

Estudo do Sistema Nefelina-Kalsilita em Rochas Vulcânicas da Província Alcalina de Goiás (GAP), Brasil Central

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*Study of the Nepheline-Kalsilite System in Volcanic
Rocks of the Goiás Alkaline Province (GAP),
Central Brazil*

by

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*“A final philosophy of earth history must be largely founded upon the unshakable facts known
about igneous rocks.”*

– R. A. Daly (1933)

Agradecimentos (in Portuguese)

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Resumo (in Portuguese)

A Província Alcalina de Goiás (*GAP* em inglês) engloba uma grande variedade de rochas alcalinas máficas e félsicas. Estudos anteriores, na sua maioria, mantiveram o foco em três aspectos: (i) mapeamento geológico, (ii) caracterização petrográfica, e (iii) química de rocha, ainda que este de forma mais restrita. Uma investigação detalhada sobre a química mineral, principalmente no que diz respeito ao sistema nefelina-kalsilita ainda está por ser realizada. Tais minerais são de grande importância para os modelos petrológicos e genéticos da *GAP*. Neste contexto, um estudo sistemático foi realizado na presente tese com o intuito de melhor entender a presença incomum de nefelina e kalsilita juntos em rochas vulcânicas da *GAP*. A petrografia detalhada possibilitou individualizar ao menos dois grupos distintos de rochas vulcânicas: (i) rochas máficas sem feldspatos, e (ii) rochas máficas e félsicas com feldspatos. Conforme o objetivo inicial proposto, o estudo concentrou-se nas características texturais e composicionais dos minerais do sistema nefelina-kalsilita, os quais coexistem somente nas rochas sem feldspatos. Os resultados mostram que a nefelina potássica é o principal mineral félsico na matriz dessas rochas. Tanto a nefelina quanto a kalsilita se formaram a partir do magma, ou seja, são fases primárias. Além disso, observou-se que tais rochas vulcânicas não podem ser classificadas de acordo com nenhum sistema vigente (*e.g.* IUGS). Desta forma, é proposto um novo sistema de classificação modal e nomenclatura para as rochas vulcânicas com kalsilita. Este é baseado na fase mineral predominante entre melilita, leucita, kalsilita e nefelina. Assim, somente quatro nomes de rochas, dos quais três já vem sendo utilizados, são necessários para englobar todas as variações modais: katungito, ugandito, mafurito e kalsilita nefelinito. Além disso, a composição química da nefelina (e da kalsilita) obtidas neste estudo permitiram ampliar, de forma significativa, o entendimento sobre soluções sólidas destes dois minerais. Nefelina potássica e kalsilita podem ter valores de MgO relativamente elevados (*i.e.* > 0.1 wt.%) quando cristalizados a partir de magmas ultrabásicos alcalinos ricos em Mg. Isso se deve a relação de substituição $2\text{Al}^{3+} = \text{Mg}^{2+} + \text{Si}^{4+}$, a qual afeta diretamente o cálculo do excesso de sílica (Q'). Por fim, a rara associação mineral entre nefelina e kalsilita primárias sugere que os modelos atuais para a origem da *GAP* devem ser revisados.

Palavras-chave: magmatismo potássico e ultrapotássico; Província Alcalina de Goiás; química mineral; feldspatóides; kalsilita; cálculo estequiométrico; kama fugito

Abstract

The Goiás Alkaline Province (GAP) comprises a wide variety of alkaline igneous rocks. Most previous studies had a focus on field mapping and petrography, and less on petrogenesis of the related magmas. Detailed mineralogical studies are still lacking, particularly for nepheline and kalsilite, the occurrence of which has guided the current view about the genesis of the GAP magmas. For this reason, a systematic study has been carried out to better understand the unusual nepheline and kalsilite coexistence in some volcanic rocks from the GAP. Sampling was focused on lavas and subvolcanic rocks (dykes, sills and plugs) throughout the province, which may be considered representative of parental magmas. A careful petrographic study recognizes two main groups of volcanic rocks: (1) feldspar-free mafic rocks, and (2) feldspar-bearing mafic and felsic rocks. This study also entailed a detailed textural and compositional characterisation of nepheline and kalsilite, which coexist only in the feldspar-free rocks. The results show that K-rich nepheline is the main leucocratic groundmass phase and that it is of primary magmatic origin like the kalsilite. The studied rocks cannot be classified with the current (such as IUGS) nomenclature systems. Therefore, a new nomenclature approach has been proposed, whereby the kalsilite-bearing volcanic rocks are mineralogically classified by the presence of the main light-coloured constituents melilite, leucite, kalsilite and nepheline. Only four terms are required for this classification: katungite, ugandite, mafurite, and kalsilite nephelinite. Additionally, the composition of nepheline and kalsilite occurring in the feldspar-free volcanic rocks from the GAP considerably expands the current understanding about their solid solutions in nature. This study shows that both nepheline and kalsilite may have significant MgO contents (~0.3 wt.% on average) when they crystallised from Mg-rich alkaline ultrabasic magmas. The coupled substitution $2\text{Al}^{3+} = \text{Mg}^{2+} + \text{Si}^{4+}$ is the most likely explanation for the entrance of Mg into the crystal structures of these minerals; this also affects significantly the excess of silica (Q') values. The mineral assemblage with nepheline and kalsilite as primary igneous phases suggests that the parental magma(s), as well as the mantle source(s), of the GAP feldspar-free volcanic rocks should be different from that currently hypothesised, *i.e.*, it should be, at least in part, of a potassic rather than an ultrapotassic nature.

Keywords: potassic and ultrapotassic magmatism; Goiás Alkaline Province; mineral chemistry; feldspathoids; nepheline stoichiometry; kalsilite; kamafugite

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List of Minerals

All minerals cited in the present study, in alphabetical order.

Aegirine	Kalsilite
Aegirine-Augite	Leucite
Amphibole	Magnetite
Analcime	Melilite
Anorthoclase	Nepheline
Apatite	Olivine
Biotite	Perovskite
Bowlingite*	Phlogopite
Calcite	Plagioclase
Cancrinite	Sanidine
Chromite	Serpentine
Clinopyroxene	Spinel
Diopside	Tetrakalsilite
Garnet	Titanite
Iddingsite*	Trikalsilite
Kaliophilite	Zeolites

*Although obsolete according to the IMA, these are traditional descriptive terms used in the petrography of alkaline igneous rocks such as those studied in this work.

Abbreviations

a.s.l.	Above sea level
AE	Águas Emendadas*
AMO	Amorinópolis*
Ap	Apatite
ARE	Arenópolis*
BSE	Backscattered Electrons
ca.	<i>circa</i>
CAPES	Coordenação de Aperfeiçoamento de Pessoal de Nível Superior*
CETEM	Centro de Tecnologia Mineral*
cf.	<i>confer</i>
CNPq	Conselho Nacional de Desenvolvimento Científico e Tecnológico*
CPRM	Companhia de Pesquisa de Recursos Minerais*
Cpx	Clinopyroxene
CRTi	Centro Regional para o Desenvolvimento Tecnológico e Inovação*
DIO	Diorama*
DR Congo	Democratic Republic of the Congo
e.g.	<i>exempli gratia</i>
EMP	Electron Microprobe
EMPA	Electron Microprobe Analysis
FB	Fazenda Buriti*
Fm.	Geological formation
GAP	Goiás Alkaline Province
GEOROC	Geochemistry of Rocks of the Oceans and Continents
GPS	Global Positioning System
i.e.	<i>id est</i>
ibid.	<i>ibidem</i>
IG	Instituto de Geociências*
IMA	International Mineralogical Association
IUGS	International Union of Geological Sciences
Kfs	Kalsilite
Ks	Potassic end-member component of the ‘nepheline-kalsilite’ system
Lct	Leucite
LME	Laboratório de Microsonda Eletrônica*
LOD	Limit of Detection

LOI	Loss on Ignition
Mag	Magnetite
MAR	Marimbondo*
MCG	Montes Claros de Goiás*
Mll	Melilite
MM	Morro do Macaco*
mol. %	Molecular percentage
Mt.	Mount
MTA	Mata Azul*
NAL	New Aluminum Silicate
Ne	Sodic end-member component of the ‘nepheline-kalsilite’ system
NEU	Neuzinha*
Nph	Nepheline
Ol	Olivine
PAR	Paraúna*
Phl	Phlogopite
PPL	Plane-Polarised Light
Prv	Perovskite
RC	Rio Claro*
SAB	Santo Antônio da Barra*
SCLM	Subcontinental Lithospheric Mantle
SEM	Scanning Electron Microscopy
SF	Santa Fé*
TAS	Total Alkali-Silica
TEM	Transmission Electron Microscopy
TIG	Tigre*
UFG	Universidade Federal de Goiás*
UFRRJ	Universidade Federal Rural do Rio de Janeiro*
UnB	Universidade de Brasília*
WDS	Wavelength-Dispersive X-ray Spectroscopy
wt. %	Weight percentage
XPL	Cross-Polarised Light
XRF	X-ray Fluorescence
Zeo	Zeolite

All mineral abbreviations according to Warr (2021).

*Terms in Portuguese.

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Chapter 1

Introduction

1.1 Thesis Rationale

Alkaline igneous provinces are enigmatic. The Goiás Alkaline Province (GAP) located at the northern margin of the Phanerozoic Paraná Basin in central Brazil is no exception. It comprises a wide variety of mafic and ultramafic alkaline rocks, including one of the largest exposures of very rare kalsilite-bearing volcanic rocks worldwide (*e.g.* Junqueira-Brod *et al.*, 2002; Brod *et al.*, 2005). Although this province has been known since the late 1960's (Guimarães *et al.*, 1968), most of the work to date has focused either on field mapping and description (*e.g.* Junqueira-Brod *et al.*, 2002; Brod *et al.*, 2005 and references therein) or on the physicochemical aspects of the highly explosive (diatreme) volcanism (Sgarbi *et al.*, 1998; Junqueira-Brod *et al.*, 1999; 2002; 2003a; 2004; 2005a, b). Understanding the petrogenetic relations of the diverse alkaline rocks exposed in the GAP region, particularly from the point of view of their unusual mineral associations, is still not achieved.

Outline of Theory and Research on the Topic

The widespread potassic magmatism in the GAP region (formerly known as the Iporá Province – Gibson *et al.*, 1995) has been postulated as evidence for the impact of the Late Cretaceous (~85 Ma) early Trindade mantle plume head on the base of the subcontinental lithospheric mantle (SCLM) in Western Brazil, similarly to the Alto Paranaíba and Poxoréu provinces (see Gibson *et al.*, 1995; 1997). However, the lack of comprehensive mineralogy, geochemistry and geochronology studies for most of the GAP occurrences (Brod *et al.*, 2005) bounds our understanding about the role of this postulated mantle plume in the generation of the GAP parental magmas. Moreover, there is still a contentious debate whether the cause of such Late Cretaceous intraplate alkaline magmatism is indeed related to the Trindade mantle plume or not (*e.g.* Felgate, 2014; Gomes & Comin-Chiaramonti, 2017 and references therein).

A spatial and potentially temporal variation is recognized across the province with a significant variation in the mode of emplacement and in the degree of silica-undersaturation of the alkaline rocks. Less SiO₂-undersaturated (*i.e.* feldspar-bearing) rocks occur essentially in the northern GAP, as major intrusive complexes and minor dykes, sills and plugs. Strongly SiO₂-undersaturated (*i.e.* feldspar-free) rocks dominate in the central and southern portions of the province as subvolcanic bodies (diatremes, dykes and plugs), lava flows and pyroclastic deposits (Junqueira-Brod *et al.*, 2002; 2005a; Brod *et al.*, 2005). Danni (1994) suggested that the less SiO₂-undersaturated rocks were derived from alkali picrite parental magmas through fractional crystallization. The strongly SiO₂-undersaturated volcanic rocks, otherwise, exhibit a more intricate evolution, possibly involving other differentiation processes such as magma mixing and liquid immiscibility (*e.g.* Junqueira-Brod *et al.*, 2005a). The latter rocks also exhibit some evidence that suggests a possible link with carbonatite magmas within the province (*e.g.* Gaspar & Danni, 1981; Junqueira-Brod *et al.*, 2000; 2005a; Brod *et al.*, 2005; Nascimento, 2018).

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In this context, the GAP feldspar-free volcanic rocks provide a great opportunity to investigate a very unusual mineral assemblage with K-rich nepheline and kalsilite. Potassic nepheline has so far been thought to occur occasionally in a few alkaline ultrabasic lavas (*e.g.* Edgar, 1984; Wilkinson & Hensel, 1994; Antao & Nicholls, 2018). Likewise, kalsilite is a rare rock-forming mineral that occurs only in a few places in the world (Brazil, DR Congo, Italy and Uganda – *i.e.* in volcanic rocks). Moreover, the coexistence of nepheline and kalsilite has been investigated in detail only in the strongly SiO₂-undersaturated potassic lavas of the Mt. Nyiragongo volcano, DR Congo (Sahama, 1957; 1960; 1962a; Andersen *et al.*, 2012; 2014). Even so, this coexistence seems to be a very particular occurrence given that nepheline and kalsilite occur together in both the groundmass and also as remarkable exsolved phenocrysts. The relationship of such minerals exclusively in the groundmass of K-rich, Si-poor, volcanic rocks such as those from the GAP are very poorly investigated and understood.

Earlier works on the GAP (*e.g.* Gaspar & Danni, 1981; Danni, 1985; Moraes, 1988; Danni *et al.*, 1990; Danni & Gaspar, 1994) have all described the ‘nepheline-like’ mineral in the groundmass of the feldspar-free volcanic rocks as nepheline, obviously. This fact has implications for rock classification such as mela-nephelinites, and also led some authors to consider at least part of the GAP magmas as having a ‘typical’ nephelinite affinity (Gaspar & Danni, 1981; Danni *et al.*, 1990). However, and in apparent contrast, bulk rock geochemistry suggested a certain resemblance between the feldspar-free volcanic rocks from the GAP and ultrapotassic kamafugites from SW Uganda (Danni, 1985; Moraes, 1988; Danni *et al.*, 1990). Then, in 1998, two independent studies (Junqueira-Brod, 1998; Sgarbi, 1998) reported the presence of kalsilite in the GAP, a characteristic mineral of the kamafugitic rocks, and then, such rock types became the main reference for GAP studies. But there is still an intriguing question. Despite the evident K character of the GAP magmatism, K-rich nepheline is an abundant phase in the groundmass of their feldspar-free volcanic rocks. The recent literature

considers this nepheline as a secondary phase after intense subsolidus alteration of primary kalsilite (*e.g.* Danni & Gaspar, 1994; Junqueira-Brod, 1998; Brod *et al.*, 2005). Nevertheless, there is no single investigation about the ‘true’ relationship between nepheline and kalsilite in the GAP rocks.

Thus, a comprehensive investigation of the mineral phases of the nepheline-kalsilite system in the GAP rocks can be a powerful ally to understand the nature of this magmatism. Moreover, it can provide important knowledge about the petrogenesis of such kalsilite-bearing volcanic rocks worldwide. Hence, the aims of this research project are:

- to characterize the textures and compositions of the minerals of the nepheline-kalsilite system in the GAP rocks;
- to understand the genetic relationship between these mineral phases to define their primary or secondary origin;
- to investigate the processes involved in such mineral association and how this can be related to other occurrences worldwide.

In view of these main objectives, sampling was focused on collecting only volcanic and subvolcanic rocks. More than 200 samples were collected essentially from dykes, sills, plugs and lava flows throughout the province. The GPS locations of sampled outcrops are given in Appendix A.

The present work is focused on investigating systematically the relationship between nepheline and kalsilite in certain alkaline volcanic rocks of the GAP. This will be achieved using the most modern techniques available at the University of Brasília (UnB) and the University Federal of Goiás (UFG). Details of the analytical methods employed in this study can be found in the Supplementary Material. This is the first systematic mineralogical study in the GAP regarding felsic phases and will provide a basis for future detailed studies on the region, as well as for a comparison with other alkaline provinces globally.

1.2 Location and Access

The studied area (GAP) is located in the southwest of Goiás State, *ca.* 450 km from Brasília, between the towns of Rio Verde, Iporá and Santa Fé (**Figure 1.1**). The main roads to the southern and northern portions of the GAP are the BR-060 and the BR-070, respectively. The central region (*i.e.* around Iporá city) is accessed by the BR-060 until Goiânia, and then, by the GO-060 toward Barra do Garças. The road GO-174 is also an important connection between the southern and central portions of the province.

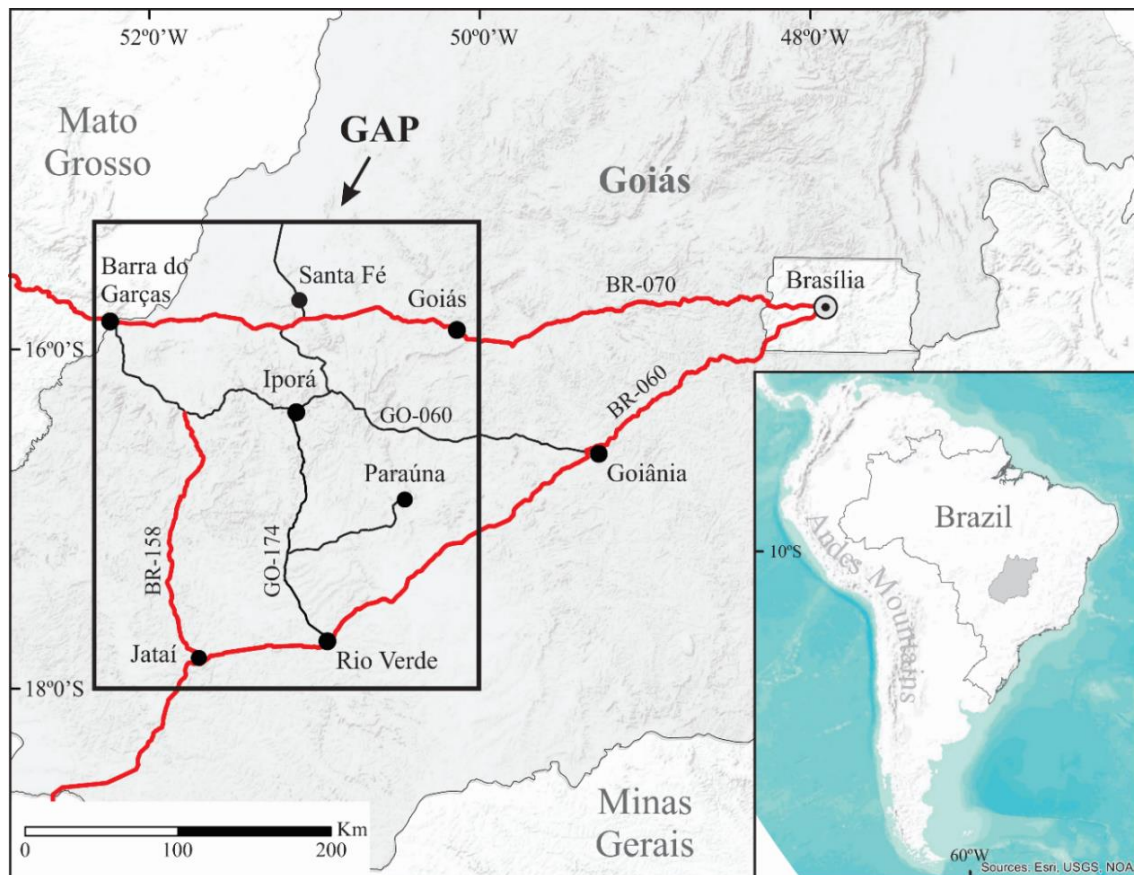


Figure 1.1 Location map and road access to the studied area (GAP). The inset shows Goiás State borders highlighted in the interior of the Brazilian territory.

1.3 Thesis Outline

This work consists of eight chapters and two appendixes. **Chapter 1** provides a brief introduction to the research topic, as well as the location of the province, and the purposes of

the study. **Chapter 2** focuses on the Goiás Alkaline Province (GAP), showing some general physiographic aspects, a complete historical background, and up-to-date geological knowledge of the province. **Chapter 3** gives the field descriptions and petrography for the most abundant rock types examined in the course of this study. **Chapter 4** relates a paper entitled “*The IUGS nomenclature on kalsilite-bearing volcanic rocks: a critical appraisal and recommendations*” which discusses the main issues related to the nomenclature of the studied rocks and proposes how this can be overcome. **Chapter 5** presents part one of two companion papers developed in partnership with Professor Michael Henderson from the University of Manchester (UK). This is entitled “*Substitution of ‘small’ divalent cations (e.g. Mg) for Si and Al in the nepheline tetrahedral framework: 1. Calculation of atomic formulae and stoichiometry parameters*”. It covers the practical effects of high Mg contents for ‘ideal’ nepheline stoichiometry. **Chapter 6** contains the second part of the two articles elaborated with Prof. Henderson. This is entitled “*Substitution of ‘small’ divalent cations (e.g. Mg) for Si and Al in the nepheline tetrahedral framework: 2. The occurrence of Mg-rich nepheline and kalsilite*”. The article discusses the possible petrological significance of the relatively high Mg values found in these minerals in the GAP rocks. **Chapter 7** presents the main contribution of this work, a draft paper entitled “*K-rich nepheline in strongly SiO₂-undersaturated alkaline mafic volcanic rocks and its petrological significance*”. It brings the textural and compositional results that have led to the publication of the previous three chapters. The manuscript also contains a discussion of the meaning of K-rich nepheline occurrences, in a global context. Finally, **Chapter 8** summarizes the main conclusions of this study, in the GAP context, and explores some ideas for future works. All **references cited** are reported afterwards.

The two appendices contain:

- The GPS locations of sampled outcrops (**Appendix A**);
- Conference abstracts presented in the course of this work (**Appendix B**);

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Also, there is a number of supplementary materials that are an essential part of this thesis. Some of them are already available on the journals' websites where the articles were published (see the relevant chapters). But they also can be readily obtained upon request from the author by using the following email address: lopesdeoliveira.italo@yahoo.com.br

Chapter 2

The Goiás Alkaline Province

In this chapter, it is presented a historical perspective of how the current geological knowledge on the Goiás Alkaline Province (GAP) has been built in the past 50 years. The chapter begins with the illustration of some general physiographic aspects (**Section 2.1**), with emphasis on the physiognomies that are often evoked in the text. Further, a brief summary of all works (to my knowledge) completed on the GAP so far is presented (**Section 2.2**), as well as a comprehensive review of the GAP occurrences (**Section 2.3**). A contextual overview of the most relevant economic aspects of the GAP follows (**Section 2.4**).

2.1 Physiographic Aspects

Climate, Vegetation and Hydrography

The climate in Central Brazil is tropical, with average temperature between 15 °C and 18 °C in the dry months (IBGE, 2002). There are two pronounced seasons: (1) the warm rainy

season from October to March, and (2) the dry cool season from April to September. The annual precipitation is around 1,600 mm (Pena *et al.*, 1975), and thus, based on the Köppen-Geiger classification (*e.g.* Beck *et al.*, 2018), the climate is defined as Aw.

The original vegetation is the typical Brazilian savannah (*i.e.* Cerrado) accompanied by riparian forests along water bodies (Pena & Figueiredo, 1972; Pena *et al.*, 1975; IBGE, 2006). However, only small portions of the original cerrado remain intact, as it has been progressively modified by farming (IBGE, 2004).

The *Cuesta* of Caiapó, in the southern portion of the GAP (**Figure 2.1**), is a major water divide with a general WSW-ENE trend (Pena & Figueiredo, 1972; Pena *et al.*, 1975). The Araguaia River is the most important drainage to the north of the *cuesta*. It has a marked NE-trend strongly influenced by the Transbrasiliiano Lineament (Cordani *et al.*, 2013; Brito Neves & Fuck, 2014), which seems to delimit GAP alkaline occurrences toward the SE (compare **Figure 2.1** and **2.7**). Two other foremost rivers (*i.e.* the Caiapó River and the Claro River – **Figure 2.1**) flow to the east margin of the Araguaia. They have a strong NW-SE structural control, similarly to the Verdão River toward the south of the *Cuesta* of Caiapó (**Figure 2.1**). Such tectonic control is probably related to large NW extensional faults formed in the GAP region during the Late Cretaceous (*e.g.* Pena & Figueiredo, 1972).

Geomorphology

The landscape contrasts significantly between the southern and the northern portions of the study area, including a topographic variation from *ca.* 900 m to 300 m a.s.l. Three main geomorphological units gathered the distinctive relief patterns: (a) the Rio Verde Plateau; (b) the Alcantilados Plateau; and (c) the Araguaia Depression. Moreover, a minor fraction of the Lower Plateau of Goiânia also occurs in the easternmost portion of the province (Mamede *et al.*, 1983; IBGE, 2006).

The Rio Verde Plateau in the southern GAP (**Figure 2.1**) is the most elevated portion of the province at *ca.* 900 m a.s.l. (Pena & Figueiredo, 1972; Mamede *et al.*, 1983). It is limited to the north by the WSW-ENE *Cuesta* of Caiapó to the N-S Caiapó River Fault (**Figure 2.1** and **2.2**). On the top of the Rio Verde Plateau, particularly in the south, extensive farming areas cover the rocks of the Phanerozoic Paraná Basin as well as their Cenozoic cover. A transition zone between the Rio Verde Plateau and the more dissected surrounding relief patterns occurs in the region between Paraúna and Iporá (**Figure 2.1**). There, the landscape is marked by some prominent mesas (*e.g.* Serra da Portaria – **Figure 2.3**) and deep structural valleys, which are controlled by the Late Cretaceous extensional tectonics (Pena & Figueiredo, 1972).

The Alcantilados Plateau (Pena & Figueiredo, 1972; Mamede *et al.*, 1983; IBGE, 2006) occurs from the *Cuesta* of Caiapó towards the north. It is a very heterogeneous lower-level plateau (*i.e.* from 400 m to 750 m a.s.l. – Mamede *et al.*, 1983) with a strongly dissected relief marked by deep river valleys (*e.g.* the Caiapó River) and by the Late Cretaceous extensional tectonics (Pena & Figueiredo, 1972; Pena *et al.*, 1975). The reddish sedimentary rocks of the Aquidauana Formation dominate the landscape, establishing abundant mesas (**Figure 2.4**). Prominent elevations with gentle slopes are typically formed by basement rocks (*e.g.* post-tectonic granites), and sometimes, they may exhibit a flat top associated with the Paraná Basin sedimentary rocks (Guimarães *et al.*, 1968).

In the north of the province the landscape changes drastically to the wide plain of the Araguaia Depression (Mamede *et al.*, 1981; 1983). This portion of the GAP is marked by extensive Cenozoic cover occurring at an average altitude of *ca.* 350 m a.s.l. (Mamede *et al.*, 1981; 1983). The sandstones of the Furnas Formation and some major Late Cretaceous alkaline bodies (*e.g.* Morro do Engenho Hill – **Figure 2.5**) are responsible for some remarkable hills that occur in this part of the Araguaia Depression (*e.g.* Justo, 1972; Chaban, 1973; Mamede *et al.*, 1981). In fact, most of the large GAP alkaline mafic-ultramafic intrusions that dominate in

the northern portion of the province are represented by prominent hills with steep slopes and up to 850 m altitude (e.g. Morro do Macaco Hill – **Figure 2.6** – Guimarães *et al.*, 1968; Pena & Figueiredo, 1972).

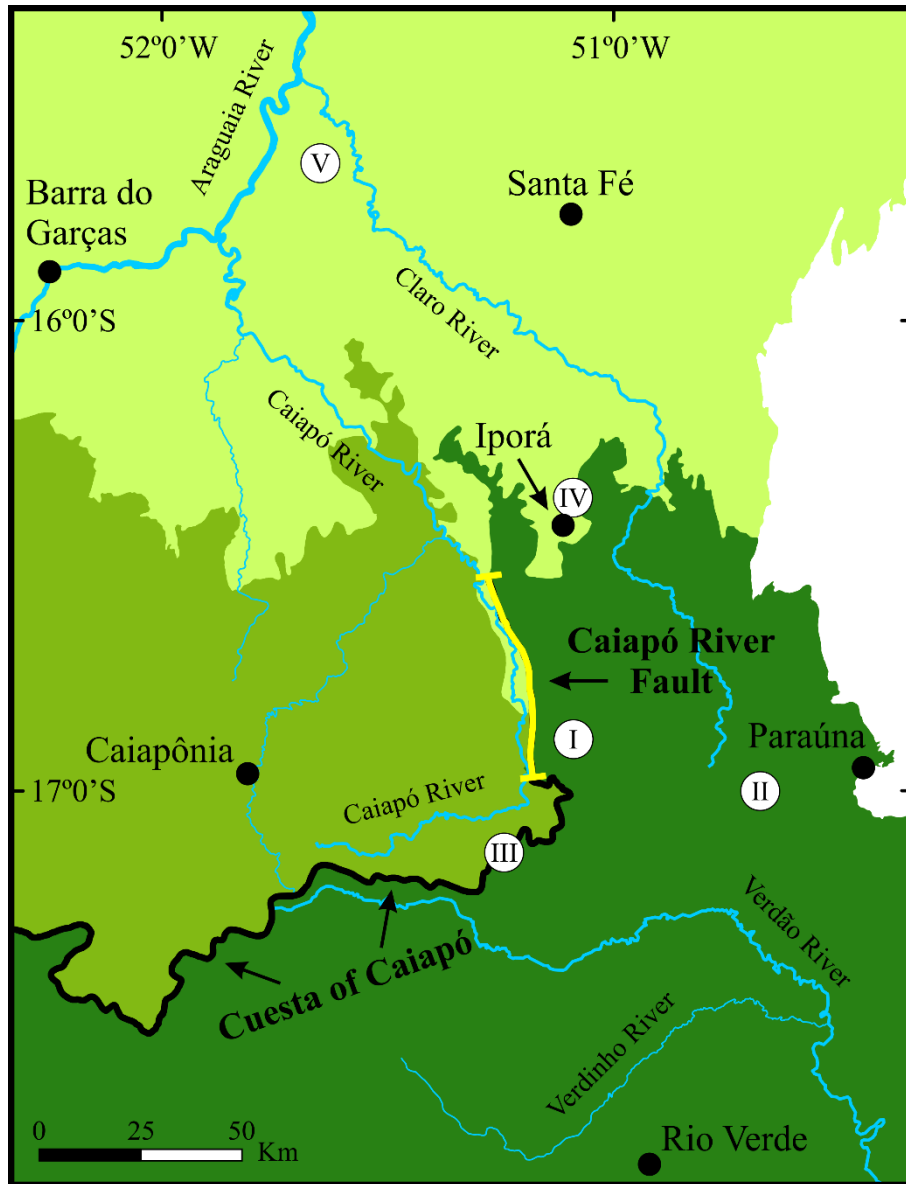


Figure 2.1 Geomorphological map showing the main units of the study area (modified after Mamede *et al.*, 1983; IBGE, 2006). The small circles (I to V) indicate the approximate location of the following landscape photos.



Figure 2.2 Front of the *Cuesta* of Caiapó adjacent to the Caiapó River Fault (location I in Figure 2.1).



Figure 2.3 View of the Serra da Portaria mesa in the Paraúna region. Note the extensive farming areas in the forefront, immediately before the mesa elevation (location II in Figure 2.1).



Figure 2.4 The reddish rocks of the Aquidauana Formation occurring as mesas in the southern portion of the Alcantilados Plateau (location III in Figure 2.1).



Figure 2.5 View from the Araguaia Depression to the north (location V in Figure 2.1). Note the Morro do Engenho alkaline mafic-ultramafic complex in the background.



Figure 2.6 View of the remarkable Morro do Macaco hill to the south (location IV in Figure 2.1). This is a geomorphological transition zone between the highlands of the plateaus, in the south, and the Araguaia Depression, in the north.

2.2 Historical Background

Guimarães *et al.* (1968) provided the first description of major alkaline igneous bodies and hypabyssal intrusions near the Iporá region. They reported a series of ultramafic rocks, alkali gabbros, and nepheline syenite intrusive into the sandstones of the Paraná Basin. Later, Glaser *et al.* (1970a, b) identified mafic alkaline lavas and breccias in the Águas Emendadas (AE) and Amarinópolis regions (see **Section 2.3**). Almost at the same time, Bez *et al.* (1971b) described widespread leucite-bearing volcanic rocks in the Santo Antônio da Barra (SAB) district, close to Rio Verde (see **Section 2.3** and **Figure 2.7**). Several works, mostly from the then recently founded Geological Survey of Brazil (*i.e.* the CPRM), contributed to mapping many other alkaline occurrences in the SW of the Goiás state during the 1970's and early 1980's (see references in **Table 2.1**).

Chapter 2: Goiás Alkaline Province

Almost all studies prior to 1985 emphasized geological mapping and field descriptions (see **Table 2.1** – red symbols). Hence, the works conducted by Danni (1974; 1978) on the petrology of some alkaline plutonic complexes in the Iporá region (*i.e.* Corrêgo dos Bois and Morro do Macaco – **Figure 2.7**) are remarkable. Studies encompassing mineral chemistry and whole-rock geochemistry improved significantly after the mid 1980's (**Table 2.1**). However, until 1998 most of the publications were restricted to the Brazilian literature, and almost half were reported as conference abstracts (see **Table 2.1** – asterisks). A marked change to GAP studies set in with Danni (1985). He was pioneer on recognizing the mafic alkaline rocks from the Amorinópolis region as belonging to the kamafugite series, including the rarest katungite type. Moraes (1988) and Danni *et al.* (1990) also suggested a kamafugite character for some lavas and breccias described in the SAB and AE regions, respectively (see **Section 2.3**). The presence of kalsilite in these rocks was, furthermore, documented (*e.g.* Junqueira-Brod, 1998; Sgarbi, 1998; Junqueira-Brod *et al.* 2000; Sgarbi & Gaspar 2002), definitely characterizing these rocks as kamafugites.

Most of the studies on the GAP region after 1990's paid attention to the kamafugites. For instance, Junqueira-Brod *et al.* (1999; 2002; 2003a; 2004; 2005a; b) carried out comprehensive studies about the volcanology of the kamafugites. Nonetheless, the studies of Danni (1994) and Danni *et al.* (1994b) concerning other alkaline mafic rocks in the GAP are remarkable. The former described numerous subvolcanic intrusions with an 'alkali picrite' composition around the Iporá region (see **Section 2.3**), whereas the latter work reported the first mantle xenoliths (spinel lherzolites) found in the province.

Isotope studies are incredibly rare on the GAP rocks (**Table 2.1**). Gibson *et al.* (1996) reported radiogenic (Sr and Nd) isotope compositions for some 'mafic potassic rocks' from the Iporá province. However, their study was focused on regional implications for the genesis of the Paraná-Etendeka tholeiitic magmatism. Sgarbi *et al.* (1998) reported stable isotope data

(oxygen) for only two SAB samples. Gaspar *et al.* (2003) and Carlson *et al.* (2007) carried out systematic radiogenic isotope studies (Sr, Nd, Hf and Os) on the GAP mantle xenoliths and kamafugites, but as Gibson *et al.* (1996), they did not focus on the source and origin of the province magmas. More recently, Felgate (2014) reported a complete dataset of mineralogy, geochemistry and radiogenic isotopes for one kamafugite sample from the Rio Verde region (see **Section 2.3**).

Brod *et al.* (2005) provided an extensive review of the knowledge on the GAP rocks and pointed out that only a few alkaline occurrences had been studied in detail so far. Amply mineralogical, geochemical and isotopic work is still missing to firmly constrain the genesis of this magmatic province. In the last 15 years a considerable break in petrological studies of the GAP occurred (see **Table 2.1**), and except for the recent studies in the Morro Preto complex (*e.g.* Nascimento, 2018), very scarce, local data were reported for these alkaline rocks (*i.e.* Kafino *et al.*, 2012, Felgate, 2014).

Table 2.1 Summary of the previous studies on GAP rocks, except for geophysical studies. *Abstracts published at conferences or symposia.

Reference	Geological Mapping	Field Description & Petrography	Mineral Chemistry	Whole Rock Geochemistry	Isotopes
01 - Guimarães <i>et al.</i> (1968)	•	•			
02 - Bez (1970) *	•	•			
03 - Faria <i>et al.</i> (1970) *	•				
04 - Glaser <i>et al.</i> (1970a) *		•			
05 - Glaser <i>et al.</i> (1970b) *	•	•			
06 - Marques & Rippel (1970) *		•			
07 - Bez <i>et al.</i> (1971a) *		•			
08 - Bez <i>et al.</i> (1971b)	•	•			
09 - Hasui <i>et al.</i> (1971)	•	•			
10 - Lessa Sobrinho & Andrade (1971)	•	•			
11 - Lessa Sobrinho <i>et al.</i> (1971) *		•			
12 - Justo (1972)		•			
13 - Pena & Figueiredo (1972a)	•	•			
14 - Pena & Figueiredo (1972b)	•	•			
15 - Chaban (1973)	•	•			
16 - Justo (1973) *		•			
17 - Chaban & Santos (1973) *		•			
18 - Figueiredo & Pena (1973) *	•	•			
19 - Pena & Figueiredo (1973) *	•	•			
20 - Danni (1974)	•	•	•	Major Elements	

Reference	Geological Mapping	Field Description & Petrography	Mineral Chemistry	Whole Rock Geochemistry	Isotopes
21 - Pena <i>et al.</i> (1975)	•	•			
22 - Barbour (1976)	•	•			
23 - Danni <i>et al.</i> (1976)	•	•			
24 - Gaspar (1977)	•	•	•		
25 - Barbour <i>et al.</i> (1978) *		•			
26 - Danni (1978)	•	•	•	Major Elements	
27 - Sousa <i>et al.</i> (1978) *		•			
28 - Barbour <i>et al.</i> (1979)	•	•			
29 - Gaspar & Danni (1979)		•	•		
30 - Gaspar & Danni (1981)	•	•			
31 - Drago <i>et al.</i> (1981)		•			
32 - Ianhez <i>et al.</i> (1983)		•		Major Elements	
33 - Moraes (1984)	•	•		•	
34 - Danni (1985)	•	•	•	•	
35 - Tompkins (1987)			•		
36 - Moraes (1988)		•		•	
37 - Danni <i>et al.</i> (1989)	•	•			
38 - Danni <i>et al.</i> (1990)		•		Major Elements	
39 - Danni & Gaspar (1992) *		•	•	•	
40 - Danni <i>et al.</i> (1992) *		•	•	•	
41 - Danni <i>et al.</i> (1993)	•	•			

Reference	Geological Mapping	Field Description & Petrography	Mineral Chemistry	Whole Rock Geochemistry	Isotopes
42 - Cerqueira & Danni (1994a) *	●	●		●	
43 - Cerqueira & Danni (1994b) *		●	●		
44 - Danni (1994)	●	●	●	●	
45 - Danni & Gaspar (1994)		●	●	●	
46 - Danni <i>et al.</i> (1994a) *	●	●		Major Elements	
47 - Danni <i>et al.</i> (1994b) *	●	●	●		
48 - Cerqueira (1995)	●	●	●	●	
49 - Junqueira-Brod (1998)		●	●	●	
50 - Sgarbi (1998)		●	●	●	●
51 - Sgarbi <i>et al.</i> (1998)		●			●
52 - Junqueira-Brod <i>et al.</i> (1999)		●			
53 - Junqueira-Brod <i>et al.</i> (2000)		●	●		
54 - Sgarbi <i>et al.</i> (2000a)		●	●		
55 - Junqueira-Brod <i>et al.</i> (2002)	●				
56 - Sgarbi & Gaspar (2002)		●	●	●	
57 - Gaspar <i>et al.</i> (2003) *				●	●
58 - Junqueira-Brod (2003)	●	●			
59 - Junqueira-Brod <i>et al.</i> (2003a) *		●			
60 - Junqueira-Brod <i>et al.</i> (2003b) *		●		●	
61 - Junqueira-Brod <i>et al.</i> (2004)		●			
62 - Reis Brod <i>et al.</i> (2004a) *			●		

Reference	Geological Mapping	Field Description & Petrography	Mineral Chemistry	Whole Rock Geochemistry	Isotopes
63 - Reis Brod <i>et al.</i> (2004b) *		•		•	
64 - Sgarbi <i>et al.</i> (2004)		•		•	
65 - Brod <i>et al.</i> (2005)			•	•	
66 - Junqueira-Brod <i>et al.</i> (2005a)		•		•	
67 - Junqueira-Brod <i>et al.</i> (2005b)		•			
68 - Carlson <i>et al.</i> (2007)		•		•	•
69 - Kafino <i>et al.</i> (2012) *		•	•		
70 - Felgate (2014)		•	•	•	•
71 - Navarro <i>et al.</i> (2014)		•		•	
72 - Martins <i>et al.</i> (2018) *		•			
73 - Nascimento (2018)	•	•	•	•	

Red symbols stand for works before 1985; black symbols for studies between 1985 and 1995; and blue symbols for those after 1998.

2.3 State of the Art

The GAP is composed of a wide variety of petrographic types, outcropping as large plutonic complexes, a number of subvolcanic bodies (sills, plugs, dykes, and diatremes), as well as lava flows and pyroclastic deposits (Junqueira-Brod *et al.*, 2002; 2005a; Brod *et al.*, 2005). These bodies occur along N50°-70°W trending Late Cretaceous extensional faults, over an area of ca. 250 x 70 km wide (*e.g.* Pena & Figueiredo, 1972; Almeida, 1983), from the town of Rio Verde, in the south, to the Araguaia River, in the north (**Figure 2.7**).

One of the most remarkable aspects of the GAP is the systematic variation in the mode of emplacement and in the degree of silica-undersaturation of the alkaline rocks across the province (Junqueira-Brod *et al.*, 2002; 2005a). In the northern GAP, less silica-undersaturated feldspar-bearing rocks are commonly found in major intrusive bodies (**Figure 2.7**). On the other hand, toward the central and southern portions of the province, strongly silica-undersaturated, feldspar-free, mafic potassic lavas, breccias, and hypabyssal intrusions dominate (Junqueira-Brod *et al.*, 2002; 2005a; Brod *et al.*, 2005).

Northern GAP

In the northern GAP (*i.e.* from the Iporá latitude to the north) outcrop the large plutonic complexes of Morro do Engenho, Santa Fé, Montes Claros, Arenópolis, Fazenda Buriti, Corrêgo dos Bois and Morro do Macaco (**Figure 2.7**). They comprise concentrically zoned alkaline intrusions that often consist of a central dunite body, surrounded by peridotites, pyroxenites and alkali gabbros, with subordinate nepheline syenites at the outside (see Junqueira-Brod *et al.*, 2002; Brod *et al.*, 2005, for further details). Interestingly, some felsic (syenites) and mafic (pyroxenites) rocks containing leucite or pseudo-leucite have been reported in the Morro do Macaco (Glaser *et al.* 1970b), Santa Fé (Lessa Sobrinho *et al.*, 1971; Sousa *et al.*, 1978; Barbour *et al.*, 1979), and Fazenda Buriti (Cerqueira, 1995) complexes.

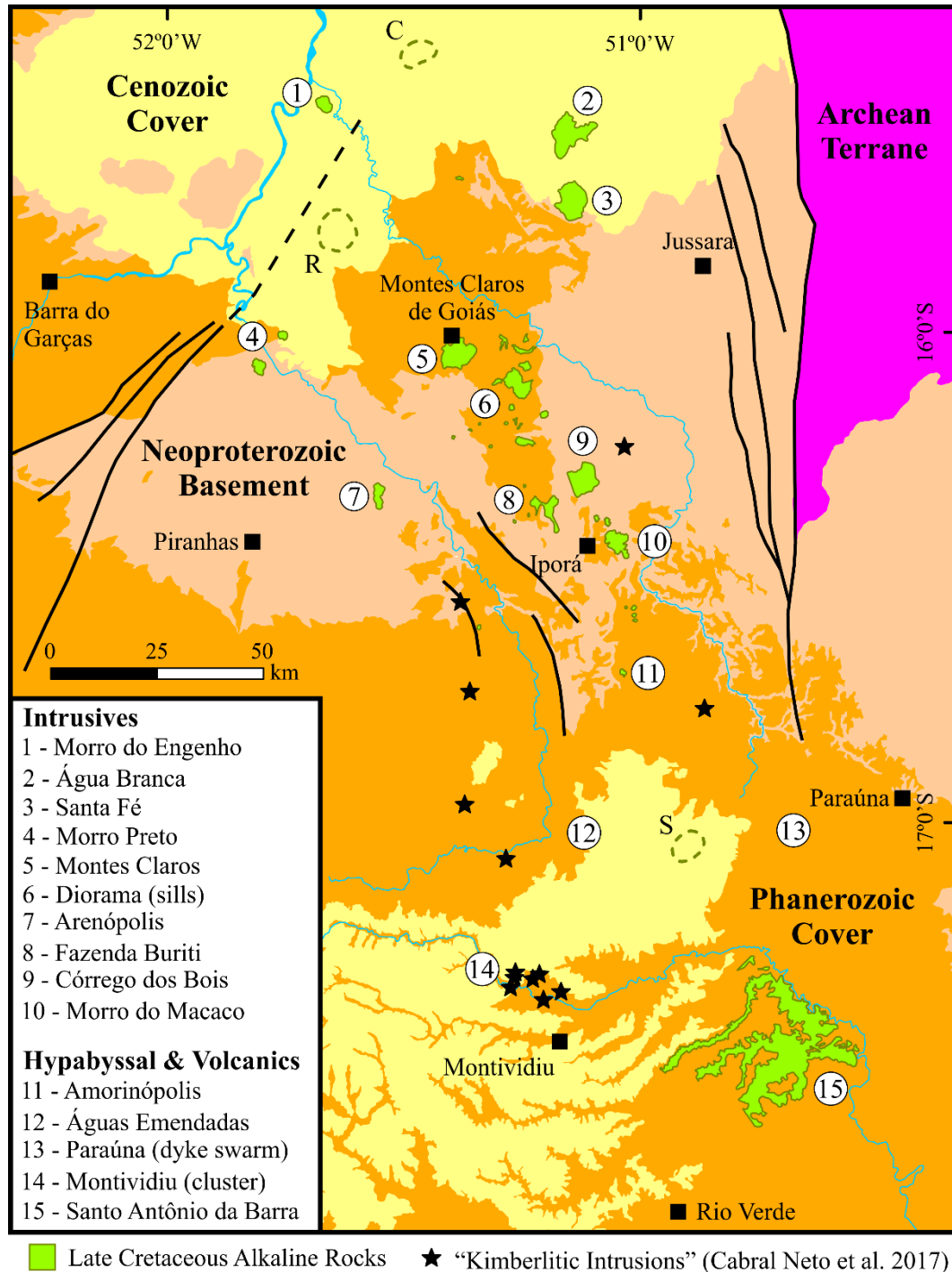


Figure 2.7 Simplified geological map of the Goiás Alkaline Province, showing the location of the main alkaline occurrences (modified after Pena & Figueiredo, 1972; Brod *et al.*, 2005; Moreira *et al.*, 2008). C, R, and S (dashed rounded areas) symbols stand respectively for Canadá Farm, Registro do Araguaia, and Santana magnetic anomalies (see text).

The alkaline plutonic complexes in the north portion of GAP are usually emplaced at the discordance between the Precambrian basement and the sandstones of the Furnas Fm., which is in good agreement with density simulations conducted by Junqueira-Brod *et al.*

(2005a). These authors proposed that volatile-rich mantle-derived alkaline magmas such as those of the GAP would be retained at the Precambrian-Phanerozoic discontinuity by density contrast, and then, generate a shallow magma chambers.

At least three other alkaline occurrences occur in the northern GAP (see **Figure 2.7**). The Água Branca body (**Figure 2.7**), not previously distinguished in its own right, outcrops as an extensive mesa (*ca.* 35 km²) in the extreme northern part of the province. It consists of a tabular intrusion into the Paleozoic rocks of the Paraná Basin, probably forming a large sill of serpentinized ultramafic rocks (*e.g.* dunites, peridotites and pyroxenites – Justo 1972; 1973), which is entirely covered by silicite blocks (Lessa Sobrinho & Andrade, 1971).

The Morro Preto alkaline-carbonatite complex (**Figure 2.7**) comprises two circular bodies (*ca.* 3 km in diameter) intrusive into Precambrian orthogneisses (Nascimento, 2018). Both intrusions outcrop essentially as weathered and silicified rocks (Pena & Figueiredo, 1972; Ianhez *et al.*, 1983; Navarro *et al.*, 2014). However, on drill core samples, Nascimento (2018) recognized it as dominated by carbonatites, which is an exception in the GAP until now. Dykes of kamafugite and unusual alkali basalts crosscut the entire complex, mainly in the southern body (Nascimento, 2018). Interestingly, veins composed of phlogopite and carbonates were described crosscutting ultramafic rocks from Morro do Engenho (Chaban, 1973) and Fazenda Canadá (Campos, 1977), but additional studies are still required to confirm if such veins also represent carbonatite melts or not.

In the Diorama region (**Figure 2.7**), the alkaline magmatism occurs mostly as sills of varied compositions (*e.g.* alkali pyroxenite, basanite, trachyte), emplaced into the sandstones of the Furnas Fm. (*e.g.* Pena & Figueiredo, 1972; Ianhez *et al.*, 1983). More than twenty small subvolcanic bodies (dykes, sills and plugs) that consist mainly of ‘alkali picrite’ have been characterized in the region NW of Iporá (Danni, 1994 – **Figure 2.8**).

In general, dykes crosscut the Precambrian basement (granites and gneisses), whereas sills are particularly emplaced into the Vila Maria and Ponta Grossa sedimentary rocks, usually forming thin (< 5 m thick) homogeneous bodies. Plugs are intrusive mostly into the Paraná Basin units, with up to 200 m diameter. Danni (1994) postulated that such alkali picrite may represent the parental magmas from which the northern GAP alkaline mafic-ultramafic complexes were derived by fractional crystallization, most likely in shallow magma chambers.

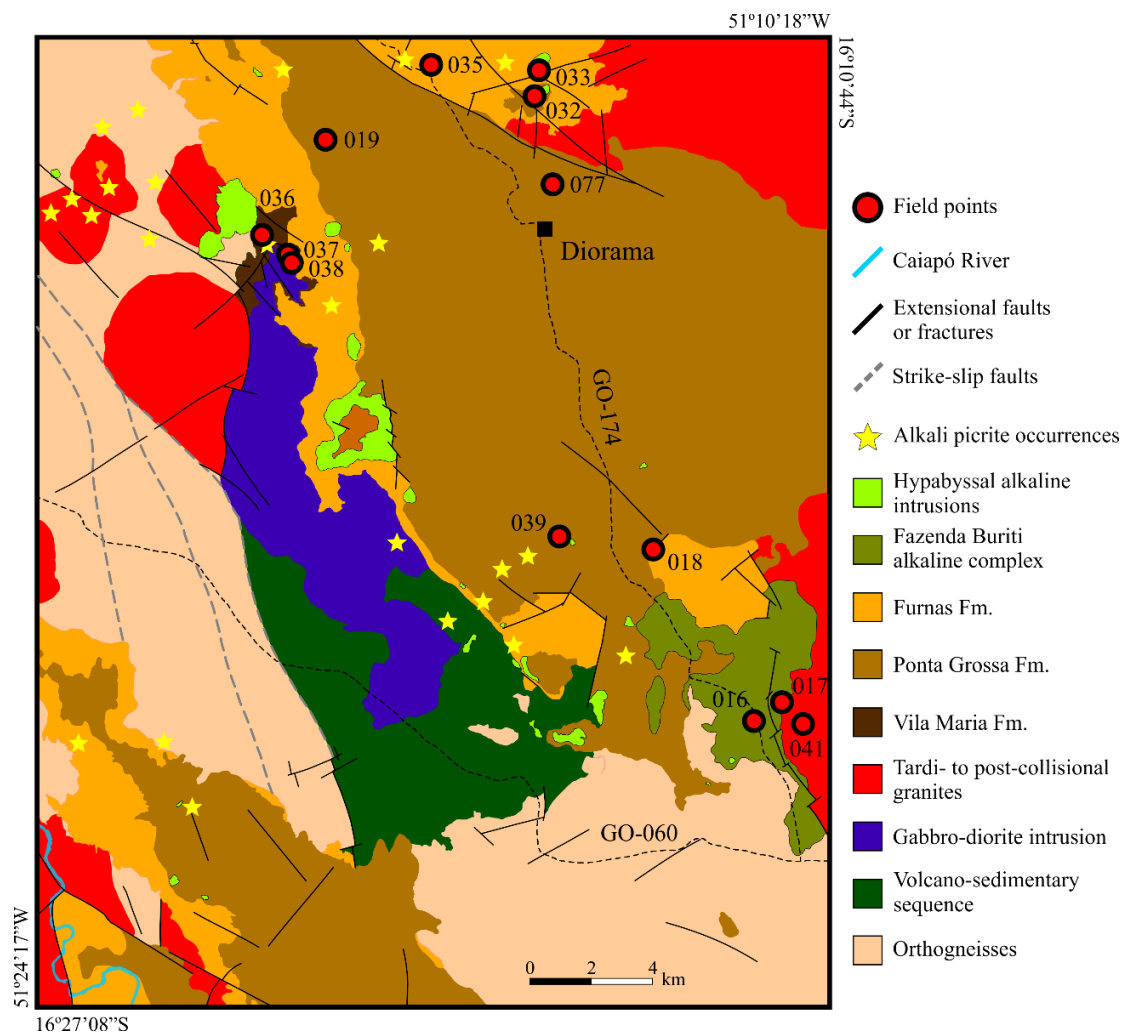


Figure 2.8 Detailed geological map of the region NW of Iporá (modified after Danni *et al.*, 1993; Danni, 1994). The numbers corresponding to the field points (see [Appendix A](#)) are indicated next to them.

Central GAP

The central portion of the province contains essentially subvolcanic bodies (diatremes, dykes and plugs). The main occurrences are located between the towns of Amarinópolis,

Montividiu and Paraúna (**Figure 2.7**). A large volcanic-subvolcanic complex associated with a few radial dykes stands out southeast of Amarinópolis (**Figure 2.7**). It is intrusive into the sedimentary rocks of the Ponta Grossa Formation, comprising mainly subvolcanic rocks with minor lavas and breccias (*e.g.* Danni, 1985 – **Figure 2.9**). These rocks are typically feldspar-free volcanic rocks, containing abundant ultramafic nodules as well as some crustal fragments (Danni, 1985; Reis Brod *et al.*, 2004). Basanite and tephrite breccias have also been reported in the centre of the complex (Danni, 1985). To the southwest of the main intrusion, there is a katungite plug with *ca.* 100 m in diameter (**Figure 2.9**). This is the only known katungite occurrence in the entire GAP so far (Danni, 1985; Danni & Gaspar, 1992; 1994).

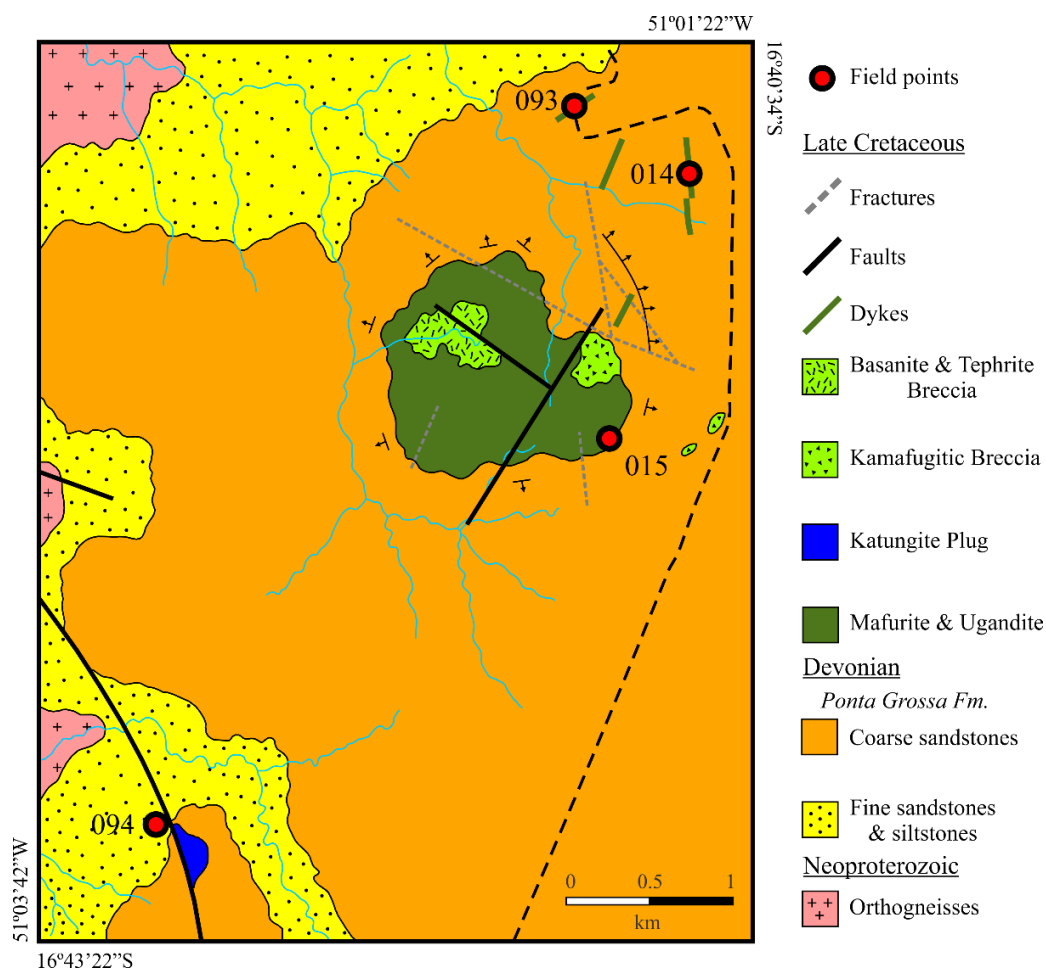


Figure 2.9 Detailed geological map of the volcanic-subvolcanic Amarinópolis complex and the adjacent region (modified after Danni, 1985; Danni *et al.*, 1993).

Another volcanic-subvolcanic association crops out in the Águas Emendadas (AE) region, almost in front of the *Cuesta* of Caiapó (**Figure 2.7**). This is dominated by diatreme structures emplaced into the sandstones of the Aquidauana Fm. and covered by the Bauru sedimentary rocks (Danni *et al.*, 1990; Junqueira-Brod *et al.*, 2004). The diatremes are filled with kamafugitic breccias, which are partially capped by small, pond-like lava flows of kamafugite and basanite compositions. Late dykes and plugs crosscut both diatremes and country rocks (*e.g.* Junqueira-Brod *et al.*, 2003b; 2004; 2005b). The explosive activity in the AE region was most likely triggered by magma mixing and volatile exsolution in shallow magma chambers (Junqueira-Brod *et al.*, 2003a; 2004; 2005a; b). In addition, textural evidence shown that CO₂ is the most important volatile phase in this volcanism (Junqueira-Brod *et al.*, 2004; 2005a; b).

Recently, CPRM reported near Montividiu town a cluster of ‘kimberlitic intrusions’, which were investigated by De Beers during the early 1990’s (Cabral Neto *et al.*, 2017 – **Figure 2.10**). Almost all of these occurrences crop out as highly weathered rocks. Nevertheless, on a drill core sample, Felgate (2014) obtained a complete geochemical and geochronological dataset for one of the intrusions (*i.e.* Rio Verde 3 – RV3 in **Figure 2.10**). Felgate (2014) also determined a kamafugite character for this intrusion, which was formerly classified as hypabyssal ‘kimberlite-like’ by De Beers. Hence, based on the absence of kimberlites in the entire GAP so far, it can be inferred that the Montividiu cluster probably represent a series of kamafugite intrusions (*i.e.* plugs or diatremes) rather than ‘true’ kimberlites.

