



Universidade de Brasília – UnB
Instituto de Geociências – IG/UnB
Programa de Pós-Graduação em Geologia

**MANGANÊS ASSOCIADO AO GRUPO ARAÍ E PARANOÁ NA
PORÇÃO NORDESTE DO ESTADO DE GOIÁS**

DISSERTAÇÃO DE MESTRADO Nº: 501

Gabriel Castro de Oliveira Domingues

Brasília/DF, 2022



**Universidade de Brasília – UnB
Instituto de Geociências – IG/UnB
Programa de Pós-Graduação em Geologia**

**MANGANÊS ASSOCIADO AO GRUPO ARAÍ E PARANOÁ NA PORÇÃO
NORDESTE DO ESTADO DE GOIÁS**

Dissertação de Mestrado N°: 501

Gabriel Castro de Oliveira Domingues

Área de concentração: Geologia regional e geoquímica

Orientadora: Prof^a. Dr^a. Adriana Maria Coimbra Horbe

Dissertação apresentada ao Programa de Pós-Graduação em Geologia do Instituto de Geociências da Universidade de Brasília, como requisito para a obtenção do grau de Mestre em Geologia.

Banca Examinadora

Prof. Dr. Roberto Ventura Santos
(Titular interno)

Prof. Dr. Márcio Fernando dos Santos Albuquerque
(Titular externo)

Brasília/DF, 2022

Ficha catalográfica

CD671m Domingues, Gabriel
Manganês associado ao Grupo Araí e Paranoá na porção
nordeste do estado de Goiás / Gabriel Castro de Oliveira
Domingues; orientador Adriana Maria Coimbra Horbe. --
Brasília, 2023.
75 p.

Dissertação (Mestrado em Geologia) -- Universidade de
Brasília, 2022.

1. Romanechita. 2. Litioforita. 3. Hausmannita. 4.
Hidrotermal. 5. Supergênico. I. Horbe, Adriana
, orient. II. Título.

AGRADECIMENTOS

Agradeço primeiramente a Prof^a. Dr^a. Adriana Maria Coimbra Horbe pela paciência e por todo suporte prestado não apenas no mestrado, mas nesse período extremamente complicado de pandemia.

À Universidade de Brasília e ao Instituto de Geociências pelos meios físicos e disponibilizados para a realização da presente pesquisa e aos professores do instituto por todos os ensinamentos.

À equipe do laboratório de raios-x (todas as gerações) pelos bons momentos e apoio ao longo desse trabalho. Carol, Rafael, Bob, Cuia, , Marcus, San Clever, João, Mariana e principalmente ao Marcinho pelas cervejadas e açaizinhos. Ao pessoal da microsonda e laminação, pelo suporte nessa reta final de trabalho.

Agradeço aos brothers.

Agradeço também a minha família, meus pais, Alberto e Isabel, e minhas irmãs, Melissa e Ana por todo o carinho e apoio. E a Gabizinha pela companhia, afeto e por todos os bons momentos.

O presente trabalho foi realizado com apoio da Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) – Código de Financiamento 001

EPÍGRAFE

Said the straight man to the late man
Where have you been?
I've been here and I've been there
And I've been in between
I talk to the wind – King crimson

LISTA DE ABREVIACÕES

OH-Mn – Óxi-hidróxidos de Mn
OH-Fe – Óxi-hidróxidos de Fe
MJ – Depósito de Monjolo
MI – Depósito de Minaçu
RZ – Depósito de Raizama
NQ – Depósito de Niquelândia
PP – Depósito de Pedra Preta
FT – Depósito de Fortaleza
VZ – Depósito de Vãozinho
CR – Depósito de Corrente
VR – Depósito de Vereda
FA – Depósito de Formosa
BL – Depósito de Brazlândia
FO – Depósito de Formoso
Pyr – Pirolusita
Cry – Criptomelana
Ms/Ilt – Muscovita/illita
Lt – Litioforita
Mnz – Monazita
Hsm – Hausmannita
Hol – Hollandite
Ro – Romanechita
Go – Goethita
He – Hematita
Brt – Barita
Qz – Quartzo

LISTA DE FIGURAS

Figura 1.2.1. Localização e vias de acesso aos locais estudados.....	11
Figura 2.1.1. Diagrama de Eh e pH de óxidos, sulfetos e carbonatos de manganês e ferro (Force & Maynard, 1991).....	13
Figura 2.1.2. Estruturas em cadeia em OH-Mn formando tuneis de diferentes tamanhos e camadas (Post, 1999).....	14
Figura 2.2.1. (A) Modelo de zona de mínimo oxigênio, com presença de águas profundas oxigenadas(B)Modelo de bacia restrita, no qual é necessária a presença de H ₂ S livre abaixo da <i>redoxline</i>	16
Figura 2.2.2 Comportamentos dos elementos terras raras em fluidos de baixa e alta temperatura (Bau & Dulski, 1999).....	17
Figura 2.2.3 Estágios de formação de minerais supergênicos de Mn a partir de (a) rodocrosita, (b) silicatos de Mn (Parc <i>et al.</i> , 1989).....	18
Figura 2.3.1 Principais domínios tectônicos da província tocantins, dando destaque para a zona interna (1) e externa (2) da faixa de dobramentos Brasília em pontilhado (Delgado <i>et al.</i> , 2003).....	19
Figura 2.3.2 Carta tectono-cronoestratigráfica dos Grupos Araí e Traíras com destaque para a unidade estudada (Martins-Ferreira <i>et al.</i> 2018a).....	21
Figura 2.3.3 Coluna estratigráfica do Grupo Paranoá na área-tipo Alto Paraíso de Goiás/Distrito Federal (Campos <i>et al.</i> 2013).....	23
Figura 2.3.4 Estruturas de brecha associados a pelitos na mina de Pedra Preta (Baeta Jr. <i>et al.</i> 1978).....	25

LISTA DE TABELAS

Tabela 2.1.1 Localidade, litotipo e acesso do Mn analisado.....	12
Tabela 3.1.1 Minerais de Mn comuns e suas abundâncias. (Maynard, 2014).....	26

RESUMO

Pequenos depósitos de Mn ocorrem na zona externa da faixa de dobramentos Brasília, um orôgeno neoproterozoico localizado no Brasil Central. Os depósitos estão associados aos grupos Araí (depósito de Monjolo), bacia paleoproterozoica do tipo rift, e Paranoá (depósitos de Minaçu, Raizama, Niquelândia, Pedra Preta, Fortaleza, Vãozinho, Corrente, Vereda, Formosa, Brazlândia, Formoso), bacia mesoproterozoica formada em margem cratônica. Esses pequenos depósitos, de origem supergênica, ocorrem em camadas, lamelas, bolsões e preenchem fraturas. O Mn do Grupo Araí é caracterizado pela presença de pirolusita, criptomelana e hausmannita subordinada, altas concentrações de U, Tl e Sr, altas razões $(La/Yb)_N$ e Eu/Eu^* e baixas razões Co/Zn e . Por outro lado, o Mn do Grupo Paranoá é caracterizado pela presença de romanechita, hollandita, litioforita, criptomelana e pirolusita, juntamente com as mais altas concentrações de Al_2O_3 , Ba, Co, Cu e Ni, e baixas razões $(La/Yb)_N$. Análise estatística dos dados (análise de componente principal) identificou que as variações químicas no Mn do Grupo Paranoá estão relacionadas a intensidade da atividade supergênica que originou romanechita e litioforita nos estágios mais avançados à medida que concentra Al, Ba, Co, Cu, Ni e Zn. Entretanto, a presença de hausmannita e as características geoquímicas (baixas razões Co/Zn e altas razões $(La/Yb)_N$ e Eu/Eu^*) indicam contribuição hidrotermal para o do Grupo Araí. As menores razões $(La/Yb)_N$ podem estar associadas a alteração supergênica e ao fracionamento nos isótopos de Sm e Nd, além dos valores mais radiogênicos de isótopos de Sr. As razões de $^{208}Pb/^{206}Pb$ e $^{207}Pb/^{206}Pb$ não variam com as razões $(La/Yb)_N$ e apresentam valores elevados de $^{206}Pb/^{204}Pb$ nas amostras MJ1 e RZ1. Os valores $\epsilon Nd(0)$ variando de -8,8 a -20,7 Ga e TDM que variam de 2,24 a 3,46 Ga indicam fonte continental antiga.

Palavras-chave: Romanechita, litioforita, hausmannita, hidrotermal, origem supergênica

ABSTRACT

Small Mn deposits occur in the external zone of Brasília fold belt, a Neoproterozoic orogen located in Central Brazil. The deposits are associated with the Arai Group (Monjolo) a Paleoproterozoic rift basin and Paranoa group (Minaçu, Raizama, Niquelandia, Pedra Preta, Fortaleza, Vãozinho, Corrente, Vereda, Formosa, Brazlânida, Formoso) a cratonic margin basin of Mesoproterozoic age. These small deposits occur as layers, plates, fillings in pockets and fractures and are considered of supergenic origin. Studies carried out by X-ray diffraction, SEM, EPMA and chemical analysis indicate the presence of pyrolusite, cryptomelane and, to a lesser extent, hausmannite together with higher concentrations of U, Tl and Sr, Co/Zn ratios and high ratios $(La/Yb)_N$ and Eu/Eu^* in the one associated with the Arai Group. Romanechite, hollandite, lithiophorite, cryptomelane and pyrolusite and higher concentrations of Al_2O_3 , Ba, Co, Cu, Ni, greater variation of REE, in addition to low ratios $(La/Yb)_N$ are the characteristic of those associated with the Paranoa Group. Statistical analysis of the data (Principal component) identified that the chemical variations in those from Paranoa Group are related to the intensity of the supergenic activity that forms romanechite and lithiophorite in the most advanced stages as it concentrates Al, Ba, Co, Cu, Ni and Zn. However, the presence of hausmannite and the geochemical characteristics (low Co/Zn ratios and high $(La/Yb)_N$ and Eu/Eu^*) indicates a hydrothermal contribution to the Arai Group. The lower ratios $(La/Yb)_N$ may be associated with supergenic alteration and fractionation in Sm and Nd isotopes, in addition to the more radiogenic values of Sr isotopes. The $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ratios do not vary with the $(La/Yb)_N$ ratios and present high values of $^{206}Pb/^{204}Pb$ in samples MJ1 and RZ1. $\epsilon Nd(0)$ values ranging from -8.8 to -20.7 Ga and TDM ranging from 2.24 to 3.46 Ga indicate ancient continental source.

Keywords: Romanechita, litioforita, hausmannita, hydrothermal, supergenic origin

SUMÁRIO

CAPÍTULO 1: APRESENTAÇÃO.....	10
1.1 Justificativa e objetivos	10
1.2 Localização e acesso	10
CAPÍTULO 2: REFERENCIAL TEÓRICO E REVISÃO BIBLIOGRÁFICA....	12
2.1. Química e mineralogia dos óxidos de Mn.....	12
2.2. Tipos de depósitos (sedimentar, hidrotermal e supergênico).....	14
2.3. Geologia regional	18
CAPÍTULO 3: MATERIAIS E MÉTODOS	26
3.1. Composição mineral, químico-mineral e geoquímica.....	27
CAPÍTULO 4: “Gênese dos depósitos de Mn do nordeste do Goiás, Brasil: Mineralogia, Geoquímica e isótopos”	Erro! Indicador não definido.
CONSIDERAÇÕES FINAIS E CONCLUSÃO	59
REFERÊNCIAS BIBLIOGRÁFICAS	61
ANEXOS	64

CAPÍTULO 1: APRESENTAÇÃO

1.1 Justificativa e objetivos

No nordeste do Goiás há vários pequenos depósitos e ocorrências de Mn na forma de bolsões, blocos, lamelas, e preenchendo fraturas, nas rochas metassedimentares dos grupos Araí e Paranoá (Guimarães, 1978; Baeta Jr. *et al.*, 1978). Os depósitos e as ocorrências de Mn são de pequeno volume e apresentam ~2 m de espessura e algumas centenas de metros de extensão. No depósito de Pedra Preta (já exaurido), de onde foram explotadas 615.310 toneladas de manganês, as camadas manganíferas se estendiam por 200 m a 300 m, com teor médio de 45,8% de MnO (Baeta Jr. *et al.*, 1978). Desses depósitos cujo conhecimento está restrito a trabalhos de campo, métodos óticos, difração de raios-x e análises químicas de SiO₂, Al₂O₃, Fe₂O₃, MnO₂, BaO e P₂O₅, foram estudados os de Pedra Preta e Buritizinho em maior detalhe. As condições de deposição na bacia, o protominério e os processos de concentração em ambiente supergênico foram debatidos, mas nunca houve um consenso.

Neste estudo, onde foram utilizados equipamentos modernos como DRX, MEV, microsonda eletrônica, ICP-MS e ICP-AES, foram realizadas a caracterização mineralógica, química e isotópica em detalhe das ocorrências de Mn do nordeste do Goiás.

Os objetivos abordados neste trabalho foram:

- i. Identificar as condições de deposição do Mn na bacia;
- ii. Identificar as possíveis fontes do Mn;
- iii. Compreender os processos de alteração supergênica;

1.2 Localização e acesso

A área de estudo situa-se em toda porção nordeste do Goiás, engloba também o Distrito Federal, e pequena porção a sudoeste de Minas Gerais. Os locais amostrados estão sumarizados e descritos na Tab.1 e Figura 1. Os acessos partindo de Brasília-DF foram realizados pela BR-010 à norte para os pontos próximos a São João d'Aliança, Colinas do Sul, Cavalcante e Niquelândia, pela BR-030 à nordeste para próximo de Formoso-MG e pela BR-020 nos pontos próximos mais próximos ao Distrito Federal (Fig 1.2.1).

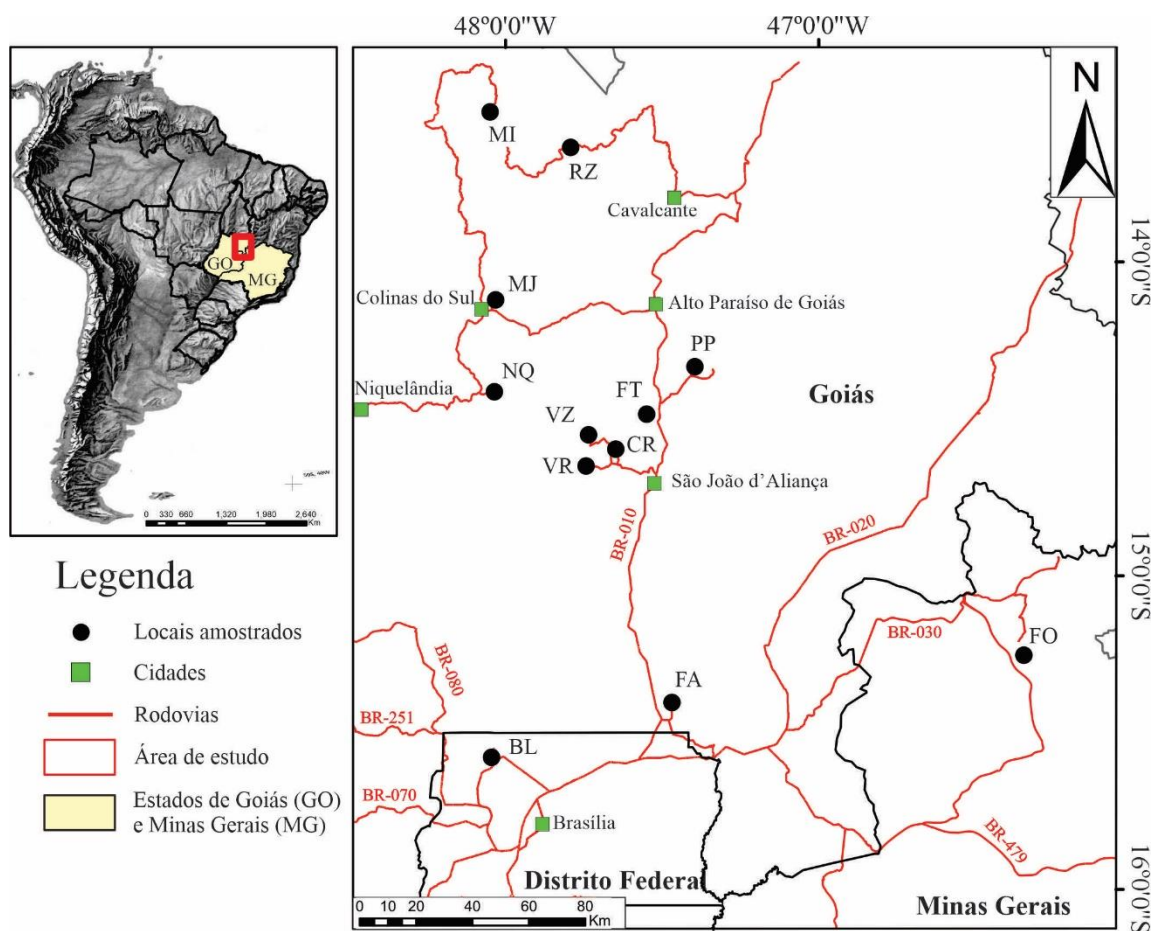


Figura 1.2.1 Localização e vias de acesso aos locais estudados, Monjolo (MJ), Minaçu (MI), Raizama (RZ), Niquelândia (NQ), Pedra Preta (PP), Fortaleza (FT), Vãozinho (VZ), Corrente (CR), Vereda (VR), Formosa (FA), Brazlândia (BL), Formoso (FO).

CAPÍTULO 2: REFERENCIAL TEÓRICO E REVISÃO BIBLIOGRÁFICA

2.1. Química e mineralogia dos óxidos de Mn

O manganês (Mn), bastante utilizado na fabricação de baterias e ligas de aço de alta resistência, é o décimo elemento mais abundante na crosta terrestre e apresenta propriedades químicas semelhantes ao ferro (Fe). É encontrado na natureza nos estados de oxidação Mn^{2+} e Mn^{3+} que apresentam raio iônico de 0,81 e 0,64Å, respectivamente, podendo nessas condições substituir o Fe^{2+} (0.76 Å) e Fe^{3+} (0.64 Å) nos minerais. No entanto, o maior estado de oxidação do Mn na natureza é Mn^{4+} (0.53 Å), que dá origem a uma variedade de óxidos (Tab 2.1.1). O Mn apresenta maior solubilidade que o Fe em condições de pH e Eh normais. Por outro lado, em condições redutoras, os sulfetos de Mn (alabandita e hauerita) apresentam menor estabilidade quando comparado com os de Fe (pirita), enquanto os carbonatos de Mn (rodocrosita e kutnahorita) apresentam maior estabilidade quando comparado com os carbonatos de Fe (Fig. 2.1.1) (Maynard, 2014).

Tabela 2.1.1 Minerais de Mn comuns e suas abundâncias. (Maynard, 2014)

Tipo	Nome	Fórmula	Abundância	Descrição
Óxidos tetraivalentes em cadeia	Pirolusita	β - MnO_2 (Tetragonal)	5	Cadeias simples de octaedros de $(MnO_6)^{8-}$
	Ramsdellita	MnO_2 (ortorrômbico)	<1	Cadeias duplas
	Nsutita	MnO_2 (hexagonal); intercrescimento de pirolusita e ramsdellita	1	Cadeias simples e duplas
	Hollandita	$(Ba)_x(Mn^{4+}, Mn^{3+})_8O_{16}$ (tetragonal)	<1	Cadeias com túneis abertos que permitem que cátions grandes sejam incorporados
	criptomelana	$(K)_x(Mn^{4+}, Mn^{3+})_8O_{16}$ (tetragonal)	9	
	Coronadita	$(Pb)_x(Mn^{4+}, Mn^{3+})_8O_{16}$ (tetragonal)	<1	
	Romanechita	$(Ba)_{0.66}(Mn^{4+}, Mn^{3+})_8O_{16}$ (monoclínico)	4	Psilomelano
Camadas (filomanganatos)	Todorokita	$(Na, Ca, K)_x(Mn^{4+}, Mn^{3+})_6O_{12} \cdot 3.5H_2O$	2	Manganita de 10 Å
	Birnessita	$(Ca, Na)(Mn)_7O_{14} \cdot 2.8H_2O$	<1	Manganita de 7 Å
	Vernadita	δ - MnO_2	<1	Comum em oxidação microbiana
Óxidos trivalentes	Litioforita	$(Al, Li)(OH)_2(Mn^{4+}, Mn^{3+})O_6(OH)_6$ (monoclínico)	1	comum em zonas supergênicas
	Bixbyita	α -(Mn, Fe^{3+}) $_2O_4$ (isométrico)	1	>30% Fe_2O_3
Óxidos divalentes	Manganosita	MnO (isométrico)	<1	
Estrutura de espinélio	Hausmannita	$Mn^{2+}Mn_2^{3+}O_4$ (tetragonal)	5	Até 7 mol% Fe_3O_4
	Jacobsita	$Mn^{2+}(Mn, Fe^{3+})_2O_4$ (isométrico)	<1	>45 mol% Fe_3O_4
Hidróxidos	Manganita	γ - $MnOOH$ (monoclínico)	8	
	Groutita	α - $MnOOH$ (ortorrômbico)	<1	
	Feitknechtita	β - $MnOOH$ (trigonal)	<1	
	Pyrochroita	$Mn(OH)_2$ (trigonal)	1	
Silicatos	Braunita	Mn_7SiO_{12}	25	Estrutura de brucita
Carbonatos	Kutnahorita	$CaMn(CO_3)_2$	2	
	Rhodochrosita	$MnCO_3$	32	

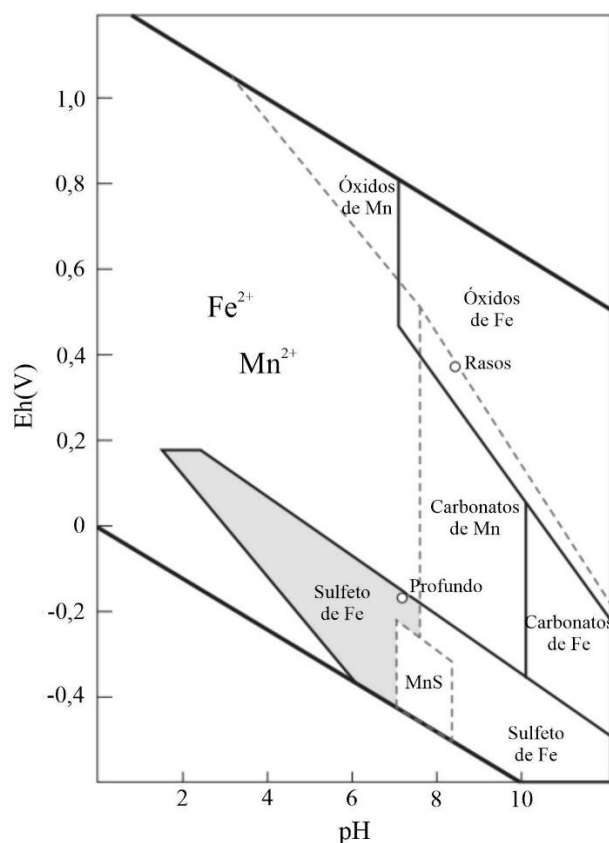


Figura 2.1.1. Diagrama de Eh e pH com delimitação pontilhada nos campos onde podem ser formados óxidos, sulfetos e carbonatos de manganês e contínuas para o ferro (Force & Maynard, 1991).

A existência de oxi-hidróxidos de Mn (OH-Mn) multivalentes permitem grande diversidade de arquiteturas atômicas. A unidade mais básica dos OH-Mn são os octaedros de MnO_6 , que ao compartilhar vértices e arestas criam arranjos estruturais em cadeia, os quais podem formar estruturas em túnel e arranjos em camada (Fig. 2.1.2, Post, 1999). As estruturas em túnel podem ser formadas por cadeias simples, duplas e triplas de octaedros de Mn. Essas estruturas podem acomodar cátions, como Ba na hollandita e romanechita, K na criptomelana, Pb na coronadita e Na e Ca na todorokita. As estruturas em camadas podem acomodar tanto cátions, como Na na birnessita e Zn na calcofanita, como octaedros de outros metais, como $\text{Al}(\text{OH})_6$ na litioforita.

A maior parte dos OH-Mn apresenta baixa cristalinidade, são criptocristalinos e ocorrem intercrescidos e misturados, o que torna complexa a sua caracterização. Desta forma, termos como *wad* são utilizados para caracterizar materiais moles, finos, marrons a pretos, que sujam a mão com facilidade, e apresentam grande variação mineralógica. O termo psilomelano é aplicado a materiais duros, cinzas a pretos, com textura botrioidal e maciça, cujo espécime mineral dominante normalmente é a romanechita (Post, 1999) (Tab. 2.1.1).

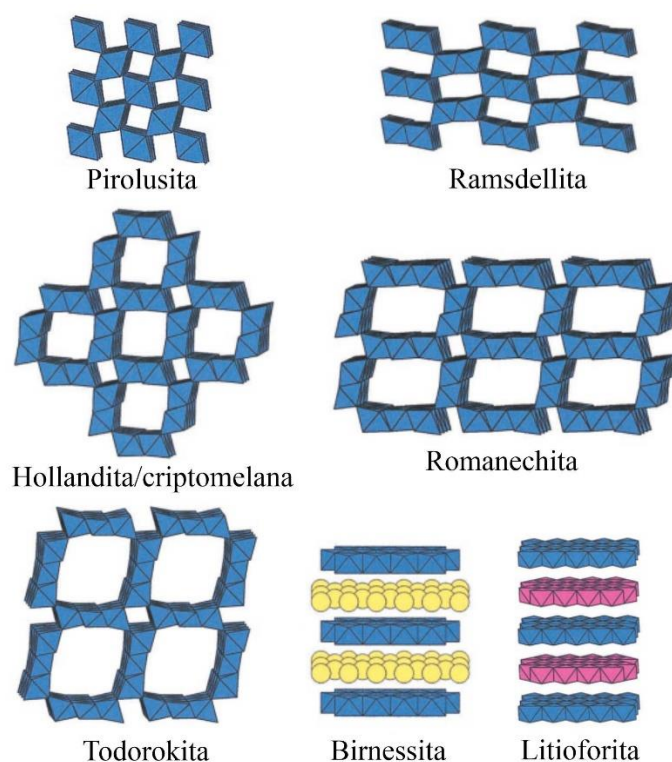


Figura 2.1.2. Estruturas em cadeia em OH-Mn formando tuneis de diferentes tamanhos em pirolusita, ramsdellita, hollandita, criptomelana, romanechita e todorokita e camadas em birnessita e litioforita. (adaptado de Post, 1999).

2.2. Tipos de depósitos (sedimentar, hidrotermal e supergênico)

Os ambientes sedimentares e hidrotermais são considerados os processos primários de deposição de Mn. Os dois podem ocorrer em grande variedade de regimes tectônicos e geoquímicos e podem ser correlatos. Os depósitos de Mn supergênico podem ser formados a partir do enriquecimento tanto do Mn hidrotermal como do sedimentar, e é controlado pelo clima, topografia e sistema de drenagem (Roy, 1992; Varentsov, 1996).

Os depósitos sedimentares se destacam por seu tamanho e distribuição espacial e temporal, e podem ocorrer também associados a rochas vulcânicas, embora em menor porte (Roy, 1992). O comportamento do Mn, que é diferente em condições óxidas (insolúvel) e anóxicas (solúvel) permite reciclagem quando as duas estão justapostas, aumentando a concentração de Mn. Em bacias permanentemente anóxicas não são encontrados depósitos de Mn, sendo necessário uma interface óxida entre sedimento e água para ocorrer a deposição (Calvert & Pedersen, 1996).

Existem dois principais modelos de deposição de Mn sedimentar: no primeiro, a presença de uma zona de ressurgência poderia causar a mobilização de óxidos de Mn de sedimentos de água profunda para sedimentos marinhos rasos, onde o topo da zona de

mínimo oxigênio coincide com a interface sedimento-água. Nesse local o Mn^{2+} pode ser re-oxidado para óxidos de Mn insolúveis, que ao serem soterrados com matéria orgânica podem ser convertidos para carbonatos de Mn durante a diagênese (Fig. 2.2.1A) (Calvert & Pedersen, 1996). O segundo modelo, conhecido como “*bathtub ring*” está associado a depósitos de grande porte e ocorre em bacias euxínicas, na qual as diferentes solubilidades de Fe e Mn sob condições sulfídicas, onde H_2S livre permite a formação preferencial de pirita, em detrimento de alabandita, cuja solubilidade é maior que os sulfetos de Fe. Esse processo permite a concentração de grandes quantidades de Mn dissolvido em águas profundas que ao entrar na interface com a água oxidante precipita na forma de óxidos. Esses óxidos quando depositados com matéria orgânica são convertidos em carbonatos de Mn durante a diagênese (Fig. 2.2.1B) (Force & Cannon, 1988). A pureza desses depósitos depende da eficiência da remoção do ferro dissolvido por meio da precipitação de pirita, podendo ocorrer associados a sulfetos, fosforitos e barita e muitos apresentam evidências de grande produtividade orgânica (Force & Cannon, 1988).

Os depósitos formados por esses processos têm como principal mineral a rodocrosita (Maynard, 2010). O Mn formado em ambiente sedimentar marinho apresenta enriquecimento em Na, K, Ca, Mg, Sr em ambiente marinho raso, associado a processos diagenéticos (Nicholson, 1992), e enriquecimentos em Co e Ni em marinho profundo, associado a precipitação direta da água do mar e processos diagenéticos (Halbach, 1986; Bau *et al.*, 2014). O comportamento dos elementos terras raras (ETR) em manganês sedimentar pode sofrer interferência de acordo com o grau de mistura com materiais detríticos (Maynard, 2010). O comportamento do Ce e Eu são os mais importantes nas análises do Mn sedimentar. Os ETR têm comportamentos semelhantes quando no estado de oxidação $3+$, mas em ambiente oxidante o Ce^{3+} pode ser convertido em Ce^{4+} que apresenta menor solubilidade, enquanto em ambiente redutor o Eu^{3+} pode passar para Eu^{2+} e substituir o Ca^{2+} em alguns minerais, como no plagioclásio. Em ambiente oxidante o Ce^{4+} é mais fortemente ligado aos óxidos de Mn, deixando o óxido formado com anomalia positiva de Ce e o fluido com anomalia negativa. A assinatura hidrotermal é caracterizada por anomalia positiva de Eu que é liberado de plagioclásio cálcico durante a passagem de fluidos quentes e redutores. As anomalias de Eu ao longo do tempo geológico apresentam maior variabilidade quando comparadas com as de óxidos de Fe, sugerindo um maior controle local na anomalia (Maynard, 2014).

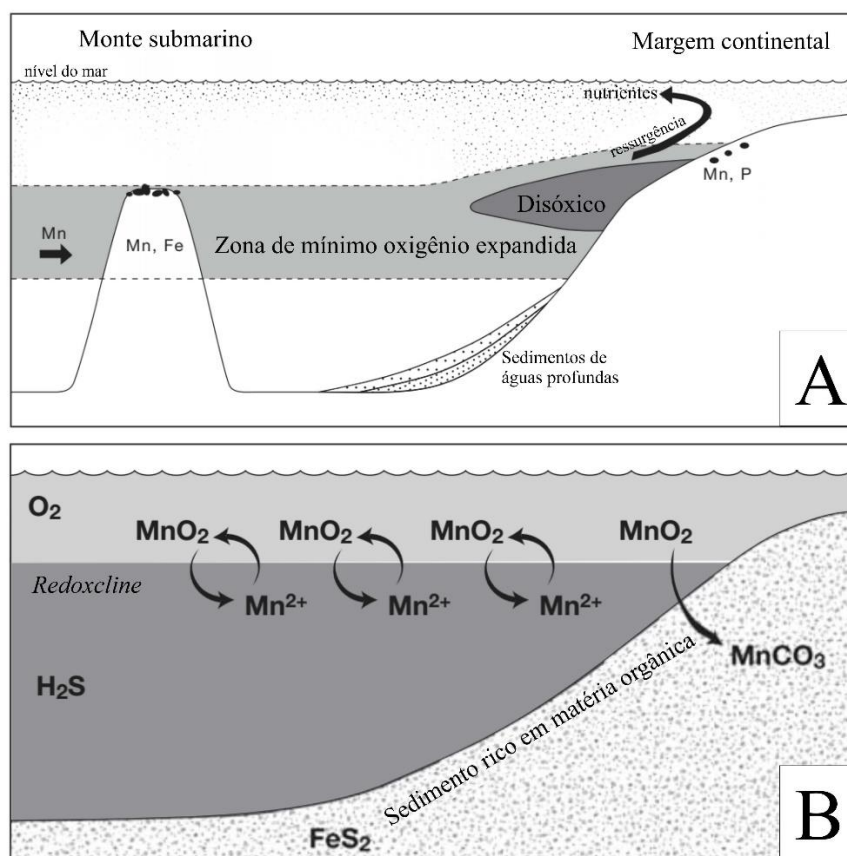


Figura 2.2.1. (A) Modelo de zona de mínimo oxigênio, com presença de águas profundas oxigenadas. (B) Modelo de bacia restrita, no qual é necessária a presença de H₂S livre abaixo da *redoxline* (Retirado de Maynard, 2014).

Os depósitos hidrotermais normalmente são pequenos quando comparados com os depósitos sedimentares e são identificados de ambientes continentais a marinhos profundos, além de presentes na forma de veios em rochas ígneas. Depósitos de Mn hidrotermais antigos ocorrem como camadas estrato-ligantes e veios em diferentes tipos de rochas de diferentes idades podendo apresentar continuidade com depósitos de ferro, apresentando razões Mn/Fe muito grandes ou muito pequenas (Roy, 1997).

Os veios hidrotermais derivados de fontes termais terrestres apresentam grande variedade de minerais. Os de baixa temperatura são formados por pirolusita, criptomelana, romanechita, hollandita e todorokita, enquanto os demais formados em temperaturas um pouco mais elevadas apresentam braunita, bixbieta, hausmannita, huebnerita e carbonatos de Mn (Roy, 1997). Barita, fluorita, calcita e quartzo são minerais acessórios comuns (Roy, 1981). Os principais minerais de Mn formados a partir de fluidos hidrotermais em fundo oceânico são todorokita e birnessita (Buatier *et al*, 2004). Os OH-Mn nesses depósitos apresentam baixa concentração de metais quando comparados com os outros depósitos marinhos e terrestres, ocorrendo enriquecimentos em As, Ba, Cu, Li, Mo, Pb, Sb, Sr, V, Zn

(Nicholson, 1992) com raras exceções que apresentam concentrações maiores de Co e Ni que indicam proximidade com a fonte de calor (Hein *et al.*, 2008). Apesar da diversidade, a maior parte dos depósitos hidrotermais de Mn e Fe apresentam baixa concentração de ETR, podendo apresentar anomalias positivas de Eu típicas de fluidos que ultrapassaram 200 °C, que diminuem conforme ocorre mistura com fluidos frios (Fig 2.2.2) (Bau, 1991; Bau & Dulski, 1999; Bau *et al.*, 2014).

