



Universidade de Brasília
Instituto de Geociências
Programa de Pós-graduação em Geologia

ESPECTROSCOPIA, CRISTALOQUÍMICA E INCLUSÕES FLUIDAS DA ESMERALDA DE MONTE SANTO, TOCANTINS, BRASIL.

Spectroscopy, Crystallochemistry and Fluid
Inclusions of the Monte Santo Emerald, Tocantins,
Brazil.

DÉBORA EZEQUIEL CAVALCANTI

Tese de Doutorado nº 202

Orientador: Prof. Dr. Valmir da Silva Souza.

Co-orientador: Prof. Dr. José de Araújo
Nogueira Neto.



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Tese de Doutorado apresentado ao Programa de Pós-Graduação em Geologia do Instituto de Geociências da Universidade de Brasília, como requisito para obtenção do título de Doutora em Geologia. Área de Concentração: Mineralogia e Petrologia.

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Ficha catalográfica elaborada automaticamente,
com os dados fornecidos pelo(a) autor(a)

EC377e Ezequiel Cavalcanti, Débora
Espectroscopia, Cristaloquímica e Inclusões Fluidas da
Esmeralda Monte Santo do Tocantins, Brasil. / Débora
Ezequiel Cavalcanti; orientador Valmir da Silva Souza;
co-orientador José de Araújo Nogueira Neto. -- Brasília,
2023.
133 p.

Tese(Doutorado em Geologia) -- Universidade de Brasília,
2023.

1. Esmeralda Monte Santo. 2. Esmeralda brasileira
V-dominante. 3. Proveniência Mineral. 4. Técnicas Analíticas
minerais. 5. Espectroscopias e Cristaloquímica. I. da Silva
Souza, Valmir , orient. II. Nogueira Neto, José de Araújo ,
co-orient. III. Título.

Dedico esse trabalho à todos os seres de luz que
habitam este vasto Universo.

Om Om Om

AGRADECIMENTOS

Agradeço à minha família, pelo apoio incessante. À minha mãe que sempre se dedicou aos filhos. Ao meu pai, que me ensinou sobre as coisas do mundo...! Aos meus sobrinhos Maycon, Gabriel, Sarah e Emanuela, que iluminam a minha vida diariamente e me trazem paz!

Agradeço à Universidade de Brasília (UnB) pelos aprendizados e incríveis oportunidades vividas; ao Instituto Nacional de Ciência e Tecnologia de Estudos Geotectônicos (INCTET - UnB), na pessoa do Prof. Dr. Reinhardt Adolfo Fuck, por todo o apoio que tornou projeto possível; ao Instituto de Física da Universidade de Brasília, onde realizei as análises espectroscópicas, comum agradecimento especial ao prof. Dr. Sebastião, ao Alexandre e à Ísis, por todo o apoio e amizade ao longo da pesquisa.

Um agradecimento especial ao meu querido professor e co-orientador Zeca que, ainda no começo do curso de graduação em geologia, me ensinou sobre o complexo e encantador universo da Mineralogia; pelas oportunidades a mim concedidas ao longo de todo o mestrado e doutorado; por ser para mim um pai. Ao professor Valmir, por aceitar me orientar, pela paciência e confiança; pela incrível e inesquecível oportunidade de conhecer a África do Sul e seus depósitos. À professora Paola, pela inspiração, por todas as discussões que me ensinam e me engrandecem e por todo o apoio ao longo dessa jornada. À Martha pela força, pelo companheirismo e por tantas ajudas ao longo do caminho. À Canile, pelo acolhimento e luz nos momentos em que eu mais precisei ultimamente; pela amizade.

Aos colaboradores do Laboratório de Microscopia Eletrônica de Varredura - MEV da UFC, ao Joel, pela grande ajuda na preparação de amostras, e apoio constante.

À todos os professores e aos funcionários do Instituto de Geociências da UnB. Aos garimpeiros do Estado de Tocantins, em especial à Dra. Lina Encarnação, detentores do título minerário das ocorrências de esmeralda onde foi realizado o presente trabalho; por autorizarem a realização da presente pesquisa e pelo fornecimento das amostras.

Às minhas queridas amigas. irmãs, companheiras e cúmplices dessa vida, Fernanda, Júlia Mariana, Úrsula, Marina, Robênia, Ianna, Cecília e Amanda, por toda a força que me deram, por me aturarem no meu melhor e no meu pior, por tornarem o meu mundo mais bonito e colorido, pelos aprendizados, pelas viagens, por tantos momentos vividos...gratidão! Aos meus amorosos companheiros dessa jornada terrena, Dipesh e Bento. Amo muito vocês!

À todos, a minha sincera Gratidão! *Namastê!*

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

Om Gam Ganapataye Namaha

" लोकाः समस्ताः सुखिनो भवन्तु "

"Lokāḥ samastāḥ sukhino bhavantu "

*"May all beings everywhere be happy and free,
and may the thoughts, words, and actions of my
own life contribute towards that happiness and
freedom for all."*

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1. INTRODUÇÃO

Esmeralda é a espécie gemológica de cor verde do mineral berilo, considerada como uma das gemas de valor comercial mais elevado. Entretanto, a esmeralda também pode ser sintetizada em laboratório ou ainda submetida a tratamento para a melhoria de sua cor e transparência. Em geral, cada ocorrência de esmeralda espalhada pelo mundo possui assinaturas geoquímica, espectroscópica, microscópica e isotópica específicas, as quais são importantes diagnósticos quanto à origem dessa gema.

A proveniência é uma importante questão econômica e social inerente à indústria das gemas. A consciência da origem e do processo de produção das "gemas" tem se tornado tão importante para os consumidores quanto o próprio produto em si. Os consumidores procuram cada vez mais conhecer a origem de suas gemas para garantir que sua compra não suporte condições desumanas de trabalho, cause problemas legais e para distinguir entre espécimes naturais, tratadas e sintetizadas.

A determinação da origem é de importância crescente no mercado de gemas. Determinar a localidade geográfica de exemplares naturais e distinguir entre esmeraldas naturais, tratadas e sintéticas nem sempre é tarefa fácil, principalmente em se tratando de gemas de qualidade superior, nas quais raramente são observadas feições diagnósticas.

Para determinar a origem de uma gema, é necessário utilizar uma combinação de técnicas analíticas avançadas complementares, que incluem principalmente a observação de características microscópicas, tais como marcas de crescimento e natureza das inclusões; determinação da composição química (elementos maiores, menores e traços); medições espectroscópicas, tais como micro-Raman, infravermelho e de absorção no ultravioleta-visível; e até mesmo análises isotópicas ($\delta^{18}\text{O}$).

O Brasil é um importante produtor de esmeraldas, com muitas ocorrências localizadas no centro-oeste, sudeste e nordeste do país. Entretanto, ainda não dispomos de um banco de dados que contemple as características específicas dessas gemas, tais como características, espectroscópicas, cristalográficas, geoquímicas, isotópicas e de ambiência geológica.

1.1 - Objetivos

O objetivo geral desta pesquisa envolve a investigação em detalhe sobre as esmeraldas de Monte Santo do Tocantins-TO, através de estudo espectroscópico,

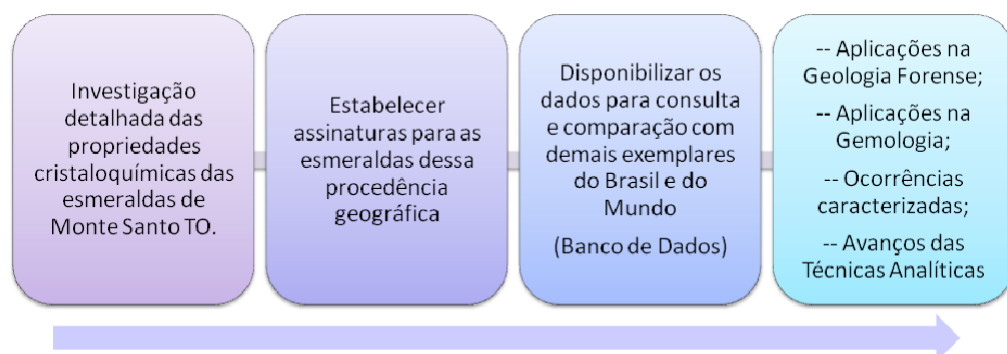
cristaloquímico e de inclusões fluidas, como suporte para estabelecer assinaturas ou *fingerprints*, que as identifiquem e as correlacionem com sua procedência geográfica (Figura 1). Nesse sentido, foram aplicadas técnicas analíticas complementares que variam de não-destrutivas a semi-destrutivas, onde a combinação de dados obtidos permite propor assinaturas com alta acurácia para as esmeraldas de Monte Santo do Tocantins (TO).

Uma investigação estatisticamente significativa que visa compor um “banco de dados”, exige um grande número de amostras de uma única localidade. Por exemplo, Kochelek *et al.* (2015) estudaram entre 10 e 30 amostras de cada local para uma análise de proveniência do rubi e da safira. Um número tão grande de amostras está disponível apenas em algumas das localidades de esmeraldas conhecidas em todo o mundo.

Para a realização dessa investigação sobre a esmeralda Monte Santo, foram analisadas cerca de 60 amostras de esmeralda de um mesmo depósito, visando compor um universo amostral estatístico representativo para essa localidade. Os resultados compõem um banco de dados das esmeraldas Monte Santo, que será disponibilizado futuramente para consulta e comparação com os demais depósitos de esmeralda do Brasil e, potencialmente, do mundo.

As aplicações dos resultados obtidos são diversas (figura 1), indo desde a sua utilização na Geologia Forense, permitindo a identificação da proveniência de lotes de esmeralda futuramente apreendidos em contrabandos; aplicações na gemologia, para fins de identificação entre espécimes naturais, tratadas e sintéticas; contribuições mineralógicas e genéticas sobre a sua formação; potenciais avanços na aplicação de técnicas analíticas em minerais (ver artigo 2).

Figura 1: Objetivos da presente pesquisa e algumas de suas aplicações.



2. - ESTADO DA ARTE DO BERILO

O berilo é um ciclossilicato de alumínio e berílio, de fórmula geral $\text{Be}_3\text{Al}_2(\text{Si}_6\text{O}_{18})$. O nome origina-se da palavra grega *beryllos*, que tem alusão à coloração mais comum deste mineral, ou seja, o verde-claro-azulado (Sauer, 1982). É marcante sua utilização como gema, porém possui também importante uso industrial como uma das principais fontes de berílio (Be), além de ser um importante mineral indicador.

2.1 - Estrutura Cristalina

O berilo pertence ao sistema hexagonal, espacial P6/mcc. Apresenta comumente hábito prismático hexagonal longo ou curto, adquirindo, por vezes, um aspecto tabular. É comum apresentar-se em cristais individuais, euédricos perfeitos e, raramente, em agregados de cristais.

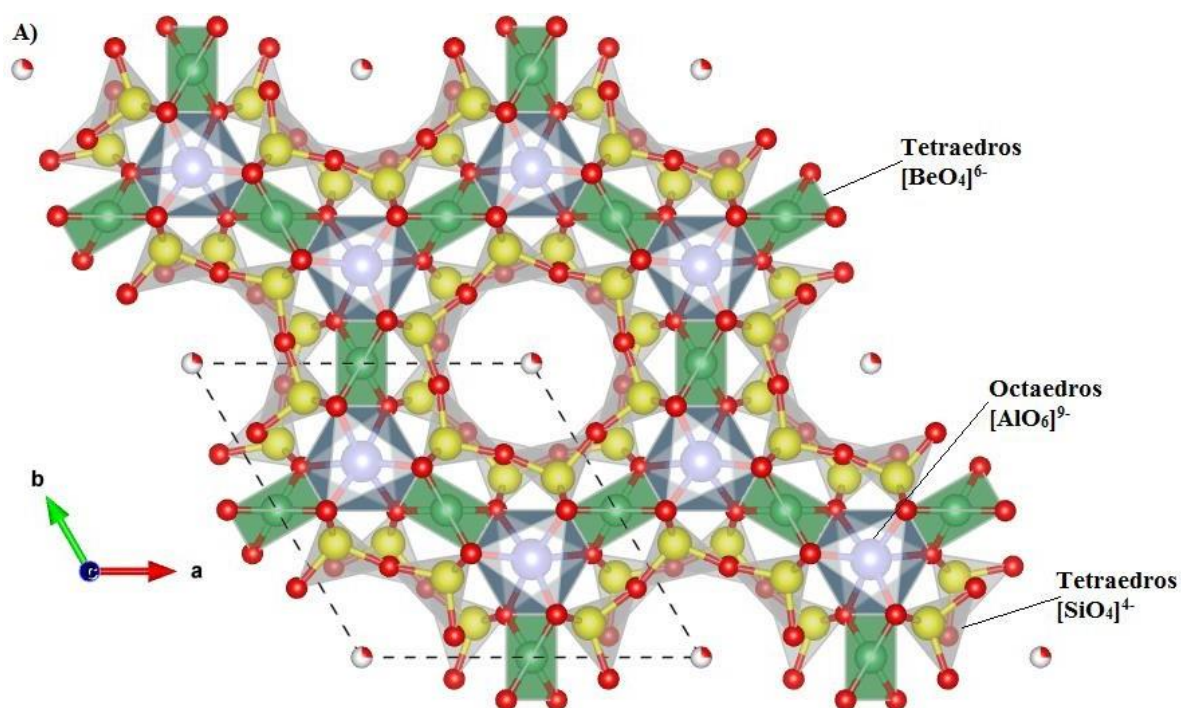
2.2 - Propriedades Cristaloquímicas

Apresenta em sua composição teórica, valores de $\text{BeO} \cong 14\%$, $\text{Al}_2\text{O}_3 \cong 19\%$ e $\text{SiO}_2 \cong 67\%$ (Deer *et al.*, 1966). As impurezas usuais, que compõem uma parte substancial da maioria das espécies de berilo, são álcalis (Na, Li, Cs, Rb, K) e em menor abundância H_2O , Ca, Mg, Mn, Fe^{2+} , Fe^{3+} , Cr, CO_2 , He e Ar (Beus, 1966). É comum a presença de elementos alcalinos em uma porcentagem de até 11%, H_2O em uma porcentagem de até 4%, além da presença de Fe, Mg, Mn, Ti, V, Cr, P, Ba, Zr, Sr, Sc, Zn e Ca em concentração de elementos traços (<0,1% em peso) e outros (Deer *et al.*, 1966).