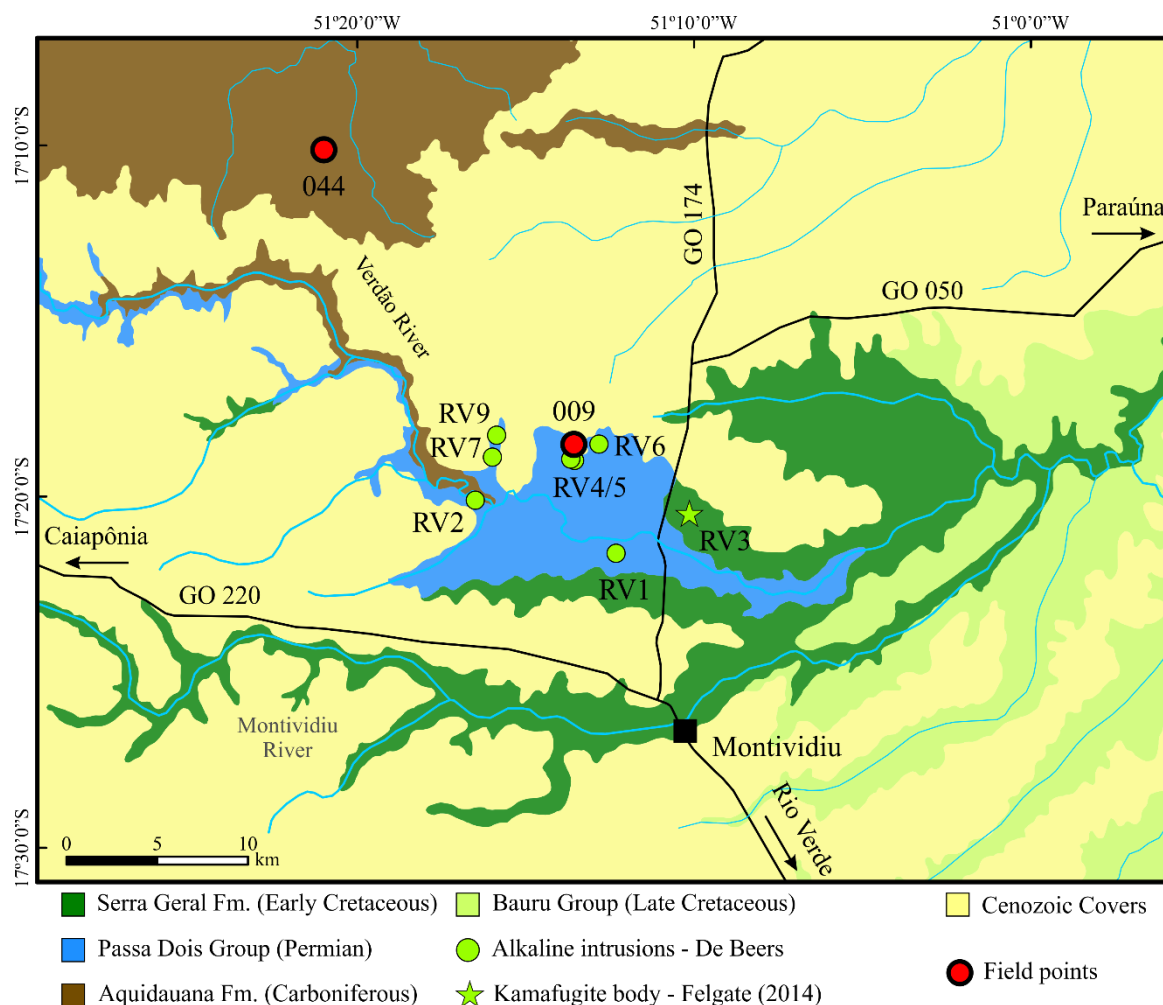


Figure 2.10 Detailed geological map of the Montividiu region showing the location of the alkaline intrusions that comprise ‘the Montividiu cluster’ (modified after Moreira *et al.*, 2008; Cabral Neto *et al.*, 2017).

In the Paraúna region (**Figure 2.7**) some plugs as well as a dyke swarm of kamafugite composition, both intrusive into the Paraná Basin sedimentary rocks occur (**Figure 2.11**). The former are relatively small (up to 300 m in diameter) and may contain mantle xenoliths (*e.g.* Danni *et al.*, 1994). The dykes, otherwise, are generally less than 10 m wide and hundreds of meters long but can exceptionally reach up to 3 km in length. Pena *et al.* (1975) related the Paraúna dyke swarm with the massive Santana Anomaly (see **Figure 2.7**). Bez *et al.* (1971a) also reported mafic lavas, breccias and pyroclastic rocks occurring close to the Serra da Portaria (**Figure 2.3**). Except for the mantle xenoliths (Danni *et al.*, 1994; Carlson *et al.*, 2007; Kafino *et al.*, 2012), the Paraúna volcanic-subvolcanic rocks are very poorly investigated.

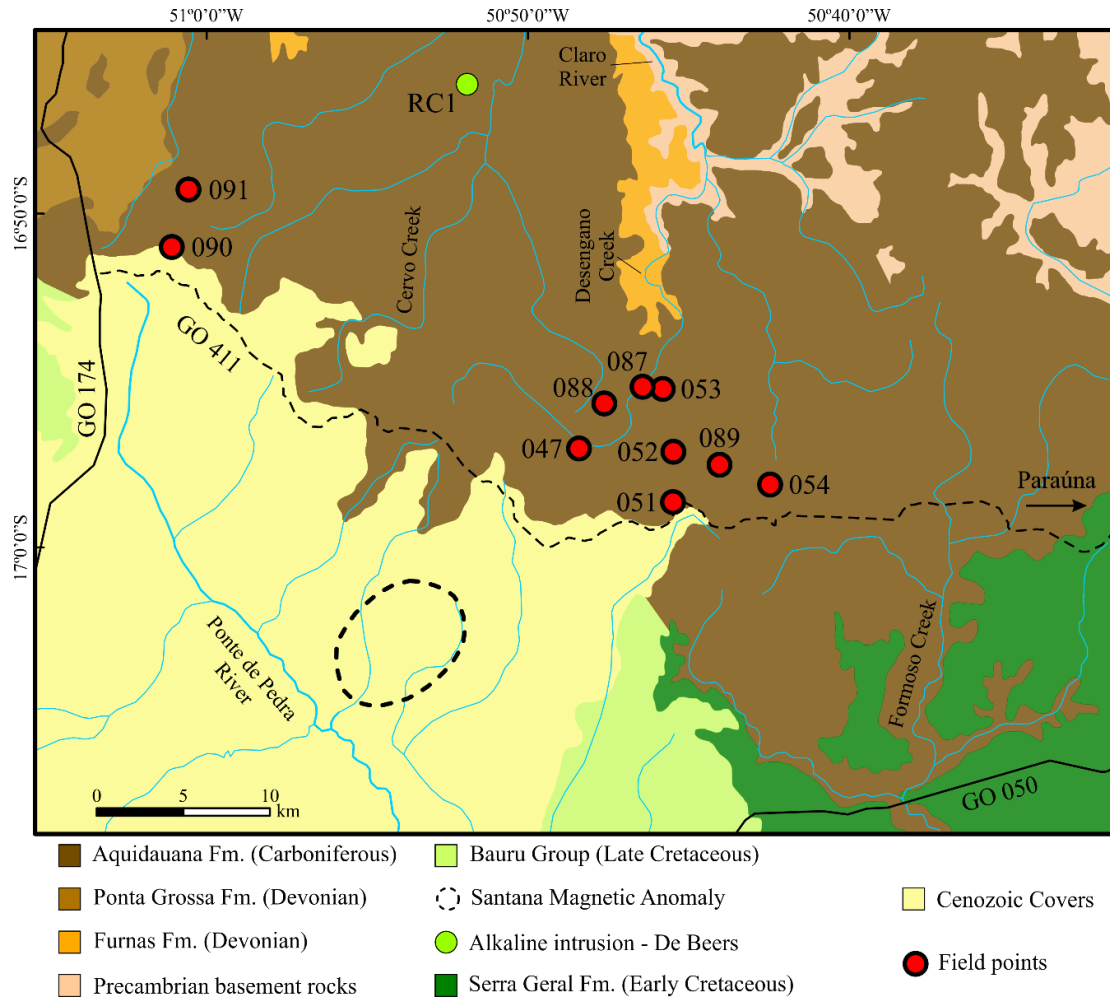


Figure 2.11 Detailed geological map of the Paraúna region (modified after Pena *et al.*, 1975; Moreira *et al.*, 2008; Cabral Neto *et al.*, 2017).

Southern GAP

Voluminous kamafugite lavas and pyroclastic deposits (at least 23 km³), locally accompanied by extrusive carbonatites, crops out near Santo Antônio da Barra (SAB), in the extreme south of the GAP (Junqueira-Brod *et al.*, 2002 – **Figure 2.7**). Several dykes and plugs composed mostly of kamafugites, with rare phonolites, also occur intrusive into the entire volcanic sequence. The SAB volcanism is limited to NE and SW by major extensional faults, and probably was controlled by N40°-50°W fractures and faults aligned across the conduits. Additionally, the numerous subvolcanic bodies (more than 80) probably acted as magma feeders of the volcanism (Gaspar & Danni 1981; Junqueira-Brod *et al.*, 2002).

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Detailed geological mapping in the SAB region established three main volcanic packages with alternating amounts of lavas and breccias. These rocks regionally overlap the tholeiitic basalt lava flows of the Serra Geral Formation (Gaspar, 1977; Moraes, 1984; Junqueira-Brod *et al.*, 2002). On the top of the volcanic sequence coeval epiclastic rocks (*i.e.* poorly-sorted sandstone and conglomerate) known as the Verdinho Formation were deposited (Gaspar & Danni, 1981). Furthermore, the sedimentary rocks of the Bauru Group covered all the SAB stratigraphy (Sgarbi & Gaspar 2002; Junqueira-Brod *et al.*, 2002; 2005a).

According to Junqueira-Brod *et al.* (2005a), the common presence of cognate nodules and disequilibrium textures indicates that shallow magma chambers occur beneath the SAB region. Moreover, carbonate-rich volcanic rocks containing up to 70% by volume of carbonate globules have been interpreted as evidence of liquid immiscibility processes (Junqueira-Brod *et al.*, 2005a). Gaspar & Danni (1981) stated that CO₂ is the main volatile phase of the SAB volcanism. Therefore, the SAB kamafugites have a complex petrogenesis involving different degrees of partial melting, fractional crystallization and almost certainly liquid immiscibility (*e.g.* Brod *et al.*, 2005; Junqueira-Brod *et al.*, 2005a).

Three other major alkaline bodies can be recognised in the GAP region based on geophysical data (see **Figure 2.7**):

- The Canadá Farm Anomaly (C – **Figure 2.7**) is the northernmost occurrence in the province. Campos (1977) reported a syenite outcrop in the Água Limpa River, and described, on drill core samples, mafic and ultramafic alkaline rocks (*e.g.* pyroxenites, nephelinites) *ca.* 50 m below the Cenozoic cover;
- The Registro do Araguaia Anomaly (R – **Figure 2.7**) similarly occurs in the northern GAP buried by thick Cenozoic cover (up to 1500 m – Dutra *et al.*, 2012). Pena *et al.*, (1975) reported the occurrence of a syenite outcrop in a lake above the anomaly region.

- The Santana Anomaly (S – **Figure 2.7**) occurs in the southern GAP, between the AE and Paraúna regions. It is covered by thick reddish latosols (up to 150 m – Prospec, 1972), but some silexite blocks with extremely altered fragments of alkaline rocks can be found in the region.

2.4 Economic Aspects

Historically two main resources, lateritic nickel and diamonds, have been targeted for exploration in the GAP region (*e.g.* Pena & Figueiredo, 1972; Pena *et al.*, 1975). Most of the alkaline mafic-ultramafic plutonic complexes in the northern portion of the province are associated with lateritic Ni deposits in their ultramafic zones (*e.g.* Lessa Sobrinho & Andrade, 1971; Justo, 1972; Chaban, 1973; Barbour, 1976; Melfi *et al.*, 1988; Biondi, 2005). These mineralizations are composed mostly of silicated ore type (*i.e.* garnierite), comprising a total estimated reserve of *ca.* 200 Mt with at least 1.1 wt.% Ni (Melfi *et al.*, 1988; Biondi, 2005).

Alluvial diamond deposits in the GAP region have been exploited by artisanal mining (*i.e.* *garimpeiros* – Svisero *et al.*, 2017), chiefly in the Bonito, Caiapó, Claro and Santa Marta rivers (*e.g.* Pena & Figueiredo, 1972; Tompkins, 1987). Bez *et al.* (1971a) earlier suggested that possible kimberlites intrusive in the Paraúna region were the most likely source of these alluvial diamonds. Similarly, Danni *et al.* (1990) proposed that leucite-bearing rocks outcropping along the *Cuesta* of Caiapó (*i.e.* in the AE region) could represent an alternative source. On the other hand, conglomerates from the Vila Maria, Furnas, Aquidauana formations, and, mainly, from the Bauru Group have been considered as the main source of the alluvial diamonds in the GAP region (Pena & Figueiredo, 1972; Tompkins, 1987). Noticeably there is a considerable debate if such diamonds derived from primary (*i.e.* the GAP alkaline rocks) or secondary sources (*i.e.* the Phanerozoic conglomerates).

A major breakthrough regarding the GAP exploration targets has taken place owing to the recent description of the kamafugite-carbonatite association in the Morro Preto complex,

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northern GAP (Nascimento, 2018). This association give rise to important world-class multi-commodity deposits such as Araxá (Nb, P, REE, Ba), Catalão I (P, Nb, Ti, Ba, REE, vermiculite), and Phalaborwa (Cu, U, Zr, P, Ti – Ribeiro *et al.*, 2014). Besides, extrusive carbonatites associated with kamaugites have been characterized in the SAB and AE regions, southern GAP (Garpar & Danni, 1981; Junqueira-Brod *et al.*, 2005a). Therefore, the existence of carbonatite magmas in the GAP increases enormously the potential of the region for multiple mineralizations, well beyond those historically known.

Chapter 3

Field Geology and Petrography

3.1 Field Characteristics

The GAP comprises a vast collection of igneous bodies, including dykes, sills, plugs, diatremes, lavas, pyroclastic deposits and major plutonic complexes (**Section 2.3**). In view of the research aims, the present study focuses on collecting those rocks that best represent magmas (*i.e.* fine-grained rocks) in as many occurrences as possible within the GAP. Hence, the main features of sampling locations for this study (**Figure 3.1**) are briefly described.

Santo Antônio da Barra

Lavas crop out through the whole SAB region. They are usually weathered to brown fertile soils. Nevertheless, fresh volcanic rocks are well exposed along the drainages (*e.g.* Verdinho River – **Figure 3.2**) or in small rounded hills. A great diversity of mafic rocks is present, varying from porphyritic to aphanitic types. They are dark grey in colour, strongly

magnetic, and may show late-stage hydraulic fracturing (**Figure 3.3**). Porphyritic types include olivine, pyroxene and leucite phenocrysts (not necessarily in the same rock) set in an aphanitic groundmass. The sample suite is divided into two groups: (1) with abundant coarse-grained phenocrysts, particularly of olivine and clinopyroxene, and (2) with sparse clinopyroxene microphenocrysts. Ultramafic nodules (< 30 mm) may be present in both. It was also found extrusive rocks very rich in carbonate globules surrounded by dark grey aphanitic groundmass (see **Figure 3.4**). Moreover, a small rounded block of vesiculated trachyte (**Figure 3.5**) was sampled from the overlying rocks of the Verdinho Fm. (Gaspar & Danni, 1981).

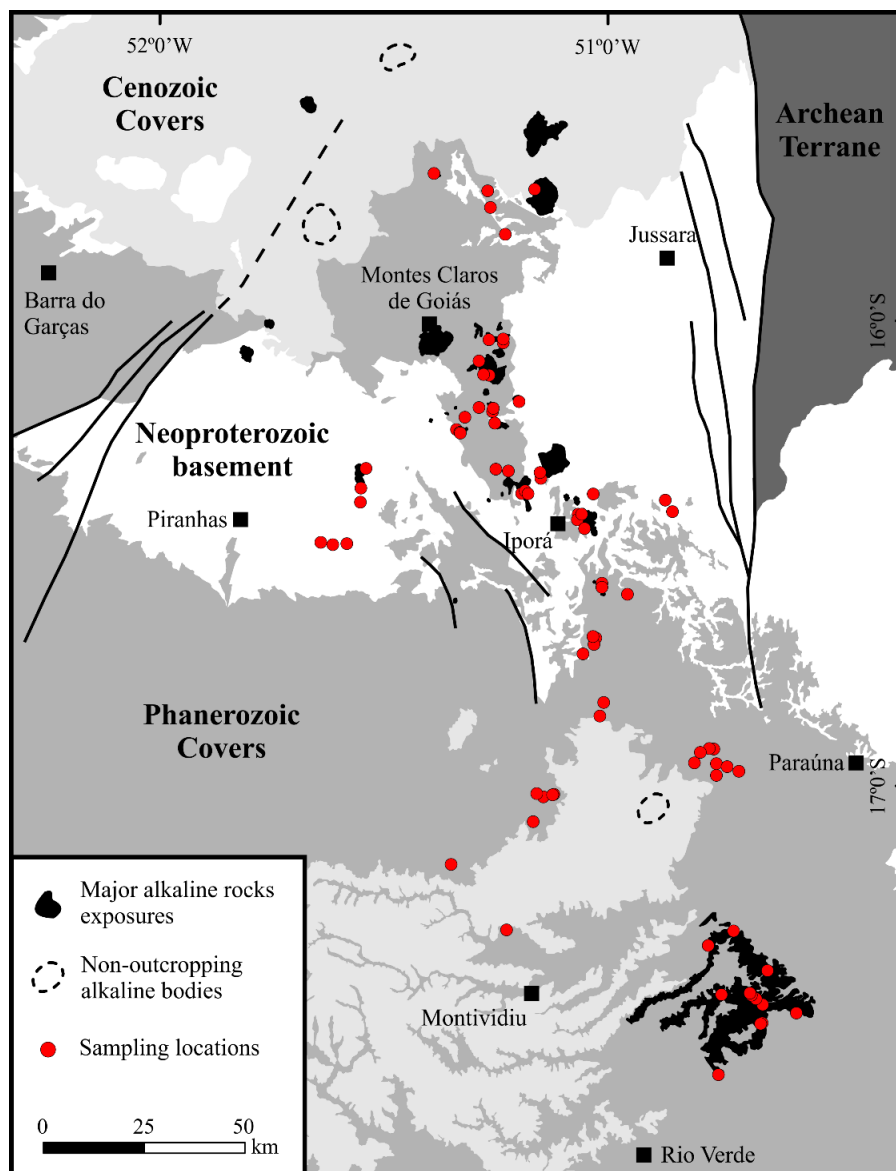


Figure 3.1 Simplified geological map of the GAP showing the sampling locations for this study.



Figure 3.2 Porphyritic autobreccia (aa lavas) outcrop along the Verdinho River (SAB 001). Note that the number in parentheses corresponds to the field points (see [Appendix A](#)) in all figures.



Figure 3.3 Typically aphanitic lava flow showing brittle, low-temperature, hydraulic fracturing filled by secondary carbonate (SAB 008). Pencil size for scale = 144 mm.

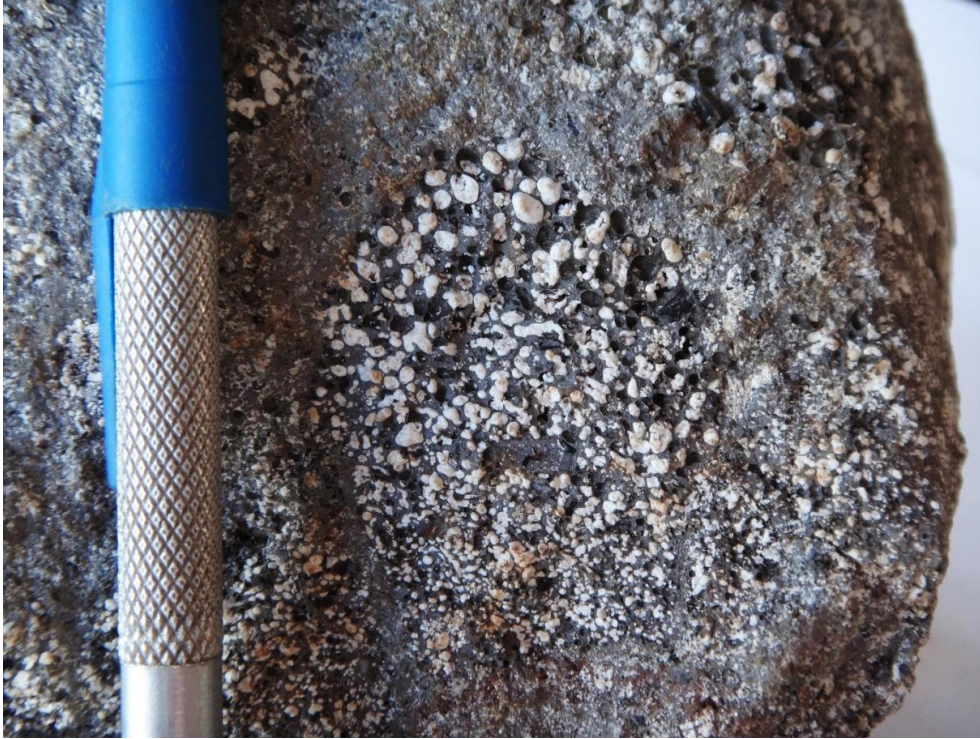


Figure 3.4 Volcanic rock composed of several dark grey rounded fragments (~50 mm) set in a light grey groundmass with pyroxene and magnetite microphenocrysts (SAB TT). The fragments contain plenty of carbonate globules in a dark grey groundmass.



Figure 3.5 Porphyritic trachyte with abundant feldspar microphenocrysts set in a pinkish grey groundmass (07/04 SB). The feldspars seem to be fairly oriented in groundmas. Also note the presence of some vesicles (up to 10 mm) filled by calcite.

Águas Emendadas

The AE region is remarkable because of its diatreme structures, which have been systematically detailed in previous studies (*e.g.* Junqueira-Brod *et al.*, 2004; 2005b). In this study, sampling was focused on dykes and on the freshest lava blocks eroded from diatremes by crosscutting drainages (**Figure 3.6**). Most of the blocks represent juvenile magma fragments erupted together with the pyroclastic rocks during explosive activity. Nevertheless, true lavas occur covering the diatreme breccias as well, and, then, may include some of the sampled lava blocks (**Figure 3.7**).



Figure 3.6 Numerous lava blocks ‘sampled’ by drainage from the Neuzinha diatreme (NEU 046).

A wide variety of mafic rocks was collected in four different diatreme bodies (Águas Emendadas, Neuzinha, Tigre and Marimbondo). The sample suite varies from aphanitic to strongly porphyritic types. The former is dark grey, strongly magnetic, occasionally containing small (< 1 mm) clinopyroxene crystals, and more rarely, phlogopite phenocrysts. Porphyritic rocks show mainly olivine, clinopyroxene and leucite phenocrysts, with minor phlogopite. In

general, coarse-grained crystals occur in large amounts set in a fine-grained groundmass. Small (< 1 mm) crystals may be abundant or scarce and are commonly associated with aphanitic groundmass. Dykes were sampled only in the Águas Emendadas body. They often comprise clinopyroxene, phlogopite, and sometimes, plagioclase microphenocrysts set in a dark grey aphanitic groundmass.



Figure 3.7 Lava flow covering the breccias on the top of the Águas Emendadas diatreme (AE 060).

Paraúna

An important dyke swarm accompanied by a small number of plugs occurs in the Serra da Portaria region (**Section 2.1**), *ca.* 45 km west of Paraúna (**Figure 3.1**). These subvolcanic bodies are mostly intrusive into the Aquidauana Fm. pinkish-reddish sandstones, which developed a mottled texture as well as thermal fractures close to the contact with the alkaline intrusions (**Figure 3.8**). The Paraúna dykes, in general, have a considerable size (~ 10 m wide), extending over hundreds of meters in the WSW-ENE direction (**Figure 3.9**). In contrast, the plugs are much smaller, often less than 50 m in diameter.



Figure 3.8 Pinkish sandstones of the Aquidauana Fm. showing mottled texture and thermal fractures associated with a nearby alkaline intrusion (PAR 088).



Figure 3.9 A sequence of blocks aligned in a preferential direction for more than 250 m, defining a dyke with ~5 m width. Note the typical columnar jointing faces on some of the blocks (PAR 053).

Chapter 3: Field Geology and Petrography

These hypabyssal bodies consist of dark grey, clinopyroxene-rich rocks, frequently exhibiting coarse-grained porphyritic textures (**Figure 3.10**). Interestingly, in all outcrops except one, olivine phenocrysts occur only in subordinate amounts. Flow texture marked by the preferential alignment of clinopyroxene prisms (**Figure 3.10**) as well as columnar jointing are common features of the Paraúna dykes. In some outcrops, the flow directions appear to be parallel to the columnar joints, whereas in others it appears to be sub-vertical, demonstrating that the magma was moving. Locally, these porphyritic rocks show a fine-grained groundmass containing leucite and phlogopite. Ultramafic nodules (up to 30 mm) also may occur, mainly in those rocks that exhibit reduced amounts of clinopyroxene phenocrysts, set in a more aphanitic groundmass.



Figure 3.10 Block of a coarse-grained porphyritic rock, showing plenty of clinopyroxene phenocrysts that are aligned because of magmatic flow (PAR 051).

In addition, during fieldwork, it has been found a singular outcrop that resembles the AE breccia pipes. It comprises a wide variety of rock types, including aphanitic (**Figure 3.11**), coarse-grained porphyritic, and leucite-rich rocks (**Figure 3.12**). The latter often shows

glomeroporphyritic texture (**Figure 3.13**) and clinopyroxene phenocrysts of up to 30 mm size. Moreover, occur some rocks very rich in carbonate globules set in a brownish grey, extremely oxidized groundmass, with olivine and clinopyroxene phenocrysts (**Figure 3.14**).



Figure 3.11 Aphanitic mafic rock with scarce and small (< 0.5 mm) clinopyroxene phenocrysts (PAR 088).



Figure 3.12 Leucite-phyric rock with abundant leucite and clinopyroxene phenocrysts set in a brownish grey aphanitic groundmass (PAR 088).



Figure 3.13 Detail of glomeroporphyritic texture formed by tiny leucite crystals surrounding a large clinopyroxene phenocryst (PAR 088).



Figure 3.14 Rock composed of abundant carbonate globules set in a brownish grey groundmass. Note the black clinopyroxene phenocrysts as well as some reddish (altered) olivine crystals close to the tip of the pencil (PAR 088).

Amorinópolis

Near the town of Amorinópolis in the central GAP (**Figure 3.1**), there are some minor intrusions (dykes, sills and plugs) as well as the large volcanic-subvolcanic complex of Amorinópolis (**Figure 3.15**). Some dark grey aphanitic dykes and plugs typically display columnar jointing (**Figure 3.16**). A few radial dykes (5 m wide) that extend for hundreds of meters, and a small plug of *ca.* 100 m diameter, occur near the Amorinópolis complex. They comprise mostly dark grey, strongly magnetic, aphanitic mafic rocks, with rare clinopyroxene microphenocrysts. Otherwise, in the Amorinópolis complex, olivine-phyric rocks with plenty ultramafic nodules (< 50 mm) dominate. To the east of the Amorinópolis town, a series of small (up to 300 m in diameter – *e.g.* Danni *et al.*, 1994a) sills and plugs consisting mainly of clinopyroxene and feldspar phenocrysts (up to 10 mm) set in a light grey (felsic) aphanitic groundmass occur.



Figure 3.15 View of the large Amorinópolis volcanic-subvolcanic complex in the background.



Figure 3.16 Columnar jointing in an aphanitic mafic dyke adjacent to the Amarinópolis complex (AMO 014). The dyke has ~5 m width and extends for more than 200 m in NNW direction.

Northern GAP

Sampling in the northern portion of the GAP consists of dykes, sills and plugs outcropping in the Arenópolis, Diorama, Iporá, Monte Claros de Goiás and Santa Fé regions (**Figure 3.1**). In the Morro do Engenho, Morro Preto, and Água Branca surrounds, was found only coarse-grained serpentinized ultramafic rocks. Extensive lateritic surface, silicite blocks, thick soils and alluvial deposits made it very difficult to locate fine-grained rocks (*e.g.* dykes) inside and outside of these complexes.

Relatively thin (< 0.5 m wide) mafic and felsic dykes occur in the other large alkaline plutonic complexes or crosscut the Precambrian basement (**Figure 3.17**). They are typically aphanitic, strongly fractured, varying from dark to light grey, and also may show textural variations most likely as a result of flow differentiation (**Figure 3.18** and **3.19**). Phlogopite, and more rarely, clinopyroxene and olivine xeno/phenocrysts (up to 10 mm) may occur set in their aphanitic groundmass (**Figure 3.19**).

It is noteworthy that most of these thin aphanitic dykes were emplaced under brittle conditions, both in basement granites and in the Late Cretaceous plutonic alkaline rocks (**Figure 3.17** and **3.18**). The common presence of irregular borders, indentation (**Figure 3.20**) and wall rock fragments (**Figure 3.21**) indicates that the magmas ascent through these dykes under turbulent flow. Additionally, chilled margins are characteristic for such dykes (**Figure 3.18** and **3.22**).



Figure 3.17 Dark grey sinuous aphanitic dyke (~0.2 m wide), strongly fractured, intruding a post-tectonic coarse-grained granite (ARE 064).



Figure 3.18 Mafic dyke (~0.4 m wide) crosscutting orthogneiss with sub-vertical (060/70°) foliation (RC 058). There is a quench zone at the dyke margins (~50 mm wide), as well as an increase in the number of vesicles filled with carbonate toward the centre of the dyke.



Figure 3.19 Dark grey aphanitic dyke (~0.2 m thickness) intrusive into Late Cretaceous coarse-grained nepheline syenite (FB 017). Note the concentration of clinopyroxene and minor olivine macrocrysts close to one of the dyke walls. The irregular margins of the dyke are also visible.



Figure 3.20 Another portion of the dark grey aphanitic dyke with ~0.2 m width (see Figure 3.19) showing remarkable indentation (FB 017).



Figure 3.21 Wall-rock xenolith of up to 30 mm width inside mafic dyke (RC 058). Note the chilled margin close to the contact zone. Interestingly, it appears that fenitization does not occur in the wall rock (*i.e.* left-hand side), which suggests that there was no escape of volatiles.

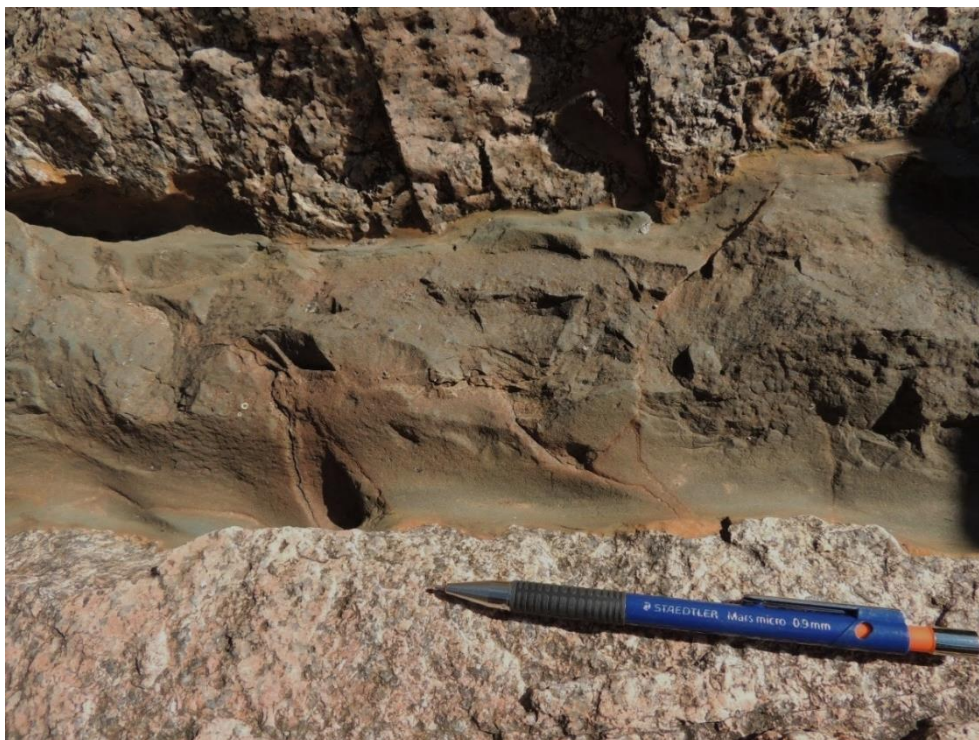


Figure 3.22 Dark grey aphanitic dyke (~0.1 m wide) intrusive into a post-tectonic pink granite (MM 023). Note the presence of chilled margins as well as a fenitized portion adjacent to the contact zone, modifying locally the colour of the granite (white rather than pink). This is evidence for escape of volatiles.

Another type of dyke occurs emplaced into the sedimentary rocks of the Paraná Basin and in the Precambrian rocks. In general, these dykes are strongly porphyritic, up to 25 m size, and extend for more than a hundred meters (**Figure 3.23**). They are composed mostly of coarse-grained olivine and clinopyroxene phenocrysts set in a dark grey, strongly magnetic, fine-grained groundmass (**Figure 3.24**). Some of these rocks may have plagioclase or leucite crystals scattered in the groundmass. Moreover, a crystal-rich dyke intrusive into Paleoproterozoic orthogneiss exhibits an extraordinary degassing texture (**Figure 3.25**).

The present study also found phonolite dykes in the northern GAP. They are a few meters wide (< 10 m) but may extend for more than a kilometre. These rocks are aphanitic or strongly porphyritic, showing the typical greenish grey colour of phonolites. Sanidine, and minor clinopyroxene, phenocrysts occur in an aphanitic groundmass. Flow texture is locally noted by the preferential orientation of sanidine phenocrysts (**Figure 3.26**).



Figure 3.23 Porphyritic mafic dyke (*i.e.* aligned blocks) have up to 10 m width and extends for more than 150 m in a NNW direction (ARE 027).



Figure 3.24 Strongly porphyritic texture of a crystal-rich dykes (ARE 028). Olivine and clinopyroxene phenocrysts may reach ~15 mm in size.



Figure 3.25 Crystal-rich mafic dyke (~1.5 m wide) intrusive into Paleoproterozoic orthogneiss (ARE 031). Note the remarkable fenitized zone (degassing feature) of ~0.5 m thickness.

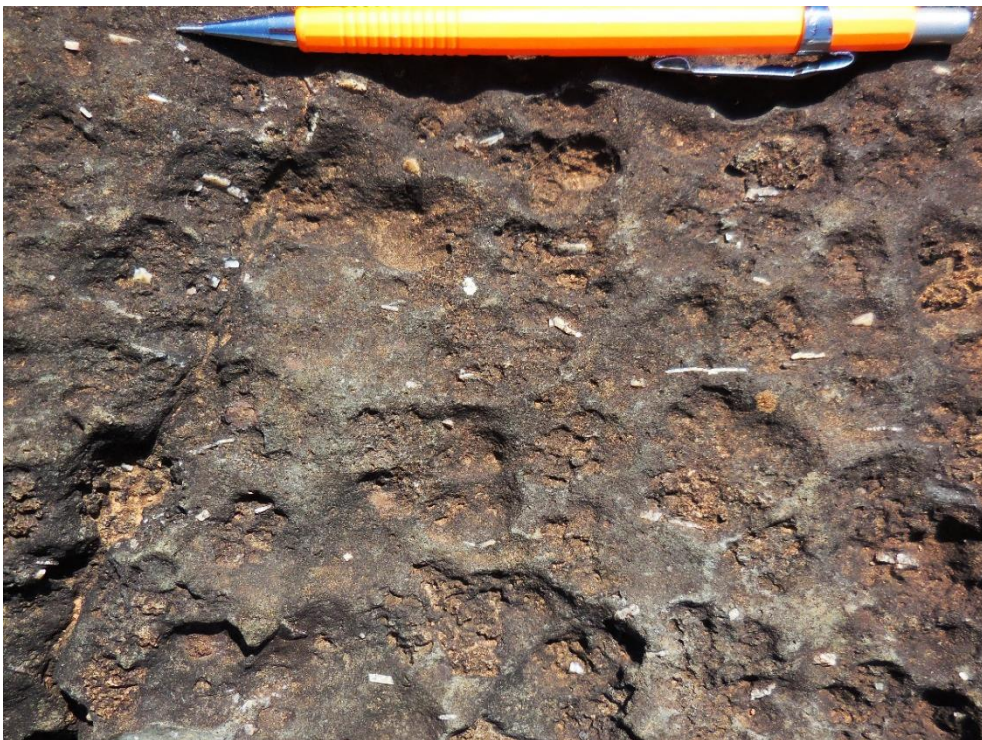


Figure 3.26 Phonolite dyke showing slightly oriented up to 20 mm large sanidine phenocrysts (MTA 061).

Sills and plugs are mostly intrusive into the sandstones of the Furnas and Ponta Grossa formations, which often show columnar jointing due to the thermal effect of the alkaline intrusions (**Figure 3.27**). Two distinct rock types appear to be associated with these bodies. The first type is characterized by scarce olivine, clinopyroxene and plagioclase microphenocrysts set into a fine-grained brownish grey groundmass. In addition, these rocks frequently display small (< 1 mm) rounded carbonate globules. The second type comprises porphyritic rocks with abundant coarse-grained olivine and clinopyroxene phenocrysts, usually set into an aphanitic, strongly magnetic, dark grey groundmass. Leucite, plagioclase and phlogopite may occur locally as tiny crystals in the groundmass.

A large trachyte sill (~300 m in size) composed of abundant feldspar phenocrysts set into a pinkish grey groundmass also crops out close to the Diorama region.



Figure 3.27 Columnar jointing in a sandstone of the Ponta Grossa Fm., which was intruded by a sill of alkaline rock (DIO 033).

3.2 Petrography

Most of the studied rocks are dark grey in colour, strongly magnetic, and exhibit a porphyritic texture dominated by olivine and clinopyroxene macrocrysts set in fine-grained or

aphanitic groundmass. Detailed petrography and electron microprobe analyses allowed to establish two distinct petrographic groups: (1) feldspar-free mafic rocks; (2) feldspar-bearing mafic and felsic rocks.

Feldspar-free Mafic Rocks

Nomenclature and classification of the volcanic and subvolcanic rocks included in this group attempt to follow, initially, the International Union of Geological Sciences (IUGS) recommendations (*i.e.* Le Maitre *et al.*, 2002). However, as discussed in the next chapter, the feldspar-free volcanic rocks of the GAP contain a rare mineral assemblage that prevents them to be classified according to any of the existing nomenclature system. Hence, the rock terms given in the following are in accordance with the recommendations of Oliveira *et al.* (2022) – see **Chapter 4**.

➤ **Kalsilite-Olivine Nephelinite (or Potassic Olivine Nephelinite)**

These rocks are leucite-poor or leucite-free types, which contain dominant nepheline with or without kalsilite in the groundmass (kalsilite can simply not have been identified yet). Olivine is almost always the only phenocryst set in a dark grey cryptocrystalline groundmass (**Figure 3.28**). The groundmass is normally composed of Fe-Ti oxides, perovskite, pale-yellow pyroxene, interstitial nepheline and/or kalsilite, carbonate and late-stage phlogopite (**Figure 3.29**). Small rounded crystals of leucite are sometimes found in the groundmass. Ultramafic nodules (up to 3 mm in size), and olivine xenocrysts with characteristic undulose extinction, may also occur in some samples (**Figure 3.30**).

Olivine phenocrysts (up to 3.5 mm) are subhedral to anhedral, often fractured, and sometimes show irregular outlines. Euhedral opaque inclusions are very common in these crystals. Microphenocrysts vary from euhedral to anhedral, occasionally being skeletal. In some samples olivine is partially altered to yellowish red ‘iddingsite’ or strong green ‘bowlingite’. These represent a mixture of various secondary minerals.

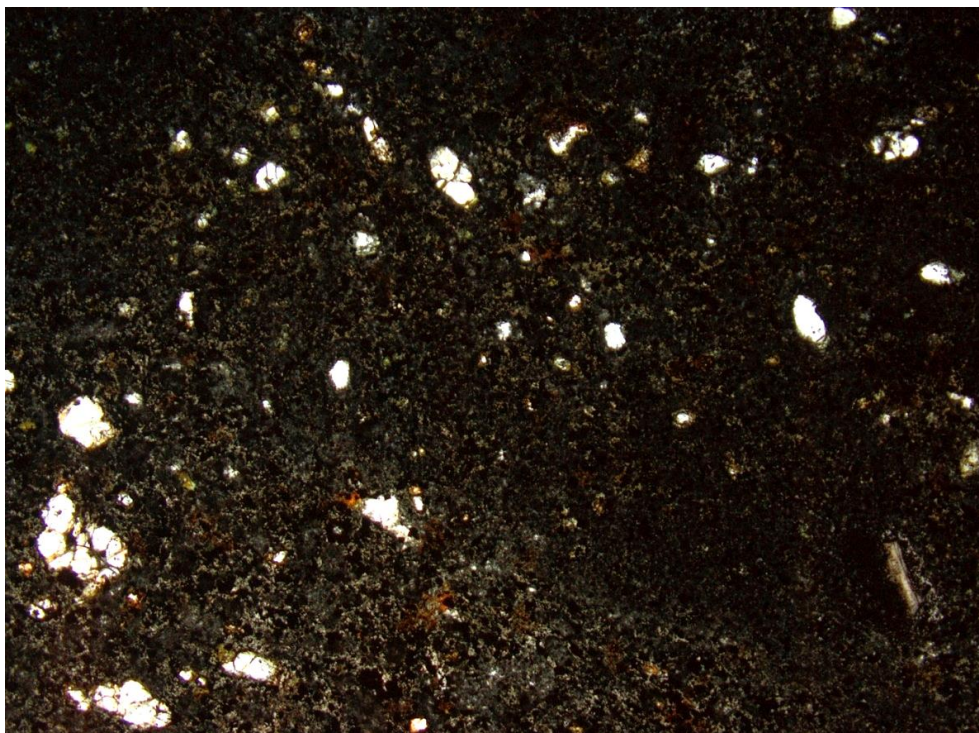


Figure 3.28 Olivine and rare pyroxene microphenocrysts (in the bottom right-hand corner) set into a cryptocrystalline groundmass. The latter is composed of pale-yellow pyroxene microlites, Fe-Ti oxides, perovskite and an interstitial felsic phase. Poikilitic phlogopite occurs as a late phase.

Neuzinha (NEU 046A) – magnification x 2.5 – PPL. Field of view is 5.7 x 4.2 mm.

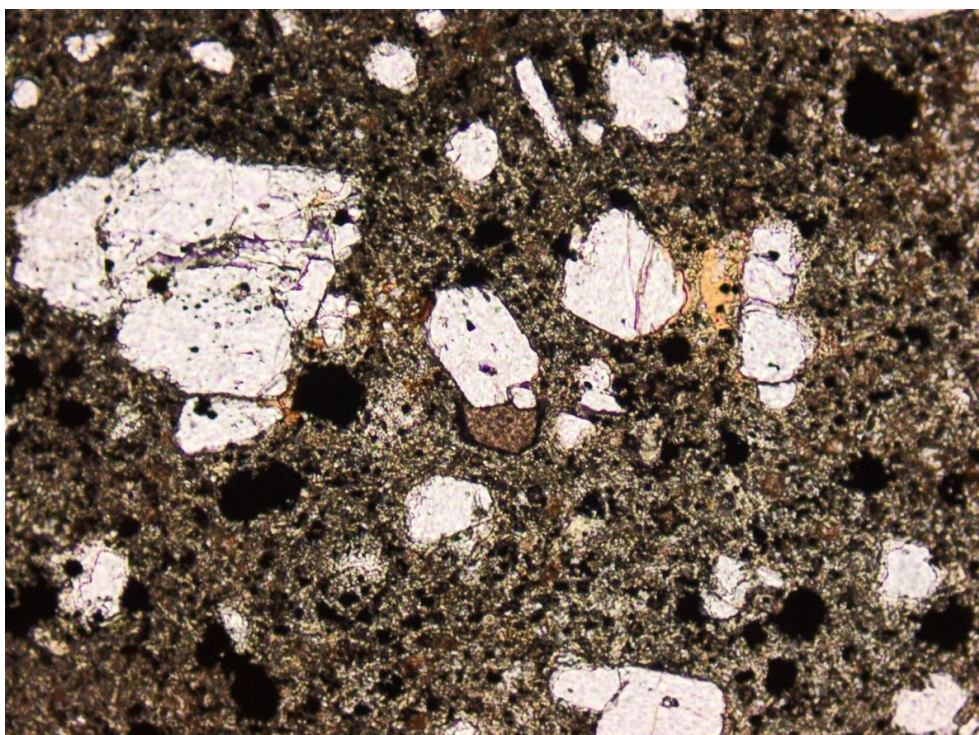


Figure 3.29 Olivine, Fe-Ti oxides and perovskite microphenocrysts (in the centre of the field of view) set into a cryptocrystalline groundmass. Phlogopite often occurs associated with olivine crystals.

Amorinópolis (AMO 015A) – magnification x 10 – PPL. Field of view is 1.4 x 1.0 mm.

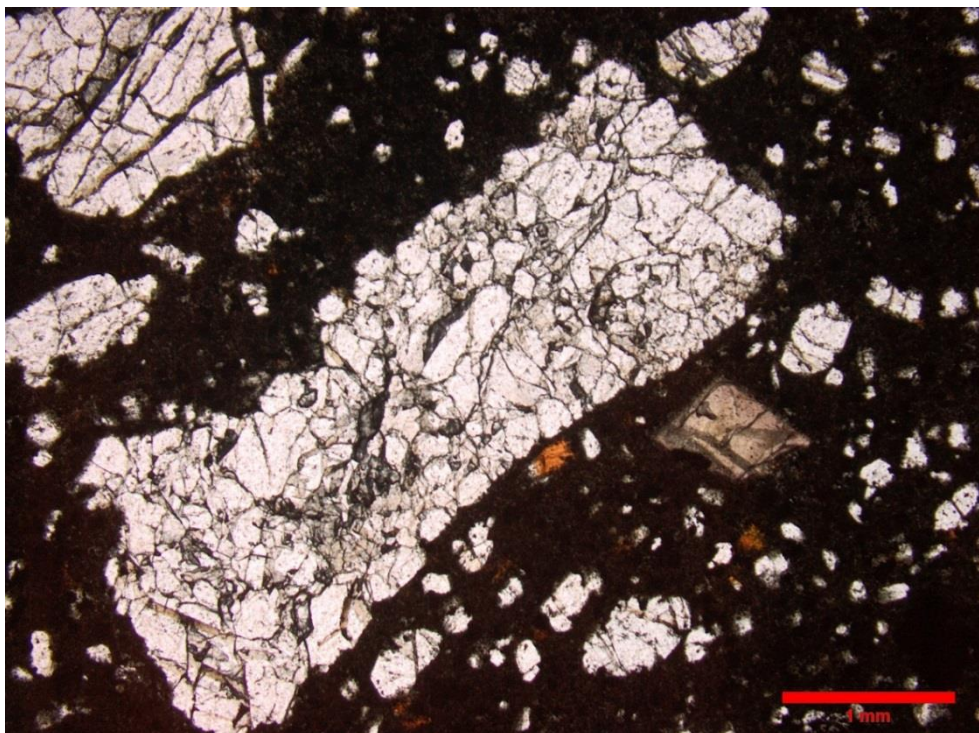


Figure 3.30 Recrystallized ultramafic nodule, composed essentially of olivine, set in a cryptocrystalline groundmass. Note the abundance of anhedral to subhedral fractured olivine crystals in the surroundings. The red scale bar is 1 mm in size for all figures at 2.5x magnification.

Amorinópolis (AMO 015A) – magnification x 2.5 – PPL. Field of view is 5.7 x 4.2 mm.

Rare clinopyroxene phenocrysts (up to 7 mm) often show pale yellow cores and pleochroic pale yellow to purple-lilac rims. These crystals may contain plenty of opaque inclusions, mainly at the rims. Microphenocrysts, when present, are devoid of inclusions and seem to have crystallized together with the rims of larger crystals. Continuous zoning and twinning are common in the clinopyroxene phenocrysts. In the groundmass, the pale-yellow clinopyroxene prisms may sometimes display flow orientation.

Poikilitic late-stage phlogopite (up to 1.2 mm) occurs widespread in the groundmass, mostly associated with olivine phenocrysts. Phlogopite also often shows a pale-orange to dark orange normal pleochroism. Fe-Ti oxides and perovskite essentially occur as microlites in the groundmass but can also be found as microphenocrysts (**Figure 3.29**).

The interstitial felsic phase is usually colourless in plane-polarised light and shows bluish grey interference colours in the XPL view, sometimes with radiating extinction. It is

probably a feldspathoid (nepheline or kalsilite – see **Chapter 4**) that has been partially altered to secondary zeolites.

➤ **Potassic Leucite-Olivine Nephelinite**

The potassic leucite-olivine nephelinites contain significant amounts of leucite in the groundmass. These rocks also contain a much larger amount of macrocrysts, both olivine and clinopyroxene (**Figure 3.31** and **3.32**). The groundmass is fine-grained and composed of abundant Fe-Ti oxides, pale-yellow clinopyroxene, perovskite, phlogopite and two distinct colourless phases. One is consistently rounded and isotropic (leucite), whereas the other (nepheline) is typically interstitial, with low interference colours, occasionally forming euhedral crystals.

Olivine occurs chiefly as phenocrysts. They are euhedral to subhedral (up to 4.8 mm), often fractured and altered to ‘iddingsite’ / ‘bowlingite’. It also may show rounded outlines, which suggests disequilibrium with the groundmass (**Figure 3.31**). Besides, small euhedral opaque inclusions are common. In some samples are found xenocrysts displaying undulose extinction, recrystallization and some deformation texture (**Figure 3.31** and **3.33**).

Clinopyroxene is the dominant phenocryst in these rocks, occasionally forming seriate and glomeroporphyritic textures. Twinning and continuous zoning patterns are common features (**Figure 3.32**). At least two types of clinopyroxene phenocrysts are recognizable. One is euhedral to subhedral (up to 8 mm), pale-beige in colour, frequently showing a marked purple-lilac rim. It commonly has irregular outlines and plenty of inclusions (Fe-Ti oxides, perovskite, apatite) along the rims, which suggests crystallization at the same time as the groundmass. The second type of clinopyroxene (up to 1.5 mm) is characterized by green cores, intermediate pale-beige zones, and dark purple outer rims (**Figure 3.34**). Tiny opaque needles seem to occur in the green cores.

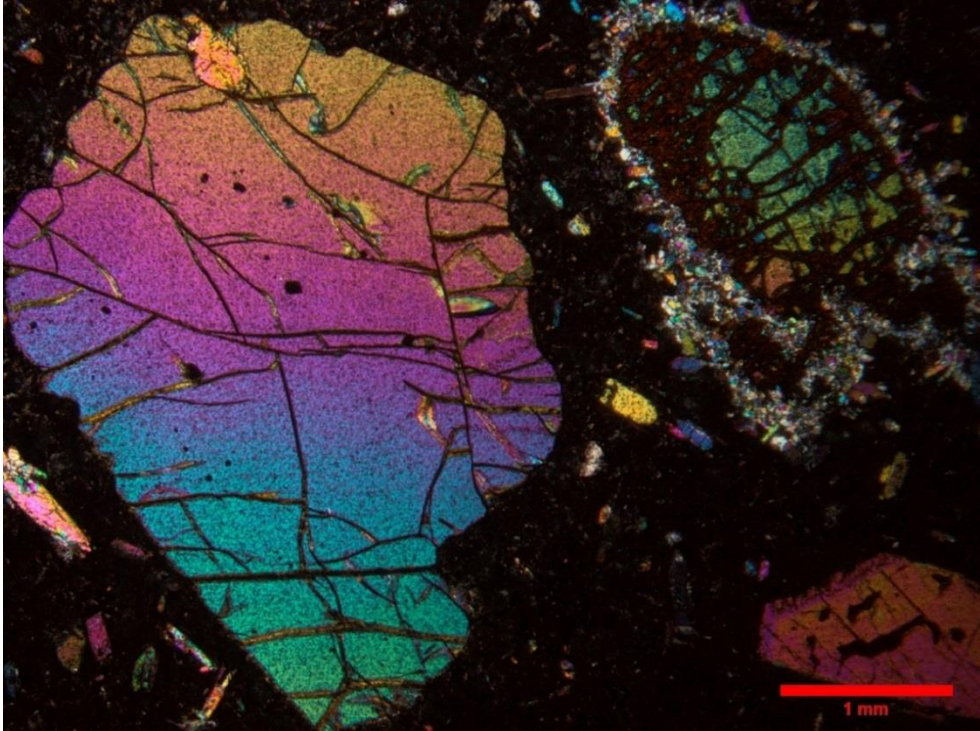


Figure 3.31 Large olivine phenocrysts set into a fine-grained groundmass. There are at least two types of olivine. The crystal in the top right-hand corner appears to be strongly recrystallized at the borders, suggesting that it is a xenocryst, whereas the crystal at the left, displays curved and embayed faces.

Paraúna (PAR 054) – magnification $\times 2.5$ – XPL. Field of view is 5.7×4.2 mm.

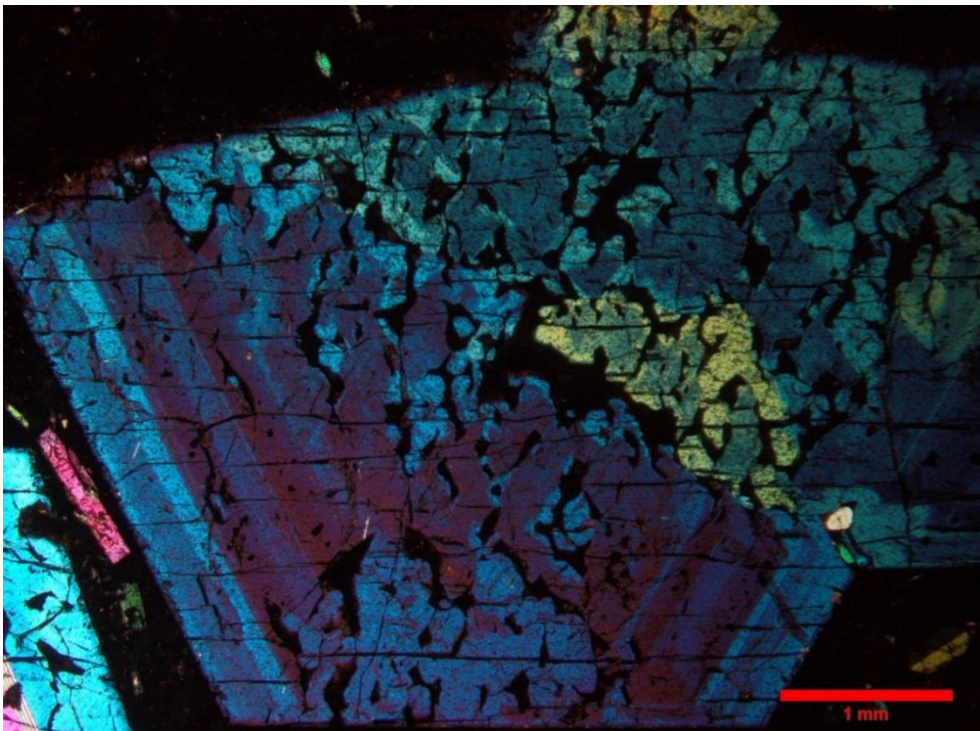


Figure 3.32 Large clinopyroxene phenocryst showing a continuous zoning pattern and plenty of melt inclusions (?).

Paraúna (PAR 054) – magnification $\times 2.5$ – XPL. Field of view is 5.7×4.2 mm.

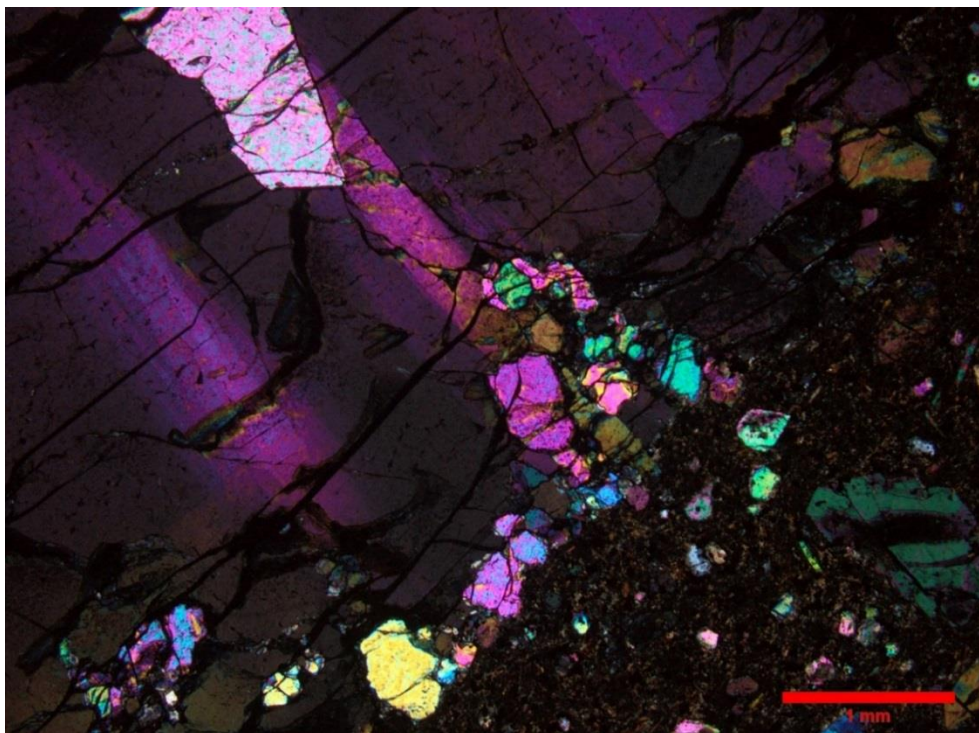


Figure 3.33 Large olivine xenocryst with undulose extinction and recrystallized rims set in a fine-grained groundmass.

Paraúna (PAR 090B) – magnification $\times 2.5$ – XPL. Field of view is 5.7 $\times$ 4.2 mm.

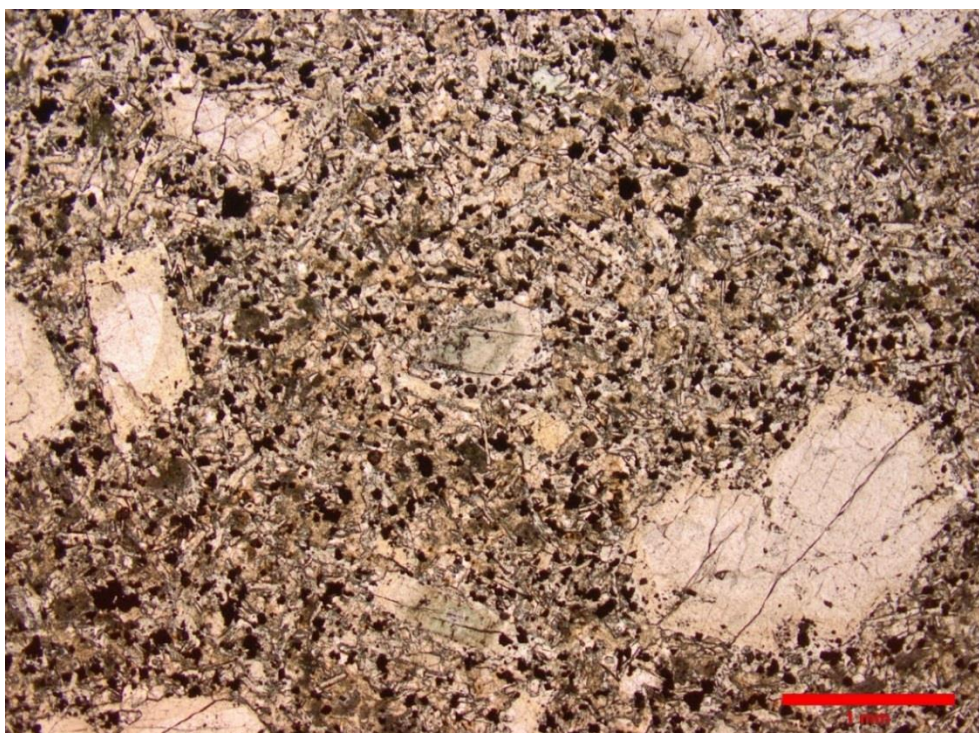


Figure 3.34 Two types of clinopyroxene phenocrysts set in a fine-grained groundmass. One type shows pale-beige core and a marked rim with abundant opaque inclusions (e.g. at the bottom right-hand corner). The other has green cores and lighter rims (e.g. in the centre of the view).

Santo Antônio da Barra (SAB 050C) – magnification $\times 2.5$ – PPL. Field of view is 5.7 $\times$ 4.2 mm.

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In some potassic leucite-olivine nephelinite samples occur notable ‘ghost’ phlogopite phenocrysts, showing pale orange to dark orange normal pleochroism. Such crystals (up to 4 mm in size) are in disequilibrium, being replaced by an assemblage of abundant opaque, clinopyroxene, isotropic and anisotropic felsic phases (probably feldspathoids), and a newly formed phlogopite.

➤ Potassic Olivine Leucitite

This group is distinguished from the others by the presence of leucite phenocrysts or microphenocrysts in addition to abundant olivine (**Figure 3.35** and **3.36**). Clinopyroxene is very rare as phenocrysts, being almost restricted to the groundmass. This is typically fine-grained, composed of abundant pale-yellow pyroxene, Fe-Ti oxides, phlogopite, apatite, rare perovskite and a brown isotropic phase (altered glass or leucite). In some samples there is an evident flow orientation of the clinopyroxene crystals in the groundmass (**Figure 3.36**). Furthermore, two types of phlogopite seem to occur. One is euhedral to subhedral laths with strongly zoned black rims. The other is a late-stage phase surrounding the olivine crystals.

Olivine and leucite phenocrysts commonly define a porphyritic seriate texture. Crystals of olivine are usually subhedral to anhedral (up to 3 mm), often fractured and altered along fractures to ‘iddingsite’ / ‘bowlingite’. Euhedral opaque inclusions are very common. These may also occur as rare phenocrysts (up to 0.9 mm). Rounded leucite phenocrysts are often strongly altered, showing brownish grey or beige colours. Leucite also have clinopyroxene inclusions, but these are uncommon.

Evidence of mixing between olivine nephelinite and olivine leucitite was found in sample NEU 046A (**Figure 3.37**). An interesting aspect is the occurrence of almost perfectly circular structures of ~1.5 mm width (**Figure 3.38**). They are composed of four- to six-sided feldspathoid (nepheline/kalsilite), pyroxene and a black isotropic phase (glass?). Phlogopite, perovskite, Fe-Ti oxides and a brownish rounded phase (leucite) may also be present.