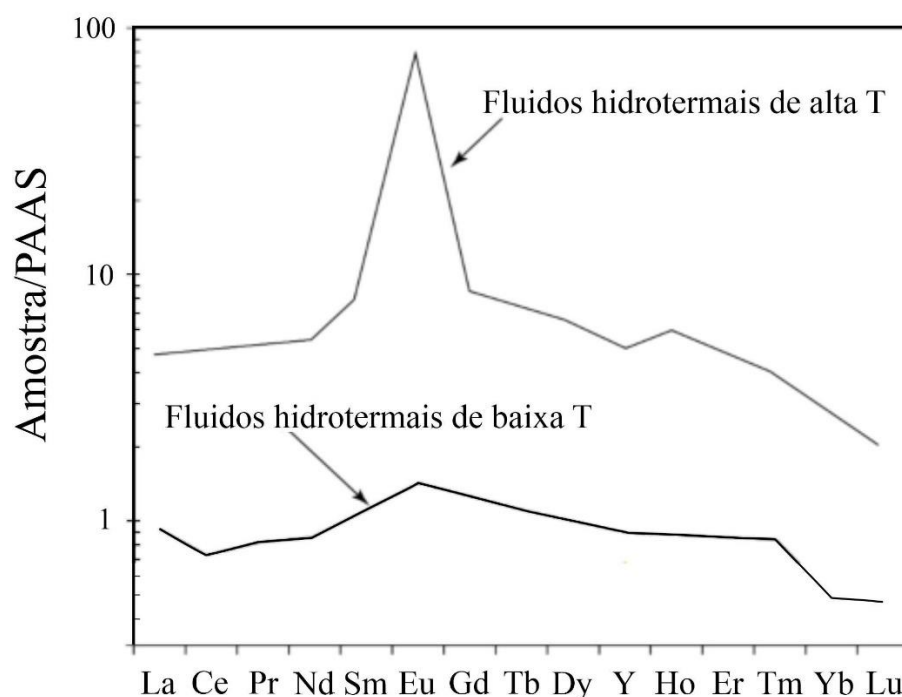


Figura 2.2.2 Comportamentos dos elementos terras raras em fluidos de baixa e alta temperatura (Bau & Dulski, 1999).

Os processos de alteração supergênica podem aumentar a concentração de Mn e transformar depósitos não econômicos em exploráveis. Os depósitos supergênicos podem ocorrer como: (1) Minérios em zonas oxidadas ou depósitos secundários associados a alterações de Mn sedimentar-diagenético, hidrotermal-sedimentar e metamórfico (formam os maiores e mais importantes depósitos); (2) Depósitos de Mn associados à processos de lixiviação, infiltração e reprecipitação, (os mais importantes desse tipo estão associados à carstes) (Varentsov, 1996). Os minerais de Mn supergênico podem se formar a partir de qualquer mineral primário de Mn, como silicatos, carbonatos ou outros óxidos (Fig 2.2.3). Os principais minerais supergênicos de Mn são cryptomelana, romanechita, nsutita, vernadita, manganita, pirolusita e litioforita (Ostwald, 1988; Dash *et al.*, 2020).

Os depósitos manganésíferos associados a zonas oxidadas e depósitos secundários associados a ambientes sedimentares marinhos comumente têm carbonatos de Mn como

protominério, nas quais as acumulações primárias ocorrem como corpos estratiformes, lamelas e concreções. A alteração do minério primário leva a formação de camadas e lamelas de pirolusita, criptomelana, nsutita e litioforita, que podem ser alternadas com rochas ferruginosas. Impregnação de OH-Mn e Fe podem ocorrer em arenitos e conglomerados. No processo de alteração ocorre a lixiviação de Ca, Mg e Na, e fixação apenas do K, Ba (Weber, 1997) não havendo mudanças no padrão de comportamentos nos ETR.

Os depósitos de Mn em carstes ocorrem nas cavidades, fraturas e em brechas na forma de cimento, e têm como principais minerais a criptomelana e litioforita. Os processos de dissolução e precipitação permitem o enriquecimento em Co, Ni, Cu e Ba (Varentsov, 1996), com o Ba apresentando o maior enriquecimento (Maynard *et al.*, 2010). Nesses depósitos quanto maior a remobilização maior o enriquecimento de Ba, o que possibilita a formação de romanechita (Garnit *et al.*, 2020; Dash *et al.*, 2020; Gutzmer *et al.*, 2012). O processo de remobilização gera diminuição na razão $(La/Yb)_n$ (Varentsov, 1996; Han *et al.*, 2017; Klueshov *et al.*, 2022; Garnit *et al.*, 2020).

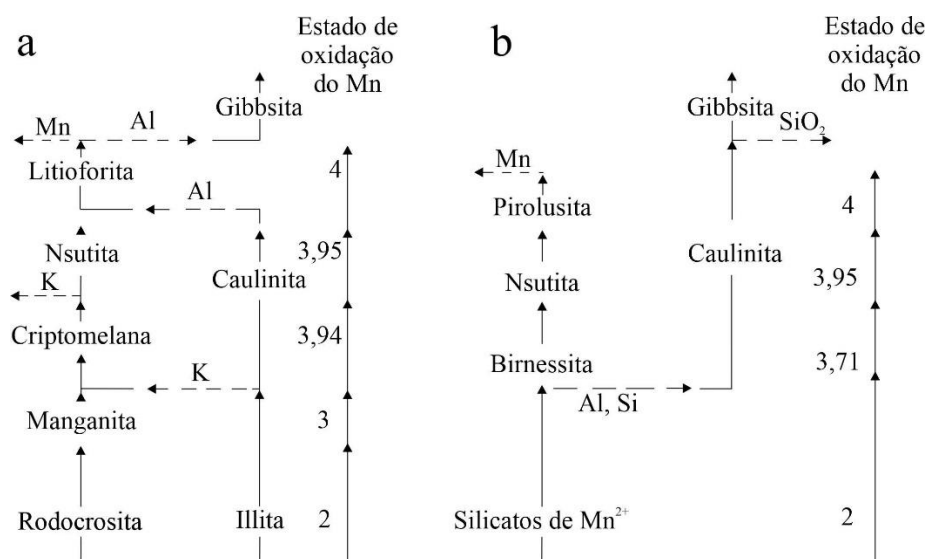


Figura 2.2.3 Estágios de formação de minerais supergênicos de Mn a partir de (a) rodocrosita, (b) silicatos de Mn. (Parc *et al.*, 1989).

2.3. Geologia regional

A província Tocantins, localizada no Brasil central, representa um orógeno brasileiro/Pan-Africano formado a partir da colisão dos cratões Amazônico, São Francisco/Congo e Paranapanema e é dividido nas faixas de dobramento Araguaia, Paraguai e Brasília. As faixas Araguaia e Paraguai estão localizadas na porção oeste da província, enquanto a Brasília está à leste (Pimentel *et al.* 2000; Fig. 2.3.1). A faixa Brasília bordeja o oeste do Craton São Francisco e suas principais unidades são sequências sedimentares,

Figura 2.3.1 Principais domínios tectônicos da província tocanzins, dando destaque para a zona interna (1) e externa (2) da faixa de dobramentos Brasília em pontilhado (Delgado *et al.*, 2003).



2.3.1. Grupo Araí

O Grupo Araí foi descrito inicialmente por Barbosa *et al.* (1969) e foi caracterizado como grupo por Dyer (1970). A idade paleoproterozoica (1,77 Ga), está relacionada a datação de riolitos encontrados na base do Grupo Araí (Pimentel *et al.*, 1991). Tanizaki *et al.* (2015) subdividiu a bacia do Grupo Araí em estágio pré-rift, sin-rift, transicional e flexural, além de definir quatro formações (Água Morna, Arraias, Caldas e Traíras). Nessa divisão, a Formação Arraias é composta pelos membros Cubículo, Prata, Buracão, Ventura e Mutum; a Formação Caldas se subdivide nos membros inferior e superior, e a Formação Traíras é composta pelos membros Boqueirão, Membro Rio Preto e Membro Rosário. No entanto, Martins Ferreira *et al.* (2018a), ao revisar as coberturas paleoproterozoicas e mesoproterozoicas da borda oeste do cráton São Francisco, elevou a formação Traíras a condição de Grupo. Nesse contexto o Grupo Traíras é composto pelas formações Caldas, Boqueirão, Rio Preto e Rosário, enquanto o Grupo Araí é representado pelas formações Arraias e Água Morna (Fig. 2.3.2). Além disso, os autores estabeleceram que as suítes intrusivas Serra da Mesa, Pedra Branca e Aurumina foram as fontes dos grupos Araí e Traíras.

Os metarcóseos grossos e quartzitos feldspáticos, juntamente com quartzitos micáceos e metaparaconglomerados da Formação Água Morna, marcam a base do Grupo Araí. A sua deposição se deu em condições continentais em sistemas de rios entrelaçados. Os metaparaconglomerados intercalados com quartzitos e derrames de basaltos e riolitos da Formação Arraias, recobrem a Formação Água Morna. A Formação Arraias é composta por sedimentos continentais e é subdividida nos membros: i) Cubículo, composto principalmente por metaconglomerado matriz suportado e por quartzitos feldspáticos, metarcóseos e metaconglomerados clasto suportados depositados em leques aluviais, ii) Prata, composto por espessos pacotes de metarcóseos e quartzitos feldspáticos com lentes de metaparaconglomerado matriz-suportado depositados em ambiente de rios entrelaçados, iii) Mutum, composto por quartzitos puros de ambiente eólicos, iv) Ventura, composto por metaconglomerados, quartzitos e intercalações métricas de metamarga e metagrauvaca depositadas em ambiente lacustre, e v) Buracão, composto por derrames de basalto, riolito, riodacito, dacitos, piroclásticas e brechas (Tanizaki *et al.* 2015).

As intercalações métricas e decamétricas de quartzitos e metaconglomerados clasto suportados da Formação Caldas marcam a base do Grupo Traíras e o fim da fase rift e as primeiras incursões marinhas. O contato dessa unidade com o Grupo Araí é marcado por discordância erosiva, enquanto seu contato com os membros superiores é transicional, com

presença de quartzito puro e metapelitos em sua porção superior. Essa Formação é recoberta pela Formação Boqueirão, que é composta por siltitos calcíferos intercalados com material carbonoso, além de quartzitos e filitos com lentes de mármore, depositados em condições marinhas rasas. A Formação Rio Preto é composta principalmente por quartzitos puros médios, em condição de plataforma siliciclástica. A Formação Rosário é composta por uma sequência psamo-pelito-carbonatada com níveis arenosos e argilosos com lentes de mármore puros, calcíticos ou dolomíticos depositadas em plataforma mista dominada por marés com eventuais episódios de tempestade.

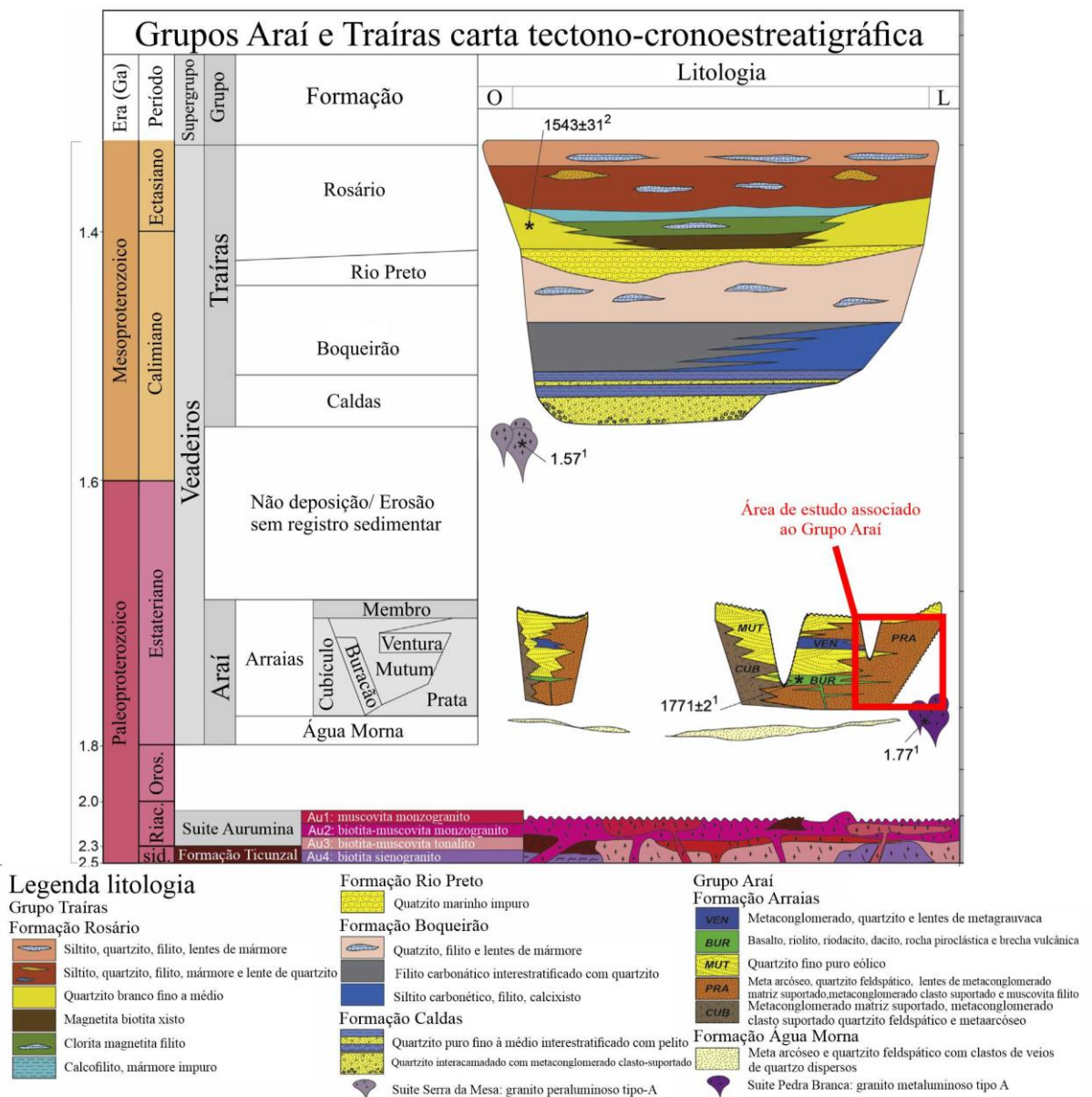


Figura 2.3.2 Carta tectono-cronoestratigráfica dos Grupos Araí e Traíras com destaque para a unidade estudada (Martins-Ferreira *et al.* 2018a).

2.3.2. Grupo Paranoá

A bacia que deu origem ao Grupo Paranoá foi controlada pelas mesmas falhas que deram origem a bacia do Araí (Martins-Ferreira *et al.*, 2018b). A bacia é de idade Steniana, interpretada como de margem passiva (Fuck *et al.* 2017) e mais especificamente como de margem cratônica que funcionaria como epicratônica em períodos de transgressão marinha (Martins-Ferreira *et al.*, 2018b). As rochas fonte dos sedimentos do Grupo Paranoá tem em sua maioria idade Riaciana (entre 2,2 e 2,0 Ga), relacionada ao ciclo Riaciano de acreção crustal que formou o paleocontinente São Francisco, constituído pela Suite Aurumina, embasamento cristalino dos Grupos Araí e Paranoá (Cuadros *et al.* 2017). Podem ser encontradas em menor proporção idades Neo e Mesoarqueanas associadas aos cratons São Francisco e o maciço de Goiás (Alkmim *et al.* 1993, Borges *et al.* 2017) e idades Estateriana e Calymiana (1,77 e 1,58 Ga) associadas aos Grupos Araí e Traíras (Matteini *et al.* 2012, Martins-Ferreira *et al.* 2018a). Souza *et al.* (2020) também identificou idades de 1.1 Ga restritas ao Topo do Grupo Paranoá.

O Grupo Paranoá, é caracterizado por sucessões marinhas rasas influenciadas por marés e tempestades (Campos *et al.*, 2013). O paraconglomerado da formação Ribeirão São Miguel, depositado em leques aluviais, marca a base do Grupo Paranoá, as demais formações em sequência marcam as variações do nível do mar na bacia ao longo do tempo. A formação Córrego Cordovil é composta por ritmitos de planície de maré (quartzitos e pelitos). A formação Serra da Boa Vista compreende quartzitos finos a médios depositados em ambiente de supramaré. A formação Serra Almécegas agrupa ritmitos depositados em ambiente de planície de maré da. A Formação Serra do Paranã reúne quartzitos médios a grossos típicos de ambiente de supramaré. A Formação Ribeirão Piçarrão é composta por metassiltitos argilosos depositados em plataforma externa com presença de lentes carbonáticas intercaladas com metarritmitos. A Formação Ribeirão do Torto engloba ardósias depositados em plataforma externa. A Formação Serra da Meia Noite é caracterizada por ritmitos arenosos depositados em inframaré, enquanto a Formação Ribeirão Contagem apresenta quartzitos finos de intermaré sobrepostos por ritmitos de planície de maré da Formação Córrego do Sansão (Fig 2.3.3). Calcários, dolomitos e estromatólitos agrupados na Formação Córrego do Barreiro indicam deposição em águas rasas e ocorrem no topo do Grupo Paranoá (Campos *et al.*, 2013, Martins-Ferreira *et al.* 2018b, Seraine *et al.* 2020).

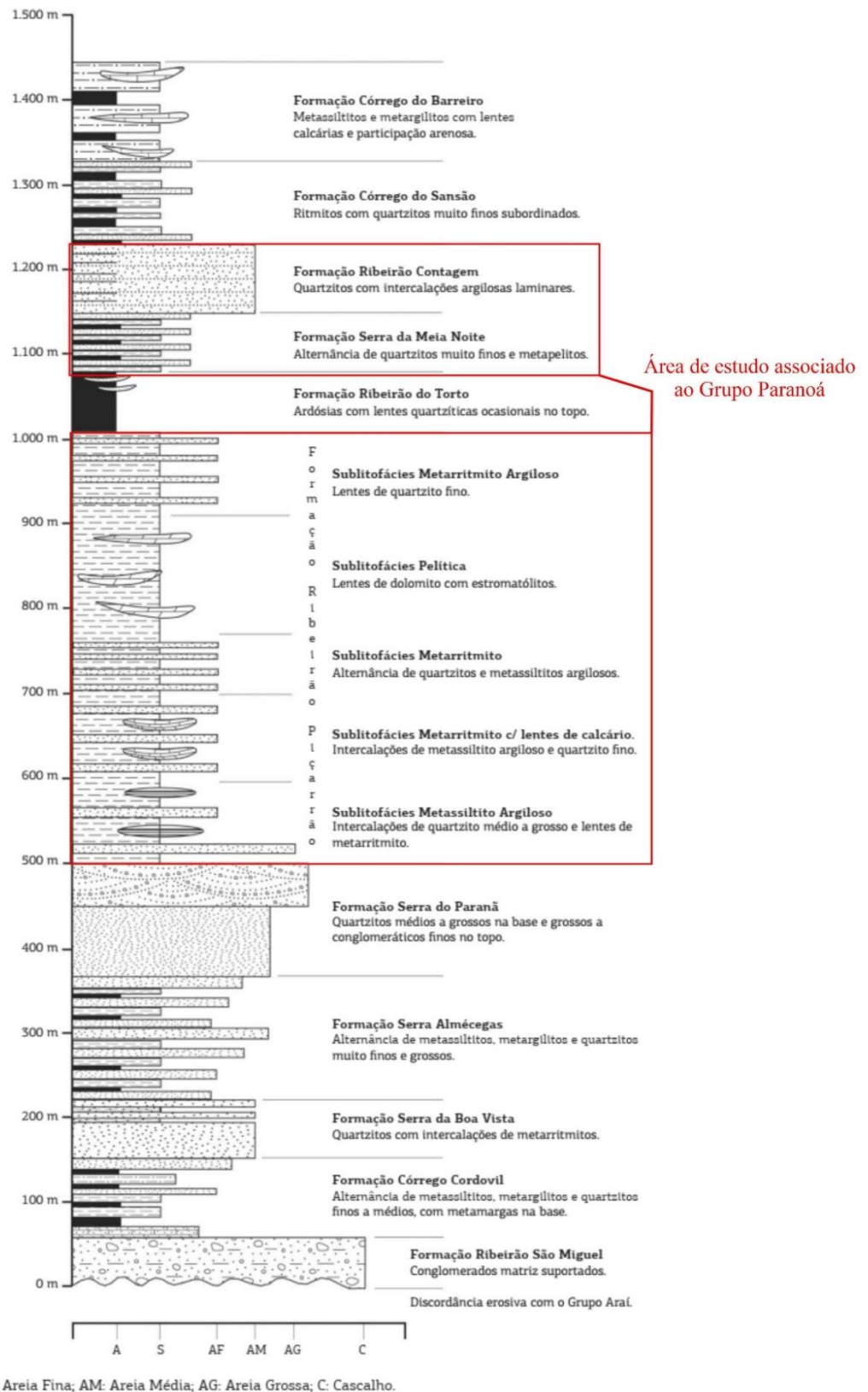


Figura 2.3.3 Coluna estratigráfica do Grupo Paranoá na área-tipo Alto Paraíso de Goiás/Distrito Federal (Campos *et al.* 2013).

Na porção central da área de estudo, o Grupo Paranoá apresenta dois domínios com grau de metamorfismo entre xisto verde baixo a anchimetamorfismo separados pela Falha

Serra do Cristal, com direção NNW-SSE (Martins-Ferreira, 2018). O domínio a leste da falha apresenta dobras suaves quilométricas com mergulho a SW, enquanto no domínio oeste as camadas estão intensamente dobradas e falhadas formando séries de dobras fechadas com eixo paralelo a direção da falha (NNW-SSE).

2.3.3. Ocorrências de Mn no Grupo Paranoá e Araí

O Mn está associado a ardósias e siltitos bastante intemperizados e ocorre principalmente como blocos, bolsões de minério pulverulento, na forma minério placoso e lamelar, e preenche fraturas e planos de acamamento (Guimarães, 1978; Baeta Jr. *et al.*, 1978).

O depósito de Pedra Preta, o maior da região, é formado por corpos alongados de minério com mergulho contrário ao acamamento (Baeta Jr. *et al.*, 1978). A estrutura mais importante associada ao minério é de brechas formadas por fragmentos angulosos de ardósia intemperizada imersas em matriz composta de argilominerais (caulinita), OH-Mn e OH-Fe (hematita e goethita). Essa matriz, localmente, pode individualizar bolsões (Guimarães, 1978). Guimarães (1978) identificou principalmente pirolusita, criptomelana, hollandita e litioforita, enquanto Baeta Jr. *et al.* (1978) identificaram, apenas pirolusita e psilomelana.

Nos depósitos de Extrema, Palmeiras e São Lourenço o minério ocorre na forma de bolsões ou preenche fraturas nos pelitos alterados. Em Extrema, o Mn ocorre na como psilomelana, pirolusita e manganita subordinada. Em Vereda ocorre pirolusita. Em outras áreas de estudo foram identificadas pirolusita, romanechita e hollandita. A sequência de mineralização manganita, psilomelana, pirolusita na forma de polianita e goethita da base para o topo é comum (Baeta Jr. *et al.*, 1978).

O minério em Vãozinho também apresenta estruturas de brecha, ocorrendo também grande número de cavidades, que muitas vezes são preenchidas por material argiloso. Em Buritizinho ocorre na forma de blocos, bolsões, preenche fraturas e como minério pisolítico que pode ter matriz argilosa ou cimento de OH-Mn, composto por pirolusita, criptomelana, e litioforita. Nesses dois depósitos há presença de fragmentos de quartzo anguloso leitoso (Baeta Jr. *et al.*, 1978; Guimarães, 1978).

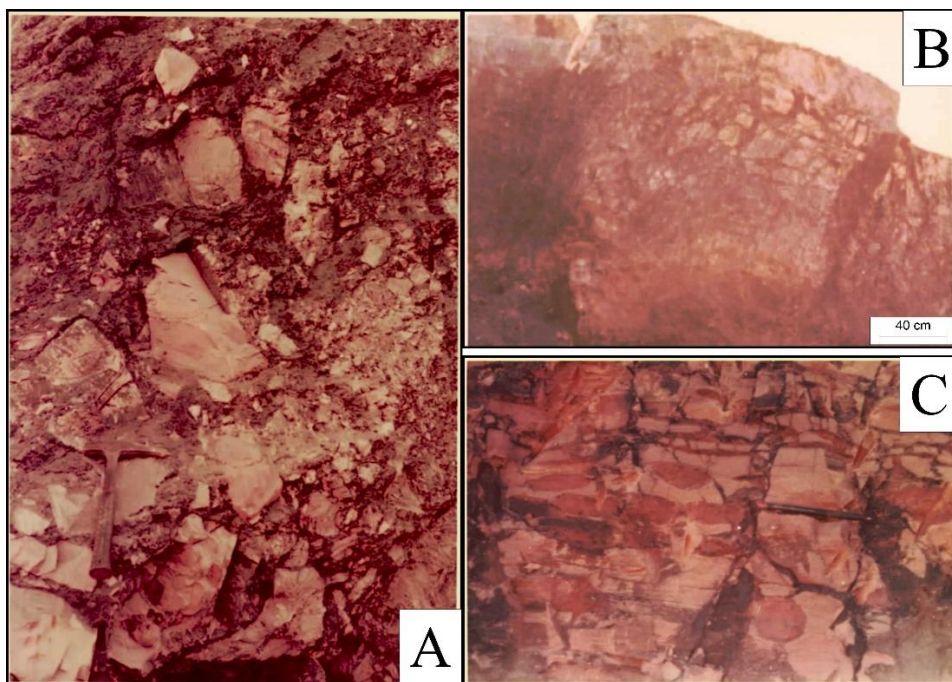


Figura 2.3.4 Estruturas de brecha associados a pelitos na mina de Pedra Preta (Baeta Jr. *et al.* 1978).

O minério foi classificado como supergênico tanto por Baeta Jr *et al.* (1978) como por Guimarães (1978). O primeiro definiu três fases para formação do minério: (1) fase de sedimentação, deposição de argilas contendo Mn em ambiente marinho; (2) deformação e baixo grau de alteração metamórfica da rocha sedimentar; (3) fase de remobilização e concentração de Mn em bacias restritas semelhantes a lagos. O Mn acumulado teria sido remobilizado durante o ciclo de erosão Velhas, onde o rebaixamento do nível de base possibilitou a deposição do Mn em zonas de fraqueza. Guimarães (1978) definiu que o enriquecimento ocorreu por meio de processos de lateritização associado a formação da superfície Sulamericana com acúmulo de Fe e Mn no solo. A retomada da erosão durante o ciclo Velhas causou a remoção do solo e a remobilização do Mn. O minério da região de São João d'Aliança apresenta teores de Mn entre 33,6 e 48,2%, de Fe que variam de 0,9 a 11,2%, Si de 0,9 a 11,7%, Al 1,2 a 13,8% e BaO de 0,7 a 5% (Baeta Jr. *et al.*, 1978).

O depósito de Monjolo, segundo Baeta Jr *et al.* (1978), é formado por uma camada de óxido de Mn (pirolusita) com 2 m de espessura intercalado com camadas de óxido de ferro com aproximadamente 5 m de espessura. Os autores associaram o depósito a lagos terciários formados durante o ciclo Sulamericano e Velhas (Baeta Jr. *et al.* 1978).

CAPÍTULO 3: MATERIAIS E MÉTODOS

Nesse estudo, foram selecionados 12 locais e coletadas 25 amostras. Desses locais, um está associado ao Grupo Araí (Monjolo) e os demais ao Grupo Paranoá (Figura 1). Os locais selecionados foram: 1. Monjolo (MJ), 2. Minaçu (Mi), 3. Raizama (RZ), 4. Niquelândia (NQ), 5. Pedra Preta (PP) 6. Fortaleza (FT), 7. Vãozinho (VZ) 8. Corrente (CR), 9. Vereda (VR), 10. Formosa (FA), 11. Brazlândia (BL), 12. Formoso (FO) (Tabela 3.1.1). Desses, os dois últimos são apenas ocorrências de óxi-hidróxidos de Mn.

Tabela. 3.1.1 Localização e vias de acesso aos locais estudados

Grupo	Depósito	Litotipo	Latitude	Longitude	Estrutura do minério	Minerais de Mn	Acesso
Paranoá	Raizama (RZ)	Quartzito	13°38'09"S	47°47'32"W	Preenchendo fratura, blocos	Romanechita, Litioforita e pirolusita	50 km a NW de Cavalcante pela GO-241 e 30 km a SW em via não pavimentada
	Niquelândia (NQ)	Metassiltito	14°24'52"S	48°02'05"W	Blocos, preenchendo fraturas	Hollandita, criptomelana e litioforita	53 km a leste de Niquelândia pela GO-132 e 4 km a leste por via não pavimentada
	Minaçu (Mi)	Quartzito	13°31'23"S	48°02'56"W	Blocos	Pirolusita e romanechita	54 km a norte de Minaçu em via pavimentada
	Corrente (CR)	Quartzito	14°35'52"S	47°38'51"W	Bolsão	Hollandita e criptomelana	3 km a norte de São João d'Aliança pela BR-010 e 26 km a oeste por via não pavimentada
	Vãozinho (VZ)	Metassiltito	14°33'08"S	47°44'03"W	bolsão, preenchendo fraturas, blocos,	Hollandita, criptomelana, litioforita e pirolusita	3 km a norte de São João d'Aliança pela BR-010 e 33 km a oeste por via não pavimentada
	Vereda (VR)	Metassiltito	14°39'06"S	47°44'36"W	Bolsão, preenchendo fraturas, blocos	Romanechita e pirolusita	3 km a norte de São João d'Aliança pela BR-010 e 32 km a oeste por via não pavimentada
	Pedra Preta (PP)	Ardósia/metassiltito	14°20'06"S	47°23'45"W	blocos	Romanechita e pirolusita	30 km a norte de São João d'Aliança pela BR-010 e 20 km a leste por via não pavimentada
	Formosa (FA)	Quartzito	15°24'16"S	47°28'09"W	Bolsão, preenchendo fraturas	Hollandita	26 km a NW de Formosa pela GO-430 e 6 km a leste por via não pavimentada
	Brazlândia (BL)	Quartzito	15°34'49"S	48°02'38"W	Blocos	Romanechita e pirolusita	27 km a leste de Brazlândia pela DF-001 e 3 km a norte por via não pavimentada
	Formoso (FO)	Calcário	15°15'14"S	46°20'45"W	Blocos	Romanechita	40 km ao sul de Formoso pela MG-400 e 23 km ao sul por via não pavimentada
	Fortaleza (FT)	Ardósia	14°29'24"S	47°32'37"W	lamelar, blocos	Romanechita, hollandita, criptomelana e pirolusita	23 km a norte de São João d'Aliança pela BR-010 e 5 km a oeste por via não pavimentada
Araí	Monjolo (MJ)	Metaparaconglomerado/Quartzito	14°07'21"S	48°01'36"W	Camada	Hausmannita, criptomelana e pirolusita	4 km a leste de Colinas do Sul pela GO-239 e 5 km a norte por via não pavimentada

3.1. Composição mineral, químico-mineral e geoquímica.

Para caracterizar os OH-Mn com o mínimo de contaminação pela rocha encaixante, as amostras foram fragmentadas e coletados apenas os fragmentos de manganês. Sempre que possível, a amostra foi lavada no ultrassom para remoção de argilominerais pertencentes a rocha encaixante. A determinação das características óticas e texturais, assim como a verificação da ausência de minerais detríticos não manganésíferos foi feita por lupa binocular. Após esse procedimento, as amostras foram pulverizadas e submetidas a análise mineralógica e química. 10 fragmentos não pulverizados foram utilizados na confecção de seções polidas (os locais escolhidos foram RZ, NQ, VZ, FT, MJ, PP, FO, BL e FA) analisadas no microscópio eletrônico de varredura (MEV, ZEISS modelo EVO LS15), operando na voltagem de 20 kV, da UNESP, Campus de Ilha Solteira, e por microsonda eletrônica (JEOL JXA-8230) onde foram analisados Na, Mg, F, Al, Si, P, Cl, K, Y, Ca, Mn, Ti, Ni, Cr, Y, Fe, Ba à 15 kV e 10 nA e Zn, Pb, Sr, Cu, Co à 20 kV e 20 nA, na Universidade de Brasília.

A análise mineralógica foi realizada por difratometria de raios-X (DRX, Rigaku-Ultima IV) com tubo de Cu acoplado e operado à 35 kV e 15 mA no Instituto de Geociências da Universidade de Brasília. A análise qualitativa foi determinada por meio do software Jade 9.0 com banco de dados PC-PDF (Powder diffraction file – ICDD). As análises químicas totais foram realizadas na ALS, onde foram determinados SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, Na₂O, K₂O, TiO₂, MnO, P₂O₅ por ICP-AES e Cr, Cs, Ga, Hf, Nb, Rb, Sn, Ta, Th, U, V, W, Y, Zr e ETR por ICP-MS, após fusão por metaborato de lítio e digestão por ácido nítrico. As, Co, Cu, Ni, Pb, Sc, Tl, Zn foram analisados por ICP-AES após digestão com quatro ácidos (HCl, HNO₃, HF, HClO₄). A perda ao fogo (LOI) foi feita por gravimetria a 1000°C.

Foi feita extração com água régia a quente para determinar o modo de ocorrência dos elementos, se associados majoritariamente aos óxi-hidróxidos de manganês e eventualmente de Fe ou aos silicatos. Nesta extração foram analisados os mesmos elementos da extração total além de Ag, Au, B, Be, Bi, Cd, Ge, In, Li, Mo, Pd, Pt, Re, S, Sb, Se, Te e isótopos de Pb (²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb) por ICP-MS, sendo usado os padrões OREAS 905, MRGeo08, OREAS 920 e OREAS-45f. Devido à falta de dados de isótopos de Pb na região foram analisadas três amostras: uma possível rocha fonte, granito da Suíte Aurumina representando o embasamento da região e dois pelitos do Grupo Paranoá representando as encaixantes dos minérios de Mn.