A estrutura do berilo (Figura 2) consiste basicamente na presença de seis tetraedros de Si–O (SiO_4) (Deer *et al.*, 1966), os quais se polimerizam para formar anéis de seis membros paralelos a (001). O empilhamento dos anéis resulta em grandes canais paralelos ao eixo "c". No interior dos anéis de cada grupo SiO_4 , dois átomos de oxigênio são compartilhados por dois outros tetraedros de SiO_4 adjacentes, de modo que o radical dos anéis seja representado por $[\text{Si}_6\text{O}_{18}]^{12-}$, com uma relação Si:O igual a 1:3. Os átomos de alumínio (Al^{3+}) e berílio (Be^{2+}) estão posicionados, alternadamente, entre os anéis, sendo cada átomo de alumínio coordenado por um grupo octaédrico de seis átomos de oxigênio $[\text{AlO}_6]^{9-}$ e cada átomo de berílio coordenado por quatro átomos de oxigênio $[\text{BeO}_4]^{6-}$, formando um tetraedro distorcido. Os átomos de oxigênio dos anéis $[\text{Si}_6\text{O}_{18}]^{12-}$ vizinhos se unem tanto lateral como verticalmente pelo

alumínio e pelo berílio.

Os canais não são uniformes em diâmetro; na verdade, eles consistem em cavidades com um diâmetro de aproximadamente 5,2 Å separadas por "gargalos" com um diâmetro de aproximadamente 2,6 Å. Esses canais podem estar preenchidos por íons alcalinos (Aurischio *et al.*, 1994), cuja presença é necessária para equilibrar as reduções nas cargas positivas quando ocorrem substituições de cátions na estrutura. Moléculas de H₂O e CO₂ neutras e gases nobres, como Ar, He, Xe e Ne, podem estar presentes em quantidades variáveis nos canais que podem, ainda, estar vazios.



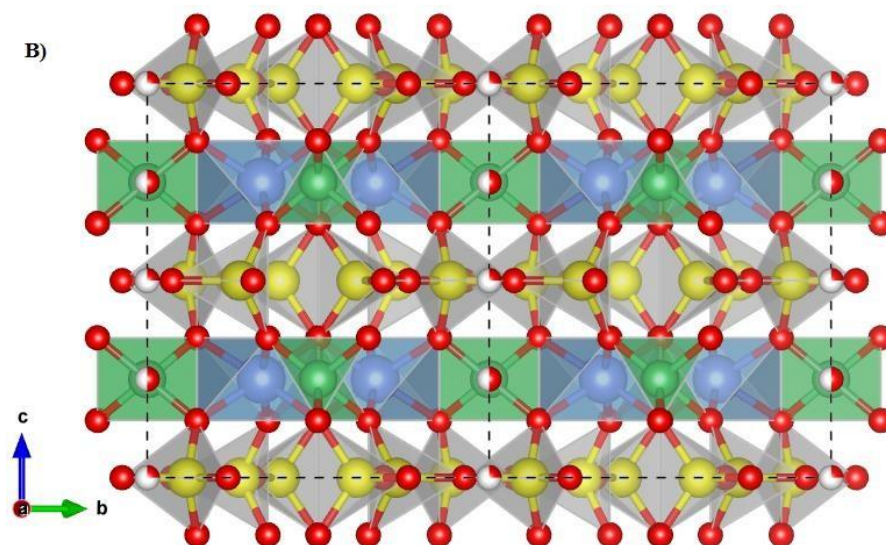


Figura 2: Estrutura do Berilo com projeção correspondente à face do prisma de primeira ordem $\{10'10\}$, com o eixo cristalográfico c vertical. Observam-se anéis hexagonais formados por seis tetraedros de Si-O, onde esses anéis são ligados e reticulados por átomos de Al^{3+} em coordenação octaédrica e por átomos de Be^{2+} em coordenação tetraédrica, formando canais ao longo do eixo c . Fonte: a autora. A) Projeção basal; B) Projeção lateral. Fonte: resultados de DRX.

2.3 - Substituições na Estrutura do Berilo

A fórmula cristaloquímica do berilo pode ser expressa por $[A]X_3Y_2T_6O_{18}$, associando as várias substituições isomórficas na estrutura do mineral e os elementos alcalinos sob a forma de íons mono e bivalentes (Tabela 1). Desta forma, o **A** representa os íons e/ou moléculas que ocupam as vacâncias e canais, tais como, H_2O , OH^- , Na^+ , Ca^{2+} , Fe^{2+} , K^+ , Cs^+ , Rb^+ , Li^+ ; o **X** os sítios tetraédricos de Be^{2+} , Al^{3+} , Li^+ , Si^{4+} ; o **Y** os sítios octaédricos de Al^{3+} , Fe^{2+} , Mg^{2+} , Fe^{3+} , Ca^{2+} , Mn^{2+} , Cr^{3+} , V^{5+} , Te^{4+} , Sc^{3+} ; e o **T** os sítios tetraédricos de Si^{4+} .

Três tipos de substituições são distinguidos: **1)** substituição octaédrica do Al^{3+} , **2)** substituição tetraédrica do Be^{2+} e **3)** limitada substituição tetraédrica do Be^{2+} e substituição octaédrica do Al^{3+} . Deficiência em Al^{3+} octaédrico é comum com substituições bivalentes resultando em ocupação do sítio **A** por compensação de carga. Berilo com alto teor em Al^{3+} tende a apresentar substituição significativa de Be^{2+} por Li^+ , enquanto o baixo teor em Al^{3+} tende a apresentar o sítio **X** completamente ocupado por Be^{2+} . O Al^{3+} , no caso de excesso, pelo seu caráter anfótero, entra nos tetraedros, substituindo Be^{2+} e Si^{4+} , enquanto o Si^{4+} , quando ocorre em excesso, pode substituir o Be^{2+} no tetraedro $[BeO_4]^{6-}$.

Análises permitem concluir que a substituição $Li^+ \rightarrow Be^{2+}$ favorece, fortemente, o mecanismo de entrada de álcalis nos canais da rede cristalina, paralelos ao eixo cristalográfico " c " (Deer *et al.*, 1966).

Estudos mostram que a maioria das substituições ocorre no local Y, no sítio octaédrico do Al, sugerindo que, para alcançar o equilíbrio de carga, a substituição de cátions divalentes por Al é acoplada à substituição de um cátion monovalente por uma vaga no local do canal (Giuliani *et al.*, 2019).

Tabela 1: Relações entre a fórmula geral do berilo $[A]X_3Y_2T_6O_{18}$, sua estrutura e a presença de álcalis como impurezas.

Elemento da Fórmula Geral	Posicionamento na Estrutura do Mineral	Impurezas e suas Representações
A	Vacâncias e Canais	Na⁺ e Ca⁺ : Raramente ocorrem nos espaços entre os anéis; comumente entre dois grupos H-O-H.
		K⁺ : ocorre em posições cognatas ao grupo H-O-H; às vezes, nas posições ocupadas pelo íon Rb ⁺ .
		Rb⁺ : ocorre em canais entre grupo H-O-H e três oxigênios de um anel ditrigonal, fortemente deformado.
		Cs⁺ : análogo ao Rb ⁺ , com uma leve distorção nos anéis;
		Fe²⁺ : ocorre nos canais ou ocupando vacâncias quando existe uma deficiência em Al ³⁺
X	Sítio Tetraédrico	OH⁻ : nota-se também a sua presença
		Be²⁺ : ocorre sob a forma de tetraedros $[BeO_4]^{6-}$ ou junto ao Si ⁴⁺ nos tetraedros $[SiO_4]^{4-}$; quando há deficiência em Si ⁴⁺ ou Al ³⁺ ocorre preferencialmente à substituição do Al ³⁺
		Li⁺ : ocorre nas posições do Be ²⁺
Y	Sítio Octaédrico	Al³⁺ : ocorre em octaedros $[AlO_6]^{9-}$; no caso de excesso, pelo seu caráter anfótero, entra nos tetraedros, substituindo Si ⁴⁺ e Be ²⁺
		Fe²⁺, Fe³⁺, Mg²⁺, Mn²⁺, Cr³⁺, Sc³⁺, V³⁺, Te⁴⁺ : ocorrem substituindo o Al ³⁺ nos octaedros $[AlO_6]^{9-}$
		Li⁺ : ocorrem em posições do Al ³⁺ , não substitui, mas pode ocupar certas vacâncias quando há alguma deficiência
T	Sítio Tetraédrico	Si⁴⁺ : ocorre em tetraedros $[SiO_4]^{4-}$ --em excesso, pode substituir o Be no tetraedro $[BeO_4]^{6-}$

Fonte: Gaines *et al.* (1997), adaptado por Carvalho (2004).

2.4 - Parâmetros Axiais do Berilo

Os autores Bragg & West (1926) foram os primeiros a determinar os parâmetros

axiais para o berilo, com valores de $a_o = 9,21\text{\AA}$ e $c_o = 9,17\text{\AA}$. Segundo Deer *et al.* (1992), as constantes de cela unitária para o berilo são $a_o = 9,21\text{\AA}$, $c_o = 9,20\text{\AA}$. Para os autores Aines & Rossman (1984) e Aurisicchio *et al.* (1994), assim como para vários outros, os parâmetros axiais para o berilo são $a_o = 9,21\text{\AA}$, $c_o = 9,19\text{\AA}$, e são os valores padrões utilizados na presente pesquisa.

Autores como Radeliffe & Campbell (1966) e Bakakin *et al.* (1970) sugerem que mudanças nas dimensões dos parâmetros axiais ocorrem quando há substituições nos sítios cristalográficos, assim como no posicionamento de íons nos canais. A razão c_o / a_o é normalmente utilizada para indicar o sítio em que as substituições ocorrem, bem como para classificá-los de acordo com essas substituições.

Deer *et al.* (1992) e Sampaio Filho *et al.* (1973), sugerem que o parâmetro a_o sofre acréscimo em sua dimensão com a entrada de outros elementos químicos (Fe, Mn, Mg, dentre outros álcalis) na estrutura do berilo, enquanto c_o permanece constante.

Bakakin *et al.* (1967) e Gandini (1999) sugerem que a entrada de álcalis e água na estrutura do berilo resulta em um acréscimo na dimensão do parâmetro c_o , enquanto o valor de a_o permanece constante ou sofre um acréscimo insignificante.

Bakakin *et al.* (1967) concluíram que a substituição parcial de Be por Li é acompanhada de aumento na dimensão dos parâmetros a_o e c_o , sendo o aumento de c_o maior. Por outro lado, a substituição parcial do Al por Li na estrutura do berilo, mantendo constante o Be, promove um aumento do eixo a_o . Os mesmos autores chamam atenção para o fato de que, devido ao grande raio iônico do Cs ($1,67\text{\AA}$), esse elemento entraria nos canalículos estruturais como íon neutralizador de carga, causando um acréscimo nas dimensões da cela unitária na direção do eixo cristalográfico a_o .