Figure 3.35 Abundant subhedral olivine phenocrysts and altered leucite microphenocrysts (the rounded, brownish crystals) set in a fine-grained groundmass.

Northern GAP (SF 071A) – magnification $\times 2.5$ – PPL. Field of view is 5.7 x 4.2 mm.

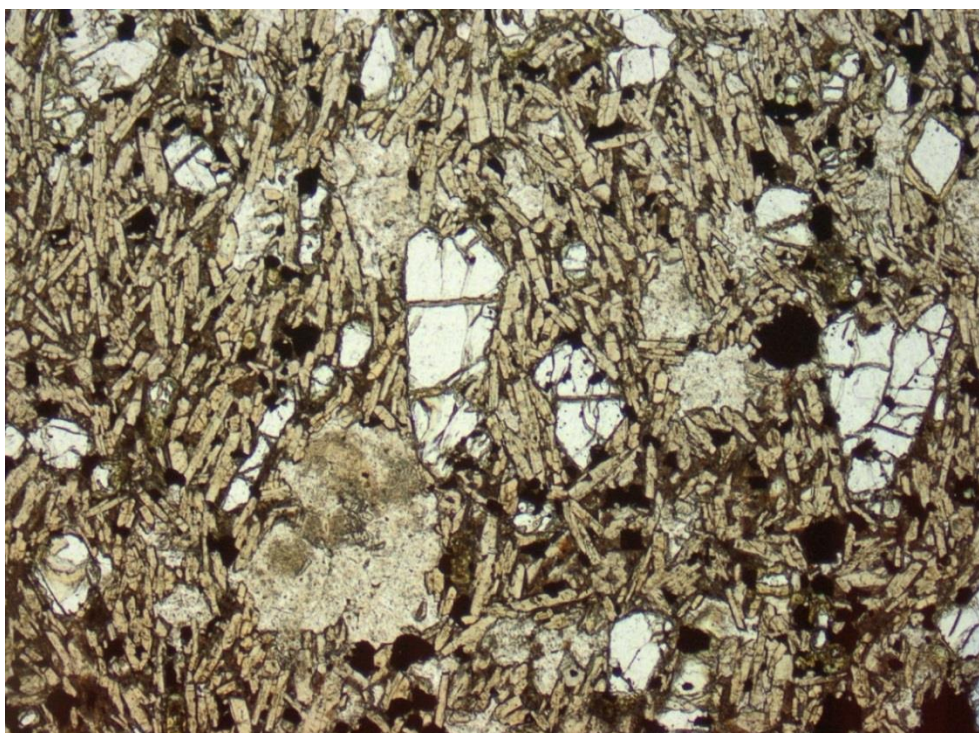


Figure 3.36 Pale-yellow clinopyroxene prisms with flow orientation in the groundmass. Note how the clinopyroxene prisms margin the olivine and altered leucite phenocrysts (at the bottom centre of the view).

Marimbondo (MAR 044B) – magnification $\times 4$ – PPL. Field of view is 3.6 x 2.6 mm.



Figure 3.37 Evidence of mixing between potassic olivine nephelinite (on left) and potassic olivine leucite (on right) magmas. Note the presence of abundant feldspathoid crystals along the contact zone and the almost perfectly circular structures at the top right corner.

Neuzinha (NEU 046A) – magnification x 2.5 – PPL. Field of view is 5.7 x 4.2 mm.

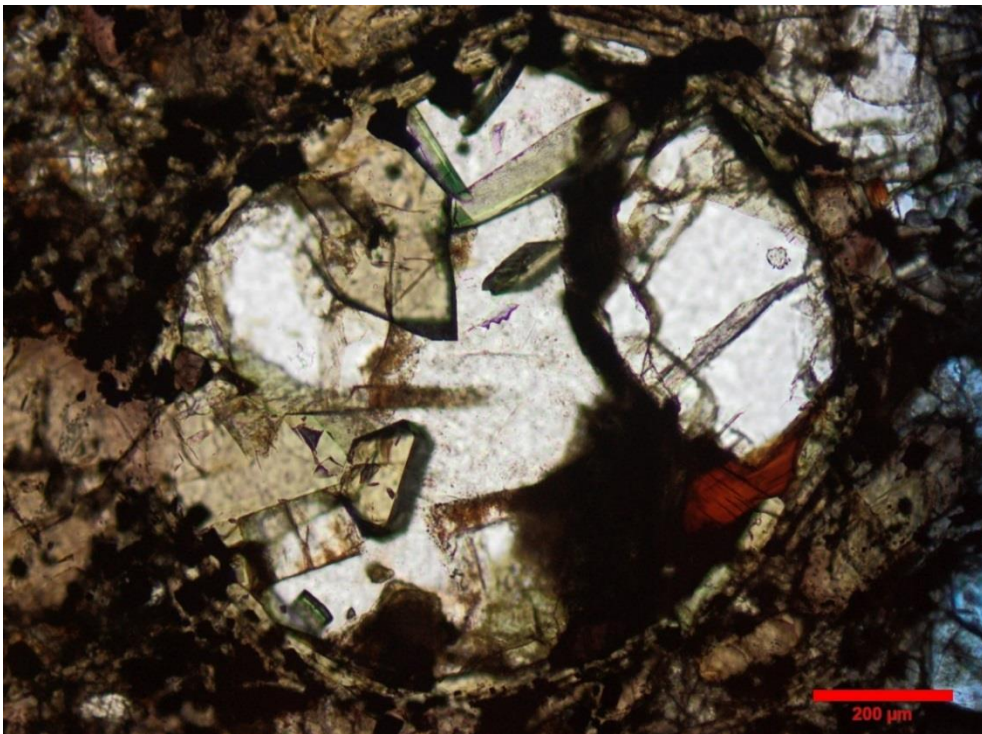


Figure 3.38 Detail of a circular structure composed of euhedral feldspathoid, greenish clinopyroxene, strong red phlogopite and a black isotropic phase (glass?). A colourless low-relief phase seems to be cancrinite.

Neuzinha (NEU 046A) – magnification x 10 – PPL. Field of view is 1.4 x 1.0 mm.

➤ **Leucitite**

Leucitites are volcanic rocks containing essentially leucite and clinopyroxene, both as phenocrysts and in the groundmass (**Figure 3.39** and **3.40**). Seriate and glomeroporphyritic textures are common. The dark brown groundmass is very fine-grained consisted of abundant euhedral Fe-Ti oxides, beige clinopyroxene microlites, leucite, as well as rare phlogopite laths and apatite needles. Abundant rounded leucite and rare clinopyroxene microphenocrysts occur in some samples (**Figure 3.40**).

➤ **Phlogopite-rich Dykes**

This group comprises some aphanitic dykes (see **Figure 3.18**) found in the northern GAP. These are composed of numerous elongated phlogopite laths (up to 3.0 mm) and minor pale yellow clinopyroxene microphenocrysts set in a brownish grey cryptocrystalline groundmass. Rounded structures (ocelli?) occupied by carbonates are common (**Figure 3.41**).

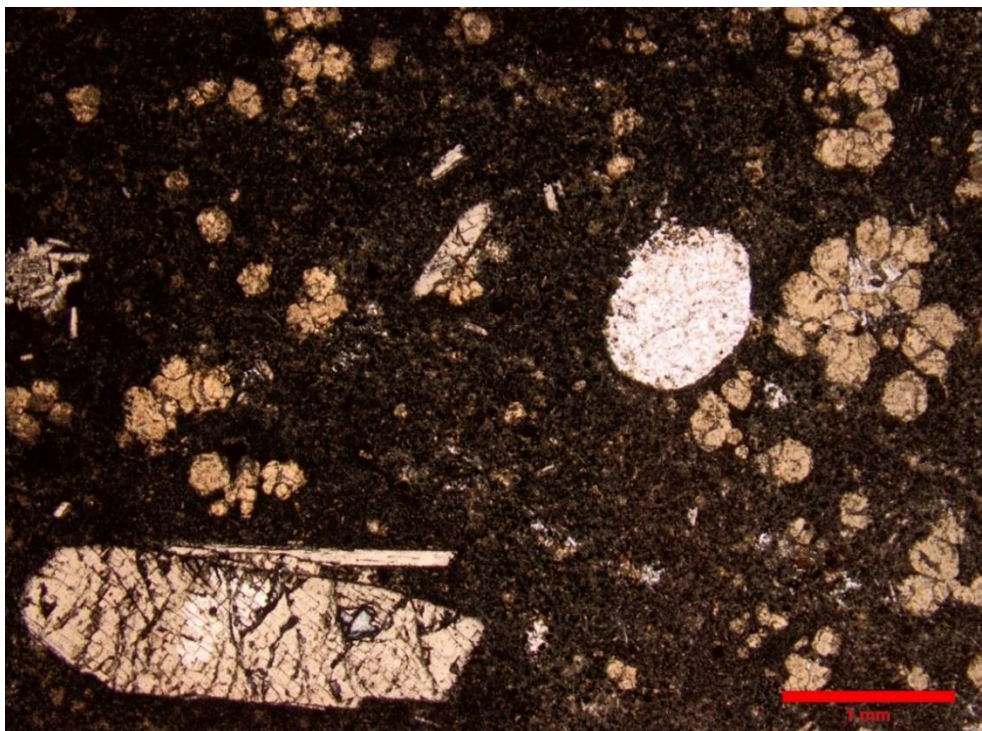


Figure 3.39 Typical altered leucite phenocrysts forming a glomeroporphyritic texture, and, set into a dark brown cryptocrystalline groundmass. Note the presence of a zoned clinopyroxene phenocryst at the bottom left, and a small vesicle filled with zeolite near to the centre of the view.

Santo Antônio da Barra (SAB 001A) – magnification x 2.5 – PPL. Field of view is 5.7 x 4.2 mm.

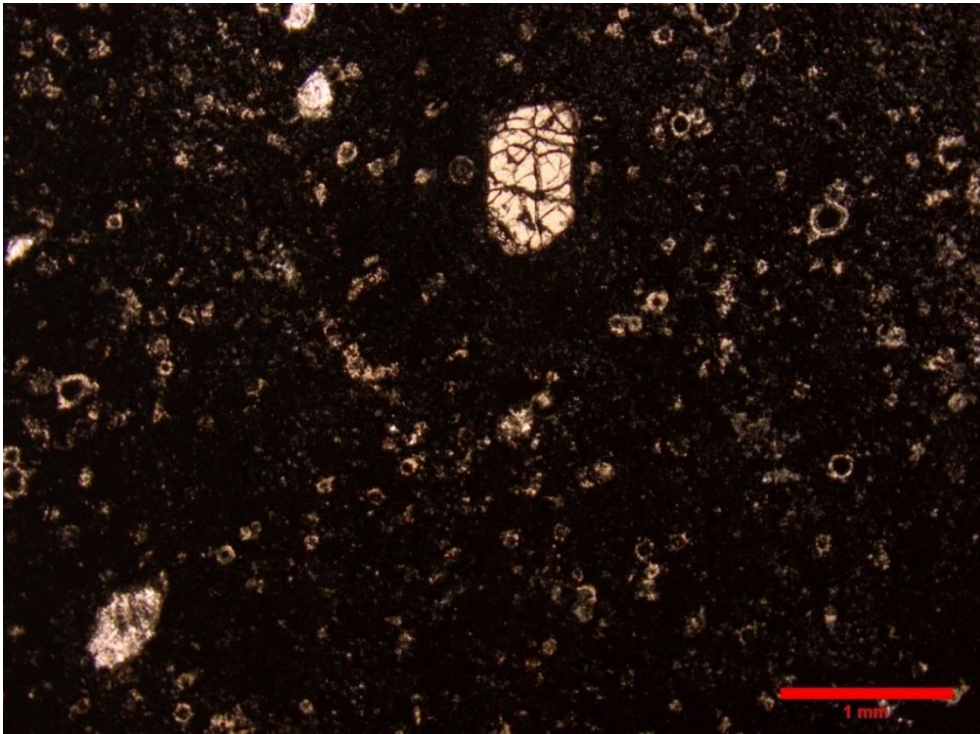


Figure 3.40 Leucite with plenty of tiny rounded leucite crystals set into a cryptocrystalline groundmass. Note the rare purple-lilac clinopyroxene microphenocrysts at the top centre.

Santo Antônio da Barra (SAB 007A) – magnification x 2.5 – PPL. Field of view is 5.7 x 4.2 mm.

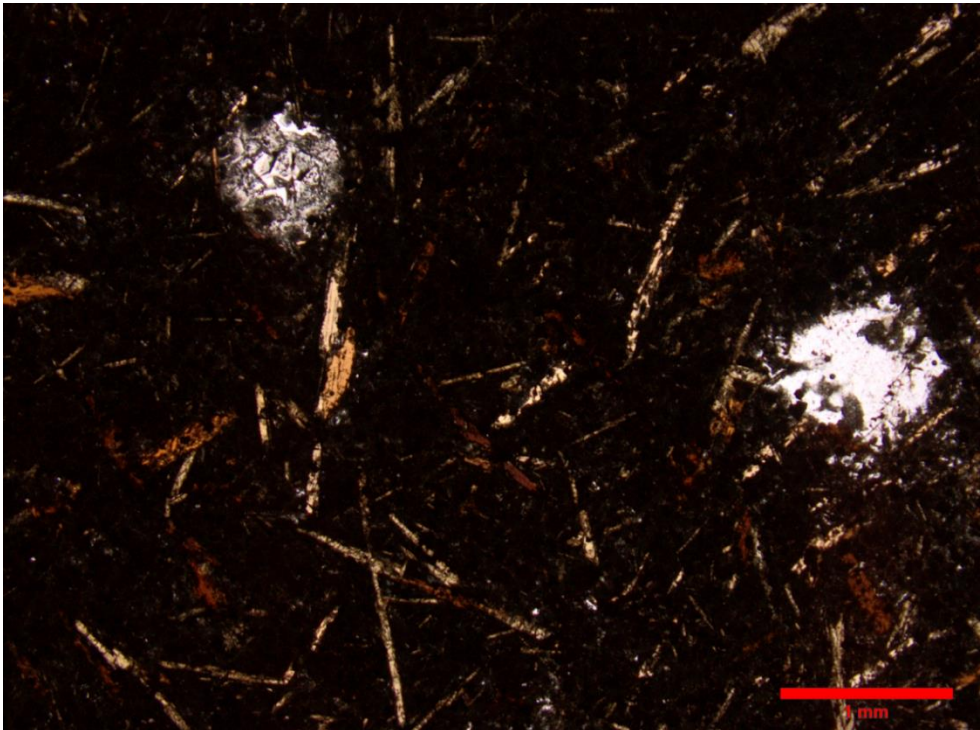


Figure 3.41 Numerous phlogopite laths and pale-yellow pyroxene microphenocrysts in a brownish cryptocrystalline groundmass. The colourless rounded zones (e.g. at the top left-hand corner) are vesicles or ocelli (?) filled with carbonate.

Northern GAP (RC 058B) – magnification x 2.5 – PPL. Field of view is 5.7 x 4.2 mm.

Feldspar-bearing Mafic Rocks

It also has been attempted to follow, as closely as possible, the IUGS recommendations for the nomenclature and classification of this group of rocks as well. However, the feldspar-bearing volcanic rocks from GAP cannot be easily classified using only one of the endorsed criteria, mineralogical or chemical, provided that:

- As can be seen below, most of these rocks appear to have equivalent amounts of both plagioclase and potassic feldspar in their fine-grained groundmass. Thus, it is very difficult, if not impossible, to estimate the modal composition.
- Post-emplacement alteration has clearly remobilized the alkali elements as long as primary leucite is often replaced by analcime (*e.g.* Danni, 1994). Thus, the TAS diagram should be used for classification only with caution.
- Some textural variations may induce wrong chemical classification, mainly in the case of the strongly porphyritic rocks (*cf.* Danni, 1994 – and text below).

In a broad sense, the plagioclase-bearing mafic rocks are classified as potassic basanite or potassic tephrite. The potassic (K) prefix is justified by the evident potassic mineralogy encompassing biotite, leucite, sanidine, anorthoclase, and K₂O-rich plagioclase (all of these phases do not necessarily occur always together). Whole-rock geochemistry also supports this classification (see below).

A first attempt to classify these rocks considered only petrography and resulted in the definition of four groups: (1) ‘basanitic rocks’; (2) ‘tephritic rocks’; (3) ‘quench-textured’ rocks; and (4) phonolites and trachytes. Groups 1 and 2 were distinguished according to the presence or absence of modal olivine, respectively.

Not surprisingly, in the TAS diagram (see Le Maitre *et al.*, 2002) the feldspar-bearing rocks with LOI < 3 wt.% plot mostly into the basanite/tephrite fields, and some plot into the

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trachyte and phonolite fields. Similar results were achieved using the R_1 - R_2 diagram (De la Roche *et al.*, 1980) and the immobile trace elements (Winchester & Floyd, 1977). Therefore, although some remobilization of the alkali elements had occurred – as evidenced by the analcimization of original primary leucite – whole-rock chemical data still remains rather consistent with the preliminary petrographic classification.

The CIPW norm calculation was also used to discriminate between basanites and tephrites. All analyses were recalculated to 100% on a volatile-free basis, and standard iron oxidation ratios ($\text{Fe}_2\text{O}_3/\text{FeO}$) were used according to Middlemost (1989). Most of the GAP volcanic rocks were extensively altered by Na_2O -rich hydrothermal fluids – for which the presence of abundant zeolites, mainly analcime, is evidence (*e.g.* Moraes, 1988; Danni, 1994; Junqueira-Brod, 1998). So, it must be expected that Fe_2O_3 content has also been modified (and increased by alteration). Therefore, the use of a ‘standard’ $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio rather than any measured iron ratio is more than justified. All analyses plotting into the U1 field of the TAS diagram are indeed basanites or tephrites, with normative albite > 5% (see Le Bas, 1989).

Interestingly, none of the studied rocks can be classified as picrite, neither based on chemical (Le Bas, 2000) nor on textural (Kerr & Arndt, 2001) criteria. This is probably due to the fact that olivine and clinopyroxene phenocrysts were carefully separated by handpicking before sample preparation for chemical analysis (see Supplementary Material – **Chapter 7**). Thus, the use of the term ‘alkali picrite’ as proposed by Danni (1994) has been disregarded. Besides, these GAP rocks clearly undergone crystal accumulation, as stated by Danni (1994), and then, they are most likely strongly porphyritic basanites.

In view of that, hereafter, it is recommended to divide the basanites of the GAP into phenocryst-poor (K-basanites) and phenocryst-rich (K-ankaramites) varieties, given that the strongly porphyritic basanites are very common in the northern GAP. It should also be noted

that the phenocryst-poor K-basanites are largely represented by the rock types initially classified as ‘quench-textured’ rocks.

➤ **Potassic Ankaramite (Phenocryst-rich Basanite)**

This group includes those feldspar-bearing rocks with significant amounts of olivine. They are commonly strongly porphyritic rocks containing clinopyroxene, olivine, leucite and feldspar phenocrysts, in this order of abundance (**Figure 3.42** and **3.43**).

There are two types of olivine phenocrysts. One comprises subhedral to anhedral (up to 4.8 mm), strongly fractured, and mostly altered to ‘iddingsite’ / ‘bowlingite’, crystals. Rounded faces and opaque inclusions are common. The second consists of euhedral microphenocrysts devoid of any kind of alteration.

Clinopyroxene phenocrysts also occur in at least two types. Inclusion-bearing euhedral to subhedral phenocrysts (up to 6.4 mm) are often characterized by colourless cores mantled by a pleochroic Ti-rich rims. The cores exhibit irregular outlines with complex zoning patterns (**Figure 3.44**), while the rims show continuous oscillatory zoning. Fe-Ti oxides as well as ‘groundmass’ inclusions are abundant (**Figure 3.44**). A second type of phenocrysts occurs as euhedral (up to 4 mm), without inclusions, crystals, and they are characterized by pale beige cores and a prominent marginal zoning. The purple-lilac rim often contains plenty of small opaque inclusions (**Figure 3.45**).

Opaque euhedral phenocrysts (up to 2 mm) are common in these rocks. They show irregular outlines, and sometimes skeletal habit.

Felsic minerals are rare as phenocrysts but they may be present in some samples. Tabular crystals of plagioclase (up to 2.7 mm) are most common (**Figure 3.42**). Strongly zoned microphenocrysts frequently have glomeroporphyritic texture. Rounded leucite phenocrysts with up to 1.4 mm are usually colourless with brownish areas due to secondary alteration to zeolites (**Figure 3.43**).

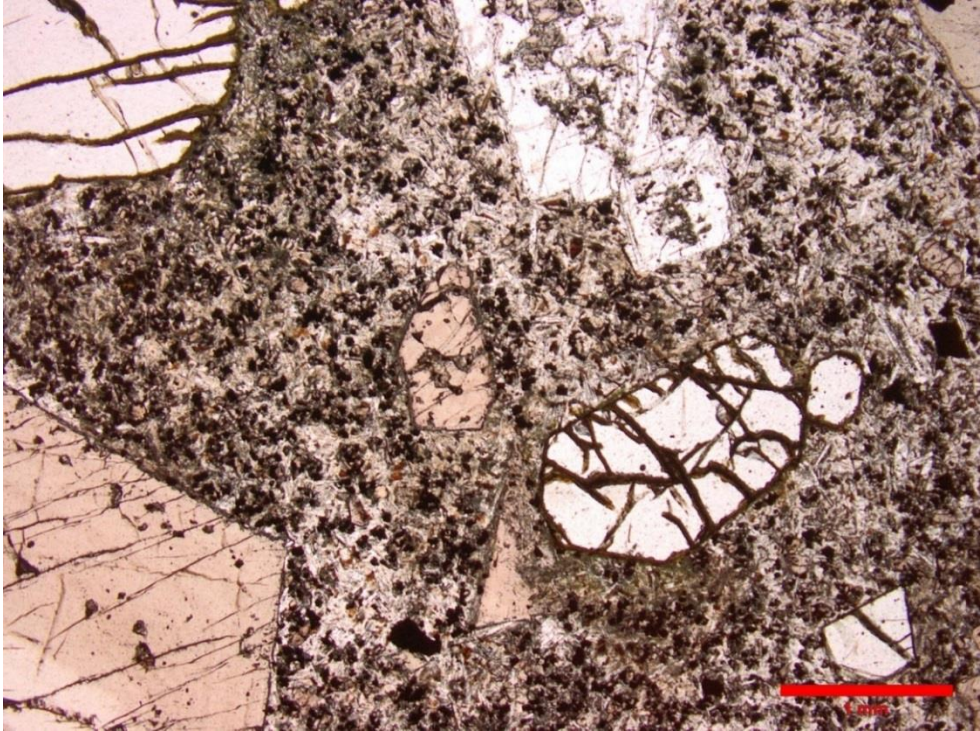


Figure 3.42 Phenocrysts and microphenocrysts of olivine, clinopyroxene and plagioclase (at the top centre) in a fine-grained groundmass composed of purplish pyroxene, feldspars, Fe-Ti oxides, phlogopite and an altered interstitial material (mostly secondary zeolite).

Northern GAP (ARE 028A) – magnification $\times 2.5$ – PPL. Field of view is 5.7×4.2 mm.

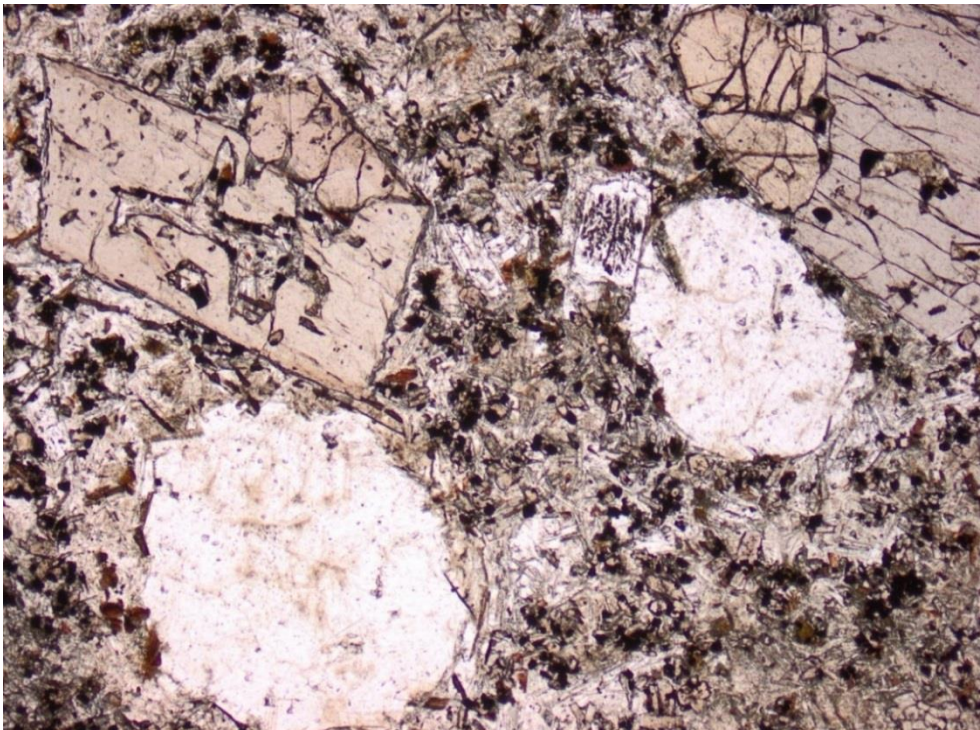


Figure 3.43 Two rounded leucite phenocrysts in fine-grained groundmass composed of purplish pyroxene, feldspars, Fe-Ti oxides, phlogopite and an altered interstitial material. Note the presence of clinopyroxene with some ‘groundmass’ enclosed (former melt inclusion?).

Northern GAP (ARE 028C) – magnification $\times 4$ – PPL. Field of view is 3.6×2.6 mm.



Figure 3.44 Inclusion-bearing glomerocrysts of pyroxene showing a complex zoning pattern in the core. A continuous purple-lilac rim highlights the contact with the groundmass.

Northern GAP (ARE 028C) – magnification $\times 2.5$ – PPL. Field of view is 5.7×4.2 mm.

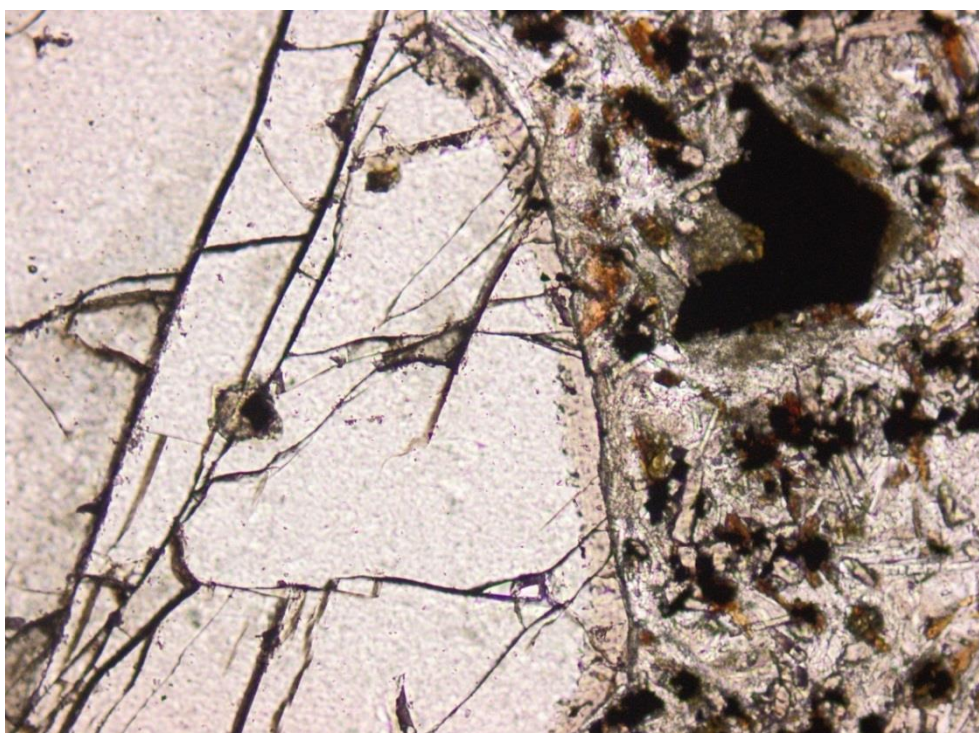


Figure 3.45 Detail of a clinopyroxene phenocrysts with a homogeneous pale beige core and prominent marginal zoning. The purple-lilac marked rim contains plenty of small opaque inclusions, suggesting crystallization together with the groundmass phases.

Northern GAP (ARE 028C) – magnification $\times 10$ – PPL. Field of view is 1.4×1.0 mm.

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The groundmass of the potassic ankaramite is typically fine-grained, hypocrySTALLINE, and composed mostly of purplish clinopyroxene, tabular feldspars, and Fe-Ti oxides (**Figure 3.46**). Phlogopite laths with light to dark orange normal pleochroism and apatite are common accessories. A brownish interstitial material, *i.e.* clay minerals and secondary zeolites, probably represent altered glass.

In SEM images (**Figure 3.47** and **3.48**) it can be seen that the felsic phases in the groundmass of these rocks are heterogeneous, with some portions being more enriched in potassium or calcium (**Figure 3.48**). This clearly implies that both potassic and calcic feldspars are present.

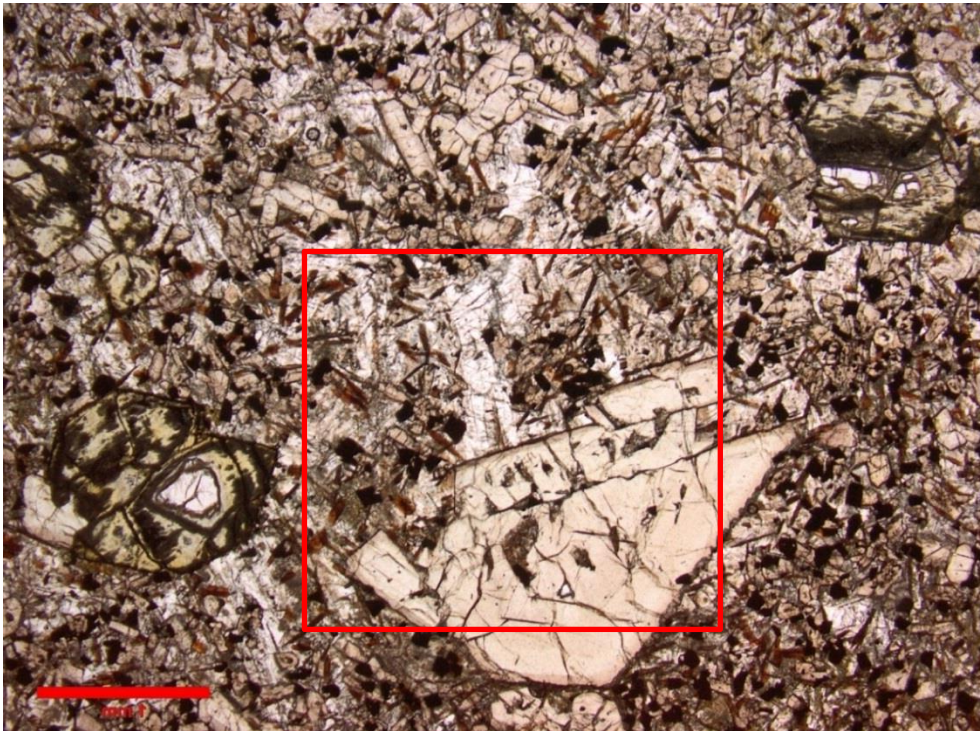


Figure 3.46 Olivine (altered to serpentine) and clinopyroxene phenocrysts in a fine-grained groundmass. Note the presence of felsic phases and phlogopite laths in the delimited area (red square).

Northern GAP (DIO 032) – magnification $\times 2.5$ – PPL. Field of view is 5.7×4.2 mm.

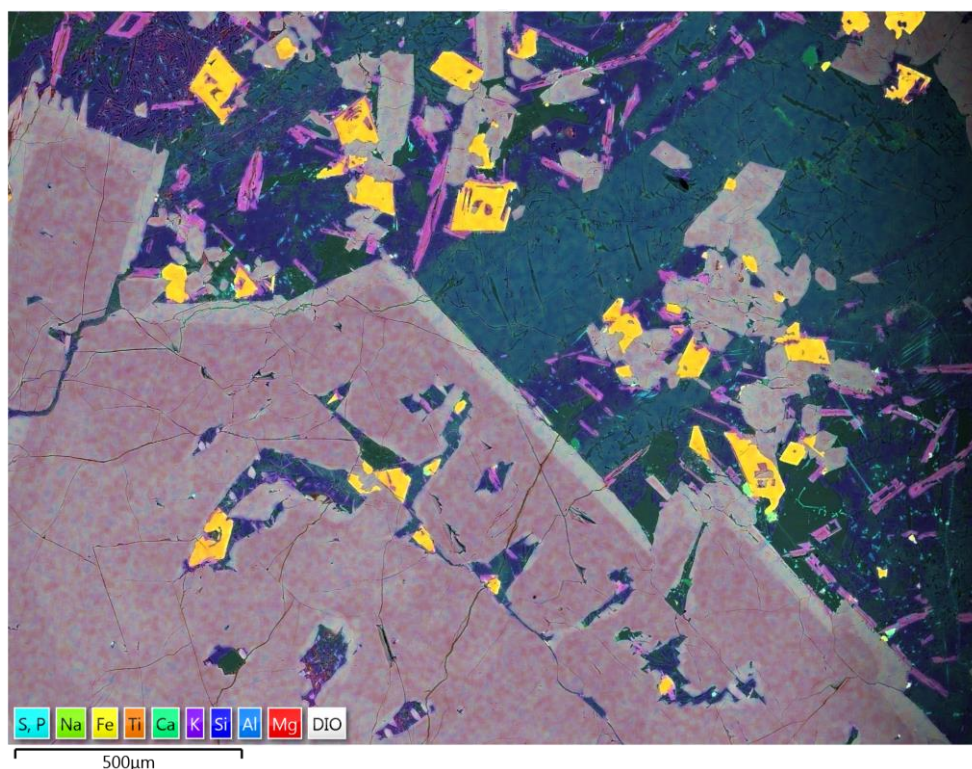


Figure 3.47 False colour SEM image of the red square area of Figure 3.46. There is an interstitial potassic phase (strong purple) predominant in the groundmass. Note the prominent marginal zoning in the clinopyroxene phenocryst. Other phases are phlogopite (stronger pink) and Fe-Ti oxides (yellow).

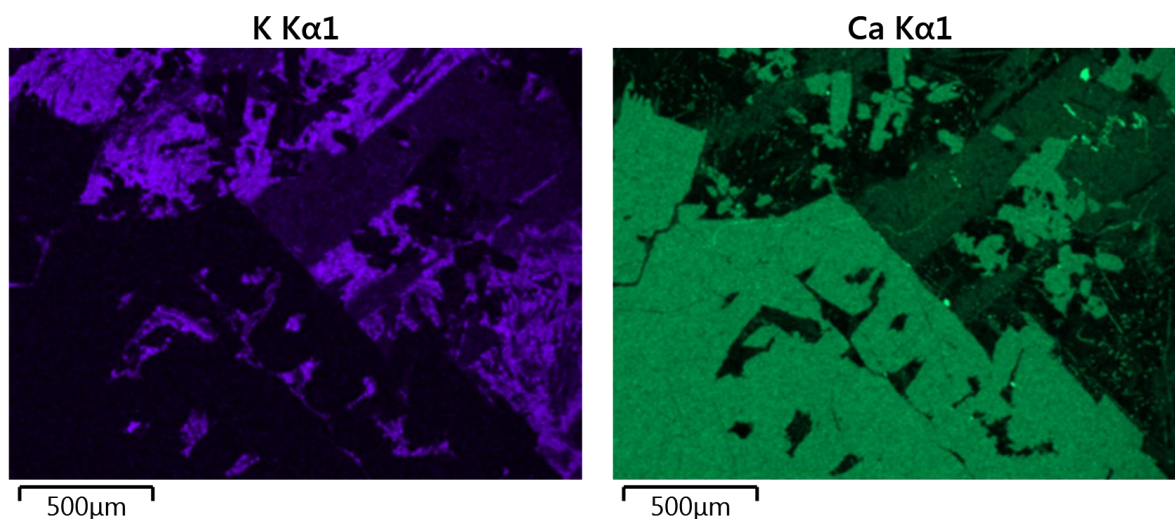


Figure 3.48 False colour SEM images showing K and Ca X-ray distributions. The groundmass is clearly composed of two distinct phases: one K-rich (potassic feldspar), and another Ca-rich (plagioclase).

➤ **Potassic Basanite (Phenocryst-Poor)**

This group includes rocks that are commonly microporphyritic and contain very rare olivine phenocrysts (up to 2 mm) in a cryptocrystalline groundmass. The phenocrysts are inclusion-free, often showing embayed faces and rounded outlines without any evidence of alteration (**Figure 3.49**). A second type of olivine occurs as abundant skeletal (**Figure 3.50**) or subhedral microphenocrysts. They usually occur as clusters giving rise to glomeroporphyritic texture. Purple-lilac clinopyroxene microphenocrysts are rare and, when present, occur as clusters (**Figure 3.51**). The dark grey groundmass is composed mostly of purplish pyroxene, Fe-Ti oxides (skeletal and euhedral), some olivine, phlogopite, and an interstitial colourless phase that seems to be concentrated in some portions of the groundmass (**Figure 3.51**). In addition, dendrites similar to feathers also occur disseminated throughout the groundmass (**Figure 3.52 and 3.53**).

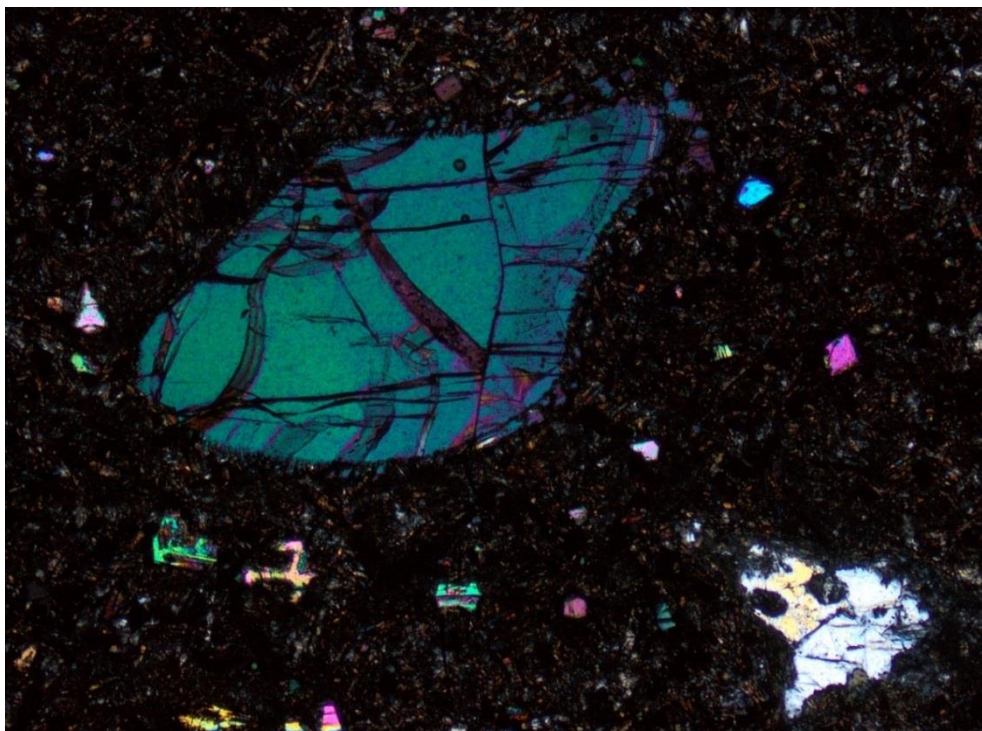


Figure 3.49 Olivine phenocryst (or xenocryst?) with rounded outline and skeletal olivine microphenocrysts in a cryptocrystalline groundmass. In this particular sample occur some resorbed quartz xenocrysts as can be seen close to the bottom right-hand corner.

Amorinópolis (AMO 014) – magnification x 2.5 – XPL. Field of view is 5.7 x 4.2 mm.

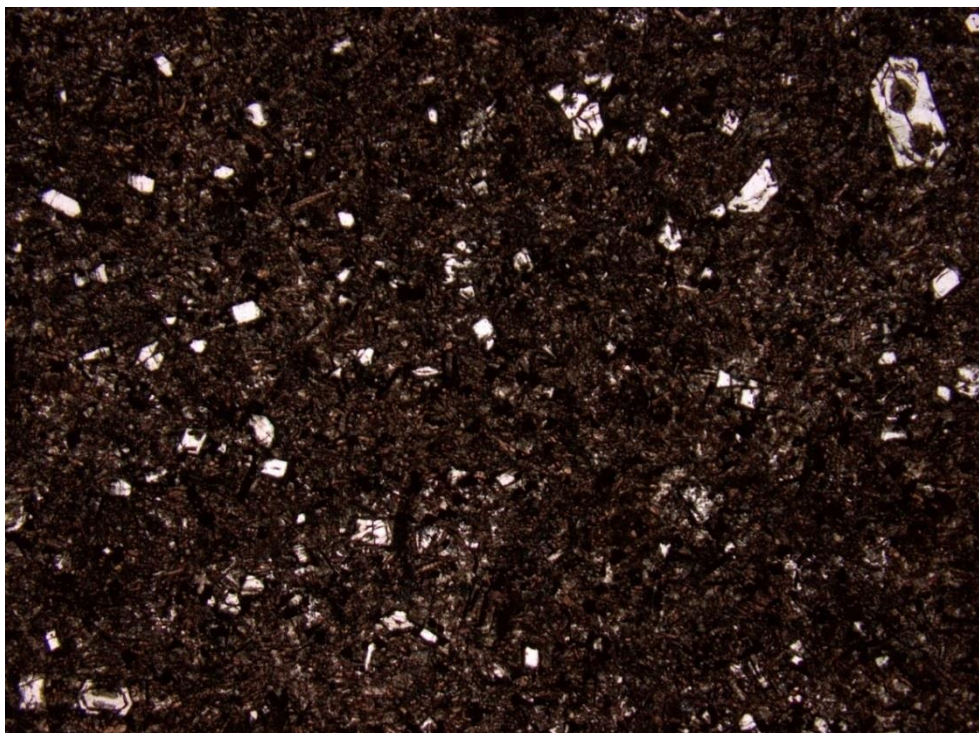


Figure 3.50 Skeletal olivine microphenocrysts in a cryptocrystalline groundmass of purplish clinopyroxene, Fe-Ti oxides (skeletal and euhedral), phlogopite, interstitial felsic phases, and dendrites.

Amorinópolis (AMO 014) – magnification x 2.5 – PPL. Field of view is 5.7 x 4.2 mm.



Figure 3.51 Skeletal olivine and minor purplish clinopyroxene microphenocrysts occurring as tiny clusters (*e.g.* to the right of the centre of the view). Also note the abundance of interstitial colourless phases close to the centre of the field of view.

Northern GAP (MCG 078B) – magnification x 2.5 – PPL. Field of view is 5.7 x 4.2 mm.



Figure 3.52 Another view of the same sample illustrating the great number of dendritic phases set in the groundmass.

Northern GAP (MCG 078B) – magnification x 4 – PPL. Field of view is 3.6 x 2.6 mm.

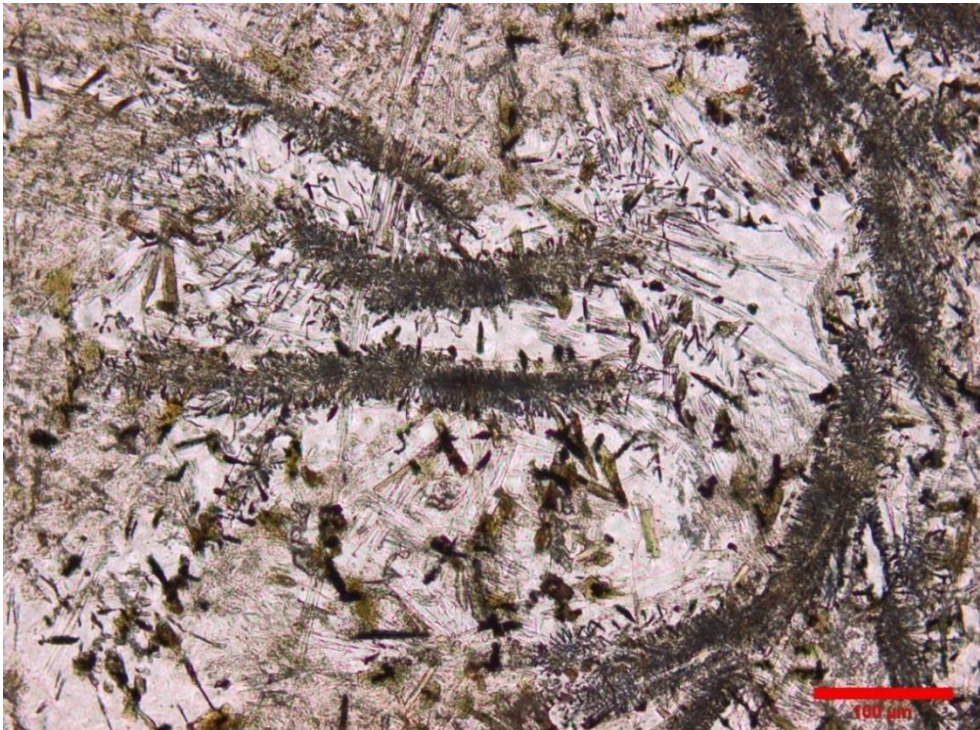


Figure 3.53 Detailed view of the dendritic mineral phases. Note their curved pattern resembling a feather. Also note the abundance of tiny brownish mafic laths, all enclosed within the colourless interstitial phase (altered feldspathoid or glass?).

Northern GAP (MCG 078B) – magnification x 20 – PPL. Field of view is 0.7 x 0.52 mm.

➤ **Potassic Tephrite and Phonotephrite**

In contrast to the potassic basanites, this group comprises olivine-poor or olivine-free feldspar-bearing mafic rocks. They are much poorer in phenocrysts, and when phenocrysts are present, these consist of clinopyroxene or feldspars. The K-tephrites are generally very fine-grained, hypocrySTALLINE rocks, with a mostly brownish grey groundmass (**Figure 3.54** and **3.55**). Pyroxene and plagioclase microphenocrysts form glomeroporphyritic textures (**Figure 3.55**). The groundmass of these rocks is composed mainly of purplish clinopyroxene, Fe-Ti oxides, phlogopite, or Ti-rich amphibole, as well as abundant feldspars (both plagioclase and potassic feldspar). Some samples also carbonate may occur (**Figure 3.55**), as well as small, rounded leucite crystals as accessories (**Figure 3.56**).

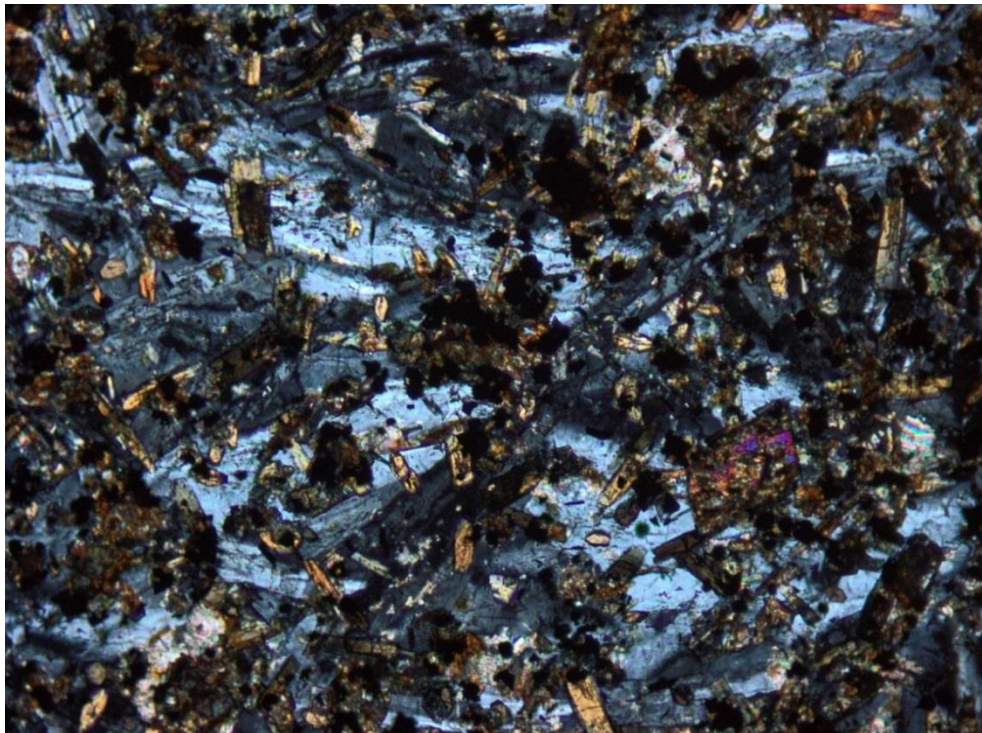


Figure 3.54 Aphanitic rock with a very fine-grained groundmass composed of similar proportions of dark and light minerals. Dark minerals are essentially Fe-Ti oxides and pleochroic light brown to dark brown amphibole. Light minerals display bluish grey interference colours and appear to be mostly feldspars.

Northern GAP (ARE 027C) – magnification x 10 – XPL. Field of view is 1.4 x 1.0 mm.

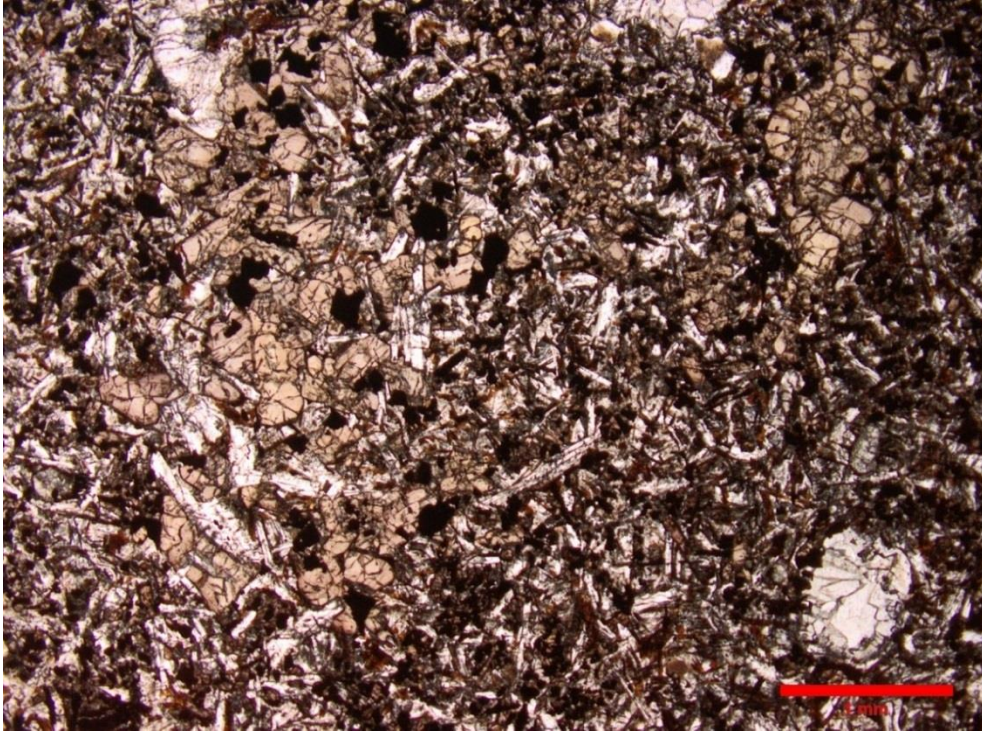


Figure 3.55 Microporphyritic rock with a fine-grained brownish groundmass composed of plagioclase, purplish pyroxene (frequently in glomeroporphyritic texture), Fe-Ti oxides, phlogopite and carbonate. The latter often occurs as spherules, as can be seen to the bottom right-hand corner.

Northern GAP (MCG 081A) – magnification x 2.5 – PPL. Field of view is 5.7 x 4.2 mm.



Figure 3.56 Another field of view of the sample above, showing a small rounded leucite crystal at the bottom centre. Also note the clusters of purple-lilac pyroxenes.

Northern GAP (MCG 081A) – magnification x 2.5 – PPL. Field of view is 5.7 x 4.2 mm.

As in the feldspar-free mafic rocks, here it has also been found evidence of magma mixing (**Figure 3.57**). In this particular sample, it seems that a clinopyroxene-phyric magma was mixed with a plagioclase- and olivine-rich magma. However, as the pyroxene phenocrysts appear to be fragments, the mixing probably occurred at lower temperature conditions. This sample also shows some circular structures, similar to those described in the previous section, but with a very different mineral assemblage.

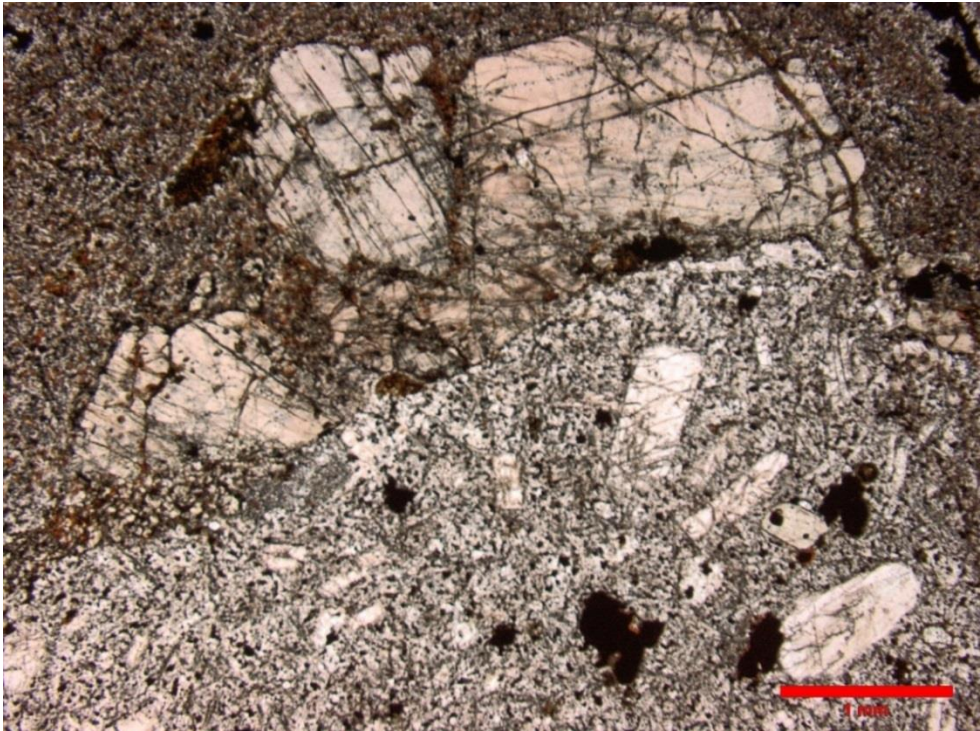


Figure 3.57 Evidence of mixing between two slightly different feldspar-bearing magmas. To the top of the field of view occurs a porphyritic tephrite, with large pyroxene phenocrysts. To the bottom half of the field of view occurs a finer grained rock with plagioclase and olivine phenocrysts.

Northern GAP (MM 042B) – magnification x 2.5 – PPL. Field of view is 5.7 x 4.2 mm.

➤ **Alkali Dolerite**

The alkali dolerite sample is somewhat equigranular (**Figure 3.58**), fine-grained, and encompasses purplish clinopyroxene, reddish orange phlogopite, zoned plagioclase, Fe-Ti oxides, long apatite needles (up to 3.0 mm), and a brownish altered felsic phase (zeolite). Clinopyroxene and Fe-Ti oxides are intimately associated with each other, sometimes forming radiating clusters. Phlogopite occurs as large poikilitic laths that often have black rims.

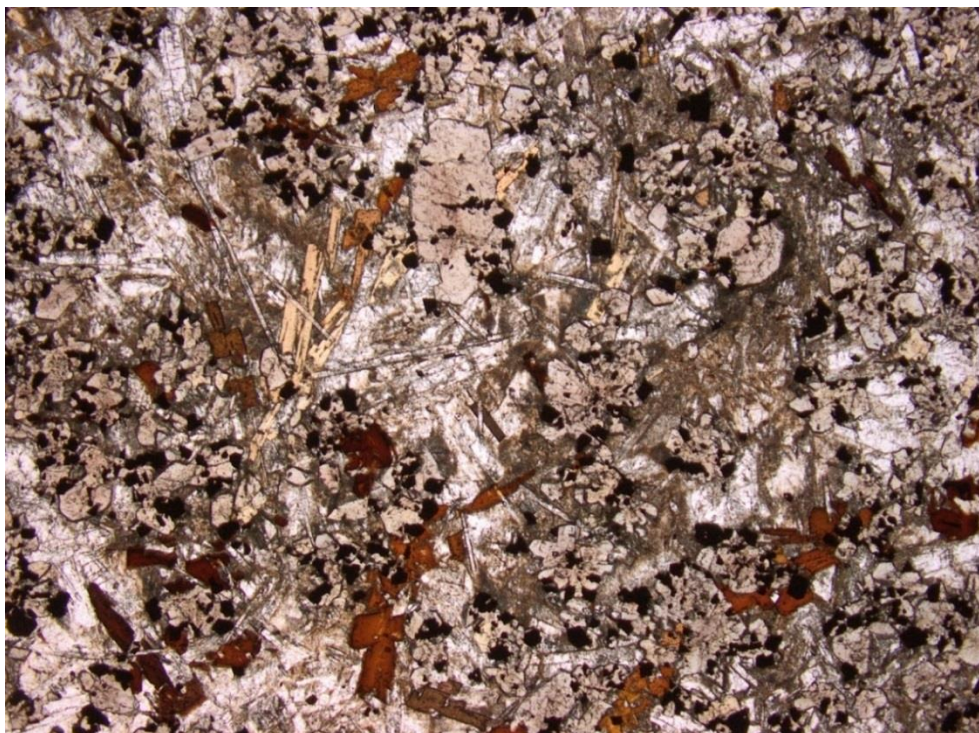


Figure 3.58 Fine-grained rock composed of purple-lilac, zoned clinopyroxene, reddish orange phlogopite, zoned plagioclase (colourless phase), Fe-Ti oxides, and long apatite needles. The brownish altered felsic phase probably represents an original feldspathoid.

Northern GAP (SF 073) – magnification x 2.5 – PPL. Field of view is 5.7 x 4.2 mm.

Phonolites

Phonolites vary from almost aphyric to strongly porphyritic. The former has rare aegirine-augite zoned microphenocrysts (**Figure 3.59**) and some Fe-Ti oxides rimmed by titanite (**Figure 3.60**). The groundmass is very fine-grained, holocrystalline, and comprising microlites of aegirine, Fe-Ti oxide and felsic minerals in an intergranular texture (**Figure 3.60**). Apatite is the main accessory. In the porphyritic phonolites the main phenocrysts are aegirine-augite, biotite, nepheline, and sanidine, besides rare titanite (**Figure 3.61**). An important difference in the porphyritic phonolites is the presence in some samples of rounded xenoliths or ocelli (?). Some are composed of carbonate and euhedral apatite (**Figure 3.62**), whereas others appear to contain clinopyroxene and cancrinite/zeolite crystals (**Figure 3.63**). The latter also show a yellowish outer rim with zoned Ti-rich garnet (**Figure 3.64**).



Figure 3.59 Almost aphyric phonolite with rare purple clinopyroxene microphenocrysts set in a greenish holocrystalline groundmass.

Northern GAP (SF 069) – magnification x 2.5 – PPL. Field of view is 5.7 x 4.2 mm.

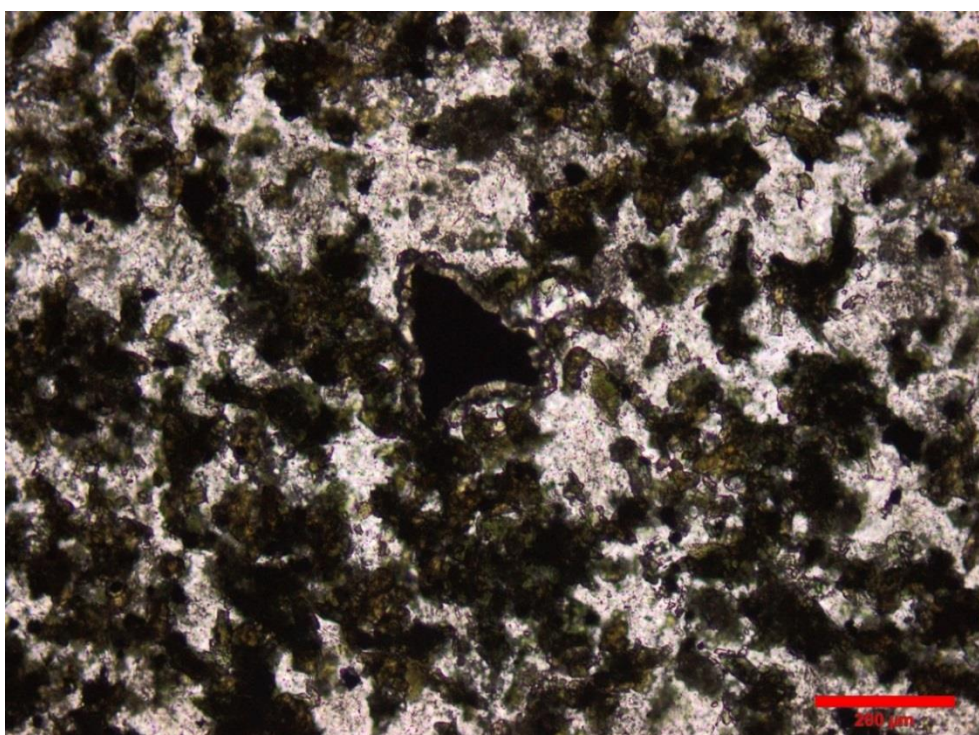


Figure 3.60 Detail of the above phonolite groundmass. It is an aggregate of microlites of aegirine, Fe-Ti oxides and felsic minerals. Note that the Fe-Ti oxide microphenocryst in the centre is rimmed by titanite.