O fracionamento dos ETR foi normalizado com relação à crosta continental superior (UCC) de McLennan (2001). As razões Ce/Ce*, Eu/Eu*, Tm/Tm* e (La/Yb)_n foram calculadas de acordo com as equações:

$$\begin{aligned} (1) \text{ Ce/Ce}^* &= (\text{Ce}/64) / [(\text{La}/30) * (\text{Pr}/7,1)] \\ (2) \text{ Eu/Eu}^* &= (\text{Eu}/0,88) / [(\text{Sm}/4,5) * (\text{Gd}/3,8)] \\ (3) \text{ Tm/Tm}^* &= (\text{Tm}/0,33) / [(\text{Er}/2,3) * (\text{Yb}/2,2)] \\ (4) \text{ (La/Yb)}_n &= (\text{La}/30) / (\text{Yb}/2,2) \end{aligned}$$

As análises isotópicas de Sm-Nd seguiram o método descrito por Gioia e Pimentel (2000). O processo de preparação de amostra consiste na mistura de 50 à 100 mg de rocha com spike, seguido de dissolução com HNO₃ e 4 ml de HF concentrado. A dissolução é seguida de evaporação e o resíduo é dissolvido novamente por HF e HNO₃ em proporção de 4 para 1 que é aquecida a 190°C por 4 dias. A solução passa por evaporação mais duas vezes sendo adicionado HNO₃ na primeira e 6N HCl na segunda. O Nd foi isolado dos demais elementos por meio da resina AG50-X2 enquanto o Sm foi separado usando a resina AG50W-X8. As análises de isotópicas de Sm-Nd e Sr foram realizadas no Thermo Scientific TRITON™ Plus Thermal Ionization Mass Spectrometer (TIMS) no laboratório de Geocronologia da Universidade de Brasília (UnB) sendo medidos separadamente em filamento de tungstênio com solução de TaF, e foram analisadas 11 amostras (de MJ, MI, RZ, NQ, PP, VZ, CR, VR, FA, BL, FO). Foi usado o padrão USGS BHVO-1 com razão ¹⁴³Nd/¹⁴⁴Nd=0.512996 ± 0.000006 (2SD; n = 7) para Sm-Nd e o NBS-987 com razão ⁸⁷Sr/⁸⁶Sr=0.710257 ± 0.000007 (2SD; n = 9). Os valores de TDM, εNd(0) e f^(Sm/Nd) foram calculados através das seguintes equações:

$$\begin{aligned} (1) \text{ } \epsilon(\text{Nd}) &= \left[\frac{(^{143}\text{Nd}/^{144}\text{Nd})_R^0}{(^{143}\text{Nd}/^{144}\text{Nd})_{\text{CHUR}}^0} - 1 \right] \times 10^4 \\ (2) \text{ Tdm} &= \frac{1}{\lambda} \ln \left[\frac{(^{143}\text{Nd}/^{144}\text{Nd})_R^0 - (^{143}\text{Nd}/^{144}\text{Nd})_{\text{dm}}^0}{(^{147}\text{Sm}/^{144}\text{Nd})_R^0 - (^{147}\text{Sm}/^{144}\text{Nd})_{\text{dm}}^0} + 1 \right] \\ (3) \text{ f}^{\text{Sm/Nd}} &= \left[\frac{(^{147}\text{Sm}/^{144}\text{Nd})_R^0}{(^{147}\text{Sm}/^{144}\text{Nd})_{\text{CHUR}}^0} - 1 \right] \end{aligned}$$

Sendo R as razões isotópicas da rocha e dm e CHUR dos reservatórios do manto depletado e chondrito, respectivamente. Todos os valores calculados no tempo zero, valores das razões medidas hoje.

A análise estatística multivariada foi feita no software Statsoft Statistica 12 pelo método de componentes principais. A análise que melhor permitiu identificar grupos de amostras similares utilizou MnO, Fe₂O₃, SiO₂, Al₂O₃, K₂O, P₂O₅, LOI, As, Ba, Co, Cu, Ni, Pb, Sr, Th, Tl, U, V, Y, Zn, Zr e ETR e dois fatores que agruparam as amostras e os elementos com base na variância.

Capítulo 4: GENESIS OF MN DEPOSITS IN NORTHEASTERN GOIÁS, BRAZIL: MINERALOGY, GEOCHEMISTRY, AND Nd-Sr-Pb ISOTOPES

Gabriel Castro de Oliveira Domingues ^a; Adriana Maria Coimbra Horbe ^a; Márcio Fernando dos Santos Albuquerque^b

^a Universidade de Brasília, Instituto de Geociências, Campus Universitário Darcy Ribeiro, 70910-900 Brasília, Distrito Federal, Brazil; ^bUniversidade Estadual Paulista, Faculdade de Ciências e Tecnologia, Campus de Presidente Prudente, São Paulo, Brazil

ABSTRACT

Small Mn deposits occur in the external zone of the Brasilia fold belt, a Neoproterozoic orogen located in Central Brazil. The deposits are associated with the Arai Group a Paleoproterozoic rift basin and with Paranoá Group a Mesoproterozoic cratonic margin basin. The Mn in these small deposits occur in thin lamellae, fractures, pockets, and surface blocks, and have supergene origin. The study carried out by X-ray diffraction, SEM, EPMA and chemical analysis, indicate hausmannite, cryptomelane (hollandite), pyrolusite paragenesis, low P₂O₅ contents, high Sr, Tl, and U concentrations, expressive positive Eu/Eu* anomalies, high (La/Yb)_N, and Mn/Fe ratios, and the lowest Co/Zn ratios are the features one of the Arai Group Mn deposits. Romanechite, hollandite, lithiophorite, cryptomelane and pyrolusite paragenesis, higher Al₂O₃, Ba, Co, Cu, Ni concentration, the highest Co/Zn ratios, and the major depletion of LREE concerning UCC are the features of those associated with the Paranoá Group. Chemical variations in the Mn from the Paranoá Group may be related to the primary processes of hydrothermal enrichment that concentrate Al, Ba, Co, Cu, Ni and Zn, and to supergene activity that forms romanechite and lithiophorite. The lower ratios of (La/Yb)_N and fractionation in Sm and Nd isotopes, in addition to the more radiogenic Sr isotopes values are also associated with supergene process. The ²⁰⁸Pb/²⁰⁶Pb and ²⁰⁷Pb/²⁰⁶Pb ratios that do not vary with the (La/Yb)_N ratios, the high ²⁰⁶Pb/²⁰⁴Pb in samples MJ1 and RZ1 samples that have high U/Pb ratios. εNd(0) values (-8.8 to -20.7 Ga) and TDM (2.24 to 3.46 Ga) indicate ancient continental source. The Mn of the Araí Group can be characterized as hydrothermal. The Mn of the Paranoá Group has a probable ancient continental source, has evidence of remobilization that increased its metal content, being related to hydrothermal or supergene processes or an overlap of the two.

1. INTRODUCTION

Marine basins are ideal sites for manganese accumulation (Nicholson, 1992). This environment can form world-class deposits in euxinic basins associated with restricted seas containing H₂S, whose origin may be related to hydrothermal influence (Force & Cannon, 1988; Roy et al., 1992; Calvert & Pedersen, 1996). Smaller deposits form in the upwelling zone (redoxline or oxygen minimum zone) of shallow marine, or in swamps, and lakes (Nicholson, 1992; Maynard, 2010). Hydrothermal influence also forms small deposits with higher concentrations of trace elements, such as Co, Cu, Pb, Ni, Tl, and others (Nicholson, 1992; Conly et al., 2011, Albuquerque et al., 2017). In addition, on the ocean floor, the oxidizing to sub-oxidizing waters (hydrogenous environment) allows the formation of Mn deposits with a high concentration of trace elements in polymetallic nodules (Halbach, 1986; Bau et al., 2014). Regardless of the type of deposit, weathering can remobilize and

reprecipitate manganese minerals as new phases, forming manganese crusts with high MnO contents sometimes, with economic importance (Nicholson, 1992; Varentsov, 1996; Carmichael *et al.*, 2017; Albuquerque *et al.*, 2017; Dash *et al.*, 2020).

Due to the ability of Mn oxyhydroxides to retain chemical elements in their structures, it is possible to identify the characteristics and geochemical heterogeneities of depositional environments (Post, 1999). In marine euxinic and upwelling basins, the manganese is Ba, Ca, K, Mg, Na, and Sr enriched due to the direct precipitation of seawater and organic matter with subsequent diagenesis (Roy, 2006; Maynard, 2010). Under hydrothermal influence such as hot fumarole fluids from oceanic or continental crust leaching, the manganese is As, Ba, Cu, Li, Mo, Pb, Sb, Sr, V, and Zn enriched (Nicholson, 1992; Maynard, 2010). In swamps and lakes of continental environment, Mn, and Ba correlate (Nicholson, 1992). Most Mn deposits have undergone supergene enrichment due to mineral dissolution and reprecipitation. In this case, the chemical composition will depend on the parent rock, the adsorption processes, and the Eh and pH conditions to form Mn oxyhydroxides Ni, Co, Ba, Al, and K enriched (Varentsov, 1996). In this condition, supergene lithiophorite, cryptomelane, hollandite, and romanechite are formed (Ostwald, 1988; Costa *et al.*, 2005; Albuquerque *et al.*, 2017; Dash *et al.*, 2020).

In Central Brazil (northeastern Goiás State), several small deposits of Mn occur as layers on the metaparaconglomerates and quartzites of the Araí Group, and in thin lamellae, fractures, pockets, and surface blocks on pelites from the Paranoá Group (Guimarães, 1978; Baeta Jr. *et al.*, 1978). These small deposits, exploited since the 1960s, present ~2 m thick average and between 200 m and 300 m long, and 33.6 to 48.2% of MnO contents. In one of these small deposits, around 615,000 tons with 45.8% MnO were exploited (Baeta Jr. *et al.*, 1978). Nevertheless, the previously carried out studies are restricted to fieldwork, optical methods, x-ray diffraction, and chemical analysis of Si, Al, Fe, Mn, and Ba (Guimarães 1978 and Baeta Jr. *et al.* 1978). According to these authors, the Mn is the product of supergene enrichment of siltstones and slates of the Paranoá Group containing cryptomelane, pyrolusite, and lithiophorite. Based on this knowlagent, and more robust and sophisticated of mineralogy, geochemistry, and Sr, Nd, and Pb isotopes analysis, this study present a new approach of the several Mn small deposits along the outer zone of the Brasília fold belt in Goiás State, Central Brazil. The goal of this study is to identify the depositional environment, the possible diagenetic influences, the source of manganese, and the transformations related to the sedimentary and supergene environments, and thus reconstruct the deposition conditions in the context of the Proterozoic basins of the Araí and Paranoá Groups.

2. GEOLOGICAL CONTEXT

The Brasília, Araguaia, and Paraguay Belts form the Tocantins Province, a Neoproterozoic orogen in Central Brazil. It was formed after the collision between the Amazonian and São Francisco paleocontinents, with contributions from the Parnaíba and Paranapanema blocks, currently covered by Phanerozoic sediments (Fuck *et al.*, 2017). The external zone of the Brasília Belt, the eastern part of the Tocantins Province, constitutes several lithostratigraphic units commonly separated by thrusts and reverse faults (Dardenne, 2000; Valeriano *et al.*, 2008).

In the study area, schists and paragneisses of the Ticunzal Formation (Marini *et al.* 1984) comprise the oldest rocks (> 2.2 Ga, T_{DM} : 2.0-2.8 Ga) of the Brasília Fold Belt external zone (Pimentel *et al.*, 2004; Botelho *et al.*, 2006; Cuadros *et al.*, 2017; Fuck *et al.*, 2014).

Intersecting the Ticunzal Formation there are several granitoid bodies related to the Aurumina Suite (U-Pb 2.18 to 2.12 Ga; Botelho *et al.*, 2006a; Fuck *et al.*, 2014; Sousa *et al.*, 2016; Cuadros *et al.*, 2017).

Overlaying the basement rocks occurs a volcano-sedimentary sequence of the Araí Group and the sedimentary sequence of the Paranoá Group, respectively. The Paranoá Group overlaps the rocks of the Araí Group. The Sthaterian Araí Group is a rift-type basin that evolved into a sag-type in the western portion of the São Francisco craton, which underwent uplift and erosion between 1.75 and 1.55 Ga (Martins-Ferreira *et al.*, 2018). The Araí Group comprises metasedimentary and metavolcanosedimentary rocks divided into the Água Morna and Arraias formations, the pre-rift and rift phases, respectively. Coarse meta-arkoses and feldspathic quartzites, together with micaceous and metaparaconglomerates quartzites from the Água Morna Formation, mark the base of the Araí Group. Its deposition took place under continental conditions in braided river systems. Metaparaconglomerates interlayered with quartzites and basalt and rhyolite flow from the Arraias Formation overlies the Água Morna Formation. According to Tanizaki *et al.*, (2015), the Arraias Formation is subdivided into the following members: i) Cubículo, mainly composed of matrix-supported metaconglomerates and feldspathic quartzites, metarkoses, and clast-supported metaconglomerates deposited in alluvial fans, ii) Prata, which consists of thick packages of metarkoses and feldspathic quartzites with matrix-supported metaparaconglomerate lenses deposited in an environment of braided rivers, iii) Mutum, which gathers aeolian quartzites, iv) Ventura, composed of metaconglomerates, quartzites and metric intercalations of metamarl and metawackes deposited in a lake environment, and v) Buracão, volcanic member, which comprise basalt, rhyolite, rhyodacite, dacites, pyroclastic rocks, and breccias.

Despite Tanizaki *et al.*, (2015) considering the Traíras Formation part of Araí Group, Martins-Ferreira *et al.*, (2018) elevated the Traíras Formation to the status of a Group. In this context, the Traíras Group is composed of the Caldas, Boqueirão, Rio Preto, and Rosário formations, while the Araí Group is represented by the Arraias and Água Morna formations.

The Paranoá Group is characterized by shallow marine successions influenced by tides and storms (Campos *et al.*, 2013). According to Campos *et al.*, (2013), the paraconglomerate of the Ribeirão São Miguel Formation, deposited in alluvial fans, marks the base of the Paranoá Group, and the other formations in sequence mark the sea level variations in the basin over time. The Córrego Cordovil Formation comprises tidal rhythmites (quartzites and pelites). The Serra da Boa Vista Formation gathers fine to medium quartzites deposited in a supratidal environment. The Serra Almécegas formation groups rhythmites deposited in a tidal environment. The Serra do Paranã Formation consists of medium to coarse quartzites typical of the supratidal environment. The Ribeirão Piçarrão Formation is composed of clayey metasiltstones deposited on an external platform with the presence of carbonate lenses interspersed with metarrhythmites. The Ribeirão do Torto Formation includes slates deposited on an external platform. The Serra da Meia Noite Formation is characterized by sandy rhythmites deposited in infratidal, while the Ribeirão Contagem Formation presents fine intertidal quartzites superimposed by tidal plain rhythmites of the Córrego do Sansão Formation. Limestones, dolomites, and stromatolites grouped in the Córrego do Barreiro Formation indicate deposition in shallow waters and occur at the top of the Paranoá Group (Campos *et al.*, 2013, Martins-Ferreira *et al.* 2018, Seraine *et al.* 2020).

Zircon distribution patterns show a dominant Rhyacian source and a minor contribution of Statherian, Neoproterozoic, and Paleoproterozoic sources both to Araí and Paranoá

groups (Martins-Ferreira *et al.*, 201a). In this context, The Aurumina Suite is one of the main sources for both Araí and Paranoá Group, and it is mostly related to the Rhyacian cycle of crustal (~2.2 and 2.0 Ga) accretion that formed the São Francisco paleocontinent (Cuadros *et al.* 2017). Neo and Mesoarchean populations are assigned to the São Francisco craton and Goiás Massif can be found in smaller proportions (Borges *et al.* 2017) and Staterian and Calymian ages (1.77 and 1.58 Ga) associated with the Araí and Traíras groups (Matteini *et al.* 2012, Martins-Ferreira *et al.* 2018a). In addition, Souza *et al.* (2020) also identified ages of 1.1 Ga restricted to the top of the Paranoá Group.

3. MATERIALS AND METHODS

In this study, 12 sites of small Mn deposits were selected from where 26 samples were collected. Among these sites, one is associated with the Araí Group (Monjolo), and eleven with the Paranoá Group (Fig. 1). The selected locations were: 1. Monjolo (MJ), 2. Minaçu (MI), 3. Raizama (RZ), 4. Niquelândia (NQ), 5. Pedra Preta (PP) 6. Fortaleza (FT), 7. Vãozinho (VZ) 8. Corrente (CR), 9. Vereda (VR), 10. Formosa (FA), 11. Brazlândia (BL), 12. Formoso (FO) (Table 1).

Table 1. Location and lithotype of deposits/occurrences

Group	Deposit	Lithotype	Latitude	Longitude	Ore structure	Mn minerals
Araí	Monjolo (MJ)	Metaparaconglomerate/ quartzite	14° 07'21"S	48° 01'36"W	Layered	Hausmannite, cryptomelane and Pyrolusite
	Raizama (RZ)	Quartzite	13°38'09"S	47°47'32"W	Filling fracture, blocks	Romanechite, Lithiophorite and pyrolusite
	Niquelândia (NQ)	Metasiltite	14°24'52"S	48° 02'05"W	Filling fracture, blocks	Hollandite, cryptomelane and lithiophorite
	Minaçu (Mi)	Quartzite	13°31'23"S	48° 02'56"W	blocks	Pyrolusite and romanechite
Paranoá	Corrente (CR)	Quartzite	14°35'52"S	47°38'51"W	blocks	Hollandite and cryptomelane
	Vãozinho (VZ)	Metasiltite	14°33'08"S	47°44'03"W	Pocket, filling fracture, blocks	Hollandite, cryptomelane. lithiophorita and pyrolusite
	Vereda (VR)	Metasiltite	14°39'06"S	47°44'36"W	Pocket, filling fracture, blocks	Romanechite and pyrolusite
	Pedra Preta (PP)	Slate/metasiltite	14°20'06"S	47°23'45"W	blocks	Romanechite and pyrolusite
	Formosa (FA)	Quartzite	15°24'16"S	47°28'09"W	Pocket, filling fracture	Hollandite
	Brazlândia (BL)	Quartzite	15°34'49"S	48° 02'38"W	Blocks	Romanechite and pyrolusite
	Formoso (FO)	Limestone	15°15'14"S	46°20'45"W	Blocks	Romanechite
	Fortaleza (FT)	Slate	14°29'24"S	47°32'37"W	Platy, blocks	Romanechite, hollandite. cryptomelane and pyrolusite

The samples were broken and only the Mn fragments were collected, to obtain the Mn composition with minimal contamination by the host rock. The samples were ultrasound cleaned to remove contaminants whenever possible. The determination of the optical and textural features, as well as the verification of the purity of the sample, was carried out in the stereoscope. After this procedure, the samples were crushed and pulverized in a mortar and submitted for mineralogical and chemical analysis. The mineralogical analyses were performed by X-ray diffraction (XRD, Rigaku-Ultima IV) with a Cu tube and operated at 35 kV and 15 mA at the Geosciences Institute of the University of Brasília. Qualitative analyses were performed using the Jade 9.0 program with a PC-PDF database (Powder diffraction file – ICDD).

Moreover, fragments were selected and used for the preparation of polished sections to be analyzed in the scanning electron microscope (SEM) and by electronic microprobe (EPMA). The SEM analyses were performed in a ZEISS microscope model EVO LS15 at 20 kV of voltage, after Au-Pd coating, in a UNESP, Campus de Ilha Solteira. The electronic microprobe (EMPA, JEOL JXA-8230) analyses were carried out at Brasília University, after carbon coating. The selected elements for mineral geochemistry analyses were Na, Mg, F, Al, Si, P, Cl, K, Y, Ca, Mn, Ti, Ni, Cr, Y, Fe, and Ba analyzed at 15 kV and 10 nA, and Zn, Pb, Sr, Cu, and Co at 20 kV and 20 nA.

The bulk chemical analyses were performed at ALS Laboratory Service, where SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, Na₂O, K₂O, TiO₂, MnO, P₂O₅ were determined by ICP-AES and Cr, Cs, Ga, Hf, Nb, Rb, Sn, Ta, Th, U, V, W, Y, Zr, and REE by ICP-MS, both after fusion by lithium metaborate and digestion by nitric acid. As, Co, Cu, Ni, Pb, Sc, Tl, and Zn were analyzed by ICP-AES after digestion with four acids (HCl, HNO₃, HF, HClO₄). The loss of ignition (LOI) was determined by gravimetry at 1000°C. The aqua regia leaching was carried out to determine the mode of occurrence of the elements, whether associated mainly with Mn oxyhydroxides and eventually Fe or silicates. The leaching rates for each element have been calculated by the ratio between the concentration of the element obtained through leaching, divided by the concentration of the element in the total extraction. In this extraction, the same elements of the total extraction were analyzed in addition to Ag, Au, B, Be, Bi, Cd, Ge, In, Li, Mo, Pd, Pt, Re, S, Sb, Se, Te and Pb isotopes (²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb) by ICP-MS.

Sm-Nd isotopic analyses followed the method of Gioia and Pimentel (2000). Sm-Nd and Sr isotopic analyses were performed using the Thermo Scientific TRITON™ Plus Thermal Ionization Mass Spectrometer (TIMS) at the Geochronology Laboratory of the University of Brasília (UnB). The USGS BHVO-1 standard with a ratio ¹⁴³Nd/¹⁴⁴Nd = 0.512996 ± 0.000006 (2SD; n = 7) was used for Sm-Nd and the NBS-987 with a ratio 87Sr/86Sr = 0.710257 ± 0.000007 (2SD; n = 9). These isotopes were determined in the total sample.

Multivariate statistical analyses were performed using the STATISTICA 12 software using the principal components method. First, factor analyses were performed in both Araújo and Paranoá groups to select the elements above 0.7 or 0.6 of factor loading for supporting the task of interpretation (just in the second loaded matrix of Paranoá Group deposits were used elements with of > 0.6 factor loading). For the Araújo Group deposits were used components 1 and 2 with 71.1 and 25.5% of the variance and were just considered MnO, SiO₂, Al₂O₃, K₂O, LOI, As, Ba, Co, Cu, Ni, Pb, Rb, Sc, Sr, Th, Tl, U, V, Y, Zr, and REE. On the other hand, the Paranoá Group multivariate statistical analyses involved two loaded matrices, once in the first matrix most of the elements were associated with two samples that

have anomalous content of trace elements. In the first matrix were used components 1 and 2 with 44.03 and 32.3% of the variance. Therefore, MnO, SiO₂, Al₂O₃, K₂O, MgO, TiO₂, Co, Cu, Ni, Nb, Rb, Th, U, Y, and REE were considered for the Paranoá Group. In addition, on the second matrix, based on components 1 and 2 with 40.04 and 26.25% of the variance, MnO, SiO₂, Al₂O₃, K₂O, TiO₂, P₂O₅, LOI, Ba, Ni, Rb, Th, V, Zn, and Zr were used.

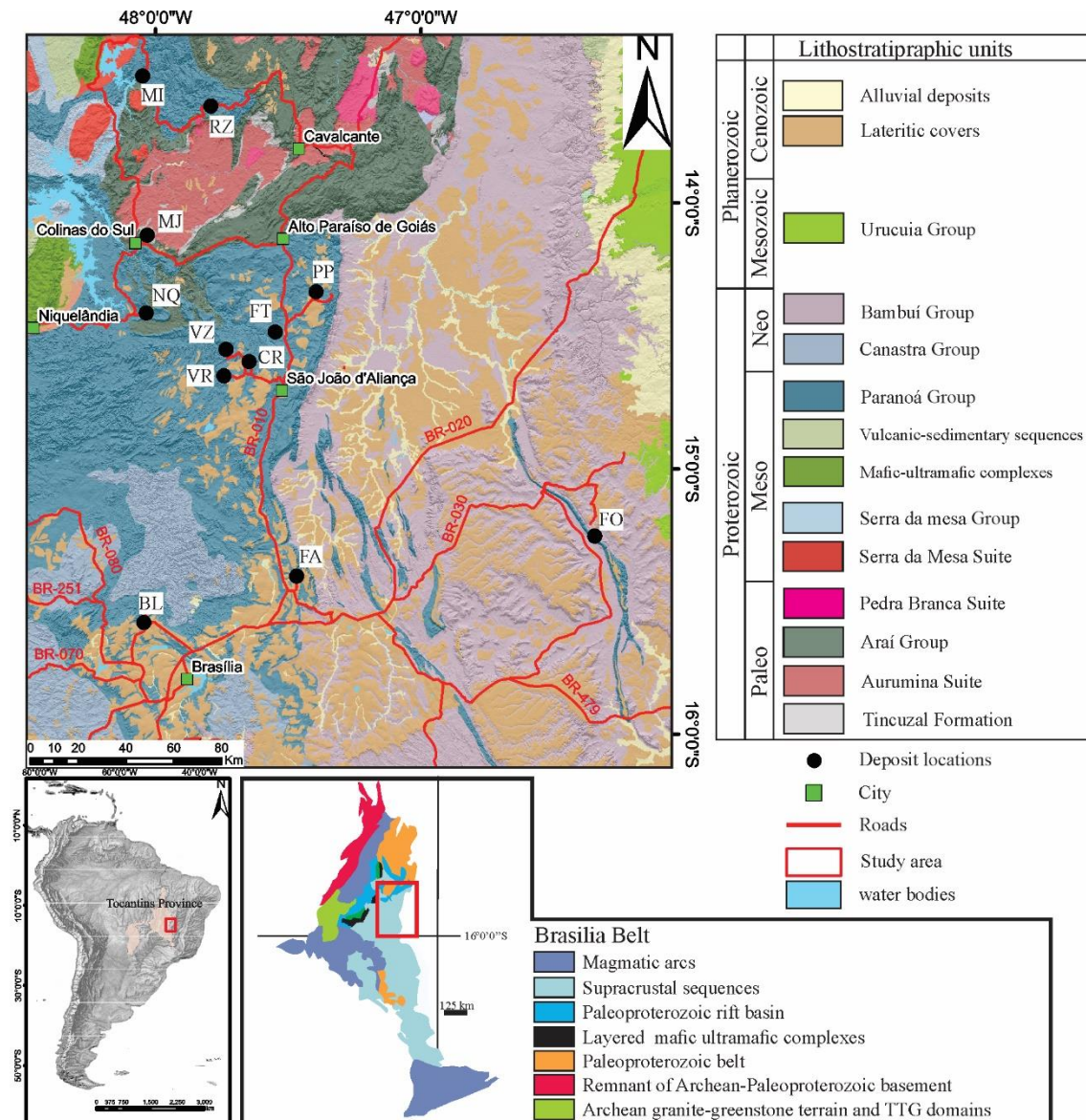


Figure 1. Geological map with access roads and sampled points. Monjolo (MJ), Minaçu (MI), Raizama (RZ), Niquelândia (NQ), Pedra Preta (PP), Fortaleza (FT), Vaizinho (VZ), Corrente (CR), Vereda (VR), Formosa (FA), Brazlândia (BL), Formoso (FO). Modified Brasília Belt from Delgado et al. (2013).

4. RESULTS

The Mn oxyhydroxides Araí Group hosted, represented by MJ deposit, is included in the Prata Member of the Arraías Formation. The massive Mn is hosted in layers up to 7 m thick (Fig. 2A and B) and occurs interstratified with weathered white matrix-supported

metaconglomerates and quartzites. The Mn layers grades laterally to powdery Mn levels, with major fracture concentrations (Fig. 2C).

The Mn oxyhydroxides Paranoá Group hosted, represented by the RZ, NQ, MI, CR, VZ, VR, PP, FA, BL, FO, and FT deposits, were divided into four types according to the mode of occurrence, characteristics, and morphologies (Table 1): (1) Mn thin lamellae interstratified with the red to purple slates which, sometimes, are folded (samples FT1, FT2, FT4, Fig. 2D, E, and F); (2) Mn filling fractures in the quartzites and metasiltstones. The fractures have millimeters to a few centimeters in width by meters in extension. In addition, there are fractures filled by Mn-veins measuring 0.5 m in width by ≤ 5 in extension (samples RZ2, VZ1, Fig. 2G, H, I and J); (3) Mn as powdery pockets up to 1 m in diameter, and between 2 and 7 m deep widespread into the quartzites and metasiltstones (samples RZ3, CR1, CR2, VZ3, VR2, FA1, FA2, Fig. 2K); (4) hard and shining Mn as centimetric to metric massive surface blocks enveloped by slates and metasiltstones saprolites, and, sometimes in reddish soils (samples NQ1, MI1, PP1, BL1, FO1, Fig. 2L). Colluvium deposits were also described over quartzite in RZ deposit (Fig. 2I). These Mn modes, and morphologies found at Paranoá Group are associated with grayish and pinkish friable quartzites from the Serra da Meia Noite Formation (samples from CR, RZ, FA, MI) and from the Ribeirão Contagem Formation (sample from BL). The other deposits (PP, NQ, FT, VZ, VR samples) are associated with pink to whitish slates and yellow to reddish metasiltstone from the Ribeirão Piçarrão Formation. The quartzites, as well as the slates and metasiltstones, are quite weathered (Table 1, fig. 2D, E, I, J). Only in the FO sample, the Mn oxyhydroxides as massive blocks are associated, with limestone, probably from the top of the Paranoá Group.

Associated with Mn oxyhydroxides, ferruginous zones occur as massive, microlamellar, and specular hematite and in the metaparaconglomerates of Araújo Group. Rare millimeter to centimeter crystals of martite may occur widespread in hematite. In the Paranoá Group, colloform goethite fills the fractures of the slates and metasiltstones. These zones can also be powdery yellowish to botryoidal grey-brown masses with columnar structure.

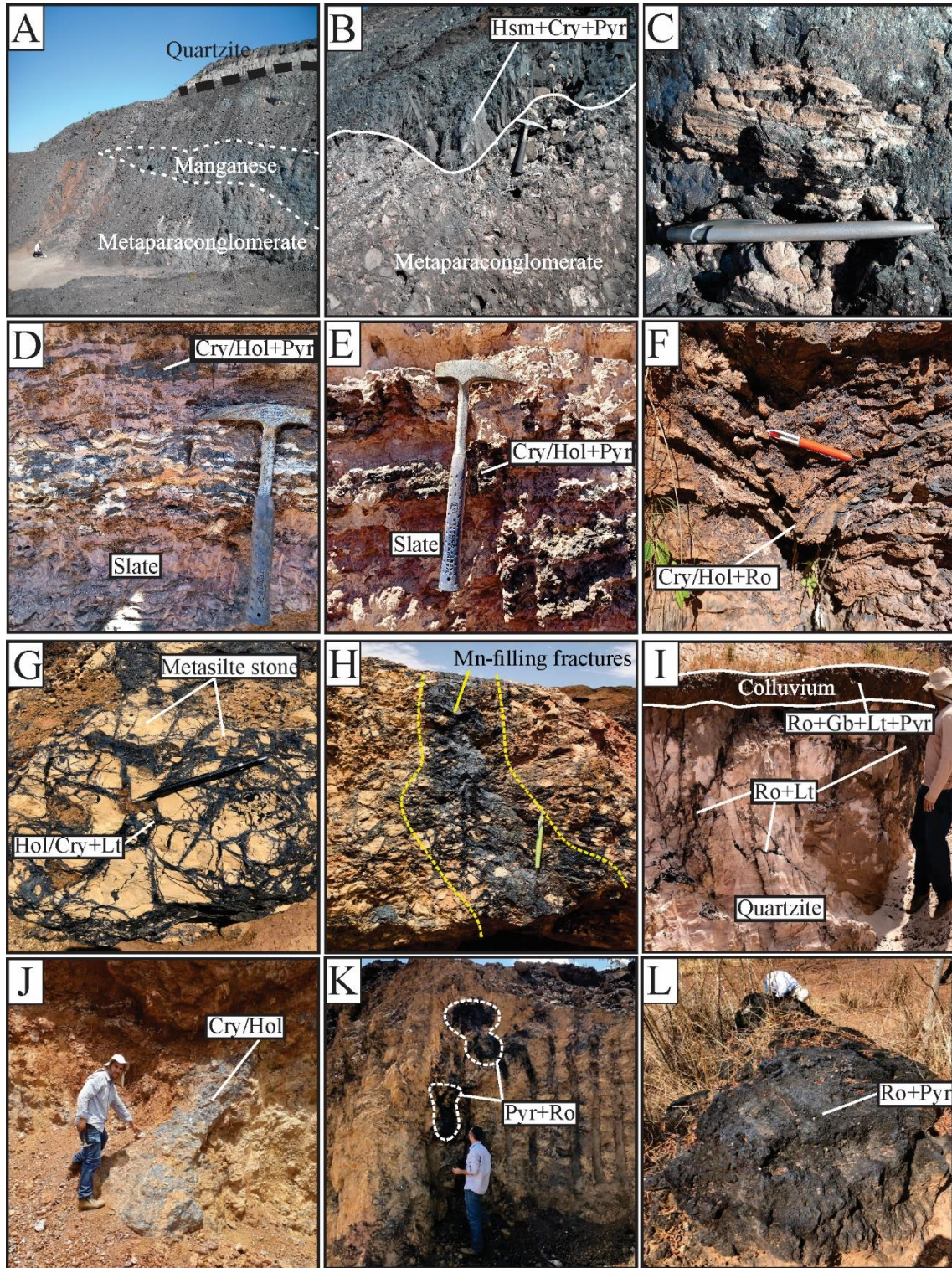


Figure 2. (A) mining front with Mn level interstratified with metaparaconglomerate and quartzite, in MJ; (B) Level of massive Mn oxyhydroxides composed of hausmannite (Hsm), cryptomelana (Cry), pyrolusite (Pyr) in contact with metaparaconglomerate in MJ. (C) Mn oxy-hydroxides filling fractures in MJ; (D) Interstratified manganese oxyhydroxides in slate, composed of cryptomelana, hollandite and pyrolusite in FT. (E) Interstratified manganese oxyhydroxides in very weathered; (F) Mn oxy-hydroxide co-folded with slate, in FT (G) Fractures in yellowish siltstone filled with hollandite (hol), cryptomelan and lithiophorite, in VZ (H) Yellow siltstone with Mn-filling fractures, in VZ; (I) fractures in weathered quartzite

filled with lithiophorite (Lt) and romanechite (Ro) and presence of colluvium with romanechite, lithiophorite, pyrolusite and gibbsite in RZ. (J) Metric fracture filled with Mn oxy-hydroxides, in VZ; (K) Pockets of powdery pyrolusite and romanechite in VR. (F) Massive Mn block composed of cryptomelane and hollandite (Hol) in VZ. (L) Massive Mn oxyhydroxide block with romanechite and pyrolusite in Formoso.