Mesmo que não seja considerada regra ou se tenha consenso sobre as variações dos parâmetros a_o e c_o , em função das impurezas químicas presentes na estrutura do berilo, sabe-se que o valor do eixo c na sua estrutura pode variar conforme a quantidade de álcalis presente nos canais estruturais. Sendo assim, conforme o tipo de berilo (se mais ou menos rico em álcalis) maior ou menor será a mudança na dimensão do eixo c_o .

Bakakin *et al.* (1970) e Aurisicchio *et al.* (1988, 1994) separam o berilo em 5 tipos: octaédrico [**O** = (Na, Cs, Rb, K)AlMe₂+Be₃Si₆O₁₈.nH₂O e c/a de 0,991 a 0,996]; transição entre o tipo octaédrico e normal (**O–N**); “normal” (**N** = Al₂Be₃Si₆O₁₈.nH₂O e c/a 0,997 – 0,998); transição entre o tipo normal e tetraédrico (**N–T**); e tetraédrico [**T** = (Na, Cs, Rb, K)Al₂Be₂LiSi₆O₁₈.nH₂O e c/a de 0,999 a 1,003].

Segundo Aurisicchio *et al.* (1988) o berilo "normal" (tipo **N**) é o berilo que apresenta ambas substituições tetraédrica e octaédrica, ou ainda, o berilo sem qualquer tipo de substituição catiônica, se aproximando mais da sua fórmula teórica.

No tipo **T** ocorre substituição parcial do berílio por lítio e, às vezes, por silício, no sítio tetraédrico, o que acarreta a entrada de elementos alcalinos no canal. No tipo **O** ocorre substituição parcial do Al por Fe, Mg, Sc, Mn dentre outros elementos, no sítio octaédrico.

2.5 - Canais no Berilo e Moléculas H₂O

Existem dois sítios no canal do berilo, um sítio cristalográfico maior (~5,1 a 5,2 Å), e um sítio cristalográfico menor (~2,6 a 2,8 Å). Acredita-se que elementos alcalinos, como K, Na, Rb e Cs, preenchem a estrutura do berilo, balanceando a carga em desequilíbrio, e se acomodando nos canais (Figura 3A). Dentro dos canais, Na⁺ é incorporado, preferencialmente, ao centro dos anéis de Si, no sítio cristalográfico menor 2b (0,0,0), onde pode estar em coordenação com uma única molécula de água tipo II, chamada "tipo IIs" ou mesmo em coordenação com duas moléculas de água tipo II, chamada "tipo IIId" (Aurisicchio *et al.*, 1994) (Figura 3), enquanto Cs⁺, Rb⁺ e K⁺, por seus raios iônico maiores, incorporam preferencialmente o sítio cristalográfico maior 2a (0,0,1/4) entre os anéis. Alguns autores acreditam que em berilo com baixa concentração de água, tanto átomos de Na como moléculas de H₂O ocorrem no sítio 2a, enquanto o sítio 2b permanece vazio.

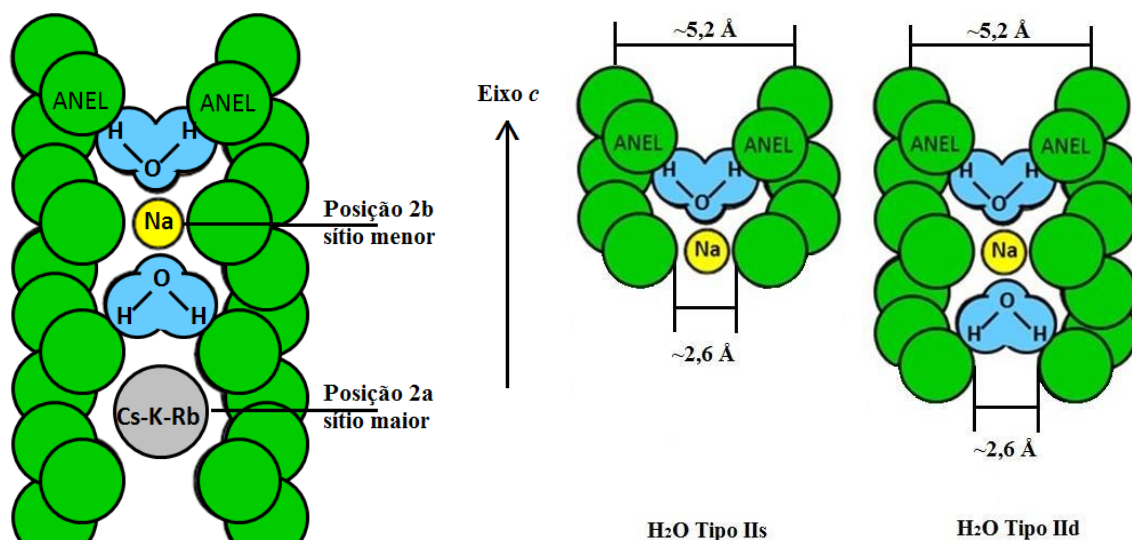


Figura 3: Seção esquemática dos canais do berilo, onde são demonstrados, ao longo do eixo *C*, (A) os sítios cristalográficos maior 2a e menor 2b, dentro dos canais, com suas possíveis ocupações e tipos moleculares de

água; e (B) as diferentes coordenações de H₂O (tipo IIs e II_d) com o cátion alcalino Na. Fonte: Modificadas por Cavalcanti (2017), de Wood & Nassau (1967) e Aurisicchio *et al.* (1994).

Dois tipos de arranjos possíveis das moléculas de água nos canais estruturais do berilo, identificados por espectroscopia de absorção no infravermelho por Wood & Nassau (1967) e Aurisicchio *et al.* (1994) são amplamente aceitos. No primeiro arranjo, para a água tipo I, as moléculas do eixo H-H se posicionam paralelas ao eixo *c*₀ do berilo. No segundo arranjo, na água tipo II, o eixo H-H é perpendicular ao eixo *c*₀, como pode ser observado na Figura 4. Esse fato implica na presença de álcalis como impureza nos canais, produzindo a atração eletrostática que provoca a rotação da molécula de água, de forma que o íon O²⁻ fique ao lado do elemento alcalino.

Um terceiro tipo de água (tipo III) foi proposto por Mashkovtsev & Lebedev (1992). A água tipo III é associada a cátions alcalinos pesados preenchendo o canal, e as moléculas do eixo H-H são orientadas paralelas ao eixo *c* do berilo, assim como a água tipo I, contudo, os cátions são situados a uma maior distância das moléculas de água, produzindo bandas ativas na região espectral do infravermelho.

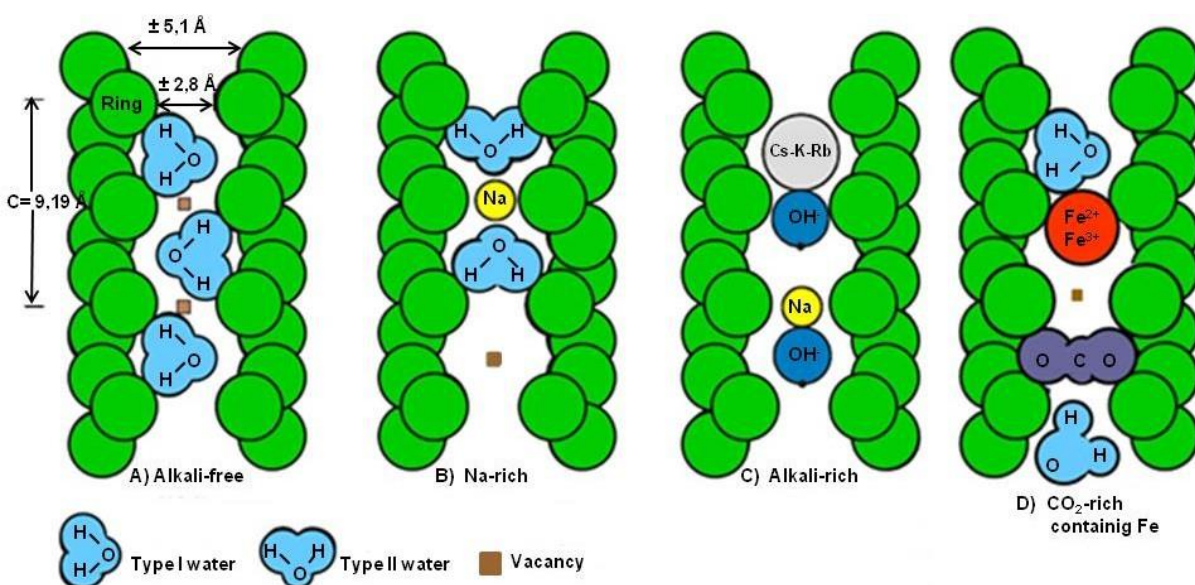


Figura 4: Esquemas paralelos ao eixo *c*, apresentando as duas orientações espaciais das moléculas de H₂O (tipo I e tipo II) no berilo. a) Berilo livre de álcalis, com H₂O tipo I e vacâncias; b) Berilo rico em sódio, com H₂O tipo II; c) Berilo rico em álcalis, estimulando grupos OH⁻. Fonte: Modificadas por Cavalcanti (2017), de Wood &

Nassau (1967), Wood & Nassau (1968), Aines & Rossman (1984), Aurisicchio *et al.* (1994) e Mathew *et al.* (1998).

Embora o conteúdo de água em berilo seja difícil de medir, sua relação com a concentração de Na₂O permite que este conteúdo seja calculado usando certas equações, como a proposta por Henry *et al.* (2021):

$$\text{H}_2\text{O (in wt\%)} = [0.6097 \times \text{Na}_2\text{O (wt\%)}] + 1.6290$$

2.6 - Causas de Cor no Berilo

As causas de cor de um mineral geralmente não estão relacionadas unicamente a um fator ou à presença de um único elemento, mas sim de uma combinação de fatores que podem ser: presença de um ou mais elemento(s) incorporado(s) em sua estrutura cristalina substituindo outro(s) elemento(s); presença de um elemento incorporado em canais ou como impurezas; proporções entre elementos com diferentes estados de oxidação (ex: Fe²⁺ / Fe³⁺); efeito de transferência de carga entre metal e ligante, onde o ligante geralmente é o oxigênio (LMCT); transferência de carga intervalente (IVCT).

A cor de um mineral é representada, na maioria dos casos, pela absorção seletiva de luz. Os mecanismos que provocam essas absorções são representados pelas transições eletrônicas nos orbitais mais externos dos átomos (geralmente elementos *3d* e *4f* da tabela periódica, dispersos no mineral ou em suas inclusões), pela transferência de carga entre elementos químicos do material e por centros de cor (Cavalcanti *et al.*, 2017). Algumas absorções podem ainda estar relacionadas a estruturas de maior escala, como as formadas pela “Teoria das Bandas”.

A grande variedade de cores em berilo está relacionada principalmente à presença de impurezas sob a forma de íons de metais de transição (elementos cromóforos) (Tabela 2), nos interstícios da estrutura cristalina do mineral, aliada ao seu posicionamento no retículo cristalino, seu estado de oxidação e transferências de carga (Tabela 3). Trata-se, portanto, de um mineral alochromático (Černý & Hawthorne, 1976; Dana & Hurlbut Jr., 1976). Alguns cristais de berilo não apresentam distribuição homogênea de cor, gerando um zonamento, fruto da variação composicional durante o crescimento do cristal (Sinkankas, 1981; Schwarz, 1987).

Fe²⁺, Fe³⁺, Mn²⁺, Mn³⁺, Cr³⁺ e V³⁺, podem substituir o Al³⁺, o Be²⁺, ou ambos.

Deficiência em Al³⁺ resulta na substituição e incorporação de íons mono e bivalentes (Gaines,

et al., 1997). O Fe é um dos principais cromóforos em berilo azul, verde e amarelo, cuja cor depende do número de coordenação (valência), posição na estrutura do mineral e da quantidade relativa entre Fe^{2+} e Fe^{3+} (Viana *et al.*, 2001a; 2001b; 2002a).

Esmeralda foi definida como “o berilo verde amarelado, verde ou verde azulado que revela distintas bandas de absorção de Cr e/ou V nas faixas violeta, vermelha e azul de seus espectros de absorção” (Schwarz & Schmetzer, 2002). Quantitativamente, as substituições de Cr e V variam entre 25 (Wood & Nassau, 1968) e 34.000 ppm (Andrianjakavah *et al.*, 2009) para Cr e de 34 ppm (Zwaan *et al.*, 2012) para 10.000 ppm (Rondeau *et al.*, 2008) para V.

Sc também é considerado um elemento cromóforo, que pode conferir uma cor verde pálida aos minerais (Mellini *et al.*, 1982).

Tabela 2: Elementos cromóforos nos berilos e suas consequentes espécies gemológicas.