Northern GAP (SF 069) – magnification x 10 – PPL. Field of view is 1.4 x 1.0 mm.

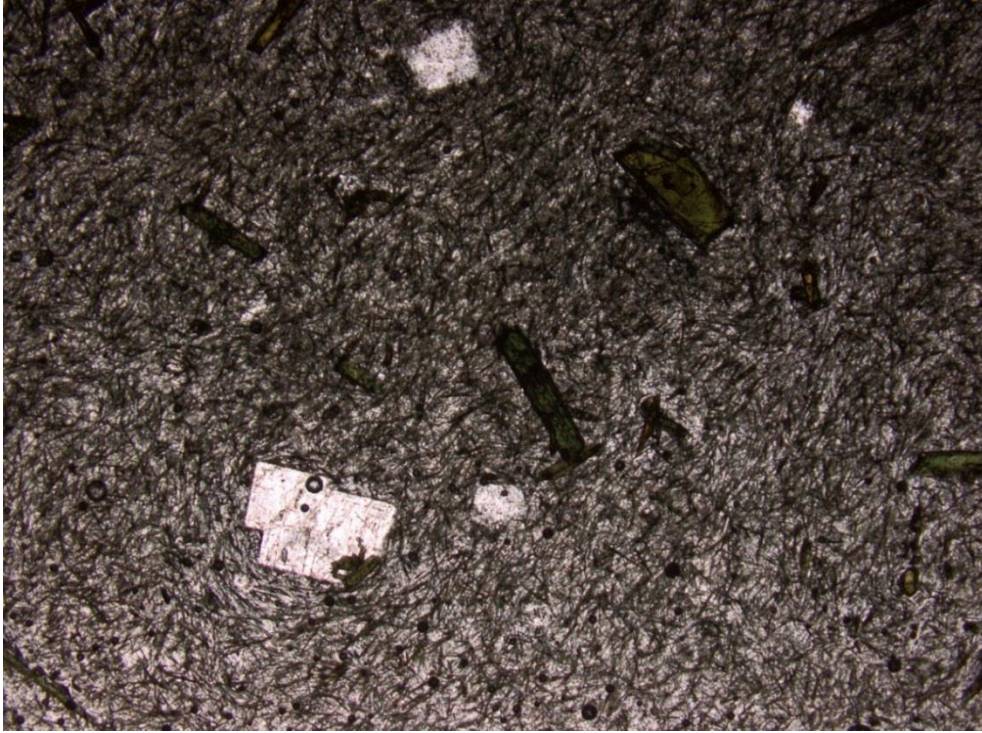


Figure 3.61 Porphyritic phonolite with some green clinopyroxene microphenocrysts as well as euhedral nepheline (colourless phase) in a typical greenish grey groundmass.

Northern GAP (MTA 061A) – magnification $\times 2.5$ – PPL. Field of view is 5.7 x 4.2 mm.

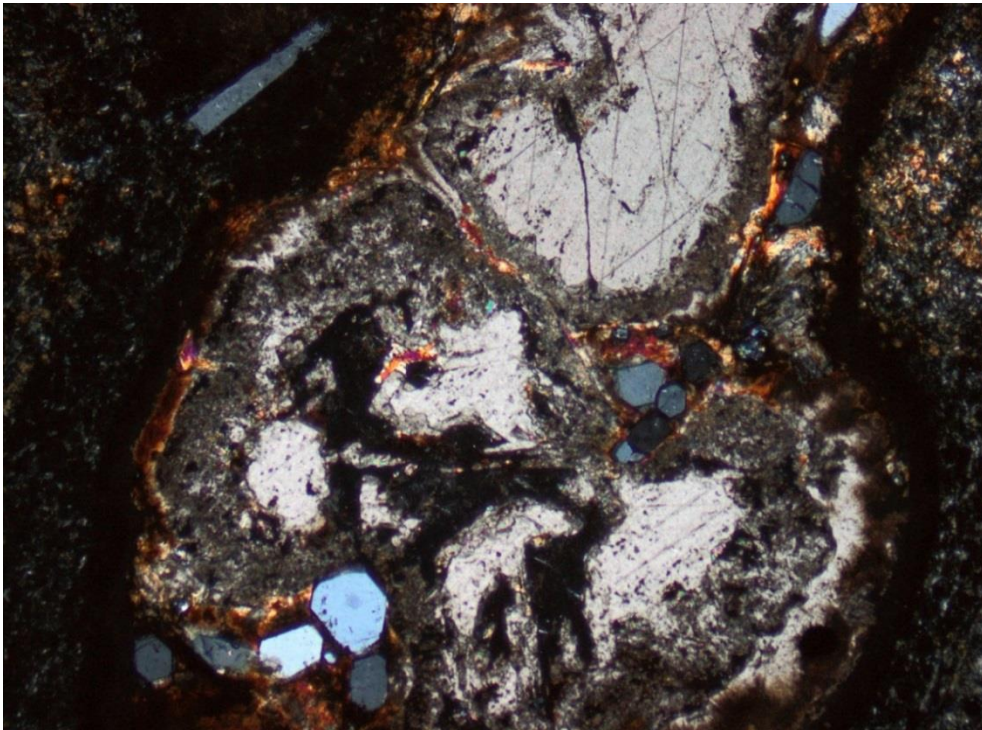


Figure 3.62 Rounded xenolith (?) or ocelli (?) mostly composed of carbonate and some euhedral apatite crystals (bluish grey interference colours) in phonolitic groundmass.

Northern GAP (RC 059B) – magnification $\times 4$ – XPL. Field of view is 3.6 x 2.6 mm.



Figure 3.63 Another view of rounded xenolith (?) or ocelli (?) composed of pectolite crystals in a cancrinite and zeolite matrix. The whole structure is surrounded by a yellowish-brown material that seems to be reaction rim to the phonolitic groundmass.

Northern GAP (RC 059B) – magnification x 4 – PPL. Field of view is 3.6 x 2.6 mm.



Figure 3.64 Detail of the other rim of the rounded structure above. Pseudo-hexagonal, high-relief, strongly zoned yellowish-brown crystals are Ti-rich garnet.

Northern GAP (RC 059B) – magnification x 10 – PPL. Field of view is 1.4 x 1.0 mm.

Chapter 4

The IUGS Nomenclature on Kalsilite-Bearing

Volcanic Rocks: A Critical Appraisal and

Recommendations

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Abstract

The current IUGS recommendations for nomenclature of kalsilite-bearing volcanic rocks do not consider the possible coexistence of kalsilite (KAlSiO_4) and nepheline ($\text{KNa}_3\text{Al}_4\text{Si}_4\text{O}_{16}$), nor do they address volcanic rocks containing kalsilite, other than the archetypal kamafugites. This review highlights the most important shortcomings in the existing IUGS nomenclature against the classical literature and the most recent reports on kalsilite-bearing volcanic rocks. In addition, a new modal classification system, more logical and complete, is proposed. This scheme follows the IUGS principles as far as possible and denotes an updated version of the most applied historical terminology. Based on the presence of the main light-coloured constituents of kalsilite-bearing volcanic rocks, only four rock names are required for petrographic classification: kalsilite nephelinite (nepheline dominant), katungite (melilite dominant), mafurite (kalsilite dominant), and ugandite (leucite dominant). Such terminology should only be applied for volcanic rocks that definitely contain kalsilite. This requires the use of advanced analytical methods (*e.g.* electron microprobe analysis coupled with back-scattered electron imaging), besides conventional transmitted-light microscopy, as kalsilite and nepheline are optically indistinguishable. The coexistence of these two minerals in K-rich volcanic rocks is much more common than previously recognised. Volcanic rocks with kalsilite can be separated into potassic and ultrapotassic groups. This highlights a major problem concerning the indiscriminate use of the term kamafugite and the existing confusion between the modal and chemical classifications of kalsilite-bearing volcanic rocks. Our recommendations are purely based on descriptive attributes.

Keywords: alkaline volcanic rocks; classification; kalsilite; nepheline; potassic and ultrapotassic magmas

Chapter 4: Nomenclature of Kalsilite-Bearing Volcanic Rocks

4.1. Introduction

Almost 20 years ago, the International Union of Geological Sciences (IUGS) published the second edition of the book “*Igneous Rocks: A Classification and Glossary of Terms*” (Le Maitre *et al.*, 2002), which had been conceived as the outcome of a collective international effort to establish a modern systematic classification scheme for igneous rocks. The remarkable work of the IUGS Subcommittee on the Systematics of Igneous Rocks undeniably clarifies the nomenclature for the vast majority of common igneous rocks, but some problems have remained (see, *e.g.* Tappe *et al.*, 2005). Most of the unresolved issues involve the group of seemingly ‘exotic’ potassic and ultrapotassic alkaline volcanic rocks, including the kalsilite-bearing ones.

In recent years, significant attention has been paid to the recognition and classification of leucitites, lamproites and kimberlites (*e.g.* Mitchell, 2020 and references therein). However, a comparable effort regarding the nomenclature of the kalsilite-bearing rocks seems to be lacking. One reason for this may be the fact that such rocks are considered extremely rare (*e.g.* Hatch *et al.*, 1972; Mitchell & Bergman, 1991) and, contrary to the well-known kimberlites and lamproites that source diamonds, no significant economic importance has so far been found for kalsilite-bearing volcanic rocks. These rocks, though, are of paramount importance in identifying tectonic settings, mantle enrichment processes, or continental rift initiation, *inter alia*. Furthermore, such K-rich volcanic rocks are intimately associated with CO₂-rich mantle sources and carbonatite magmatism (*e.g.* Stoppa & Cundari, 1998; Bailey & Collier, 2000; Brod *et al.*, 2000; Castorina *et al.*, 2000; Stoppa *et al.*, 2003; Junqueira-Brod *et al.*, 2005a; Rosenthal *et al.*, 2009; Foley *et al.*, 2011; Stoppa & Schiazza, 2013; Muravyeva & Senin, 2018).

The present paper reviews the classical works related to petrographic descriptions and classification of the kalsilite-bearing volcanic rocks, with the intent to discuss some important shortcomings in the current IUGS systematics. We, therefore, propose a new petrographic

(modal) classification system. This system is based on the IUGS principles established by Le Bas & Streckeisen (1991) and also on the old, well-established, terminology for these kalsilite-bearing rocks. In addition, the proposed scheme enables the systematic classification of these rocks into one of the two distinct groups (*i.e.* potassic and ultrapotassic) established here. This concept was not previously recognized by Woolley *et al.* (1996) and Le Maitre *et al.* (2002) in the earlier IUGS revisions of the nomenclature of kalsilite-bearing volcanic rocks. Our recommendation will be useful to clarify the petrogenesis of this ‘exotic’ group of rocks and shed some light on the existing confusion regarding their mineralogical vs chemical classifications.

4.2 Problematics of the IUGS Scheme

The IUGS Subcommittee deliberated on the nomenclature and classification of kalsilite-bearing rocks only after the publication of the first edition of their recommendations (*cf.* Le Maitre *et al.*, 1989; Woolley *et al.*, 1996). Woolley *et al.* (1996) emphasised that “...*the hierarchical system presented here is not definitive and has minimal genetic content*” (*ibid.*, p. 176). Even so, they assumed that volcanic rocks with kalsilite were restricted to the ultrapotassic kamafugitic series of Sahama (1974). However, it had already been known earlier that this was not the case (*e.g.* Sahama & Meyer, 1958; Sahama, 1960). This is probably the main issue with the current IUGS approved system for kalsilite-bearing volcanic rocks, and it has been ambiguously considered since then (*e.g.* Lustrino *et al.*, 2020 and references therein). As a matter of practicality, though, the acronym **kamafugite** (**katungite**, **mafurite**, **ugandite**; see below) will be employed here as well but always indicating its *sensu stricto* or *sensu lato* meaning according to the original definition of Sahama (1974; *sensu stricto*: *Rocks of kamafugitic affinity are potassium-rich alkaline rocks strongly undersaturated in silica and cover both chemically and mineralogically a considerable diversity of types* [Sahama, 1974, p. 96]; *sensu lato*: *A name for the distinctive series of consanguineous rocks katungite, mafurite*

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and ugandite [Le Maitre et al., 2002, p. 95] or Synonymous for any kalsilite-bearing volcanic rock regardless of its chemical affinity).

Several authors (Mitchell, 1996; Tappe *et al.*, 2003; Junqueira-Brod *et al.*, 2005a, b) have pointed out problems with the IUGS classification scheme for kalsilite-bearing volcanic rocks. First, the scheme is somewhat self-contradictory in removing local rock names but still retain's the term kamafugite (Mitchell, 1996; Tappe *et al.*, 2003). In addition, the IUGS Subcommittee excluded the rock name ugandite from the kalsilite-bearing rocks scheme under the assumption that ugandite does not contain kalsilite (Woolley *et al.*, 1996; Le Maitre *et al.*, 2002). However, there is conspicuous evidence, both descriptive (Holmes, 1942a; Combe & Holmes 1945) and quantitative (Tappe *et al.*, 2003; Gurenko & Sobolev, 2018), that kalsilite occurs in all three archetypal rock types of the Bunyaruguru volcanic field, SW Uganda, *i.e.* in katungite, ugandite and mafurite. This IUGS decision brings still more confusion to the literature when suggesting that ugandite “*is more logically classified as an olivine leucitite*” (Le Maitre *et al.*, 2002, p. 12). Consequently, some rocks lacking modal kalsilite have been classified as ugandite (see Prelević *et al.*, 2005). The inappropriate use of this rock name also prevents discussions on the conceivable genetic relationships between all types of kalsilite-bearing volcanic rocks.

A second shortcoming of the IUGS recommendations arises from the inadequate mineral assemblages considered by the IUGS Subcommittee (Le Maitre *et al.*, 2002, table 2.5). Their oversimplified mineralogy does not effectively reflect the modal variations among the kalsilite-bearing volcanic rocks (*e.g.* Junqueira-Brod *et al.*, 2005a, b). Holmes and co-workers categorically defined a continuous spectrum of volcanic rocks formed by various combinations of the essential minerals clinopyroxene (originally described as augite), leucite, kalsilite and melilite, in conjunction with more or less olivine (Holmes, 1942a, b; 1950; Combe & Holmes, 1945). Phlogopite (originally described as biotite) does not belong to the critical

minerals (Holmes, 1950; Sahama, 1974), but may occur in some varieties of these rocks (Supplementary Data – **Table A1**). In our point of view, there is a general misunderstanding concerning the mineral assemblages found in the archetypal kamafugites (*sensu stricto*), and consequently, in part of the kalsilite-bearing volcanic rocks. This probably led some authors (e.g. Mitchell & Bergman, 1991; Edgar, 1996; Woolley *et al.*, 1996) to assumptions that clearly changed the original meanings of the terms katungite, ugandite and mafurite as defined by Combe & Holmes (1945). An example of such a controversial statement is “...*katungite grades to ugandite, a variety containing leucite and augite in place of kalsilite and melilite, respectively*” (Mitchell & Bergman, 1991, p. 14).

Some mafic potassic alkaline volcanic rocks with a very uncommon mineral assemblage, which contain both nepheline and kalsilite in their groundmass, have also been found in central Brazil (Brod *et al.*, 2005). Trying to apply the IUGS guidelines to these rocks led us to the question of how to classify these kalsilite-bearing rocks. According to the hierarchical IUGS classification scheme, step 4 (Le Maitre *et al.*, 2002, p. 6) mandates: “*if a rock contains modal kalsilite go to section 2.5 – Kalsilite-bearing Rocks*”. However, there is no mention of nepheline in this section (Le Maitre *et al.*, 2002, p. 12). The IUGS recommendations on the nomenclature of kalsilite-bearing volcanic rocks obviously have neither considered the coexistence of kalsilite and nepheline, nor the possibility of other volcanic rocks containing kalsilite – besides those of the archetypal kamafugites of Sahama (see Woolley *et al.*, 1996; Le Maitre *et al.*, 2002). Note that the expression ‘**archetypal kamafugites**’ is used hereafter in the sense of Sahama (1974), who considered as archetypal the areas of the Toro Ankole province, SW Uganda, as well as the two occurrences of Umbria, Italy. Venanzite and coppaelite are, thus, also regarded as standard members of the kamafugitic series as katungite, ugandite and mafurite.

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The IUGS nomenclature (Le Maitre *et al.*, 2002) has been rarely applied, and when it was done, it was frequently reported alongside the historical terminology (*e.g.* Tappe *et al.*, 2003; Junqueira-Brod *et al.*, 2005a, b; Rosenthal *et al.*, 2009; Foley *et al.*, 2011; Muravyeva *et al.*, 2014; Gurenko & Sobolev, 2018; Muravyeva & Senin, 2018). A brief search in the GEOROC database for rock name entries referring to kalsilite-bearing volcanic rocks resulted in 46 katungite, 84 ugandite, 65 mafurite, 26 kalsilitite, and 271 indiscriminate kamafugite entries (**Figure 4.1**). No entry was found for venanzite and coppaelite, but some variations of the melilitite root name that better conforms with the IUGS recommendations have essentially been applied only to the Italian kalsilite- and melilite-bearing lavas (*e.g.* Stoppa & Cundari, 1995; 1998; Peccerillo, 2017). When searching with Google Scholar, very similar statistics were obtained. Our investigation also detected some nephelinite, and even ankaratrite entries, with kalsilite as a qualifier in their root names, which are not considered by the current IUGS scheme.

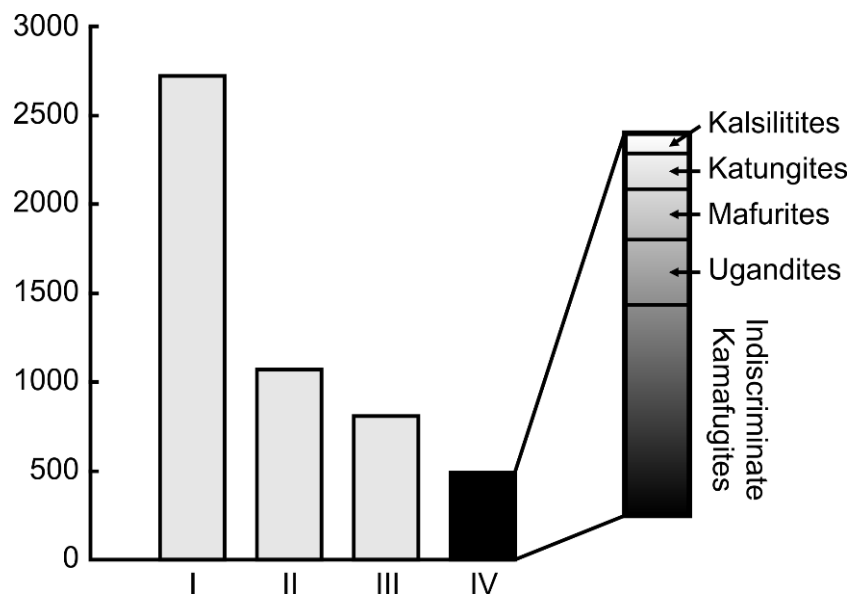


Figure 4.1 Frequency of entries of some general rock names of alkaline volcanic rocks in the GEOROC database. (I) nephelinites; (II) leucitites; (III) melilitites; (IV) kalsilite-bearing volcanic rocks. For comparison only, all rocks named kamafugite were considered here as containing modal kalsilite, although this is considered highly unlikely. The data were retrieved from the GEOROC database in September 2020.

4.3 Previous Work – Some Insights from History

Historical Terminology

In 1942, Arthur Holmes (Holmes, 1942a) in association with Bannister & Hey (1942) first discovered the presence of kalsilite in highly potassic ultrabasic lavas of the Toro-Ankole province, SW Uganda. Over the next 50 years, volcanic rocks with kalsilite were recognised at only two other localities: (1) central Italy; and (2) Mt. Nyiragongo, DR Congo (*e.g.* Edgar, 1984; Mitchell & Bergman, 1991). As a consequence, the terminology of the kalsilite-bearing volcanic rocks was restricted to a few terms (**Table 4.1**).

Table 4.1 Historical terminology of kalsilite-bearing volcanic rocks.

Rock Term	Type Locality	Original Reference
Katungite	SW Uganda	Holmes (1937)
Ugandite	SW Uganda	Holmes & Harwood (1937)
Mafurite	SW Uganda	Holmes (1942a)
Venanzite	Central Italy	Sabatini (1899)*
Coppaelite	Central Italy	Sabatini (1903)

*See Holmes (1942b).

The term **katungite** was proposed by Holmes (1937) after the extinct Katunga volcano in Toro Ankole province, SW Uganda. It was originally defined as “*an alkali ultrabasic rock with more potash than soda, the essential minerals being melilite and olivine; the potash may be present in glass, zeolites, potash-rich nepheline, kaliophilite, leucite, or biotite; special varieties may be distinguished by appropriate mineralogical prefixes, e.g. leucite katungite, biotite katungite*” (*ibid.*, p. 210). Holmes (1942a) and Combe & Holmes (1945) later recognised that kalsilite rather than kaliophilite occurs in katungite.

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The term **ugandite** broadly refers to melanocratic (olivine-rich) types of olivine leucitite (see Combe & Holmes, 1945; Holmes, 1945; Lloyd *et al.*, 1991). This term was first applied to feldspar-bearing rocks from the Bufumbira volcanic field (see Holmes & Harwood, 1937), in the NW of Virunga province, SW Uganda (*e.g.* Lloyd *et al.*, 1991). These rocks are currently classified as olivine basanites (Lloyd *et al.*, 1991). However, comparable melanocratic rocks found in the Bunyaruguru volcanic field in the Toro-Ankole province have also been classified as ugandite (see Holmes, 1937; 1942a; 1945; 1950; Combe & Holmes, 1945). These ugandites, however, clearly lack feldspars and encompass substantial amounts of perovskite instead of chromite in their groundmass (Lloyd *et al.*, 1991). Furthermore, kalsilite ugandite and melilite ugandite varieties have been described, but only from the Bunyaruguru field (Holmes, 1942a; Combe & Holmes, 1945).

After the discovery of kalsilite, Holmes (1942a) introduced the new term **mafurite**, together with the possible leucite mafurite and biotite mafurite varieties, for kalsilite-bearing lavas found in and around the Mafuru craters, Bunyaruguru field. The archetypal mafurite is composed of olivine, clinopyroxene, kalsilite, perovskite and black ore (opaques), together with minor biotite (less than 5%) and interstitial glass. According to Holmes (1942a), “*the rock could be called olivine-rich mela-kalsilitite, but as leucite and biotite varieties also occur and require distinguishing names, such a term would be unduly awkward*” (p. 199). Varieties containing a little melilite or leucite are rather common and are transitional to katungite and ugandite, respectively (*e.g.* Holmes, 1942a; Combe & Holmes, 1945).

The historical names **venanzite** and **coppaelite** derive from the small magmatic centres located at San Venanzo and Cupaello in the Intra-Apennine province of central Italy (*e.g.* Peccerillo, 2017). Venanzite was first described, independently, by Sabatini (1899) and Rosenbusch (1899) as a new rock type composed of melilite, leucite, olivine and minor phlogopite (see Holmes, 1942b). Based on the petrographic and chemical resemblances

between this rock type and the SW Uganda kalsilite-bearing rocks, Holmes (1942b) first anticipated that kalsilite could be a possible mineral phase in the San Venanzo lavas. Its occurrence was confirmed 10 years later (Bannister *et al.*, 1953).

The Cupaello lava (*i.e.* coppaelite) represents a very particular olivine-poor kalsilite-bearing rock type that had earlier been described by Sabatini (1903) as a ‘melilitic pyroxenite’ and that consisted of clinopyroxene, melilite, and minor mica (*i.e.* phlogopite) in a glassy groundmass. Chemical analyses made during the first half of the past century recorded extremely variable K₂O contents for these lavas (see Holmes, 1942b), which did not lead to a suspicion of the existence of kalsilite. The recognition of kalsilite in this ‘exotic’ rock type was only achieved in the mid-1960s as reported by Gragnani (1972) and Sahama (1974).

Historical Classification

Our early efforts to classify kalsilite-bearing rocks led us to a comprehensive review of the petrographic descriptions given by Holmes and co-workers in their classical studies on the volcanic areas of SW Uganda (Holmes & Harwood, 1932; 1937; Combe & Holmes, 1945; Holmes, 1937; 1942a; 1945; 1950; 1952). This region lies in the Western Branch of the East African Rift System and covers several volcanic fields (*e.g.* Katwe-Kikorongo, Bunyaruguru, Bufumbira – Holmes, 1950; Lloyd *et al.*, 1991), each with rocks of their own petrographic characteristics, which reflects their variable K/Na ratios, and consequently, their potassic or ultrapotassic chemical affinity. Knowledge about these early findings is essential to understand the rationale of the nomenclature of kalsilite-bearing lavas promoted in the classical papers (see also Sahama & Meyer, 1958).

In a first attempt to systematize the classification of kalsilite- and leucite-bearing volcanic rocks from the Bunyaruguru field, Holmes (1942a) considered the relationship between the leucite-kalsilite and augite-melilite mineral pairs. Olivine, perovskite and opaque minerals are common to all rock types, except for those rare olivine-free rocks called ‘proto-

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katungite'. One of the most remarkable contributions of Holmes (1942a) is probably also one of the most misunderstood. Holmes proposed that the main rock types (*i.e.* katungite, ugandite and mafurite) could be distinguished by pairs of the four critical minerals; for example, dominant augite and kalsilite identify a rock as a mafurite, although minor leucite and melilite might be present as well. Holmes never forbade the joint occurrence of augite, melilite, leucite and kalsilite, asserting that “...*rocks containing all four of the critical minerals have not been detected, but there seems to be no theoretical reason for supposing that such rocks do not exist*” (Holmes, 1942a, p. 211). Indeed, Combe & Holmes (1945) characterized a complete petrographic series between the ugandite and mafurite end-members, and between mafurite and katungite, including lavas containing all four of the critical minerals concomitantly (*i.e.* leucite-melilite mafurite; kalsilite-melilite ugandite). Unfortunately, this important aspect was disregarded, and may have led to the significant problems with the IUGS scheme as described above.

Holmes (1950) was the first to propose a triangular classification diagram (**Figure 4.2**), although he had considered rather awkward vertices with leucite and augite (L), kalsilite and augite (K), and melilite and potash-rich glass (M). Even after he noticed a complementary relationship between augite and melilite, Holmes still retained the exclusivity of the term katungite, and so adopted the formerly well-known term **alnöite** for augite- and biotite-bearing katungite varieties (see also Higazy, 1954). Note that alnöite is now considered an important melilite-bearing ‘end-member’ of the ultramafic lamprophyre group, according to Tappe *et al.* (2005). In his original work, Sahama (1974) summarized this earlier classification scheme considering that all the mineral assemblages of the kalsilite-bearing volcanic rocks could be characterized in a triangle with leucite, kalsilite, and melilite apices (**Figure 4.3**). These light-coloured minerals, together with olivine and clinopyroxene, represent the essential constituents of the katungite, ugandite and mafurite petrographic series.

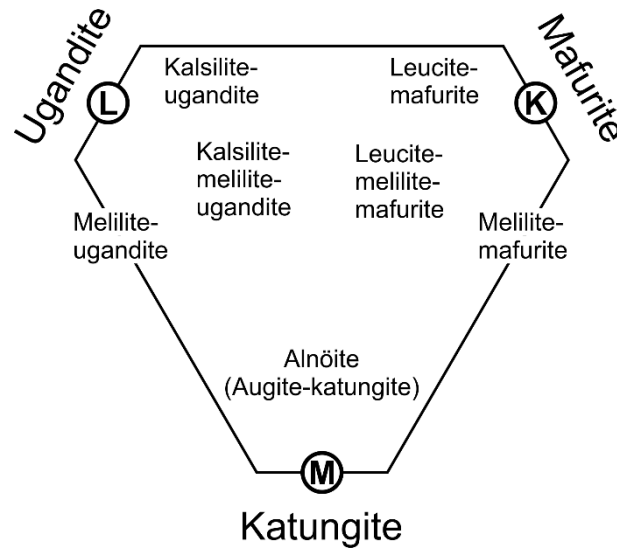


Figure 4.2 Ternary classification diagram for the mafic potassic volcanic rocks of the Toro-Ankole province, SW Uganda. L – leucite and augite, K – kalsilite and augite, M – melilite and potash-rich glass (modified after Holmes, 1950). Note that alnöite is now considered a melilite-bearing ‘end-member’ of ultramafic lamprophyres (see Tappe *et al.*, 2005).

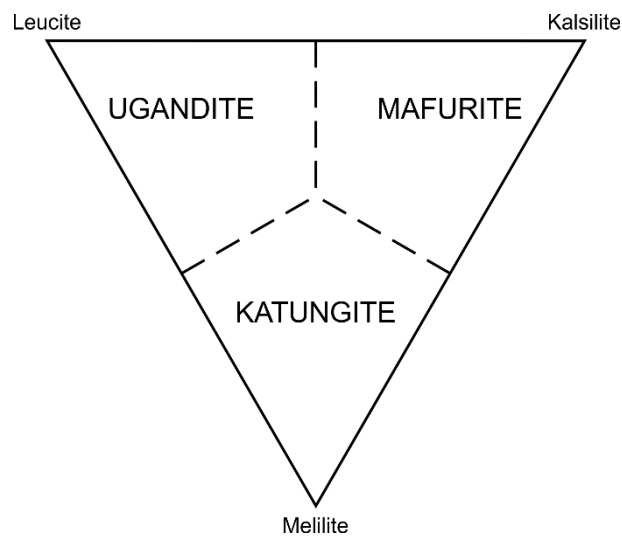


Figure 4.3 Classification scheme for the Toro-Ankole kalsilite-bearing rocks (modified after Sahama, 1974).

Further attempts to ‘simplify’ the original nomenclature of the archetypal kalsilite-bearing rocks proved unsuccessful. Hatch *et al.* (1961, 1972) tried to introduce terms such as ‘olivine kalmafite’ (kalsilite plus mafic minerals) and ‘olivine leumafite’ (leucite plus mafic minerals) in place of the original geographically based names mafurite and ugandite, respectively. In their view, the existing nomenclature of the mafic feldspathoidal lavas (*i.e.* nephelinite, leucitite, melilitite, kalsilitite) presented a false impression of their mineral

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compositions, considering that clinopyroxene and olivine often exceed the proportions of the distinctive light-coloured phases. On the other hand, Lloyd *et al.* (1991) attempted to apply a more ‘common’ mineralogical classification that resulted in very cumbersome terms (*e.g.* olivine-leucite-kalsilite-melilite clinopyroxene-rich lava), which hampered any possible correlation with the previous terminology. Moreover, according to modal compositions (see Lloyd *et al.*, 1991, table 12), the mineral names were given in decreasing order of abundance, which is the opposite of the use recommended by the IUGS (Le Maitre *et al.*, 2002).

4.4 The Coexistence of Kalsilite and Nepheline – A Challenge to Nomenclature

Combe & Holmes (1945) already anticipated the complications arising from the kalsilite and nepheline coexistence in a remarkable statement: “*The optical properties of the kalsilite are such that in the absence of evidence to the contrary the mineral would be identified as nepheline*” (*ibid.*, p. 369). With purely optical transmitted-light microscope means, kalsilite cannot be distinguished from nepheline (*e.g.* Holmes, 1942a; Sahama, 1960; Deer *et al.*, 2004). The optical distinction is possible only if the two mineral phases occur in strictly parallel orientation in the same crystal (for more details, see Sahama, 1960). If kalsilite and nepheline do not occur in parallel orientation or occur as separate crystals, other analytical methods such as X-ray powder diffraction or electron microprobe analysis (EMPA) must be employed (Sahama, 1960; Deer *et al.*, 2004). Therefore, any petrographic classification system involving kalsilite will need to be based on data from advanced instrumental techniques. Nevertheless, it is obviously expected that in the 21st Century back-scattered electron imaging coupled with EMPA can be used to clarify the nature and abundances of fine-grained colourless phases in the groundmass of volcanic rocks.

Kalsilite (ideally KAlSiO_4 ; the ‘so-called’ Ks chemical component) may contain ~20 mol.% of NaAlSiO_4 (*i.e.* the ‘so-called’ Ne component) in solid solution. On the other hand, ‘ideal’ nepheline must contain one-fourth of K substituting for Na (*i.e.* $\text{KNa}_3\text{Al}_4\text{Si}_4\text{O}_{16}$ – see

also Hålenius *et al.*, 2018). In addition, in ultrabasic volcanic rocks, particularly in those K-rich ones, the composition of nepheline can reach ~60 mol.% of Ks. The solid solution between ‘ideal’ nepheline and almost pure kalsilite is incomplete and marked by a miscibility gap at temperatures below ~1000 °C (for further details, see Tuttle & Smith, 1958; Ferry & Blencoe, 1978; Hovis *et al.*, 2009). In the classical works (*e.g.* Holmes, 1952), also because the original protagonists were unaware of these experimental facts, the presence or absence of kalsilite was largely based on interpretation of whole-rock chemical data, more specifically on K₂O and Na₂O contents. As an example, potassic nephelinites (originally termed ‘potash ankaratrites’ – Holmes & Harwood, 1932; Holmes, 1952) from the Katwe-Kikorongo volcanic field, SW Uganda, were considered analogous to the archetypal kalsilite-bearing rocks of the nearby Bunyaruguru field, but with K-rich nepheline instead of kalsilite – given that their K₂O/Na₂O ratios were not as high as those from Bunyaruguru (Holmes, 1952; Sahama, 1974), as well as on a classical ‘wet-chemical’ analysis of grain separates (see Sahama & Wiik, 1952). Thus, the joint occurrence of kalsilite and nepheline in the kamafugitic series, as well as the presence of kalsilite in other mafic potassic volcanic rocks, were never investigated appropriately.

Several lines of evidence indicate that kalsilite and nepheline may occur together more commonly than originally expected. Sahama first reported the coexistence of these two feldspathoids in the forms of complex phenocrysts with perthite-like exsolutions and as individual, well separated crystals in the groundmass of some potassic lavas of the active Mt. Nyiragongo volcano, DR Congo (*e.g.* Sahama, 1957; 1960; 1962a). More recently (*e.g.* Lloyd *et al.*, 1991; 1996; 2002), some rocks from the Katwe-Kikorongo field, SW Uganda, were described as containing kalsilite or nepheline, or both phases together, as intergrowths in groundmass. It is interesting to note that Holmes & Harwood (1932) already predicted a K-rich phase similar to, and coexisting with, nepheline, until then supposedly kaliophilite, in the groundmass of the Katwe-Kikorongo lavas. Then, kalsilite and nepheline were also found

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together in mafic potassic volcanic rocks of central Brazil (Brod *et al.*, 2005), and possibly in China (Yu *et al.*, 2003) as well. Besides, various studies indicate that minor nepheline could occur also in the groundmass of some archetypal kalsilite-bearing volcanic rocks from central Italy and SW Uganda (*e.g.* Sahama, 1974; Velde & Yoder, 1978; Edgar & Arima, 1981; Cundari & Ferguson, 1991; Tappe *et al.*, 2003; Gurenko & Sobolev, 2018; Lustrino *et al.*, 2020).

4.5 A New Classification Proposal

Rationale

The current IUGS nomenclature for kalsilite-bearing volcanic rocks proved to be unclear. The revised classification system proposed in this work is largely based on the petrographic descriptions of Holmes and co-workers, on the triangular diagram of Sahama (1974), and on new findings related to kalsilite and nepheline coexistence. We attempt to: (1) clarify the use of the most familiar historical terms (*e.g.* ugandite), improving their definitions as far as possible; (2) establish that nepheline may be a common mineral in kalsilite-bearing volcanic rocks; and (3) elucidate the complicated nomenclature of some unusual, feldspar-free, mafic potassic lavas (*e.g.* Holmes potash ankaratrites) where both kalsilite and nepheline may coexist in the groundmass.

Any useful petrographic classification for kalsilite-bearing volcanic rocks should recognise the complete data base of mineral assemblages (modal mineral compositions from the global literature about these rocks are listed in Supplementary Data – **Table A1**). According to the classical works (*e.g.* Holmes, 1942a; 1945; 1950; Combe & Holmes, 1945; Sahama, 1974), olivine, clinopyroxene, kalsilite, leucite and melilite are the critical (*i.e.* essential) minerals of the archetypal kalsilite-bearing rocks. This mineralogy has also been found in the Italian and Brazilian counterparts (*e.g.* Tappe *et al.*, 2003; Supplementary Data – **Table A1**).

However, as discussed above, nepheline, too, seems to be particularly important in some ‘potassic nephelinites’ that have been hitherto overlooked as possible kalsilite-bearing volcanic rocks. On the other hand, phlogopite is no longer considered an essential phase, as it represents specific crystallization conditions of mafic potassic magmas (see Yoder, 1986), and more importantly, this will avoid overlap with the terminology of lamprophyres, lamproites and related rocks (*e.g.* Tappe *et al.*, 2005; 2021). In addition, it is fundamental to note that primary feldspars, particularly plagioclase, and amphiboles are completely absent in these rocks (*e.g.* Holmes 1945; 1950; Lloyd *et al.*, 1991).

The kalsilite-bearing volcanic rocks are dominantly mafic, melanocratic rocks, in which clinopyroxene, and occasionally olivine, constitute the most abundant phases (*e.g.* Hatch *et al.*, 1972; Lloyd *et al.*, 1991; Woolley *et al.*, 1996), with the exception of some rare, glass-rich katungite from SW Uganda (*e.g.* Holmes, 1937). On this account, the uneven distribution of the main light-coloured constituents (**Figure 4.4**) makes them perfectly suitable for petrographic classification purposes. Furthermore, we have noted a remarkable chemical constraint in the alkali ratio of kalsilite-bearing volcanic rocks that separates them into two distinct (1) potassic and (2) ultrapotassic groups.

Nomenclature

Because of the problems with the IUGS recommendations, most specialists have preferred to apply Sahama’s (1974) criteria (*i.e.* his triangular diagram) for the purpose of petrographic classification of kalsilite-bearing volcanic rocks. Consequently, the traditional type-locality based terms katungite, ugandite and mafurite have remained resolutely in the international literature, whereas the cumbersome mineralogical names endorsed by the IUGS have been ignored. What is more, the terms venanzite and coppaelite have scarcely been used so far, being almost exclusively restricted to older literature (see Gallo *et al.*, 1984 and references therein), except for some Italian authors (*e.g.* Stoppa *et al.*, 1997; Stoppa & Cundari,

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1998; Lustrino *et al.*, 2020). On these grounds, hereafter the terms katungite, ugandite and mafurite are established as root names recommended for petrographic classification of volcanic rocks containing modal kalsilite.

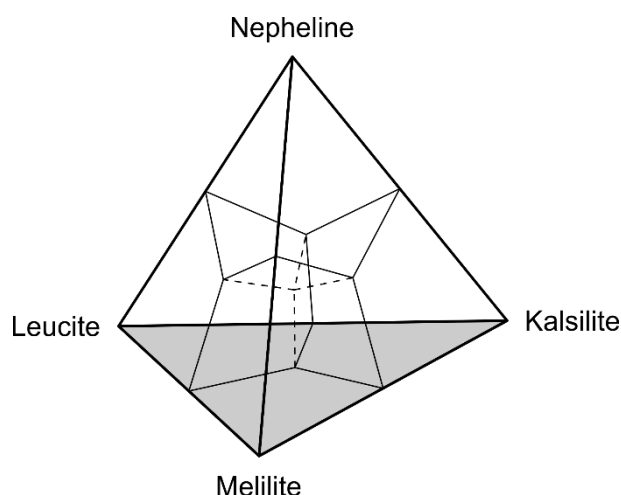


Figure 4.4 The main light-coloured constituents of kalsilite-bearing volcanic rocks (adapted from Sahama 1962b). The grey basal-plane of the tetrahedron illustrates the most likely position, in this diagram, of the ‘archetypal kamafugites’ assemblages. However, they should not be restricted to this plane as nepheline occurs in, at least, three of these rock types (venanzite, katungite and ugandite – see text for discussion). Note that there is no boundary between nepheline and kalsilite (or any other mineral) because of the difficult estimation of their respective proportions. It must be clear, though, that each of the rock names defined in this work (*i.e.* katungite, ugandite, mafurite and kalsilite nephelinite) comprises an equal 3D-volume inside the tetrahedron, extended towards the respective vertexes.

The recommendation of these three root names basically respects their original definitions (see Historical Terminology section), but some modifications are required. First, kalsilite is a mandatory constituent for all root names. This implies that ugandite is no longer synonymous with ‘olivine leucitite’ (as recommended by Le Maitre *et al.*, 2002). The term ugandite has been problematic ever since it was coined by Holmes & Harwood (1937), as it has been applied even to olivine-rich, feldspar-bearing volcanic rocks (see Lloyd *et al.*, 1991). However, as ugandite is widely accepted as an ‘end-member’ of the kamafugitic series (*sensu stricto*), we have decided to keep it as a recommended root name but give it a more restricted definition to avoid further misconceptions (*i.e.* hereafter ugandite should be used only for leucite-bearing volcanic rocks with modal kalsilite; see also **Table 4.2**). Second, nepheline is

included as a common minor phase in the definitions of all the root categories (*i.e.* katungite, ugandite and mafurite; see **Table 4.2**). Note that nepheline has not been reported in mafurites so far (see Supplementary Data – **Table A1**). But, as already discussed, nepheline occurs in the groundmass of some archetypal kalsilite-bearing rocks (venanzite, katungite and ugandite). Mass balance calculations indicate that ~5% of nepheline may occur in the ugandites from SW Uganda, ~6% in the Italian venanzites, and up to 15% in the glass-rich katungites from SW Uganda (values based on whole-rock and mineral chemistry data referenced in Supplementary Data – **Table A2**). However, it is critical to note that these numbers must be considered maximum estimates only, as clinopyroxene, kalsilite, melilite, perovskite and even the glass phase could also carry significant Na₂O contents. Nepheline, thus, likely occurs as a minor phase only.

In spite of these trivial, but very important modifications, the root names katungite, ugandite and mafurite are defined following Sahama's (1974) triangular diagram, whereby melilite, leucite and kalsilite are the discriminating constituents (**Figure 4.5**), and together with clinopyroxene and olivine, they comprise all the essential minerals of these kalsilite-bearing rocks. The defining assemblages listed in **Table 4.2** clarify the conditions required to classify each rock type under its proper name. If a rock contains modal kalsilite, but melilite is the dominant light-coloured phase, the rock should be called katungite; if leucite is dominant over kalsilite or melilite, the rock should be called ugandite; and if kalsilite is the main diagnostic constituent, the rock should be called mafurite. The presence of all five critical phases at the same time is not required to classify these rocks. It must be emphasized, however, that these root names should be applied only if modal kalsilite has been confirmed. Generally, these rock types have an ultrapotassic chemical character, except for some katungites (see **Figure 4.6**).

It is logical to infer from the main light-coloured constituents (**Figure 4.4**) that there should be a kalsilite-bearing volcanic rock in which nepheline is the dominant phase. Some

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mafic potassic lavas that until now have been overlooked, perfectly fit this category (*e.g.* kalsilite-bearing melilitite nephelinites from Mt. Nyiragongo – Sahama & Meyer, 1958; Sahama, 1962b; 1973; Demant *et al.*, 1994; Platz *et al.*, 2004; Andersen *et al.*, 2012; 2014). Such potassic volcanic rocks undeniably contain modal kalsilite, but they are often dominated by nepheline, with more or less melilitite, and rarely leucite (see, *e.g.* Sahama, 1960; Lloyd *et al.*, 1991; 1996). Nonetheless, the terminology of these rather ‘unusual’ feldspar-free volcanic rocks appears to have never been appraised by IUGS (see Woolley *et al.*, 1996; Le Maitre *et al.*, 2002).

Table 4.2 Modal classification of kalsilite-bearing volcanic rocks in comparison with other feldspar-free volcanic rocks based on their diagnostic mineralogy. Nephelinite, melilitite and leucitite defining assemblages follow the IUGS guidelines (see Le Maitre *et al.*, 2002). The dashed line marks the entrance of kalsilite into the mineral assemblages below the line. In general, the volcanic types become progressively more potassic from the top to the bottom of the table (adapted from Gill, 2010; table 9.2).

Rock Name	Common Mineralogy						Defining Assemblage
	Cpx	Ol	Nph	Lct	Mll	Kls	
Nephelinite	●	○	●	○	< 10%	-	Dominant Nph
Melilitite	●	○	○	○	●	-	Dominant Mll
Leucitite	●	○	○	●	< 10%	-	Dominant Lct
Kalsilite Nephelinite	●	○	●	○	○	●	Kls + Dominant Nph
Katungite	●	●	*	○	●	●	Kls + Dominant Mll
Ugandite	●	●	*	●	○	●	Kls + Dominant Lct
Mafurite	●	●	*	○	○	●	Dominant Kls

Mineral abbreviations according to Whitney & Evans (2010). Cpx – clinopyroxene; Ol – olivine; Nph – nepheline; Lct – leucite; Mll – melilitite; Kls – kalsilite. Perovskite and Ti-magnetite are accessory minerals common to all kalsilite-bearing rocks; Phlogopite may occur as a type mineral depending on the physical conditions of crystallization of the potassic magmas (see Yoder, 1986). Essential minerals (solid circles); Type minerals (open circles); Minor minerals (asterisks); Absent (hyphen).

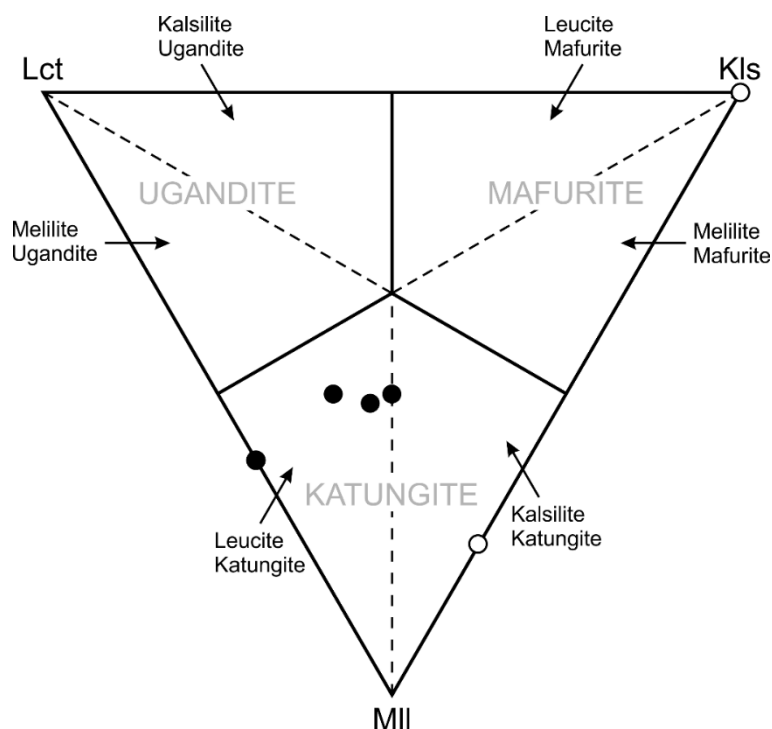


Figure 4.5 Modal classification of kalsilite-bearing volcanic rocks (after Sahama, 1974; fig. 2) based on relative amounts of leucite (Lct), kalsilite (Kls) and melilite (Mll). The fields for some more specific names are indicated as well, for specialist use. Representative modes (see Supplementary Data – Table A1) for samples of the archetypal venanzite (solid circles) and coppaelite (open circles) are plotted for comparison (see text for discussion).

The majority (if not all) of the nepheline-dominated mafic potassic lavas carrying kalsilite cannot be accurately classified as one of the formerly defined kalsilite-bearing types (*i.e.* katungite, ugandite and mafurite). Kalsilite is almost certainly far less abundant than nepheline (see Holmes, 1952; Sahama & Meyer, 1958), although it may have been largely under-estimated in conventional optical petrography. In addition, these ‘unusual’ rock types generally have only a slightly potassic chemical affinity (see **Figure 4.6**), whereas the archetypal kalsilite-bearing rocks have a distinct ultrapotassic character (*e.g.* Sahama & Meyer, 1958; Sahama, 1974; Foley *et al.*, 1987). Therefore, an additional rock name is required to properly classify the kalsilite-bearing volcanic rocks, whereby modal nepheline is the dominant light-coloured phase (**Table 4.2**). These rocks have been mostly classified as potassic nephelinites, which is appropriate in terms of a chemical classification but regrettably hides the modal kalsilite constituent. Thus, a more useful petrographic classification could make use of

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one of the prefixes *kalsilite* or *kalsilite-bearing* in place of potassic (e.g. kalsilite nephelinite, kalsilite-bearing melilite nephelinite, etc.). Hereafter, **kalsilite nephelinite** is recommended as the specific name to be used to classify this category of kalsilite-bearing volcanic rocks.

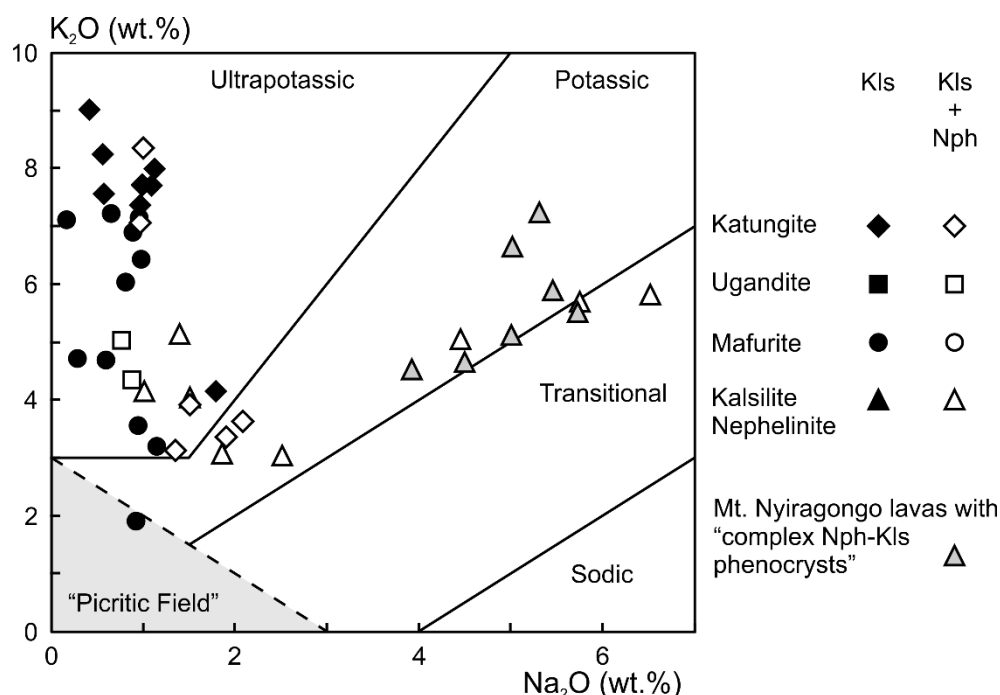


Figure 4.6 Chemical affinity of the kalsilite-bearing volcanic rocks. The alkali contents are plotted only for those rock types for which corresponding quantitative EMPA kalsilite data have been reported (see Supplementary Data – Table A2). All analyses were recalculated to 100% on a volatile-free basis. The boundary lines for sodic, transitional and potassic fields are based on Le Bas *et al.* (1986), Middlemost (1991) and Comin-Chiaramonti *et al.* (1997); ultrapotassic boundary line according to Foley *et al.* (1987); ‘picritic field’ after Le Maitre *et al.* (2002). All samples were reclassified according to our scheme; for those with available mode (Supplementary Data – Table A1), we used the dominant light-coloured phase; for those without a mineral mode, we followed the original petrographic descriptions as far as possible. Mineral abbreviations as in Table 4.2.

Additional Qualifiers

In their classical papers, Holmes and co-workers extensively employed mineral prefixes to categorise all varieties of kalsilite-bearing rocks described until then (e.g. melilite mafurite, kalsilite ugandite, leucite katungite). There is a complete petrographic series involving the three rock types katungite, ugandite and mafurite (Holmes, 1942a; 1950; Combe & Holmes, 1945). Thus, we recommend to add mineral qualifiers to the three root names whenever a more specific

terminology is required (see **Figure 4.5**). However, the accurate measurement of mineral mode in the kalsilite-bearing volcanic rocks is troublesome, if not impossible. Though often porphyritic, these rocks generally have very fine-grained groundmass, sometimes including glassy material. The difficulty to distinguish amid kalsilite and nepheline optically has been discussed above, and to achieve this quantitatively is nearly impossible. Henceforth, it is strongly recommended that any mineral qualifier should be added only after careful examination of a large suite of rock samples, as similarly required for the classification of ultramafic lamprophyres (see Tappe *et al.*, 2005). In addition, and in accordance with Holmes (1942a), it is proposed that phlogopite should be used as a qualifier only if it occurs at more than 15% of modal abundance.

Despite the obvious mineral qualifiers (see **Figure 4.5**), on some occasions terms such as ‘olivine-poor’ or ‘olivine-free’ may be added to the recommended root names (*i.e.* katungite, ugandite and mafurite). Based on the classical petrographic descriptions and the modal compositions gathered in this study (Supplementary Data – **Table A1**), modal olivine proportions $\leq 5\%$ seem to form a reasonable upper limit for the use of the olivine-poor prefix. On the other hand, to keep consistency with the IUGS rationale of the more common feldspathoidal volcanic rocks (*i.e.* nephelinite, melilitite and leucitite), olivine is considered a type mineral in the new kalsilite nephelinite specific name only (**Table 4.2**). Thus, if necessary, olivine or olivine-bearing prefixes should be added to this term (*e.g.* kalsilite-olivine nephelinite). Other qualifiers (*e.g.* glass-rich katungite) should follow the IUGS recommendations (Le Maitre *et al.*, 2002, p. 4).

Procedure

In summary, to give all the kalsilite-bearing volcanic rocks a proper name, two vital aspects should be followed: (1) a rock must contain modal kalsilite; and (2) it should be classified by one of the four rock names redefined in this work (**Table 4.2**). Before the

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application of our scheme, though, it is recommended to follow the revised hierarchical IUGS classification system after Tappe *et al.* (2005), with only a minor alteration: at steps 4 and 5, if the rock contains modal kalsilite and it is volcanic, use the following rock names according to the main light-coloured mineral phase:

- (a) if it is kalsilite, the rock is a mafurite;
- (b) if it is leucite, the rock is a ugandite;
- (c) if it is melilite, the rock is a katungite;
- (d) if it is nepheline, the rock is a kalsilite nephelinite.

4.6 Applications of the New Classification System

The following three cases shall illustrate the successful application of this newly proposed classification scheme.

Intra-Apennine Province, Italy

The kalsilite-bearing lavas from central Italy have been commonly regarded by their type localities, San Venanzo and Cupaello (*e.g.* Sahama, 1974; Gallo *et al.*, 1984; Foley *et al.*, 1987; Cundari & Ferguson, 1991). At San Venanzo, the kalsilite-bearing lavas (*i.e.* venanzites) have long been classified as olivine melilitite (*e.g.* Mittempergher, 1965; Holm *et al.*, 1982; Cundari & Ferguson, 1991; Castorina *et al.*, 2000; Panina *et al.*, 2003; Peccerillo, 2017). Similarly, most of the Cupaello lavas have been classified as kalsilite melilitite instead of coppaelite (*e.g.* Gragnani, 1972; Stoppa & Cundari, 1995; Isakova *et al.*, 2017). In addition, some portions of these lavas were already regarded as kalsilitite, based on the paucity of melilite (Cundari & Ferguson, 1991; Stoppa & Cundari, 1995).

According to the IUGS (Le Maitre *et al.*, 2002), venanzite should be termed ‘kalsilite-phlogopite-olivine-leucite melilitite’ and coppaelite ‘kalsilite-phlogopite melilitite’. These names are very restrictive, even when considering samples from their type localities only (see

Stoppa & Cundari, 1995; Lustrino *et al.*, 2020). In the view of Lustrino *et al.* (2020), for instance, the San Venanzo kalsilite-bearing lavas lacking leucite cannot be classified as venanzite (or into any other IUGS recommended category for kalsilite-bearing rocks) and would have to be classified as olivine melilitite. However, these rocks contain modal kalsilite and, therefore, should be assigned to a more specific group of kalsilite-bearing rocks (see Woolley *et al.*, 1996, p. 185).

In our classification scheme, all the kalsilite-bearing lavas from San Venanzo are classified as katungite. The ‘true’ venanzite can be more specifically classified as leucite katungite based on its modal composition (see Supplementary Data – **Table A1; Figure 4.5**). Consequently, the facies lacking leucite could be readily termed leucite-free katungite or simply katungite (*i.e.* the leucite-free prefix is not required as leucite is not an essential mineral under this root name). Interestingly, the resemblance between venanzite and katungite has been well-known (Sahama, 1974; Peccerillo *et al.*, 1988; Tappe *et al.*, 2003) and the term ‘leucite-rich katungite’ was already proposed as a synonym for venanzite (see Holmes, 1937; 1942a).

In the Cupaello lavas, on the other hand, olivine is not as abundant as in samples from San Venanzo (see Supplementary Data – **Table A1**). Hence, the kalsilite-bearing volcanic rocks could be classified as olivine-poor katungite (kalsilite melilitite) or olivine-poor mafurite (kalsilitite) depending on the facies of the lava flow (see Stoppa & Cundari, 1995). However, terms such as kalsilite melilitite and/or kalsilitite are so straightforward that they may be more useful in this special circumstance. Note that our new nomenclature emphasizes the importance of kalsilite rather than melilite in the cases of San Venanzo and Cupaello lavas (*cf.* Bailey & Collier, 2000; Castorina *et al.*, 2000).

Goiás Alkaline Province, Brazil

Some mafic potassic volcanic rocks from central Brazil have a rather uncommon mineral assemblage, with both nepheline and kalsilite in their groundmass (Brod *et al.*, 2005).

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These rocks have been classified according to Sahama's (1974) criteria as mafurite, leucite mafurite, ugandite, and rare katungite (*e.g.* Sgarbi & Gaspar, 2002; Brod *et al.*, 2005; Junqueira-Brod *et al.*, 2005a; b). However, K-rich nepheline, rather than kalsilite, and leucite are the main light-coloured phases. Melilite rarely occurs, and except for some leucite-phyric types, nepheline is always present as an interstitial groundmass phase. The presence of abundant nepheline has been hitherto interpreted as a result of intense subsolidus alteration of primary kalsilite (Brod *et al.*, 2005; Junqueira-Brod *et al.*, 2005a, b). Whereas this is surely the case in some of these rocks, new petrographic and mineral chemical results indicate that nepheline is typically of primary magmatic origin.

Based on these new findings, the mafic potassic kalsilite-bearing rocks of the Goiás Alkaline Province cannot be appropriately classified according to either Sahama's (1974) criteria or the IUGS recommendations (Le Maitre *et al.*, 2002). Besides, to date kalsilite has not been found in the 'so-called' ugandite rock type. Hence, using our new classification system, these kalsilite-bearing rocks are classified as kalsilite-olivine nephelinite (instead of mafurite), leucite-bearing kalsilite-olivine nephelinite (instead of leucite mafurite), and katungite. The latter includes only those melilite-rich types where kalsilite has been confirmed. Otherwise, these feldspar-free rocks should be classified, based on their modal compositions, as olivine-melilite leucitite (*cf.* Danni & Gaspar, 1994). In fact, all rock types without confirmation of kalsilite should be classified according to the existing IUGS nomenclature systems (*e.g.* olivine leucitite rather than ugandite).

Katwe-Kikorongo Field, SW Uganda

For the Katwe-Kikorongo volcanic field, Holmes and co-workers, early on, proposed the terms potash ankaratrite and leucite ankaratrite for clinopyroxene-phyric mafic potassic lavas resembling melanocratic olivine nephelinites or ankaratrites (see Holmes & Harwood, 1932; Holmes, 1952). Perhaps uncertain about the presence of modal kalsilite, Holmes (1950)

still projected the kalsilite ankaratrite type but it is not clear if this type indeed occurs, as petrographic descriptions have not been given anywhere (*cf.* Holmes, 1950; 1952). Besides, some recent studies considered these Holmes ‘ankaratrites’ as a type of potassic nephelinite (*e.g.* Tappe *et al.*, 2003; Rosenthal *et al.*, 2009).