4.1 MINERALOGY OF Mn OXYHYDROXIDES

In the Araújo Group, the interstratified massive Mn layers, the powdery Mn levels, with Mn in fractures have the same mineralogy, cryptomelane, and pyrolusite with minor amounts of hausmannite (Fig. 3). Despite that, hausmannite and cryptomelane are more abundant in Mn massive layers, whereas the pyrolusite is the main phase at powdery Mn. Cryptomelane occurs as cryptocrystalline masses and as spongy forms (Fig. 4A). Moreover, it constitutes at least three main phases of cryptomelane remobilization according to the order of fractures and, sometimes, veinlets (fig. 4B, C). The pyrolusite is cryptocrystalline and occurs in fractures within the masses of cryptomelane and bordering the hausmannite and pseudomorphic cryptomelane (Fig. 4D). Hausmannite is less abundant, it occurs in the form of euhedral crystals partially or entirely replaced by pseudomorphic pyrolusite and cryptomelane (Fig. 4D).

In the Paranoá Group, the Mn occurs as lamellae, filling fractures, and constitutes powdery pockets in the sandstones, siltstones, slates, and surface blocks. Hollandite, romanechite, cryptomelane, and pyrolusite are the main phases (Fig.3). Lithiophorite is found in fractures and rarely in surface blocks.

Hollandite and cryptomelane are cryptocrystalline occur as massive, spongy, acicular, porous, lamellae, colloform, filling fractures, and fibrous texture (Fig. 4E, F, G, H). Sometimes, whenever cryptomelane and hollandite are acicular, they occur filling cavities or in their edges (Fig. 4G).

Romanechite has a great variety of textures: a) It is fibrous and acicular in RZ and BL; b) massive in FO and BL; c) colloform in PP and FT (Fig. 4I, J, K); d) fills fractures in RZ and forms massive blocks on the surface in MI, PP, BL, and FO. Lithiophorite is cryptocrystalline and displays colloform and massive textures. It borders cavities in VZ and involves fragments of massive and fibrous romanechite in RZ (Fig. 4H, I). In both places, it fills fractures.

Pyrolusite occurs as crystals smaller than 300 µm with well-defined cleavage, commonly associated with romanechite, and rarely with cryptomelane and hollandite (Fig. 4K, L). Pyrolusite is replaced by romanechite in FT and PP deposits, this is replaced by pyrolusite in BL deposit (Fig. 4L) and occurs mainly in massive and powdery Mn.

The accessory minerals of the Mn of the Paranoá Group are goethite, quartz, illite/muscovite, barite, and monazite. Goethite has a colloform texture and occurs mainly in NQ and VZ deposits. Quartz grains and illite/muscovite are immersed in hollandite, cryptomelane, and romanechite Fig. 4E, J). Barite is enclosed in quartz grains in FO and anhedral monazite borders cavities in the RZ deposit (Fig. 4I, J).

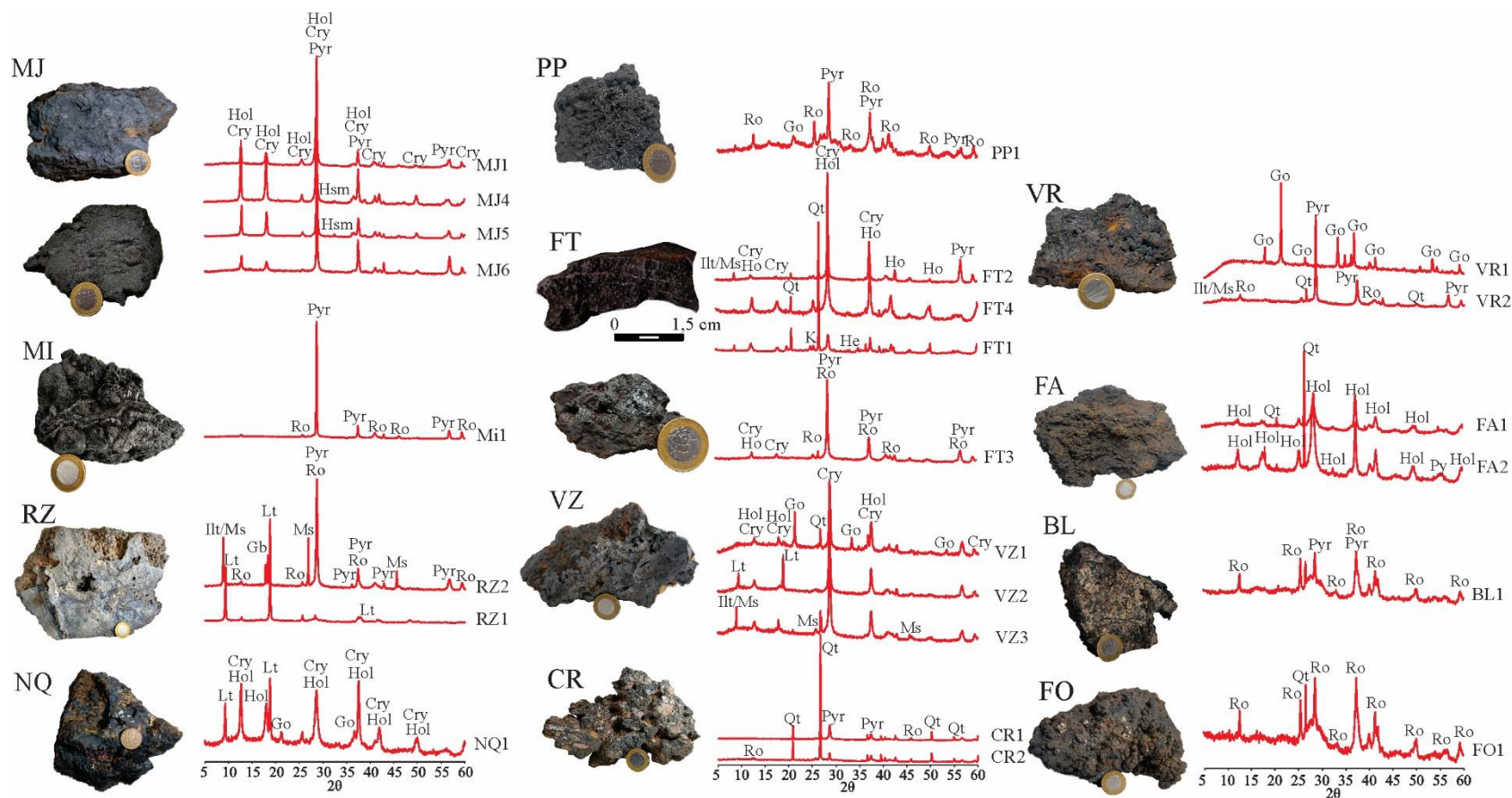


Figure 3. Samples and minerals associated with the Mn deposits of the Araí and Paranoá Groups. Pyr-pyrolusite, Cry-cryptomelana, Hsm-hausmannite, Qt-quartz, He-hematite, Ms-muscovite/illite, Lt-lithiophorite, Holhollandite, Ro-romanechite, Go-goethite, K-kaolinite, Gb-gibbsite.

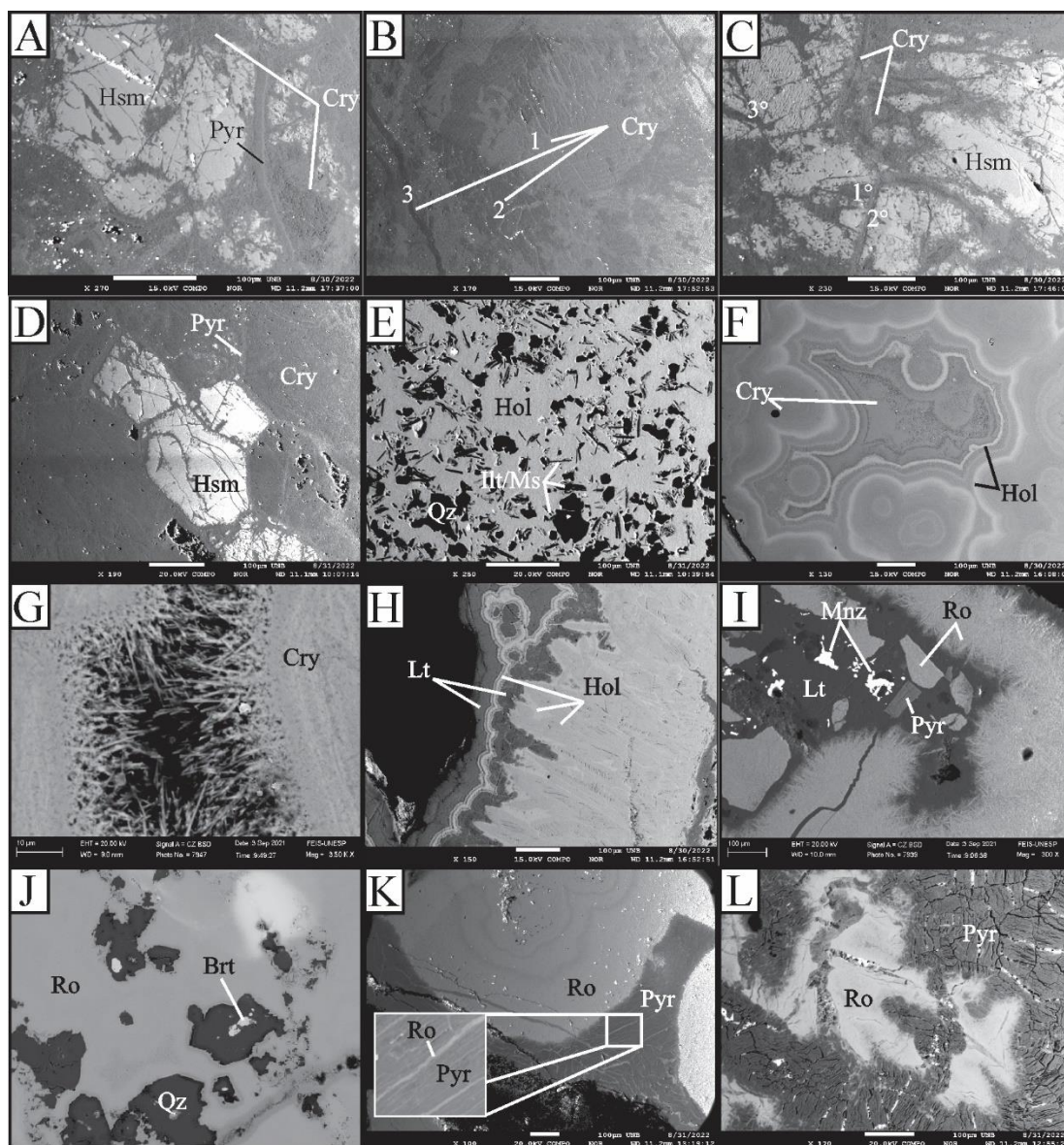


Figure 4. SEM microphotography. (A) Hausmannite crystals with fractures filled by cryptocrystalline cryptomelane, presence of spongy cryptomelane and pyrolusite venules. (B) Several generations of cryptomelane in cryptocrystalline form and in venules. (C) Cryptomelane filling Hausmannite fractures. (D) Euhedral crystals of hausmannite (Hsm) are replaced by pyrolusite (Pyr) and spongy cryptomelane (Cry) in MJ. (E) In FT, Hollandite cement involves quartz grains (Qz) and illite/muscovite plates (Ms/Ilt). (F) Cryptomelane and hollandite with coloform texture in NQ, forming banded and concentric features (G) Acicular cryptomelane bordering cavity in NQ. (H) Elongated pyrolusite crystals replaced by hollandite (Hol) and lithiophorite (Lt) with coloform texture in VZ. (I) Fibrous Romanechite and fragments of massive Romanechite and pyrolusite immersed in lithiophorite cement, presence of anhedral Nd-monazite (Mnz) on the edges of cavities in RZ. (J) Quartz grains with corroded edges and barite inclusions immersed in romanechite cement in FO. (K) Colloform Romanechite and filling pyrolusite fractures in FT. (L) Massive Romanechite (Ro) being replaced by pyrolusite with well-defined cleavage in BL.

4.2 ELECTRONIC MICROPROBE

Concerning the Araí Group, the hausmannite has only MnO (88.84 to 91.55%), while pyrolusite with 93.3 to 97.8% of MnO₂ contains up to 0.73% K₂O and 0.47% BaO. Cryptomelane (MnO₂: 89.17 to 97.82%) displays high K₂O between 1.08 and 6.32%, and small amounts of Al₂O₃ (up to 0.52%) and BaO (up to 1.62%) (Table 2 and Fig. 5A and B).

Unlike what occurs in the Araí Group, the pyrolusite and cryptomelane of the Paranoá Group are BaO and Al₂O₃ enriched and K₂O and MnO₂ depleted (Fig. 5A and B). Therefore, in the Paranoá Group, pyrolusite contains 86.4 to 98.3% of MnO₂, up to 0.21% K₂O and up to 0.89% BaO (Table 2). Cryptomelane (MnO₂: 81.97 to 92.55%) has 1.78 and 4.53% of K₂O, and significant amounts of BaO ($\leq 3.37\%$).

Hollandite (MnO₂: 67.48 to 90.8%), displays high BaO and FeO contents between 2.08 and 10.45% and up to 13.52%, respectively. Some of them were classified as Fe-hollandite due to the high FeO content (Table 2). The high Al₂O₃, P₂O₅, and K₂O contents in hollandite reach up to 5.40%, 1.10%, and 2.82%, respectively. In the BaO-Al₂O₃-K₂O diagram, it is possible to distinguish two types of hollandite: i) Al₂O₃ and BaO enriched and associated with powdery and massive Mn, and ii) with higher K₂O content, related to the Mn interstratified with slate.

Romanechite has 67.66-82.14% MnO₂, and 16.05% of BaO. The Al₂O₃ and FeO contents are lower than those of hollandite (up to 2.96% and 1.24% respectively). Lithiophorite, which is naturally aluminous, has up to 21.80% Al₂O₃ and significant concentrations of BaO, CoO, CuO, NiO, and ZnO between 1 and 2.52% (Table 2). Two types of lithiophorite in the Mn of the Paranoá Group are recognized by greater or lesser enrichment in NiO and CuO (Fig. 5C) (Table 2).

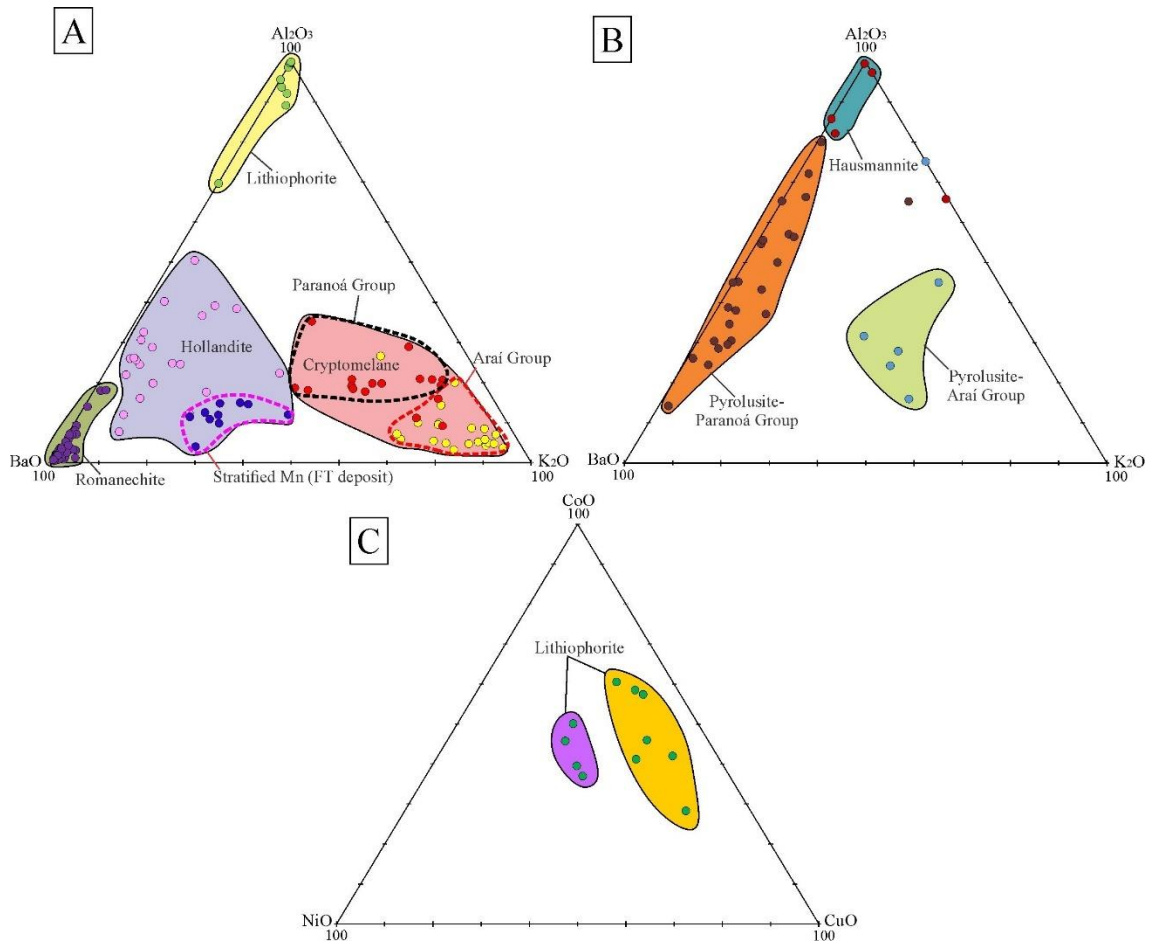


Figure 5. Al_2O_3 -BaO-K₂O and CoO-NiO-CuO ternary diagrams with the main Mn minerals. (A) The hollandites associated with the interstratified Mn and those from the other sites are differentiated, in addition to differentiating the cryptomelanes associated with the Araí and Paranoá Groups. (B) The pyrolusites of the Araí Group have more K₂O when compared to the amounts of BaO, while those of the Paranoá Group have more K₂O and a more variable amount of Al_2O_3 . (C) Lithiophorites show two varieties when compared with their NiO and CuO concentrations.

Table 2. Mineral chemistry determined by EPMA of different Mn minerals associated with the Araí and Paranoá Groups. MnO* calculated according to Antao et al. 2019. H₂O** is calculated by the difference of the sum by 100. In lithiophorite H₂O**=H₂O+LiO₂.

	Araí Group						Paranoá Group											
theoretical formula	Hausmannite		Pyrolusite		Cryptomelane		Cryptomelane		Hollandite			Romanechite			Pyrolusite		Lithiophorite	
	(Mn ²⁺ Mn ³⁺) ₃ O ₄		MnO ₂		K(Mn ⁴⁺ Mn ³⁺) ₈ O ₁₆		K(Mn ⁴⁺ Mn ³⁺) ₈ O ₁₆		Ba(Mn ⁴⁺ Mn ³⁺) ₈ O ₁₆			(Ba. H ₂ O) ₂ (Mn ⁴⁺ Mn ³⁺) ₅ O ₁₀			MnO ₂		(Al,Li)Mn ⁴⁺ O ₂ (OH) ₂	
MnO ₂	-	-	97.49	93.34	89.17	96.82	87.34	92.55	86.66	76.87	74.83	76.82	76.17	74.60	86.36	98.33	52.04	56.08
Mn ₂ O ₃	67.92	65.91	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
MnO*	30.51	29.61	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Fe ₂ O ₃	0.43	0.32	0.24	0.38	0.27	0.34	0.52	0.16	0.21	0.16	0.10	0.46	0.15	0.08	0.15	0.12	0.10	1.88
SiO ₂	<0.04	<0.04	0.15	0.15	<0.04	0.11	0.12	0.06	0.14	0.21	0.25	0.16	0.63	0.15	0.12	0.31	0.46	0.11
Al ₂ O ₃	0.49	0.47	0.30	0.44	0.33	0.24	1.22	0.60	0.73	2.57	5.40	0.15	2.48	0.39	0.20	0.17	20.89	17.01
CaO	<0.03	<0.03	0.05	<0.03	<0.03	0.04	0.10	0.03	0.05	0.03	0.10	0.21	0.13	0.15	0.03	0.04	0.06	0.08
MgO	0.08	0.11	0.07	<0.02	0.03	<0.02	<0.02	<0.02	0.05	<0.02	<0.02	0.06	<0.02	0.05	<0.02	0.04	0.05	0.25
Na ₂ O	0.04	<0.03	0.09	0.03	0.10	0.06	0.23	0.05	<0.03	0.05	0.08	<0.03	0.07	0.08	0.05	0.10	0.11	0.05
K ₂ O	<0.02	<0.02	0.53	0.68	5.44	1.81	4.53	1.78	1.86	0.54	2.02	0.58	0.12	0.03	<0.02	0.05	0.02	0.59
TiO ₂	<0.23	<0.23	<0.23	<0.23	<0.23	<0.23	<0.23	<0.23	<0.23	<0.23	<0.23	<0.23	<0.23	<0.23	<0.23	<0.23	<0.23	<0.23
P ₂ O ₅	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	0.15	<0.06	0.25	0.07	1.10	0.23	0.21	0.30	0.31	0.23	0.43	0.23
BaO	0.08	<0.07	0.40	0.46	1.05	0.34	0.58	0.64	4.14	11.55	6.39	12.01	15.19	16.14	<0.07	0.24	0.97	0.89
CoO	0.01	<0.01	<0.01	0.01	0.01	0.01	0.37	0.01	0.05	0.04	0.18	0.07	0.30	0.13	0.03	<0.01	1.97	0.59
Cr ₂ O ₃	0.14	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	0.07	0.11	<0.09	<0.09	<0.09	<0.09	<0.09	0.11
CuO	<0.02	<0.02	<0.02	<0.02	0.02	<0.02	<0.02	<0.02	0.02	0.03	0.11	0.03	0.11	0.02	0.03	<0.02	1.73	0.60
NiO	<0.08	0.08	<0.08	0.12	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	0.11	<0.08	<0.08	<0.08	<0.08	<0.08	1.62	1.30
PbO	0.03	0.04	<0.03	0.11	<0.03	0.12	<0.03	0.06	0.11	0.08	<0.03	1.74	0.15	0.16	0.41	0.29	<0.03	0.07
SrO	<0.03	<0.03	0.04	0.11	0.10	0.07	0.07	<0.03	<0.03	<0.03	<0.03	0.09	0.03	<0.03	<0.03	<0.03	<0.03	<0.03
V ₂ O ₃	0.12	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	0.11	<0.11	0.13	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11
ZnO	0.13	0.14	0.04	0.10	<0.02	0.09	0.16	<0.02	0.08	0.05	0.24	<0.02	<0.02	0.02	0.03	0.05	0.83	0.66
H2O**	0.03	3.32	0.61	4.08	3.49	0.00	4.61	4.06	5.65	7.66	9.03	7.16	4.28	7.70	12.28	0.04	18.72	19.50

4.3 GEOCHEMISTRY

4.3.1 Main elements

Overall, the Mn deposits display high MnO contents, between 52 and 72.8% (Fig. 6, Tab. 3). However, in the FT and CR there are samples with MnO contents varying from 21.3 to 36.8%, due to the high amounts SiO₂ (49.7%) assigned to the quartz, kaolinite, and muscovite (Table 3). Al₂O₃ between 3.81% and 15.55% is associated with lithiophorite in RZ and NQ deposits and illite/muscovite in FT deposit.

Concerning the K₂O amounts, there are some remarks to be done: i) In Araí Group Mn deposits the K₂O between 2 to 4.03% (samples MJ1, MJ4, and MJ5) is related to the cryptomelane enrichment over pyrolusite and hausmannite, while the K₂O content at 0.29% (sample MJ6) demonstrate the pyrolusite are abundant over cryptomelane; ii) In the Paranoá Group Mn deposits (NQ1, FT1 and FT4, and VZ2), the K₂O between 1.04 and 2.5% is associated to the cryptomelane+hollandite+lithiophorite paragenesis (in NQ and VZ) and muscovite/illite (in FT); iii) in the FT2, FT3, and FA deposits of the Paranoá Group, the K₂O contents between 0.37 to 0.54% are related to the hollandite+cryptomelane+pyrolusite+romanechite (in FT3) and to the hollandite+(pyrolusite) paragenesis; iv) according to the mineral abundance, the K₂O contents varying from 0.08 to 0.61% in of the Paranoá Group Mn deposits, are linked to pyrolusite+romanechite (MI deposit); romanechite+pyrolusite (PP, and BL); lithiophorite+romanechite+pyrolusite (muscovite/illite; RZ deposit); and romanechite+pyrolusite+muscovite/illite (VRdeposit); romanechite paragenesis.

Fe₂O₃ varies between 0.02% and 15.75%, except in ferruginous zones where the Fe₂O₃ ranges from 28% to 80.8%. These high Fe₂O₃ contents are related to the predominance of goethite and hematite in VR and MJ deposits, respectively. The ferruginous zones present low MnO content (0.19-2.85%; Table 3). CaO, MgO, Na₂O, TiO₂, and P₂O₅ do not exceed 1%. The highest MnO/Fe₂O₃ ratios are found in MJ, MI, RZ, and FO (MnO/Fe₂O₃ =152.3-2815) deposits and the lowest in ferruginous zones (MnO/Fe₂O₃<0.03).

4.3.2 Trace elements

Among all the small Mn deposits, there is a significant variation in trace element concentrations (Fig. 6, Tab. 3). Ba, Co, Cu, Sr, Ni, and Zn are the most concentrated trace elements in all deposits (Table 3). Some trace elements deserve to be highlighted, Sr (≤ 3295 ppm), U (≤ 143 ppm), and Tl (≤ 327 ppm), more concentrated in the Araí Group deposits (Table 3). On the Paranoá Group deposits, Ba (PP, FO, BL, and FA: 113301-136140 ppm), Co, Cu, and Ni (RZ1 and NQ: 872-8380 ppm, 936-3080 ppm, and 222-1765 ppm, respectively), V (CR: 723-855 ppm), and REE (FT1 and RZ1: 1139 and 2500 ppm) are highlighted. Both Araí and Paranoá deposits register some ultrahigh Zn contents (1335-2460 ppm).

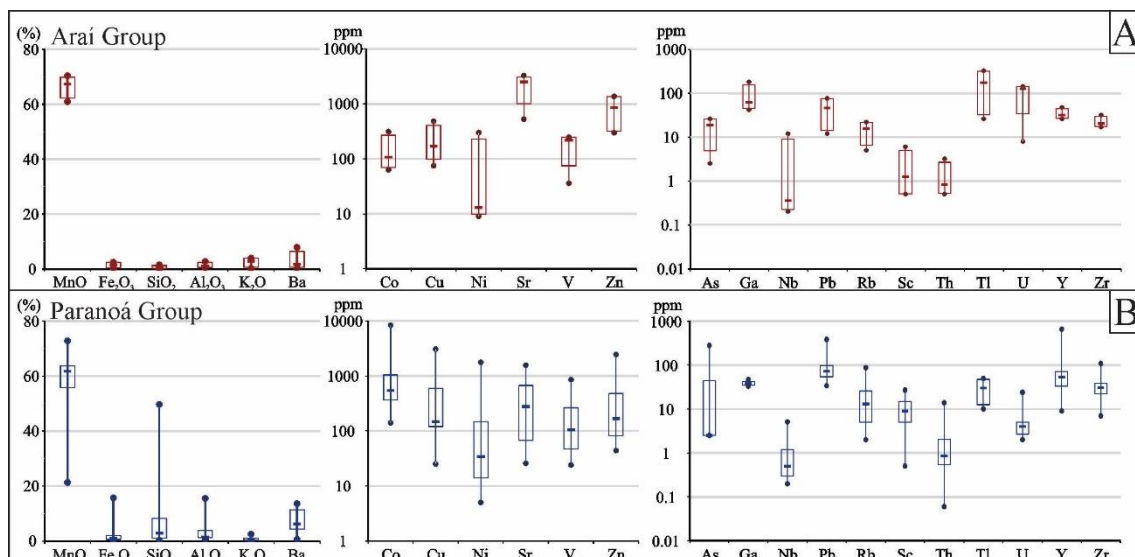


Figure 6. Box and whisker diagram showing the variation in chemical composition in the studied locations. Oxides and Ba in wt% and trace elements in ppm A: MJ, Araí Group; (B) Paranoá Group.

Overall, concerning the UCC-normalized trace elements of the Mn deposits, As, Ba, Co, Cu, and Ga are enriched, and Hf, Nb, Rb, Sc, Th, and Zr are depleted or close to the UCC average (Fig. 7). The Araí Group deposits are featured by the most pronounced Sr, Tl, U, and Zn enrichment. However, the sample MJ6 of the Araí Group also displays Ni and Pb enrichment and Sr close to the UCC average. On the other hand, Tl is also above the UCC average in the Paranoá Group Mn deposits, though less pronounced. Pb is close to the UCC average or is enriched in all the Paranoá Group Mn deposits. Ni, Y, and Zn are UCC-enriched in NQ1, VZ2, VZ1, and RZ1. In addition, V is enriched in the RZ1, and much more enriched in the CR. The Paranoá Group Mn deposits also has high Co/Zn ratios (0.70 to 14, 4, table 3).

The Araí Group Mn deposits are LREE UCC-enriched over HREE as shown by high $(La/Yb)_N$ varying from 1.63 to 4.9 (Table 3). Moreover, positive Eu anomalies ($Eu/Eu^* = 1.74$ to 2.34) also characterize these deposits, although the MJ6 presents a negative Eu anomaly ($Eu/Eu^* = 0.88$). Slight positive Ce anomalies were also identified at MJ1, MJ4, and MJ6 ($Ce/Ce^* = 1.2$ to 1.43). Overall, the Paranoá Group Mn deposits present a flat-REE pattern as shown by $(La/Yb)_N$ varying from 0.68 to 1.05, except in the sample FT1 ($(La/Yb)_N = 1.42$) and samples from RZ, NQ, PP, (sample FT3), VZ and BL ($(La/Yb)_N < 0.53$). Negative or absence of Eu anomalies ($Eu/Eu^* = 0.03$ to 1.18) occurs, despite two samples (FT2 and FT4) presenting slight positive anomalies ($Eu/Eu^* = 1.22$ to 1.37). The Paranoá Group Mn deposits are featured by the highest positive Ce anomalies ($Ce/Ce^* = 1.20$ to 5.55) as occurring in NQ, PP, FT, CR, FA, BL, and FO. Nevertheless, negative Ce anomalies ($Ce/Ce^* = 0.11$ to 0.76) also occur in MI, RZ, VZ, and VR deposits.

Table 3. Chemical composition major and minor oxides in % by weight. trace elements in ppm.