Metais de Transição	Espécie Gemológica	Tonalidades
Cr^{2+} , V^{3+} , Fe^{2+} , Fe^{3+}	Esmeralda	Verde-intensa, verde-grama, verde-alface
Fe^{2+} , Ba^{3+}	Água-marinha	Azul, azul-esverdeada, verde-amarelada, verde-azulada
Fe^{2+} , Mn, Ti	Heliodoro	Amarelo-dourado, amarelo-esverdeada, amarelo-acastanhada, âmbar
Mn, Fe, Li	Morganita	Rósea a rosa-salmão
Mn, Ti, Li, Nb	Berilo vermelho	Vermelho-groselha a vermelho-salmão
Na, Li^1	goshenita	Incolor, branca, amarela ou azulada

¹ a presença dos metais de transição na estrutura do mineral não está relacionada, necessariamente, às tonalidades desta espécie. Fonte: Correia Neves *et al.* (1984); Schwarz (1987); Castañeda *et al.* (2000).

Tabela 3: Causas de cor em espécies de berilo.

Cor	Espécie	Causa	Referências Bibliográficas
Azul-escuro	<i>Maxixe</i>	NO_3^- centros de cor devido à irradiação	Andersson (1979)
Azul-escuro	tipo <i>Maxixe</i>	CO_3^{2-} centros de cor devido à irradiação	Andersson (1979)
Azul-claro	Água-marinha azul	Fe^{2+} em canais estruturais	Goldman <i>et al.</i> (1978)
Azul muito escuro	Água-marinha azul	transferência de carga intervalência (IVCT) $\text{Fe}^{2+} - \text{O} - \text{Fe}^{3+}$	Goldman <i>et al.</i> (1978)
Verde (amarelo + azul)	Água-marinha verde	transferência de carga $\text{O}^{2-} \rightarrow \text{Fe}^{3+}$ e Fe^{2+} nos canais estruturais	Fritsch & Rossman (1988)
Amarelo a laranja	heliodoro	transferência de carga $\text{O}^{2-} \rightarrow \text{Fe}^{3+}$	Goldman <i>et al.</i> (1978)
Rosa	morganita	Mn^{2+} em coordenação octaédrica	Wood & Nassau (1968)
Verde-grama Verde claro a escuro	esmeralda	Cr^{3+} e/ou V^{3+} em coordenação octaédrica	Wood & Nassau (1968)
vermelho	berilo vermelho	Mn^{3+} em coordenação octaédrica	Shigley & Foord (1984)

Fonte: Adaptado de Fritsch & Rossman (1988).

3. - FORMAÇÃO DA ESMERALDA

De um modo geral, esmeralda é um berilo com concentrações anômalas de cromo e vanádio, resultando em cristais verdes. Geralmente Cr, V e Be ocorrem em ambientes geológicos completamente distintos, sendo este, o fator limitante na sua formação. Mais comumente, formam-se em ambientes geológicos que envolvem metassomatismo, marcados pela introdução de fluidos ricos em Be em contato com rochas ou fluidos ricos em cromo (Cr^{3+}) e/ou vanádio (V^{3+}), sob condições específicas de temperatura e pressão.

O berílio é um elemento litófilo, que tem uma forte afinidade pelo oxigênio, levando à produção de berilo e crisoberilo (BeAlO_4) em temperaturas mais altas, e em temperaturas médias a baixas, com sílica, formando minerais silicatados, como berilo, bertrandita [$\text{Be}_4\text{Si}_2\text{O}_7(\text{OH})_2$] e micas. Estes minerais têm uma densidade relativamente baixa ($\rho = 2,76$) e estão concentrados na crosta ($\rho_{\text{crosta}} = 2,7$). O berílio está presente nos granitos da crosta e nos enxames de diques de pegmatitos, aplitos e veios de quartzo associados. Por outro lado, cromo e o vanádio são metais de transição de alta densidade que geralmente se concentram no núcleo e no manto da Terra. Embora Cr e V mostrem afinidades litófilas e siderófilas, eles tendem a formar soluções sólidas com ferro para formar, por exemplo, cromita (FeCr_2O_4) a altas temperaturas. O cromo e o vanádio são mais altamente concentrados nas rochas máfico-ultramáficas metamorfizadas da litosfera oceânica.

A formação de esmeraldas requer a circulação de fluidos entre depósitos de Be e Cr-V para mobilizar esses elementos. Metassomatismo e interação fluido-rocha é o principal mecanismo de mobilização de elementos em rochas sedimentares (*black shale*) ou graníticas, para Be, e em rochas máfico-ultramáficas metamorfizadas para Cr e V.

3.1 - Classificação Genética de Depósitos de Esmeralda

Historicamente, depósitos de esmeralda foram classificados em três tipologias abrangentes. O primeiro e mais abundante tipo de depósito (*schist-type*), em termos de produção, é o tipo relacionado a pegmatitos dessilicatados que se formaram através da interação de fluidos metassomáticos com pegmatitos ricos em berílio, ou corpos graníticos, que intrudiram em rochas ricas em cromo ou vanádio, como rochas máfico-ultramáficas e vulcânicas, ou folhelhos derivados dessas rochas.

Um segundo tipo de depósito, responsável pela maior parte da esmeralda de qualidade gemológica, é o tipo sedimentar, que geralmente envolve a interação, ao longo de

falhas e fraturas, de salmouras ricas em Be, e da interação evaporítica com folhelhos e rochas sedimentares contendo V.

O terceiro tipo, e comparativamente mais raro, é o depósito metamórfico-metassomático. Neste modelo de depósito, fluidos crustais mais profundos circulam ao longo de falhas ou zonas de cisalhamento e interagem com xistos metamorfizados, carbonatos e rochas ultramáficas, e Be e Cr ($\pm$ V) podem ser transportados para o local de deposição através dos fluidos ou já estarem presentes nas rochas metamórficas interseccionadas por falhas ou zonas de cisalhamento (Giuliani *et al.*, 2019).

Todos os três modelos de depósitos de esmeralda requerem algum nível de atividade tectônica e, frequentemente, a atividade tectônica continuada pode resultar no metamorfismo de um depósito tipo sedimentar ou magmático pré-existente. No extremo, em níveiscrustais mais profundos, o metamorfismo de alto grau pode resultar na fusão parcial de rochas metamórficas, obscurecendo a distinção entre depósitos do tipo metamórfico e magmático (Giuliani *et al.*, 2019).

Pela ambiguidade desses esquemas de classificação e por não serem particularmente úteis quando se trata de entender os mecanismos e condições que levaram à formação de um depósito de esmeralda, Giullinai *et al.* (2019) propuseram uma nova classificação, com base no ambiente geológico (magmaico ou metamórfico); tipo de rochas hospedeiras (rochas máfico-ultramáficas, rochas sedimentares e granitóides); grau de metamorfismo; estilos de mineralização (veios, *pods*, zona de cisalhamento); tipo de fluidos circulantes e sua temperatura, pressão e composição química.

A nova classificação explica a formação em múltiplos estágios dos depósitos e as idades de formação, bem como a provável remobilização da mineralização prévia de berílio, como as intrusões pegmatíticas nas rochas máfico-ultramáficas. Tais novas considerações usam o conceito de modelos genéticos baseados em estudos empregando assinaturas (*fingerprints*) geoquímicas, de isótopos estáveis e radiogênicos, e de inclusões fluidas e sólidas. As ocorrências e depósitos de esmeraldas são classificados em dois tipos principais:

Tipo I: *Tectonic magmatic-related*, com sub-tipos hospedados em:

(IA) Rochas Máfico-ultramáficas (Brasil, Zâmbia, Rússia e outros);

(IB) Rochas Sedimentares (China, Canadá, Noruega, Cazaquistão, Austrália);

(IC) Rochas Graníticas (Nigéria);

Tipo II: *Tectonic metamorphic-related*, com sub-tipos hospedados em:

(IIA) Rochas Máfico-ultramáficas metamorfizadas M-UMR (Brasil, Áustria);

(IIB) Rochas Sedimentares - *Black shales* (Colômbia, Canadá, USA);

(IIC) Rochas Metamórficas (China, Afeganistão, EUA);

(IID) Depósitos tipo I metamorfizados e remobilizados, ou relacionados a intrusões graníticas ocultas (Áustria, Egito, Austrália, Paquistão) e alguns depósitos não classificados.

3.2 - Ocorrências de Esmeralda no Mundo

Esmeralda é rara, mas é encontrada em todos os cinco continentes (Figura 1). Colômbia, Brasil, Zâmbia, Rússia, Zimbábue, Madagascar, Paquistão e Afeganistão são os maiores produtores de esmeralda do Mundo. Depósitos de esmeralda ocorrem principalmente em rochas pré-cambrianas no leste do Brasil, África Oriental, África do Sul, Madagascar, Índia e Austrália, e em sequências metavulcano-sedimentares mais jovens ou ofiolitos na Bulgária, Canadá, China, Índia, Paquistão, Rússia e Espanha. Por outro lado, os depósitos de esmeralda colombianos, que produzem a maioria das esmeraldas de alta qualidade do mundo, são únicos porque estão localizados em rochas meta-sedimentares, os *black shales* do Cretáceo Inferior da bacia da Cordilheira Oriental. Outros depósitos são hospedados em veios do tipo Alpino, também chamados de filões/fissuras (*clefts*) do tipo Alpino. Esmeralda é encontrada em veios e cavidades nos Alpes Europeus (Binntal), bem como nos Estados Unidos (Hiddenite). As esmeraldas nigerianas são únicas e estão localizadas em pegmatitos lenticulares do tipo *pods* (Giuliani *et al.*, 2019).

Os depósitos e ocorrências de esmeralda no mundo foram agrupadas por Giuliani *et al.* (2019), segundo os seus tipos geológicos, ou seja, seus ambientes de formação, conforme pode ser observado na figura 5 a seguir.

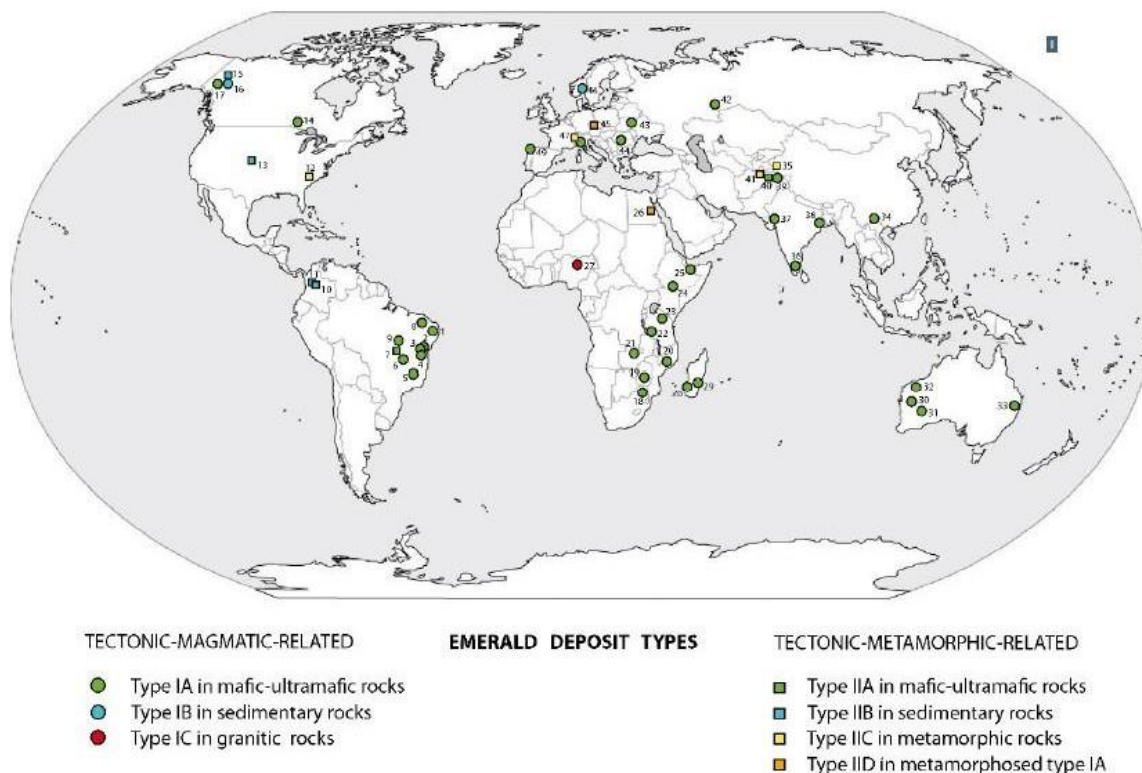


Figura 5: A localização dos depósitos e ocorrências de esmeraldas em todo o mundo relatados seguindo os seus ambientes geológicos. Fonte: Giuliani *et al.*, 2019.