As discussed earlier, kalsilite has been found in the groundmass of some of the Katwe-Kikorongo lavas – ‘so-called’ olivine melilitite and K-nephelinite (Lloyd *et al.*, 1996; 2002). From our point of view, these kalsilite-bearing volcanic rocks should be classified as katungite and kalsilite (olivine) nephelinite, respectively. In addition, it should be noted that Holmes (1950, 1952) employed the term ‘ankaratrite’ also to reflect an abundance of clinopyroxene and relatively little olivine content in the Katwe-Kikorongo lavas – in comparison with the ugandite-mafurite series of the Bunyaruguru volcanic field. This use resembles the obsolete application of the term ‘melanephelinite’ (see Le Bas, 1989, p. 1304). Thus, we suggest that the use of the terms potash ankaratrite and leucite ankaratrite in the sense of Holmes (1952) or Sahama (1974) be discontinued (see, *e.g.* Prelević *et al.*, 2005; Caran, 2016).

4.7 Concluding Remarks

Despite criticisms about exclusively mineralogically-based classifications for the potassic alkaline volcanic rocks (*e.g.* Foley *et al.*, 1987; Mitchell, 1996), the IUGS recommendations of igneous rocks nomenclature (*i.e.* Le Maitre *et al.*, 2002) remain the reference book for non-specialists. Therefore, in view of the problems discussed in this paper, our new classification scheme is an improvement of the current IUGS system. Nevertheless, there are still some important aspects regarding the classification of kalsilite-bearing volcanic rocks that should be carefully considered.

The introduction of the specific name **kalsilite nephelinite** here clearly indicates that this is a special case of nephelinite (*i.e.* nephelinite *sensu lato*). Similarly, katungite is a special case of melilitite-bearing rocks, and ugandite is a special case of leucite-bearing rocks. Only

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mafurite is a unique case amongst all kalsilite-bearing volcanic rocks. According to the IUGS rationale, the equivalent nomenclature to these terms would be kalsilite-olivine melilitite, kalsilite-olivine leucitite and olivine kalsilitite, respectively. However, we do not endorse the use of these ‘common’ IUGS terms in order to avoid false suggestions of possible cogenetic associations that may not be real (*e.g.* katungite have a potassic or ultrapotassic character but typical olivine melilitite have a transitional or sodic chemical affinity, which implies distinctly different origins). Besides, most specialists have favoured the simplicity of the historical terminology, which by now is deeply entrenched in the literature. Furthermore, the IUGS fourth principle of classification states that “...*the terms to be used in any classification should follow, as far as possible, those which are currently and widely accepted as being useful terms*” (Le Bas & Streckeisen, 1991, p. 826).

The current ‘non-genetic’ IUGS modal nomenclature system does not consider the origin of kalsilite (or any other essential mineral) as a criterion for classifying igneous rocks (Le Maitre *et al.*, 2002; see also Le Bas & Streckeisen, 1991). Only the kimberlite and lamproite schemes currently adopted by the IUGS consider the primary or secondary origin of their constituents. But these are mineralogical-genetic classifications based on countless detailed petrographic and petrogenetic studies conducted over the last four decades (see Mitchell, 2020 and references therein). The state-of-the-art on kalsilite-bearing volcanic rocks does not allow this type of classification yet, especially if one considers that the coexistence of kalsilite and nepheline has been investigated in-depth only in the Nyiragongo potassic lavas (*e.g.* Sahama, 1957; 1960; 1962a; Andersen *et al.*, 2012; 2014). And even in this case, it is evident that more systematic investigations are needed before any conclusive interpretation can be arrived at.

However, it should be noted that besides the primary magmatic origin, kalsilite and nepheline can also be formed by subsolidus, metasomatic and contamination processes (Deer *et al.*, 2004). Lustrino *et al.* (2020) argued that the kalsilite-bearing rocks of Italy are products

of very different processes, and only those rocks with primary kalsilite (*i.e.* kalsilite resulting from the igneous crystallization of a melt) can be considered as ‘real’ kamafugites (*sensu lato*). Meanwhile, Lima *et al.* (2020) demonstrated that kalsilite and nepheline occurring in very particular hypabyssal rocks from SE Brazil are products of reaction of a kimberlite melt with Si-rich crustal xenoliths. It is clear that the simple presence of modal kalsilite is not enough to consider this mineral a primary phase, and therefore, detailed textural and petrographic analyses are mandatory in the search for the proper name of a kalsilite-bearing volcanic rock.

Volcanic rocks containing kalsilite cannot be classified by simple optical petrography due to their common fined-grained textures and the virtually impossible optical distinction between kalsilite and nepheline. Hence, if a feldspar-free volcanic rock contains a nepheline-like mineral – coupled with a potassic or ultrapotassic chemical affinity (see below) and when more detailed petrography is unavailable (*i.e.* modal kalsilite cannot be recognized), it is recommended to use the non-specific terms **potassic nephelinite** and/or **potassic melilitite**. The potassic prefix is very useful to identify analogous rock types for petrogenetic purposes. Besides, the simple root names nephelinite and melilitite traditionally suggest a sodic chemical affinity, which is inappropriate in the context of kalsilite-bearing rocks.

Holmes (1942a) already recognised that heteromorphism can be quite extensive in the kalsilite-bearing volcanic rocks given that the mineral pairs leucite-melilite and kalsilite-augite chemically overlap each other (see also Yoder, 1986). As a consequence, a chemical classification system designed specifically to discriminate these rocks has not yet been achieved. Nonetheless, there seems to be a systematic correlation between modal mineralogy and chemical affinity of the kalsilite-bearing volcanic rocks (**Figure 4.6**). Based on the available data, mafurites and ugandites are so far recognized as ultrapotassic (Supplementary Data – **Table A2**). In contrast, katungites can be potassic or ultrapotassic, whereas kalsilite nephelinites typically have a slightly potassic character, except for one or two ultrapotassic

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samples (see **Figure 4.6**). This systematic may be useful as a guide to the rock nomenclature after the confirmation of modal kalsilite. If the chemical data plot into the ultrapotassic field (**Figure 4.6**), the rock almost certainly would be classified as katungite, ugandite or mafurite. If not, then it would be a kalsilite nephelinite or a potassic katungite. These criteria are particularly useful for the feldspar-free volcanic rocks containing only nepheline-like minerals as the main light-coloured phases. However, in leucite-bearing rocks, one should be cautious about the strict application of any chemical classification because of common analcimization (*i.e.* the transformation of primary leucite to secondary analcime accompanied by exchange of K and Na – see Ngwenya & Tappe, 2021 and references therein).

The IUGS systematics for kalsilite-bearing volcanic rocks (*i.e.* Le Maitre *et al.*, 2002) have promoted the general idea that modal kalsilite is limited to kamafugites (*sensu stricto*). This, at least in part, has led to confusion in the literature concerning the application of the terms ‘kamafugite’ and ‘kamafugitic affinity’. We believe that this subject deserves further comprehensive discussion that is, however, beyond the scope of this work. Nevertheless, some critical points must be clarified here. As defined earlier, the acronym ***kamafugite*** was introduced by Sahama (1974) based on the original nomenclature of the archetypal kalsilite-bearing rocks of the Toro-Ankole province, SW Uganda (*e.g.* Combe & Holmes, 1945). But despite the origin of the name, kamafugite is a chemically-defined term initially proposed to categorize some ultrapotassic volcanic and subvolcanic rock types as a distinct group (see Sahama, 1974). The presence of kalsilite or any other mineral was not part of the definition (note, according to Sahama [1974, table 2] some potash ankaratrites also can be considered as having kamafugitic affinity, although they do not contain modal kalsilite – *ibid.*, p. 100). Therefore, the long-standing paradigm that a volcanic rock containing kalsilite is a kamafugite (*sensu stricto*) is no longer true. Also, not all volcanic rocks with a kamafugitic affinity must have modal kalsilite (*e.g.* ultramafic lamprophyres – see Foley *et al.*, 1987; Rosenthal *et al.*,

2009). Only the kalsilite-bearing volcanic rocks with an ultrapotassic chemical affinity (so far mafurites, ugandites and some katungites) can be regarded as a kamafugite (*sensu stricto*), as the other chemical parameters also agree with the Foley *et al.* (1987) criteria. On the other hand, the potassic kalsilite-bearing volcanic rocks should not be characterised by the same criteria, as they fail the primary premise of being ultrapotassic (Foley *et al.*, 1987).

Thus, it must be emphasised once more that the nomenclature system outlined here for the kalsilite-bearing volcanic rocks is a strictly petrographic/modal classification, whereas the terms kamafugite or kamafugitic affinity refer to a chemical classification.

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Supplementary Data

Supplementary data for this paper are available at Journal of Petrology online.

Chapter 5

Substitution of 'Small' Divalent Cations (e.g. Mg)

for Si and Al in the Nepheline Tetrahedral

Framework

Part 1. Calculation of atomic formulae and stoichiometry parameters

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Abstract

A recent review paper on nepheline solid solutions dealt mainly with sodic varieties from nepheline syenites and differentiated alkali basaltic sills. Excel spreadsheets were provided for recalculating cell formulae in terms of the stoichiometric parameters $\Delta\text{Al}^{\text{cavity}}$ cation charge and $\Delta\text{T}^{\text{framework charge}}$ and molecular percentages of the end-members Ne, Ks, Ca-nepheline, and excess Si (Q^{xs}). Small amounts of tetrahedral divalent species (usually < 0.10 wt.% but with up to 0.33 wt.% MgO) were related to a stuffed-tridymite end-member of ideal formula $\text{K}_8\text{Mg}_4\text{Si}_{12}\text{O}_{32}$ (denoted KsT^{2+} -nepheline), although the equations used to calculate these end-members only considered Si, Al and Fe^{3+} as tetrahedral framework species. Recently, K-rich nepheline and kalsilite which contain up 0.54 wt.% MgO have been found in some feldspar-free mafic potassic volcanic rocks from central Brazil. Equations have been developed to deal rigorously with the presence of significant amounts of Mg (and Mn) in recalculating nepheline solid-solution parameters. In two related communications reworked spreadsheets are provided with examples of their use. High quality microprobe analyses of nepheline and kalsilite from magmatic rocks must include analyses for Mg and Mn and, if possible, estimates of Fe^{2+} contents.

Keywords: nepheline stoichiometry, tetrahedral T^{2+} cations, end-member calculations, coupled $\Delta\text{Al}^{\text{cavity cation charge}}$ and $\Delta\text{T}^{\text{framework charge}}$ parameters, estimating Fe valence, excel calculation spreadsheets

5.1 Introduction

In a recent paper reviewing the recalculation of atomic cell formulae for nepheline solid solutions (Henderson, 2020), the approach followed by Barth (1963) was adopted to report the molecular proportions of the end-member molecules for nepheline (Ne, $\text{Na}_8\text{Al}_8\text{Si}_8\text{O}_{32}$), kalsilite (Ks, $\text{K}_8\text{Al}_8\text{Si}_8\text{O}_{32}$), Ca-nepheline (CaNe , $\square^{\text{Ca}}_4\text{Ca}_4\text{Al}_8\text{Si}_8\text{O}_{32}$, *cf.* anorthite), and excess Si (Q^{xs} , $\square^{\text{Si}}_8\text{Si}_{16}\text{O}_{32}$). Following Barth, it was emphasized that the entry of Ca into extra-framework cavity sites and excess Si into the three-dimensional framework is accompanied by formation of a fixed numbers of vacant sites in the cavities (denoted $\square^{\text{Ca}}$ and $\square^{\text{Si}}$). Many authors have not reported the presence of Mg (and Mn) in nepheline compositions and some consider these elements might be present as impurity or alteration phases (*e.g.* Dollase & Thomas, 1978). Henderson (2020) considered that small divalent atoms (*e.g.* Mg) could substitute for quadrivalent and trivalent tetrahedral cations in the framework to form the nepheline/kalsilite end-member molecule $\text{K}_8\text{T}^{2+}_4\text{Si}_{12}\text{O}_{32}$. Note that Ne_{total} would include Al and Fe^{3+} as T^{3+} components and Ks_{total} would contain both T^{3+} and T^{2+} components. Henderson pointed out that, in examples where MgO had been analysed for specifically by other authors, its concentration level was generally less than 0.1 wt.%. It was assumed that such small concentrations would have little effect on the calculation of excess Si values which, in any case, would be the main repository for the effects of any analytical error as explained by Henderson (2020). However, it was recommended that nepheline analyses should also include reliable MgO and MnO contents; and that Na determination should be carried out with low beam currents and an unfocussed electron beam to minimise Na loss (Morgan & London, 2005).

Recently, it has been recognized that some strongly Si-undersaturated (*i.e.* feldspar-free) mafic potassic/ultrapotassic volcanic rocks from central Brazil contain K-rich nepheline and kalsilite with relatively high Mg contents (up to 0.54 wt.% MgO), which show a strong positive correlation with Fe contents. To take account of these data some of the equations from table 2

in Henderson (2020) need to be modified to include terms for the tetrahedral divalent element content. This stoichiometric approach is also used to assess whether the valence state of Fe could be deduced.

In this paper we present revised equations for the calculation of stoichiometric nepheline formulae with revised spreadsheets for both the original ‘total Na’ and ‘corrected Na’ spreadsheets, along with consideration of a new approach for estimating Fe valence; the necessary explanations of the spreadsheet derivation and use are included as well.

5.2 Variables and Equations in Spreadsheets 1 (‘total Na’) and 2 (‘corrected Na’)

Deducing the changes necessary for the recalculations follows the same approach used by Henderson (2020) where end-member nepheline component compositions and hypothetical nepheline (and kalsilite) solid solution compositions are used to confirm the validity of the formulae. For spreadsheet 1, these include data for the end-members Ne, Ks, CaNe, excess Si’ (Q’, $\square_{\text{Si}_8\text{Si}_{16}\text{O}_{32}}$), $\text{K}_8\text{T}^{2+}_4\text{Si}_{12}\text{O}_{32}$ (denoted KsT^{2+} here) and a hypothetical solid solution $\square_{\text{Ca}_{0.4}\square_{\text{Si}_{0.8}}\text{Na}_4\text{K}_{2.4}\text{Ca}_{0.4}\text{Al}_6\text{Si}_9\text{O}_{32}}$. The latter component contains 1.6 atoms of excess Si which accounts for the Si vacancy of 0.8 ‘atoms’, whereas the Ca vacancy value matches the amount of Ca in the cavity site (see Henderson, 2020).

The numbering of equations 1 to 14 is identical in **Table 5.1** to the original formulae given in Henderson (2020, table 2), however, the new versions of equations 1, 2 and 10, and the formulation of the $\Delta\text{Al}^{\text{cc}}$ and $\Delta\text{T}^{\text{ch}}$ stoichiometry parameters, must also include the atomic proportions of the sum of tetrahedral T^{2+} atoms (normally mainly Mg). These changes can be rationalized as follows:

$\Delta\text{Al}^{\text{cc}}$, replacement of one Si by one Al in the framework is accompanied by the entry of one univalent alkali element cation into a cavity within the ‘stuffed-tridymite’ framework (Buerger, 1954). The substitution of one divalent T^{2+} (e.g. Mg) for one Si in the framework therefore allows the entry of two univalent cavity cations; thus, double the

atomic proportion of the T^{2+} species is equivalent to one T^{3+} (Al) species. The redefinition shown in **Table 5.1** (top row) is required to quantify how the positive charges on the framework cations match those for the contents of the interframework cavities.

ΔT^{ch} ; the change here is straightforward so that the correct average T site valency is calculated (**Table 5.1**, second row).

Si^{xs1} ; the original formulation (Henderson 2020) is correct as long as tetrahedral T^{3+} cations (Al and Fe^{3+}) are the only framework cations to be associated with the cavity cations. However, we have shown that entry of a framework divalent cation is associated with the entry of one extra univalent cavity cation which explains the necessity of adding the associated extra T^{2+} term to match the amount of extra M^+ (Equation 1). The same explanation accounts for the addition of the T^{2+} term to the Q^{cav2} calculation (Equation 10, **Table 5.1**).

Si^{xs2} ; the ideal end-member for the KsT^{2+} phase has a Si/Mg ratio of 3 ($K_2MgSi_3O_8$) so that this requires the additional amount of $3T^{2+}$ to be subtracted from the total Si amount to give an estimate of the excess Si in Equation 2.

Equation 15; the modification to the calculation of the peraluminous parameter Cn % follows the change to the ΔAl^{cc} term (see above).

Equation 16; we consider that it makes sense to calculate a value for the Si/Al ratio that has a value of 1 for the component of a solid solution that only has a value for the T^{3+} end-members. Thus, the calculation shown here subtracts the atomic proportion T^{2+} from the total Si; that value represents the Si associated with the extra univalent cavity cation amount. The T^{3+} term is increased by the amount of framework T^{2+} that is equivalent to the total T^{3+} . However, note that analyses with high T^{2+} contents will be displaced from those with low T^{2+} in plots of Si/Al vs $\Delta Al^{cc}/\Delta T^{ch}$ as defined by Henderson (2020).

The equations in **Table 5.1** are used here to update the two spreadsheets that were attached to the Henderson (2020) paper on nepheline. These revised spreadsheets are attached to the present paper as Supplementary files 1 (total Na file) and 2 (corrected Na file). We have rerun the original Henderson (2020) dataset with the revised spreadsheet and have confirmed the original delta values except some with significant MgO contents (see below). **Table 5.2** shows the key data for model end-member compositions and for representative published analyses of nephelines and kalsilites. The Henderson (2020) paper concentrated on sodic nephelines which constituted the database compiled for that work, many being from syenitic rocks where feldspathoids coexist with essential alkali feldspars. The present data set now includes analyses for potassic nephelines and kalsilites, some of which are from more basic rock types, including foidites, where nepheline might not coexist with alkali feldspar. We have also updated the equations in Supplementary file 2 (corrected Na file) to match those in **Table 5.1**; however, we have chosen to define equation 17 using the $Q^{(\text{Si-Al})}$ proportion to estimate the vacancies associated with the excess Si content (*i.e.* $Q^{(\text{Si-Al})}/2$; see Henderson, 2020). In **Spreadsheet 2** and in **Table 5.2** (columns 16 and 17) we also clarify how the possible presence of a cancrinite component in a Na-rich nepheline solid solution can be estimated.

We have adopted the composition of an ideal water-free, basic hydroxycancrinite as a possible cancrinite end-member (*e.g.* Hassan & Grundy, 1991; Deer *et al.*, 2004). This phase has the ideal composition SiO_2 38.668, Al_2O_3 32.809, Na_2O 26.592 wt.% and the formula can be written as $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{OH})_2$; the atomic formula can thus be calculated on an anhydrous basis as $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{25} + \text{H}_2\text{O}$. The aluminosilicate framework has a stuffed tridymite structure based on linked six rings of tetrahedra similar to those in nepheline. This framework has 6Na as network modifying cavity cations with the other two Na complexed with the hydroxyls occupying the large cancrinite ‘cages’. However, the atomic formulae for cancrinite compounds is usually calculated on the basis of 12 tetrahedral $\text{Si} + \text{Al} + \text{Fe}^{3+}$ cations (*e.g.* Deer *et al.*, 1966,

2004; Hassan & Grundy, 1991), and the same cation and anion numbers would be obtained on the basis of a 25 oxygen anhydrous phase calculation (see **Spreadsheet 1**, bottom rows). Henderson (2020) recalculated cancrinite phase compositions on a 32 oxygen basis for direct comparison with the data for nephelines from different rock types but incorrectly defined this phase as having the formula $\text{Na}_8[\text{Al}_8\text{Si}_8\text{O}_{32}].(\text{NaOH})_2.n\text{H}_2\text{O}$. In **Table 5.2** of this paper and in **Spreadsheet 2** we show that to report the nepheline-like framework for cancrinite on an 8 cation basis it is necessary to multiply the tetrahedral cation numbers by the factor $1\frac{1}{3}$ to convert from 12 to 16; in that case a 25 oxygen cancrinite cell should be recalculated on a $25 * 1\frac{1}{3}$ oxygen ($33\frac{1}{3}$ O) basis (see last two columns in **Table 5.2**). In **Spreadsheet 2** we show how the amount of excess Na in a cancrinite-like component can be calculated as the amount of Na in the nepheline solid solution that can be correlated with that cancrinite-like phase. However, we continue to calculate these phases on a 32 oxygen, nepheline-cell basis, which would have the anhydrous end-member cancrinite-like formula of $\text{Na}_{10.24}[\text{Al}_{7.68}\text{Si}_{7.68}\text{O}_{32}]$ and the proportion of Na present as a hydroxycancrinite phase could be estimated as $\text{Na}^{\text{xs}} * 100/10.240$ mol.% (Supplementary **Spreadsheet 2**).

5.3 Explanation of Changes

The first 3 columns in **Table 5.2** show end-member compositions for end-members Ne and Ks together with the intermediate Na_3K -nepheline ‘compound’. Also shown are data for the ‘tridymite end-member’ (Q), the Ca-nepheline composition (CaNe), and the hypothetical, stuffed tridymite KsT^{2+} -end-member. Based on the 32 oxygen nepheline unit cells, the first three compositions show the stoichiometric number of tetrahedral framework sites ($T = 16$) and cavity cation sites ($M = 8$) making totals of 24 sites per unit cell. No cation site vacancies are present. The CaNe data show the presence of 16 T sites and 4 Ca atoms in the M sites (20 cations); thus 4 of the cavity sites are vacant (denoted $\square^{\text{Ca}}$ here). The tridymite end-member has only Si in the T sites (16) and all the potential cavity cation sites are empty showing the presence

of 8 vacant sites (denoted $\square^{\text{Si}}$ here). The KsT^{2+} -end-member also has filled T sites (12Si plus 4Mg) and all cations sites are filled with K. None of these examples has excess Si. The 7th column shows the composition of a hypothetical sample that is a solid solution containing Ne (50 mol.%), Ks (15%), CaNe (10%), KMg-nepheline (15%) and an excess silica component (Q^{xs}) of 10%. The 16 tetrahedral framework sites contain 9.4 Si, 6 Al, and 0.6 Mg atoms ($T = 16$). The cavity cations are 4 Na, 2.4 K and 0.4 Ca (total 6.8 atoms) leading to 0.4 vacancies associated with the entry of Ca, and 0.8 vacancies associated with 1.6 atoms of excess Si in the framework; thus, the species for all the 8 cavity cation sites are accounted for. The cell formulae given in **Table 5.2** for these compositions were calculated using **Spreadsheet 1** together with the data for the delta parameters and the nepheline end-member mol.% values. The equations defined in **Table 5.1** are shown to be correct when applied to the wt.% oxide analytical data that are input to the spreadsheet (column 8 forward).

The $\Delta\text{Al}^{\text{cc}}$ and $\Delta\text{T}^{\text{ch}}$ stoichiometry parameter values (**Table 5.1**) are effectively zero for the end-member compositions shown here, but the wt.% values given for the solid solution in column 7 have finite, very small values with a $\Delta\text{Al}^{\text{cc}}/\Delta\text{T}^{\text{ch}}$ ratio of 1.130 which is the expected ratio for a Si-rich nepheline solid solution (Henderson, 2020). In **Table 5.2** columns 8 and 9 give data for two natural nepheline analyses referred to in Henderson (2020), columns 10 and 11 have analysed data also considered by Henderson (2021), column 12 is the average of 5 analyses for kalsilite from Brazilian kamafugitic rocks (Sgarbi & Valença, 1995), and columns 13 to 15 are for naturally occurring kalsilite analyses from Deer *et al.* (2004; analyses 7, 8, 13); Columns 16 and 17 give the data for the hydroxycancrinite referred to above.

Henderson (2020) stressed the importance of the analysis of the nepheline in **Table 5.2** column 8 (Dawson *et al.*, 1995) in that it contained a much higher MgO content (0.33 wt.%) than any of the other samples from the syenite database that have reliable electron microprobe analyses. This sample has 2.45 mol.% of the chosen KsT^{2+} end-member and Henderson

commented that the relatively high Mg content would not affect the calculated excess silica value for Q^{xs} which was his chosen Q' parameter. The other equations for calculating Q' (**Table 5.2**) confirm that Q^{Si} , Q^{cav2} , and $Q^{(Si-Al)}$ are all dependent on the T^{2+} content; note that Henderson stressed the importance of obtaining reliable microprobe data for Mg and Mn in this mineral. However, the ΔAl^{cc} and ΔT^{ch} stoichiometry parameters used in that paper did not contain terms for T^{2+} atoms (*cf.* Dollase & Thomas, 1978) and show a higher value for ΔT^{ch} , and thus a lower $\Delta Al^{cc}/\Delta T^{ch}$ ratio than expected for a reliable nepheline analysis. Note that the original delta data are also given in **Table 5.2**. The newly defined delta values take account of the T^{2+} content (**Table 5.1**) and the 'new' values are lower with a delta ratio of 1.132 confirming that it is reliable nepheline analysis. The 'old' delta parameters for the analyses given in columns 9 to 11 in **Table 5.2** also show $\Delta Al^{cc}/\Delta T^{ch}$ ratios that depart from the values expected for good analyses while the newly defined ratios are all entirely consistent with them being reliable analyses with the lower $\Delta Al^{cc}/\Delta T^{ch}$ reflecting their Si-rich character. It is clear that MgO plus MnO contents of as low as 0.12 wt.% show the importance of using the newly defined delta parameters, which in turn points to the importance of obtaining reliable analyses for these elements in nepheline. Each of these four nephelines shows a range of estimates for the different Q' values reflecting their different levels of non-stoichiometry.

Compositions shown in columns 12-14 are microprobe analyses for groundmass kalsilite in K-rich alkaline volcanic rocks; based on the newly defined delta parameters all are reliable analyses with the first two showing significant MgO contents of ~0.5 wt.% MgO. The analysis given in column 15 is from an ultrabasic mafurite from Uganda and is based on 'classical' wet chemical analyses (Potts, 1987; chapter 2) of a separated mineral with ~1-2% of impurity phases. Sahama (1954) commented that some of the Fe, Mg and Ca might come from the impurities, but suggests that kalsilite itself contains significant amounts of these elements. The 'new' ΔAl^{cc} and ΔT^{ch} parameters and ratios are all consistent with the kalsilite analysis

being reliable, although the wide range of the differently defined Q' values must reflect the contributions from impurity phases. However, the chemically analysed separate values for Fe³⁺ and Fe²⁺ in this sample, and for others in Smith & Sahama (1954), all look plausible (average Fe³⁺/Fe²⁺ for 14 samples 3.9 ± 1.3), confirming that the main valence state for Fe in magmatic rocks is Fe³⁺ (see below).

Finally, the last two columns give the calculated composition for the hypothetical hydroxycancrinite end-member with cell formulae calculated to both 32 and 33½ oxygens; note that the correct data for cell formulae have much smaller delta parameters for the 33½ O cell than for the incorrect 32 O cell, but both have the same ideal $\Delta Al^{cc}/\Delta T^{ch}$ ratio of 1.143.

We also deal with the revised corrected Na file (**Spreadsheet 2**). Henderson (2020, 2021) used the $Q^{(Si-Al)}/2$ parameter in the estimation of 'excess' Na and we have continued with that approach here. The results for representative nephelines and kalsilites are detailed in **Spreadsheet 2** and summarized in **Table 5.3**. This calculation was developed by Henderson (2020) to quantify the presence of a possible cancrinite solid solution component in nephelines from peralkaline, silica-undersaturated magmatic rock series. Inevitably, analyses with deficient alkalis compared with Al and Fe³⁺ (apparent normative *Cn*) would show negative Na^{xs} values and vice versa; thus, Henderson advised caution regarding the application of this calculation as a petrogenetic tool. The same advice is relevant here but we provide data for two groups of nephelines. The first four analyses in **Table 5.3** (columns 1 to 4) are all from basic, alkaline hypabyssal sills or volcanic rocks which are characterized by very high excess Q', high Ne and generally low Ks; such phases might have crystallized at relatively high temperatures and before alkali feldspar was precipitated. Gibb & Henderson (1978) pointed out that such compositions plotted outside of the stability field of nepheline and might thus have formed metastably. Such a process might explain their high excess Q' contents (up to ~20 mol.%) and low Ks contents with bulk compositions approaching that of a hypothetical anhydrous analcime

composition. More research is needed to understand such compositions. The other analyses in **Table 5.3** are for nephelines, mainly from foidites and nepheline syenites, with more normal silica contents (40 - 46 wt.% SiO₂) with variable Q^(Si-Al) from ~10 to 1 mol.%; these are generally more potassic and most are likely to have equilibrated with alkali feldspars. Note that the ‘peralkaline’ samples from Oldoinyo Lengai and Shombole volcanoes (columns 6, 11-15) have a range of excess Q values (1.5-6 mol.%), and variable Na^{xs} levels which are difficult to calculate reliably because of analytical and stoichiometric uncertainties; however, the Shombole sample (column 15) has the highest Na^{xs} of 0.53 atoms / 32 O which is equivalent to ~5 mol.% of the hydroxycancrinite end-member (*cf.* vishnevite). Better and complete analyses are required to assess these parameters more carefully.

5.4 Fe Valence Considerations

Feldspars are the main aluminosilicate minerals and are essentially stoichiometric with only trivalent Al and Fe³⁺ substituting for Si in the tetrahedral framework sites. Nepheline, by contrast, has a much more ‘flexible’ structure and ‘small’ divalent tetrahedral cations (mainly Mg with less common Mn) are commonly present in minor concentrations, especially in K-rich nepheline solid solutions and kalsilite (see **Chapter 6**). These phases are enriched in Fe and it is possible, if Mg and Mn are present, that a significant amount of Fe²⁺ might also be present. Ideally, microprobe analyses of these phases should include determination of both oxidation states of Fe but this is far from straightforward. Specialized techniques that could provide useful information include application of K- and L-edge X-ray absorption spectroscopies (XAS), the latter being particularly rich in information on the chemical and structural state of multivalent transition elements in minerals and glasses (*e.g.* Cressey *et al.*, 1993; Henderson & Foland, 1996; Schofield *et al.*, 2014). Microprobe and high-resolution imaging techniques include Fe K-edge X-ray absorption spectroscopy (EXAFS and XANES; *e.g.* Fiege *et al.*, 2017; Suga *et al.*, 2021), scanning transmission X-ray microscopy (STXM; Carrière *et al.*, 2019; Pattammattel

et al., 2021; Suga *et al.*, 2021); X-ray photo electron emission spectroscopy (XPEEM; Schofield *et al.*, 2014; Pattammattel *et al.*, 2021), and electron energy-loss spectroscopy (EELS; Brown *et al.*, 2017; Pattammattel *et al.*, 2021). The first three techniques require synchrotron radiation and the last specialized TEM facilities; none are in routine application for petrological and geochemical research on magmatic rocks but note that Baudouin (2016) has used Fe K-edge XANES to analyse a nepheline phenocryst from a Mg-poor nephelinite from Tanzania and has reported an Fe³⁺/total Fe ratio of 0.93. We have considered how stoichiometric recalculation methods (*e.g.* Droop, 1987), based on an ideal 16.0 T-site framework, could be used to recalculate a wt.% oxide analysis with all Fe recorded as FeO using the formula: Fe³⁺ atoms = $2 * 32 * (1 - 16/\text{sum T site cations})$ per 32 O. However, we have already used strict stuffed-tridymite stoichiometric considerations to define the various proportions of the chosen nepheline end-members; indeed, the estimation of the amount of an excess (or deficiency) of Na, reflecting the presence of a cancrinite molecule (or analytical error), negates this possibility. Nevertheless, we consider below how it might be possible to assess whether a significant Fe²⁺ component could be indicated based on the variation of the $\Delta\text{Al}^{\text{cc}}$ and $\Delta\text{T}^{\text{ch}}$ stoichiometry parameters.

Spreadsheet 3 has key data for assessing the Fe valences in model and analysed nephelines and kalsilites. Model compounds include KsFe end-members $\text{K}_8\text{Fe}^{3+}_8\text{Si}_8\text{O}_{32}$ (composition A, **Table 5.4**) and $\text{K}_8\text{Fe}^{2+}_4\text{Si}_{12}\text{O}_{32}$ (B, **Table 5.4**) and the three solid solutions $\text{K}_8\text{Fe}^{3+}_{3.85}\text{Fe}^{2+}_{2.08}\text{Si}_{10.08}\text{O}_{32}$ (50:50 wt.% end-members; C, **Table 5.4**), $\text{K}_8\text{Fe}^{3+}_{5.88}\text{Fe}^{2+}_{1.06}\text{Si}_{9.06}\text{O}_{32}$ (75:25 wt % end-members; D, **Table 5.4**) and the hypothetical composition $\text{K}_8\text{Al}_{6.94}\text{Fe}^{3+}_{0.69}\text{Fe}^{2+}_{0.19}\text{Si}_{8.18}\text{O}_{32}$ (85KsAl:10KsFe³⁺:5KsFe²⁺ wt.% end-members; E, **Table 5.4**). All of these have strict stuffed-tridymite formulae with 8 cavity cations and 16 T-site frameworks with no excess Si and no vacancies and thus have effectively zero values for the delta parameters. The spreadsheet shows three rows for each solid solution: a purple highlighted

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row for the stoichiometric compositions; a brown highlighted row for total Fe shown as Fe_2O_3 and a green highlighted row for total Fe as FeO . For each data set with total Fe calculated as wt.% FeO , the total T-site atom sum is > 16.000 reflecting that the cation numbers are too high because not enough oxygen was declared in the wt.% compositional data. As expected, the $\Delta\text{Al}^{\text{cc}}$ and $\Delta\text{T}^{\text{ch}}$ parameters both have large positive values with a $\Delta\text{Al}^{\text{cc}}/\Delta\text{T}^{\text{ch}}$ greater than that for a stoichiometric cell formula; note that larger the overestimate of an Fe^{2+} content the more positive both delta values will be (see **Table 5.1** with equations for calculating $\Delta\text{Al}^{\text{cc}}$ and $\Delta\text{T}^{\text{ch}}$).

The size of the delta parameters reflects the amount of non-stoichiometry that has been introduced in calculating all the Fe as either ferric or ferrous; in addition, the relative displacement from $\Delta\text{Al}^{\text{cc}}/\Delta\text{T}^{\text{ch}} = 0$ provides information for estimating the actual values for the two oxidation states. We have shown above that entry of a T^{2+} framework cation has twice the effect on causing a framework-cation / cavity-cation valence mismatch compared to that for entry of a T^{3+} framework component; thus, an overestimate of Fe^{2+} , compared with Fe^{3+} , seriously increases the $\Delta\text{Al}^{\text{cc}}$ parameter. For example, the 50:50 solid solution (sample C) discussed above has a ‘reduced-Fe’ delta (denoted ΔAlFe^{2+}) parameter of +4.1; the positive parameter implies that 4.1 too few atoms of Fe^{3+} have been declared. By comparison, an ‘oxidized-Fe’ ΔAlFe^{3+} has a value of -2.0 and this negative sign is consistent with 2.0 atoms too many atoms of Fe^{3+} having been declared. These two delta values define the extremes of the non-stoichiometries for a mixing model with a total range of non-stoichiometry of $4.1 + 2.0 = 6.1$; this value is equivalent to the average number of Fe atoms shown by the oxidised- and reduced-Fe data sets (6.02). If we treat these data in terms of a lever-rule, the balance would be at the strict stoichiometry, lever-rule-pivot position of $\Delta\text{Al}^{\text{cc}} = 0.000$ with a value for Fe^{3+} close to 4.1 atoms/32 O and a value for $\text{Fe}^{2+} \sim 2.0$ atoms/32 O. Using the Droop (1987) calculation based on 32 O and 16 T atoms for the reduced Fe data for composition C would give an $\text{Fe}^{3+} = 3.846$ and a corrected $\text{Fe}^{2+} = 2.076$. These two sets of values are similar but the former are only

approximations because they are based on end-member estimates, both are calculated to 32 oxygens cells but with different numbers of T-site atoms (*i.e.* 17.023 for Fe²⁺ cell and 15.495 for Fe³⁺; see **Table 5.4**). Data for model composition E (**Table 5.4**), which has Fe contents more likely to be found for natural nepheline/kalsilite samples, give delta-based values of Fe³⁺ = 0.698, Fe²⁺ = 0.186, total Fe = 0.884 atoms/32 O compared with actual values of 0.690, 0.186, and 0.876, respectively (see **Table 5.4**). Note that the estimates for Fe³⁺ and Fe²⁺ contents can be converted to equivalent wt.% Fe₂O₃ and FeO values by reversing the atomic formulae calculations as defined in the footnote to **Table 5.4**. Using these values along with analytical data for the other components in **Spreadsheet 1** will then give the correct atomic values and molecular end-member compositions incorporating the deduced ‘model’ Fe valence data.

Reliably analysed natural nepheline/kalsilite minerals with reasonably high total Fe contents with a significant amount of each Fe oxidation state the delta parameters should show similar relationships to those described here for the stoichiometric model compositions and it might be possible to predict the amounts of the different oxidation states. Thus, we have tested this approach to provide approximate values for the amounts of Fe²⁺ that might be present for two Fe-rich nepheline samples considered by Henderson (2020) and for a published Fe- and Mg-rich kalsilite sample (Tappe *et al.*, 2003). The data provided in **Spreadsheet 3** and **Table 5.4** show that all three analyses show positive $\Delta\text{Al}^{\text{cc}}$ and $\Delta\text{T}^{\text{ch}}$ values when using total iron as Fe²⁺ in the calculation and negative values when total Fe³⁺ is used; these relationships are consistent with Fe being present in both oxidation states and the relative values for the $\Delta\text{Al}^{\text{cc}}$ parameters for the all-Fe²⁺ and all-Fe³⁺ datasets can be used to estimate the relative proportions of the two valency states for each sample. **Table 5.4** (bottom two rows) gives the estimated values for Fe³⁺ and Fe²⁺ (atoms per 32 O) and the equivalent wt.% values for these three samples. Thus, we suggest that the nepheline analyses of Dawson (1995) and Dawson & Hill (1998) are consistent with 15-20% of the total Fe being present as FeO while the Tappe *et al.*

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(2003) kalsilite might have ~10% of the total Fe as FeO. This approach is particularly relevant for Mg- and Fe-rich potassic nephelines and kalsilites and we will consider this matter further in **Chapter 6**.

Table 5.1 Formulae for calculations based on 32 oxygen nepheline structure unit cell modified for entry of divalent cations (T^{2+}) into tetrahedral sites.

Basis	Formulae	Eq. #
Stoichiometry tests vs ideal tridymite with 16 T-site cations and 32 oxygen in the framework		
Change in T charge minus cavity cation charge:	$\Delta[(T^{3+} + 2T^{2+}) - (M^+ + 2M^{2+})]$	ΔAl^{cc}
Total analysed T charge minus charge for 16 T:	$[(4 * T^{4+} + 3 * T^{3+} + 2 * T^{2+}) - 16 * \text{mean T charge}]$	ΔT^{ch}
Cell formula parameter calculation		
Excess Si, Si^{xs}	$Si^{xs1} = Si^{total} - Na - K - 2Ca - T^{2+}$	1
	$Si^{xs2} = Si^{total} - Al - 3T^{2+}$	2
Total sites, 24	$Q^{xs} \% = (24 - 3Na - 3K - 6Ca) \times 100 / 24$	3
	$Ne \% = 3Na \times 100 / 24$	4
	$Ks \% = 3K \times 100 / 24$	5
	$CaNe \% = 6Ca \times 100 / 24$	6
	$KsT^{2+} \% = 6T^{2+} \times 100 / 24$	14
	$Cn \% = [(Al + Fe^{3+} + 2T^{2+}) - (Na + K + 2Ca)] \times 100 / 21.333$	15
	$Si/Al = (Si - T^{2+}) / (Al + 2T^{2+})$	16
Framework sites only, 16	$Q^{Si} \% = Si^{xs1} \times 100 / 16$	7
	$Q^{(Si-Al)} = Si^{xs2} \times 100 / 16$	8
Cavity sites only, 8	$Q^{cav1} \% = (8 - Na - K - 2Ca) \times 100 / 8$	9
	$Q^{cav2} \% = (24 - \text{total Si} - Al - Fe^{3+} - T^{2+} - Na - K - 2Ca) \times 100 / 8$	10
	$Ne \% = Na \times 100 / 8$	11
	$Ks \% = K \times 100 / 8$	12
	$CaNe \% = 2Ca \times 100 / 8$	13
Excess Na calculation		
Based on Si^{xs2} equation 2, above	$Na \text{ in neph} = 8 - K - 2Ca - (Si^{total} - Al - 3T^{2+}) / 2$	17
	$Na^{xs} = Na^{total} \text{ from analysis} - Na \text{ in Nph}$	18

Footnotes: T = tetrahedral cations in framework; M = atoms in interframework cavity cation sites. Possible T-site occupants : $T^{4+} = Si, Ti, Ge$; $T^{3+} = Al, Fe^{3+}, Cr^{3+}$; $T^{2+} = Mg, Fe^{2+}, Mn, Ni, Co, Zn$; $M^+ = Na, K, Rb$; $M^{2+} = Ca, Sr, Ba$

Table 5.2 End-member nepheline group compositions and atomic and molecular formulae data calculated in Spreadsheet 1.

Wt.%	Ne	Ne _{0.75} Ks _{0.25}	Ks	CaNe	Q	KsT ²⁺ Ne	Ne ₅₀ Ks ₁₅ - CaNe ₁₀ - KsT ²⁺ ₁₅ Q ^{xs} ₁₀	Dawson <i>et al.</i> 1995 Nph	T&N 1996 Nph	Berkesi 2020 Nph	Paslick 1996 Nph	S&V 1995 Kls	Edgar 1979 Kls	A&C 1984 Kls	Sahama 1954 Kls	Hydroxy cancrinite 32 O	Hydroxy cancrinite 33.333 O
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
SiO ₂	42.296	41.130	37.988	43.193	100.000	57.268	48.930	42.1	54.13	43.33	43.56	39.55	38.93	39.22	38.50		38.669
TiO ₂									0.20			0.10	0.24		0.09		
Al ₂ O ₃	35.887	34.898	32.233	36.649			26.500	28.6	26.91	32.19	32.35	27.19	27.72	25.83	26.27		32.809
Cr ₂ O ₃													0.06				
Fe ₂ O ₃								5.2	1.70	2.17	0.84	5.08	2.99	5.37	5.07		
FeO	-	-	-	-	-	-	-								0.53		
MnO										0.03		0.02	0.11		0.02		
MgO						12.805	2.095	0.33	0.37	0.05	0.08	0.47	0.48		0.87		
CaO				20.156			1.943	0.06	1.16	0.07	0.19	0.04	0.13	0.15	0.44		
SrO											0.18						
BaO											0.28	0.12		0.16			
Na ₂ O	21.815	15.910					10.739	15.6	15.58	15.09	17.74	1.39	0.54	1.27	2.07		26.592
K ₂ O		8.060	29.777			29.926	9.793	7.07	1.79	7.29	3.89	26.51	28.79	27.44	24.85		
Total	100.00	100.00	100.00	100.00		100.00	100.00	98.96	101.85	100.22	99.11	100.45	99.99	99.44	98.71		100.00
Atoms/32O																	
Si	8.000	8.000	8.000	8.000	16.000	12.000	9.400	8.377	9.837	8.380	8.424	8.321	8.277	8.416	8.247	7.680	8.000
Ti									0.27			0.016	0.038	0.000	0.015		
Al	8.000	8.000	8.000	8.000			6.000	6.707	5.763	7.337	7.373	6.742	6.946	6.533	6.632	7.680	8.000
Cr													0.010				
Fe ³⁺								0.779	0.232	0.316	0.122	0.804	0.478	0.867	0.817		
Fe ²⁺												0	0.000	0.000	0.095		
Mn										0.005		0.004	0.020	0.000	0.004		
Mg						4.000	0.600	0.098	0.100	0.014	0.023	0.147	0.152	0.000	0.278		
Ca				4.000			0.400	0.013	0.226	0.015	0.034	0.045	0.030	0.034	0.101		
Sr											0.020		0.000	0.000	0.000		
Ba											0.021	0.010	0.000	0.013	0.000		
Na	8.000	6.000					4.000	6.018	5.489	5.658	6.652	0.567	0.223	0.528	0.860	10.240	10.267
K		2.000	8.000			8.000	2.400	1.795	0.415	1.798	0.960	7.116	7.809	7.512	6.791		
Total cations	24.000	24.000	24.000	20.000	16.000 ⁸	24.000	22.800	23.787	22.090	23.522	23.634	23.731	23.983	23.904	23.839	23.040	24.000
Total T	16.000	16.000	16.000	16.000	16.000	16.000	16.000	15.961	15.960	16.051	15.942	16.034	15.922	15.816	16.087	15.360	16.000
Na ^{xs}																2.560	2.667
Δ(Al-cats) old								-0.353	-0.360	0.167	-0.277	-0.174	-0.666	-0.736	-0.403		
Δ(T _{valency})								-0.484	-0.508	0.113	-0.285	-0.475	-0.891	-0.650	-1.02		
ΔAl/ΔT								0.73	0.71	1.478	0.972	0.366	0.748	1.132	0.395		

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$\Delta(\text{Al-cats})$	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	-0.000024	-0.157	-0.160	0.206	-0.231	0.137	-0.312	-0.736	0.350	-0.332	-0.0001
new																	
$\Delta(T_{\text{valency}})$	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	-0.000022	-0.138	-0.144	0.181	-0.204	0.120	-0.274	-0.650	0.305	-0.290	-0.0001
$\Delta\text{Al}/\Delta T$							1.130	1.132	1.107	1.136	1.134	1.138	1.140	1.133	1.145	1.143	1.143
Mol.%																	
Ne total	100	75					50	75.23	72.72	70.73	83.14	7.10	2.78	6.60	10.75		
Ks total		25	100				15	22.43	5.19	22.48	11.42	88.94	97.61	93.90	84.89		
CaNe				100			10	0.32	5.65	0.36	2.02	0.36	0.74	1.20	2.52		
Q^{xss}					100		10	2.02	20.55	6.43	2.84	3.61	-1.14	-1.70	1.84		
Cn							0	-0.74	-0.75	0.96	-1.08	0.64	-1.46	-3.45	1.64		
Q^{Si}								2.75	21.30	5.47	3.92	2.97	0.33	1.75	0.20		
Q^{cav2}								2.51	20.55	5.79	3.56	3.18	-0.16	0.60	0.75		
$Q^{(\text{Si-Al})}$								3.74	22.30	4.18	5.37	2.15	2.28	6.35	-1.98		
Mol % PRS[§]																	
Ne								74.2	72.72	72.6	82.7	0.78	2.71	6.18	11.47		
Ks								22.1	5.50	23.1	11.9	98.71	95.07	87.87	90.64		
Q'								3.68	21.78	4.29	5.34	0.50	2.22	5.94	-2.12		

[§] PRS refers to Petrogeny's Residua System Ne-Ks-Quartz

&Note that no cavity cations are present in the 'tridymite' end-member.

Nph = nepheline; Kls = kalsilite

Analyses:

1. NaAlSiO_4 , Ne; 2. $\text{Na}_3\text{KAl}_4\text{Si}_4\text{O}_{16}$, 'ideal' nepheline; 3. KAlSiO_4 , Ks; 4. $\text{CaAl}_2\text{Si}_2\text{O}_8$, Ca-Ne; 5. Si_2O_4 Q; 6. $\text{K}_2\text{MgSi}_3\text{O}_8$, KsT^{2+} -Ne; 7. $\text{Na}_{50}\text{Ks}_{15}\text{CaNe}_{10}\text{KsM}_{15}\text{Q}_{10}$; 8. Dawson *et al.*, 1995; 9. Trupia & Nicholls, 1996; 10. Berkesi *et al.*, 2020; 11. Paslick *et al.*, 1996; 12. Sgarbi & Valença, 1995; 13. Edgar, 1979; 14. Allan & Carmichael, 1984; 15. Sahama, 1954; 16. and 17. Ideal hydroxycancrinite – $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$

Table 5.3 Data from corrected Na spreadsheet showing results for ‘excess’ Na and possible cancrinite contents.

	1 G&H 1978	2 W&H 1994	3 Cuccien 2018	4 Melluso 2018	5 Paslick 1996	6 Berkesi 2020	7 Melluso 2012	8 Blancher 2010	9 Zhu 2016	10 Andersen 2017	11 Dawson 1995	12 D&H 1998	13 M&D 2007	14 K&P 1991	15 Peterson 1989	16 Hamada 2019	17 Tappe 2003	18 Tappe 2003
SiO ₂	50.30	51.82	52.03	51.66	43.56	43.33	44.34	42.34	42.79	45.65	42.10	40.30	41.21	43.59	41.80	42.56	42.31	38.46
TiO ₂									0.04							0.06	0.05	0.09
Al ₂ O ₃	30.50	29.81	29.32	28.49	32.35	32.19	32.31	34.38	32.62	31.48	28.60	28.00	30.75	31.30	31.54	32.27	32.42	29.35
Fe ₂ O ₃		0.40	0.73	2.30	0.84	2.17	0.73	0.37	2.13	1.06	5.20	8.02	4.46	2.41	2.62	1.07	0.93	2.48
Cr ₂ O ₃																0.03		0.04
FeO																		
MgO					0.08	0.07			0.04	0.02	0.33					0.12	0.13	0.32
MnO						0.03			0.03								0.03	
CaO	0.18	0.00	0.44	0.42	0.19	0.07	0.99	3.16	0.11	0.00	0.06		0.20	0.18	0.20	0.15	0.06	
SrO					0.18		0.52			0.00								
BaO					0.28												0.05	0.05
Na ₂ O	16.70	16.65	15.32	15.36	17.74	15.09	15.67	14.95	16.52	16.54	15.60	15.20	15.51	16.86	16.21	14.32	16.42	2.08
K ₂ O	2.24	2.15	2.44	2.14	3.89	7.29	4.64	4.20	6.28	5.39	7.07	8.30	7.95	5.52	8.15	9.00	6.81	26.35
Total	99.92	100.83			99.11	100.24	99.20	99.40	100.56	100.14	98.96	99.82	100.08	99.86	100.52	99.58	99.21	99.22
Corrected framework cell																		
Si	9.33	9.50	9.56	9.51	8.45	8.35	8.55	8.15	8.25	8.74	8.40	8.12	8.16	8.47	8.25	8.34	8.30	8.15
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01
Al	6.67	6.44	6.35	6.18	7.40	7.31	7.34	7.80	7.42	7.10	6.72	6.65	7.17	7.17	7.34	7.45	7.50	7.33
Fe ³⁺	0.00	0.06	0.10	0.32	0.12	0.31	0.11	0.05	0.31	0.15	0.78	1.22	0.66	0.35	0.39	0.16	0.14	0.40
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Fe ²⁺	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mg	0.00	0.00	0.00	0.00	0.02	0.02	0.00	0.00	0.01	0.01	0.10	0.00	0.00	0.00	0.00	0.04	0.04	0.10
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ca	0.04	0.00	0.09	0.08	0.04	0.01	0.20	0.65	0.02	0.00	0.01	0.00	0.04	0.04	0.04	0.03	0.01	0.00
Sr	0.00	0.00	0.00	0.00	0.02	0.00	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ba	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na	6.06	5.99	5.67	5.79	6.47	5.83	5.79	5.52	6.17	5.97	5.89	5.76	5.77	6.11	5.67	5.38	6.02	0.81
K	0.53	0.50	0.57	0.50	0.96	1.79	1.14	1.03	1.55	1.32	1.80	2.13	2.01	1.37	2.05	2.25	1.71	7.12

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Framework O	32.00	32.00	32.00	32.00	32.00	32.00	32.00	32.00	32.00	32.00	32.00	32.00	32.00	32.00	32.00	32.00	32.00	32.00
Excess Na	-0.05	-0.07	-0.22	-0.31	0.20	-0.19	0.07	0.05	0.01	0.16	0.14	0.18	0.18	0.24	0.53	0.06	0.23	0.05
Delta Al cc	0.008	0.009	0.031	0.044	-0.029	0.027	-0.010	-0.008	-0.001	-0.024	-0.020	-0.026	-0.026	-0.034	-0.077	-0.009	-0.033	-0.006
Delta T ch	0.007	0.008	0.028	0.039	-0.026	0.024	-0.008	-0.007	-0.001	-0.021	-0.017	-0.023	-0.023	-0.030	-0.067	-0.008	-0.029	-0.006
DelA/DelT	1.12	1.11	1.11	1.11	1.13	1.14	1.13	1.14	1.14	1.13	1.14	1.14	1.14	1.13	1.14	1.14	1.14	1.14
%Vishnev	-0.51	-0.64	-2.12	-3.00	1.98	-1.86	0.65	0.52	0.10	1.61	1.34	1.76	1.76	2.34	5.20	0.58	2.25	0.44
Ne total	75.75	74.83	70.92	72.35	80.87	72.87	72.39	69.05	77.10	74.65	73.67	72.01	72.14	76.40	70.85	67.26	75.22	10.12
NaAl	75.75	74.14	69.65	68.37	79.34	68.94	71.06	68.38	73.23	72.74	63.91	56.80	63.83	71.99	65.98	65.28	73.51	5.17
NaFe	0.00	0.69	1.26	3.98	1.53	3.93	1.32	0.67	3.86	1.91	9.75	15.21	8.30	4.41	4.87	1.97	1.72	4.94
Ks total	6.63	6.29	7.15	6.28	12.03	22.41	14.27	12.89	19.32	16.45	22.48	26.68	25.09	17.11	25.66	28.12	21.31	89.05
CaNe	0.89	0.00	2.17	2.07	0.99	0.36	5.11	16.29	0.57	0.00	0.32	0.00	1.06	0.94	1.06	0.79	0.32	0.00
KsT ²⁺	0.00	0.00	0.00	0.00	0.58	0.63	0.00	0.00	0.41	0.14	2.45	0.00	0.00	0.00	0.00	0.88	1.08	2.53
Q xs	16.73	18.88	19.77	19.29	6.11	4.36	8.23	1.77	3.02	8.91	3.53	1.31	1.71	5.56	2.44	3.83	3.15	0.84
Q Si	16.69	18.84	19.63	19.09	5.21	4.23	6.82	1.81	3.03	9.02	3.62	1.43	1.83	5.72	2.80	3.87	3.21	0.77
Q cav.	16.73	18.88	19.77	19.29	6.11	4.36	8.23	1.77	3.02	8.91	3.53	1.31	1.71	5.56	2.44	3.83	3.15	0.84
Q(Si-Al)	16.64	18.78	19.43	18.81	5.39	4.06	6.88	1.85	3.03	9.16	3.74	1.59	2.00	5.94	3.28	3.96	3.41	0.85
Ne total	76.50	74.83	72.48	73.88	81.68	73.14	76.29	82.49	77.54	74.65	73.91	72.01	72.91	77.12	71.60	67.79	75.46	10.12
Ks total	6.69	6.29	7.31	6.42	12.15	22.49	15.04	15.40	19.43	16.45	22.55	26.68	25.36	17.27	25.93	28.34	21.38	89.05
Q(Si-Al)	16.81	18.80	19.93	19.31	5.48	4.09	7.36	2.21	3.05	9.14	3.75	1.59	2.01	5.97	3.28	3.98	3.41	0.85

Sample sources: 1. Gibb & Henderson, 1978; 2. Wilkinson & Hensel, 1994; 3. Cuccienello *et al.*, 2018; 4. Melluso *et al.*, 2018; 5. Paslick *et al.*, 1996; 6. Berkesi *et al.*, 2020; 7. Melluso *et al.*, 2012; 8. Blancher *et al.*, 2010; 9. Zhu *et al.*, 2016; 10. Andersen *et al.*, 2017; 11. Dawson *et al.*, 1995; 12. Dawson & Hill, 1998; 13. Mitchell & Dawson, 2007; 14. Kjarsgaard & Peterson, 1991; 15. Peterson, 1989; 16. Hamada *et al.*, 2019; 17 and 18. Tappe *et al.*, 2003.

Table 5.4 Valence characterization for Fe model compounds and three high-Fe nepheline group minerals.

	KFe ²⁺ Ne	KFe ³⁺ Ne	KFe ss 0.5A 0.5B C	KFe ss C	KFe ss C	KFe ss 0.75A 0.25B D	KFe ss D	KFe ss D	KAlFe ss 0.85KAl E	KAlFe ss E All Fe ²⁺	KAlFe ss E All Fe ³⁺	Dawson et al (1995) Nepheline		Dawson & Hill (1998) Nepheline		Tappe <i>et al.</i> (2003) Kalsilite	
Oxides in wt. %	A	B		All Fe ²⁺	All Fe ³⁺		All Fe ²⁺	All Fe ³⁺				All Fe ²⁺	All Fe ³⁺	All Fe ²⁺	All Fe ³⁺	All Fe ²⁺	All Fe ³⁺
SiO ₂	52.05	32.13	42.09	42.09	42.09	37.11	37.11	37.11	38.10	38.10	38.10	42.1	42.1	40.3	40.3	38.10	38.10
TiO ₂																0.10	0.10
Al ₂ O ₃									27.40	27.40	27.40	28.6	28.6	28.0	28.0	23.70	23.70
Cr ₂ O ₃																0.02	0.02
Fe ₂ O ₃		42.69	21.35		32.83	32.02		37.78	4.27		5.43		5.20		8.02		6.47
FeO	20.75		10.37	29.58		5.19	34.00		1.04	4.88		4.68		7.22		5.82	
MnO																0.0	0.0
MgO												0.33				1.41	1.41
CaO												0.06					
BaO																0.20	0.20
Na ₂ O												15.6	15.6	15.2	15.2	0.94	0.94
K ₂ O	27.20	25.18	26.19	26.19	26.19	25.69	25.69	25.69	29.19	29.19	29.19	7.07	7.07	8.30	8.30	27.84	27.84
Total	100.00	100.00	100.00	97.86	101.11	100.00	96.79	100.58	100.00	99.57	100.12	98.44	98.57	99.02	99.82	98.14	98.78
Atoms/32(O)																	
Si	12.000	8.000	10.077	10.722	9.764	9.059	9.976	8.911	8.186	8.275	8.162	8.480	8.377	8.258	8.101	8.467	8.340
Ti																0.017	0.016
Al									6.937	7.013	6.917	6.790	6.707	6.762	6.634	6.208	6.114
Cr																0.003	0.003
Fe ³⁺	4.000	8.000	3.846		5.731	5.882		6.828	0.690		0.885		0.777		1.213		1.065
Fe ²⁺			2.077	6.301		1.059	7.644		0.186	0.875		0.788		1.237		1.082	
Mn																	
Mg												0.099	0.098			0.460	0.460
Ca												0.013	0.013				
Ba																0.017	0.017
Na												6.093	6.018	6.039	5.924	0.405	0.399
K	8.000	8.000	8.000	8.512	7.751	8.000	8.810	7.870	8.000	8.087	7.952	1.817	1.799	2.170	2.129	7.893	7.775
Total cations	24.000	24.000	24.000	25.534	23.246	24.000	26.429	23.609	24.000	24.262	23.930	24.080	23.787	24.466	24.002	24.560	24.191

Chapter 5: Nepheline Stoichiometry – Part 1

Sum T (= S)	16.000	16.000	16.000	17.023	15.495	16.000	17.619	15.740	16.000	16.175	15.954	16.157	15.961	16.257	15.949	16.244	16.000
16/S				0.940			0.908			0.989		0.990		0.984		0.985	
^{8s} Calc. Fe ³⁺				3.846			5.881			0.692		0.621		1.011		0.960	
Δ(Al-cats)	0.0000x	0.0000x	0.0000x	+4.09	-2.02	0.00000 x	+6.48	-1.04	- 0.00000 1	+0.698	-0.186	+0.629	-0.157	+1.028	-0.206	+0.972	-0.106
Δ(T _{valency})	0.0000x	0.0000x	0.0000x	+3.33	-1.83	0.00000 x	+5.07	-0.93	- 0.00000 1	+0.603	-0.163	+0.546	-0.138	+0.882	-0.181	+0.833	-0.092
ΔAl/ΔT	1.143	1.143	1.143	1.227	1.102	1.143	1.277	1.122	1.143	1.157	1.141	1.165	1.137	1.165	1.140	1.167	1.145
⁵ Fe cats/32 O Fe ³⁺ , Fe ²⁺ Wt. Fe ₂ O ₃ ; FeO												Fe ³⁺ 0.63; Fe ²⁺ 0.16		Fe ³⁺ 1.03; Fe ²⁺ 0.21		Fe ³⁺ 0.97; Fe ²⁺ 0.11	
												4.15; 0.94 wt. %		6.67; 1.22 wt. %		5.83; 0.57 wt. %	

[&]Based on total Fe as FeO in wt. % analysis.

^sEstimated model Fe³⁺ and Fe²⁺ atoms per 32 oxygens and 16.000 ΣT cations (i) Fe³⁺ = 2 * 32 * (1-16/sumT) and (ii) (Fe²⁺ = total Fe per 32O * 16/ΣT) (Droop, 1987)

[£] Fe valence from ΔAl^{cc}; Equivalent wt. % Fe oxides: Fe₂O₃ = (model Fe³⁺ * ΣO/32) * (159.69/2) * (ΣT/16); FeO = (model Fe²⁺ * ΣO/32) * 71.85 * (ΣT/16)

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We thank Jack Zussman for his encouragement at an early stage of this nepheline stoichiometry ‘journey’, the constructive comments of an anonymous referee, also Roger Mitchell for his patient and detailed suggestions, and overall for the editorial input. I.L.O. also thanks the Brazilian National Council for Scientific and Technological Development (CNPq) for the doctorate scholarship (GM/GD 146955/2016-1).