Samples	Araí Group				Paranoá Group								
	MJ1	MJ4	MJ5	MJ6	MI1	RZ1	RZ2	NQ1	PP1	FT1	FT2	FT3	FT4
MnO	68.40	66.17	70.35	60.92	72.80	56.30	63.90	61.70	58.00	21.30	55.80	61.70	52.00
Fe ₂ O ₃	2.55	2.03	1.01	0.40	0.12	0.02	1.89	6.10	8.49	3.49	1.39	1.69	1.05
SiO ₂	0.55	0.22	0.74	1.57	0.47	0.99	2.64	0.96	0.81	41.20	9.17	1.86	8.19
Al ₂ O ₃	1.67	0.68	0.56	2.76	0.73	8.04	4.76	3.81	0.68	15.55	3.52	2.03	4.44
CaO	0.05	0.02	0.03	0.06	0.15	0.12	0.12	0.10	0.12	0.03	0.08	0.15	0.02
MgO	0.03	0.01	0.03	0.08	0.06	0.04	0.08	0.02	0.04	0.24	0.09	0.04	0.07
Na ₂ O	0.10	0.11	0.13	<0.01	0.03	0.03	0.04	0.11	0.02	0.07	<0.01	<0.01	0.01
K ₂ O	2.00	4.03	3.95	0.29	0.23	0.13	0.38	2.50	0.08	1.84	0.54	0.54	1.18
TiO ₂	0.01	0.02	0.02	0.01	0.01	0.01	0.06	0.02	0.01	0.23	0.08	0.02	0.10
P ₂ O ₅	0.06	<0.01	<0.01	0.08	0.22	0.29	0.11	0.58	0.56	0.06	0.47	0.44	0.25
LOI	9.13	19.30	11.90	13.80	11.80	12.35	13.05	10.85	9.43	9.80	12.00	12.70	11.05
As	<5	25	26	12	<5	<5	<5	19	281	<5	115	115	<5
Ba	79355	13347	22523	5370	61621	104792	55800	43081	121810	44248	35828	43889	76045
Co	128	88	63	314	634	8380	872	4790	1080	140	224	356	459
Cu	482	75	176	165	133	3080	1745	936	139	25	46	411	155
Ga	42	182	70	54	39	41	47	36	35	35	46	46	39
Hf	0.2	0.6	0.5	0.6	0.2	<0.2	1	0.4	0.2	1.8	0.7	0.4	0.9
Nb	0.3	0.2	12	0.4	<0.2	<0.2	0.9	0.3	0.2	5.1	1.4	0.5	4.4
Ni	13	13	9	300	63	1765	222	990	24	14	16	52	6
Pb	77	20	12	72	170	52	105	99	54	35	69	76	66
Rb	11	22	20	5	3	2	13	30	3	88	26	15	41
Sc	2	<1	<1	6	11	8	17	5	6	16	12	26	15
Sr	2450	3295	2579	526	1445	252	268	430	138	26	50	290	66
Th	0.6	1.1	0.5	3.2	0.3	0.1	2.6	0.8	0.17	13.9	3.7	0.7	3.1
Tl	50	297	327	26	<10	<10	<10	<10	<10	<10	<10	<10	<10
U	143	111	143	8	3	24	20	4	3	3	3	5	3
V	247	192	248	36	106	280	214	37	103	51	189	109	92
Y	26	34	30	48	56	661	53	146	53	33	40	66	43
Zn	383	300	1365	1335	399	1640	217	1235	75	52	88	171	148
Zr	17	22	19	32	23	37	63	22	7	68	31	34	34
La	134.00	50.00	109.00	83.00	75.00	438.00	65.00	16.00	9.00	68.00	48.00	43.00	50.00
Ce	251.00	121.00	60.00	290.00	109.00	144.00	282.00	74.00	102.00	920.00	465.00	201.00	181.00
Pr	17.10	7.91	9.60	25.85	21.8	194.50	20.10	5.37	3.99	21.10	20.80	26.30	20.20
Nd	63.00	34.00	40.00	96.00	82.2	888.00	66.00	23.2	16.9	80	82	105	85
Sm	15.10	9.69	7.40	21.39	21.2	224.00	13.80	6.45	5.1	15.85	18.80	23.30	19.15
Eu	6.88	5.10	3.36	3.68	3.29	51.90	2.29	1.01	0.38	2.97	4.53	4.74	4.89
Gd	14.40	10.80	11.15	18.22	14.6	223.00	10.15	14.95	5.55	10.85	16.15	19.85	14.60
Tb	1.87	1.47	1.36	2.27	2.51	32.70	1.78	2.68	0.99	1.76	2.43	3.22	2.39
Dy	8.98	6.57	6.34	12.02	14.45	173.50	10.25	16.55	6.24	8.60	11.75	16.90	12.25
Ho	1.53	1.28	1.21	1.68	2.8	30.30	2.30	4.1	1.53	1.52	1.98	3.23	2.23
Er	3.02	3.16	2.94	4.21	7.47	73.10	6.24	10.65	4.18	3.90	4.56	8.59	5.75
Tm	0.46	0.42	0.37	0.53	1.16	10.55	1.07	1.43	0.7	0.61	0.64	1.20	0.82
Yb	2.00	2.25	1.86	3.51	6.61	60.40	6.85	7.7	3.93	3.50	3.39	7.18	5.32
Lu	0.35	0.39	0.28	0.54	1.05	9.15	1.19	1.31	0.65	0.57	0.56	1.17	0.81
ΣREE	519	254	255	562	363	2553	489	185	161	1139	681	465	404
MnO/Fe ₂ O ₃	26.82	32.60	69.65	152.30	607	2815.00	33.81	10	6.8	6	40	37	50
Co/Zn	0.33	0.29	0.05	0.24	1.59	5.11	4.02	3.88	14.40	2.69	2.55	2.08	3.10
(Cu+Co+Ni)	623	176	248	779	830	13225	2839	6716	1243	179	286	819	620
(La/Yb) _N	4.90	1.63	4.29	1.73	0.83	0.53	0.70	0.15	0.16	1.42	1.04	0.44	0.68
Eu/Eu*	2.19	2.34	1.74	0.88	0.88	1.09	0.91	0.48	0.34	1.06	1.22	1.04	1.37
Ce/Ce*	1.20	1.38	0.42	1.43	0.62	0.11	1.78	1.85	3.93	5.55	3.35	1.36	1.30
Tm/Tm*	1.28	1.07	1.08	0.94	1.13	1.08	1.12	1.08	1.18	1.13	1.11	1.04	1.01

Tabela 3. Continuation

Amostra	Paranoá Group									
	VZ1	VZ2	VZ3	CR1	CR2	VR2	FA1	FA2	BL1	FO1
MnO	57.60	70.40	63.60	36.80	33.20	63.70	58.90	63.50	62.30	65.60
Fe ₂ O ₃	15.75	1.91	0.92	0.49	0.61	1.08	1.46	1.02	0.92	0.22
SiO ₂	2.91	0.30	6.05	47.00	49.70	2.98	7.99	3.08	2.45	1.76
Al ₂ O ₃	1.40	1.35	2.45	1.35	1.44	1.27	1.68	1.49	1.20	1.18
CaO	0.17	0.19	0.26	0.06	0.09	0.27	0.14	0.23	0.13	0.29
MgO	0.07	0.03	0.11	0.06	0.06	0.11	0.04	0.03	0.09	0.09
Na ₂ O	0.05	0.05	0.06	0.04	0.04	0.01	0.03	0.05	0.02	0.05
K ₂ O	1.04	1.15	1.12	0.25	0.17	0.61	0.37	0.85	0.20	0.32
TiO ₂	0.03	<0.01	0.07	0.06	0.10	0.05	0.02	0.03	0.02	0.02
P ₂ O ₅	0.75	0.72	0.24	0.22	0.16	0.20	0.26	0.26	0.32	0.32
LOI	12.85	13.35	11.60	6.28	6.25	11.75	9.32	9.40	9.76	11.35
As	44	<5	<5	69	37	<5	<5	<5	28	<5
Ba	6270	17465	49440	43350	66189	66995	113301	114197	136140	130319
Co	587	1730	558	392	530	491	262	210	401	1100
Cu	128	664	139	118	134	291	30	28	308	407
Ga	41	38	42	42	41	44	33	33	35	34
Hf	0.4	0.6	0.8	1.1	2.7	0.6	0.6	0.6	0.6	0.3
Nb	0.7	0.8	1.1	1.2	1.7	0.5	0.4	0.4	0.4	0.3
Ni	148	753	28	14	32	61	34	5	11	79
Pb	57	69	77	35	34	72	96	76	382	244
Rb	25	25	28	10	5	16	6	12	6	5
Sc	4	<1	11	4	4	9	11	5	6	27
Sr	426	747	1570	59	38	877	70	126	436	980
Th	0.86	0.84	2.04	1.93	1.89	1.87	0.5	0.6	1.2	0.4
Tl	50	40	20	<10	<10	10	<10	<10	<10	<10
U	2	5	5	5	4	13	2	2	5	8
V	46	28	74	723	855	24	56	28	119	408
Y	44	64	97	20	25	114	12	9	53	71
Zn	603	2460	226	130	163	151	60	44	365	504
Zr	20	24	39	45	109	28	25	22	33	10
La	14.00	5.00	27.00	27.00	13.00	133.00	21.00	13.00	13.00	97.00
Ce	28.00	9.60	100.00	143.00	39.00	256.00	274.00	140.00	127.00	792.00
Pr	3.35	1.52	9.79	12.2	4.39	54.6	7.32	5.01	5.78	29.20
Nd	13.50	6.30	45.20	41.00	14.40	219.00	22.00	16.00	29.00	101.00
Sm	4.21	1.38	15.85	9.76	3.19	55	5.09	4.00	12.10	22.00
Eu	1.43	0.37	4.18	1.21	0.23	11.45	0.005	0.37	1.96	4.46
Gd	7.69	3.52	18.8	5.56	2.63	44.3	2.71	1.95	17.50	17.90
Tb	1.78	0.88	3.35	0.95	0.49	7.05	0.56	0.41	2.88	3.11
Dy	12.1	8.27	20.2	4.81	3.01	37.8	2.70	1.95	14.20	17.55
Ho	2.59	2.39	3.8	0.9	0.74	6.76	0.51	0.32	2.67	3.50
Er	6.10	6.75	9.43	2.16	2.10	16.35	1.29	0.88	5.63	8.75
Tm	0.91	1.06	1.37	0.38	0.4	2.46	0.27	0.21	0.81	1.44
Yb	4.31	5.86	7.67	1.91	2.13	13.3	1.44	0.96	3.86	7.91
Lu	0.61	0.84	1.10	0.32	0.33	1.81	0.26	0.19	0.63	1.23
ΣREE	100	54	268	251	86	858	339	185	237	1106
MnO/Fe ₂ O ₃	4	37	69	75	54	59	40	62	68	298
Co/Zn	0.97	0.70	2.47	3.02	3.25	3.25	4.37	4.77	1.10	2.18
(Cu+Co+Ni)	863	3147	725	524	696	843	326	243	720	1586
(La/Yb) _N	0.23	0.07	0.26	1.02	0.44	0.73	1.05	1.01	0.25	0.90
Eu/Eu*	1.18	0.79	1.14	0.77	0.37	1.09	0.03	0.62	0.63	1.06
Ce/Ce*	0.94	0.76	1.40	1.81	1.20	0.69	5.09	3.93	3.33	3.40

Tm/Tm*	1.21	1.15	1.10	1.28	1.29	1.14	1.35	1.56	1.18	1.18
--------	------	------	------	------	------	------	------	------	------	------

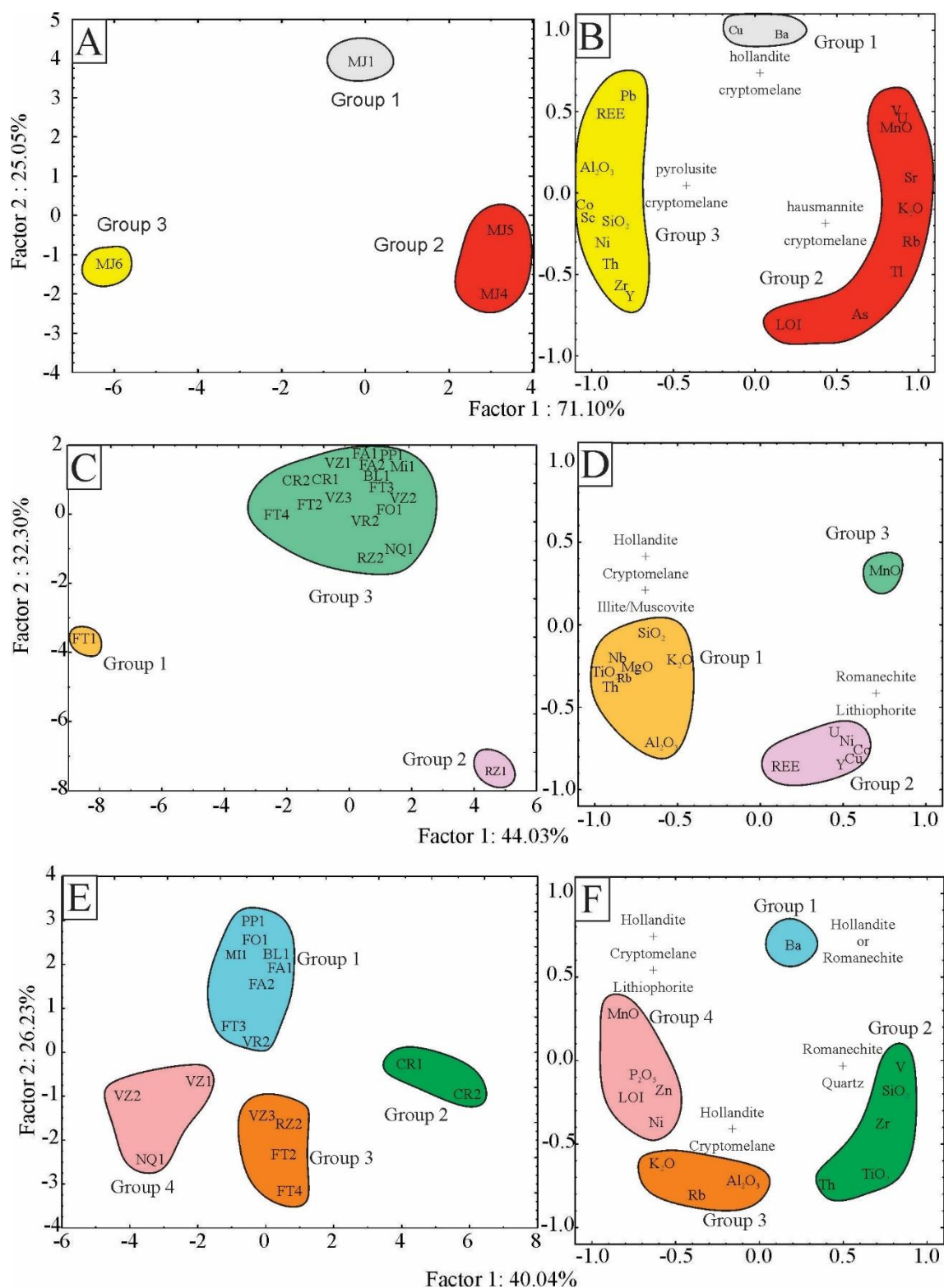


Figure 7. (A) principal component analysis and the groups of the samples associated with the Araí Group identified in MJ; (B) Geochemical correlations and associated mineral paragenesis; (C) Groups of samples identified through principal component

analysis of all Paranoá Group samples, with only the separation of samples FT1 and RZ1 from the others.; (D) Geochemical associations for all samples of the Paranoá Group with mineral parageneses of Sample FT1 and RZ1; (E) Principal component analysis and sample groups of Paranoá without samples FT1 and RZ1; (F) Geochemical association and mineralogy present in the other samples of the Paranoá Group.

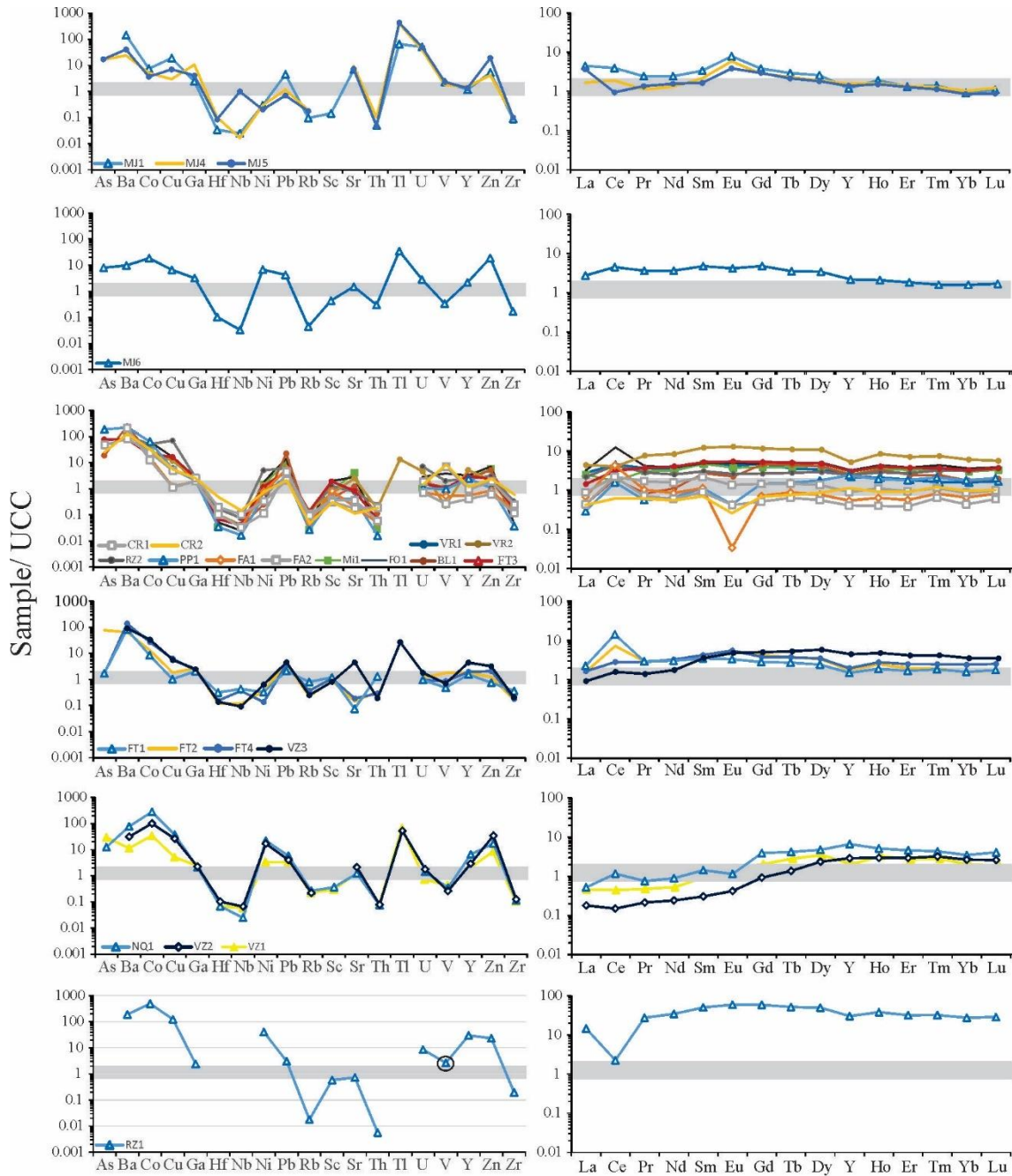


Figure 8. Normalized trace element diagrams for McLennan's Upper Continental Crust (2001) for the groups identified through principal component analysis.

4.3.3 Leaching by aqua regia

Based on the leaching rates in aqua regia in 11 samples of the Mn deposits, four groups of elements were identified (Fig. 8): (1) Ce, Co, Cu, Fe, Ni, Sr, and Zn with leaching rates of 90% in almost all samples, indicating direct association with Mn oxyhydroxides; (2) Nb, Ti, and Zr with leaching rates above 85% in the Araí Group Mn deposits and below 51% in those of the Paranoá Group, indicating that these elements are associated with silicates and heavy minerals; (3) Th has the lowest leaching rate (25%) in the MJ (Araí Group); while the Al, La, Th, U, and V have variable leaching rates, between 45% and 100% in those of the Paranoá deposits. The Al leaching rates vary from 53 to 74% in CR1, FO1, and BL1. La leaching rates vary from 60 to 65% in BL1, NQ1, and RZ1. The Th leaching rates are between 25 to 64% in MJ1, RZ1, VZ1, PP1, and FO1. The U leaching rates in VZ1 and FA are 65-66%, while the V rates in VR2 and NQ1 vary from 50 to 59%, respectively. These lower leaching rates of < 50% are associated with heavy minerals and the higher leaching rates of > 50% with Mn oxyhydroxides. (4) The lower Pb leaching rates <38% in most samples (except in MI, BL, and FO between 61 and 93%) indicate an association with heavy minerals.

Among the elements analyzed only in aqua regia leaching (Au, Ag, Be, Bi, Cd, Ge, Hg, In, Li, Mo, Pd, Pt, Re, Sb, Se, and Te), Li and Mo are the most concentrated in RZ1 sample (1160 ppm and 52.7 ppm, respectively), while in all samples the Au and Re are the least concentrated (> 0.03 ppm). Among the other elements, the highest concentrations of Ag (11.2 ppm in BL1), Be (22 ppm in FO1), Cd (21.4 ppm in NQ1) and Sb (11.6 ppm in VR2) stand out (Fig. 9).

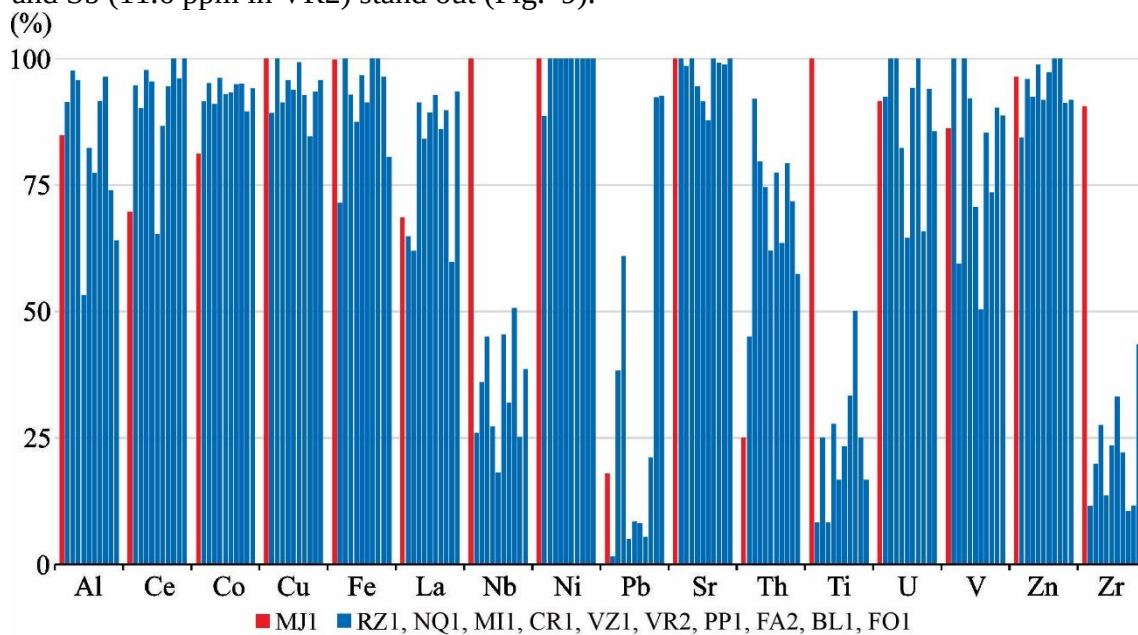


Figure 9. Lixiviation rate in aqua regia in relation to total chemical analyses. In red, MJ1 associated with the Araí Group and in blue, those are associated with the Paranoá Group.

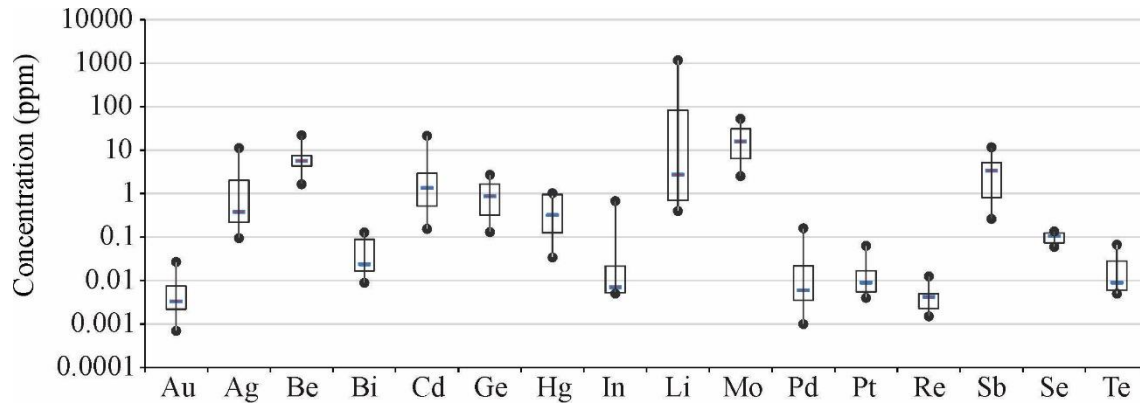


Figure 10. Box and whisker diagrams showing the variation of trace elements in ppm analyzed by aqua regia leaching only.

4.4 Pb, Sr, and Sm-Nd ISOTOPES

The $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios analyzed in the aqua regia solution show significant variation. The most radiogenic ratio of $^{206}\text{Pb}/^{204}\text{Pb}$ is in the MJ1 ($^{206}\text{Pb}/^{204}\text{Pb} = 78.557$), which has the highest concentration in U (131 ppm). The most radiogenic values of $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ in CR (45,625 and 111.375, respectively) do not correlate with Pb, Th, and U concentrations (Tab. 4). In the other Paranoá Group Mn samples, the $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios vary between 17.814 and 59.75; 15.814 and 22.571; 35.464 and 44.643, respectively. The $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios present their lowest values in the MJ1 sample ($^{207}\text{Pb}/^{206}\text{Pb} = 0.239$; $^{208}\text{Pb}/^{206}\text{Pb} = 0.451$), associated with the Araújo Group. The RZ1 sample, Paranoá Group, presents the lowest values of $^{207}\text{Pb}/^{206}\text{Pb}$ (0.603) and $^{208}\text{Pb}/^{206}\text{Pb}$ (1.366) (Tab. 4).

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the raw samples vary a lot. The most radiogenic are in RZ1, NQ1, PP1, FA2, and BL1 (between 0.74265 and 0.76742) and the least in MJ, MI, and FO (between 0.71842 and 0.72479). The ϵNd varies from -20.7 to -13 and it is extremely radiogenic in BL ($\epsilon\text{Nd} = -8.8$). The T_{DM} varies between 2.24 and 3.46 Ga (Table 4).

Table 4. Pb, Nd, Sr and Nd isotopic ratios and U, Th, Pb, Sm, Nd and Sr concentrations in ppm.

Samples	MJ1	MI1	RZ1	NQ1	PP1	VZ1	CR1	VR2	FA2	BL1	FO1
²⁰⁶ Pb/ ²⁰⁴ Pb	78.557	18.81	37.429	20.426	23.606	22.232	59.75	21.197	17.814	18.997	18.707
²⁰⁷ Pb/ ²⁰⁴ Pb	18.763	16.654	22.571	15.842	17.03	17.196	45.625	16.408	15.814	16.241	16.595
²⁰⁸ Pb/ ²⁰⁴ Pb	35.464	38.959	51.143	40.405	42.727	44.643	111.375	40.704	37.07	38.847	38.233
²⁰⁷ Pb/ ²⁰⁶ Pb	0.239	0.885	0.603	0.776	0.721	0.773	0.764	0.774	0.888	0.855	0.887
²⁰⁸ Pb/ ²⁰⁶ Pb	0.451	2.071	1.366	1.978	1.810	2.008	1.864	1.920	2.081	2.045	2.044
U	131	3.12	22.2	4.15	3.13	1.29	4.12	12.25	1.315	4.7	6.85
Th	0.138	0.239	0.027	0.736	0.108	0.534	1.44	1.45	0.5	0.854	0.241
Pb	13.8	103.5	0.825	37.9	2.94	4.81	1.76	5.87	16.1	353	226
U/Pb	9.493	0.030	26.909	0.109	1.065	0.268	2.341	2.087	0.082	0.013	0.030
Th/Pb	0.010	0.002	0.033	0.019	0.037	0.111	0.818	0.247	0.031	0.002	0.001
εNd (0)	-20.50	-17.05	-	-20.70	-15.70	-20.05	-14.7	-18.20	-13.54	-8.82	-15.70
TDM Ga	2.14	1.88	-	2.16	1.78	2.11	1.70	1.97	1.61	1.26	1.78
Sm	15.199	20.869	-	6.605	4.742	4.367	9.743	55.552	3.447	11.304	21.944
Nd	62.261	81.121	-	22.966	16.207	13.272	40.052	222.439	15.037	27.859	101.309
Sm/Nd	0.244	0.257	-	0.288	0.293	0.329	0.243	0.250	0.229	0.406	0.217
¹⁴⁷ Sm/ ¹⁴⁴ Nd	0.148	0.156	-	0.174	0.177	0.199	0.147	0.151	0.139	0.245	0.131
¹⁴⁷ Sm/ ¹⁴⁴ Ndr	0.11	0.11	-	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11
⁸⁷ Sr/ ⁸⁶ Sr ±	0.72479	0.72422	0.76742	0.75675	0.74911	0.73032	0.73063	0.73301	0.7558	0.74265	0.71842
2SE	±7	±6	±1	±4	±4	±1	±7	±3	±1	±4	±3
Rb	12.1	2.91	3.39	32	1.67	21.30	2.79	12.05	11.80	3.97	4.05
Sr	2720	1515	281	424	146	390	55.8	770	125	431	990
Rb/Sr	0.004	0.002	0.012	0.075	0.011	0.055	0.050	0.016	0.094	0.009	0.004

¹⁴⁷Sm/¹⁴⁴Ndr = recalculated to be able to calculate TDM. f_{Sm/Nd} = -0.44

DISCUSSION

The mineralogical variations justify the geochemical differences between the Mn deposits. They are related to the presence of hausmannite and the absence of lithiophorite, and romanechite in the Araí Group Mn deposit (MJ), concerning the other deposits of the Paranoá Group. On the other hand, cryptomelane and pyrolusite are common in both the Araí and Paranoá groups deposits. Therefore, the Araí Group Mn deposit is characterized by hausmannite-cryptomelane(hollandite)-pyrolusite paragenesis, low P₂O₅ contents, high Sr, Tl, and U concentrations, expressive positive Eu/Eu* anomalies (Fig. 7), high (La/Yb)_N and Mn/Fe ratios, and the lowest Co/Zn ratios (Fig 10A, Table 3). These geochemical characteristics together with the restricted nature of the deposit (small size deposits), and the lower concentrations of Co+Ni (Fig. 10A, Table 3), typical elements associated with supergene and ocean floor deposits, indicate possible hydrothermal control at the time of Mn deposition (Toth, 1980; Nicholson, 1992; Hein *et al.*, 1997; Maynard, 2010). In addition, the low Zr, Th, Nb, and Hf contents (Table 3) in the Araí Group Mn deposit suggest low continental sediment input. This fact, together with the more radiogenic Nd isotopic signature (ε_{Nd(0)} = -20.5) compared to unaltered Araí Group rocks (ε_{Nd(0)} = -21.93 to -24.09; Pimentel *et al.*, 2001; Silva *et al.*, 2021), and the opposite Pb isotopic behavior (lower ²⁰⁷Pb/²⁰⁶Pb and ²⁰⁸Pb/²⁰⁶Pb) relative to the other deposits, ratifies the hydrothermal origin (Fig 11C).

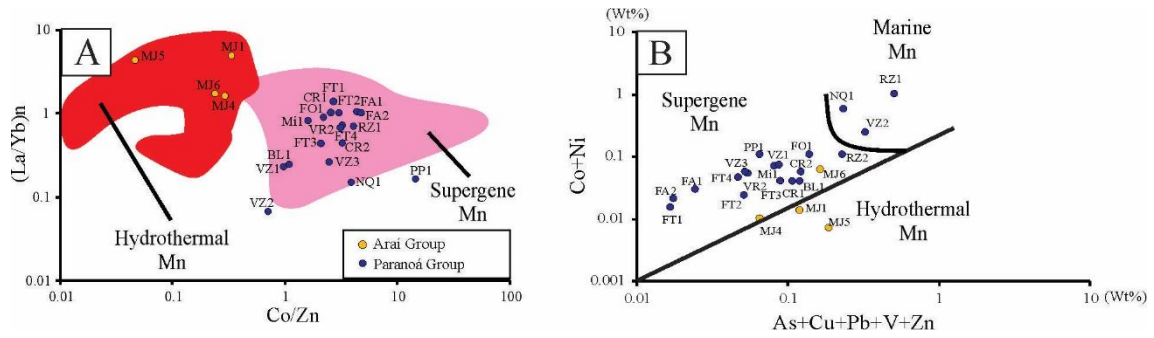


Figure 11. (A) Ratio $(La/Yb)_N$ by Co/Zn showing the different behaviors in the Araí and Paranoá Groups. (Hydrothermal Mn: Del Rio-Salas *et al.*, 2013; Hein *et al.*, 2008) (Supergenic Mn: Garnit *et al.*, 2020; Mishra *et al.*, 2006; Pharoe *et al.*, 2020). (B) Separation of supergene, hydrothermal and marine Mn (modified from Nicholson, 1992).

The multivariate statistical analysis revealed three main geochemical associations for the Araí Group deposits (Fig. 12): i) Ba-Cu association, characteristic of the Mn powdery type of the MJ1 sample, due to the hollandite occurrence (identified by XRD) and their capacity to scavenge Cu in their lattice, such as reported by Albuquerque *et al.* (2017), Garnit *et al.* (2020); ii) MnO, K₂O, LOI, As, Rb, Sr, Tl, U, and V association, related to the massive, hard and shining Mn of the MJ4 and MJ5 samples. This association is intrinsically linked to cryptomelane over hausmannite predominance and their preference for most trace elements which include As, Rb, Sr, Tl, U, and V (Post, 1999, Duan *et al.*, 2020). The microprobe data from Araí Group cryptomelane, indicate reasonable V₂O₃ and SrO contents varying from 0.13 to 0.1% and 0.04 to 0.2%, respectively. Moreover, at least three generations of cryptomelane along the fractures or venules, together with the high Tl contents with until 327 ppm in the MJ4 and MJ5 samples, are indicative of hydrothermal origins, such as discussed by Gołbiowska *et al.*, (2016) and Albuquerque *et al.*, (2017); iii) Al₂O₃, SiO₂, Co, Ni, Sc, Pb, Th, Zr, Y, and REE association relative to the Mn powdery type of MJ6 sample, and controlled by the pyrolusite and cryptomelane association. Low amounts of Al₂O₃ and SiO₂ in the whole rock geochemistry (Table 3) may be assigned to small Al₂O₃ and SiO₂ contents into pyrolusite and cryptomelane lattice (SiO₂= 0.092 to 0.474% and 0.013 to 0.340%; Al₂O₃=0.228 to 0.487% and 0.118 to 0.516%, respectively). Sc, Th, Zr, Y, and REE may be assigned to small amounts of heavy minerals. Moreover, due to the low sediment input from the continent, these elements, together with Co, Ni, and Pb, are probably related to the cryptomelane and pyrolusite capacity of trap trace and REE elements (Braun *et al.*, 1990; Ohta and Kawabe, 2001). On the hand, the leaching rates > 50% ratify the Mn's ability to trap Al, Ce, Co, Cu, Fe, Nb, Ni, Sr, Ti, U, V, Zn, and Zr. However, Th and Pb with leaching rates below 50% (Fig. 8) seem to be associated with heavy minerals, instead of Mn minerals.

The Paranoá Group Mn deposits interstratified in the reddish slate and siltstones bedding, and along a set of fractures, pockets and blocks in the surface, are characterized by the presence of romanechite, hollandite, and lithiophorite reflecting the highest Ba and Al₂O₃ concentrations, the highest Co/Zn ratios, and the major depletion of LREE concerning UCC. Two multivariate statistical analyzes were necessary to effectively separate the samples belonging to the Paranoá Group (Fig. 12D, F). The first separated three geochemical associations, dividing 2 samples with the most anomalous composition (FT1 and RZ1) from the other samples: 1) Al₂O₃, SiO₂, K₂O, MgO, TiO₂,

Rb, Nb, Th association, relating to sample FT1, which contains hollandite and cryptomelane, but also large amounts of illite/muscovite; 2) Co, Cu, Ni, U, Y and REE association, relating to sample RZ1 with large amounts of lithiophorite, Co and Co enrichment and monazite with U and Y; 3) the other samples are correlated only with MnO, which underwent a second process of multivariate analysis (Fig. 12E, F).

The second multivariate statistical analysis separated the remaining samples in four groups (Fig. 12E, F): i) Ba which grouped the powdery Mn and surface blocks samples, being related to romanechite+pyrolusite and hollandite+pyrolusite paragenesis and little contribution of terrigenous minerals; ii) SiO₂, TiO₂, Th, V and Zr association, related to CR deposit, which is associated with large amounts of quartz, the presence of Th, V, Zr may possibly be related to the resistate minerals; iii) Al₂O₃, K₂O, Rb association, being related to the stratified and powdery Mn, composed of hollandite, cryptomelane and the presence of illite/muscovite with Rb being related to this minerals; iv) MnO, P₂O₅, LOI, Ni, Zn association, related to Mn filling fractures in samples VZ1 and VZ2, and surface massive block in NQ1, linked to hollandite, cryptomelane and lithiophorite.