3.3 - Ocorrências de Esmeralda no Brasil

O Brasil é um dos principais produtores de esmeralda do mundo, depois da Colômbia e Zâmbia, com ocorrências de esmeralda localizadas nos estados de Minas Gerais (Nova Era-Itabira, Piteiras, Capoeirana), Bahia (Socotó, Carnaíba, Salininha), Goiás (Santa Terezinha de Goiás), Ceará (Tauá), Rio Grande do Norte (Fazenda Bonfim, Paraná) e Tocantins (Monte Santo do Tocantins).

A principal produção brasileira é de depósitos do tipo I (correlatas ao magmatismo tectônico) em Minas Gerais (74%) e Bahia (22%) sendo o mais importante exemplo de ocorrências de esmeralda no Brasil, o distrito de mineração de Nova Era-Itabira em Minas Gerais, localizado no Quadrilátero Ferrífero.

Em 1978, o depósito de Itabira foi descoberto em uma propriedade privada chamada “Fazenda Itabira” (Bastos, 1981). Após três anos de desenvolvimento, a mina foi mecanizada e denominada mina de Belmont (Hänni *et al.*, 1987). Em 1988, esmeraldas foram descobertas em Capoeirana perto de Nova Era, 10 km a sudeste da mina de Belmont (Souza *et al.*, 1992). Em 1998, o depósito de Piteiras foi descoberto, e está localizado a 15 km a sudeste da cidade de Itabira, entre as minas de Belmont e Capoeirana. A zona mineralizada se estende por mais

de 5 km e as minas estão localizadas em duas zonas de empurrão (orogênese brasileira) justapondo rochas ultramáficas e granitos altamente deformados chamados de “Borrachudos” (Rondeau *et al.*, 2003).

Os depósitos de esmeralda brasileiros estão parcialmente associados a zonas de cisalhamento recortando rochas máfico-ultramáficas metamorfizadas. A ausência de influência magmática em sua formação é limitada por estudos de campo, geoquímicos, de inclusão de fluidos e de isótopos estáveis (Giuliani *et al.*, 1997). É o caso do depósito de Santa Terezinha de Goiás e da ocorrência de Itaberaí. A importância econômica desse tipo de depósito (tipo II) está diminuindo devido a esmeraldas menores, disseminação de esmeraldas e maior custo de mineração artesanal que hoje representa apenas 4% da produção total do Brasil.

O depósito de Santa Terezinha de Goiás produziu cerca de 155 toneladas de esmeralda entre 1981, data da descoberta, e 1988 (Biondi, 1990). A infiltração de fluidos hidrotermais é controlada por estruturas tectônicas, como as zonas de empurrão e cisalhamento. Os veios pegmatíticos estão ausentes e a mineralização é estratiforme. A esmeralda é disseminada dentro de flogopititos e carbonato-talco xistos flogopitizados da sequência metavulcânica sedimentar de Santa Terezinha (Biondi, 1990; Giuliani *et al.*, 1990).

No nordeste do Brasil, inseridas na Província Borborema (PB), a ocorrência de esmeralda mais antiga conhecida é a de Tauá-CE, reconhecida desde 1950 pela extração de esmeraldas através de atividades garimpeiras, sendo classificada como um depósito do Tipo I (Giuliani *et al.*, 1997) e considerada de baixa importância econômica devido à baixa qualidade dos cristais encontrados (Schwarz *et al.*, 1988; Giuliani *et al.*, 1997). As ocorrências estão relacionadas a corpos pegmatíticos de pequena expressão em faixas de biotita-xisto e tremolito intercalados em gnaisses de duas micas, onde a intrusão destes veios teria provocado metassomatismo das encaixantes (Castelo Branco *et al.*, 1988).

O depósito de esmeralda da Fazenda Bonfim, inserido na PB, é um exemplo de depósito do tipo metassomático, o qual resulta da interação metassomática entre os fluidos graníticos de pegmatitos e as rochas metavulcano-sedimentares, principalmente as rochas de composição básica-ultrabásica ou seus equivalentes metamórficos, afetados por dobras e deformações complexas (Giuliani *et al.*, 1990; Beurlen *et al.*, 2009; Oliveira & Ali, 2011). O contato entre os pegmatitos e as rochas ultramáficas é caracterizado por um zoneamento metassomático, individualizado por uma lente de flogopita xisto, bordejando diretamente a intrusiva ácida, em contato brusco. As esmeraldas ocorrem concentradas nas lentes de flogopita xisto, dispersas em pequenos cristais em grande quantidade (Santiago, 2017).

A ocorrência de Salininha (Bahia) foi descoberta na década de 1960 por Sauer, que conseguiu a autenticidade da gema verde encontrada na região, através de análises e certificação emitida pelo GIA (Gemological Institute of América) em agosto de 1963. Devido à ausência de cromo, fato este imprescindível na época para que o berilo verde fosse denominado de esmeralda, ele utilizou a informação que detinha sobre ocorrências de esmeraldas de outras regiões do mundo, como as encontradas na Rússia e na África, que também tinham somente o Vanádio como elemento cromóforo, assim como a de Salininha.

A descoberta de esmeraldas na região de Carnaíba (Bahia) ocorreu em 1963 e deu origem à mineração e garimpagem de esmeralda de qualidade gemológica. Griffon *et al.* (1967) apresentaram o primeiro estudo de detalhe da jazida de esmeralda de Carnaíba, identificando a relação da mineralização em rochas ultramáficas metassomatizadas com intrusões pegmatíticas. A esmeralda ocorre nas faixas de biotita-flogopita-xistos, com bolsões caulínicos, em menor frequência nos talco-xistos e, mais raramente, no núcleo de quartzo dos pegmatitos e no biotitito. Na região de Socotó, a esmeralda foi descoberta em 1983, inserida no mesmo contexto geológico da região de Carnaíba.

3.4 - As Ocorrências de Esmeralda de Tocantins

As ocorrências de esmeraldas estudadas localizam-se na porção central do Estado de Tocantins, no contexto geológico do Cinturão Araguaia. A área dos garimpos está localizada a sul do município de Monte Santo do Tocantins, nas proximidades do município de Paraíso do Tocantins (Figura 6).

A descoberta de esmeralda se deu durante a abertura de uma cisterna em setembro de 1996. Sua divulgação resultou em um grande fluxo de garimpeiros para a área, levando à criação da Cooperativa de Garimpeiros de Monte Santo do Tocantins - COOPERGEMAS (CPRM, 1997).

1.1.1 - Contexto Geológico Local e Controles da Mineralização

Localmente, a região de Paraíso do Tocantins é caracterizada geologicamente pelas seguintes unidades:

A - Complexo Colméia: constituído por rochas gnáissicas e migmatíticas;

B - Grupo Rio do Coco: sequência vulcano-sedimentar representada por anfibolitos, anfibólio xistos magnesianos, que constituem as rochas vulcânicas máfico-ultramáficas, e formações ferríferas;

C - Grupo Estrondo: constituído predominantemente por mica xistos (granada-biotita xisto, biotita-muscovita xistos) e quartzitos;

D - Granitos Intrusivos;

E - Coberturas Sedimentares (Bacia do Parnaíba): constituída por siltitos, argilitos e folhelhos.

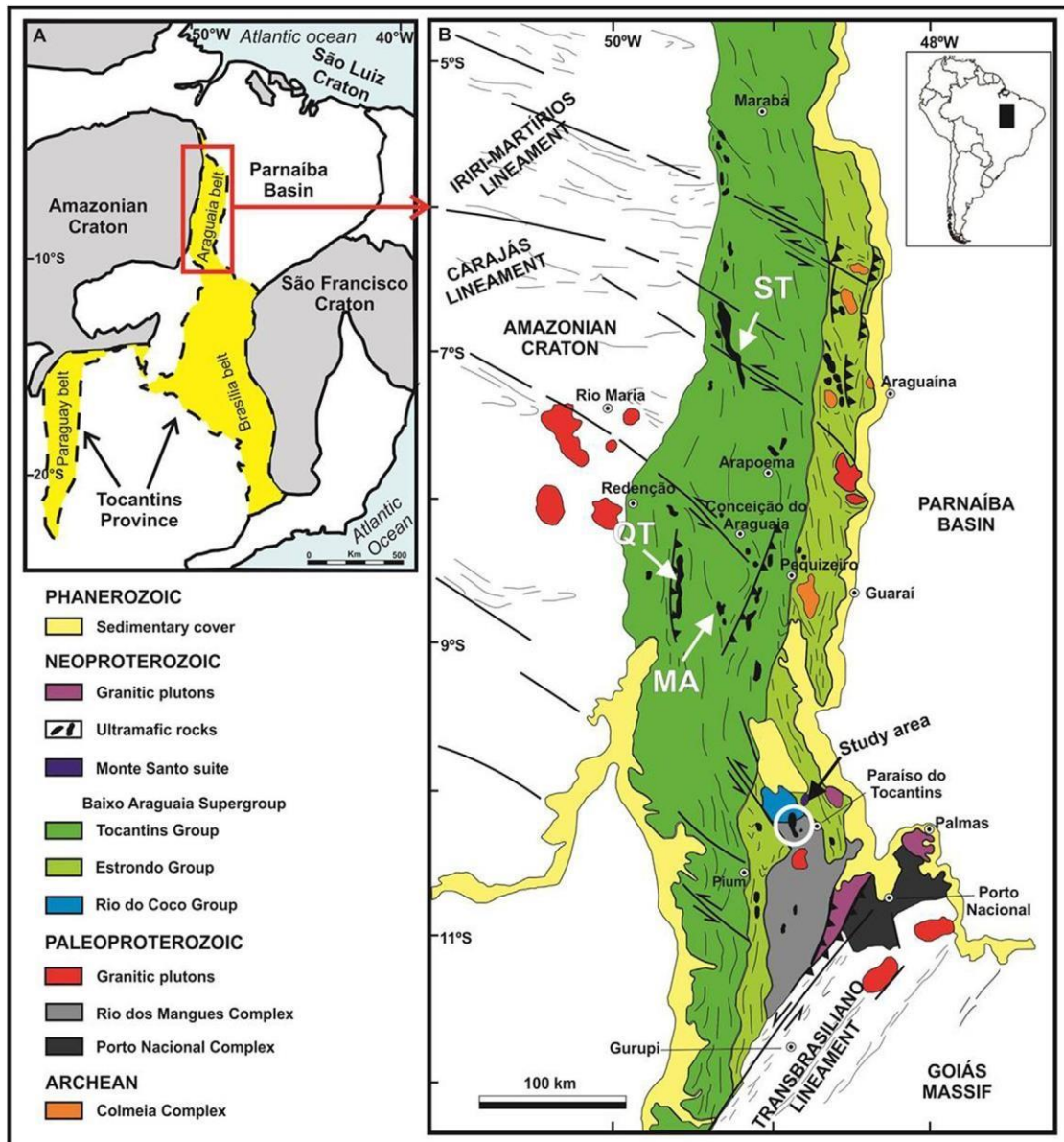


Figura 6: A) Mapa tectônico esquemático do Brasil Central, com destaque para a Província Estrutural do Tocantins e o Cinturão Araguaia. Adaptado de Delgado & Pedreira (1995). (B) Mapa geológico do Cinturão Araguaia destacando a área de estudo. Adaptado de Alvarenga *et al.* (2000) e Souza *et al.* (2019).

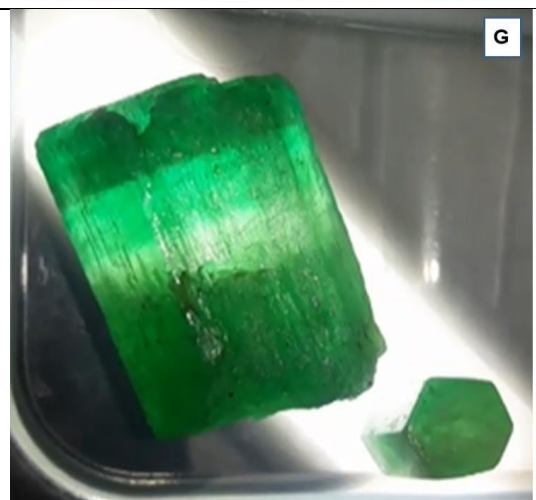
A zona mineralizada dos garimpos de Monte Santo do Tocantins está situada na zona de contatotectônico entre o biotita-granito e as rochas máfico-ultramáficas (anfíbolitos e hidrotermalitos). Neste ambiente primário, as esmeraldas ocorrem em bolsões, como cristais dispersos no biotito, e associadas a agregados de quartzo, tremolita, flogopita e biotita.