Chapter 6

Substitution of 'Small' Divalent Cations (e.g. Mg)

for Si and Al in the Nepheline Tetrahedral

Framework

Part 2. The Occurrence of Mg-rich Nepheline and Kalsilite

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Abstract

Natural nepheline usually contains very small amounts of MgO (< 0.1 wt.%), although these examples are mainly from Mg-poor alkaline igneous rocks such as nepheline syenites. However, this work shows that nepheline and kalsilite with much higher MgO concentrations can occur in the groundmass of strongly SiO₂-undersaturated, feldspar-free, mafic volcanic rocks (*i.e.* olivine-rich foidites). Furthermore, a strong positive correlation is evident between their Mg and Fe contents. The occurrence of Mg-rich nepheline and kalsilite seems to be related to their derivation from Mg-rich magmas when compared to most of host rocks investigated so far. Additionally, the physicochemical condition of crystallization seems to have an important role in the incorporation of ‘small’ divalent cations by these minerals. The prevalence of Mg-rich nepheline and kalsilite as late magmatic phases and the divergent Mg and Fe relationships for phenocrysts and ‘quenched’ groundmass crystals support this hypothesis. The positive correlation between Mg and Fe contents reflects their strong geochemical affinity and the entrance of Fe³⁺, Fe²⁺ and Mg²⁺ cations into the same crystallographic site of nepheline and kalsilite structures. The calculation of atomic formulae and stoichiometry parameters for nepheline-group minerals where data for the T²⁺ cations (*e.g.* Mg²⁺) are incorporated gives more reliable compositional parameters (see **Chapter 5**). Calculated excess silica values (Si’) are significantly affected when the coupled substitution $2\text{Al}^{3+} = \text{Mg}^{2+} + \text{Si}^{4+}$ is considered. Thus, specific analyses of ‘small’ divalent cations are essential to obtain more realistic values of excess Si’, in particular, for nepheline and kalsilite that crystallized from Mg-rich, Si-poor, mafic-ultramafic alkaline lavas.

Keywords: nepheline-group minerals, stoichiometry calculations, mafic volcanic rocks, minor elements, Fe valence

6.1 Introduction

The chemistry of nepheline solid solutions has attracted considerable interest for nearly a century because of its compositional variation in diverse rock types (*e.g.* Bannister & Hey, 1931; Miyashiro, 1951; Smith & Sahama, 1954; Tilley, 1954; Barth, 1963; Velde & Yoder, 1978; Henderson & Gibb, 1983; Wilkinson & Hensel, 1994; Blancher *et al.*, 2010). As a consequence, it is well established that natural nephelines are not restricted to the ‘ideal composition’ $\text{Na}_3\text{KAl}_4\text{Si}_4\text{O}_{16}$ (*cf.* Hålenius *et al.*, 2018) as they usually contain some excess Si’ (*e.g.* Henderson, 2020). In addition, small amounts of Ca^{2+} (up to 3.5 wt.% CaO) might occur with the alkali atoms in the cavity cation ‘Na-sites’ (see Antao & Hovis, 2021) and some Fe^{3+} commonly replaces Si^{4+} and Al^{3+} in the tetrahedral framework. It also has been proposed that ‘small’ divalent cations (mainly Mg, but also Fe^{2+}) could occur in the tetrahedral sites according to the coupled substitution $2\text{Al}^{3+} = (\text{Mg}, \text{Fe})^{2+} + \text{Si}^{4+}$ (see Henderson, 2020 and references therein).

In general, it is expected that very low contents of Mg (and Mn) occur in most natural nephelines (see Deer *et al.*, 2004; table 6). Indeed, Henderson (2020) pointed out that Mg tends to be the most important ‘small’ divalent cation reported for this mineral based on a new database of 310 published analyses. Henderson (2020) also assumed that the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio is relatively high (see below). However, prior to the development of the electron microprobe, small amounts of Mg, Mn, Fe and Ti were commonly reported in the classical ‘wet-chemical’ analysis of nepheline and kalsilite grain separates (Bannister & Hey, 1931; 1942; Sahama, 1954; Neuvonen, 1956). Subsequently these have been considered to reflect the presence of alteration products or mineral impurities (Dollase & Thomas, 1978). Hence, the presence of Mg in natural nephelines and kalsilites has not been systematically investigated.

Nonetheless, while investigating the composition of nepheline and kalsilite in mafic potassic volcanic rocks from central Brazil, the first author observed that relatively large

amounts of Mg (average ~0.3 wt.% MgO) occur in these minerals and that a strong positive correlation exists between Mg and Fe contents. The companion paper by Henderson & Oliveira (2022) has established how ‘small’ divalent cations (*e.g.* Mg, Mn, Fe²⁺, *etc.*) are incorporated in the calculation of nepheline/kalsilite atomic formulae.

In this work, we present and discuss some examples that reveal the significance of the Mg (and Fe) contents in nepheline and kalsilite. These observations are based on recently assembled databases of published and new wavelength-dispersive electron microprobe analyses of these minerals, taken exclusively from alkaline ultrabasic volcanic rocks (see below). Additionally, we verify the significance of the higher amounts of Mg (and Fe) for the calculation of nepheline/kalsilite end-member components using the revised equations presented in our companion paper (Henderson & Oliveira, 2022).

6.2 Magnesium as an Important Minor Element in Nepheline and Kalsilite

Roedder (1951) was the first to suggest that the occurrence of Mg could be important in natural kalsilite, and its hexagonal counterparts nepheline and kaliophilite, mainly when they have crystallized from Mg-rich alkaline magmas. At that time, though, there was only one ‘wet-chemical’ analysis of a kalsilite-rich mineral separate (*i.e.* Bannister & Hey, 1942) with 3.7 wt.% MgO and 5.0 wt.% CaO, elements which were mostly attributed to inclusions of phlogopite and diopside. The compositions shown in the larger dataset of Deer *et al.* (2004; table 7) indicate that kalsilite from volcanic rocks can actually have significant amounts of MgO (average ~0.4 wt.%). As far as we are aware, that work is the most extensive compilation of kalsilite compositions published. While researching the composition of nepheline and kalsilite in strongly SiO₂-undersaturated mafic potassic volcanic rocks (*i.e.* feldspar-free assemblages), the first author assembled comprehensive databases of 168 kalsilite compositions (137 published and 31 new electron microprobe WDS data) and 315 nepheline analyses (144 published; 171 unpublished) taken only from feldspar-free volcanic rocks (*i.e.* foidites). These

databases were compiled at the Institute of Geosciences, University of Brasília, and have been used in the current papers.

It has long been recognized that variations in the composition of natural nephelines are intimately related to their igneous paragenesis and crystallization conditions (see Miyashiro, 1951; Tilley, 1954; Barth, 1963; Edgar, 1984; Wilkinson & Hensel, 1994). However, almost all previous studies of nepheline composition have dealt with ‘common’ alkaline igneous rocks (*e.g.* nepheline syenites, phonolites, alkali basalts, *etc.*) where nepheline is associated with feldspars. Thus, as many of these feldspar-bearing rocks represent late-stage products of magmatic differentiation, it can be anticipated that nepheline crystallized from such Mg-poor residual magmas will only contain minor amounts of MgO. This might have led to a biased view of the small concentrations of MgO (usually < 0.1 wt.%; Henderson, 2020) so far reported in most natural nephelines.

K-rich nepheline, rather than kalsilite, is the main light-coloured mineral of strongly porphyritic (olivine- and clinopyroxene-phyric) mafic potassic volcanic rocks of the Goiás Alkaline Province, central Brazil (*e.g.* Brod *et al.*, 2005; Oliveira *et al.*, 2021). The fine-grained groundmass of some of these rocks include both nepheline and kalsilite occurring interstitially as individual, well separated crystals, together with abundant clinopyroxene, magnetite and perovskite. Leucite (commonly replaced by analcime), and rarely melilite, may or may not be present. Post-magmatic, secondary phases, are mainly analcime and other zeolites. The Mg content of these K-rich nephelines varies from 0.05 to 0.51 wt.% MgO (average 0.22 wt.%; $n = 120$). In addition, there is a good positive correlation ($R^2 = 0.62$) between the Mg and Fe contents, even in a single rock sample (see **Figure 6.1**, sample AMK-01). In comparison with nepheline, kalsilite has consistently higher amounts of Mg, ranging from 0.24 to 0.54 wt.% MgO (average 0.35 wt.%; $n = 31$), and also shows a positive correlation between Mg and Fe contents (**Figure 6.2**).

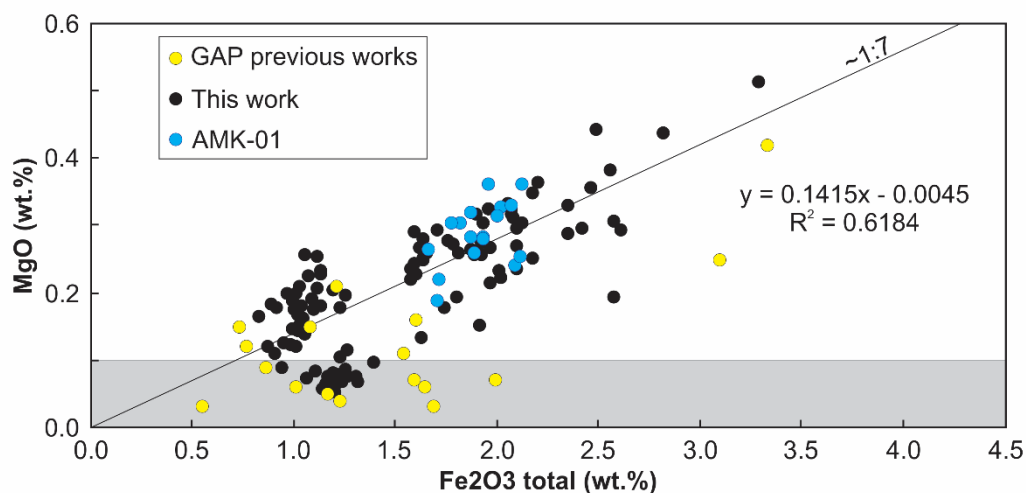


Figure 6.1 Plot of MgO vs total Fe₂O₃ (wt.%) reliable data (see text) of groundmass nepheline from Goiás Alkaline Province (GAP) potassic foidites. The correlation between MgO and total Fe (as Fe₂O₃) is close to a 1:7 ratio ($n = 120$), suggesting that for every ~ 3.5 Fe atoms there is one Mg²⁺ cation in the structure of these nephelines (NB. atom/cation numbers corrected for a.p.f.u.). Also note that more than 80% of analyses have MgO contents > 0.1 wt.% (grey area); this is in marked contrast to most values reported for igneous nephelines (*cf.* Henderson, 2020).

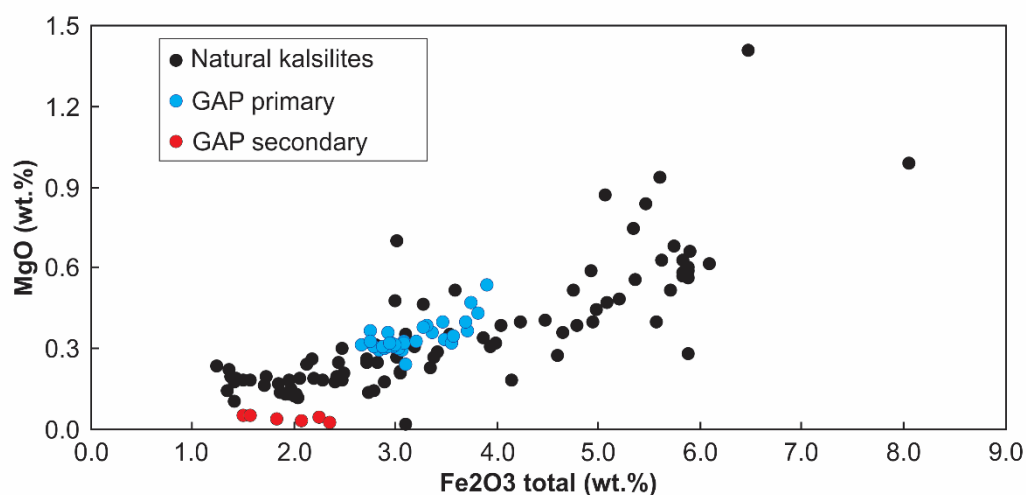


Figure 6.2 Plot of MgO vs total Fe₂O₃ (wt.%) reliable data (see text) of groundmass kalsilite from Goiás Alkaline Province potassic foidites compared to natural kalsilites worldwide (database compiled by ILO). All plotted data are EMPA except for one reliable ‘wet-chemical’ analysis (Sahama, 1954).

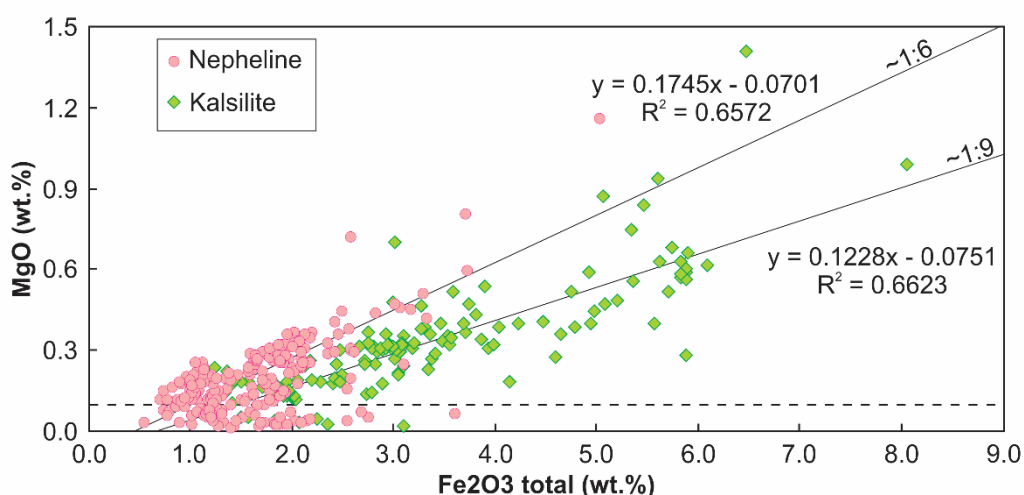


Figure 6.3 A comparison between the new nepheline and kalsilite Mg / Fe databases. All data points plot above 0.5 wt.% total Fe_2O_3 and most of them (~80%) show MgO contents > 0.1 wt.% (dashed line). The correlation between MgO and total Fe (as Fe_2O_3) is ~1:9 for all kalsilites ($n = 121$) and ~1:6 for groundmass nephelines ($n = 187$); phenocrysts of nepheline were not included because they show a very distinct trend (see Figure 6.4).

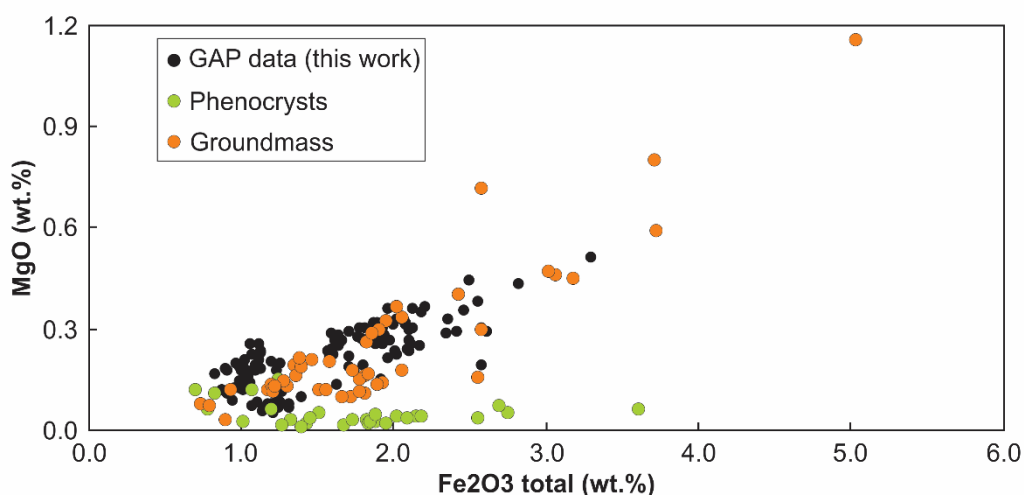


Figure 6.4 Nepheline database analyses grouped according to their mode of occurrence. Groundmass nepheline, including this work data, show a positive correlation between MgO and total Fe. In contrast, nepheline phenocrysts plot in a trend almost parallel to the horizontal axis, being enriched in total Fe but poor in MgO.

The unusually high concentrations of MgO found in nepheline and kalsilite from the Goiás Alkaline Province also can be observed in our new ‘global’ databases (**Figure 6.3**). Nephelines with MgO contents as high as 0.25 wt.% are not uncommon, and values with up to 0.59 wt.% (Gurenko & Sobolev, 2018), 0.80 wt.% (Baudouin, 2016), and 1.16 wt.% (Prelević

et al., 2005) have occasionally been reported for nepheline in the groundmass of other olivine-rich foidites. Likewise, groundmass kalsilites from K-rich volcanic rocks have Mg and total Fe content that can reach up to 1.41 wt.% MgO and 8.05 wt.% Fe₂O₃ (*e.g.* Tappe *et al.*, 2003). It is evident that kalsilite shows a wider range of MgO and total Fe₂O₃ in comparison to nepheline (see **Figure 6.3**). As both minerals occur essentially as late magmatic phases in the groundmass of these alkaline volcanic rocks, a possible explanation could be that kalsilite, in general, is derived from more Mg-rich magmas. However, the explanation is not straightforward. There are examples of kalsilite and nepheline coexisting in the groundmass of the same rock sample with very contrasting Mg and Fe values (*e.g.* Andersen *et al.* 2012); thus, his sample A2274 has kalsilite with 0.40 wt.% MgO and 4.71 wt.% Fe₂O₃, on average, and nepheline with 0.07 wt.% MgO and 0.76 wt.% Fe₂O₃, on average. A similar case is noted for our new EMP data for sample AMK-1. These patterns suggest that the magmatic compositions are not the only controlling factor for Mg and Fe incorporation in these two minerals (see below). In addition, the iron content of nepheline seems to be related to the Fe oxidation state and the amount of alkalis in the system (Edgar, 1984); however, the case of kalsilite is more complicated as it appears to be independent of the composition of the parental magma.

The positive correlation between Mg and Fe contents is shown by the compositions in both the nepheline and kalsilite databases (see **Figure 6.3**), but, the occurrence of Mg-rich nepheline seems to be restricted to groundmass nephelines (see **Figure 6.4**). In contrast, nepheline phenocrysts tend to have lower MgO contents (usually < 0.15 wt.%), regardless of their high amounts of total Fe (up to 3.6 wt.% Fe₂O₃). It should be emphasized, though, that most of the groundmass compositions used in **Figure 6.4** are from nephelines associated with kalsilite in strongly Si-undersaturated mafic potassic/ultrapotassic volcanic rocks, whereas the phenocrysts data are exclusively from Mg-poor nephelinites (see Dawson, 1998; Platz *et al.*, 2004; Baudouin *et al.*, 2016), pointing to the Mg-content of nepheline being dependent on

magma composition. However, it is evident that more systematic investigations and a greater number of nepheline/kalsilite analyses which have reliably analysed MgO data are required before any conclusive interpretation can be established.

It is clear that the positive correlation of Mg and Fe contents in nepheline and kalsilite described in this work is the opposite of the ‘normal’ magmatic trend, where Fe/Mg increases (or Mg/Fe decreases) with differentiation driven by the crystallization of ferro-magnesian minerals. In this context it is useful to refer to the work of Gurenko & Sobolev (2018) where their whole-rock and mineral databases show increasing Fe/(Fe+Mg) with fractionation in the parent rocks, increasing Fe/(Fe+Mg) in phenocrystic olivine, phenocryst and groundmass clinopyroxene, and groundmass mica. In contrast, their data for groundmass nepheline and kalsilite compositions show a coupled Fe and Mg trend leading to a fairly constant Fe/(Fe+Mg) ratio within the rock series. These relationships are comparable to those found in the Goiás Alkaline Province feldspar-free volcanic rocks and their mineral data (Brod *et al.*, 2005; Oliveira *et al.* in prep.). It is likely, therefore, that the strong positive correlation between Mg and Fe observed for nepheline and kalsilite can be explained, at least in part, by a combination of mineral crystal-chemical properties and geochemical affinities; thus, cations with similar ionic sizes and valences (*i.e.* Fe^{3+} , Fe^{2+} , Mg^{2+} , Mn^{2+}) can enter the same crystallographic site in the stuffed-tridymite framework (Henderson, 2020). Based on the prevalence of Mg-rich nepheline and kalsilite in the groundmasses of Mg-rich alkaline volcanic rocks, it is reasonable to assume that significant amounts of Mg might be incorporated preferentially by the nepheline and kalsilite structure when these minerals crystallized during rapid cooling to form the groundmass phases. Under these conditions, more Mg^{2+} cations would be available for all the crystallizing phases and the high-temperatures would make the mineral structures more expanded and able to accept ‘small’ divalent cations into the tetrahedral framework sites. Indeed, we suggest that the amount of Mg incorporated might depend on the cooling rate of the

particular lava pulse, with faster quenching locking-in the earlier high-temperature Mg-rich compositions. We emphasize, again, that further research, including experimental petrology studies, are required before any reliable interpretation can be established for the detailed nepheline and kalsilite relations in the strongly Si-undersaturated alkaline volcanic rocks.

The recognition of Mg as an important minor element in natural nepheline and kalsilite leads to numerous avenues of possible research. In this context, it is worth mentioning recent studies on the existence of a high-pressure compound (*i.e.* the NAL phase) that can be recrystallized to composite inclusions of a low-pressure assemblage of Mg-rich nepheline-kalsilite solid solution and (Mg,Fe)Al₂O₄-rich spinel during the exhumation of diamond-bearing, super-deep mantle to the Earth's surface (Walter *et al.*, 2011; Thomson *et al.*, 2014; Zedgenizov *et al.*, 2014; Kimura *et al.*, 2021).

6.3 Data Reliability

At the outset, we recommend that all EMP studies of nepheline and kalsilite should include rigorous determination of all the divalent cations (*i.e.* Mg, Mn, Ca, Sr, and Ba). In addition, care should be taken to avoid loss of Na under the electron beam (*i.e.* if possible using a beam current 2-5 nanoamps with a spot size 5-20 μm ; Morgan & London, 2005; Campbell *et al.*, 2016; and/or using a rastered beam). According to Henderson (2020), high quality nepheline data should have: (1) values for both $\Delta\text{Al}^{\text{cc}}$ and $\Delta\text{T}^{\text{ch}}$ parameters within ± 0.6 ; (2) values for the $\Delta\text{Al}^{\text{cc}}/\Delta\text{T}^{\text{ch}}$ ratio between 1.0 and 1.25; (3) CaO contents < 3.5 wt.%; (4) the sum of tetrahedral cations within the range 15.9-16.1; and (5) only limited differences between the excess Si' parameters (see Henderson 2020 for further details). In this study, we also extend this approach to kalsilite data. Hence, all data presented here (**Figure 6.1-4**), and their interpretations, are based exclusively on the most reliable K-rich nepheline and kalsilite analyses.

Regardless of the high contents of MgO and total Fe₂O₃ noted in the previous section, a wider range of values have occasionally been reported in the literature (see Prelević *et al.*, 2005;

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Andersen *et al.*, 2014; Isakova *et al.*, 2017) and their reliability should be assessed. Firstly, a large number of nepheline analyses are considered unreliable because of their high totals of tetrahedral cations (*i.e.* the sum of T-cations > 16.1). This is undoubtedly a consequence of unsuitable analytical conditions, involving significant Na loss (also see Henderson, 2020). Secondly, K-rich nepheline and kalsilite from feldspar-free volcanic rocks generally contain much smaller CaO contents (usually < 0.5 wt.%) than most natural nephelines reported to date. Thus, we evaluate the CaO contents for individual spot analyses compared to the average composition for a single sample; any outlier with an unusually high CaO content can be rejected. About seventy nepheline analyses have been considered unreliable on the basis of their unacceptable stoichiometric parameters combined with our ‘new’ ‘Ca-rich’ approach. In addition, the nepheline data for exsolved nepheline-kalsilite phenocrysts (see Andersen *et al.*, 2012) were omitted as they represent a post-magmatic, subsolidus process. Within the kalsilite database, 21 analyses do not report MgO contents; 16 analyses are unreliable on the basis of at least one of the five criteria above (most are from a single sample from Andersen *et al.*, 2014); and 6 analyses have been considered anomalously rich in CaO. In addition, the four ‘acceptable’ analyses from Isakova *et al.* (2017) were rejected because of their low analytical totals (95.0–98.2 wt.%), which probably result from the ‘robust’ analytical conditions employed. Even so, the extremely high values of total Fe (up to 12.6 wt.% FeO; Isakova *et al.*, 2017) reported for kalsilites, which occur as daughter phases of primary melt inclusions, merit further consideration.

A direct consequence of the use of the ‘new’ **Spreadsheet 1** (see Henderson & Oliveira, 2022) for data reliability is that a much narrower range of $\Delta\text{Al}^{\text{cc}}/\Delta\text{T}^{\text{ch}}$ ratios has been obtained for reliable analyses when compared with the range established by Henderson (2020). In the case of the nepheline database used in this study, when considering only the reliable analyses, this parameter varies from 1.125 to 1.147 (average 1.140; $n = 217$). For reliable kalsilite

analyses, the ‘new’ $\Delta\text{Al}^{\text{cc}}/\Delta\text{T}^{\text{ch}}$ ratio shows an even narrower range of values (1.137 to 1.146, with an average of 1.142; $n = 127$). Hereafter, we recommend that $\Delta\text{Al}^{\text{cc}}/\Delta\text{T}^{\text{ch}}$ ratios between 1.1 and 1.2 should be accepted as indicating high quality microprobe nepheline and kalsilite analyses.

6.4 *Application of the Revised Spreadsheets*

As noted by Henderson & Oliveira (2022), the revised **Spreadsheet 1** for calculation of nepheline-group minerals atomic formulae and stoichiometry parameters including the T^{2+} cations (*e.g.* Mg^{2+}) gives more sensible compositional parameters for analyses which report MgO contents, particularly for the $\Delta\text{Al}^{\text{cc}}/\Delta\text{T}^{\text{ch}}$ ratio. In **Table 6.1**, we show a comparison between the values obtained for published representative Mg-rich nepheline and kalsilite compositions using both the earlier ‘old’ equations as defined by Henderson (2020) and the revised spreadsheets. The analysed Fe-oxide components reported are those given in the original publications but note that the choice of using Fe_2O_3 or FeO values for these EMP data is a personal choice of the analyst; in all cases the atomic formulae are given here in **Table 6.1** with all iron as Fe^{3+} . The atomic formulae, stoichiometry parameters, and end-member compositions are calculated with the revised **Spreadsheet 1** (Henderson & Oliveira, 2022) and the data for the sample set are attached here as the version denoted **Spreadsheet 1A**; in this spreadsheet we also show how the Fe valence could be assessed based on Fe calculated as both Fe^{3+} or Fe^{2+} ‘end-members’ (see Henderson & Oliveira, 2022). Note that **Spreadsheet 1A** is attached to this paper as a supplementary file together with an additional file explaining how to use the EXCEL file.

Table 6.1 shows that all ‘previous’ values of the $\Delta\text{Al}^{\text{cc}}/\Delta\text{T}^{\text{ch}}$ ratio are < 1.0 , which implies that all these analytical data should be considered unreliable. However, the ‘revised’ delta values have an average $\Delta\text{Al}^{\text{cc}}/\Delta\text{T}^{\text{ch}}$ ratio of 1.141 for both nepheline and kalsilite showing that these Mg-rich analyses are, actually, all reliable. It is clear that the contrasting values

mentioned above are not due to the high amounts of MgO, but simply reflect the importance of correctly incorporating data for Mg (and other T^{2+} cations) in the stoichiometry calculation. For instance, assuming that Mg had not been specifically analysed in all previous cases, both the original and the new spreadsheets will give acceptable $\Delta Al^{cc}/\Delta T^{ch}$ ratios (*i.e.* within the 1.0-1.25 range). However, when considering the coupled substitution $2Al^{3+} = Mg^{2+} + Si^{4+}$, the excess Si' is significantly affected if the MgO concentrations are not given (compare the values of the $Q^{(Si-Al)}$ parameter in **Table 6.1**, particularly for columns 4, 6, 9 and 15). The Si^{total} is directly related to this coupled substitution as demonstrated by Henderson & Oliveira (2022; table 1). Thus, robust analyses of T^{2+} cations (mainly Mg but also Mn and reliably-estimated Fe^{2+}) are essential to determine more realistic values of excess Si', particularly, for K-rich nepheline and kalsilite crystallised from Mg-rich alkaline ultrabasic magmas (*i.e.* feldspar-free assemblages).

Of course, the reliability of these estimates depends on the analytical errors for all of the elements present. We have shown that overestimation of the proportion of Fe^{3+} cations would shift the ΔAl^{cc} values to more negative values and overestimation of Fe^{2+} cations would lead to more positive values (Henderson & Oliveira, 2022); clearly the overall proportions of M^{+} vs M^{2+} cations would be equally important. In particular, the contents of divalent species for both framework and cavity cation sites are crucial as both have doubled cation coefficients for the calculation of ΔAl^{cc} values; hence reliable determinations for Ca, Sr, and Ba and Mg, Mn, and Fe^{2+} are essential. Nepheline/kalsilite compositions showing stuffed-tridymite stoichiometry would have negative $\Delta AlFe^{3+}$ and positive $\Delta AlFe^{2+}$ values (see above) and would plot in the appropriate quadrant of **Figure 6.5**. Those close to stoichiometry would plot in adjacent quadrants but very close to the relevant boundary axis. In addition, serious analytical errors would lead to significant departures from stuffed-tridymite stoichiometric delta parameters with both $\Delta AlFe^{2+}$ and $\Delta AlFe^{3+}$ parameters being positive or negative (see **Figure 6.5**). However,

the numerical difference between these two values (*e.g.* $\Delta\text{AlFe}^{2+} - \Delta\text{AlFe}^{3+}$) should match the value for the total of Fe atoms. Displacement of both these delta values would define the overall nature of the framework/cavity cation valence mismatches, although if all of the divalent element species have been estimated reliably it might be that underestimation of the actual Na content is the most likely problem (see above). Thus, if the Na content is underestimated due to Na loss in the electron beam the $\Delta\text{Al}^{\text{cc}}$ would have anomalously high positive values (see **Figure 6.5**). Note also that a small analytical error for Na would modify the delta parameters for samples plotting in the northwest quadrant and would adjust the plotted sample in **Figure 6.5** to either a higher or lower $\text{Fe}^{3+}/\text{Fe}^{2+}$ apparent ratio. Clearly, high analytical accuracy for all elements is paramount.

Finally, we will consider whether the Fe valence model could be evaluated following the approach suggested in Henderson & Oliveira (2022) with the objective of estimating possible Fe^{3+} and Fe^{2+} contents. Only reliable nepheline and kalsilite analyses with both Fe oxidation states present are likely to provide reliable results for this approach by having positive ΔAlFe^{2+} and negative ΔAlFe^{3+} values. Supplementary **Spreadsheet 1A** shows the compositions for representative nepheline/kalsilite analyses which have Fe reported as both FeO and Fe_2O_3 . Nepheline analyses in **Table 6.1** columns 1, 3, 5, 9 and kalsilites in columns 11, 12, 13, 14, 16 and 17 all show positive values for ΔAlFe^{2+} and negative values for ΔAlFe^{3+} (see **Figure 6.5**). As shown by Henderson & Oliveira (2022), the former numbers reflect the possible atomic proportions of Fe^{3+} and the latter values those for Fe^{2+} . The pairs of values for each sample can be extracted from the spreadsheet and are summarized in the bottom portion of **Table 6.1** along with the equivalent wt.% values of the ferric and ferrous oxides. Note that nepheline and kalsilite from the different parent rocks both show a range of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios, but better analytical data are required to assess the significance of such estimates. This method requires rigorous analyses for all cation components, in particular the T^{2+} cations, but we emphasize that

bulk analyses with Fe-oxide concentrations > 2 wt.% would probably deliver significantly more reliable calculated delta values and, in turn, more robust excess Si values and Si/Al ratios.

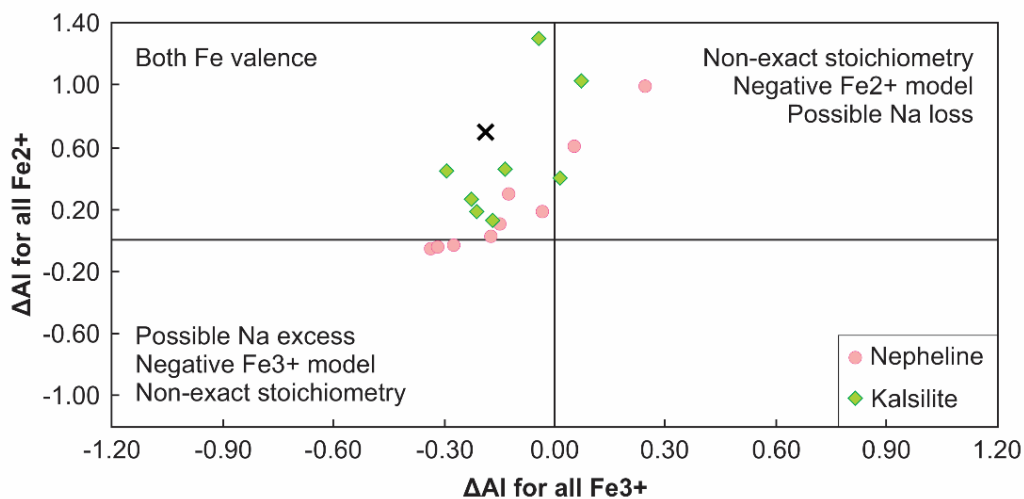


Figure 6.5 Plot of ΔAlFe^{2+} vs ΔAlFe^{3+} values calculated for the representative compositions of K-rich nepheline and kalsilite shown in Table 6.1. Also plotted are data for the hypothetical composition $\text{K}_8\text{Al}_{6.94}\text{Fe}^{3+}_{0.69}\text{Fe}^{2+}_{0.19}\text{Si}_{8.18}\text{O}_{32}$ (i.e. 85KsAl:10KsFe³⁺:5KsFe²⁺ wt.% end-members; see Chapter 5, table 4, composition E) as reference (black cross). Note that nepheline compositions in columns 2, 4, 6, 7, 8 and kalsilite in columns 10 and 15 of Table 6.1 have both ΔAlFe^{2+} and ΔAlFe^{3+} parameters either positive or negative; all these analyses have been considered reliable, but the discrepancy in their ΔAlFe^{2+} and ΔAlFe^{3+} values suggest that: (1) they do not show the exact stuffed-tridymite stoichiometry; (2) unsuitable analytical conditions may have caused some Na loss or; (3) some alteration product (Na excess) might be present.

Table 6.1. Stoichiometry parameters calculated for Mg-rich nepheline and kalsilite compositions using the ‘old’ and the ‘new’ spreadsheets (see text).

[Ref.]	Daws [1]	J-B <i>et al.</i> [2]	Platz <i>et al.</i> [3]	Prelev <i>et al.</i> [4]	Ander <i>et al.</i> [5]	G&S [6]	B&P [7]	Lustri <i>et al.</i> [8]	This work	Gallo <i>et al.</i> [9]	Lloyd <i>et al.</i> [10]	Tappe <i>et al.</i> [11]	Brod <i>et al.</i> [12]	Ander <i>et al.</i> [5]	G&S [6]	Lustri <i>et al.</i> [8]	This work
#	1 Nph	2 Nph	3 Nph	4 Nph	5 Nph	6 Nph	7 Nph	8 Nph	9 Nph	10 Kls	11 Kls	12 Kls	13 Kls	14 Kls	15 Kls	16 Kls	17 Kls
Wt. %																	
SiO ₂	41.00	40.21	39.62	43.87	41.23	42.79	40.50	41.15	41.69	39.20	39.07	37.85	37.95	37.25	38.91	38.82	38.24
TiO ₂		0.06	0.03		0.10	0.06	0.02	0.03	b.d.l.	0.05		0.09	0.08	b.d.l.	0.05	0.03	0.05
Al ₂ O ₃	32.50	32.62	32.57	27.55	32.46	30.36	31.09	31.94	30.25	29.90	28.77	23.57	29.90	27.12	26.62	30.15	28.28
Cr ₂ O ₃							0.03					0.01					b.d.l.
Fe ₂ O ₃	1.73							1.81	2.82		3.10		2.48			1.87	3.72
FeO		1.44	1.32	4.53	1.22	3.35	1.71			2.24		7.24		4.02	5.29		
MnO		b.d.l.	b.d.l.	0.08	b.d.l.	b.d.l.	0.02	b.d.l.	b.d.l.		0.02	b.d.l.	0.01	b.d.l.		0.01	b.d.l.
MgO	0.12	0.16	0.21	1.16	0.19	0.59	0.30	0.16	0.44	0.21	0.35	0.99	0.18	0.41	0.60	0.14	0.36
CaO	0.46	0.06	0.13	0.48	0.08	0.04	3.77	0.07		0.08	0.11	0.02	0.04		0.01	b.d.l.	0.03
SrO			0.02		b.d.l.				b.d.l.					b.d.l.			0.09
BaO			0.11	0.13		0.01			b.d.l.			0.26	0.13	b.d.l.	0.27		0.13
Na ₂ O	14.90	15.00	14.29	12.12	14.09	15.50	11.02	14.86	14.66	1.38	1.74	0.77	1.94	0.69	2.33	1.60	2.24
K ₂ O	8.49	9.64	9.55	10.96	10.36	7.79	8.81	9.49	8.64	27.30	27.26	27.64	27.20	28.65	25.48	27.48	26.06
Total	99.20	99.19	97.85	100.88	99.74	100.49	97.27	99.51	98.62	100.36	100.42	98.44	99.91	98.13	99.57	100.08	99.20
Atoms/32(O)																	
Si	8.102	7.993	7.975	8.600	8.135	8.326	8.152	8.147	8.309	8.183	8.213	8.263	8.028	8.107	8.240	8.153	8.145
Ti		0.009	0.005		0.015	0.009	0.003	0.005		0.008		0.015	0.013		0.008	0.004	0.008
Al	7.569	7.642	7.727	6.365	7.550	6.962	7.375	7.452	7.107	7.356	7.128	6.065	7.454	6.957	6.643	7.463	7.101
Cr							0.005					0.002					
Fe ³⁺	0.257	0.239	0.222	0.743	0.201	0.545	0.288	0.269	0.422	0.391	0.490	1.322	0.395	0.732	0.937	0.295	0.596
Fe ²⁺																	
Mn				0.013			0.003				0.004		0.002			0.002	
Mg	0.035	0.047	0.063	0.339	0.057	0.172	0.089	0.048	0.130	0.065	0.110	0.322	0.057	0.131	0.191	0.042	0.115
Ca	0.097	0.013	0.028	0.101	0.017	0.008	0.814	0.014	0.026	0.018	0.025	0.005	0.009		0.001		0.006
Sr			0.002														0.011
Ba			0.009	0.010		0.001						0.022	0.011		0.023		0.011
Na	5.709	5.781	5.577	4.607	5.391	5.848	4.302	5.706	5.664	0.559	0.709	0.326	0.796	0.289	0.956	0.650	0.925
K	2.140	2.445	2.452	2.741	2.609	1.932	2.262	2.397	2.198	7.270	7.310	7.698	7.340	7.955	6.883	7.363	7.082
Σ cations	23.910	24.170	24.060	23.520	23.975	23.802	23.293	24.038	23.857	23.850	23.998	24.040	24.103	24.171	23.882	23.971	24.002
Using equations from Henderson (2020)																	
Si/Al	1.035	1.015	1.004	1.210	1.051	1.110	1.064	1.056	1.104	1.057	1.078	1.120	1.024	1.054	1.088	1.051	1.059
Σ T-site	15.928	15.884	15.929	15.709	15.900	15.841	15.823	15.874	15.839	15.938	15.831	15.666	15.889	15.795	15.828	15.914	15.850
Δ(Al - cats)	-0.2175	-0.3698	-0.1586	-0.4614	-0.2845	-0.2901	-0.5228	-0.4099	-0.3863	-0.1174	-0.4511	-0.6898	-0.3265	-0.5555	-0.3076	-0.2550	-0.3679
Δ(T charge)	-0.2528	-0.4070	-0.2491	-1.0341	-0.3495	-0.5598	-0.6224	-0.4436	-0.5692	-0.2179	-0.5960	-1.1769	-0.3889	-0.7188	-0.6065	-0.3013	-0.5262

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$\Delta\text{Al}/\Delta\text{T}$	0.8603	0.9086	0.6366	0.4462	0.8139	0.5182	0.8399	0.9242	0.6786	0.5386	0.7568	-0.5861	0.8397	0.7728	0.5073	0.8464	0.6991
Q^{xs}	-0.55	-3.14	-1.35	5.38	-0.44	2.54	-2.38	-1.64	1.06	1.69	-0.86	-0.98	-2.19	-3.05	1.40	-0.16	-0.80
Q^{Si}	0.36	-1.56	-0.80	6.44	0.71	3.36	-0.22	0.13	2.46	2.04	0.90	1.25	-0.84	-0.86	2.25	0.90	0.56
Q^{cav2}	-0.09	-2.28	-1.24	4.62	0.09	2.37	-1.33	-0.66	1.45	1.65	-0.16	-0.83	-1.54	-2.13	1.17	0.37	-0.38
$Q^{\text{(Si-Al)}}$	1.72	0.75	0.19	9.33	2.49	5.18	3.05	2.69	4.87	2.77	3.72	5.56	1.20	2.62	4.17	2.50	2.86
Using 'new' equations - improved for T2+ cations																	
Si/Al	1.021	0.997	0.980	1.056	1.029	1.040	1.027	1.037	1.050	1.031	1.033	0.990	1.002	1.003	1.012	1.034	1.014
Σ T-site	15.963	15.931	15.992	16.061	15.957	16.014	15.916	15.921	15.968	16.003	15.944	15.989	15.948	15.927	16.018	15.958	15.966
$\Delta(\text{Al} - \text{cats})$	-0.1468	-0.2750	-0.0325	0.2432	-0.1710	0.0548	-0.3374	-0.3149	-0.1266	0.0133	-0.2246	-0.0454	-0.2094	-0.2926	0.0737	-0.1669	-0.1369
$\Delta(\text{T charge})$	-0.1286	-0.2406	-0.0284	0.2136	-0.1499	0.0481	-0.2958	-0.2763	-0.1111	0.0117	-0.1970	-0.0397	-0.1833	-0.2560	0.0645	-0.1464	-0.1199
$\Delta\text{Al}/\Delta\text{T}$	1.1411	1.1431	1.1445	1.1384	1.1405	1.1397	1.1407	1.1399	1.1389	1.1403	1.1403	1.1436	1.1427	1.1426	1.1419	1.1401	1.1417
Q^{xs}	-0.55	-3.14	-1.35	5.38	-0.44	2.54	-2.38	-1.64	1.06	1.69	-0.86	-0.98	-2.19	-3.05	1.40	-0.16	-0.80
Q^{Si}	0.14	-1.85	-1.19	4.24	0.36	2.28	-0.80	-0.17	1.65	1.63	0.19	-0.76	-1.21	-1.68	1.06	0.63	-0.16
Q^{cav2}	-0.09	-2.28	-1.24	4.62	0.09	2.37	-1.33	-0.66	1.45	1.65	-0.16	-0.83	-1.54	-2.13	1.17	0.37	-0.38
$Q^{\text{(Si-Al)}}$	1.06	-0.14	-0.99	2.72	1.43	1.94	1.31	1.80	2.44	1.55	1.59	-0.48	0.10	0.15	0.60	1.67	0.69
Mol.% PRS¹																	
Ne	71.95	70.37	70.15	60.89	66.44	73.69	64.51	69.19	70.30	7.02	8.70	4.08	9.77	3.50	12.12	7.98	11.48
Ks	26.98	29.76	30.85	36.23	32.15	24.35	33.92	29.06	27.28	91.42	89.73	96.40	90.13	96.35	87.27	90.38	87.84
Q'	1.07	-0.13	-1.00	2.88	1.41	1.96	1.57	1.75	2.42	1.56	1.57	-0.48	0.10	0.15	0.61	1.64	0.69
Mol.% Ne-Ks²																	
Ne	72.7	70.3	69.5	62.7	67.4	75.2	65.5	70.4	72.0	7.1	8.8	4.1	9.8	3.5	12.2	8.1	11.6
Ks	27.3	29.7	30.5	37.3	32.6	24.8	34.5	29.6	28.0	92.9	91.2	95.9	90.2	96.5	87.8	91.9	88.4
Fe cats/32(O)																	
Fe3+	0.111		0.190		0.031				0.298		0.268	1.303	0.187	0.444		0.129	0.463
Fe2+	0.147		0.033		0.171				0.127		0.225	0.045	0.209	0.293		0.167	0.137
Wt.%																	
Fe ₂ O ₃	0.75		1.26		0.21				1.98		1.68	7.78	1.17	2.69		0.82	2.87
FeO	0.89		0.19		1.03				0.76		1.27	0.24	1.18	1.60		0.95	0.77

¹PRS refers to Petrogeny's Residua System Ne-Ks-Quartz. ²Ne-Ks refers to Nepheline-Kalsilite Binary System Ne-Ks.

Abbreviations in top rows: b.d.l. below detection limit; Nph – nepheline; Kls – kalsilite. References and sample ID: [1] Dawson (1998), table 2, sample WN4421; [2] Junqueira-Brod (1998), table A4.3, 96AE08; [3] Platz *et al.* (2004), table 6, #96.660; [4] Prelević *et al.* (2005), suppl. dataset KAG, NV01/6; [5] Andersen *et al.* (2012), suppl. table 5, S80 – nepheline / A2274 – kalsilite; [6] Gurenko & Sobolev (2018), suppl.2 table C1.7, #11529 – nepheline / #11497 – kalsilite; [7] Baudouin & Parat (2020), suppl. table A1, Kw5; [8] Lustrino *et al.* (2020), suppl. table 1e, SAV8 – nepheline / SAV6 – kalsilite; [9] Gallo *et al.*, (1984), table 1, SV16; [10] Lloyd *et al.* (1991), table 11, S23,160; [11] Tappe *et al.* (2003), table 4, C4793gm; [12] Brod *et al.* (2005), table 5, sabM01.

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Chapter 7

K-rich Nepheline in Strongly SiO₂-Undersaturated Alkaline Mafic Volcanic Rocks and its Petrological Significance

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Abstract

The present knowledge about the composition of natural nepheline solid solutions is based mostly on research into the chemistry of nephelines coexisting with feldspar minerals. These nephelines are generally Na-rich and exhibit considerable excess of silica (Q') in comparison with the ideal formulae $\text{Na}_3\text{KAl}_4\text{Si}_4\text{O}_{16}$. Potassic (or K-rich) nephelines, as anticipated, are those with more potassium than in the ideal nepheline. Such potassic compositions are quite rare. They are usually associated with K-rich and Si-poor volcanic rocks. Based on a detailed textural and chemical investigation of nepheline that coexists with kalsilite in strongly SiO_2 -undersaturated, feldspar-free, volcanic rocks from central Brazil, we discuss here broadly the petrological importance of the potassic nepheline compositions. Both K-rich nepheline and kalsilite coexisting in the groundmass of these volcanic rocks are primary magmatic phases. We propose that they were already formed as separate phases under a subsolvus condition during rapid undercooling of the parental magma. A novel compilation of data revealed that potassic nepheline is not restricted to K-rich host rocks. The compositions with more K than in the ideal chemical formulae have been found also in groundmass nepheline from lavas with characteristic sodic affinity such as those from Madagascar and from the East African Rift System (*e.g.* Oldoinyo Lengai volcano). This allows concluding that other factors rather than the sodic or potassic chemical affinity of parental magma must control the crystallisation of potassic nepheline. We postulate that the silica activity in the magmatic system, together with the strong site preference for Na and K in the nepheline structure, are two key factors in controlling the composition of natural nepheline solid solutions.

Keywords: nepheline-kalsilite system; crystal structure; Goiás Alkaline Province; mineral composition; silica activity

7.1 Introduction

Nepheline (Nph), the most common feldspathoid (Brooks, 2021), is a distinctive mineral of SiO₂-undersaturated alkaline igneous rocks. It occurs as a primary magmatic phase in many extrusive and intrusive rock types of a wide range of compositions (see, *e.g.* Deer *et al.*, 2004 and references therein). Consequently, it is well-established that the composition of nepheline in igneous rocks depends on the chemistry of the parental magma and the physical conditions of crystallization (*e.g.* Bowen & Ellestad, 1936; Miyashiro, 1951; Tilley, 1954; Hamilton, 1961; Barth, 1963; Edgar, 1984; Wilkinson & Hensel, 1994). In deep-seated host rocks (*i.e.* those plutonic rocks that crystallized at rather low temperatures and slow cooling rates), nepheline commonly exhibits a narrow compositional range that approaches the ‘ideal composition’ of Na₃KAl₄Si₄O₁₆ – independent of bulk rock chemistry (see also Blancher *et al.*, 2010 and references therein). Unlike nepheline of slowly cooled plutonic rocks, that in volcanic rocks varies significantly in composition, deviating from the ‘ideal’ Na:K ratio of 3:1 towards both Na-rich and K-rich specimens (Deer *et al.*, 2004). Nonetheless, nepheline with more K than in the ideal composition is rather uncommon and, so far, has been thought to occur occasionally in a few alkaline ultrabasic lavas, mostly potassic ones (*e.g.* Edgar, 1984; Wilkinson & Hensel, 1994; Antao & Nicholls, 2018; Hamada *et al.*, 2019; Antao & Hovis, 2021).

However, as recently pointed out by Oliveira & Henderson (2022), until now most of the knowledge about nepheline chemistry has been based on research into feldspar-bearing assemblages, particularly in plutonic rocks (*e.g.* Blancher *et al.*, 2010 and references therein). The compositional variation of nepheline in strongly SiO₂-undersaturated volcanic rocks (*i.e.* feldspar-free assemblages) remains virtually unexplored, except maybe for the work of Velde & Yoder (1978). This is despite an increasing number of nepheline electron microprobe analyses that have been reported for such volcanic rocks in the last two decades (*e.g.* Melluso

et al., 2011; Andersen *et al.*, 2012; 2014; Cucciniello *et al.*, 2017; Minissale *et al.*, 2019; Mazzeo *et al.*, 2021; see also Supplementary Data – **Nepheline Database**).

In this study, we examine a very unusual mineral assemblage that occurs in some strongly SiO₂-undersaturated, mafic, potassic to ultrapotassic volcanic rocks of the Goiás Alkaline Province (GAP) in central Brazil (*e.g.* Brod *et al.*, 2005). In these rocks, both K-rich nepheline and kalsilite have been found to occur together in the groundmass, in the form of individual homogeneous grains. Hitherto, the coexistence of K-rich nepheline and kalsilite is only poorly documented in volcanic rocks (Oliveira *et al.*, 2022) and except for the notable occurrence in the potassic lavas of Mount Nyiragongo, DR Congo (*e.g.* Sahama, 1957; 1960; 1962a; Platz *et al.*, 2004; Andersen *et al.*, 2012; 2014), and a rare kalsilite-bearing hypabyssal xenolith collected from pyroclastic deposits of the Roman Province, Italy (*e.g.* Aurisicchio & Federico, 1985; Federico *et al.*, 1994), no other case has so far been investigated in detail.

For this paper, it is provided 203 new electron microprobe analyses, backscattered electron images, and compositional maps (for Na and K) to characterize the K-rich nepheline in the GAP volcanic rocks and to determine its primary or secondary nature. Special attention is paid to the relationship of K-rich nepheline to kalsilite. We then discuss the petrogenetic significance of the K-rich nepheline compositions in feldspar-free volcanic assemblages by comparing our data with the nepheline databases of Deer *et al.* (2004) and Henderson (2020), and our newly assembled database (see Supplementary Data – **Nepheline Database**), with data taken exclusively from alkaline ultrabasic volcanic rocks.

7.2 Background – Nepheline Structure, Chemistry and Phase Relations

The ‘so-called’ nepheline-kalsilite system is an excellent example of the interrelationships between structure, chemistry, thermodynamics, and phase equilibrium behaviour within a mineral series (Hovis *et al.*, 2009). Until recently (*cf.* Hålenius *et al.*, 2018), the International Mineralogical Association (IMA), as well as a large part of the geological

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community, have considered the mineral nepheline (Nph) as the ‘pure’ sodic end-member of the binary chemical system NaAlSiO_4 (Ne) – KAlSiO_4 (Ks). Nevertheless, based on considerable evidence from previous experimental, theoretical, and mineral composition investigations (*e.g.* Bannister & Hey, 1931; Tilley, 1954; Buerger *et al.*, 1954; Hahn & Buerger, 1955; Tuttle & Smith, 1958; Donnay *et al.*, 1959; Hamilton & Mackenzie, 1960; Barth, 1963; Dollase & Thomas, 1978; Ferry & Blencoe, 1978; Hovis *et al.*, 2009; among others) it has long been recognised that nepheline represents, in fact, an intermediate compound in the Ne-Ks binary system, with a composition of $\text{Ne}_{75}\text{Ks}_{25}$ (*i.e.* ideally, nepheline is a mineral phase that consists of 75 mol.% NaAlSiO_4 and 25 mol.% KAlSiO_4 end-member components).

The ideal formula of nepheline ($\text{Na}_3\text{KAl}_4\text{Si}_4\text{O}_{16}$ – Hålenius *et al.*, 2018) and, thus, its stoichiometry can be explained in part by its crystal structure. The nepheline structure is based on a tridymite-type framework (‘stuffed derivative’ – see Buerger, 1954), in which half of the Si atoms in the tetrahedral (T) sites are replaced by Al atoms. The negative charge is balanced by alkali atoms (Na, K) occupying spaces (or cavities) along the crystallographic c-axis. In addition, the crystal structure of nepheline is slightly distorted in comparison with the tridymite structure due to the small size of the sodium ion (Buerger *et al.*, 1954) and, thus, it holds interframework cavities (or alkali sites) of two different kinds. The large hexagonal (A) sites comprise 2 *apfu* (*i.e.* atoms per formula unit) and accommodate, preferentially, K and vacancies. The small, distorted, oval-shaped (B) cavities cover the other alkali sites (= 6 *apfu*) that are mainly occupied by Na, with minor Ca; in K-rich nepheline, however, K must enter also into the smaller B site to occupy it before the more appropriate A cavity positions (*e.g.* Buerger *et al.*, 1954; Hahn & Buerger, 1955; Merlino, 1984; Deer *et al.*, 2004; Hovis *et al.*, 2009; Antao & Nicholls, 2018; Hamada *et al.*, 2019; Antao & Hovis, 2021).

In nature, the most important chemical substitution in nepheline is K for Na atoms (Donnay *et al.*, 1959). Across the Ne-Ks system, the $\text{Na} \leftrightarrow \text{K}$ substitution triggers significant

changes in the unit-cell parameters (a, c and volume) of the crystalline phases. In nepheline solid solutions (*i.e.* between Ne₁₀₀ and ~Ne₃₀ – **Figure 7.1**), there is a linear increase of the lattice parameters with increasing Ks content. However, two remarkable discontinuities occur at the compositions Ne₇₅ and ~Ne₄₀₋₃₀ (*e.g.* Bannister & Hey, 1931; Smith & Sahama, 1954; Smith & Tuttle, 1957; Donnay *et al.*, 1959; Hovis *et al.*, 2009; Antao & Nicholls, 2018; Antao & Hovis, 2021). The first break is clearly related to the ‘ideal’ structure of nepheline and marks the entrance of the large K⁺ cations into the smaller B sites. The second discontinuity, otherwise, occurs close to the structural transition nepheline-tetrakalsilite [note: tetrakalsilite is a high-temperature, almost certainly, metastable phase that occurs between the stability fields of nepheline (Nph) and kalsilite (Kls) solid solutions – compare **Figure 7.1**. It contains three distinct alkali sites and only occurs within a narrow compositional range (Ne_{37.5}Ks_{62.5} to Ne₂₀Ks₈₀) – see Sahama (1957), Sahama & Smith (1957), Tuttle & Smith (1958), Merlino (1984), Hovis *et al.* (2009) and Antao & Hovis (2021) for further details].

Natural nepheline usually contains excess Si (hereafter expressed as Q’ end-member component – see Henderson, 2020 and Henderson & Oliveira, 2022) and a minor amount of other substitute cations such as Ca²⁺ and Fe³⁺ (*e.g.* Bannister & Hey, 1931; Smith & Sahama, 1954; Donnay *et al.*, 1959; Dollase & Thomas, 1978; Henderson, 2020). When Si⁴⁺ exceeds Al³⁺ (plus Fe³⁺) in the tetrahedral framework sites, or the monovalent cavity cations (Na⁺, K⁺) are replaced by divalent ones (Ca²⁺), the charge balance is usually compensated by vacancies at the cavity cation positions (see Barth, 1963; Henderson, 2020). Moreover, Mg seems to be an important minor element, particularly in K-rich phases that crystallised from Mg-rich, Si-poor alkaline magmas (Oliveira & Henderson, 2022).

As illustrated in **Figure 7.1**, in terms of phase relations, nepheline has a large stability field in the Ne-Ks binary system forming an extensive solid solution in the compositional range Ne₁₀₀-Ne₃₀ (Tuttle & Smith, 1958). At high temperatures ($T \geq 1000$ °C) and compositions more

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potassic than $\sim\text{Ks}_{60}$ ($=\text{Ne}_{40}$) a number of polymorphs can occur (*e.g.* trikalsilite, tetrakalsilite, kaliophilite, *etc.* – Sahama, 1957; Tuttle & Smith, 1958; also see Mugnaioli *et al.*, 2020). These are ‘transitional’ to kalsilite, which has the most stable structure for compositions close to KAlSiO_4 at low temperatures ($T < 850\text{ }^{\circ}\text{C}$). Thus, nepheline and kalsilite have distinct, yet related, crystal structures. Furthermore, experimental studies have demonstrated that despite the extensive solid solution at high temperatures, there is a large miscibility gap between K-rich nepheline and kalsilite solid solutions at lower temperatures (see **Figure 7.1**). The nepheline-kalsilite ‘solvus’ reaches its maximum at $\sim 1070\text{ }^{\circ}\text{C}$, in a composition $\sim\text{Ne}_{30}$ (*i.e.* an extremely K-rich nepheline). At moderate to low temperatures ($T = 400\text{--}500\text{ }^{\circ}\text{C}$), the miscibility gap is similar to that for the alkali feldspars and extends from ‘ideal’ nepheline (*i.e.* Ne_{75}) to almost ‘pure’ kalsilite (Tuttle & Smith, 1958; Ferry & Blencoe, 1978; Hovis *et al.*, 2009). Accordingly, potassic nepheline and kalsilite would theoretically be expected to occur together in more K-rich, Si-poor lavas. Indeed, a significant number of studies have reported their coexistence in the groundmass of some rare mafic potassic and ultrapotassic volcanic rocks, even though very poor attention has so far been paid to such assemblages (Oliveira *et al.*, 2022).

It is noteworthy that both crystallographic and experimental data support that the stoichiometric formula of natural nepheline is $\text{Na}_3\text{KAl}_4\text{Si}_4\text{O}_{16}$. As previously seen, marked changes in the structural relations take place at this composition (Ne_{75}), which also constrains the ‘sodic limb’ of the miscibility gap with decreasing temperatures. Note that the solvus does not cross the ‘ideal’ nepheline composition (Tuttle & Smith, 1958; Ferry & Blencoe, 1978; Hovis *et al.*, 2009; see **Figure 7.1**). These aspects led Tuttle & Smith (1958), Donnay *et al.* (1959) and Ferry & Blencoe (1978) to suggest that nepheline solid solutions may involve two binary sub-systems at low temperatures (*i.e.* the Na-rich and K-rich compositional regions in **Figure 7.1**), in which the exchange of K for Na atoms behaves somewhat differently.