The low (La/Yb)_N ratios may be associated with hollandite and romanechite which, according to Kuleshov *et al.* (2022), is expected in the final stages of weathering and has also been identified in crusts formed in karsts in the Guizhou province in southwest China (Han *et al.*, 2017) and in hollandite and romanechite formed by infiltration in Tunisia and Morocco Mn deposits (Garnit *et al.*, 2020). Lithiophorite according to Parc (1989) marks the reaction of hollandite/cryptomelane with kaolinite. The Al₂O₃ in the lithiophorite structure increases its stability in a surface environment and can be considered the final product of the weathering of Mn oxides (Dowding & Fey, 2007). All lithiophorite associated with the Paranoá Group occur in filling fractures and are associated with samples with low (La/Yb)_N values.

These geochemical groups indicate a transformation sequence of minerals in the Mn of the Paranoá Group. It starts with cryptomelane, gradually passes to hollandite, and romanechite due to the addition of Ba and loss of K₂O (Gutzmer *et al.*, 2012), and ends with lithiophorite, which is the mineral with the highest Al₂O₃ content and the most stable on the surface (Dash *et al.* 2020) (Fig. 13). However, the paragenesis of lithiophorite and hollandite may be associated with hydrothermal processes, such as those in Erzgebirge metallogenic province. where lithiophorite and hollandite occur associated with hydrothermal veins (Burisch *et al.* 2020) which in the Paranoá group can be reinforced by the absence of terrigen and resistate minerals in most samples.

Most of the samples associated with the Paranoá Group have f^{Sm/Nd} similar to those of the Aurumina Suite and have higher values when compared to pelites from the Paranoá Group, the other samples have higher f^{Sm/Nd} values (Fig. 11A), with the samples having the lowest ratios (La/Yb)_N (<0.25) (Fig. 10A) that may be associated with supergenic processes (Peng *et al.*, 2014; Ma *et al.* 2010; Öhlander *et al.*, 2000)

The more radiogenic ⁸⁷Sr/⁸⁶Sr ratios (⁸⁷Sr/⁸⁶Sr > 0.74265) (Table 4) are mainly associated with the lower (La/Yb)_N ratios (Fig. 10B). This behavior is like that observed in the supergene alteration of the hydrothermally enriched Mn ore from the giant Kalahari deposit (Vafeas, 2019), suggesting the possibility of remobilization followed by supergene alteration for the Paranoá Group Mn samples.

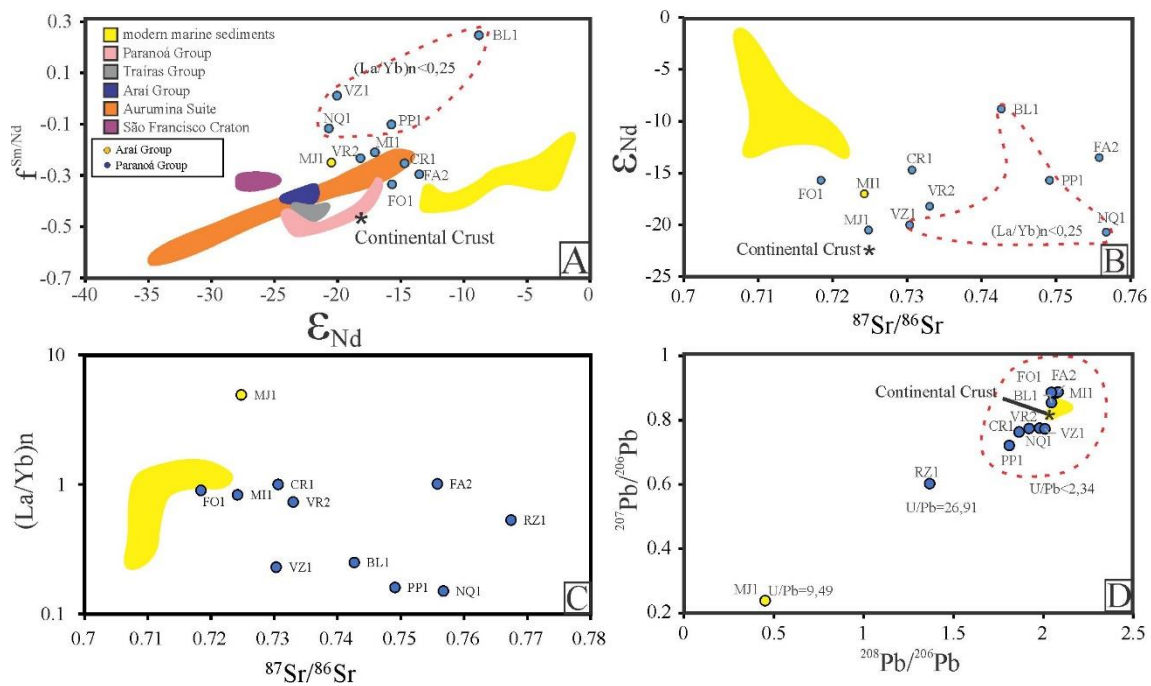


Figure 12. (A) Isotope ratios of Sm and Nd compared with the rocks of the Paranoá Group, Araí, their possible source rocks and sediments from current oceans and crustal averages. São Francisco Craton (Santos Pinto *et al.*, 1998), Suite Aurumina (Cuadros *et al.*, 2017), Araí Group (Silva *et al.*, 2021), Traíras and Paranoá Group (Pimentel *et al.*, 2001), modern marine sediments (Othman *et al.*, 1989), *upper continental crust (Taylor & McLennan, 1985). (B) Nd and Sr isotopic ratios compared to modern marine sediments, upper continental crust, continental crust (White, 2013). (C) Pb isotopic ratios compared with modern marine sediments and upper continental crust (Asmerom & Jacobsen, 1993).

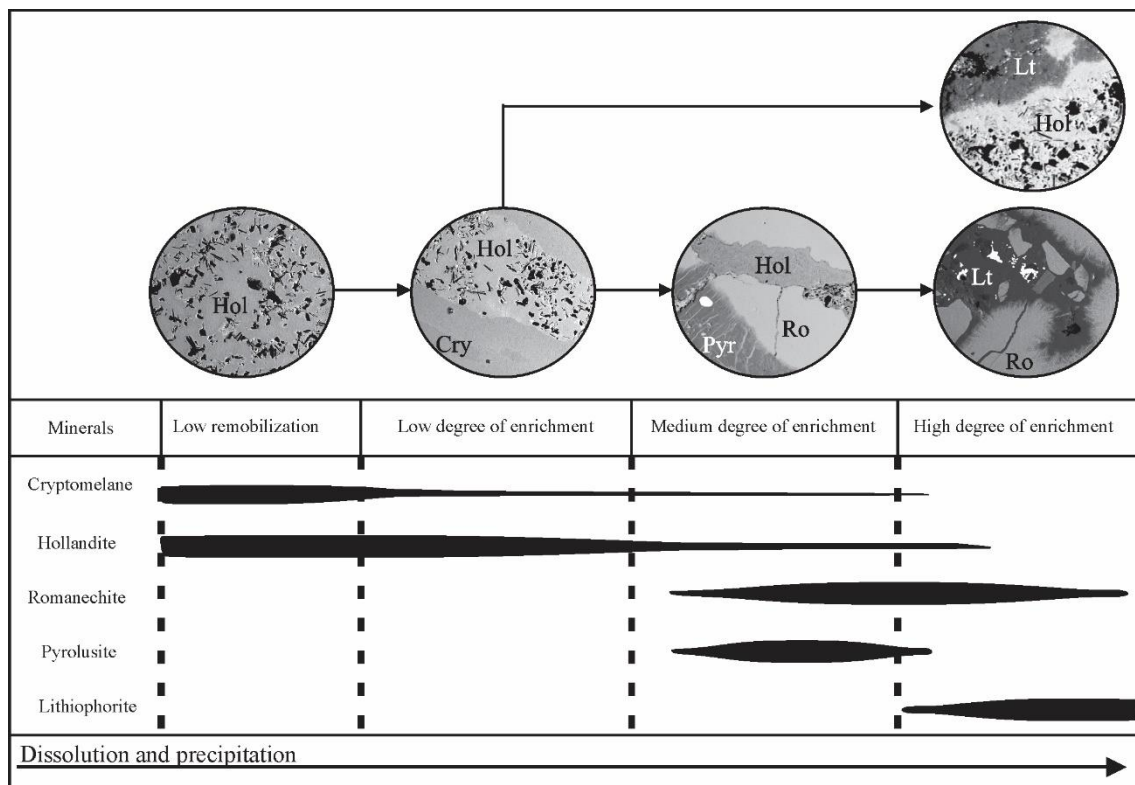


Figure 13. Mn oxide evolution process associated with the Paranoá Group.

6. CONCLUSIONS

The Mn oxyhydroxides in the Brasília fold belt, located in Central Brazil, are associated with the Araí and Paranoá Groups. The mineralogy and geochemistry with hausmannite and low Co/Zn ratios, high (La/Yb)_N and Eu/Eu* ratios of the Araí Group Mn deposit probably has a hydrothermal origin.

The Mn oxyhydroxides of the Paranoá Group with the highest concentrations of Al₂O₃ and Ba and the highest fractionation in the REE are indicative of supergene origin. The concentrations of Co, Ni, Cu and Zn associated with litiophorite and the presence of romanechite and hollandite may be associated with supergene Mn from infiltration or through hydrothermal processes and may be an overlap of the two.

Smaller (La/Yb)_N ratios may be associated with a greater degree of supergene alteration and are associated with fractionation in the isotopes of Sm and Nd, in addition to presenting more radiogenic Sr. The Pb isotope analyses indicate that the supergenic process had no influence on the ratios of these isotopes and that the RZ1 and MJ1 samples have higher concentrations of U/Pb, which differentiate them from the other analyzed samples.

ACKNOWLEDGEMENTS

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) – Finance Code 001 and by the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq-Project nº 137234/2019-8). The results presented here are part of the master thesis of Mr. Domingues G. C. O (first author). The authors are thankful to the Instituto de Geociências (IG-Unb) and the Programa de Pós-graduação da Universidade de Brasília (IGD-Unb).

REFERENCES

- Albuquerque, M. F. dos S., Horbe, A. M. C., & Botelho, N. F. (2017). Genesis of manganese deposits in southwestern Amazonia: Mineralogy, geochemistry and paleoenvironment. *Ore Geology Reviews*, 89, 270–289.
- Alvarenga, C. J. S. de, Botelho, N. F., Dardenne, M. A., Lima, O. N. B. de, Machado, M. A. 2007. Nota Explicativa da Folha SD.23-V-C-V (Cavalcante) – escala 1:100.000. UnB/CPRM, Goiás, 76 p.
- Asmeron, Y., Jacobsen, S.B., 1993. The Pb isotopic evolution of the Earth: inferences from river water suspended loads. *Earth Planetary Science Letters*. 115, 245–256
- Baêta, Jr. J. D. A., Martins, E. G., Leite, E. A., Ramos, J. B., Sá, J. A. G., Ribeiro, M. B. & Pires, P. R. O. 1978. Projeto Manganês no Centro-Sul de Goiás. Relatório Final, DNPM/CPRM. Escala 1:50.000. Goiânia, 256 p.
- Bau, M., & Dulski, P. (1999). Comparing yttrium and rare earths in hydrothermal fluids from the Mid-Atlantic Ridge: implications for Y and REE behaviour during near-vent mixing and for the YrHo ratio of Proterozoic seawater. *Chemical Geology*, 155, 77–90.
- Bau, M., Schmidt, K., Koschinsky, A., Hein, J., Kuhn, T., & Usui, A. (2014). Discriminating between different genetic types of marine ferro-manganese crusts and nodules based on rare earth elements and yttrium. *Chemical Geology*, 381, 1–9.
- Botelho, N.F., Alvarenga, C.J.S. de, Meneses, P.R., D’el-Rey Silva, L.J.H. 1999. Suíte Aurumina: Uma suíte de granitos paleoproterozóicos, peraluminosos e sintectônicos na Faixa Brasília. In: SBG, Simp. Geol. Centro-Oeste, 7, Brasília, Anais pp.17.
- Botelho, N.F., Fuck, R.A., Dantas, E.L., Laux, J.H., Junges, S.L. 2006a. The Paleoproterozoic peraluminous Aurumina granite suite, Goiás and Tocantins, Brazil: geological, whole rock geochemistry and U-Pb and Sm-Nd isotopic

- constraints. In: Alkmim, F.F., Noce, C.M. (Eds.). The Paleoproterozoic record of the São Francisco Craton, Brazil. Field guide and abstracts. IGCP509: Paleoproterozoic Supercontinents & Global Evolution. p. 92.
- Borges, C.C.A., Toledo, C.L.B., Silva, A.M., Chemale, F., Jost, H., Lana, C.C., 2017. Geochemistry and isotopic signatures of metavolcanic and metaplutonic rocks of the Faina and Serra de Santa Rita greenstone belts, Central Brazil: evidence for a Mesoarchean intraoceanic arc. *Precambrian Research*, 292, 350-377.
- Braun, J., Pagel, M., Muller, J., Bilong, P., Michard, A., Guillet, B., 1990. Cerium anomalies in lateritic profiles. *Geochimica et Cosmochimica Acta*, 54, 781-795.
- Callender, E., Bowser, C. J., 1976. Freshwater ferromanganese deposits. In *Handbook of strata-bound and stratiform ore deposits* (pp. 341-377). Elsevier scientific publishing company, Amsterdam 1997.
- Calvert, S. E., & Pedersen, T. F. (1996). Sedimentary Geochemistry of Manganese: Implications for the Environment of Formation of Manganiferous Black Shales. *Economic Geology*, 91, 36-47.
- Campos, J. E. G., Dardenne, M. A., Freitas-Silva, F. H., Martins-Ferreira, M. A. C. (2013). Geologia do Grupo Paranoá na porção externa da Faixa Brasília. *Brazilian Journal of Geology*, 43, 461-476.
- Carmichael, S. K., Doctor, D. H., Wilson, C. G., Feierstein, J., McAleer, R. J. (2017). New insight into the origin of manganese oxide ore deposits in the Appalachian Valley and Ridge of northeastern Tennessee and northern Virginia, USA. *Bulletin of the Geological Society of America*, 129, 1158-1180.
- Conly, A. G., Scott, S. D., & Bellon, H. (2011). Metalliferous manganese oxide mineralization associated with the Boléo Cu-Co-Zn district, Mexico. *Economic Geology*, 106, 1173-1196.
- Costa, M. L.; Fernandez, O. J. C.; Requelme, M. E.R. (2005) Depósito de Manganeês do Azul, Carajás: estratigrafia, Mineralogia, geoquímica e Evolução Geológica. In: Caracterização de depósitos minerais em distritos mineiros da Amazônia. DNPM-CT/Mineral-ADIMB.
- Cuadros, F. A., Botelho, N. F., Fuck, R. A., & Dantas, E. L. (2017). The peraluminous Aurumina Granite Suite in central Brazil: An example of mantle-continental crust interaction in a Paleoproterozoic cordilleran hinterland setting? *Precambrian Research*, 299, 75-100.
- Dardenne, M.A., 2000. The Brasília fold belt. In: Cordani, U.G., Milani, E.J., Thomaz Filho, A., Campos, D.A. (Eds.), 2000. Tectonic Evolution of South America. 31st International Geological Congress. SBG, Rio de Janeiro, pp. 231-263.
- Dash, N., Nayak, B., & Mohapatra, B. K. (2020). The Supergene Mn-minerals in Gangpur Group, Eastern India and their Genesis. *Journal of the Geological Society of India*, 96, 337-348.
- Dekoninck, A., Bernard, A., Barbarand, J., Saint-Bezar, B., Missenard, Y., Lepretre, R., Saddiqi, O., & Yans, J. (2016). Detailed mineralogy and petrology of manganese oxyhydroxide deposits of the Imini district (Morocco). *Mineralium Deposita*, 51(1), 13-23.
- Dowding, C. E., & Fey, M. v. (2007). Morphological, chemical and mineralogical properties of some manganese-rich oxisols derived from dolomite in Mpumalanga province, South Africa. *Geoderma*, 141, 23-33.
- Duan, J., Fu, Y., Zhang, Z., Xiao, J., & Wu, C. (2020). Genesis of the Dounan manganese deposit of southeast Yunnan, China: Constraints from the mineralogy and geochemistry of micronodules. *Journal of Geochemical Exploration*, 214, 106541.

- Fernandes, N. A., Olivo, G. R., Layton-Matthews, D., Voinot, A., Chipley, D., Leybourne, M., Reith, W., Leduc, E., Diniz-Oliveira, G., Kyser, T. K. (2021). Metal sources in the proterozoic vazante-paracatu sediment-hosted zn district, Brazil: Constraints from pb isotope compositions of metasiliciclastic units. *Canadian Mineralogist*, 59, 1187–1205.
- Force, E. R., & Cannon, W. F. (1988). Depositional Model for Shallow-Marine Manganese Deposits around Black Shale Basins. *Economic Geology*, 83, 93–117.
- Fuck, R.A., Dantas, E.L., Pimentel, M.M., Botelho, N.F., Armstrong, R., Laux, J.H., Junges, S.L., Soares, J.E., Praxedes, I.F., 2014. Paleoproterozoic crust-formation and reworking events in the Tocantins Province, central Brazil: A contribution for Atlantica supercontinent reconstruction. *Precambrian Research* 244, 53–74.
- Fuck, R.A., Pimentel, M.M., Alvarenga, C.J., Dantas, E.L., 2017. The Northern Brasília Belt. In: São Francisco Craton, Eastern Brazil. Springer International Publishing Switzerland 2017, pp. 205–220.
- Garnit, H., Kraemer, D., Bouhlef, S., Davoli, M., & Barca, D. (2020). Manganese ores in Tunisia: Genetic constraints from trace element geochemistry and mineralogy. In *Ore Geology Reviews*, Vol. 120. Elsevier B.V.
- Gołębiowska B., Rzepa G., Pieczka A. (2015). Exceptional Tl-bearing manganese oxides from Zalas, Krakow area, southern Poland. *Mineralogia*, 46, 3-18.
- Gioia, S. M. C. L.; Pimentel, M. M. (2000) The Sm-Nd isotopic method in the Geochronology Laboratory of the University of Brasília. *Anais da Academia Brasileira de Ciências*, 72, 219-245.
- Guimarães, E. M., 1978. Os depósitos de manganês de S. João D’Aliança – GO. M.Sc. dissertation (unpubl.), Universidade de Brasília, Brasil. 129 p.
- Gutzmer, J., du Plooy, A. P., & Beukes, N. J. (2012). Timing of supergene enrichment of low-grade sedimentary manganese ores in the Kalahari Manganese Field, South Africa. *Ore Geology Reviews*, 47, 136–153.
- Halbach, P. (1986). Processes controlling the heavy metal distribution in pacific ferromanganese nodules and crusts. *Geologische Rundschau*, 75, 235–247.
- Han, G., Song, Z., & Tang, Y. (2017). Geochemistry of rare earth elements in soils under different land uses in a typical karst area, Guizhou Province, Southwest China. *Canadian Journal of Soil Science*, 97, 606–612.
- Hein, J. R., Koschinsky, A., Halbach, P., Manhein, F. T., Bau, M. Kang, J., Lubick, N., 1997 Iron and manganese oxide mineralization in the pacific. In *Manganese Mineralization: Geochemistry and Mineralogy of the Terrestrial and Marine Deposits* (pp. 123-138). Geological Society Special Publication 1997.
- Kuleshov, V. N., Bychkov, A. Y., & Sviridov, L. I. (2022). Specific Features of the Rare Earth Element Distribution in Rocks and Ores of the Porozhinsk Manganese Deposit (Yenisei Ridge, Krasnoyarsk Region). *Lithology and Mineral Resources*, 57, 299–314.
- Ma, J., Wei, G., Xu, Y., & Long, W. (2010). Variations of Sr-Nd-Hf isotopic systematics in basalt during intensive weathering. *Chemical Geology*, 269, 376–385.
- Ma, Y., Liu, C. (2001). Sr isotope evolution during chemical weathering of granites. *Science of China*, 44, 726–734.
- Marini, O.J., Fuck, R.A., Dardenne, M.A. and Danni, J.C.M., 1984. Provincia Tocantins: setores central e sudeste. In: F.F.M. de Almeida and Y. Hasui (Editors), *O Pr6-Cambriano do Brasil*. Bliicher, São Paulo, 205-264
- Martins-Ferreira, M.A., Chemale, F., Dias, A.N.C., Campos, J.E.G., 2018a. Proterozoic intracontinental basin succession in the western margin of the São Francisco

- Craton: constraints from detrital zircon geochronology. *Journal of South American Earth Sciences*, 81, 165–176.
- Matteini, M., Dantas, E.L., Pimentel, M.M., de Alvarenga, C.J.S., Dardenne, M.A., 2012. U–Pb and Hf isotope study on detrital zircons from the Paranoá Group, Brasília Belt
Brazil: constraints on depositional age at Mesoproterozoic–Neoproterozoic transition and tectono-magmatic events in the São Francisco craton. *Precambrian Res.* 206, 168–181.
- Maynard, J. B. (2010). The chemistry of manganese ores through time: A signal of increasing diversity of earth-surface environments. *Economic Geology*, 105, 535–552.
- McLennan, S. M. (2001). Relationships between the trace element composition of sedimentary rocks and upper continental crust. *Geochemistry Geophysics Geosystems*, 2, 1–24.
- Nicholson, K. (1992). Contrasting Mineralogical-Geochemical Signatures of Manganese Oxides' Guides to Metallogenesis. *Economic Geology*, 87, 1253–1264.
- Ohta, A., Kawabe, I., 2001. REE (III) adsorption onto Mn dioxide (d-MnO₂) and Feoxyhydroxide: Ce (III) oxidation by d-MnO₂. *Geochimica et Cosmochimica Acta*, 65, 695–703.
- Öhlander, B., Ingri, J., Land, M., & Schöberg, H. (2000). Change of Sm-Nd isotope composition during weathering of till. *Geochimica et Cosmochimica Acta*, 64, 813–820.
- Ostwald, J. (1984). Two varieties of lithiophorite in some Australian deposits. *Mineralogical Magazine*, 48, 383–391.
- Ostwald, J. (1988). Mineralogy of the Groote Eylandt manganese oxides: a review. *Ore Geology Reviews*, 4, 3–45.
- Ostwald, J. (1993). Manganese oxide mineralogy, petrography and genesis, Pilbara Manganese Group, Western Australia. *Mineral. Deposita*, 28, 198–209.
- Othman, D., White, W.M. and Patchett, J. 1989. The geochemistry of marine sediments, island arc magma genesis, and crust-mantle recycling. *Earth and Planetary Science Letters*, 94, 1–21
- Parc, S., Nahon, D., Tardy, Y., Vieillard, P. (1989). Estimated solubility products and fields of stability for cryptomelane, nsutite, birnessite, and lithiophorite based on natural lateritic weathering sequences. *American Mineralogist*, 74, 466–475.
- Peng, B., Rate, A., Song, Z., Yu, C., Tang, X., Xie, S., Tu, X., & Tan, C. (2014). Geochemistry of major and trace elements and Pb-Sr isotopes of a weathering profile developed on the Lower Cambrian black shales in central Hunan, China. *Applied Geochemistry*, 51, 191–203.
- Pimentel, M. M., Dardenne, M. A., Fuck, R. A., Viana, M. G., Junges, S. L., Fischel, D. P., Seer, H. J., & Dantas, E. L. (2001). Nd isotopes and the provenance of detrital sediments of the Neoproterozoic Brasília Belt, central Brazil. *Journal of South American Earth Sciences*, 14, 571–582.
- Post, J. E. (1999). Manganese oxide minerals: Crystal structures and economic and. *Proceedings of the National Academy of Sciences USA*, 96, 3447–3454.
- Pracejus, B., Bolton, B. R., Frakes, L. A. (1988). Nature and development of supergene manganese deposits, Groote Eylandt, Northern Territory, Australia. *Ore Geology Reviews*, 4, 71–98.

- Rollinson, H. and Pease, V., 2021. Using Geochemical Data: to Understand Geological Processes, Cambridge University Press, Cambridge.
- Roy, S. (2006). Sedimentary manganese metallogenesis in response to the evolution of the Earth system: *Earth Science Reviews*, 77, 273–305.
- Roy, S. (1997). Genetic diversity of manganese deposition in the terrestrial geological record Hydrothermal manganese deposits. In *Manganese Mineralization: Geochemistry and Mineralogy of the Terrestrial and Marine Deposits* (pp. 5-27). Geological Society Special Publication.
- Roy, S. (1992). Environments and processes of manganese deposition. *Economic Geology*, 87, 1218–1236.
- Santos Pinto, M., Peucat, J., Martin, H., & Sabaté, P. (1998). Recycling of the Archaean continental crust: the case study of the Gavião, State of Bahia, NE Brazil. *Journal of South American Earth Sciences*, 11, 487–498.
- Seraine, M., Campos, J.E.G., Martins-Ferreira, M.A.C., Giorgioni, M., Angelo, T.V., 2020. Tectonic significance of abrupt immature sedimentation in a shallow cratonic margin basin: the Arkose Level, Mesoproterozoic Paranoá Group. *Journal of South America Earth Science*. 97 p.102397.
- Silva, C. C., da Silva Souza, V., Botelho, N. F., & Dantas, E. L. (2021). Contribution to petrogenesis of the Paleoproterozoic Basaltic Magmatism from the Araí continental rift, central Brazil. *Journal of South American Earth Sciences*, 110, 103345.
- Sousa, I.M.C., Giustina, M.E.S.D., Oliveira, C.G., 2016. Crustal evolution of the northern Brasília Belt basement, central Brazil: A Rhyacian orogeny coeval with a pre-Rodinia supercontinent assembly. *Precambrian Research* 273, 129–150.
- Tanizaki, M.L.N., Campos, J.E.G., Dardenne, M.A., 2015. Estratigrafia do Grupo Araí: Registro de rifteamento paleoproterozoico no Brasil Central. *Brazilian J. Geol.* 45, 95–108.
- Taylor, D., Dalstra, H. J., Harding, A. E., Broadbent, G. C., & Barley, M. E. (2001). Genesis of High-Grade Hematite Orebodies of the Hamersley Province, Western Australia. *Economic Geology*, 96, 837–873.
- Taylor, S.R., McLennan, S.M., 1985. *The Continental Crust its Composition and Evolution*. Blackwell Scientific Publications, Oxford, 312 pp.
- Vafeas, N. A., Blignaut, L. C., Viljoen, K. S., & le Roux, P. (2019). An investigation into the $^{87}\text{Sr}/^{86}\text{Sr}$ radiogenic isotope geochemistry of the manganese ore of the Kalahari manganese field with a view on hydrothermal fluid flow and related rare earth element enrichments. *South African Journal of Geology*, 122, 237–248.
- Valeriano, C.M., Pimentel, M.M., Heilbron, M., Almeida, J.C.H., Trouw, R.A.J., 2008. Tectonic evolution of the Brasília Belt, Central Brazil, and early assembly of Gondwana. In *West Gondwana: Pre-Cenozoic Correlations Across the South Atlantic Region* (pp. 197–210) Geological Society, London, Special Publications. 294.
- Varentsov, I.M., 1996, *Manganese ores of supergene zone: Geochemistry of formation*: Dordrecht, Kluwer Academic Publishers, 342 p.
- White, W.M., 2013. *Geochemistry*. Wiley-Blackwell, Chichester 312 pp.

CONSIDERAÇÕES FINAIS E CONCLUSÃO

Os oxi-hidróxidos de Mn que ocorrem na faixa de dobramentos Brasília, localizado no Brasil Central, estão associados aos Grupos Araí e Paranoá. A ocorrência presente no Grupo Araí está na forma de camadas interestratificados com metaparaconglomerados e quartzitos do Membro Prata. As ocorrências associadas ao Grupo Paranoá estão na forma de lamelas, preenchendo fraturas, em bolsões com Mn pulverulento e na forma de blocos, ocorrendo associado aos quartzitos friáveis da Formação Serra da Meia Noite e Formação Ribeirão Contagem e aos pelitos da Formação Ribeirão Piçarrão.

A mineralogia e a geoquímica com hausmannita e baixas razões Co/Zn, altas de $(La/Yb)_N$ e Eu/Eu^* nos OH de Mn do Grupo Araí, são indicativas de hidrotermalismo. Enquanto nas do Grupo Paranoá apresentando romanechita e litioforita sugerem uma forte contribuição supergênica para os depósitos, apresentando maiores concentrações de Al_2O_3 , Ba e um fracionamento nos ETR e razão $(La/Yb)_N$ menor que 1 para a maior parte das amostras.

As maiores concentrações de Co, Cu, Ni e Zn estão associadas a litioforita, que pode ser considerada a última fase a ser formada, o que indica que seu acúmulo está associado ao processo de enriquecimento supergênico. A combinação de baixos valores de $(La/Yb)_N$ com presença de hollandita e romanechita podem sugerir que os depósitos se tratam de depósitos de infiltração, que são comumente associados a carstes. O modo de ocorrência desse tipo de depósito é na forma cimento em brechas de colapso e preenchendo fraturas.

As baixas razões $(La/Yb)_N$ ($(La/Yb)_N < 0,25$) estão associados maiores fracionamentos nas razões isotópicas de Sm e Nd, além de valores mais radiogênicos de isótopo de Sr. Os isótopos de Pb não apresentam fracionamento com as variações de $(La/Yb)_N$. As amostras apresentam razões $^{208}Pb/^{206}Pb$ e $^{207}Pb/^{206}Pb$ próximas da média crustal, as amostras RZ1 e MJ1 apresentam valores menores quando comparados com a média crustal.

Os OH-Mn em lamelas são considerados menos remobilizados e apresentam comportamento dos ETR semelhante a composição da Crosta Continental. A presença de hollandita e litioforita nesses depósitos e a identificação de manganita em trabalhos anteriores indicam um proto-minério formado por carbonato de Mn. Esse carbonato pode ter sido depositado em ambiente transgressivo e associado a zonas de ressurgência, visto a existência de elementos presentes em zona de alta produtividade, como Ba e

P₂O₅ no Mn, assim como elementos que são adsorvidos em matéria orgânica como Co, Ni, Cu e Zn.

O estudo mais detalhado dos OH-Mn presente em lamelas que pode ser considerado o menos remobilizado pode trazer informações sobre o proto-minério e sobre as condições deposicionais do Mn na bacia do Paranoá.

O estudo mais detalhado dos OH-Mn com análises de geoquímica pontual (LA-ICPMS) nos minerais associados ao Mn remobilizado e ao menos remobilizado com diferentes (La/Yb)_N podem fornecer informações importante de como funciona o fracionamento dos ETR em Mn supergênico e como ocorre o fracionamento dos isótopos de Sm, Nd e Sr.

AGRADECIMENTOS

O presente trabalho foi realizado com apoio da Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) – Código de Financiamento 001

REFERÊNCIAS BIBLIOGRÁFICAS

- Alvarenga, C.J.S. de, Botelho, N.F., Dardenne, M. A., Lima, O.N.B. de, Machado, M. A. 2007. Nota Explicativa da Folha SD.23-V-C-V (Cavalcante) - escala 1:100.000. UnB/CPRM, Goiás, 76 p.
- Baêta, Jr. J. D. A., Martins, E. G., Leite, E. A., Ramos, J. B., Sá, J. A. G., Ribeiro, M. B. & Pires, P. R. O. 1978. Projeto Manganês no Centro-Sul de Goiás. Relatório Final, DNPM/CPRM. Escala 1:50.000. Goiânia, 256 p.
- Bau, M. (1991) Rare-earth element mobility during hydrothermal and metamorphic fluid-rock interaction and the significance of the oxidation state of europium. *Chem. Geol.* 93, 219-230.
- Bau, M., & Dulski, P. (1999). Comparing yttrium and rare earths in hydrothermal fluids from the Mid-Atlantic Ridge: implications for Y and REE behaviour during near-vent mixing and for the YrHo ratio of Proterozoic seawater. *Chemical Geology*, 155, 77–90. [https://doi.org/https://doi.org/10.1016/S0009-2541\(98\)00142-9](https://doi.org/https://doi.org/10.1016/S0009-2541(98)00142-9)
- Bau, M., Schmidt, K., Koschinsky, A., Hein, J., Kuhn, T., & Usui, A. (2014). Discriminating between different genetic types of marine ferro-manganese crusts and nodules based on rare earth elements and yttrium. *Chemical Geology*, 381, 1–9. <https://doi.org/10.1016/j.chemgeo.2014.05.004>
- Botelho, N.F., Alvarenga, C.J.S. de, Meneses, P.R., D’el-Rey Silva, L.J.H. 1999. Suíte Aurumina: Uma suíte de granitos paleoproterozóicos, peraluminosos e sin-tectônicos na Faixa Brasília. In: SBG, Simp. Geol. Centro-Oeste, 7, Brasília, Anais pp.17.
- Buatier, M.D., Guillaume, D., Wheat, C.G., Hervé, L., and Adatte, T. (2004) Mineralogical characterization and genesis of hydrothermal Mn oxides from the flank of the Juan the Fuca Ridge. *American Mineralogist*, 89, 1807-1815.