Foi sugerido pela CPRM (1997), de acordo com a classificação genética de Schwarz (1987), que estas ocorrências são do tipo I, caracterizadas pela associação de rochas máfica-ultramáficas ou seus derivados metamórficos, fornecendo Cr, V, Fe, e de pegmatitos fornecendo Be, a partir da interação de seus fluidos.

Os garimpeiros denominam de "friso" a porção da rocha onde encontra-se a mineralização, conforme pode ser observado na figura 7 a seguir. As rochas hospedeiras das esmeraldas são predominantemente mica xistos (Figura 7B) de composição biotítica flogopítica ou actinolita-tremolita xistos. Foram observadas algumas amostras onde cristais de esmeralda encontram-se encaixados no contato do granito albitizado com o xisto (Figura 7C).

Figura 7: A) Galeria do garimpo G5, com destaque para o "friso" (porção da rocha onde encontra-se a mineralização, segundo a linguagem dos garimpeiros). B) Cristais de esmeralda contidos no xisto; C) Cristais de esmeralda encaixados no contato do granito albitizado com o xisto; D) Lote de amostras da esmeralda MonteSanto; E) Amostras hexagonais euédricas de esmeralda; F) Amostras de esmeralda mostrando variação na cor verde; G) Amostras de esmeralda apresentando zonamento de cor.





2 - MATERIAIS E MÉTODOS

A presente pesquisa foi desenvolvida pela aplicação das seguintes etapas de trabalho e procedimentos analíticos:

2.1 - Amostragem

Uma primeira etapa de campo e coleta de amostras foi realizada no município de Paraíso do Tocantins-TO, em maio de 2019. No total, foram visitados nove garimpos, dentre eles, alguns ativos e outros inativos, segundo informações fornecidas pelos próprios garimpeiros. A aquisição de amostras se deu por doação de cristais de esmeralda e rochas encaixantes contendo ou não cristais de esmeralda.

O garimpo denominado G4 encontra-se temporariamente inativo para a realização de melhorias na sua infraestrutura, em atendimento às exigências do órgão regulador ANM (Agência Nacional de Mineração). O mesmo possui um *shaft* com elevador semi-mecanizado, além de galpões contendo equipamentos utilizados no desmonte da rocha para a obtenção de cristais de esmeralda. Neste garimpo, os cristais de esmeralda encontram-se encaixados em biotita-xisto. As amostras oriundas desse garimpo possuem a melhor qualidade gemológica dentre as amostras observadas e coletadas na região, onde as mesmas apresentam boa transparência, um baixo grau de fraturamento e inclusões nos cristais. As principais amostras foram adquiridas nesse garimpo (Figura 7).

2.1.1 - Preparação de Amostras

Tomou-se o cuidado de utilizar as amostras onde pelo menos uma face do cristal pudesse ser identificada, entre euédricas e subédricas, a fim de obter um espaço amostral representativo. As amostras coletadas foram catalogadas e separadas em grupos, de acordo com uma escala de cor (Figura 8), com o intuito de observar a relação entre a cor e os resultados obtidos. Cerca de 60 amostras de esmeralda foram selecionadas, preparadas e analisadas. As amostras foram georreferenciadas com o ponto de extração *in situ* do "garimpo (G4)", seguido da numeração utilizada para a catalogação das amostras.



Figura 8: A) Amostras adquiridas no garimpo G4, catalogadas e separadas segundo uma escala de cor, onde observar-se-á a relação da cor com os resultados da composição química e das análises espectroscópicas.

2.2 - Técnicas Analíticas

A aplicação de técnicas analíticas minerais avançadas ainda não é amplamente conhecida ou utilizada no Brasil. O mineralogista tradicionalmente treinado foi instruído a analisar propriedades físicas, ópticas e mecânicas na identificação e caracterização dos minerais (cor, cor do traço, brilho, clivagem, fratura, dureza e densidade), além de usar um microscópio óptico. Num panorama mais otimista, até um difratômetro de raios-X e alguns dispositivos diferentes para determinações de química analítica, como por exemplo microsonda eletrônica ou fluorescência de raios-X, visando caracterizar uma rocha ou mineral.

Os tempos mudaram, e hoje os problemas e direções de pesquisa são muitas vezes diferentes daqueles do passado e novas abordagens e 'ferramentas' de estudo são necessárias. Portanto, a aplicação de uma única ou duas técnicas analíticas já não é mais suficiente para caracterizar um mineral. A experiência mostra que, em geral, diferentes métodos analíticos devem ser usados de forma complementar. Se o objetivo é entender a natureza físico-química de algum material ou um sistema de fases (por exemplo, uma rocha ou uma interface de fluido mineral) em um sentido completo, deve-se aplicar uma série de técnicas diferentes, de modo que elas se complementem.

As técnicas analíticas utilizadas na presente investigação foram: métodos essencialmente espectroscópicos como espectroscopias *Raman*, de absorção molecular na região do infravermelho, por transformada de *Fourier* (FTIR), e de absorção molecular na região ultravioleta-visível-infravermelho proximal (UV-Vis-NIR); análise química utilizando Microsonda Eletrônica; estudo cristalográfico por Difração de Raios-X em monocristal; e

estudo das Inclusões Fluidas. A aplicação combinada dessas técnicas fornece resultados de alta acurácia, de modo a permitir estabelecer *fingerprints* para minerais e gemas, além de permitir uma melhor compreensão sobre o sistema de formação dos mesmos.

O fluxograma a seguir (Figura 9) apresenta as técnicas analíticas utilizadas de forma sintética e didática, associando-as com o objetivo pretendido.

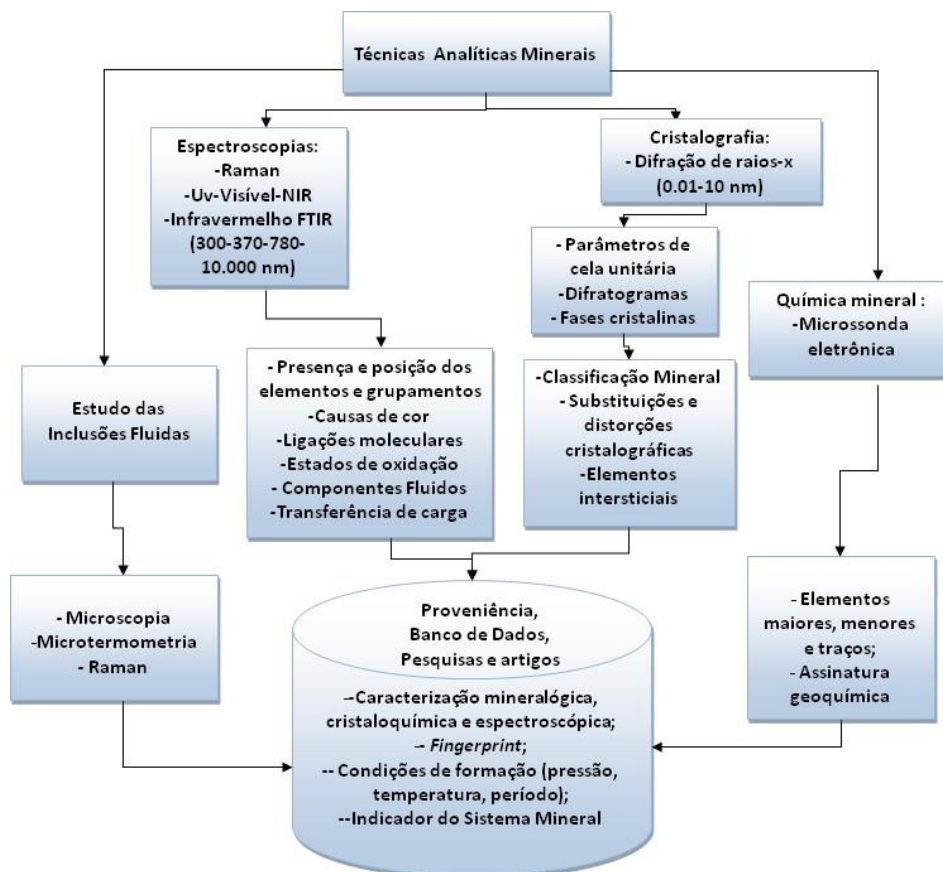


Figura 9: Fluxograma das técnicas analíticas utilizadas e seus respectivos objetivos.

2.2.1 - Difração de Raios-X pelo Monocristal

Alguns autores sugerem que mudanças e distorções nos parâmetros axiais ocorrerem quando há substituições de elementos em sítios cristalográficos, assim como no posicionamento de íons nos canais. A distorção pode ocorrer, ainda, pela entrada de elementos de transição, álcalis e água nos canais vazios, balanceando a carga deste mineral. A razão entre parâmetros axiais é normalmente utilizada para indicar o sítio em que as substituições ocorrem, bem como para classificar o berilo de acordo com essas substituições.

Para a determinação de tais parâmetros, utilizamos a difração de raios-X pelo método do monocristal. Através de tratamento de dados obtidos e utilizando *Software* para esse fim (por exemplo *Vesta* ou *Mercury*), foi possível construir os modelos cristalográficos reais para as amostras analisadas. Na análise de difração de raios-X em monocristal, dezesseis cristais de esmeralda foram analisados. As amostras foram preparadas para que atingissem granulometria aproximada de 1 mm, necessária para a realização das análises de DRX pelo método do monocristal.

As coletas de dados dos 16 cristais analisados foram realizadas em um difratômetro modelo *Bruker Kappa APEX II DUO*, utilizando radiação $\text{Mo-K}\alpha$ ($\lambda = 0,71073$), à temperatura ambiente. As análises foram realizadas no Laboratório de Cristalografia Estrutural - Raios-X em Monocristal do Departamento de Física da Universidade Federal do Ceará-UFC. Os parâmetros de cela foram obtidos utilizando o refinamento pelo “método dos mínimos quadrados” em F^2 . As estruturas cristalográficas foram obtidas utilizando um programa cristalográfico, o *software Vesta*®.

2.2.2 - Espectroscopia Raman

A espectroscopia Raman vem sendo cada vez mais utilizada no meio gemológico como uma ferramenta para a identificação das espécies minerais. Por estar diretamente relacionada aos átomos e ligações moleculares presentes, é única e específica para cada tipo de material. Essa técnica analítica permite a caracterização de diferentes tipos de água nos canais do berilo, distingue entre gemas naturais e sintéticas, assim como auxiliar na separação entre exemplares de diferentes localidades.

As assinaturas micro-Raman das amostras foram coletadas em temperatura ambiente ($\pm 25^\circ \text{C}$), através do equipamento de espectroscopia Raman *LabRAM HR Evolution*, da marca *Horiba*, que realiza medidas com microscópio confocal *Raman* acoplado a uma CCD (*ChargeCoupled Device*) usando laser de diodo semiconductor com grade de 1800 linhas/mm. Foi utilizado como fonte de excitação um laser verde (532 nm) e analisada a faixa entre 150 e 5.500cm^{-1} , o que permite o estudo de efeitos de fotoluminescência, além do efeito Raman.

As análises micro-Raman foram realizadas no Laboratório de Espectroscopia Óptica do Instituto de Física-IF da Universidade de Brasília-UnB. Os espectros Raman foram gerados no *software OriginPro 9.0* e foi realizada *baseline* nos espectros utilizando o *software LabSpec*.

2.2.3 - Espectroscopia na Região do Infravermelho por Transformada de Fourier (FTIR)

A partir da espectroscopia na região do infravermelho, obtêm-se informações sobre as moléculas ou sobre os grupos de átomos e seus respectivos arranjos. Além da identificação dos materiais, o método pode ser utilizado para análise quantitativa de fases, caracterização de componentes fluidos presente nos materiais (ex: H₂O, CO₂, CH₄ e outros), vibrações fundamentais dos grupamentos (ex: hidroxila) e dos sítios estruturais (ex: tetraedros e octaedros), dentre outras, o que permite distinguir entre gemas naturais e sintéticas, assim como auxiliar na separação entre exemplares de diferentes localidades.

As análises de espectroscopia na região do infravermelho foram realizadas no equipamento *Perkin Elmer Spectrum 400 FT-IR / FT-NIR Spectrometer*. Os dados foram coletados entre 6.000 e 400 cm⁻¹, com uma resolução de 4 cm⁻¹. Para amostras sólidas, foram formadas pastilhas, comprimindo a amostra moída com brometo de potássio (KBr) em pó sob alta pressão. Essas pastilhas são chamadas de pastilhas de KBr e foram confeccionadas na proporção de 2% de amostra para a quantidade geralmente usada de KBr, ou seja, 0,3 g de KBr e 0,006 g de amostra pulverizada na fração 200 mesh.

As alíquotas para análise de FTIR foram moídas e maceradas manualmente em gral de ágata. O gral de ágata foi escolhido e utilizado por ser composto exclusivamente por sílica, evitando assim possíveis contaminações durante a preparação das amostras.