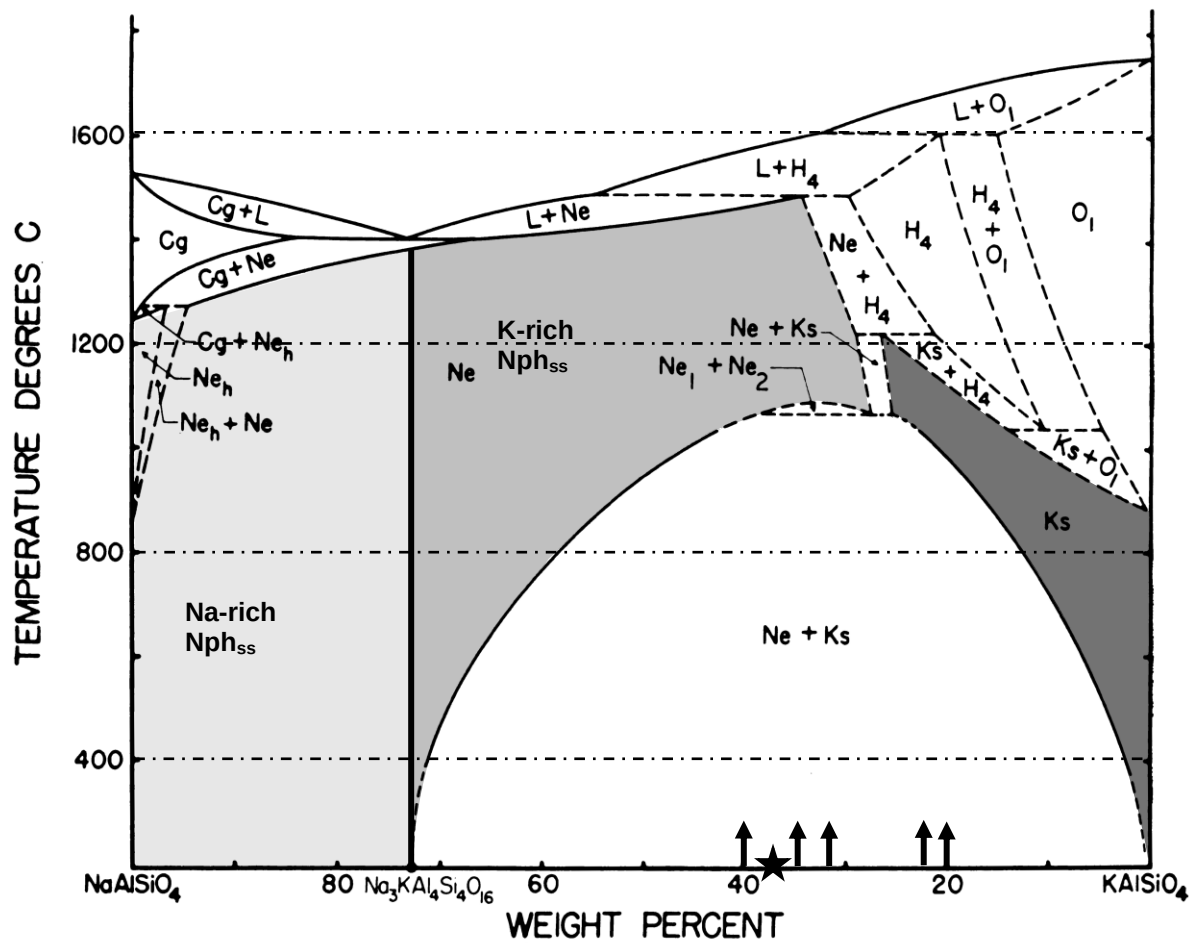


Figure 7.1 Simplified phase diagram for the binary system NaAlSiO_4 (Ne) – KAlSiO_4 (Ks) at 1 atm (modified after Deer *et al.*, 2013, after Tuttle & Smith, 1958). Dashed lines are inferred phase boundaries. The vertical arrows mark important changes of lattice parameters for each literature source (1 = Donnay *et al.*, 1959 and Antao & Hovis, 2021 [$\sim\text{Ne}_{40}$]; 2 = Hovis *et al.*, 2009 [$\sim\text{Ne}_{35}$ to Ne_{20}]; 3 = Antao & Nicholls, 2018 [$\sim\text{Ne}_{32}$ to Ne_{23}]). Black star = ‘ideal’ tetrakalsilite composition ($=\text{Ne}_{37.5}$) from Hovis *et al.* (2009). All these authors agree about the discontinuity at $\text{Na}_3\text{KAl}_4\text{Si}_4\text{O}_{16}$ ($=\text{Ne}_{75}$). Note that Na-rich nephelines display a positive correlation of c/a lattice parameter ratio with composition, whereas K-rich ones show a negative correlation (see Antao & Nicholls, 2018; Antao & Hovis, 2021). The relative displacement of the various discontinuity points at the nepheline-tetrakalsilite transition likely reflects the uncertainties of the referred works. It is also shown the possible extent of the tetrakalsilite stability field, which is poorly constrained. Note that the original abscissa scale is given in weight per cent (wt.%) of the NaAlSiO_4 end-member. This has been converted to the equivalent molecular per cent (mol.%) using the following equation: $\text{mol.\% Ne} = 100 * [(\text{wt.\% Ne} / 142.057) / (\text{wt.\% Ne} / 142.057 + \text{wt.\% Ks} / 158.165)]$.

7.3 Methodology

Samples Acquisition

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The Late Cretaceous mafic potassic-ultrapotassic magmatism of the Goiás Alkaline Province comprises a great variety of igneous manifestations, including dykes, sills, plugs, diatremes, lava flows, pyroclastic deposits and major differentiated plutonic complexes (see Brod *et al.*, 2005 and references therein). We conducted systematic sampling during several exploratory field trips in the province between July 2015 and November 2018. Despite the intense tropical weathering prevailing in the area, we managed to collect remarkably fresh outcrop samples suitable for detailed petrological and geochemical studies. Samples were collected from as many localities as possible throughout the province in order to obtain a representative set of volcanic and subvolcanic types (note: the GPS coordinates of the samples investigated in this work are given in Supplementary Data – **Table A1**; for a map location see Brod *et al.*, 2005; Junqueira-Brod *et al.*, 2005a, b; Carlson *et al.*, 2007). For this study, twelve rather fresh rock samples from large dykes (up to 10 m wide; extending over hundreds of meters), small plugs (up to 50 m wide), lava blocks from diatremes, and lava flows were selected, avoiding hydrothermal alteration, weathering effects, and occasional xenoliths or visible xenocrysts.

X-ray Fluorescence Analysis (XRF)

Major element concentrations for whole-rock samples were obtained by X-ray fluorescence spectrometry at the Regional Centre of Technology and Innovation (CRTi) of the Federal University of Goiás (UFG) using a Bruker S8 TIGER WDXRF spectrometer equipped with a Rh X-ray tube. On-line calibration and corrections were done using the Bruker GeoQuant M[®] software package, which is based on a wide range of certified reference materials, including natural rock and mineral standards (for more information see www.bruker.com). Precision and accuracy of the X-ray fluorescence analyses were monitored by in-run measurements of two in-house rock standards (Supplementary Data – **Table A2**). Analytical uncertainties are better than 2% for all major oxides, except for total Fe₂O₃ (< 3%). The limits

of quantification provided by CRTi-UFG were 0.1 wt.% for all elements. Analysis totals including loss on ignition (LOI) are within the acceptable limits of 99.0 to 101.0 wt.%. Sample preparation procedures are detailed in Supplementary Data – **Appendix 7A**.

Electron Microprobe Analysis (EMPA)

Quantitative chemical analyses of the minerals of interest (*i.e.* nepheline and kalsilite) were carried out at both the Electron Microprobe Laboratory (LME) of the Institute of Geoscience (IG), University of Brasília (UnB), and the CRTi-UFG. Both facilities use a JEOL JXA-8230 SuperProbe electron probe micro-analyser, equipped with five wavelength-dispersive X-ray spectrometers coupled with several analysing crystals (TAP, PET and LiF) and one energy-dispersive X-ray spectrometer. Backscattered electron (BSE) images and X-ray compositional maps for Na and K were acquired at the CRTi-UFG only. All polished thin sections for transmitted-light petrography and mineral chemistry studies were prepared at the IG-UnB. More details of sample preparation, operating conditions, reference materials, and limits of detection (LOD) are given in Supplementary Data – **Appendix 7A** and **Tables A3 to A5**.

Reliability of EMPA Data

Nepheline is an aluminosilicate mineral that may be tricky to analyse, whereby significant migration of alkali ions (particularly Na⁺) may occur in routine WDS EMPA (see, *e.g.* Reed, 2005; Morgan & London, 2005). Additionally, it is an anhydrous phase that can, however, contain small but significant, amounts of H₂O (up to 0.55 wt.% – Beran & Rossman, 1989; Balassone & Beran, 1995; Johnson, 2006). These aspects alone should be enough for a more critical evaluation of nepheline analyses. In this study, we conducted EMPA in two separate laboratories with distinct analytical conditions – even though the same type of micro-

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analyser was employed at both analytical facilities (see Supplementary Data – **Appendix 7A**). This allowed us to verify data reliability.

Overall, few researchers have devoted much attention to the analytical reliability of nepheline compositions (*e.g.* Bannister & Hey, 1931; Dollase & Thomas, 1978; Henderson, 2020). Following the previous works, Henderson (2020) established a number of criteria for evaluating the acceptability of nepheline microprobe analyses. These are based on the strict nepheline stoichiometry (*i.e.* a unit-cell with 32 oxygen-basis, 16 tetrahedral cations, 8 cavity cations, Si = Al) and robust protocols for calculating the molecular end-members. Moreover, Oliveira & Henderson (2022) recently revised some of these criteria taking into account that significant amounts of Mg can be found in nepheline and kalsilite occurring in ultrabasic, feldspar-free, volcanic rocks.

Accordingly, as a first step for checking data reliability, we have used the following criteria: (1) values for both ΔAl^{cc} (*i.e.* the difference between the sum of trivalent and divalent tetrahedral cations and the sum of equivalent cavity cations) and ΔT^{ch} (*i.e.* the difference between the total analysed T charge and the ‘ideal’ value for 16 mean T charge) stoichiometric parameters should be within ± 0.6 (note that for ‘ideal’ nepheline ΔAl^{cc} and ΔT^{ch} are zero); (2) values for the $\Delta Al^{cc} / \Delta T^{ch}$ ratio should be between 1.1 and 1.2 (‘ideal’ nepheline = 1.143); (3) The sum of T cations within the range 15.900 – 16.100 *apfu*; and (4) only minor differences should be noted among the excess Si parameters (see Henderson, 2020 and Henderson & Oliveira, 2022 for further details). Oliveira & Henderson (2022) also noted that K-rich nepheline and kalsilite in feldspar-free volcanic rocks generally contain much less Ca than in ‘common’ alkaline rocks (*e.g.* nepheline syenites). Thus, analyses with anomalously high CaO contents (usually > 0.5 wt.%) in comparison with the average abundance of this element in a given sample were rejected, too.

Based on these criteria, approximately half of an overall 203 new nepheline analyses were found to be non-reliable and not represent high-quality electron microprobe data. We noted, however, that a single criterion ($T > 16.100$) is responsible for most of these rejections ($n = 54$). In addition, except for a few analyses on samples NEU 10C and NEU 46B, all the rejected data have values for the sum of T cations < 16.150 . Looking at the full dataset, it became evident that the analyses that give much higher T values, in general, also have low analytical totals (**Figure 7.2**). Besides, the greatest part of these data came from the CRTi-UFG. This suggests a systematic error, maybe some loss of Na, presumably triggered by the more robust instrumental operating conditions (*i.e.* higher current densities – Morgan & London, 2005) employed, notably, for the CRTi analyses.

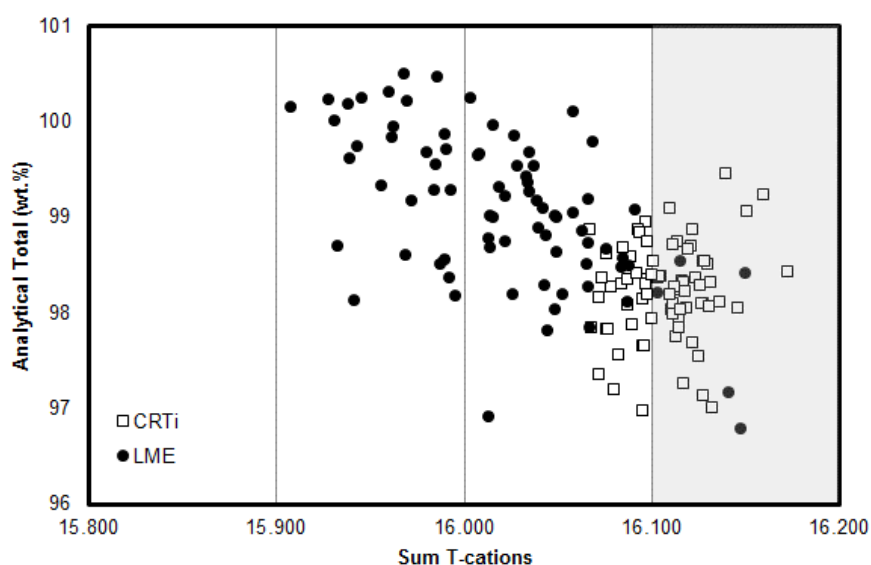


Figure 7.2 Plot of analytical total (data in wt.%) against the sum of tetrahedral *T* cations (in *apfu*) for the electron microprobe (WDS) nepheline raw data obtained for this study at two analytical facilities (CRTi and LME). Plotted are all reliable data ($n = 104$) and also the non-reliable data rejected only by the sum of *T* cation criterion ($n = 54$). All data points are individual spot analyses of homogeneous groundmass grains.

To confirm our suspicion that the actual Na content of at least part of the nepheline analyses may be underestimated, we compared two sets of data obtained for a single sample (AMK 01) at both laboratories. It is clear in **Figure 7.3** that except for Na_2O and analytical total values, all other data show a good correlation. This implies that some loss of Na might have

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occurred during the CRTi EMPA. Assuming that the LME data are correct, *i.e.* they represent the ‘true’ values for the composition of nepheline in the sample AMK 01, the Na deficiency in the CRTi analyses is ~10.6 %, on average. This corresponds to ~1.5 wt.% of Na₂O, on average, which is close to the difference between the means of the analytical totals for each laboratory (1.7 wt.%). The comparable values support the view that Na loss is a real problem, and consequently, the reason for the former rejection of a substantial part of our nepheline data.

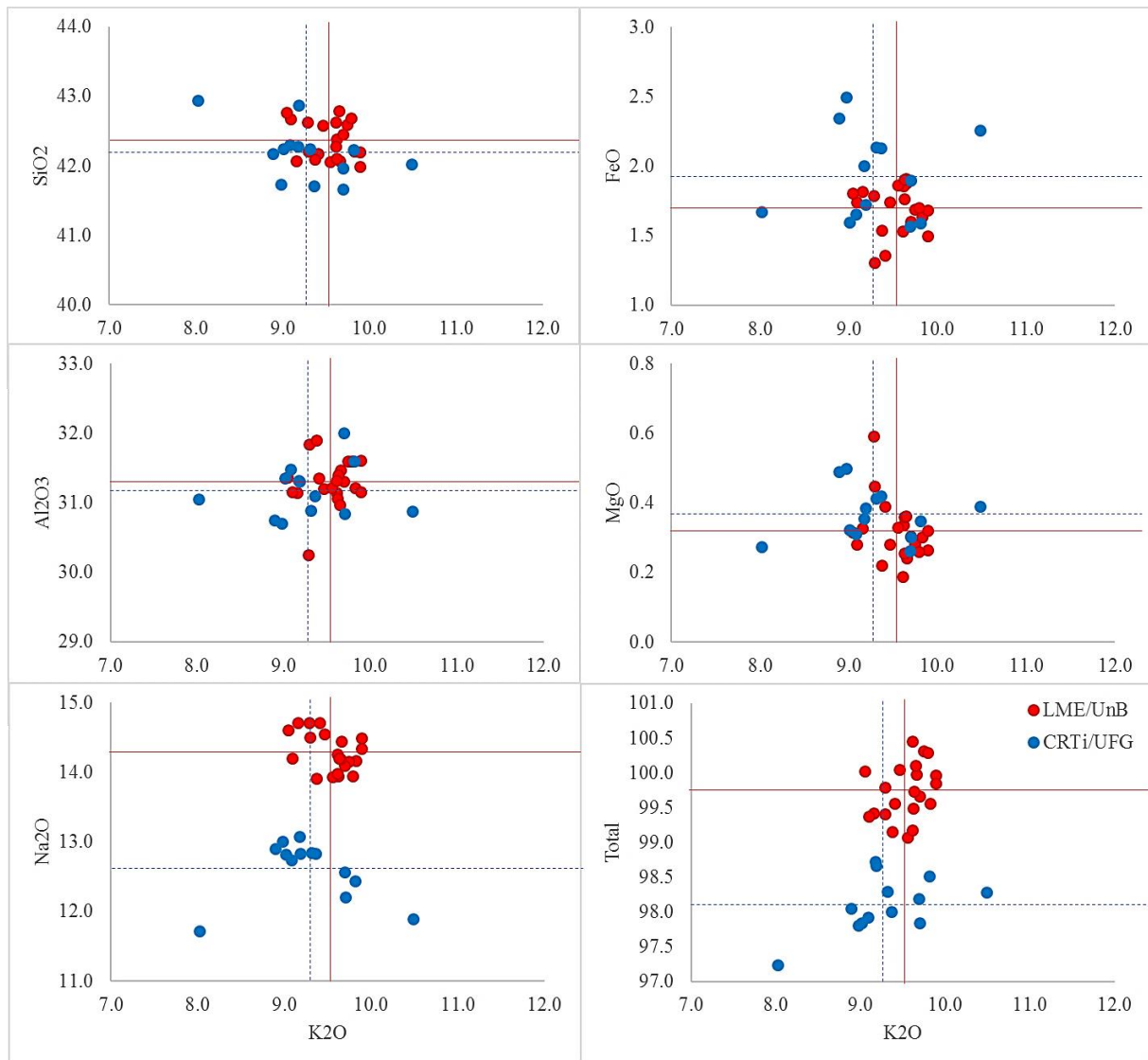


Figure 7.3 A comparison of nepheline compositions (raw data) from sample AMK 01 obtained at the two analytical facilities (CRTi and LME). The red and blue, solid and dashed lines, in all six panels, represent the average values for each dataset (red = LME-UnB; blue = CRTi-UFG). All values are reported in weight per cent (wt.%).

A second comparison was then done to check the reliability of the CRTi analyses, independently. In this case, two sets of data acquired for sample AMO 94A using the same analytical conditions but with a difference of six months were compared to each other (**Figure 7.4**). In summary, the internal reproducibility of the EMPA at the CRTi-UFG is really good. All major and minor elements analysed show, on average, variations smaller than 1.5 rel.%. Note that the analysed grains were selected randomly in both analytical sessions and, therefore, at least part of these relative differences must be attributed to the naturally occurring changes in the composition of nepheline within the sample AMO 94A. Accordingly, the consistently low totals of the CRTi analyses (**Figure 7.2**) can be, in fact, explained by an underestimate of the Na contents.

Based on Morgan & London (2005), we can estimate a Na lost between 10 and 15% for the EMPA data obtained at CRTi (20 nA, 3-5 μm) and about 5-10% for the EMPA from LME (10 nA, 3-5 μm). The value of 10% is a good estimate in the first case scenario provided that it matches the 10.6% of Na loss calculated earlier for sample AMK 01. However, there is no evidence of Na loss in the case of the most reliable analyses from LME, *i.e.* in those data acquired using a 10 nA beam current and 5 μm beam diameter (sample AMK 01; see **Figure 7.3**). Thus, we can conclude that the Na loss largely observed for the CRTi analyses was mainly caused due to a comparatively stronger beam current (20 nA). However, it cannot be ignored that some LME data also show evidence of a minor Na loss (see **Figure 7.2**), which was almost certainly triggered by the smaller electron beam diameter (3 μm) employed for some analyses.

Despite the Na loss problem discussed above, we decided to accept all nepheline data that had first been rejected because of the sum of the T cation criterion. Henceforth, only those analyses with high CaO contents ($n = 26$), or that fit more than one reliability criteria ($n = 19$) were completely rejected. The reasoning behind this is that (1) most of the earlier rejected analyses have sums of T cations just slightly above the limit of 16.100 (indeed almost all are

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below 16.150 *apfu*); (2) the deficit of Na could be estimated with some degree of certainty, at least for one sample (AMK 01); this allowed a possible data correction (see below); (3) the Na loss does not invalidate the key interpretations of the present study; it only limits further discussions, for instance, about the iron oxidation state (see Oliveira & Henderson, 2022) or a possible excess of alkalis (*e.g.* Henderson, 2020); and (4), even though part of the EMPA were not accepted as high-quality stoichiometric data, they are still appreciated for the purpose of mineral identification, mainly in cases where nepheline and kalsilite coexist in the groundmass.

The estimates of Na loss discussed above led us to consider the possibility of a correction of ‘non-reliable’, accepted, data. However, this cannot be done simply by applying a uniform correction factor (*e.g.* adding 10% Na₂O) for all analyses. The amount of Na loss under the electron beam is not linear, *i.e.* it depends on the total of Na₂O contents of each individual nepheline crystal, and as will be seen in the following, the K-rich nepheline of the present study displays an extensive range of compositions. Also, many factors such as small changes in the electric power supply during the EMPA section, variations in the polishing of each sample, imperfections in the carbon coating, *etc.*, should certainly influence the amount of Na loss. Furthermore, the loss of Na may result in a relative increase in Si and Al concentrations (*e.g.* Morgan & London, 2005). In this way, we opted to use a stoichiometric parameter – the occupancy of the cavity cation sites ($A + B = 8$ *apfu*), including the vacancy (for further details, see the ‘excess Na’ calculation from Henderson, 2020) – to ‘normalise’ all the acceptable nepheline data ($n = 158$). For this, it was assumed that all iron occurs as Fe³⁺ and that the abundances of all important elements apart from Na (*i.e.* Si, Al, K, Ca, Fe and Mg) were rigorously determined. The calculation was done using the revised ‘corrected Na’ spreadsheet after Henderson & Oliveira (2022). Note that, hereafter, it is always indicated to which dataset we are referring – to the original ‘raw data’ or the ‘normalised’ (corrected) data.

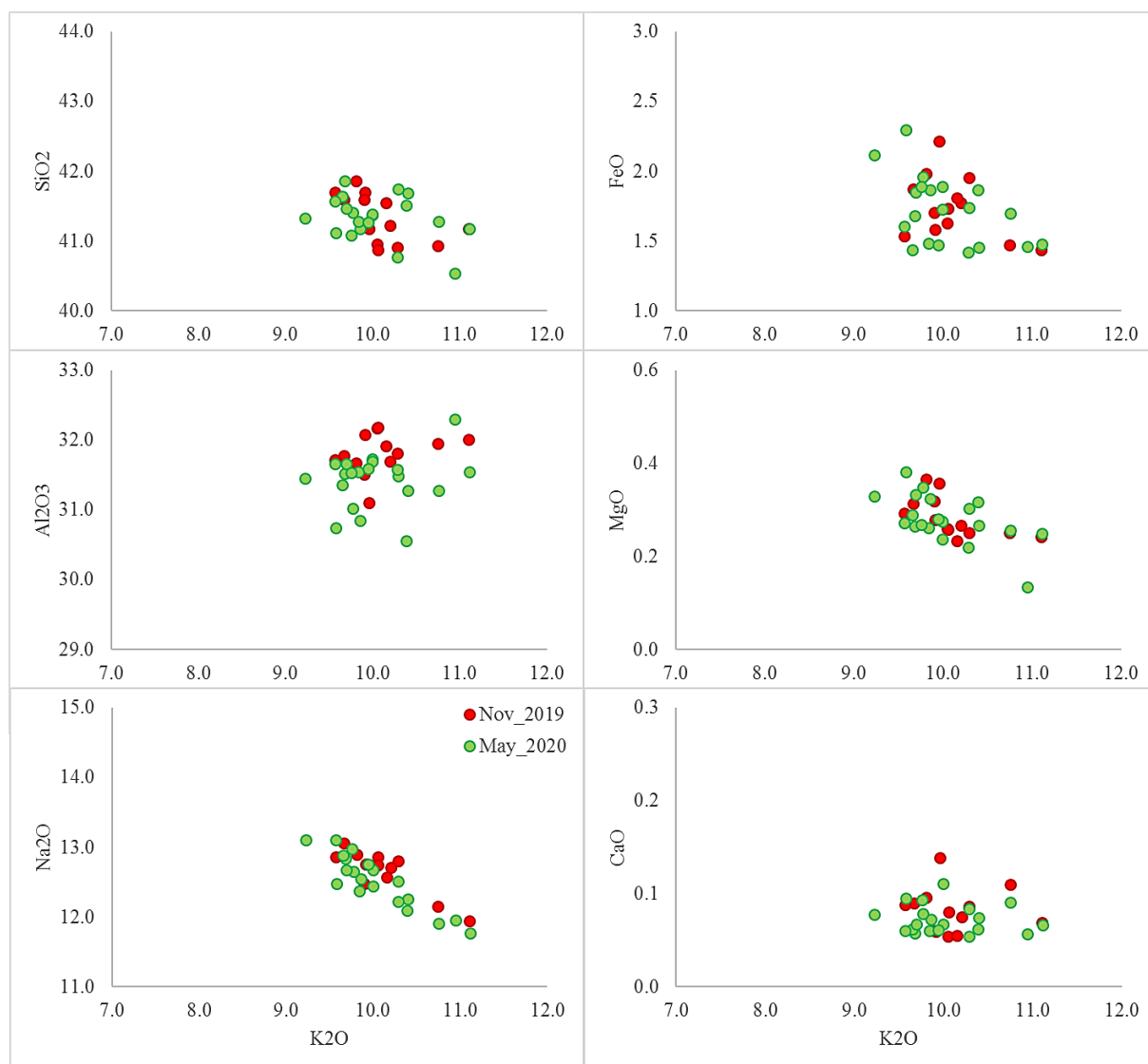


Figure 7.4 A comparison of nepheline compositions (raw data) from sample AMO 94A obtained at CRTi during two analytical sessions separated by six months. All values are reported in weight per cent (wt.%).

7.4 Results

Petrography

The strongly SiO_2 -undersaturated (*i.e.* feldspar-free) volcanic and subvolcanic rocks from the Goiás Alkaline Province display a great variety of textures and modal mineralogy. Besides, the coexistence of nepheline and kalsilite makes it impossible to classify these rocks by strictly following any of the widely used nomenclature schemes (*i.e.* Le Maitre *et al.*, 2002 or Sahama, 1974; for further discussion, see Oliveira *et al.*, 2022). On a macroscopic scale, the

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studied rocks are dark grey, strongly magnetic, mafic, melanocratic, and show a porphyritic (or microporphyritic) texture with olivine, clinopyroxene (diopside), and rarely phlogopite macrocrysts (up to 8.0 mm in size) in an aphanitic groundmass. As a more detailed petrographic classification is not relevant for the present study, hereafter, the studied rocks will be grouped under the generic terms of olivine-phyric and clinopyroxene-phyric, in accordance with their macrocryst assemblages. In the olivine-phyric case, nearly all macrocrysts are olivine (**Figure 7.5a**). In the clinopyroxene-phyric rock types, the assemblages of macrocrysts can consist solely of clinopyroxene (*e.g.* sample PAR 89A); clinopyroxene with more or less olivine (**Figure 7.5b**); or clinopyroxene, phlogopite, and rare olivine (*e.g.* sample SAB 04). Note: ‘macrocryst’ is a purely descriptive term (*i.e.* it has no genetic connotation such as xenocryst or phenocryst) that is used for comparatively large crystals (> 0.5 mm) enclosed in a fine-grained groundmass (see, *e.g.* Mitchell, 1997).

Apart from the mafic macrocrysts, the groundmass phases are very similar in all rocks. They comprise abundant pale-yellow clinopyroxene, Ti-magnetite, perovskite, phlogopite, and accessory apatite. In addition, there are two melilite-rich samples (**Table 7.1**). It is noteworthy that perovskite is commonly abundant in the olivine-phyric rocks but quite rare in the clinopyroxene-phyric ones. A characteristic ‘nepheline-like’ interstitial mineral also occurs as the most conspicuous light-coloured phase in our samples (**Figure 7.5c, d**). This phase may be accompanied by leucite (usually replaced by analcime) and/or melilite as the main light-coloured minerals, but not invariably (see **Table 7.1**). Post-magmatic, secondary phases, are essentially analcime and other zeolites.

Note that the term ‘nepheline-like’ has been employed in the previous paragraph to emphasise that both nepheline and/or kalsilite can be found in these rocks, but they cannot be distinguished with a petrographic transmitted-light microscope. The application of X-ray diffraction or electron microbeam methods is a prerequisite to resolving this difficulty (see

Oliveira *et al.*, 2022 and references therein). In this study, we have employed backscattered electron imaging (**Figure 7.6**) and Na and K compositional mapping (**Figure 7.7** and **7.8**) to identify this ‘nepheline-like’ mineral in the groundmass. BSE images coupled with WDS EMPA were very useful for the recognition of K-rich nepheline as a key felsic phase in the groundmass of the studied rocks (see **Figure 7.6**). In contrast, BSE images were not so helpful for the purpose of kalsilite identification, as kalsilite and clinopyroxene solid solutions shown very similar BSE intensities (or grey levels – see **Figure 7.7** and **7.8**) and could not be easily distinguished. Na and K compositional maps supported by single-spot WDS microprobe analyses were most effective to confirm the presence of kalsilite. At this point, it must be noted that not all of our samples have been explored for kalsilite occurrence yet.

➤ **K-rich nepheline in the Goiás Alkaline Province (GAP) – Occurrence, Textural relationships, and Mineral assemblages**

Though not so abundant as the mafic constituents, K-rich nepheline is definitely an essential mineral in all rocks of the present study (see **Table 7.1**). This mineral rarely occurs as microphenocrysts (*e.g.* sample TIG 45B), but it is always present as interstitial, late magmatic phase in groundmass (**Figure 7.6**). Two remarkable aspects of nepheline in the studied rocks must be noted: (1) regardless of whether the coexisting leucite is preserved or totally replaced by analcime, the nearby crystals of nepheline are always homogeneous (**Figure 7.6**); (2) as far as we could see, nepheline appears to be pristine in all our samples and never demonstrate any evidence of subsolidus exsolution (see discussion section). Zeolitization of nepheline crystals is seemingly limited, although minor amounts of interstitial analcime (and other zeolites) are common in almost all samples of this work.

Within other light-coloured minerals, K-rich nepheline occurs in a variety of mineral associations, with or without leucite, melilite, and/or kalsilite. Nepheline together with leucite (partially to entirely altered) occur in sample SAB 04 (**Figure 7.6a**; see also **Table 7.1** for other

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examples). Nepheline can be found either with abundant melilite and rare leucite (sample PAR 89A) or with accessory melilite only (sample PAR 52A – **Figure 7.6b**). In addition, K-rich nepheline can occur together with kalsilite in three distinct assemblages of light-coloured phases: (1) nepheline and kalsilite (samples AMO 94B, NEU 10C, NEU 46B); (2) nepheline, kalsilite and melilite (sample AMO 94A), and (3) nepheline, kalsilite, melilite and leucite (sample AMK 01). In all these assemblages, nepheline and kalsilite always occur as separate homogeneous crystals in the groundmass (**Figure 7.6c, d**). For all samples for which compositional maps were acquired, kalsilite was confirmed in groundmass coexisting with K-rich nepheline. It is also important that rocks with cryptocrystalline groundmass (**Figure 7.5b**), in principle, give the impression to contain only nepheline as a felsic constituent. But, the compositional maps confirmed that significant amounts of nepheline and kalsilite coexist, in random distribution in groundmass (see **Figure 7.7** and **7.8**).

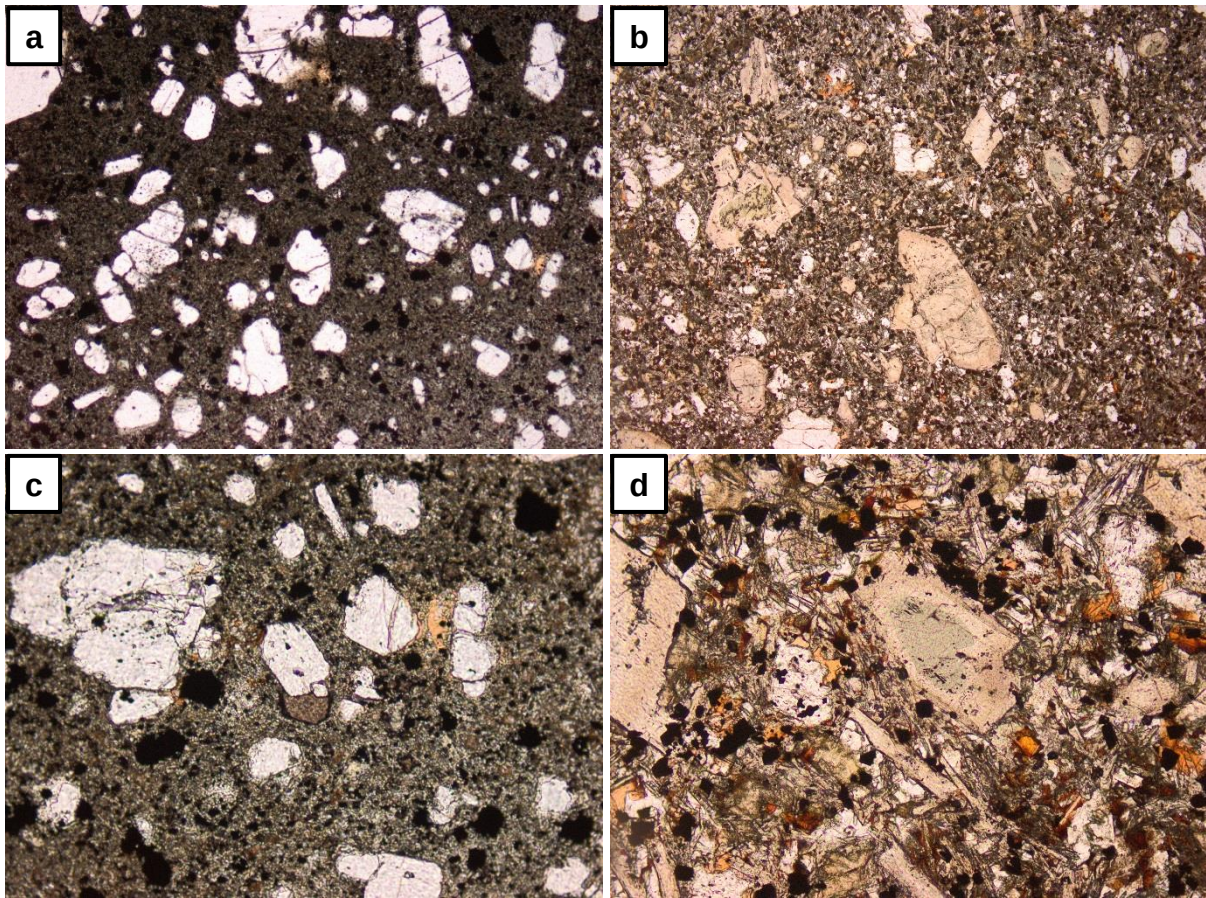
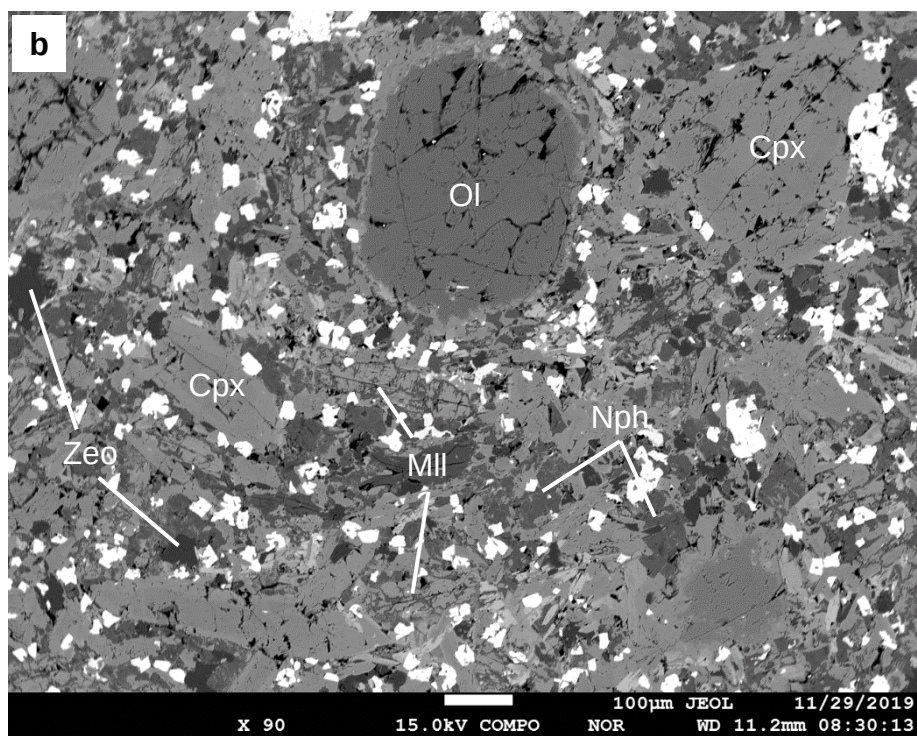
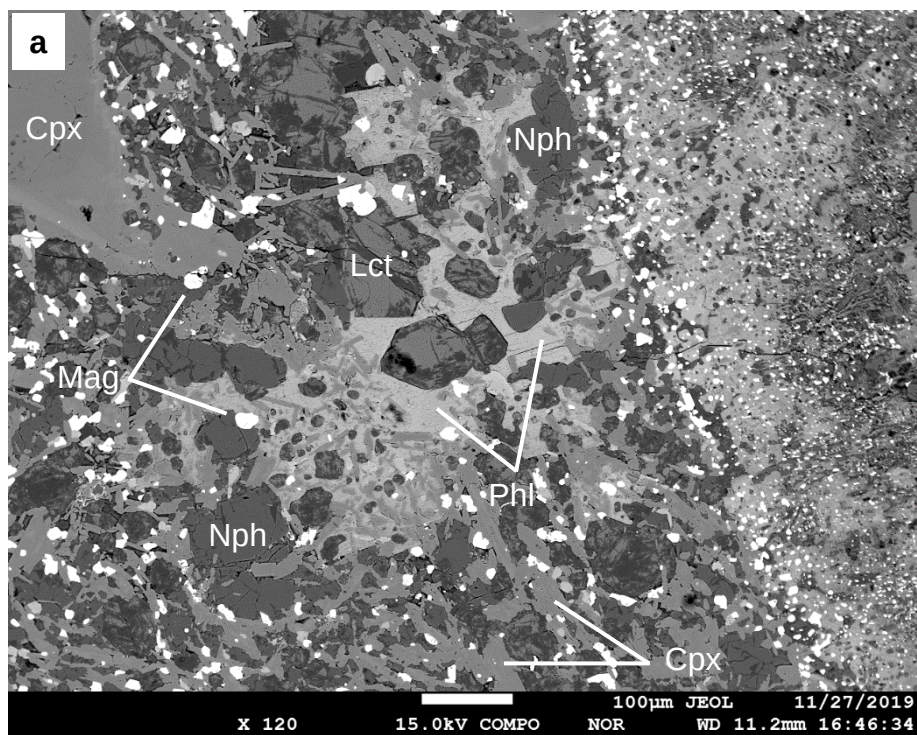
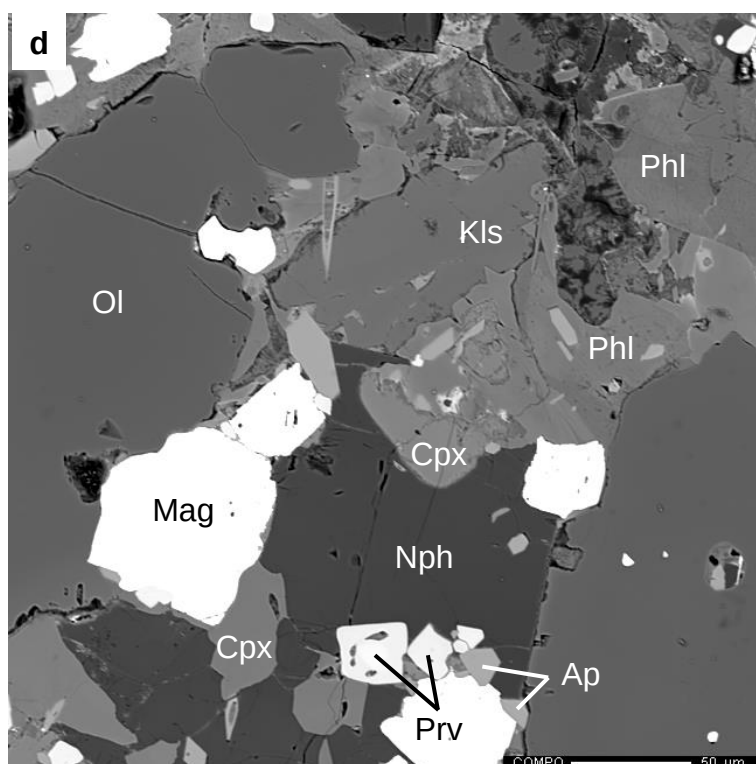
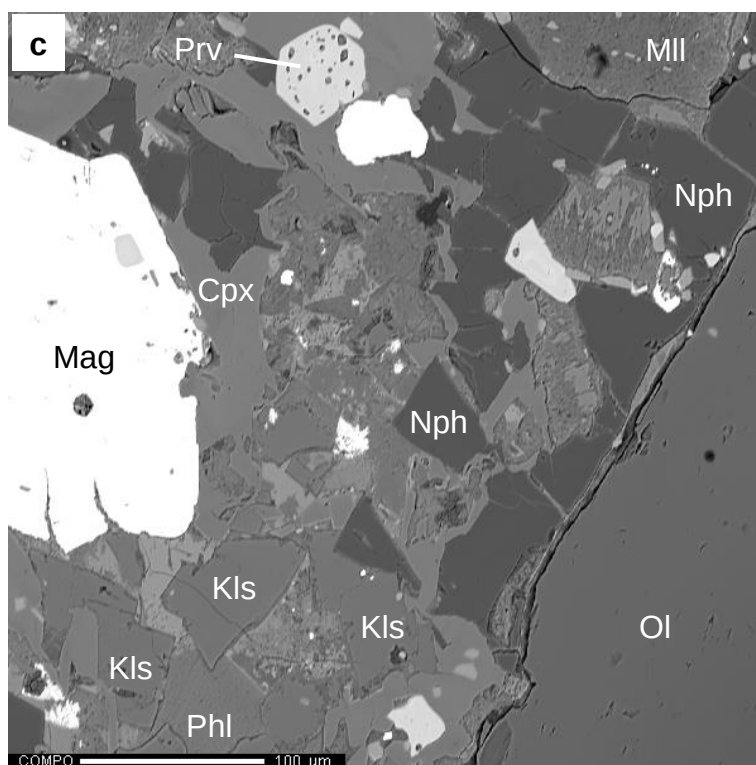


Figure 7.5. Typical petrographic features of the samples of this study in plane-polarized light. a) General view of the microporphyritic texture of olivine-phyric rock types – sample AMO 15A. Abundant olivine macrocrysts (up to 3.5 mm) and Fe-Ti oxides in very-fine grained groundmass. b) Porphyritic texture of clinopyroxene-phyric rock types – sample RC 59D. This particular sample contains abundant zoned clinopyroxene macrocrysts with minor amounts of comparatively smaller olivine macrocrysts set in a microcrystalline groundmass. c) Detail of groundmass in olivine-phyric rocks – sample AMO 15A. This groundmass comprises abundant microlites of clinopyroxene, Fe-Ti oxides, perovskite, minor phlogopite, and an interstitial colourless phase (K-rich nepheline). d) Detail of groundmass in a clinopyroxene-phyric rock type – sample RC 59D. This groundmass is composed of abundant prisms or needles of clinopyroxene, Fe-Ti oxides, phlogopite, an interstitial colourless phase (K-rich nepheline), and accessory apatite and perovskite.





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Figure 7.6. Backscattered electron images. a) Textural aspects of nepheline (Nph) together with leucite (Lct) replaced to various degrees by analcime (Anl) (sample SAB 04). Note the part of a large clinopyroxene (Cpx) macrocryst at the top-left corner of the image. To the right side of the image is a partly resorbed phlogopite (Phl) macrocryst. Partially to totally altered leucite with clinopyroxene, Ti-magnetite (Mag), nepheline, and the second generation of poikilitic phlogopite make up the groundmass mineralogy. The nepheline crystals are consistently homogeneous, even when they are close to the most altered portions of leucite (dark stripes). b) Characteristic relationships between nepheline (Nph) and the groundmass phases of a melilite-bearing rock (sample PAR 52). Zoned olivine (Ol) and clinopyroxene macrocrysts are set in a groundmass of clinopyroxene, altered melilite (Mll) laths, Ti-magnetite (white), nepheline, accessory apatite (Ap), and secondary zeolites (Zeo – mostly analcime). The black patches in macrocrysts are holes in the thin section. c) Mineralogical relationships in the groundmass of sample AMO 94A. Note the random distribution of both nepheline and kalsilite (Kls) crystals. Nepheline clearly occurs as a late interstitial phase that encloses the other minerals. Perovskite (Prv) occurs as an important minor phase. Note the homogeneously smooth aspects of both nepheline and kalsilite. d) Detail of the relationship between nepheline and kalsilite in the groundmass of sample AMK 01. Again, both minerals are generally homogeneous, with only small inclusions of other mineral phases. It is evident that even when in contact, the nepheline and kalsilite crystals keep their integrity.

Table 7.1 Mineral assemblages of the volcanic rocks of the Goiás Alkaline Province (GAP) investigated in this study. A – abundant, includes macrocrysts and groundmass crystals; m – minor phase (type mineral); r – rare (accessory); Zeo – zeolites other than analcime. Mineral abbreviations according to Warr (2021).

Sample	Type	Ol	Cpx	Mag	Prv	Phl	Mill	Nph	Kls	Lct ¹	Ap	Other
AMK 01	Ol-phyric	A	m	✓	✓	r	✓	✓	✓	✓	r	
AMK 02	Ol-phyric	A	✓	✓	✓	m		✓		m	r	
AMO 15A	Ol-phyric	A	✓	✓	✓	m		✓		r	r	Zeo
AMO 94A	Ol-phyric	A	✓	✓	✓	r	✓	✓	✓		r	
AMO 94B	Ol-phyric	A	✓	✓	✓	r		✓	✓			Zeo
NEU 10C	Ol-phyric	A	✓	✓	r	✓		✓	✓			
NEU 46B	Ol-phyric	A	✓	✓	r	✓		✓	✓			Zeo
PAR 52	Ol-, Cpx-phyric	✓	A	✓		m	m	✓				Zeo
PAR 89A	Cpx-phyric	r	✓	✓		r	✓	✓		r	r	Zeo
RC 59D	Ol-, Cpx-phyric	✓	✓	✓	r	m		✓			r	Zeo
SAB 04	Phl-, Cpx-phyric	r*	A	✓	r	m		✓		✓		Zeo
TIG 45B	Ol-, Cpx-phyric	r*	A	✓	m	r		✓		✓	r	

*occur only as macrocrysts. ¹ includes leucite and analcime.

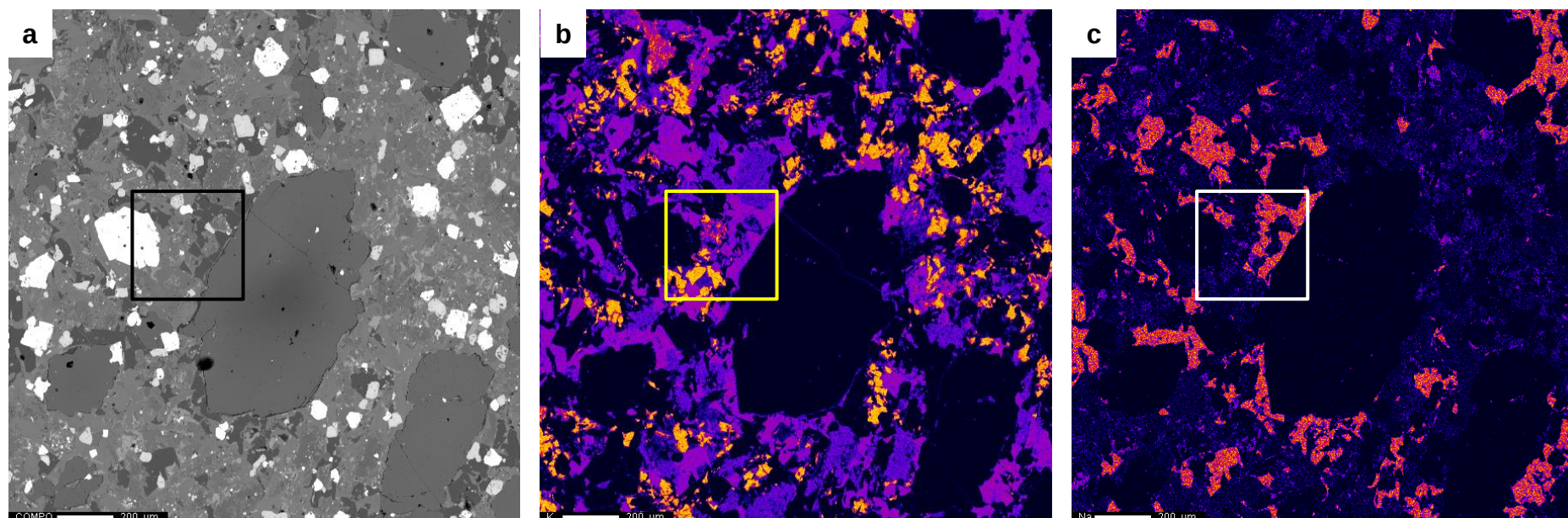


Figure 7.7 Backscattered electron image (a) and X-ray compositional maps for K ($K\alpha$) (b) and Na ($K\alpha$) (c) from sample AMO-94A. The field of view is 1.92 x 1.74 mm. The warmer colours (red, orange, yellow) indicate higher contents of an element, whereas the cooler colours (purple, dark blue, black) indicate relatively lower contents of the same element. The bright yellow areas in (b) indicate the crystals of kalsilite (~26 wt.% K_2O) in the groundmass. The orange areas in (c) indicate the crystals of K-rich nepheline (~10 wt.% K_2O). Note the correspondence between the orange areas in (c) with the smooth purple areas in (b) and the dark grey areas in (a). Also note that kalsilite is very difficult to distinguish from other groundmass phases (mainly clinopyroxene) using the grey levels of the BSE image only. It is also indicated the area detailed in Figure 7.6c (the coloured rectangles in the three images).

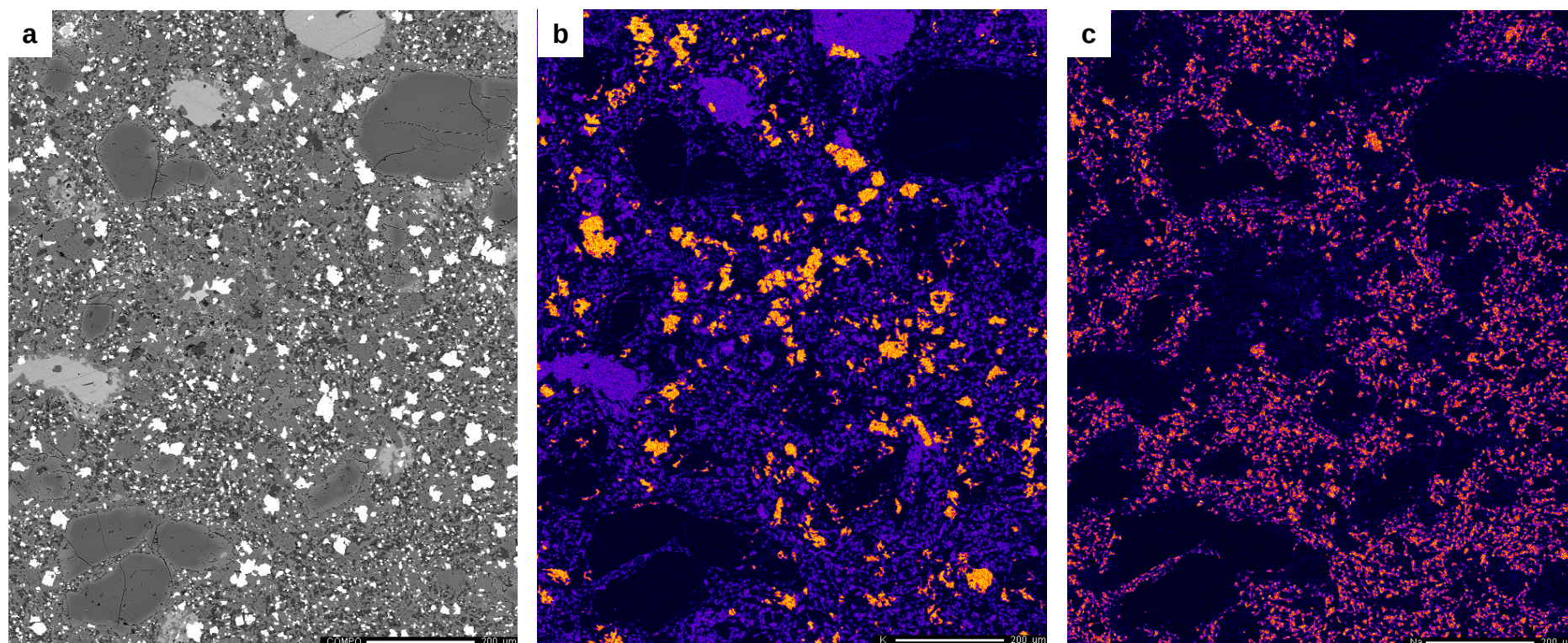


Figure 7.8. BSE image (a) and X-ray compositional maps for K ($K\alpha$) (b) and Na ($K\alpha$) (c) for sample NEU-46B. The field of view is 1.2 x 0.975 mm. The ‘thermal’ colour / X-ray intensity scale is equal to that for Figure 7.7. Note that this sample has ‘large’ phlogopite crystals (~9 wt.% K_2O) that appear as continuous blue areas in (b) and light grey areas in (a). The kalsilite crystals, which contain much more K than phlogopite, occur again as bright yellow areas randomly distributed in groundmass. The tiny orange areas in (c) indicate the interstitial K-rich nepheline crystals in the groundmass.

Mineral Chemistry

Traditionally, nepheline compositions are reported in terms of three molecular end-members (Ne, Ks, and Q' – as previously defined), but, until recently, no systematic way on how best to calculate these end-members had been given in the literature (compare, *e.g.* Wilkinson & Hensel, 1994; Worley & Cooper, 1995; Blancher *et al.*, 2010; see also Henderson, 2020 for further discussion). Fortunately, Henderson (2020) published a comprehensive review of the diverse procedures and proposed a consistent approach to standardise such calculations based on strict nepheline stoichiometry (*i.e.* $\text{Na}_6\text{K}_2\text{Al}_8\text{Si}_8\text{O}_{32}$). Accordingly, molecular formulae and stoichiometry parameters for all nepheline solid solutions discussed hereafter were recalculated following the guidelines of Henderson (2020) and Henderson & Oliveira (2022) and using the Excel files provided by the latter. Importantly, the abbreviations Ne and Ks have been employed in the present study to refer exclusively to the molecular end-member components. The mineral phases nepheline (Nph) and kalsilite (Kls) are abbreviated according to Warr (2021) after Whitney & Evans (2010).

The average compositions of the reliable nepheline analyses for each rock sample are given in Supplementary Data – **Table B1**. Except for one microphenocryst from sample TIG 45B, all data discussed in this work are individual spot analyses (near core) of homogeneous nepheline grains in the groundmass. The complete dataset (including the non-reliable data) is available in Supplementary Data – **Nepheline Database**.

The overall compositions of this study are similar to the ones previously reported for strongly SiO_2 -undersaturated mafic volcanic rocks of the GAP (*e.g.* Danni & Gaspar, 1994; Junqueira-Brod, 1998; Sgarbi, 1998; Junqueira-Brod *et al.*, 2000; Sgarbi & Gaspar, 2002; Brod *et al.*, 2005 – see also Supplementary Data – **Table B1**). Most nephelines contain more potassium than the ideal chemical formula (*i.e.* $\text{K}_2\text{O} = 8.06$ wt.%), with K_2O values from 7.51

to 11.93 wt.%. This implies high proportions of the KAlSiO_4 molecule (*i.e.* Ks component) in their compositions ($\text{Ne}_{75.2}\text{Ks}_{24.8}$ to $\text{Ne}_{61.0}\text{Ks}_{39.0}$). These values enlarge the compositional range of nephelines found in the GAP volcanic rocks towards higher K-rich varieties (see **Figure 7.9a**). Notably, Ks contents are not homogeneous within a single sample. In fact, it is quite the opposite. Nepheline grains from most of the investigated samples display Ks variations that correspond to almost half of the whole compositional range of the province (see **Figure 7.10**).

The silica excess (Q') in the studied potassic nephelines is relatively small (up to 5.2 mol.%; mostly < 3.5 mol.%), with some analyses even being Si-deficient (*i.e.* having negative Q' values – see Supplementary Data – **Nepheline Database**). The relatively low Q' contents are in agreement with those observed by Wilkinson & Hensel (1994) as typical for nepheline in feldspar-free assemblages. In addition, it is noted that the different samples show a range of differences for the levels of minor elements determined. On the whole, the K-rich nephelines from the GAP volcanic rocks have very low amounts of Ca (< 0.15 wt.% CaO, on average), Sr (0.08 – 0.4 wt.% SrO), and Ba (0.04 – 0.16 wt.% BaO). However, the calcium concentrations are much smaller in olivine-phyric rocks than in clinopyroxene-phyric ones (0.1 and 0.2 wt.% CaO, on average, respectively). Manganese and titanium also seem to be of minor importance in the compositions of these K-rich nephelines, being rarely reported above the limits of detection, and when they are, they are usually less than 0.1 wt.% oxide (see Supplementary Data – **Table A5** and **Nepheline Database**).

On the other hand, as recently reported by Oliveira & Henderson (2022), total Fe (as Fe_2O_3) and especially Mg are important minor elements found in the potassic nephelines from GAP feldspar-free volcanic rocks. The Fe_2O_3 content is usually < 2.5 wt.% (~ 1.7 wt.%, on average; $n = 158$), as normally expected for natural nephelines (*e.g.* Deer *et al.*, 2004), but it may exceptionally reach up to 3.56 wt.%, as in sample AMK 02 (see Supplementary Data – **Nepheline Database**). The MgO content varies from 0.05 to 0.91 wt.%, with the average at

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0.26 wt.% (n = 158). This value is remarkably high compared with the small amounts of MgO generally reported for most natural nephelines (< 0.1 wt.%), but it is not uncommon for other alkaline ultrabasic, feldspar-free, volcanic rocks (Oliveira & Henderson, 2022).

The calculation of atomic formulae and stoichiometry parameters shows that the main chemical variations observed in the investigated K-rich nephelines occur as a consequence of various cation substitutions. **Figure 7.9** shows that a continuous solid solution series is found for the GAP nephelines, whereby their compositions are related by the simplest $\text{Na}^+ \leftrightarrow \text{K}^+$ substitution. As expected, there is a strong negative linear correlation between Na and K, almost matching the 1:1 ratio but with rather scattered data (**Figure 7.9b**). This behaviour is, however, improved significantly when Na is plotted against K plus vacancy (**Figure 7.9c**). The linear trend plots just along the 1:1 ratio, supporting that vacancies in the nepheline structure are indeed associated with the alkali sites (see, *e.g.* Hahn & Buerger, 1955). Moreover, according to some authors (*e.g.* Hamilton & Mackenzie, 1960; Barth, 1963; Dollase & Thomas, 1978; Hovis *et al.*, 1992), vacancy is restricted to the large A sites only. Thus, following Antao & Nicholls (2018), we calculate the amount of K atoms in each cavity site assuming that (1) the B sites are fully occupied by Na, Ca and K atoms; and (2) the remaining K^+ ions enter into the A site. The correlation between total vacancy and the K in the A site is shown in **Figure 7.9d**. All data plot almost exactly along the 2 *apfu* line (*i.e.* the total occupancy for the A site). Note that vacancies in the alkali sites are relatively low (< 0.5 *apfu*), mirroring the low CaO and excess of Si from these samples. Minor deviations from the best trendline can be related to small amounts of Sr and Ba, which have been considered for the total vacancies calculation but not for the A site occupation (as the site preference is unknown for Sr and Ba). However, based on the ionic size considerations and synthetic compounds (see Deer *et al.*, 2004), it is conceivable that both Sr and Ba, as ‘large’ divalent cations, may enter preferentially into the

larger A site together with the K atoms. Unfortunately, no clear relationship could be observed for these two elements in our dataset.