- Calvert, S. E., & Pedersen, T. F. (1996). Sedimentary Geochemistry of Manganese: Implications for the Environment of Formation of Manganiferous Black Shales. *Economic Geology*, 91, 36–47. <http://pubs.geoscienceworld.org/segweb/economicgeology/article-pdf/91/1/36/3492176/36.pdf>
- Campos, J. E. G., Dardenne, M. A., Freitas-Silva, F. H., & Martins-Ferreira, M. A. C. (2013). Geologia do Grupo Paranoá na porção externa da Faixa Brasília. *Brazilian Journal of Geology*, 43(3), 461–476. <https://doi.org/10.5327/Z2317-48892013000300004>
- Dardenne, 2000
- Dardenne, M.A., 2000. The Brasília fold belt. In: Cordani, U.G., Milani, E.J., Thomaz Filho, A., Campos, D.A. (Eds.), 2000. Tectonic Evolution of South America. 31st International Geological Congress. SBG, Rio de Janeiro, pp. 231–263.
- Dash, N., Nayak, B., & Mohapatra, B. K. (2020). The Supergene Mn-minerals in Gangpur Group, Eastern India and their Genesis. *Journal of the Geological Society of India*, 96(4), 337–348. <https://doi.org/10.1007/s12594-020-1562-5>
- Force, E. R., & Cannon, W. F. (1988). Depositional Model for Shallow-Marine Manganese Deposits around Black Shale Basins. *Economic Geology*, 83, 93–117.
- Force, E.R., and Maynard J.B., 1991, Manganese: Syngenetic deposits on the margins of anoxic basins: Reviews in Economic Geology, 5, 147–159.
- Fuck, R.A., Pimentel, M.M., Alvarenga, C.J., Dantas, E.L., 2017. The Northern Brasília Belt. In: São Francisco Craton, Eastern Brazil. Springer International Publishing Switzerland 2017, pp. 205–220. <https://doi.org/10.1007/978-3-319-01715-0>
- Garnit, 2020
- Garnit, H., Kraemer, D., Bouhlef, S., Davoli, M., & Barca, D. (2020). Manganese ores in Tunisia: Genetic constraints from trace element geochemistry and mineralogy. In *Ore Geology Reviews* (Vol. 120). Elsevier B.V. <https://doi.org/10.1016/j.oregeorev.2020.103451>
- Gioia, S. M. C. L.; Pimentel, M. M. (2000) The Sm-Nd isotopic method in the Geochronology Laboratory of the University of Brasília. *Anais da Academia Brasileira de Ciências*, 72(2), 219-245.
- Guimarães, E. M., 1978. Os depósitos de manganês de S. João D’Aliança – GO. M.Sc. dissertation (unpubl.), Universidade de Brasília, Brasil. 129 p.
- Gutzmer, 2012
- Gutzmer, J., du Plooy, A. P., & Beukes, N. J. (2012). Timing of supergene enrichment of low-grade sedimentary manganese ores in the Kalahari Manganese Field, South Africa. *Ore Geology Reviews*, 47, 136–153. <https://doi.org/10.1016/j.oregeorev.2012.04.003>
- Gutzmer, J., du Plooy, A. P., & Beukes, N. J. (2012). Timing of supergene enrichment of low-grade sedimentary manganese ores in the Kalahari Manganese Field, South Africa. *Ore Geology Reviews*, 47, 136–153. <https://doi.org/10.1016/j.oregeorev.2012.04.003>
- Halbach, P. (1986). Processes controlling the heavy metal distribution in pacific ferromanganese nodules and crusts. *Geologische Rundschau*, 75(1), 235–247. <https://doi.org/10.1007/BF01770191>
- Hein, J. R., Schulz, M. S., Dunham, R. E., Stern, R. J., & Bloomer, S. H. (2008). Diffuse flow hydrothermal manganese mineralization along the active Mariana and southern Izu-Bonin arc system, western Pacific. *Journal of Geophysical Research: Solid Earth*, 113(8). <https://doi.org/10.1029/2007JB005432>
- Martins-Ferreira, M. A. C., Campos, J. E. G., & von Huelsen, M. G. (2018). Tectonic evolution of the Paranoá basin: New evidence from gravimetric and stratigraphic data. *Tectonophysics*, 734–735(April), 44–58. <https://doi.org/10.1016/j.tecto.2018.04.004>

- Martins-Ferreira, M. A. C., Campos, J. E. G., von Huelsen, M. G., & Neri, B. L. (2018). Paleorift structure constrained by gravity and stratigraphic data: The Statherian Araí rift case. *Tectonophysics*, 738–739(December 2017), 64–82. <https://doi.org/10.1016/j.tecto.2018.05.014>
- Martins-Ferreira, M. A. C., Campos, J. E. G., von Huelsen, M. G., & Neri, B. L. (2018). Paleorift structure constrained by gravity and stratigraphic data: The Statherian Araí rift case. *Tectonophysics*, 738–739(December 2017), 64–82. <https://doi.org/10.1016/j.tecto.2018.05.014>
- Maynard, J. B. (2010). The chemistry of manganese ores through time: A signal of increasing diversity of earth-surface environments. *Economic Geology*, 105(3), 535–552. <https://doi.org/10.2113/gsecongeo.105.3.535>
- Maynard, J. B. (2013). Manganiferous Sediments, Rocks, and Ores. In *Treatise on Geochemistry: Second Edition* (Vol. 9, pp. 327–349). Elsevier Inc. <https://doi.org/10.1016/B978-0-08-095975-7.00711-7>
- McLennan, S. M. (2001). Relationships between the trace element composition of sedimentary rocks and upper continental crust. *Geochemistry Geophysics Geosystems*, 2, 1–24.
- Nicholson, K. (1992). Contrasting Mineralogical-Geochemical Signatures of Manganese Oxides' Guides to Metallogenesis. *Economic Geology*, 87, 1253–1264.
- Ostwald, J. (1988). MINERALOGY OF THE GROOTE EYLANDT MANGANESE OXIDES: A REVIEW. *Ore Geology Reviews*, 4, 3–45.
- Post, J. E. (1999). Manganese oxide minerals: Crystal structures and economic and. *Proc Natl Acad Sci USA*, 96(March), 3447–3454.
- Roy, S. (1992). Environments and processes of manganese deposition. *Economic Geology*, 87(5), 1218–1236. <https://doi.org/10.2113/gsecongeo.87.5.1218>
- Roy, S. (1997). Genetic diversity of manganese deposition in the terrestrial geological record Hydrothermal manganese deposits. In *Manganese Mineralization: Geochemistry and Mineralogy of the Terrestrial and Marine Deposits* (pp. 5–27). Geological Society Special Publication 1997.
- Roy, S., 1981, Manganese deposits, Academy Press, London, pp. 451.
- Tanizaki, M.L.N., Campos, J.E.G., Dardenne, M.A., 2015. Estratigrafia do Grupo Araí: Registro de rifteamento paleoproterozoico no Brasil Central. *Brazilian J. Geol.* 45, 95–108. <https://doi.org/10.1590/23174889201500010007>
- Valeriano, C.M., Pimentel, M.M., Heilbron, M., Almeida, J.C.H., Trouw, R.A.J., 2008. Tectonic evolution of the Brasília Belt, Central Brazil, and early assembly of Gondwana. In *West Gondwana: Pre-Cenozoic Correlations Across the South Atlantic Region* (pp. 197–210) Geological Society, London, Special Publications. 294.
- Varentsov, I.M., 1996, Manganese ores of supergene zone: Geochemistry of formation: Dordrecht, Kluwer Academic Publishers, 342 p.
- Weber, F. (2013). Evolution of Lateritic Manganese Deposits. In *Soils and Sediments* (97–124). Springer-Verlag Berlin. <https://doi.org/10.1016/B978-0-08-095975-7.00711-7>

ANEXOS

Tabela A1. Composição química lixiviação óxidos maiores em %, traços em ppm.

	MJ1	RZ1	NQ1	Mi1	CR1	VZ1	VR2	PP1	FA2	BL1	FO1	P1	P2	RT22
Mn	>50000	>50000	>50000	>50000	>50000	>50000	>50000	>50000	>50000	>50000	>50000	20.500	7.800	495.000
Fe	1.780	0.010	4.320	0.078	0.300	10.650	0.690	6.050	0.720	0.620	0.124	3.830	4.730	2.910
Al	0.750	3.890	1.970	0.370	0.380	0.610	0.520	0.330	0.760	0.470	0.400	1.710	1.140	2.200
Ca	1.320	0.170	0.250	0.750	0.060	0.270	0.480	0.120	0.190	0.230	0.520	0.010	0.010	0.370
Mg	<0.01	<0.01	<0.01	0.010	<0.01	0.010	0.030	<0.01	<0.01	0.020	0.020	0.090	0.020	1.150
Na	0.080	0.042	0.104	0.024	0.013	0.024	0.033	0.008	0.034	0.018	0.026	0.006	0.012	0.090
K	1.670	0.100	2.060	0.180	0.070	0.770	0.400	0.060	0.700	0.140	0.230	0.680	0.370	1.620
Ti	0.007	<0.001	0.003	<0.001	0.010	0.003	0.007	0.002	0.009	0.003	0.002	0.032	0.016	0.216
P	0.016	0.092	0.262	0.104	0.100	0.328	0.080	0.262	0.125	0.145	0.142	0.015	0.007	0.064
As	56.500	8.680	90.800	42.100	103.000	95.100	35.900	320.000	44.300	77.300	10.200	0.450	0.060	0.050
Ba	>10000	>10000	>10000	>10000	>10000	5730.000	>10000	>10000	>10000	>10000	>10000	221.000	57.700	368.000
Co	104.000	7670.000	4560.000	577.000	377.000	546.000	458.000	1025.000	199.500	359.000	1035.000	26.600	9.440	95.800
Cr	33.900	0.950	1.950	0.290	1.220	1.350	0.640	1.940	1.750	0.620	0.640	29.400	36.200	60.100
Cu	482.000	2750.000	936.000	121.500	113.000	120.000	289.000	129.000	23.700	288.000	390.000	2.170	4.080	30.500
Ga	17.600	4.770	7.880	10.800	12.900	12.100	13.300	9.110	7.680	11.250	6.630	4.540	4.300	9.110
Nb	0.353	0.026	0.108	0.045	0.327	0.127	0.227	0.064	0.203	0.101	0.116	0.081	0.097	0.339
Ni	18.150	1565.000	1040.000	63.000	15.850	160.000	61.500	27.500	10.050	15.200	79.100	2.350	8.690	38.500
Pb	13.800	0.825	37.900	103.500	1.760	4.810	5.870	2.940	16.100	353.000	226.000	12.300	5.310	2.090
Rb	12.100	3.390	32.000	2.910	2.790	21.300	12.050	1.675	11.800	3.970	4.050	28.100	16.700	154.000
Sc	2.270	10.300	4.770	10.750	3.510	3.870	8.660	5.510	4.480	4.620	23.500	4.640	3.680	2.840
Sr	2720.000	281.000	424.000	1515.000	55.800	390.000	770.000	146.000	125.000	431.000	990.000	7.310	3.880	25.200
Th	0.138	0.027	0.736	0.239	1.440	0.534	1.450	0.108	0.500	0.854	0.241	7.830	6.360	5.600
Tl	134.500	17.400	50.200	28.200	15.750	132.000	93.200	35.300	67.800	48.700	92.500	0.155	0.062	0.921
U	131.000	22.200	4.150	3.120	4.120	1.290	12.250	3.130	1.315	4.700	6.850	1.110	0.657	0.449
V	213.000	299.000	22.000	120.500	666.000	32.500	12.100	87.900	20.600	107.500	362.000	18.900	17.700	31.700
Y	23.400	661.000	169.500	64.200	17.750	42.400	126.000	57.300	7.460	51.100	74.500	8.960	3.180	5.680
Zn	369.000	1385.000	1185.000	369.000	128.500	554.000	147.000	119.000	90.400	333.000	463.000	6.500	8.300	91.500
Zr	15.400	4.250	4.380	6.330	6.120	4.710	9.290	1.550	2.300	3.850	4.350	20.000	8.690	2.980
La	91.600	284.000	9.670	68.300	22.400	11.350	123.000	7.570	11.850	7.830	90.400	19.350	5.360	14.650
Ce	175.000	136.000	66.900	106.500	136.500	25.700	222.000	96.400	140.500	122.000	792.000	25.000	7.820	29.300
Au	0.001	0.005	0.002	0.008	0.003	0.002	0.013	0.003	0.002	0.004	0.027	0.001	0.000	0.001
Ag	0.217	0.842	0.378	2.040	0.124	0.370	0.561	0.095	0.312	11.200	3.250	0.055	0.007	0.032
B	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	10.000	10.000	<10
Be	4.290	2.110	5.000	7.490	5.630	6.060	15.000	5.990	1.640	4.330	22.000	0.700	0.340	0.180
Bi	0.117	0.009	0.053	0.089	0.030	0.024	0.023	0.024	0.017	0.128	0.016	0.242	0.234	0.034
Cd	0.154	0.821	21.400	2.510	1.655	1.330	0.942	0.522	0.275	6.420	2.930	0.002	0.004	0.007
Cs	0.066	0.148	0.258	0.136	0.306	0.347	1.460	0.191	0.632	0.728	0.377	0.804	0.743	7.520
Ge	2.710	2.260	0.318	1.655	0.131	1.120	1.445	0.873	0.489	0.277	0.668	0.073	0.056	0.094
Hf	0.179	0.028	0.050	0.037	0.166	0.060	0.149	0.027	0.077	0.038	0.054	0.540	0.226	0.117
Hg	0.034	0.952	1.005	0.127	0.112	0.236	0.324	0.354	0.229	0.318	1.020	0.010	0.010	0.004
In	0.675	<0.005	<0.005	0.005	0.005	0.007	0.007	<0.005	0.011	0.025	0.006	0.012	0.009	0.007
Li	6.900	1160.000	433.000	0.400	0.900	82.700	1.900	0.600	11.900	0.700	2.700	1.800	0.500	41.700
Mo	24.400	52.700	6.330	8.990	2.530	4.250	27.900	30.900	15.650	40.700	14.000	0.120	0.070	0.520
Pd	0.160	0.042	0.001	0.008	0.005	0.007	0.004	0.002	0.004	0.015	<0.001	<0.001	<0.001	<0.001
Pt	0.063	0.015	0.005	0.009	<0.002	<0.002	0.008	0.012	0.019	0.004	0.006	<0.002	<0.002	<0.002
Re	0.002	0.005	0.004	0.005	0.012	0.006	0.004	0.002	0.002	0.004	0.003	0.001	<0.0002	0.013
Sb	4.240	0.809	0.550	1.230	0.261	4.110	11.600	2.610	3.380	5.180	6.650	0.482	0.180	<0.005
Se	0.099	<0.003	0.123	0.073	0.060	0.074	0.077	0.124	0.112	0.123	0.134	0.008	0.007	0.150
Sn	0.390	<0.01	0.080	0.010	0.120	0.050	0.060	0.040	0.080	0.100	0.060	0.980	0.410	0.540
Ta	0.081	0.017	0.094	0.074	0.128	0.137	0.077	0.024	0.057	0.038	0.036	<0.005	<0.005	0.025
Te	0.028	0.011	0.067	0.009	0.008	0.028	0.009	0.006	0.006	0.005	0.009	0.005	0.011	0.008
W	77.700	68.400	151.000	161.500	470.000	185.500	114.000	76.400	59.600	147.000	83.400	61.400	25.300	500.000

Imagem de Elétrons 3

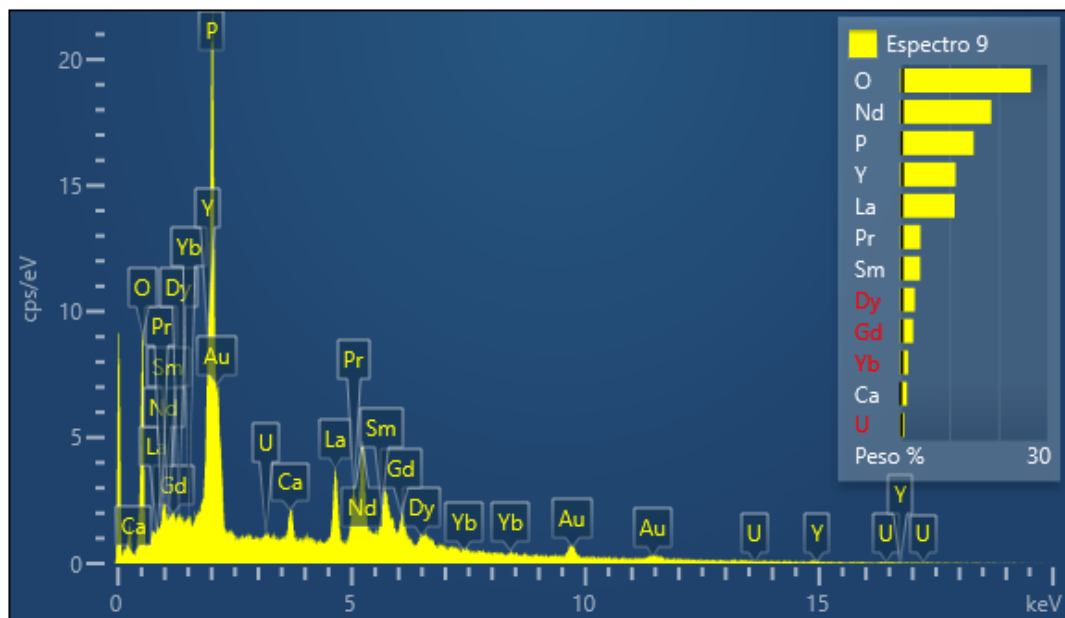
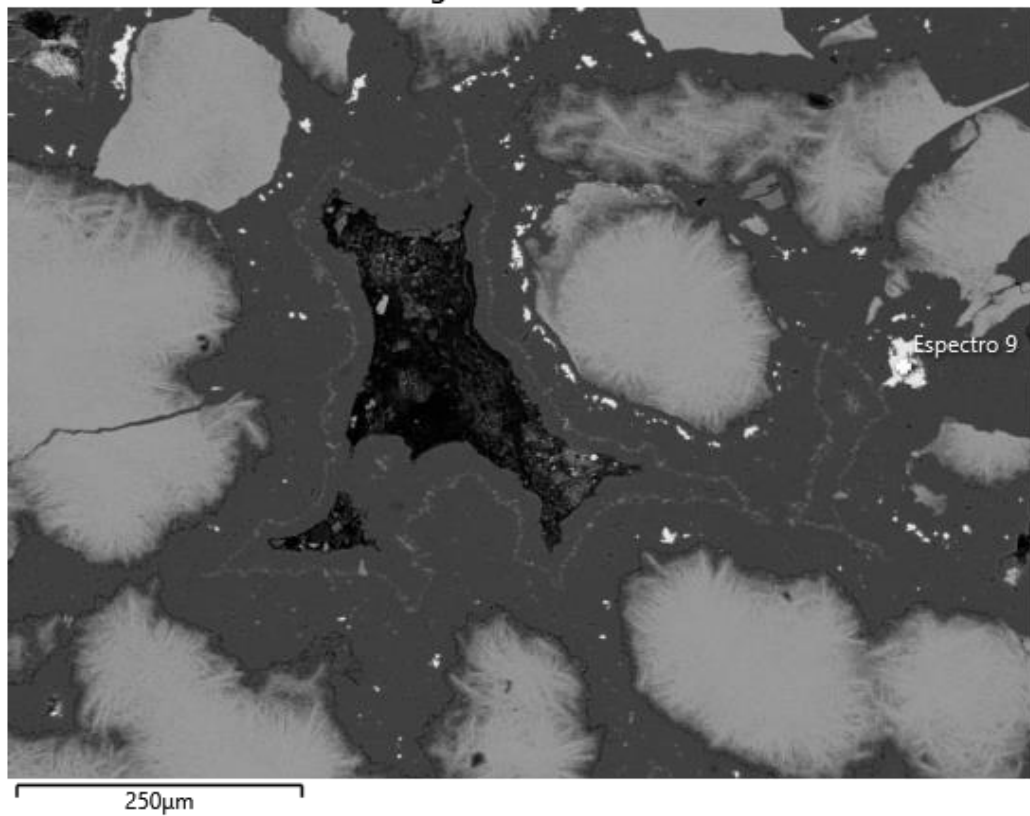


Figura A1. Imagem MEV e EDS de fosfato de terras raras em RZ1.

Imagem de Elétrons 4

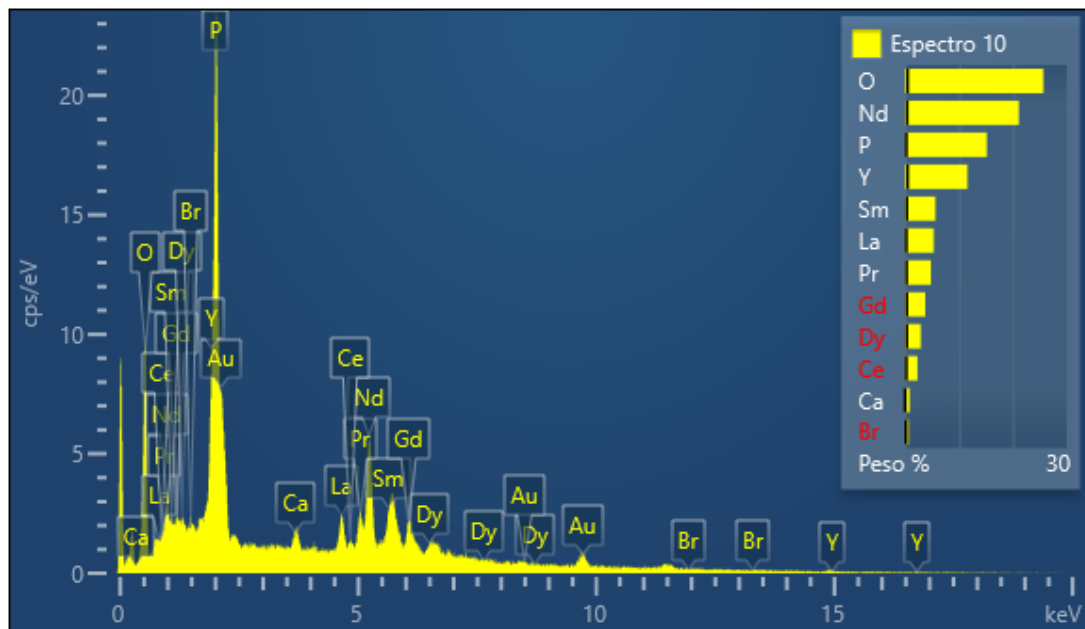
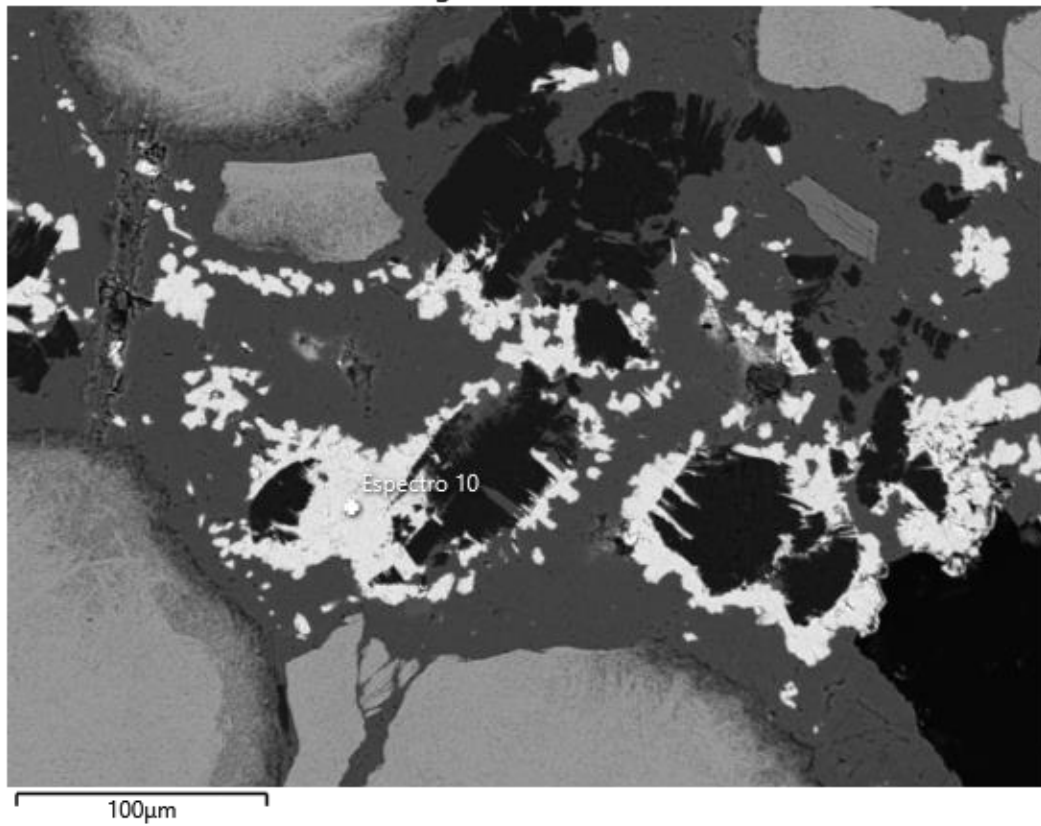


Figura A2. Imagem MEV e EDS de fosfato de terras raras em RZ1.

Imagem de Elétrons 14

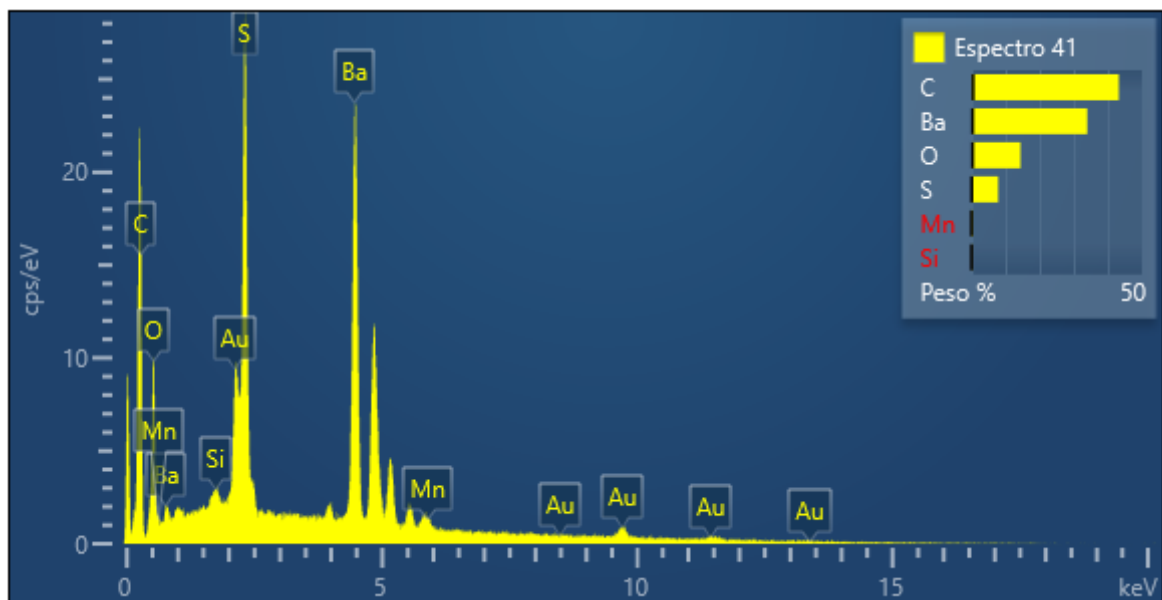
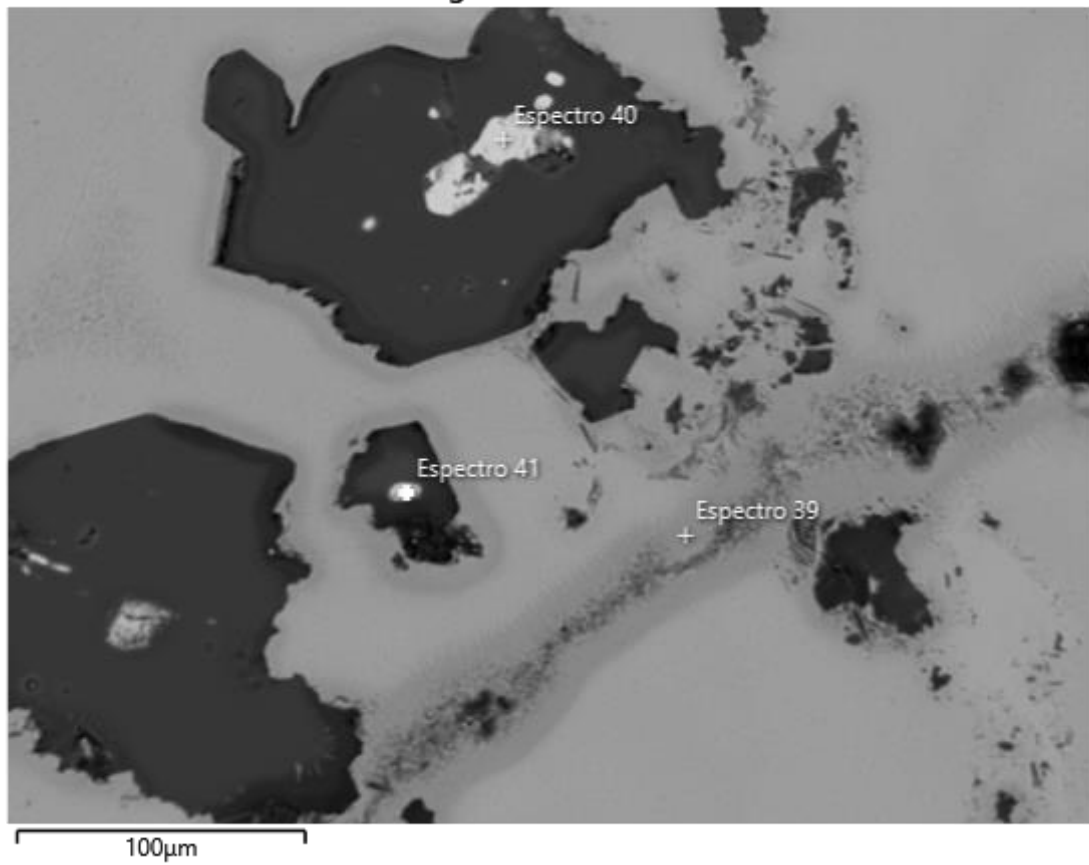


Figura A2. Imagem MEV e EDS de barita inclusa em grãos de quartzo em FO.

Tabela A2. Composição química da pirolusita.

		Pyrolusite																			
	Sample	MnO ₂	FeO	SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	BaO	CoO	Cr ₂ O ₃	CuO	NiO	PbO	SrO	V ₂ O ₃	ZnO	Soma
Araí Group	MJ5	96.074	0.275	0.130	0.361	0.023	0.055	0.099	0.342	0.057	0.011	0.099	0.003	0.000	0.005	0.079	0.012	0.000	0.000	0.070	97.694
	MJ5	97.789	0.173	0.474	0.487	0.010	0.000	0.000	0.161	0.000	0.088	0.000	0.005	0.042	0.000	0.070	0.000	0.052	0.018	0.059	99.428
	MJ5	97.492	0.219	0.152	0.296	0.054	0.072	0.086	0.525	0.000	0.000	0.400	0.000	0.012	0.000	0.000	0.015	0.037	0.000	0.036	99.395
	MJ5	93.338	0.338	0.153	0.441	0.008	0.000	0.031	0.677	0.000	0.045	0.463	0.006	0.000	0.000	0.116	0.108	0.105	0.040	0.102	95.971
	MJ5	95.564	0.308	0.092	0.370	0.035	0.031	0.126	0.396	0.167	0.045	0.404	0.001	0.000	0.005	0.138	0.000	0.033	0.068	0.000	97.783
	MJ5	94.534	0.281	0.120	0.228	0.004	0.054	0.083	0.730	0.004	0.020	0.473	0.024	0.056	0.000	0.164	0.019	0.046	0.013	0.067	96.921
Paranoá Grupo	RZ1	97.639	0.103	0.217	0.131	0.155	0.050	0.007	0.003	0.094	0.088	0.156	0.042	0.000	0.234	0.006	0.118	0.019	0.032	0.070	99.164
	NQ1	97.967	0.152	0.305	0.161	0.094	0.000	0.066	0.065	0.111	0.095	0.021	0.015	0.130	0.000	0.000	0.037	0.000	0.000	0.007	99.226
	VZ2	94.730	0.244	0.088	0.878	0.102	0.000	0.036	0.139	0.064	0.599	1.015	0.076	0.001	0.000	0.031	0.081	0.084	0.020	0.142	98.330
	PP1	86.356	0.132	0.119	0.200	0.028	0.000	0.052	0.002	0.000	0.310	0.048	0.031	0.000	0.034	0.050	0.415	0.013	0.000	0.027	87.816
	PP1	87.730	0.150	0.179	0.154	0.029	0.000	0.018	0.015	0.000	0.288	0.101	0.018	0.047	0.000	0.103	0.156	0.000	0.000	0.022	89.010
	PP1	91.589	0.162	0.212	0.160	0.068	0.013	0.005	0.003	0.105	0.403	0.130	0.034	0.000	0.026	0.000	0.150	0.000	0.000	0.009	93.069
	PP1	94.969	0.094	0.169	0.170	0.079	0.031	0.001	0.003	0.000	0.300	0.133	0.036	0.077	0.000	0.003	0.711	0.000	0.000	0.015	96.791
	PP1	93.234	0.115	0.235	0.202	0.106	0.011	0.019	0.006	0.000	0.433	0.072	0.064	0.000	0.015	0.000	0.794	0.018	0.045	0.000	95.368
	PP1	90.826	0.175	0.155	0.206	0.081	0.000	0.030	0.029	0.028	0.481	1.210	0.058	0.000	0.000	0.000	0.108	0.000	0.000	0.000	93.387
	PP1	96.021	0.164	0.125	0.186	0.038	0.000	0.040	0.025	0.086	0.280	0.161	0.033	0.000	0.011	0.000	0.037	0.000	0.000	0.009	97.216
	PP1	92.066	0.193	0.249	0.248	0.094	0.040	0.005	0.032	0.002	0.309	0.436	0.048	0.000	0.064	0.105	1.055	0.019	0.044	0.151	95.159
	BL1	92.840	0.172	0.199	0.159	0.103	0.034	0.067	0.029	0.147	0.272	0.369	0.000	0.040	0.041	0.000	0.267	0.040	0.051	0.027	94.858
	BL1	98.327	0.109	0.312	0.169	0.037	0.038	0.096	0.049	0.000	0.227	0.237	0.000	0.053	0.000	0.060	0.292	0.018	0.000	0.054	100.078
	BL1	89.069	0.143	0.140	0.226	0.056	0.017	0.059	0.028	0.000	0.137	0.147	0.000	0.023	0.000	0.000	0.311	0.000	0.003	0.044	90.403
	BL1	94.557	0.175	0.175	0.324	0.081	0.027	0.000	0.000	0.000	0.319	0.172	0.000	0.000	0.041	0.038	0.385	0.069	0.013	0.082	96.458
	BL1	87.341	0.182	0.117	0.238	0.051	0.003	0.028	0.016	0.013	0.250	0.105	0.010	0.064	0.011	0.025	0.333	0.008	0.045	0.000	88.841
	BL1	92.896	0.119	0.217	0.157	0.097	0.016	0.083	0.000	0.108	0.193	0.192	0.000	0.000	0.058	0.000	0.203	0.000	0.000	0.000	94.338
	FT3	90.938	0.116	0.336	0.734	0.121	0.014	0.000	0.166	0.000	0.800	1.505	0.014	0.000	0.011	0.053	0.079	0.026	0.000	0.101	95.014
	FT3	91.367	0.163	0.208	0.934	0.088	0.000	0.000	0.209	0.107	0.718	2.016	0.023	0.000	0.016	0.000	0.102	0.024	0.021	0.111	96.107
	FT3	94.756	0.192	0.341	0.293	0.197	0.071	0.021	0.013	0.091	0.812	0.816	0.011	0.000	0.061	0.092	0.050	0.025	0.018	0.000	97.860
	FT3	94.057	0.106	0.271	0.813	0.111	0.006	0.005	0.087	0.216	0.905	1.237	0.042	0.085	0.034	0.119	0.008	0.000	0.000	0.065	98.166
	FT3	94.689	0.129	0.210	0.922	0.083	0.036	0.000	0.194	0.000	0.562	2.649	0.037	0.043	0.055	0.042	0.031	0.000	0.000	0.131	99.813
	FT3	90.698	0.297	0.308	0.918	0.093	0.055	0.001	0.103	0.000	0.844	2.001	0.025	0.052	0.044	0.020	0.042	0.000	0.015	0.007	95.524
	FT3	92.383	0.241	0.356	0.582	0.178	0.072	0.028	0.032	0.000	0.718	0.887	0.009	0.000	0.025	0.000	0.084	0.047	0.093	0.056	95.792

Tabela A3. Hausmannita Chemical composition.