As análises espectroscopia na região do infravermelho foram realizadas no equipamento *Perkinelmer Spectrum 400 FT-IR / FT-NIR Spectrometer*, no Laboratório de Espectroscopia Óptica do Instituto de Física-IF da Universidade de Brasília-UnB. Os espectros IR foram gerados no *software OriginPro 9.0* e foi realizada *baseline* nos espectros utilizando o *software LabSpec*.

2.2.4 - Espectroscopia de Absorção no Ultravioleta-Visível e Infravermelho Proximal (UV-Vis-NIR)

A espectroscopia na região ultravioleta-visível e infravermelho proximal é uma das técnicas mais eficazes da identificação das causas de cor em minerais, além de ser utilizada para a identificação e caracterização de minerais e de outros compostos químicos orgânicos/inorgânicos.

As esmeraldas *schist-hosted*/correlatas ao magmatismo, geralmente apresentam um conteúdo de Fe muito mais alto do que as esmeraldas hidrotermais/metamórficas. Esta distinção química é facilmente observada usando a espectroscopia UV-Vis-NIR.

Para os ensaios de espectroscopia na região da luz visível foram utilizados pequenos blocos serrados e com uma de suas faces polidas. Algumas amostras são desbastadas até que atinjam uma espessura fina o suficiente que permita que a luz as atravesse.

O equipamento utilizado para essas análises é o espectrômetro *UV-Vis UV-2600 Shimadzu Corporation* do Laboratório de Espectroscopia Óptica do Instituto de Física-IF da UnB, e tem como fonte de radiação eletromagnética uma lâmpada de tungstênio que cobre a região espectral do visível e uma de deutério que cobre a região do ultravioleta.

Os espectros foram gerados no *software OriginPro 9.0*. A região do espectro selecionada para estudo dos berilos é de 300 – 850 nm. Essa região cobre toda a faixa da luz visível (Vis, 370 – 750 nm), parte da região do ultravioleta (UV, 300 – 370 nm) e parte da região do infravermelho proximal (NIR, 750 – 850 nm). Os dados foram adquiridos no intervalo entre 200 e 1.400 nm.

2.2.5 - Estudo das Inclusões Fluidas

A esmeralda é um dos melhores minerais hospedeiros para estudos de inclusões fluidas. Nos últimos 50 anos, a observação de inclusões em gemas, particularmente em esmeraldas, foi uma base essencial para identificação, análise de qualidade e determinação de proveniência. Com a descoberta de novas ocorrências, muitas sobreposições entre exemplares de diferentes depósitos vêm sendo registradas, fazendo-se necessária a aplicação de técnicas analíticas complementares.

Em muitos casos, uma separação pode ser feita com base na análise de inclusões fluidas. As esmeraldas hidrotermais/metamórficas (tipo II) freqüentemente apresentam inclusões multifásicas do tipo *jagged*, enquanto as esmeraldas *schist-hosted*/magmáticas geralmente revelam inclusões multifásicas do tipo *blocky* ou irregulares. Essa diferença está provavelmente relacionada a variações na maneira como os fluidos foram originalmente aprisionados, bem como sua evolução após o aprisionamento, enquanto as esmeraldas foram mantidas a alta temperatura e pressão antes de serem exumadas à superfície (Giuliani *et al.*, 2019).

2.2.5.1 - Microscopias

A microscopia ou petrografia convencional tem por finalidade realizar uma análise e classificação das inclusões fluidas (IF), com base nas propostas de Shepherd *et al.* (1981) e Van Den Kerkhof & Hein (2001). Os grupos de IF foram divididos e descritos com base em modo de ocorrência, relação espacial e temporal, morfologia, número de fases, proporção de fases e natureza dos fluidos.

O estudo de inclusões foi realizado em 6 lâminas bipolidas com 1 mm de espessura, confeccionadas no Laboratório de Laminação do Instituto de Geociências-IG da UnB. Destas lâminas, 3 possuem orientação paralela e as demais são perpendiculares em relação ao eixo cristalográfico c. A petrografia de inclusões minerais foi realizada à temperatura ambiente ($\pm 25^\circ\text{C}$), com auxílio de microscópio Olympus com luz polarizada, modelo BX-51, contendo objetivas de 20x, 40x, 80x e 100x, acoplado com sistema de obtenção de imagens em software específico.

2.2.5.2 - Microtermometria

Na microtermometria, notam-se as mudanças nas fases fluidas decorrentes das variações na temperatura, podendo caracterizar composição química, densidade, salinidade, pressão e temperatura dos fluidos mineralizantes, que predominavam durante o aprisionamento da inclusão, a cristalização ou recristalização do mineral hospedeiro (Fuzikawa, 1985).

Os dados microtermométricos foram adquiridos utilizando uma platina de resfriamento e aquecimento LTS420 da *LINKAM*, com intervalo de temperatura entre -200 e 420°C , acoplada a um microscópio petrográfico com objetivas de longa distância com aumento de 10 a 50x. A calibração da platina foi realizada com inclusões fluidas sintéticas de $\text{H}_2\text{O}-\text{NaCl}$, aplicando taxas de velocidade de 5 a $15^\circ\text{C}/\text{min}$, com uma precisão estimada de $\pm 0,2^\circ\text{C}$ para o congelamento ($+25^\circ$ a -100°C) e $\pm 2^\circ\text{C}$ para o aquecimento (até 420°C).

Para as fases fluidas presentes nas inclusões que não podem ser determinados pela microtermometria, é de grande utilidade a aplicação de outros métodos analíticos, como a espectroscopia *Raman*.

2.2.6 - Microsonda Eletrônica (EMPA)

A Microsonda Eletrônica é um equipamento de análise com alta resolução espacial, permitindo a determinação da composição química de partículas com diâmetro mínimo analisável inferior a 1 micrômetro por meio de um conjunto de detectores de dispersão de comprimento de onda acoplados (WDS). É expressa, geralmente, em porcentagem de óxidos.

A análise via microsonda eletrônica foi utilizada para medir a concentração de elementos maiores, menores e traços da esmeralda Monte Santo. Estas análises ajudam a estabelecer as assinaturas geoquímicas para discriminação da origem geográfica mineral. A relativa diversidade química das esmeraldas de depósitos mundiais permite a confiança na determinação da origem em a maioria dos casos. Essas análises foram realizadas utilizando-se uma microsonda eletrônica JEOL JXA-8230, com cinco detectores WDS com os cristais LDE1, LDE2, TAP, PET/L-H e LIF-L/H. Um espectrômetro de dispersão de energia JEOL (EDS) acoplado ao microscópio também foi usado para controle. As análises foram realizadas sob tensão de aceleração de 15 kV, 20 nA de corrente e abertura de feixe de 5 µm. O tempo de análise variou de 20 a 80 s por elemento, de acordo com a abundância esperada no mineral.

Para a análise, as amostras foram revestidas com material condutor (carbono) em um evaporador a vácuo JEOL-JEE-420.

A preparação das amostras foi realizada no Laboratório de Microscopia do IG-UnB, Brasil. A análise de Microsonda Eletrônica (EMPA) foi realizada no Centro Regional para o Desenvolvimento Tecnológico e Inovação-CRTI da Universidade Federal de Goiás-UFG, Brasil.

3 – RESULTADOS

3.1 – Artigos Científicos

Com os resultados das análises obtidas até o presente momento e suas interpretações, foram elaborados os seguintes artigos científicos:

- ✓ *Emerald Fingerprinting by Spectroscopic Analysis: Monte Santo Emeralds from Tocantins State, Brazil.* (Submitted to date). *Mineralogical Magazine*, 2022;
- ✓ *Raman Spectroscopy of Emeralds: Challenging Analytical Problems with Cr-Fluorescence* (Submitted to date). *Vibrational Spectroscopy*, 2022;
- ✓ *Crystallochemical Characterization of Brazilian Emeralds.* (Submitted to date). *Journal of Applied Crystallography*, 2023.

O trabalho "*Raman Spectroscopy of Emeralds: Challenging Analytical Problems with Cr-Fluorescence*" merece destaque, por ser inédito em apresentar uma metodologia que visa resolver as limitações da técnica de espectroscopia Raman em esmeraldas e outros minerais que apresentam Cr-fluorescência.

Os artigos listados a seguir encontram-se em elaboração ou sob revisão por parte dos co-autores:

- ✓ *Geographic Origin Determination of Emeralds: a contribution to the separability of the Monte Santo Emerald and its Counterparts.* (em elaboração).
- ✓ *The Monte Santo Emeralds, Central Brazil: Mineral Chemistry and Fluid Inclusions Data* (sob revisão). Revista pretendida: *Mineralium Deposita*;
- ✓ *Forensic Gemmological Investigation on a Green Colored Crystal of Unknown Provenance: a Natural Emerald?* (sob revisão).

3.2 - Trabalhos Publicados e/ou Apresentados

Os seguintes trabalhos foram publicados e/ou apresentados durante o doutorado:

- ✓ Estudo espectroscópico preliminar em turmalinas bicolores, azuis e verdes oriundas da Província Borborema, Estado do Ceará, Brasil. Resumo expandido In: XII Congresso Ibérico de Geoquímica - CIG / XX Semana da Geoquímica, 2019, Évora, Portugal;

- ✓ Spectroscopic characterization of Brazilian emeralds from Tocantins State: Preliminary results (Aceito). In: Goldschmidt 2020, Hawaii;
- ✓ Origin Determination of Brazilian Emeralds: A Preliminary Study of Samples from Tocantins State, Brazil (Aceito). In: 36th International Geological Congress - 36 IGC - Delhi - Índia, 2020;

Mineralogical Magazine

Emerald fingerprinting by spectroscopic analysis: Monte Santo emeralds from Tocantins state, Brazil. --Manuscript Draft--

Manuscript Number:	
Full Title:	Emerald fingerprinting by spectroscopic analysis: Monte Santo emeralds from Tocantins state, Brazil.
Short Title:	
Article Type:	Article
Section/Category:	General submission
Keywords:	Spectroscopic Fingerprint, Brazilian Emerald, Spectroscopies, Mineralogy, Gem Provenance, Monte Santo Emerald.
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Order of Authors Secondary Information:	
Manuscript Region of Origin:	BRAZIL
Abstract:	Monte Santo emeralds occur in the Araguaia Belt, Tocantins, central Brazil. The deposit was discovered in 1996 and is becoming an important source of emeralds, since they are typically of excellent quality and compare with some of the finest emeralds worldwide. Provenance is an important economic and societal issue inherent to the gems industry. Consumers increasingly aim to know the origin of their gems to ensure that their purchase does not support inhumane working conditions, cause legal problems, and to distinguish between natural, treated, and synthesized stones. In general, every emerald has a specific spectroscopic, geochemical, isotopic and microscopic signature, which are important diagnoses as to the origin of the gemstone. Spectroscopic analyses provide a non-destructive to minimally-destructive tool to record emerald fingerprints through spectra. This study presents, for the very first time, detailed spectral data for the Monte Santo emerald, in order to establish its fingerprints, making it possible to compare and distinguish it from other important emerald deposits worldwide. About sixty emerald samples from the Monte Santo emerald deposit were

	analyzed by spectroscopic methods, such as Raman spectroscopy, ultraviolet-visible-near-infrared spectroscopy (UV-Vis-NIR) and Fourier transform infrared spectroscopy (FTIR). Fluid H ₂ O types I, II and CO ₂ components were detected, as well as data to determine the chromophore elements, their ionic charge and probable position in the crystalline structure. The presence of all three elements (vanadium, chromium and iron), as detected by the UV-Vis-NIR spectra, appears to be a suitable diagnosis for these emeralds. The results also allowed us to classify the Monte Santo samples as alkali-rich emeralds.
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Emerald fingerprinting by spectroscopic analysis: Monte Santo emeralds from Tocantins state, Brazil.

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ABSTRACT

Monte Santo emeralds occur in the Araguaia Belt, Tocantins, central Brazil. The deposit was discovered in 1996 and is becoming an important source of emeralds, since they are typically of excellent quality and compare with some of the finest emeralds worldwide. Provenance is an important economic and societal issue inherent to the gems industry. Consumers increasingly aim to know the origin of their gems to ensure that their purchase does not support inhumane working conditions, cause legal problems, and to distinguish between natural, treated, and synthesized stones. In general, every emerald has a specific spectroscopic, geochemical, isotopic and microscopic signature, which are important diagnoses as to the origin of the gemstone. Spectroscopic analyses provide a non-destructive to minimally-destructive tool to record emerald fingerprints through spectra. This study presents, for the very first time, detailed spectral data for the Monte Santo emerald, in order to establish its fingerprints, making it possible to compare and distinguish it from other important emerald deposits worldwide. About sixty emerald samples from the Monte Santo emerald deposit were analyzed by spectroscopic methods, such as Raman spectroscopy, ultraviolet-visible-near-infrared spectroscopy (UV-Vis-NIR) and Fourier transform infrared spectroscopy (FTIR). Fluid H₂O types I, II and CO₂ components were detected, as well as data to determine the chromophore elements, their ionic charge and probable position in the crystalline structure. The presence of all three elements (vanadium, chromium and iron), as detected by the UV-Vis-NIR spectra, appears to be a suitable diagnosis for these emeralds. The results also allowed us to classify the Monte Santo samples as alkali-rich emeralds.