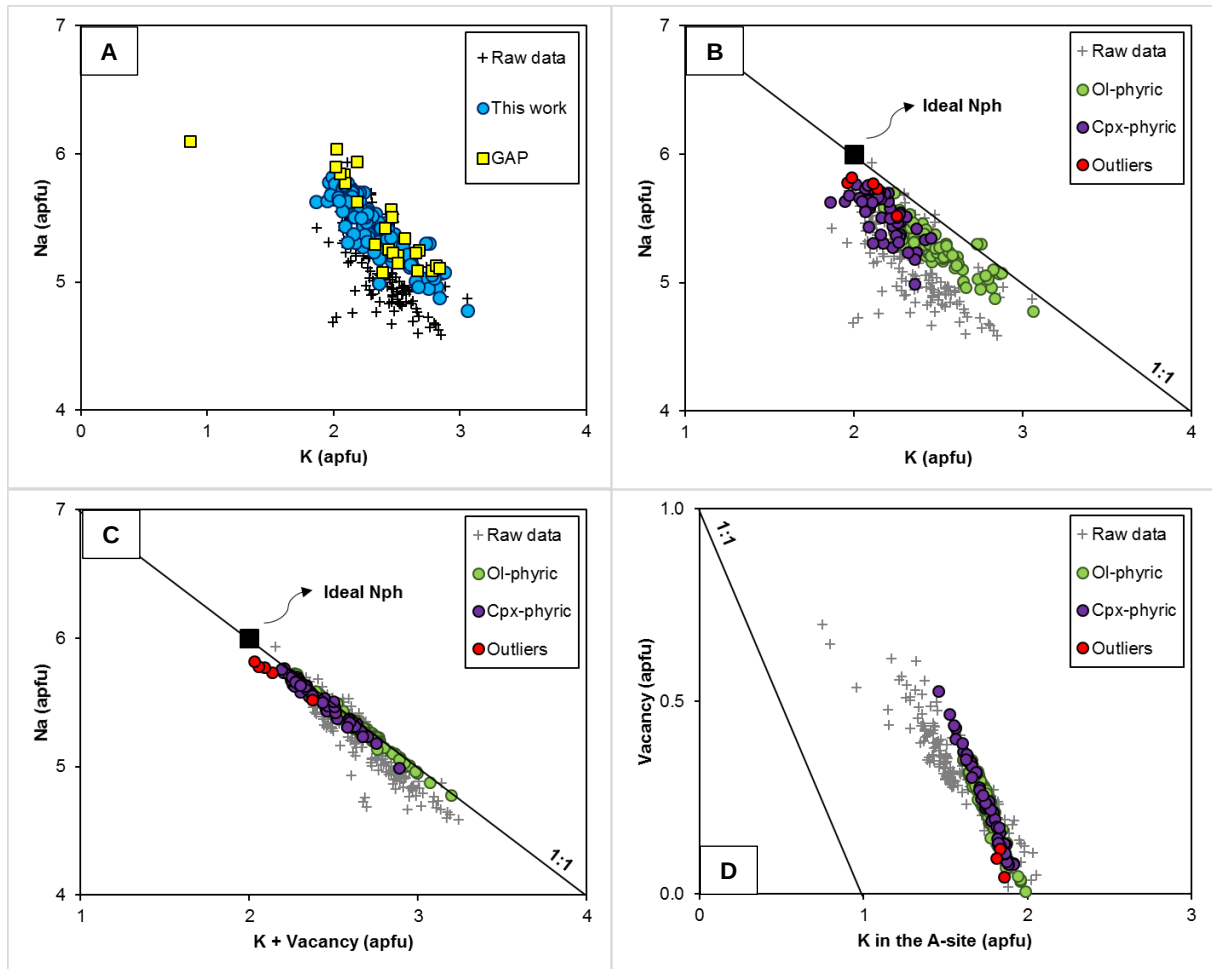


Figure 7.9 Na, K and vacancy relationships in K-rich nephelines from GAP feldspar-free volcanic rocks. Our raw data are represented by crosses, in all panels. All other data points have been normalised for cavity cation sites equal to 8 apfu (see data reliability section). a) Comparison of previous nepheline data published from the GAP volcanic rocks (data source as in Table B1) and this work, in terms of Na and K (apfu). b) Variations of Na and K according to the rock types defined in this work. Note that virtually all analysed nepheline contains more potassium than the ideal formulae. Also note that nephelines from olivine-phyric rocks contain more K-rich compositions. Outliers are those analyses from sample NEU 46B, which are slightly awkward in terms of tetrahedral cation distribution (see Figure 7.11). Even so, we plotted them in conjunction with other data, as these K-rich nephelines coexist with kalsilite in the groundmass of this sample. c) Na vs K plus vacancy relationship for the same data. d) Vacancy vs K in the A-site relationship.

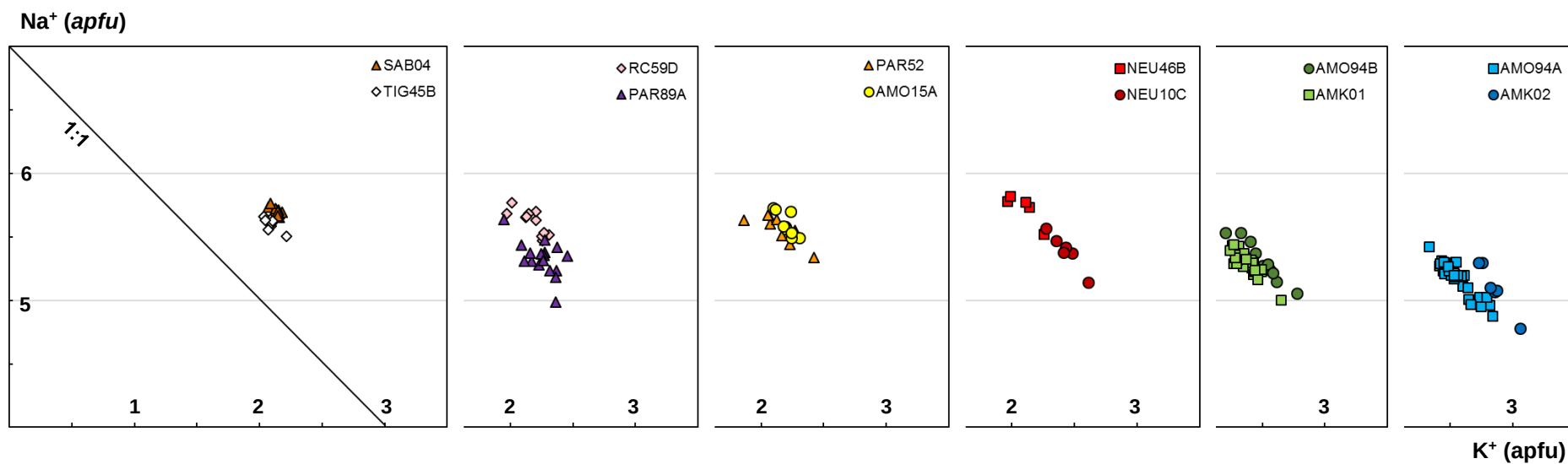


Figure 7.10 Nepheline compositions individualised for each studied rock sample and plotted in terms of Na and K concentrations (*apfu*). All charts have equal dimensions as well as horizontal and vertical scales. Clinopyroxene-phyric samples are plotted in the first three diagrams from left to right. Note that, in general, the Na content decreases and the K content increases from left to right.

The distribution of the main tetrahedral framework cations in K-rich nephelines from the samples of this study are shown in **Figure 7.11**. Si and Al have an antithetic behaviour and, as can be noted in **Figure 7.11a**, their relationship differs between the nephelines from olivine-phyric and clinopyroxene-phyric rock-types. Generally, nepheline solid solutions of the latter contain a higher Si, for a given Al, content.

It is widely accepted that ferric iron (Fe^{3+}) is a common substitute for Al in the tetrahedral framework sites of nepheline (*e.g.* Smith & Sahama, 1954; Donnay *et al.*, 1959; Brown, 1970; Henderson, 2020). Thus, in **Figure 7.11b** is plotted the sum of Si and Fe^{3+} against Al. Note how the correlation moves toward the 1:1 ratio, supporting the $\text{Al} \leftrightarrow \text{Fe}^{3+}$ substitution in the T sites. Also note that the olivine-phyric data points now show practically the same trend as clinopyroxene-phyric ones. This suggests that K-rich nepheline in olivine-phyric rocks should contain more Fe^{3+} , which is confirmed by plotting total Fe (here reported as Fe^{3+} only) against Al (**Figure 7.11c**). The amount of total Fe in nepheline from olivine-phyric rocks are consistently higher than in clinopyroxene-phyric group. Besides, the former shows a somewhat negative correlation for Fe^{3+} values $> 0.2 \text{ apfu}$. Quite to the opposite, ferric iron seems to be relatively insensitive to Al variations in nepheline from clinopyroxene-phyric rocks.

Recently, Oliveira & Henderson (2022) established that Fe and Mg may show a positive linear correlation in K-rich nepheline and kalsilite from the groundmass of strongly SiO_2 -undersaturated volcanic rocks. Here, such behaviour is detailed by correlating Fe^{3+} , and particularly Mg, with the other tetrahedral cations. **Figure 7.11d** illustrates the relationship between Mg and Al. It should be noted that, as for ferric iron, the nephelines from olivine-phyric rocks also have higher contents of Mg in comparison with those from clinopyroxene-phyric rocks. However, in both cases, there is an antithetic behaviour between Mg and Al. This suggests that Mg should substitute Al at least in some proportion. More importantly, such correlation reinforces the current thinking where Al can be substituted by ‘small’ divalent

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cations (such as Mg) in the nepheline structure by following the reaction $2\text{Al}^{3+} \leftrightarrow \text{Si}^{4+} + \text{Mg}^{2+}$ (e.g. Roeder, 1951; Henderson, 2020; Oliveira & Henderson, 2022). Accordingly, the sum of all main tetrahedral cations (Si, Fe^{3+} and Mg) other than Al is plotted against Al (**Figure 7.11e**) to illustrate this coupled substitution. All normalised data plot exactly on the 1:1 ratio, which would be expected if the above relation indeed occurs. It must be noted, though, that in this case, it is a somewhat artificial effect of our data correction, which implies 16 T cations. However, looking at the raw data, it can be seen that the above substitution involving Al, Si and Mg is correct.

Figure 7.11d shows that a few data points from samples AMK 02; NEU 46B and PAR 52 have much higher Mg for a given Al content. In the Fe^{3+} against Mg diagram (**Figure 7.11f**), these ‘outliers’ follow a linear trend almost parallel to the ‘main’ Fe-Mg trend, but it is also clear that is more enriched in Mg. The reason for this particular behaviour is not clear, but it has been suggested that these data might not represent near-core analyses. Dawson & Hill (1998) reported analyses for the rims of groundmass nephelines extremely rich in Fe. Those authors regrettably did not determine the MgO concentrations, but Mg could be as high as the Fe content. This question certainly deserves further investigation.

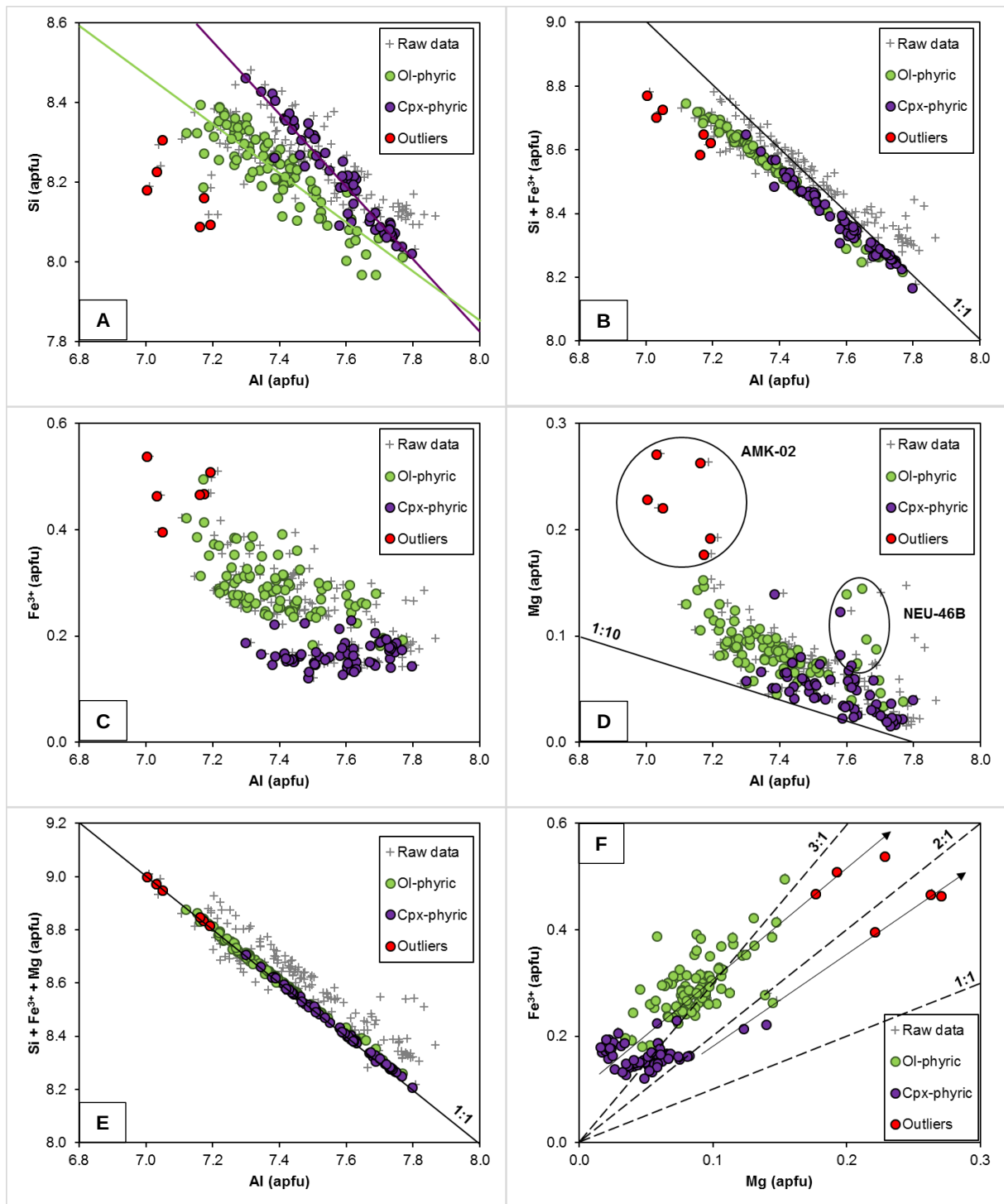


Figure 7.11. Relationships of Si, Al, Fe³⁺ and Mg in K-rich nephelines from GAP feldspar-free volcanic rocks. Our raw data are represented by crosses, in all panels. All other data points have been normalised for cavity cation sites equal to 8 apfu (see data reliability section). a) Si vs Al relationship. Coloured lines represent the best regression line for each group of analyses (rock-type). Outliers are analyses from sample AMK-02 and obviously are not included in the regression for olivine-phyric data. b) (Si + Fe³⁺) vs Al relationship. c) Fe³⁺ vs Al relationship. Note the differences in the total Fe content for nephelines of different rock types. Outliers as in (a). d) Mg vs Al relationship. As in the previous diagram, note the differences in

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Mg content for nephelines of each rock group. The two ‘outliers’ from the clinopyroxene-phyric group are analyses from sample PAR 52. e) (Si + Fe³⁺ + Mg) vs Al relationship. Note that the raw data also plot around the 1:1 ratio, confirming the coupled substitution reaction between Si, Mg and Al. f) Fe³⁺ vs Mg relationship. The arrows are plotted along the best regression line for each group of analyses. Both regression lines give the approximate ratio of 2Fe:1Mg, which suggests that for each two iron atoms that enter into the T sites replacing Al, one coupled substitution of Si + Mg should occur.

7.5 Discussion

Potassic Nepheline in the GAP Volcanic Rocks: Primary or Secondary?

The potassic-ultrapotassic character of the strongly SiO₂-undersaturated mafic volcanic rocks of the Goiás Alkaline Province (GAP) is well-established (*e.g.* Danni, 1985; Moraes, 1988; Danni & Gaspar, 1994; Junqueira-Brod, 1998; Sgarbi, 1998; Junqueira-Brod *et al.*, 2000; Sgarbi & Gaspar, 2002; Brod *et al.*, 2005; Carlson *et al.*, 2007). Even so, K-rich nepheline instead of kalsilite is the most common and abundant felsic phase in the groundmass of these rocks (*i.e.* ‘the kamafugitic series’ of Brod *et al.*, 2005). Thus, the conspicuous presence of K-rich nepheline has been until now intriguing, particularly because of the presence of kalsilite together with nepheline.

In igneous petrology, primary minerals are those that crystallised directly from a melt during magmatic crystallisation. Secondary phases, on the contrary, are those forming after the rock has been completely solidified (*i.e.* in subsolidus condition). Some previous works (*e.g.* Danni & Gaspar, 1994; Junqueira-Brod, 1998; Junqueira-Brod *et al.*, 2000; Brod *et al.*, 2005) considered that subsolidus alteration by Na-rich fluids could be responsible for the genesis of K-rich nepheline in the GAP volcanic rocks, from primary kalsilite (*i.e.* nepheline would be a secondary phase). However, in the present study, new significant evidence has been gathered, which has led us to re-examine the initial interpretation of secondary origin of the potassic nepheline.

In the newly studied samples, both nepheline and kalsilite crystals are homogeneous, even when they are in contact with each other (**Figure 7.6c-d**). It is also noted that these two phases are arbitrarily distributed in the groundmass (see **Figure 7.7** and **7.8**). Furthermore, we did not find any evidence that could indicate subsolidus exsolution, either in nepheline or in kalsilite. All these features suggest that K-rich nepheline and kalsilite crystallised as separate phases in equilibrium with each other. Moreover, K-rich nepheline occurs adjacent to leucite partially or completely replaced by secondary analcime, and even then, the potassic nepheline retains its integrity (see **Figure 7.6a**). This is further evidence against a post-magmatic origin. If the K-rich nepheline has been formed by a sodic alteration of primary kalsilite (such as analcime after leucite), it should follow that the same physicochemical formation parameters applied as to analcime, *i.e.* $T < 450\text{ }^{\circ}\text{C}$ (Wilkinson & Hensel, 1994). This would imply that nepheline compositions near the ‘ideal composition’ should have been formed, which is only rarely observed in the GAP volcanic rocks (see **Figure 7.9b**).

Additionally, the variations in the composition of K-rich nepheline also support their primary magmatic origin. Textural and chemical re-equilibration is expected when extensive subsolidus modification occurs. Nepheline in the investigated volcanic rocks, however, shows large compositional ranges, even within a single sample (**Figure 7.10**). The overall GAP nepheline compositions outline an extensive solid solution series that is comparable to that reported for potassic nepheline in recent potassic lavas from Mt. Nyiragongo (*e.g.* Minissale *et al.*, 2019; and also, Supplementary Data – **Nepheline Database**). The variable nepheline compositions within a single rock sample are indicative of non-equilibrium crystallisation caused by rapid magma cooling during the formation of the fine-grained groundmass. Moreover, as noticed earlier by Sgarbi (1998), the very high K_2O contents (up to 11.9 wt.%) of K-rich nepheline require high temperatures of crystallisation ($T > 600\text{ }^{\circ}\text{C}$), as the amount of potassium that can enter into the nepheline structure reduces with decreasing temperature (*e.g.*

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Tuttle & Smith, 1958; Ferry & Bencloë, 1978; Hovis *et al.*, 2009; see **Figure 7.1**). The strong positive correlation between total Fe and Mg recently described from K-rich nephelines and kalsilites from mafic alkaline volcanic rocks also point to a magmatic crystallisation (Oliveira & Henderson, 2022). Furthermore, a significant positive linear correlation occurs between the maximum Ks values for the K-rich nephelines and the bulk-rock SiO₂ content of their host rocks. This will be discussed in more detail later, but it supports the primary magmatic origin for the potassic nepheline of the GAP feldspar-free volcanic rocks.

It must be emphasised, though, that despite the evidence for the primary origin of the K-rich nepheline, the possibility of minor subsolidus re-equilibration should not be totally excluded. Some studied samples (SAB 04 and TIG 45B; see **Figure 7.10**) have very homogeneous nepheline compositions close to the ‘ideal’ formulae. The less potassic compositions can be readily explained by the presence of abundant leucite in the groundmass (*e.g.* Sahama, 1960), but the consistency in their nepheline compositions draws our attention.

The Joint Occurrence of Potassic Nepheline and Kalsilite in Groundmass:

Hypersolvus vs Subsolvus Crystallization

On the basis of our interpretation that potassic nepheline and kalsilite are primary igneous minerals, a petrological explanation about their co-occurrence is needed. The mineral assemblage with K-rich nepheline and kalsilite in the groundmass of some K-rich, Si-poor, volcanic rocks is not exclusive to the GAP. This association is very well documented in the mafic potassic lavas from Nyiragongo volcano, Virunga Province, Western Branch of the East African Rift System (*e.g.* Sahama, 1957; 1960; 1962a; Platz *et al.*, 2004; Andersen *et al.*, 2012; 2014). Moreover, based on electron microprobe data from the literature, Oliveira *et al.* (2022) verified that nepheline and kalsilite occur together in, at least, a dozen of rock samples from different localities around the world (*e.g.* Allan & Carmichael, 1984; Cundari & Ferguson,

1991; Lloyd *et al.*, 1991; Tappe *et al.*, 2003; Brod *et al.*, 2005; Lustrino *et al.*, 2020; among others). These authors have also recognised that these two minerals may coexist in volcanic rocks with either potassic or ultrapotassic chemical affinity.

Igneous petrologists have frequently pointed to post-magmatic processes, mainly subsolidus exsolution, or ambiguous groundmass intergrowths as explanations for the joint occurrence of nepheline and kalsilite. This view is most likely due to a series of exsolution features kindly described by Th. G. Sahama in what he called ‘complex nepheline-kalsilite phenocrysts’ found in some lavas from Mt. Nyiragongo (*e.g.* Sahama, 1957; 1960; 1962a). In this case, Sahama (1960) proposed a very elaborate interpretation for the origin of these complex phenocrysts. Here, it is relevant to know that extremely K-rich nepheline phenocrysts ($\sim\text{Ks}_{70}$) must have crystallised at hypersolvus conditions ($T > 1100\text{ }^{\circ}\text{C}$). These crystals probably invert to the tetrakalsilite structure at $\sim 1000\text{ }^{\circ}\text{C}$, and then, at temperatures below $\sim 870\text{ }^{\circ}\text{C}$ a homogeneous phase splits up into less K-rich nepheline and kalsilite. The striking exsolution textures were preserved only because of a fast cooling rate after lava extrusion, given that the initial K-rich phenocrysts were unstable in their host magma (see Sahama, 1960 for further details). More recent data from Andersen *et al.* (2012) corroborated the crystallisation model given by Sahama (1960), showing that groundmass nepheline has much less potassic compositions ($\sim\text{Ks}_{35-37}$) than the bulk nepheline-kalsilite phenocrysts – note that Andersen *et al.* (2012) made various defocused electron beam analyses yielding an average composition at $\sim\text{Ks}_{68.6}$ ($n = 23$) for the complex phenocrysts. To the best of our knowledge, despite the above case, such perthitic intergrowth between nepheline and kalsilite has been characterized in detail only in some hypabyssal granular xenoliths from Italy (*e.g.* Velde & Yoder, 1978; Aurisicchio & Federico, 1985). These rocks, however, behave more like plutonic ones, with varied thermal histories and slower cooling rates. Accordingly, we can assume that nepheline-kalsilite

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exsolution in volcanic rocks may involve specific conditions, although it cannot be ignored the fact that this is a subject very poorly investigated.

Based on the absence of evidence that could indicate that post-magmatic subsolidus exsolution actually operates in our samples, together with the textural and chemical aspects discussed in the first topic of this section, it is hard to believe that the coexisting K-rich nepheline and kalsilite in the groundmass of the feldspar-free volcanic rocks from GAP are products of a hypersolvus crystallisation. Hence, following Sahama (1960) and Carmichael *et al.* (1974), we anticipate that K-rich nepheline and kalsilite must have crystallised as separate phases directly from the magma under subsolvus conditions. The co-precipitation below the ‘solvus’ of the nepheline-kalsilite system had already been postulated by the above authors to explain the coexistence of these two minerals as separate grains in the groundmass of some strongly SiO₂-undersaturated lavas that resemble closely volcanic rocks from the GAP.

Accordingly, K-rich nepheline and kalsilite may coexist in the groundmass of volcanic rock in a comparable way to the coexistence of two feldspars in less SiO₂-undersaturated alkaline volcanic rocks. To produce a two-phase area in the subsolidus field of the Ne-Ks system, the solidus of the magmatic system must intersect the solvus curve of this binary system. The ‘solvus’ between potassic nepheline and kalsilite has been defined experimentally only for the NaAlSiO₂ – KAlSiO₄ chemical components (*e.g.* Tuttle & Smith, 1958; Ferry & Blencoe, 1978; Hovis *et al.*, 2009; see **Figure 7.1**). The behaviour of the ‘solvus’ is thus undetermined in more complex chemical systems. But in an analogy to the effect of calcium in the feldspar system (*e.g.* Carmichael *et al.*, 1974), it is fairly reasonable to assume that the uppermost temperature of the Ne-Ks solvus curve can be slightly increased by the addition of extra chemical elements. Note that the GAP nepheline-bearing hosts are all mafic and contain very high amounts of CaO as well as MgO and Fe₂O₃ (see Supplementary Data – **Table B2**).

On the other hand, and maybe this is more realistic in view of the available data, the decrease of the solidus temperature for the bulk magma system must be considered. The SiO₂-undersaturated alkaline magmas that gave rise to the GAP nepheline-bearing hosts were enriched in volatiles (mainly CO₂) and, evidently, in alkalis (*e.g.* Junqueira-Brod *et al.*, 2005a; Brod *et al.*, 2005; Carlson *et al.*, 2007). These components can reduce drastically the solidus temperature of the magmatic systems. Sgarbi *et al.* (1998) reported oxygen isotope temperatures (for the clinopyroxene-magnetite pair) for two GAP volcanic rocks. According to the authors, the values of *ca.* 1060 – 1050 °C represent intermediate temperatures between the crystallisation temperatures of the phenocrysts and the groundmass. In the same work, Sgarbi *et al.* (1998) also gave temperatures between 920 and 820 °C for the crystallisation of groundmass from comparable rocks of the Alto Paranaíba Igneous Province. In addition, Andersen *et al.* (2014) stated that the recent lavas from Mt. Nyiragongo, which also can be considered analogous to those from the GAP investigated here (although the GAP is less differentiated), have eruption temperatures ≥ 980 °C. Furthermore, these authors established that a mineral assemblage with nepheline, kalsilite and combeite could have crystallised at a near-solidus temperature of ~600 °C. Though the extremely low temperatures obtained by Andersen *et al.* (2014) may be specific for peralkaline residual liquids capable of crystallising combeite, virtually all the temperatures discussed fall below the maximum temperature (*ca.* 1070 °C – Tuttle & Smith, 1958) obtained for the experimental ‘solvus’ in the binary Ne-Ks system. Therefore, it is conceivable that the potassic nepheline and kalsilite coexisting in the groundmass of the mafic potassic, feldspar-free, volcanic rocks from the GAP formed by a subsolvus crystallisation process.

K-rich Nepheline Solid Solutions: The Influence (or not) of the Chemical Affinity of the Parental Magmas

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Bowen & Ellestad (1936) were the first to prove that nepheline composition depends on the chemical environment where it crystallises. Since then, and from the subsequent work of Miyashiro (1951), it became clear that the chemical and physical conditions of crystallisation govern the ultimate composition of natural nepheline solid solutions (see also Tilley, 1954; Hamilton, 1961; Barth, 1963; among others). Accordingly, K-rich nepheline has usually been associated with a few occurrences of K-rich and Si-poor alkaline lavas worldwide (*e.g.* Edgar, 1984; Wilkinson & Hensel, 1994; Deer *et al.*, 2004; Antao & Nicholls, 2018).

However, in our specific search for potassic nepheline analyses occurring in strongly SiO₂-undersaturated volcanic rocks to compile a new database (see Supplementary Data – **Nepheline Database**) we realised that such potassic compositions are not restricted to the K-rich lavas only. Besides, to our surprise, the range of nepheline compositions varies somewhat independently of the bulk alkali ratio of the host rocks (**Figure 7.12**). The archetypal ultrapotassic rocks from SW Uganda and central Italy (see, *e.g.* Oliveira *et al.*, 2022) contain groundmass nepheline with relatively low Ks content (Ks₂₄ to Ks₃₁) if compared to K-rich nephelines from potassic lavas of their ‘type-locality’ (*i.e.* Mt. Nyiragongo – Ks₂₁ to Ks₄₁). Most remarkably, though, is that even classical sodic affinity volcanic rocks such as those of Madagascar or from Mt. Oldoinyo Lengai (an active carbonatite volcano) have K-rich nepheline compositions that cover a significant range of variation (Madagascar – Ks₂₄ to Ks₄₁; Oldoinyo Lengai – Ks₂₆ to Ks₃₈; see **Figure 7.12**).

Velde & Yoder (1978) already noted such behaviour for the nepheline solid solution compositions in some melilite-bearing volcanic rocks. They do not necessarily reflect the bulk rock K₂O/Na₂O ratio. The reasons for that will be explored in more detail in the next topic of this section. Here, we can conclude that the presence of K-rich nepheline does not imply a potassic parental magma only. But we can affirm that in K-rich magmas, this phase may eventually occur associated with kalsilite, as demonstrated in the present study and recently

recognized by Oliveira *et al.* (2022). Therefore, the long-standing paradigm that dominant groundmass nepheline means that the rock is sodic appears to be highly questionable.

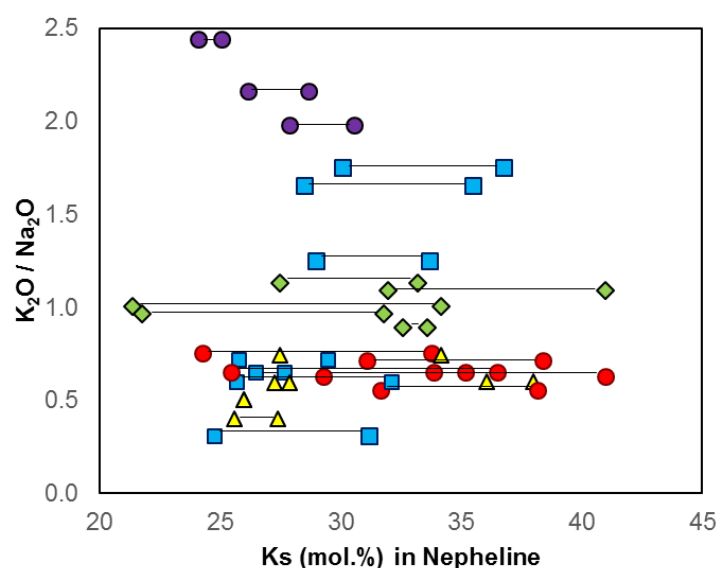


Figure 7.12 Plot of the whole-rock K_2O / Na_2O ratio of nepheline-bearing hosts vs the range of nepheline compositions (in Ks mol.%) obtained from each corresponding sample. Tie-lines connect the minimum and maximum Ks values for the same rock, or group of rocks, in the cases where only one nepheline analysis has been reported for each sample. All nepheline data are from groundmass nephelines of feldspar-free volcanic rocks. Sodic chemical affinity = $K_2O / Na_2O < 1$; Potassic chemical affinity = $K_2O / Na_2O > 1$; Ultrapotassic chemical affinity = $K_2O / Na_2O > 2$. Blue squares – this work; Purple circles – ultrapotassic lavas from SW Uganda and Italy (source: Tappe *et al.*, 2003; Gurenko *et al.*, 2018; Lustrino *et al.*, 2020); Green diamonds – potassic lavas from Mt. Nyiragongo, Congo (source: Andersen *et al.*, 2012; Minissale *et al.*, 2019); Yellow triangles – Peralkaline sodic lavas from Oldoinyo Lengai, Tanzania (source: Dawson, 1998; Keller *et al.*, 2006) and the North Tanzanian Rift (Baudouin, 2016); Red circles – sodic lavas from Madagascar (source: Melluso *et al.*, 2011; Cucciniello *et al.*, 2017; Mazzeo *et al.*, 2021). Note that the K_2O / Na_2O ratios of the ultrapotassic rocks were divided by 2 or 3 to fit the diagram scale.

We would like to clarify here some points regarding certain mineral assemblages and the erroneous association that sometimes occurs to whole-rock chemical affinity. It is well-known that leucite is not sufficient to confer an alkaline or even a potassic character to a rock (*e.g.* Foley *et al.*, 1987; Mitchell & Bergman, 1991). Thus, an assemblage with leucite and nepheline can occur in both sodic or potassic magmas with relatively small degrees of SiO_2 -undersaturation. Leucite and kalsilite, in contrast, occur in rare ultrapotassic magmas, but also with a small degree of SiO_2 -undersaturation to allow leucite formation. However, a particular

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case, previously overlooked, and that favours the crystallization of both K-rich nepheline and kalsilite is that involving strongly SiO₂-undersaturated alkaline mafic magmas, chiefly the potassic-ultrapotassic ones. In these cases, the amount of K₂O certainly would not be a limitation and given that leucite cannot crystallise in such low SiO₂ contents, the crystallization of K-rich nepheline and kalsilite would be preferred (particularly in the groundmass) to accommodate the Na, K, and alumina contents that cannot be completely incorporated by the mafic minerals (olivine, clinopyroxene, Fe-Ti oxides, melilite). The only conceivable restriction should be, in some extreme cases, crystallisation of nepheline in magmas with extremely low Na₂O contents (*e.g.* SW Uganda mafurite – Holmes, 1942; see also Oliveira *et al.*, 2022).

Silica Activity as a Key Factor Controlling Nepheline Composition in Igneous Rocks

A comparison between different data compilations (**Figure 7.13**) shows that the composition of natural nepheline covers practically the entire experimentally defined range for nepheline solid solutions (*i.e.* Ne₁₀₀ to Ne₃₀ – Tuttle & Smith, 1958). But even more relevant is to note that there is a marked contrast in the different sets of rock types that compose each database, and that appears to mirror a systematic behaviour for the variation of nepheline compositions. The published data compiled by Deer *et al.* (2004) are mostly from igneous plutonic (25 out of 35 reliable data) and feldspar-bearing (*n* = 26) rocks. Henderson (2020) gathered nepheline data mainly from nepheline syenites and high-level alkaline basaltic rocks (*n* = 292 reliable data). Hence, the two datasets comprise essentially feldspar-bearing alkaline rocks. On the other hand, our new database is for feldspar-free mafic volcanic rocks only (*i.e.* mafic foidites – olivine- and clinopyroxene-rich rocks). Here it is important to note how the nepheline compositions plotted in **Figure 7.13** seem to follow their host rock types. Almost all

feldspar-bearing rocks (blue and yellow symbols) contain only Na-rich nepheline ($K < 2 \text{ apfu}$), whereas the K-rich nepheline appears to be restricted to feldspar-free assemblages (green and red symbols).

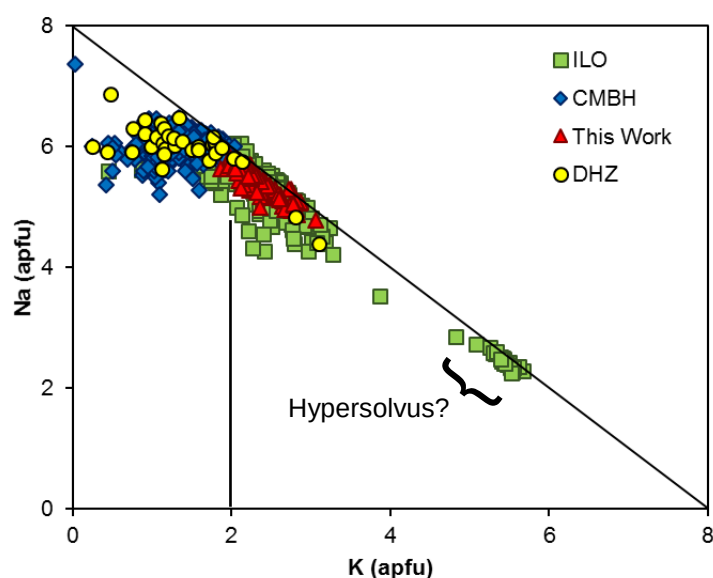


Figure 7.13. Comparison of three distinct nepheline databases with the data of this work, in terms of Na and K (*apfu*). Note that there is a remarkable ‘break’ in the distribution of natural nepheline compositions near the ideal stoichiometry (see text). DHZ – data from Deer *et al.* (2004), table 6; CMBH – data assembled and discussed by Henderson (2020); ILO – our newer database exclusively for feldspar-free volcanic rocks (available in Supplementary Data – Nepheline Database).

As previously debated, the correlation between the composition of nepheline and the chemistry of host rocks, or even, its physical crystallisation conditions, is nothing new (*e.g.* Bowen & Ellestad, 1936; Miyashiro, 1951; Tilley, 1954; Hamilton, 1961; Edgar, 1984; *etc.*). Wilkinson & Hensel (1994), for instance, established that nepheline-bearing hosts can be assigned to three main groups. Nepheline coexisting with high-temperature feldspars, in both volcanic and plutonic rocks, tends to be more enriched in Na and has relatively low excess Si ($Q' < 15 \text{ mol.}\%$). In contrast, nepheline associated with low-temperature feldspars almost always has compositions close to the ‘ideal’ formulae ($K = 2 \text{ apfu}$), with a significant excess of silica – the Q' content is always above 5 mol.% and can be as high as 20. And for feldspar-free host rocks, despite the reduced number of analyses, Wilkinson & Hensel (1994) noted that

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nepheline generally displays very low excess Si values ($Q' < 5$ mol.%) and more potassic compositions.

On that basis, and in view of the previous database comparison, we will hereafter consider two major groups, Na-rich and K-rich nepheline solid solutions, which are evidently correlated with the feldspar-bearing and feldspar-free assemblages, respectively. Yet, from another point of view, such feldspar-bearing alkaline rocks can be seen as derivatives from parental magmas that are only slightly SiO_2 -undersaturated due to the presence of feldspars together with feldspathoids. In contrast, due to the lack of feldspars, the feldspar-free rocks must have invariably been derived from magmas with lower silica activity (see Carmichael *et al.*, 1970). Velde & Yoder (1978) suggested that a controlling factor of the nepheline composition (Ks content) could be the bulk SiO_2 content of their host rock. For our samples, this is corroborated by a striking negative correlation between the maximum Ks content in nepheline and the SiO_2 content of their respective hosts (**Figure 7.14**). This kind of relationship was already noted by Donaldson *et al.* (1987), who suggested that it could be due to the temperature dependence of Na and K partitioning (note that these authors report a positive correlation between the Ne content and SiO_2 , which is equivalent to our negative Ks vs SiO_2 correlation). Significantly, Edgar (1984) also noted that nepheline in K-rich feldspar-bearing rocks does not show any important potassium enrichment relative to the Na-rich ones. He explained this by the presence of sanidine and leucite, which are early-formed minerals that incorporate K.

In addition, another somewhat indirect effect of silica activity in the composition of nepheline can be deduced from the order of crystallisation of leucite (to the former) and its abundance. Sahama (1960) and others (*e.g.* Lloyd *et al.*, 1991; Melluso *et al.*, 2011; Minissale *et al.*, 2019) claimed that the most K-rich nephelines from a particular locality occur in leucite-poor or leucite-free lavas. The explanation for this is that leucite often crystallises early,

depleting the K_2O in the liquid. Consequently, the late-stage groundmass nepheline will be relatively poor in potassium in comparison to those that crystallise without leucite or with only minor amounts of leucite in the groundmass. Even though, note that such nephelines will be usually still a K-rich variety. Here it is important to note that, as feldspars, leucite crystallises only with a certain degree of silica activity (see Carmichael *et al.*, 1970). Therefore, based on the above discussion, it is evident that silica activity is a powerful controlling factor to define the composition of natural nepheline.

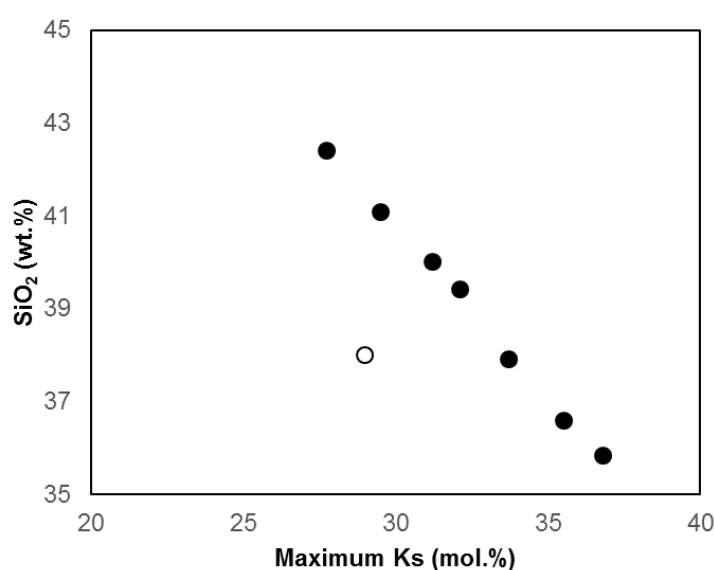


Figure 7.14 Plot of SiO_2 (in wt.%) in whole-rock samples of the nepheline-bearing hosts against the maximum Ks content (in mol.%) found in nepheline of these samples. The Ks values are reported in Supplementary Data – Table B1 or Nepheline Database. Whole-rock analyses are given in Supplementary Data – Table B2. The outlier data (open circle) refer to sample NEU 46B.

However, the effect of silica activity goes beyond whether or not early crystallisation of K-feldspar or leucite are permitted, changing the availability of K_2O in the residual liquid. The excess of silica and the potassium content in nepheline are intimately related to the crystal structure of nepheline and the strong site preference of K atoms. Barth (1963) mentioned that the main function of the 2 large alkali sites in the nepheline structure is “*willing to accept potassium ions or no ions at all*” (p. 155). This means that the amount of K atoms permitted is directly related to the need for charge balancing vacancies. In feldspar-bearing host rocks, Si

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likely replaces Al more extensively because of the high silica activity. This also means more vacancies in the A sites, and consequently, fewer cavity sites available for the entrance of K atoms. In feldspar-free host rocks (*i.e.* strongly SiO₂-undersaturated systems), there is not enough Si, but there is abundant Fe and Mg. Then, Al will be replaced more easily according to the reaction $2\text{Al}^{3+} \leftrightarrow \text{Si}^{4+} + (\text{Fe}^{2+} \text{ or } \text{Mg}^{2+})$, which does not require vacancies in contrast to the ‘common’ substitution reaction $(\text{Al}^{3+} + \text{K}^+) \leftrightarrow (\text{Si}^{4+} + \text{Vac.})$. If this explanation is correct, two chemical aspects observed in the K-rich nephelines can be explained: (1) the higher Fe and Mg concentrations with a strong positive correlation between them; and (2) the fact that high Ks contents are inversely correlated with the bulk SiO₂ contents of the system. The latter is because fewer vacancies are needed to compensate for the excess of Si charges.

7.6. Conclusion

We can draw the following major conclusions from this detailed nepheline compositional analysis:

- The detailed textural and compositional analysis of groundmass nepheline in twelve feldspar-free mafic potassic volcanic and subvolcanic rocks from the Goiás Alkaline Province (GAP) in central Brazil show that K-rich nepheline is the dominant felsic phase in the investigated rocks. The primary magmatic origin of this nepheline is attested by the absence of exsolution features, the presence of kalsilite in equilibrium, and the compositional variations found in the level of individual host rock samples.
- The textural relationship between the K-rich nepheline and kalsilite in the groundmass of the feldspar-free volcanic rocks from the GAP suggests that they already formed as separated phases. It is proposed that both K-rich nepheline and kalsilite crystallised together in the fine-grained groundmass under a subsolvus condition during rapid undercooling of the parental magma.

- A new data compilation for K-rich nepheline occurring exclusively in feldspar-free volcanic rocks revealed that this mineral composition is not limited to potassic and/or ultrapotassic host rocks. Potassic nepheline is also found in the groundmass of lavas with sodic chemical affinity.
- Our combined approach considering the crystal structure relations and the magmatic composition can readily explain why nepheline is almost always from a Na-rich specimen in Si-rich rocks (*i.e.* feldspar-bearing) and from a K-rich specimen in Si-poor rocks (*i.e.* feldspar-free). Actually, it is more a ‘prohibition’ of potassium caused by the silica activity than an ‘excess’ of sodium that gives rise to the Na-rich nephelines. All this depends on the boosted substitution of Al^{3+} for Si^{4+} ions in high silica activity environments (in the case of Na-rich nephelines) and on the substitution of 2Al^{3+} for $(\text{Si}^{4+} + \text{M}^{2+})$ in magmas with low silica activity (in the case of K-rich nephelines).

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Author Contribution Statement

ILO: conception of the main idea (lead), sampling (equal), data collection (lead), formal analysis (lead), data curation (lead), data interpretation (lead), writing – original draft (lead), writing – review & editing (lead); **JAB:** funding acquisition (lead), supervision (lead); **WUR:**

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writing – original draft (supporting), writing – review & editing (supporting); **TCJB**: sampling (equal); **TJ**: data collection (supporting), writing – original draft (supporting).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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Data Availability

The original data underlying this article are available in the article itself and in its online supplementary data. This includes a full database of nepheline compositions taking place in feldspar-free volcanic rocks.

Chapter 8

Final Considerations

The recognition of potassic nepheline as a primary magmatic phase, and its coexistence with primary kalsilite, in the strongly SiO₂-undersaturated volcanic rocks of the Goiás Alkaline Province (GAP) improves significantly the current knowledge about the source of the alkaline magmatism in central Brazil. In view of the abundance of potassic nepheline in the studied rocks, the parental magma (or magmas) of the GAP volcanic rocks must have been relatively rich in Na₂O, in comparison with those mantle-derived magmas that originate the archetypal kamafugites, which are firmly ultrapotassic. This hypothesis also clarifies the problem of the origin of the Na₂O-rich fluids that were responsible for the extensive substitution of primary leucite by secondary analcime in the GAP rocks. In all studied rocks K-rich nepheline rather than kalsilite is – by far – the more abundant felsic phase in the groundmass. This suggests that at least part of the alkaline ultrabasic rocks from the GAP should be re-evaluated as to their originally ultrapotassic character. Potassic nephelinite seems to be a very uncommon type of magma (*e.g.* Mt. Nyiragongo volcano, D.R. Congo; Katwe-Kikorongo province, SW Uganda; GAP, central Brazil; and possibly also, West Qinling province, China), though most of them may not have been recognized as such until now. However, these unusual magmas capable to crystallise K-rich nepheline and kalsilite together in the groundmass of their derivative rocks may represent an ‘intermediate’ mantle product between two more familiar ‘end-members’ – the ultrapotassic kamafugites, and the usually, but not always, sodic nephelinites.

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Appendix A

➤ **GPS locations of sampled outcrops (datum WGS-84)**

Field Point	Locality	Latitude	Longitude	Elevation	Field Info
15ISAB001	Santo Antônio da Barra	17°26'51.27"S	50°44'46.83"W	621m	Lava flow
15ISAB002	Santo Antônio da Barra	17°37'6.09"S	50°45'13.27"W	764m	Lava flow
15ISAB003	Santo Antônio da Barra	17°30'28.44"S	50°39'20.50"W	624m	Plug
15ISAB004	Santo Antônio da Barra	17°30'34.65"S	50°39'33.44"W	622m	Plug
15ISAB005	Santo Antônio da Barra	17°28'7.99"S	50°39'17.75"W	582m	Dyke
15ISAB006	Santo Antônio da Barra	17°27'22.14"S	50°40'9.98"W	576m	Lava flow
15ISAB007	Santo Antônio da Barra	17°26'53.86"S	50°40'48.17"W	571m	Sill
15ISAB008	Santo Antônio da Barra	17°26'39.13"S	50°40'59.11"W	570m	Lava flow
15IMTV009	Montividiu	17°18'31.33"S	51°13'33.72"W	836m	Dyke
15INEU010	Serra do Caiapó	17° 1'25.40"S	51° 8'38.06"W	587m	Lava block (Diatreme)
15IAMO011	Amorinópolis	16°33'55.00"S	51° 0'48.29"W	568m	Dyke
15IAMO012	Amorinópolis	16°34'25.59"S	51° 0'48.49"W	588m	Sill
15IAMO014	Amorinópolis	16°40'58.06"S	51° 1'37.82"W	717m	Dyke
15IAMO015	Amorinópolis	16°41'47.56"S	51° 1'52.24"W	770m	Plug
15IFB016	Iporá	16°22'18.41"S	51°11'33.66"W	618m	Dyke

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15IFB017	Iporá	16°21'59.49"S	51°11'4.45"W	629m	Dyke
15IFB018	Iporá	16°19'24.78"S	51°13'20.33"W	594m	Lava block?
15IDIO019	Diorama	16°12'27.14"S	51°19'9.75"W	459m	Dyke or Sill?
15IFB020	Iporá	16°20'47.41"S	51°13'12.16"W	683m	Intrusion
15IMM021	Iporá	16°25'0.10"S	51° 3'59.97"W	525m	Intrusion
15IMM022	Iporá	16°25'43.00"S	51° 4'5.30"W	577m	Dyke
15IMM023	Iporá	16°22'22.68"S	51° 1'57.25"W	492m	Dyke
15IRP024	Israelândia	16°13'43.77"S	50°50'8.67"W	362m	Dyke
15IRP025	Israelândia	16°15'15.59"S	50°52'47.01"W	408m	Intrusion
15IMP026	Morro Preto	16° 3'45.44"S	51°47'54.58"W	371m	Intrusion
15IARE027	Arenópolis	16°23'25.69"S	51°33'7.94"W	448m	Dyke
15IARE028	Arenópolis	16°28'37.10"S	51°38'26.26"W	444m	Dyke
15IARE029	Arenópolis	16°28'54.47"S	51°36'50.19"W	460m	Lava block?
15IARE030	Arenópolis	16°31'29.76"S	51°36'52.30"W	524m	Dyke?
15IARE031	Arenópolis	16°28'46.63"S	51°34'57.35"W	574m	Dyke
15IDIO032	Diorama	16°11'45.01"S	51°15'26.04"W	784m	Sill or Plug?
15IDIO033	Diorama	16°11'19.11"S	51°15'21.09"W	762m	Sill or Plug?
15IDIO034	Diorama	16°10'26.35"S	51°11'53.21"W	420m	Dyke
15IDIO035	Diorama	16°11'12.19"S	51°17'16.70"W	546m	Plug
15IDIO036	Diorama	16°14'4.25"S	51°20'17.07"W	484m	Dyke
15IDIO037	Diorama	16°14'24.47"S	51°19'49.35"W	482m	Dyke or Sill?
15IDIO038	Diorama	16°14'32.06"S	51°19'45.42"W	467m	Lava block?
15IDIO039	Diorama	16°19'11.55"S	51°14'59.87"W	599m	Lava block?
15IAMO040	Amorinópolis	16°33'10.06"S	51° 6'18.04"W	588m	Dyke

15IFB041	Iporá	16°22'21.28"S	51°10'42.32"W	675m	Dyke
15IMM042	Iporá	16°24'59.07"S	51° 3'31.31"W	540m	Dyke
15ILAJ043	Iporá	16°18'55.63"S	51°18'23.87"W	573m	Dyke
15IMAR044	Serra do Caiapó	17°10'7.61"S	51°20'59.46"W	599m	Plug
15ITIG045	Serra do Caiapó	17° 4'37.37"S	51°10'1.44"W	538m	Lava block?
15INEU046	Serra do Caiapó	17° 0'59.88"S	51° 9'30.88"W	531m	Lava block (Diatreme)
15ICSO047	Serra das Divisões	16°57'2.80"S	50°48'24.45"W	716m	Dyke
15IAE048	Serra do Caiapó	17° 1'4.92"S	51° 7'15.21"W	602m	Lava block (Diatreme)
16ISAB049	Santo Antônio da Barra	17°29'12.72"S	50°34'46.96"W	550m	Lava flow
16ISAB050	Santo Antônio da Barra	17°23'44.83"S	50°38'37.91"W	598m	Pyroclastic?
16IPAR051	Serra das Divisões	16°58'39.33"S	50°45'28.95"W	704m	Dyke
16IPAR052	Serra das Divisões	16°57'8.47"S	50°45'28.19"W	672m	Dyke
16IPAR053	Serra das Divisões	16°55'15.77"S	50°45'48.34"W	659m	Dyke
16IPAR054	Serra da Portaria	16°58'7.69"S	50°42'27.71"W	631m	Dyke
16ISAB055	Santo Antônio da Barra	17°18'39.12"S	50°43'11.24"W	607m	Lava flow
16ISAB056	Santo Antônio da Barra	17°20'32.56"S	50°46'34.06"W	657m	Pyroclastic?
16ISAB057	Santo Antônio da Barra	17°20'31.16"S	50°46'35.01"W	659m	Lava block?
16IRC058	Israelândia	16°23'11.43"S	50°52'19.31"W	400m	Dyke
16IRC059	Israelândia	16°24'39.79"S	50°51'20.75"W	430m	Dyke or Plug?
16IAE060	Serra do Caiapó	17° 1'9.50"S	51° 7'24.96"W	657m	Lava flow
16IMTA061	Iporá	16°20'21.73"S	51° 8'59.31"W	644m	Dyke
16ICB062	Iporá	16°19'35.74"S	51° 9'6.19"W	684m	Dyke
16ICB063	Iporá	16°17'37.44"S	51° 7'23.76"W	647m	Intrusion
16IARE064	Arenópolis	16°19'5.73"S	51°32'22.49"W	422m	Dyke

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16IARE065	Arenópolis	16°20'33.02"S	51°33'8.57"W	509m	Intrusion
16IARE066	Arenópolis	16°21'36.85"S	51°33'4.06"W	469m	Dyke
16IMP067	Morro Preto	16° 0'6.89"S	51°45'20.19"W	382m	Intrusion
16IME068	Morro do Engenho	15°31'17.81"S	51°39'43.98"W	348m	Intrusion
16ISF069	Santa Fé	15°42'58.77"S	51° 9'48.01"W	360m	Dyke
16ISF070	Santa Fé	15°45'48.33"S	51° 7'29.44"W	385m	Intrusion
16ISF071	Santa Fé	15°45'19.67"S	51°15'43.68"W	385m	Dyke
16ISF072	Santa Fé	15°43'9.85"S	51°16'5.86"W	370m	Dyke
16ISF073	Santa Fé	15°40'55.86"S	51°23'18.18"W	367m	Sill?
16ISF074	Santa Fé	15°48'47.77"S	51°13'45.35"W	470m	Dyke?
16ISF075	Santa Fé	15°48'0.68"S	51°10'18.44"W	525m	Wallrock
16IRP076	Israelândia	16°14'37.74"S	50°53'51.45"W	350m	Dyke?
16IDIO077	Diorama	16°13'13.06"S	51°15'7.93"W	529m	Dyke or Sill?
16IMCG078	Montes Claros de Goiás	16° 7'2.58"S	51°15'53.42"W	393m	Sill?
16IMCG079	Montes Claros de Goiás	16° 6'56.31"S	51°16'38.69"W	411m	Sill?
16IMCG080	Montes Claros de Goiás	16° 2'51.53"S	51°14'0.81"W	339m	Dyke or Sill?
16IMCG081	Montes Claros de Goiás	16° 2'21.69"S	51°14'0.31"W	328m	Sill?
16IMCG082	Montes Claros de Goiás	16° 2'27.48"S	51°15'55.41"W	348m	Dyke or Sill?
16IMCG083	Montes Claros de Goiás	16° 5'12.18"S	51°17'16.55"W	403m	Sill?
16IPG084	Palestina de Goiás	16°36'21.41"S	51°20'30.69"W	505m	Plug or Intrusion?
16IIVO085	Ivolândia	16°35'18.56"S	50°57'22.50"W	573m	Dyke?
16IAMO086	Amorinópolis	16°34'40.71"S	51° 5'52.65"W	646m	Wallrock
16IPAR087	Serra das Divisões	16°55'11.58"S	50°46'25.87"W	630m	Dyke
16IPAR088	Serra das Divisões	16°55'41.69"S	50°47'37.44"W	672m	Lava or Dyke?

16IPAR089	Serra da Portaria	16°57'32.05"S	50°44'1.97"W	662m	Dyke
16IPAR090	Serra das Divisões	16°51'0.31"S	51° 1'4.82"W	859m	Plug
16IPAR091	Serra das Divisões	16°49'16.86"S	51° 0'33.76"W	777m	Dyke?
16IMM092	Iporá	16°26'50.64"S	51° 3'7.87"W	553m	Dyke
18IAMO093	Amorinópolis	16°40'45.27"S	51° 2'0.17"W	637m	Dyke
18IAMO094	Amorinópolis	16°43'1.06"S	51° 3'19.45"W	699m	Plug

Appendix B

HISTORICAL PERSPECTIVE OF 50 YEARS OF GEOLOGICAL STUDIES OF THE CRETACEOUS ALKALINE ROCKS OF SW GOIÁS

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ABSTRACT: The story of geological studies of the alkaline rocks of SW Goiás relates closely to the history of the Geoscience Department (IG) at the University of Brasília (UnB). In 1968, during an exploratory field trip, the pioneer professors G. Guimarães, I. Glaser, and V.J. Marques recognized major alkaline mafic-ultramafic bodies and hypabyssal intrusives into the sedimentary strata of the Paraná Basin nearby the Iporá region. Soon thereafter, during a field trip related to the 24th Brazilian Geological Congress, held in Brasília, Glaser and co-workers described mafic alkaline lavas and breccias from the Águas Emendadas (AE) and Amorinópolis regions. Just about at the same time, Bez and co-workers, in a DNPM expedition, identified widespread mafic alkaline volcanism in the Santo Antônio da Barra (SAB) district, close to the Rio Verde city. Several works, mostly from the Geological Survey of Brazil, have mapped many other alkaline occurrences in the SW of Goiás throughout the 1970s and early 1980s. Notable in this period was the discovery of important lateritic nickel deposits associated with some of the main alkaline intrusions. Almost all studies prior to 1985 emphasized geological mapping and field descriptions. Former Professor J.C.M. Danni was a pioneer of petrological studies on alkaline plutons in the Iporá region. He was also responsible for most of the academic studies on the alkaline rocks of SW Goiás until his retirement in 1996. Some of the early M.Sc. projects conducted at the IG-UnB, by J.C. Gaspar and by L.C. Moraes, dealt with detailed mapping of the alkaline rocks of the SAB district. F.F.M. Almeida, in 1983, coined the term Rio Verde-Iporá Province for all alkaline rocks occurring along N50°-70°W trending extensional faults, extending over an area of 250 km length and 70 km width, from Rio Verde in the south to the Araguaia River in the north. Studies in mineral chemistry and whole-rock geochemistry became important after the mid-1980s. A benchmark occurred in 1985 when Professor Danni recognized that the mafic alkaline rocks of the Amorinópolis region belonged to the rare kamafugite series, a character which has later suggested for lavas and breccias of the SAB and AE regions as well. The presence of kalsilite, a characteristic mineral of kamafugites, was documented by two independent studies in 1998. However, until that year most of the publications were restricted to the Brazilian literature, with almost half of them having been reported as conference abstracts. After 1990, most work on the province paid attention to the kamafugites. This included comprehensive studies about the volcanology of these rocks, by T.C. Junqueira-Brod. In 2005, J.A. Brod and co-workers provided an extensive review of the up-to-date knowledge about the Goiás Alkaline Province, as it is currently known, and pointed out that detailed studies are available just for a few alkaline occurrences until then. In the last 15 years, only scarce, local data have been reported for these alkaline rocks, without any significant petrological studies, except for the recent studies on the Morro Preto complex.

KEYWORDS: ALKALINE VOLCANISM, IPORÁ, RIO VERDE, GOIÁS ALKALINE PROVINCE, KAMAFUGITE

SIGNIFICANCE OF K-RICH NEPHELINE IN STRONGLY SILICA-UNDERSATURATED MAFIC VOLCANIC ROCKS

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ABSTRACT: K-rich nepheline occur very occasionally in ultrabasic alkaline lavas. In the southern and central parts of the Goiás Alkaline Province (GAP) widespread mafic potassic magmatism took place as lavas, pyroclastic deposits, diatremes, dykes and plugs. Several authors have analysed the bulk rock chemistry firmly constraining their kamafugitic affinity. However, comprehensive mineral chemistry studies are still lacking, particularly regarding the felsic constituents of the groundmass. Although the potassic character of the GAP magmatism is unquestionable, the conspicuous presence of nepheline in their strongly SiO₂-undersaturated volcanics is intriguing. The most recent literature considers the abundance of nepheline in the GAP kamafugitic rocks as the result of intense subsolidus alteration of the original primary kalsilite. New petrography and mineral chemical data obtained from representative samples provide further insights into the meaning of nepheline in the GAP kamafugitic rocks. Most of the studied rocks have microporphyritic texture consisting of olivine and clinopyroxene phenocrysts set in an aphanitic groundmass. Nepheline, rather than kalsilite, and leucite (often altered to analcime) are the dominant felsic phases. Nepheline rarely occurs as microphenocrysts, and except for some leucite-phyric rocks, it is always present as an interstitial phase in the groundmass. Interestingly, regardless of whether coexisting leucite is unaltered or completely replaced by analcime, nepheline crystals are very homogeneous. Kalsilite seldom have been found together with nepheline in the groundmass, but their relationship is still being investigated. The nephelines analysed contain very high K₂O contents (up to 11.98 wt.%), which reflects 22.9 to 38.0 mol.% of KAlSiO₄. The composition of these K-rich nephelines also varies significantly in each rock sample (e.g. 32.8-38.0 mol.%). Variable compositions between nepheline crystals can be explained by very rapid magma cooling, which prevented the crystals to attain the equilibrium. The uncommon high K₂O contents found in the GAP nephelines indicate high temperatures of crystallization given that the amount of potassium that can enter into the Na alkali site in the nepheline structure decreases with the temperature. Also, a positive correlation between K-rich nepheline composition and whole-rock silica content support their magmatic origin. The occurrence of K-rich nepheline associated with kalsilite in the groundmass of K-rich Si-poor rocks are not exclusive from the southern and central GAP. This association is very well documented in the mafic potassic lavas of the active Nyiragongo volcano, Virunga Province, Western branch of the East African rift system. In view of the abundance of primary magmatic nepheline in the GAP kamafugitic rocks, their parental magmas must be relatively enriched in Na₂O compared with those from archetypal kamafugites (SW Uganda and central Italy). Such hypothesis also clarifies the problem of the origin of Na₂O-rich fluids that were responsible for the extensive replacement of leucite by analcime in the GAP rocks. In all the rocks studied K-rich nepheline, instead of kalsilite, is by far the most abundant felsic phase in the groundmass. This implies that some of the strongly SiO₂-undersaturated mafic rocks from GAP might be re-evaluated as to their originally potassic or ultrapotassic character.

KEYWORDS: POTASSIC MAGMATISM, KAMAFUGITE, GOIÁS ALKALINE PROVINCE