		Hausmannite																			
	Sample	MnO	FeO	SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	BaO	CoO	Cr ₂ O ₃	CuO	NiO	PbO	SrO	V ₂ O ₃	ZnO	Soma
Araí Group	MJ5	91.55	0.391	0.031	0.485	0.018	0.075	0.042	0.000	0.126	0.008	0.080	0.006	0.138	0.000	0.045	0.026	0.000	0.121	0.128	93.27
	MJ5	88.84	0.285	0.027	0.474	0.000	0.109	0.003	0.000	0.056	0.000	0.002	0.000	0.043	0.001	0.079	0.038	0.000	0.000	0.138	90.10
	MJ5	90.12	0.282	0.009	0.509	0.000	0.120	0.000	0.014	0.000	0.027	0.000	0.015	0.131	0.000	0.000	0.003	0.012	0.000	0.097	91.34
	MJ5	89.64	0.350	0.000	0.442	0.002	0.061	0.000	0.014	0.069	0.000	0.082	0.006	0.000	0.000	0.007	0.016	0.015	0.020	0.103	90.82
	MJ5	91.50	0.350	0.014	0.460	0.000	0.061	0.086	0.236	0.000	0.042	0.003	0.018	0.076	0.000	0.004	0.074	0.013	0.080	0.121	93.14

Tabela A4. Composição química litioforita

		Litioforita																			
	Sample	MnO ₂	FeO	SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	BaO	CoO	Cr ₂ O ₃	CuO	NiO	PbO	SrO	V ₂ O ₃	ZnO	Soma
Paranoá Group	RZ1	56.657	0.079	0.021	21.797	0.023	0.036	0.072	0.004	0.112	0.018	0.037	1.024	0.000	1.031	0.429	0.000	0.027	0.000	0.856	82.224
	RZ1	55.799	0.076	0.018	21.702	0.010	0.055	0.000	0.006	0.000	0.187	0.137	2.087	0.000	1.164	0.315	0.089	0.046	0.067	0.798	82.556
	RZ1	51.485	0.110	0.373	21.197	0.017	0.063	0.000	0.012	0.021	0.257	0.087	2.516	0.001	1.204	1.298	0.059	0.000	0.000	0.461	79.161
	RZ1	55.920	0.236	2.132	16.013	0.082	0.072	0.117	0.036	0.000	0.202	6.955	1.274	0.066	0.683	0.826	0.098	0.000	0.024	0.190	84.927
	RZ1	56.745	0.066	0.014	21.087	0.011	0.000	0.055	0.015	0.000	0.044	0.037	0.505	0.000	1.040	0.239	0.066	0.000	0.000	0.722	80.646
	RZ1	56.809	0.125	0.140	19.599	0.012	0.057	0.046	0.264	0.000	0.144	1.076	1.273	0.032	0.966	0.978	0.019	0.028	0.000	0.875	82.444
	RZ1	56.685	0.052	0.040	20.961	0.034	0.053	0.048	0.021	0.030	0.095	0.000	2.098	0.075	1.273	0.281	0.001	0.000	0.063	0.899	82.709
	RZ1	52.041	0.089	0.464	20.886	0.064	0.048	0.109	0.017	0.000	0.430	0.967	1.975	0.000	1.735	1.623	0.009	0.024	0.000	0.825	81.306
	RZ1	53.966	0.051	0.011	20.279	0.000	0.082	0.070	0.011	0.000	0.023	0.084	1.333	0.139	1.198	0.366	0.024	0.004	0.048	0.727	78.414
	RZ1	52.332	0.078	0.072	20.427	0.000	0.087	0.069	0.031	0.000	0.181	0.154	2.392	0.022	1.097	0.460	0.108	0.000	0.002	0.968	78.479
	RZ1	57.455	0.104	0.025	21.077	0.005	0.000	0.017	0.008	0.126	0.017	0.010	0.940	0.000	1.088	0.208	0.099	0.000	0.000	0.673	81.852
	RZ1	56.450	0.082	0.048	21.317	0.013	0.035	0.053	0.000	0.000	0.145	0.035	1.536	0.076	1.149	0.197	0.006	0.000	0.073	1.026	82.241
	VZ2	56.000	0.282	0.014	19.893	0.046	0.000	0.072	0.004	0.158	0.050	0.154	1.415	0.031	1.441	0.183	0.000	0.000	0.000	0.392	80.135
	VZ2	60.979	0.056	0.115	15.393	0.076	0.069	0.072	0.762	0.089	0.282	1.126	0.401	0.000	0.325	0.524	0.358	0.011	0.000	0.893	81.529
	VZ2	54.846	0.058	0.013	19.439	0.039	0.030	0.000	0.033	0.132	0.008	0.250	1.877	0.022	1.219	0.213	0.019	0.012	0.020	0.429	78.659
	VZ2	55.271	0.494	0.015	20.682	0.000	0.061	0.020	0.006	0.000	0.030	0.080	1.226	0.044	1.189	1.119	0.059	0.044	0.004	0.732	81.076
	VZ2	53.189	0.278	0.048	20.681	0.019	0.044	0.000	0.036	0.000	0.000	0.004	2.057	0.000	1.289	0.412	0.031	0.048	0.021	0.437	78.595
	VZ2	54.815	0.249	0.196	18.474	0.072	0.037	0.018	0.011	0.000	0.006	0.000	1.410	0.024	1.346	0.497	0.022	0.000	0.000	0.637	77.814
	VZ2	56.081	1.691	0.114	17.013	0.083	0.249	0.047	0.585	0.059	0.232	0.889	0.586	0.111	0.602	1.301	0.067	0.000	0.003	0.660	80.373

Tabela A5. Composição química da criptomelana

		Criptomelana																			
	Amostra	MnO ₂	FeO	SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	BaO	CoO	Cr ₂ O ₃	CuO	NiO	PbO	SrO	V ₂ O ₃	ZnO	Soma
Grupo Araí	MJ5	92.169	0.175	0.043	0.336	0.000	0.007	0.149	4.271	0.000	0.002	0.185	0.011	0.056	0.055	0.114	0.000	0.124	0.000	0.049	97.746
	MJ5	92.649	0.285	0.021	0.248	0.079	0.000	0.164	5.096	0.000	0.000	0.419	0.017	0.003	0.000	0.000	0.000	0.099	0.106	0.146	99.332
	MJ5	94.303	0.255	0.069	0.187	0.042	0.101	0.064	3.117	0.156	0.013	0.304	0.011	0.019	0.021	0.024	0.069	0.097	0.000	0.108	98.961
	MJ5	94.490	0.168	0.013	0.299	0.076	0.000	0.150	5.402	0.025	0.017	0.390	0.014	0.000	0.000	0.000	0.079	0.207	0.024	0.007	101.361
	MJ5	92.816	0.234	0.037	0.226	0.076	0.045	0.142	5.660	0.174	0.005	0.246	0.029	0.000	0.010	0.000	0.116	0.206	0.071	0.054	100.147
	MJ5	91.427	0.141	0.018	0.387	0.070	0.030	0.134	4.684	0.000	0.000	1.622	0.000	0.020	0.000	0.080	0.000	0.041	0.032	0.000	98.687
	MJ5	95.509	0.159	0.303	0.139	0.040	0.099	0.061	1.334	0.000	0.013	0.475	0.009	0.012	0.000	0.000	0.082	0.060	0.000	0.042	98.337
	MJ5	97.380	0.126	0.219	0.118	0.028	0.034	0.023	1.142	0.000	0.000	0.111	0.000	0.054	0.000	0.010	0.090	0.131	0.074	0.000	99.541
	MJ5	89.170	0.245	0.034	0.330	0.007	0.025	0.102	5.441	0.000	0.000	1.045	0.009	0.070	0.015	0.063	0.000	0.104	0.045	0.014	96.718
	MJ5	97.140	0.181	0.088	0.188	0.051	0.064	0.104	1.349	0.000	0.042	0.351	0.010	0.021	0.000	0.000	0.042	0.085	0.039	0.000	99.755
	MJ5	97.754	0.243	0.096	0.417	0.086	0.000	0.073	2.155	0.000	0.000	0.336	0.000	0.076	0.000	0.013	0.081	0.046	0.000	0.057	101.433
	MJ5	95.801	0.144	0.052	0.134	0.050	0.062	0.098	3.417	0.131	0.000	0.602	0.009	0.009	0.000	0.000	0.054	0.162	0.000	0.054	100.779
	MJ5	97.827	0.189	0.097	0.105	0.046	0.023	0.149	1.596	0.099	0.043	0.123	0.000	0.079	0.036	0.049	0.096	0.171	0.038	0.001	100.768
	MJ5	96.821	0.304	0.113	0.235	0.035	0.000	0.061	1.812	0.129	0.000	0.339	0.011	0.000	0.005	0.018	0.125	0.070	0.000	0.086	100.164
	MJ5	97.114	0.238	0.140	0.261	0.014	0.016	0.064	2.091	0.000	0.024	0.402	0.003	0.052	0.000	0.000	0.093	0.076	0.000	0.029	100.616
	MJ5	97.287	0.158	0.340	0.516	0.044	0.000	0.059	1.076	0.052	0.093	0.351	0.013	0.000	0.000	0.026	0.066	0.056	0.066	0.034	100.236
	MJ5	89.802	0.278	0.068	0.362	0.049	0.007	0.116	5.156	0.099	0.052	1.179	0.019	0.050	0.004	0.000	0.102	0.168	0.058	0.087	97.656
	MJ5	93.821	0.318	0.048	0.274	0.028	0.000	0.069	4.963	0.036	0.070	0.624	0.000	0.000	0.018	0.024	0.000	0.141	0.000	0.065	100.498
	MJ5	96.515	0.326	0.114	0.436	0.037	0.030	0.068	1.620	0.000	0.041	0.130	0.000	0.000	0.040	0.011	0.000	0.103	0.013	0.055	99.538
	MJ5	94.274	0.343	0.047	0.413	0.036	0.051	0.233	4.217	0.000	0.004	0.269	0.000	0.000	0.005	0.000	0.000	0.114	0.039	0.000	100.045
	MJ5	94.257	0.263	0.055	0.332	0.000	0.019	0.128	6.316	0.000	0.025	0.379	0.034	0.000	0.000	0.060	0.050	0.000	0.000	0.111	102.029
Grupo Paranoá	NQ1	87.860	0.290	0.085	1.141	0.119	0.005	0.302	3.942	0.000	0.093	0.447	0.395	0.000	0.018	0.000	0.019	0.014	0.000	0.215	94.945
	NQ1	89.910	0.203	0.059	1.007	0.035	0.000	0.294	2.912	0.024	0.035	1.183	0.187	0.000	0.035	0.000	0.100	0.005	0.000	0.080	96.069
	NQ1	87.337	0.469	0.124	1.220	0.096	0.006	0.231	4.528	0.016	0.146	0.577	0.374	0.000	0.008	0.043	0.000	0.075	0.015	0.163	95.427
	NQ1	91.000	0.080	0.117	1.308	0.142	0.032	0.260	4.164	0.051	0.083	0.796	0.300	0.010	0.000	0.000	0.095	0.111	0.000	0.194	98.743
	NQ1	84.803	0.164	0.115	1.573	0.581	0.016	0.078	3.510	0.000	0.310	3.372	0.271	0.000	0.020	0.029	0.000	0.188	0.020	0.187	95.237
	NQ1	86.383	0.611	0.060	0.849	0.224	0.022	0.241	3.883	0.053	0.090	0.608	0.409	0.019	0.000	0.043	0.000	0.129	0.003	0.289	93.916
	NQ1	91.764	0.192	0.000	0.497	0.139	0.030	0.292	4.192	0.042	0.048	0.756	0.357	0.070	0.000	0.048	0.079	0.064	0.000	0.227	98.797
	NQ1	85.687	0.322	0.099	1.227	0.141	0.000	0.239	4.090	0.106	0.147	0.607	0.334	0.000	0.078	0.000	0.178	0.047	0.052	0.144	93.498
	VZ2	81.975	1.703	0.133	1.513	0.361	0.006	0.032	3.808	0.127	0.703	1.960	0.147	0.052	0.029	0.000	0.223	0.091	0.000	0.127	92.991
	VZ2	83.112	1.676	0.116	1.360	0.522	0.099	0.057	3.784	0.020	0.554	1.987	0.155	0.128	0.029	0.000	0.089	0.026	0.007	0.161	93.882
	VZ2	84.004	1.424	0.052	1.338	0.320	0.031	0.096	3.900	0.000	0.723	2.022	0.209	0.051	0.069	0.000	0.046	0.054	0.051	0.249	94.639
	VZ2	83.433	3.611	0.098	1.342	0.479	0.079	0.067	3.313	0.000	0.603	2.788	0.149	0.000	0.058	0.000	0.082	0.102	0.000	0.174	96.377
	VZ2	85.595	0.795	0.023	0.643	0.486	0.016	0.094	4.074	0.096	0.622	1.057	0.179	0.000	0.043	0.000	0.251	0.121	0.000	0.187	94.281
	FT4	92.551	0.148	0.063	0.595	0.028	0.006	0.051	1.778	0.121	0.049	0.640	0.008	0.000	0.008	0.000	0.065	0.019	0.082	0.000	96.211
	FT4	85.892	0.184	0.235	2.829	0.044	0.000	0.073	2.954	0.000	0.113	2.257	0.060	0.000	0.001	0.064	0.074	0.024	0.000	0.041	94.846
	FT4	90.225	0.149	0.042	0.619	0.005	0.000	0.102	1.980	0.011	0.000	0.899	0.034	0.000	0.024	0.067	0.082	0.041	0.090	0.000	94.370
	FT3	84.451	0.235	0.304	2.064	0.127	0.000	0.159	4.292	0.063	0.059	0.788	0.014	0.000	0.000	0.000	0.168	0.033	0.028	0.020	92.805

Tabela A6. Composição química da hollandita

Hollandita																					
Amostra	MnO ₂	FeO	SiO2	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	BaO	CoO	Cr ₂ O ₃	CuO	NiO	PbO	SrO	V ₂ O ₃	ZnO	Soma	
Grupo Paranoá	NQ1	81.658	0.660	0.194	1.251	0.026	0.015	0.126	0.961	0.043	0.149	8.250	0.112	0.067	0.049	0.000	0.069	0.014	0.000	0.113	93.757
	NQ1	84.364	0.222	0.027	0.690	0.021	0.005	0.169	0.934	0.000	0.054	7.349	0.137	0.043	0.009	0.001	0.000	0.044	0.030	0.111	94.210
	NQ1	84.592	0.256	0.099	1.720	0.002	0.000	0.338	2.821	0.164	0.105	3.188	0.292	0.000	0.046	0.014	0.074	0.018	0.012	0.000	93.742
	NQ1	84.459	0.241	0.076	1.687	0.058	0.000	0.157	2.258	0.000	0.051	5.635	0.216	0.000	0.021	0.156	0.175	0.000	0.000	0.131	95.320
	NQ1	87.053	0.153	0.071	1.000	0.018	0.028	0.178	1.849	0.000	0.140	5.292	0.259	0.032	0.026	0.066	0.093	0.005	0.113	0.088	96.465
	VZ2	74.827	0.723	0.251	5.402	0.104	0.009	0.076	2.015	0.088	1.097	6.387	0.179	0.074	0.111	0.106	0.008	0.000	0.097	0.240	91.794
	VZ2	67.485	0.419	0.139	6.816	0.077	0.055	0.089	0.644	0.000	0.428	6.057	1.157	0.076	0.277	0.048	0.154	0.033	0.000	0.224	84.178
	RZ1	79.273	0.130	0.235	4.729	0.043	0.005	0.132	2.401	0.000	0.846	5.188	0.151	0.022	0.297	0.028	0.169	0.000	0.000	0.239	93.888
	RZ1	73.585	0.086	0.255	4.783	0.080	0.045	0.120	1.728	0.018	0.905	6.544	0.191	0.170	0.217	0.059	0.270	0.021	0.041	0.115	89.232
	FT4	88.563	0.154	0.187	0.894	0.020	0.001	0.057	1.688	0.000	0.027	3.479	0.046	0.000	0.000	0.000	0.112	0.000	0.000	0.040	95.268
	FT4	89.879	0.115	0.146	0.236	0.012	0.000	0.127	1.660	0.002	0.000	4.000	0.066	0.168	0.028	0.032	0.010	0.000	0.053	0.044	96.577
	FT4	90.808	0.173	0.117	0.647	0.014	0.000	0.069	1.504	0.108	0.000	2.294	0.029	0.032	0.019	0.017	0.162	0.013	0.026	0.007	96.039
	FT4	82.248	0.537	0.349	3.188	0.017	0.000	0.053	0.823	0.333	0.070	9.028	0.070	0.032	0.000	0.000	0.056	0.000	0.000	0.030	96.833
	FT4	81.793	0.480	0.329	2.828	0.020	0.000	0.000	0.610	0.079	0.230	9.469	0.036	0.008	0.000	0.000	0.093	0.013	0.000	0.001	95.988
	FT4	89.372	0.218	0.173	0.662	0.000	0.020	0.062	2.413	0.020	0.392	2.474	0.031	0.000	0.000	0.114	0.000	0.022	0.000	0.000	95.973
	FT4	89.702	0.134	0.165	0.640	0.031	0.026	0.026	1.967	0.000	0.362	3.917	0.050	0.000	0.021	0.000	0.045	0.000	0.035	0.050	97.171
	FT4	86.663	0.190	0.138	0.728	0.051	0.050	0.007	1.864	0.000	0.246	4.138	0.047	0.000	0.018	0.000	0.113	0.000	0.000	0.081	94.334
	FT4	88.391	0.124	0.118	0.924	0.042	0.008	0.101	1.913	0.271	0.278	4.559	0.034	0.000	0.000	0.000	0.056	0.004	0.007	0.073	96.904
	FT4	86.140	0.157	0.099	0.790	0.055	0.033	0.044	1.608	0.132	0.035	4.517	0.011	0.000	0.051	0.012	0.110	0.103	0.000	0.000	93.898
	FT4	85.781	0.121	0.087	0.795	0.000	0.038	0.107	1.700	0.011	0.000	2.824	0.025	0.000	0.056	0.000	0.044	0.007	0.000	0.007	91.604
	FT4	86.920	0.108	0.123	0.765	0.021	0.000	0.073	1.868	0.005	0.142	3.819	0.039	0.000	0.031	0.000	0.127	0.058	0.000	0.016	94.116
	BL1	81.430	0.185	0.293	2.169	0.057	0.036	0.043	0.192	0.026	0.303	3.035	0.000	0.001	0.003	0.000	0.407	0.033	0.011	0.011	88.235
	FT3	90.495	0.086	0.282	0.929	0.076	0.014	0.000	0.219	0.000	0.840	2.084	0.000	0.140	0.009	0.000	0.086	0.017	0.005	0.027	95.309
	FT3	79.807	0.240	0.783	4.106	0.057	0.000	0.012	0.388	0.000	0.626	8.117	0.081	0.051	0.010	0.000	0.014	0.059	0.000	0.046	94.398
	FT3	85.307	0.137	0.247	2.130	0.028	0.000	0.121	0.294	0.000	0.594	5.796	0.015	0.065	0.031	0.000	0.096	0.079	0.081	0.020	95.041
	FT3	78.433	0.162	0.491	4.622	0.008	0.000	0.032	0.532	0.007	0.252	9.961	0.029	0.044	0.044	0.095	0.079	0.038	0.125	0.065	95.019
	FT3	88.617	0.291	0.513	1.327	0.088	0.012	0.000	0.258	0.053	0.662	3.591	0.022	0.000	0.000	0.034	0.081	0.024	0.055	0.025	95.652
	FT3	71.848	0.255	1.463	3.920	0.029	0.001	0.077	0.641	0.185	0.108	10.450	0.065	0.095	0.090	0.000	0.014	0.000	0.090	0.000	89.331
	FT3	81.361	0.101	0.190	2.747	0.031	0.030	0.061	1.649	0.013	0.094	6.810	0.045	0.000	0.026	0.005	0.000	0.012	0.040	0.000	93.215
	FT3	80.301	0.142	0.124	2.030	0.072	0.027	0.098	1.338	0.000	0.952	9.293	0.076	0.000	0.043	0.064	0.151	0.051	0.015	0.057	94.834
	FT3	76.057	0.887	1.036	3.040	0.051	0.099	0.058	1.585	0.175	0.413	7.639	0.076	0.000	0.038	0.041	0.060	0.086	0.065	0.044	91.450
	FT3	76.703	0.735	0.307	2.550	0.081	0.044	0.036	1.469	0.000	0.436	8.872	0.065	0.000	0.000	0.000	0.102	0.000	0.113	0.057	91.570

Tabela A7. Composição química Fe-hollandita.

Fe-hollandita																					
	Amostra	MnO ₂	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	BaO	CoO	Cr ₂ O ₃	CuO	NiO	PbO	SrO	V ₂ O ₃	ZnO	Soma
Grupo Paranoá	VZ2	57.329	15.024	0.462	5.278	0.325	0.268	0.051	1.168	<0.23	0.741	2.485	0.425	<0.09	0.070	0.327	0.580	0.083	<0.11	0.129	82.007
	FT3	65.581	14.059	0.297	1.926	0.047	<0.02	0.051	1.136	<0.23	0.343	8.366	0.061	<0.09	<0.02	<0.08	0.060	<0.03	0.120	<0.02	90.698

Tabela A8. composição química da romanechita.

Romanechita																					
Amostra	MnO ₂	FeO	SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	BaO	CoO	Cr ₂ O ₃	CuO	NiO	PbO	SrO	V ₂ O ₃	ZnO	Soma	
Grupo Paranoá	RZ1	76.169	0.138	0.626	2.479	0.125	0.000	0.066	0.122	0.023	0.205	15.186	0.304	0.000	0.106	0.011	0.149	0.031	0.007	0.014	95.760
	RZ1	77.252	0.094	0.558	1.601	0.107	0.024	0.048	0.129	0.000	0.142	15.563	0.163	0.000	0.098	0.010	0.135	0.000	0.124	0.000	96.047
	RZ1	77.616	0.210	0.341	1.072	0.178	0.068	0.026	0.088	0.000	0.133	15.721	0.211	0.000	0.095	0.121	0.118	0.039	0.040	0.030	96.108
	RZ1	76.784	0.144	0.307	1.254	0.114	0.000	0.031	0.071	0.238	0.126	15.968	0.192	0.032	0.083	0.055	0.106	0.005	0.000	0.055	95.564
	RZ1	77.949	0.148	0.379	1.332	0.184	0.000	0.068	0.181	0.020	0.163	15.204	0.179	0.087	0.071	0.028	0.152	0.088	0.039	0.000	96.272
	RZ1	75.211	0.071	0.213	0.726	0.141	0.029	0.084	0.134	0.104	0.174	14.146	0.179	0.047	0.084	0.033	0.144	0.063	0.000	0.000	91.584
	RZ1	73.586	0.079	0.974	2.961	0.195	0.008	0.019	0.244	0.000	0.154	13.334	0.432	0.000	0.229	0.129	0.154	0.064	0.078	0.059	92.699
	RZ1	76.017	0.132	0.330	1.127	0.177	0.083	0.120	0.148	0.000	0.149	15.851	0.173	0.000	0.076	0.069	0.110	0.078	0.016	0.000	94.656
	FT4	82.146	0.218	0.234	2.632	0.026	0.009	0.038	0.364	0.215	0.218	11.563	0.028	0.070	0.000	0.000	0.017	0.004	0.000	0.000	97.782
	PP1	74.188	0.094	0.111	0.462	0.105	0.031	0.048	0.099	0.168	0.228	13.127	0.099	0.077	0.019	0.125	0.056	0.000	0.027	0.000	89.064
	PP1	73.686	0.176	0.101	0.422	0.088	0.007	0.064	0.077	0.000	0.276	15.260	0.099	0.034	0.020	0.000	0.023	0.005	0.123	0.000	90.460
	PP1	75.238	0.136	0.118	0.364	0.092	0.025	0.056	0.049	0.093	0.376	14.681	0.167	0.126	0.010	0.000	0.484	0.034	0.000	0.000	92.049
	PP1	75.604	0.159	0.097	0.351	0.035	0.000	0.080	0.000	0.000	0.341	16.352	0.229	0.093	0.000	0.103	0.311	0.000	0.123	0.030	93.908
	PP1	74.529	0.145	0.138	0.318	0.084	0.069	0.152	0.024	0.174	0.363	15.871	0.149	0.138	0.005	0.071	0.205	0.000	0.040	0.000	92.474
	PP1	74.977	0.113	0.089	0.450	0.151	0.081	0.090	0.055	0.206	0.285	15.926	0.081	0.049	0.000	0.000	0.194	0.000	0.000	0.051	92.799
	PP1	74.600	0.068	0.145	0.393	0.146	0.052	0.080	0.030	0.000	0.297	16.137	0.135	0.010	0.023	0.000	0.162	0.022	0.015	0.025	92.339
	PP1	75.001	0.166	0.122	0.530	0.083	0.000	0.055	0.016	0.000	0.335	14.134	0.187	0.000	0.026	0.000	0.084	0.058	0.000	0.000	90.797
	PP1	75.161	0.159	0.133	0.244	0.202	0.061	0.069	0.051	0.084	0.366	15.090	0.107	0.073	0.015	0.002	0.070	0.000	0.120	0.042	92.049
	PP1	77.066	0.103	0.107	0.494	0.087	0.000	0.113	0.022	0.079	0.328	15.204	0.113	0.055	0.029	0.072	0.104	0.007	0.000	0.000	93.983
	PP1	75.867	0.121	0.117	0.359	0.166	0.049	0.019	0.066	0.000	0.248	15.803	0.078	0.105	0.000	0.107	0.106	0.017	0.131	0.044	93.401
	PP1	75.279	0.159	0.129	0.332	0.164	0.076	0.048	0.042	0.000	0.289	15.463	0.072	0.055	0.036	0.051	0.092	0.000	0.145	0.080	92.512
	PP1	78.430	0.128	0.139	0.428	0.169	0.066	0.039	0.502	0.000	0.351	12.948	0.081	0.020	0.000	0.010	0.073	0.017	0.000	0.039	93.440
	PP1	73.591	0.347	0.078	0.413	0.071	0.022	0.053	0.030	0.039	0.327	15.454	0.179	0.000	0.063	0.080	0.515	0.037	0.101	0.000	91.400
	PP1	75.737	0.174	0.047	0.320	0.071	0.015	0.006	0.033	0.000	0.403	16.616	0.223	0.105	0.000	0.044	0.084	0.000	0.082	0.093	94.053
	PP1	74.791	0.169	0.044	0.307	0.039	0.008	0.000	0.034	0.000	0.311	15.881	0.165	0.060	0.021	0.000	0.154	0.030	0.159	0.015	92.188
	PP1	76.297	0.125	0.051	0.254	0.154	0.031	0.038	0.027	0.000	0.337	16.266	0.118	0.000	0.016	0.017	0.126	0.009	0.043	0.047	93.958
	PP1	79.877	0.164	0.160	0.649	0.126	0.045	0.055	0.169	0.025	0.346	8.386	0.130	0.000	0.000	0.042	0.923	0.021	0.029	0.000	91.147
	FO1	76.817	0.411	0.162	0.148	0.205	0.060	0.000	0.577	0.050	0.229	12.013	0.072	0.110	0.030	0.000	1.738	0.093	0.125	0.000	92.840
	FO1	77.916	0.120	0.190	0.115	0.350	0.062	0.036	0.318	0.029	0.278	13.276	0.136	0.063	0.028	0.028	0.189	0.106	0.058	0.000	93.298
	FO1	77.234	0.287	0.166	0.195	0.177	0.034	0.000	0.083	0.111	0.378	15.345	0.118	0.000	0.038	0.000	0.519	0.057	0.029	0.045	94.815
	FO1	72.516	0.144	0.238	0.139	0.249	0.036	0.063	0.114	0.000	0.335	14.102	0.099	0.045	0.021	0.000	0.195	0.006	0.015	0.042	88.360
	FO1	75.611	0.121	0.214	0.116	0.216	0.062	0.065	0.126	0.059	0.413	14.940	0.108	0.018	0.000	0.000	0.218	0.032	0.104	0.001	92.424
	FO1	78.408	0.112	0.192	0.198	0.414	0.114	0.000	0.329	0.000	0.259	13.927	0.107	0.073	0.024	0.001	0.142	0.136	0.000	0.037	94.473
	FO1	79.689	0.105	0.244	0.219	0.349	0.190	0.080	0.158	0.043	0.346	14.517	0.113	0.106	0.013	0.000	0.166	0.015	0.104	0.068	96.525
	FO1	77.740	0.137	0.223	0.354	0.455	0.216	0.078	0.225	0.095	0.274	14.039	0.131	0.000	0.026	0.000	0.157	0.000	0.033	0.014	94.197
	FO1	76.904	0.198	0.170	0.141	0.206	0.061	0.077	0.112	0.104	0.321	15.527	0.084	0.042	0.040	0.000	0.229	0.032	0.076	0.000	94.324
FO1	67.967	0.241	0.185	0.404	0.314	0.059	0.055	0.369	0.092	0.145	11.455	0.111	0.018	0.035	0.000	0.522	0.176	0.000	0.068	82.217	
FO1	79.386	0.170	0.199	0.154	0.149	0.055	0.001	0.129	0.063	0.239	14.571	0.135	0.000	0.004	0.000	0.285	0.005	0.002	0.039	95.585	
FO1	76.969	0.061	0.174	0.187	0.307	0.038	0.034	0.248	0.000	0.269	14.593	0.126	0.000	0.039	0.009	0.170	0.084	0.089	0.000	93.397	
FO1	78.590	0.150	0.102	0.153	0.170	0.038	0.090	0.109	0.095	0.318	14.777	0.107	0.000	0.000	0.023	0.480	0.053	0.148	0.025	95.429	
FO1	76.457	1.236	0.620	0.363	0.252	0.082	0.091	0.304	0.009	0.251	13.708	0.083	0.000	0.000	0.175	1.270	0.063	0.097	0.071	95.131	
FO1	77.631	0.388	0.216	0.110	0.252	0.077	0.019	0.105	0.000	0.389	14.954	0.125	0.000	0.033	0.000	0.080	0.057	0.051	0.030	94.515	
FO1	73.966	0.195	0.176	0.113	0.283	0.123	0.000	0.187	0.050	0.331	14.731	0.121	0.032	0.073	0.071	0.280	0.066	0.065	0.040	90.903	
BL1	77.473	0.109	0.089	0.316	0.098	0.038	0.132	0.080	0.079	0.221	15.441	0.023	0.000	0.000	0.000	0.247	0.005	0.084	0.000	94.434	

BL1	79.073	0.176	0.058	0.163	0.094	0.045	0.066	0.016	0.217	0.340	16.046	0.031	0.000	0.000	0.000	0.240	0.044	0.000	0.002	96.611
BL1	75.533	0.054	0.110	0.551	0.084	0.017	0.022	0.075	0.000	0.288	15.041	0.047	0.000	0.000	0.034	0.418	0.009	0.000	0.055	92.338
BL1	76.286	0.109	0.114	0.914	0.063	0.010	0.040	0.132	0.000	0.321	15.008	0.036	0.000	0.030	0.000	0.397	0.019	0.008	0.005	93.492
BL1	79.664	0.105	0.133	1.137	0.078	0.003	0.049	0.156	0.000	0.259	14.949	0.057	0.000	0.030	0.017	0.407	0.000	0.027	0.046	97.117
BL1	76.261	0.094	0.097	0.751	0.074	0.020	0.090	0.127	0.039	0.271	15.454	0.066	0.028	0.033	0.000	0.341	0.011	0.031	0.000	93.787
BL1	75.247	0.083	0.112	0.459	0.079	0.005	0.031	0.092	0.063	0.252	15.459	0.037	0.027	0.000	0.000	0.369	0.037	0.014	0.031	92.397
BL1	75.686	0.122	0.081	0.836	0.031	0.012	0.045	0.091	0.000	0.204	15.143	0.045	0.000	0.034	0.001	0.115	0.004	0.000	0.000	92.449
BL1	79.512	0.164	0.142	1.187	0.038	0.006	0.051	0.069	0.075	0.281	15.727	0.043	0.074	0.021	0.000	0.318	0.000	0.059	0.061	97.828
BL1	80.739	0.114	0.096	0.608	0.066	0.039	0.068	0.058	0.113	0.245	15.750	0.053	0.000	0.044	0.000	0.253	0.067	0.026	0.000	98.340
FT3	75.053	0.121	0.152	0.576	0.050	0.000	0.081	0.093	0.000	0.406	15.947	0.056	0.012	0.045	0.070	0.064	0.021	0.028	0.041	92.816
FT3	76.620	0.075	0.118	0.067	0.143	0.043	0.073	0.076	0.000	0.494	14.981	0.048	0.010	0.050	0.046	0.026	0.011	0.030	0.022	92.933
FT3	75.881	0.036	0.142	0.172	0.117	0.032	0.009	0.058	0.014	0.437	15.707	0.065	0.075	0.026	0.025	0.000	0.000	0.000	0.056	92.852
FT3	76.672	0.053	0.130	0.282	0.169	0.060	0.014	0.064	0.000	0.434	14.808	0.126	0.050	0.088	0.000	0.002	0.000	0.010	0.044	93.006
FT3	75.867	0.151	0.171	0.656	0.223	0.055	0.057	0.230	0.031	0.268	14.334	0.081	0.001	0.069	0.000	0.080	0.019	0.161	0.019	92.473
FT3	76.572	0.113	0.094	0.290	0.077	0.030	0.000	0.086	0.000	0.351	15.666	0.043	0.116	0.059	0.056	0.037	0.037	0.016	0.000	93.642
FT3	75.227	0.148	0.130	0.116	0.155	0.013	0.034	0.032	0.007	0.401	15.755	0.072	0.000	0.076	0.000	0.041	0.000	0.111	0.000	92.319