Keywords: Spectroscopic Fingerprint, Brazilian Emerald, Spectroscopies, Mineralogy, Gem Provenance, Monte Santo Emerald.

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Introduction

Beryl ($\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$) is chemically complex and a highly compositionally variable gem-forming mineral, found in a variety of geologic settings worldwide. Emerald is the green gemological variety of beryl, which is considered one of the "four precious gems" and generally the most valuable after diamond and ruby (Giuliani, et al., 2019). Although considered rare, emerald is found on all five continents. Brazil is an important emerald producer, with many occurrences in the southeast and northeast of the country.

The emerald occurrences studied here are located in the central portion of Tocantins, central Brazil, in the geological context of the Brasiliano Araguaia Belt. Emeralds were discovered in Tocantins in 1996. Their dissemination resulted in a large flow of prospectors ("garimpeiros" in Portuguese) to the area, leading to the creation of the "Cooperativa de Garimpeiros de Monte Santo - COOPERGEMAS" (CPRM, 1997). The mining area is located in the southern part of Monte Santo city, and Paraíso do Tocantins is the closest municipality. Emeralds occur in pockets, as scattered crystals in biotite, and are associated with aggregates of quartz, tremolite, flogopite and biotite (Figure 1). According to Schwarz's classification (Schwarz, 1987), CPRM (1997) suggested that these are type I occurrences, characterized by the association of mafic-ultramafic rocks or their metamorphic derivatives (amphibolites and shales), supplying Cr, V, Fe, and pegmatites supplying Be, via the interaction of their fluids.



Fig. 1. (A) Prospect G5 gallery, highlighting the "frizo" (Brazilian term prospectors use for the portion of rock where mineralization occurs); (B) Emerald crystals contained in the schist; (C) Emerald crystals embedded in the contact between albitized granite and schist.

The Araguaia Belt (CA) is a Neoproterozoic to Cambrian orogenic belt, located in the northern portion of the Tocantins Province (Figure 2), formed during the Brasiliano/Pan-African Orogeny (Almeida, et al., 1976) (Hasui, et al., 1977) (Alvarenga, et al., 2000). It is about 1200 km long in the N-S direction and 110 km wide in the E-W direction, bordered to the north and east by the Parnaíba Basin, to the west by the Amazonian Craton, to the southwest by the Bananal Basin and limited to the south and southeast by the Transbrasiliano Lineament. It is composed of Archean and Paleoproterozoic basement rocks, Neoproterozoic supracrustal rocks and syn- to post-collisional granitic rocks of the Ediacaran/Cambrian interface. In this geological context, emerald occurs near or inside the contact zone between small bodies of albite granite and amphibolites/shales (Figure 1).

The wide variety of colors in beryl is related mainly to the presence of impurities in the form of transition metal ions (e.g. Fe, Mn, Cr, V chromophore elements) in the interstices of the crystalline structure of the mineral, allied to its positioning in the crystalline reticulum, its oxidation state and charge transfers. The variations in the chemical composition of beryl, particularly in terms of its alkali and H_2O content, are closely correlated with the geochemical and paragenetic characteristics of the geological systems where beryl varieties are generated (Beus, 1966).

The aim of this research is to define the position of certain bands and features in the spectra obtained, in order to establish a fingerprint of the Monte Santo emeralds, by means of spectroscopic analysis. The combination of the three spectroscopic methods can provide accurate results, allowing to distinguish the Monte Santo emeralds from their counterparts, contributing to establishing their origin.

Emerald's geographic origin determination starts with a coarse separation into one of two groups based on their geological conditions of formation: Type I - tectonic magmatic-related and type II - tectonic metamorphic-related groups from Giuliani et al. (2019) and Giuliani & Groat (2019).

The type I - tectonic magmatic-related, also known as schist-hosted emerald, presents higher alkali and Fe contents. This group is represented by emeralds from Zambia (Kafubu), Russia (Urals), Ethiopia (Kenticha), Brazil (Carnaíba, Socotó, Itabira, Fazenda Bonfim, Pirenópolis), South Africa (Gravelotte), Madagascar (Ianapera, Mananjary), Zimbabwe (Sandawana), Norway (Eidsvoll), China (Dyakou), Canada (Lened), Australia (Emmavile, Torrington), Kazakstan (Delgebetey), Nigeria (Kaduna), among others.

The type II - tectonic metamorphic-related or hydrothermal/metamorphic, known as non-schist type emerald, displays lower alkali and Fe contents. This group contains emeralds from Colombia, Afghanistan (Panjsher), China (Davdar), Brazil (Itaberaí, Santa Terezinha de Goiás), Pakistan (Swat-Mingora), Australia (Poona), Zambia (Musakashi) and others.

In many cases, this separation can be made based on gemological properties, since magmatic related emeralds generally have much higher Fe and alkali contents than hydrothermal/metamorphic emeralds. This chemical distinction is easily seen by means of spectroscopic analyses.

Wood & Nassau (1967, 1968) and Aurisicchio et al. (1994) found that type I H₂O occurs as an isolated molecule and type II H₂O is associated with alkaline elements, indicating a high concentration of charge-compensating alkaline ions, such as Cs⁺, Na⁺, Li⁺, K⁺, Rb⁺, etc. The presence of alkalis as impurities in the channels produces an electrostatic attraction that causes water molecules to rotate in such a way that the O²⁻ ion remains next to the alkali. The alkali cations at the channel sites balance charge deficiencies that can occur as a result of heterovalent substitutions at octahedral and/or tetrahedral sites.

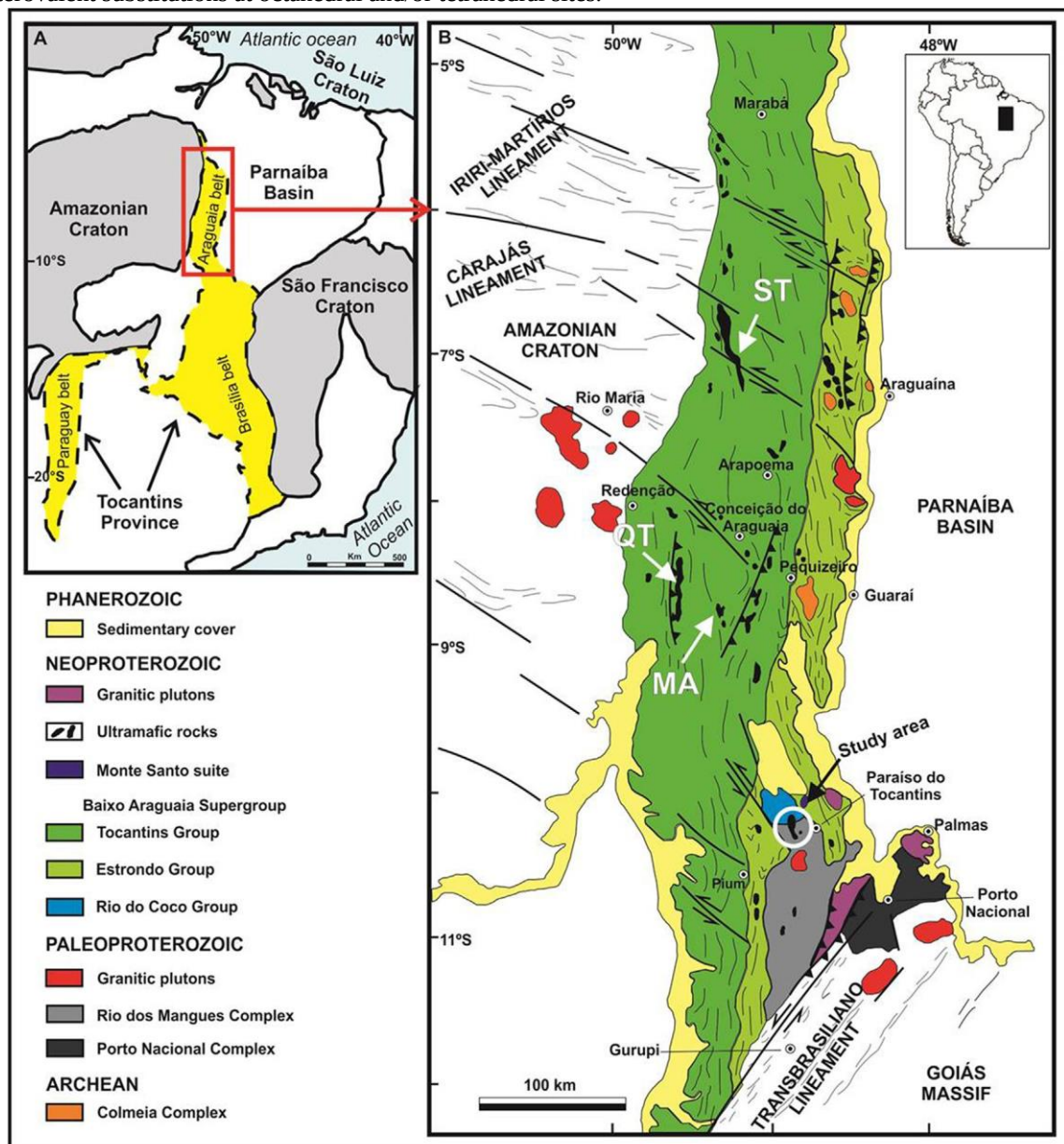


Fig. 2. (A) Schematic tectonic map of Central Brazil, with the Tocantins Structural Province and the Araguaia Belt highlighted. Adapted from Delgado & Pedreira (1995) (Bersani, et al., 2014). (B) Geological map of the Araguaia Belt highlighting the study area. adapted from Alvarenga et al. (2000) and Souza et al. (2019).

Materials and Methods

Samples and Preparation

A batch of emerald samples, mostly consisting of crystal fragments ranging from pale to intense green, was acquired during a field trip to the mine. Care was taken to use the samples where at least one face of the crystal could be identified, either subhedral or euhedral, in order to obtain a representative sample space. The samples were catalogued and separated according to a color scale (Figure 3B), showing the relationship between the color and the results of spectroscopic analysis. When possible, polarized spectra of oriented samples were collected to obtaining ordinary ray (o-ray) and extraordinary ray (e-ray) spectra. In addition to the batch, two euhedral samples presenting a light green-bluish color were also analyzed (Figure 3C).

About 60 emerald samples were selected, prepared and analyzed. The samples were georeferenced with the point of the extraction in situ at the "garimpo (G4)" (mining site), followed by the numbering used for sample cataloguing.

All the sample preparations and spectroscopy analyses were performed at Universidade de Brasília (UnB) Laboratory of Optical Spectroscopy of the Institute of Physics.



Fig. 3. (A) Samples from "garimpo G4"; (B) Batch of samples catalogued and separated according to a color scale, in order to obtain the relationship between color and spectroscopic results; (C) Euhedral samples analyzed, exhibiting a light green-bluish color.

Raman spectroscopy

In recent years, the use of Raman spectroscopy as a gemological tool has largely increased, in particular in the conservation science field where a non-destructive and contactless identification is required (Bersani et al. 2014).

In many experimental techniques, such as the electronic microprobe, OH^- and H_2O molecules can be difficult to detect. Thus, their content in a mineral is often calculated, not measured. OH^- and H_2O can be detected by X-ray diffraction or neutrons. However, simpler, faster and non-destructive methods to detect OH^- and H_2O in a sample are Raman and infrared spectroscopies.

The Raman signatures of the samples were collected at room temperature with the Raman LabRAM HR Evolution spectrometer (HORIBA, Scientific, Palaiseau, France), which performs measurements using a semiconductor diode laser with 1800 lines/mm grid and a confocal Raman microscope coupled to a CCD (Charge Coupled Device). The measurements were collected using a green laser (532 nm) as excitation source and an output power of 10 mW, focused on the samples by an OLYMPUS 50x objective microscope. The spectral range between 150 and 5500 cm^{-1} was analyzed, to study the photoluminescence effects and obtain Raman spectra.

The data obtained were saved in X and Y files and the Raman spectra produced in OriginPro 9.0® software. The spectrum baseline was determined using LabSpec® software. For some samples, two distinct Raman spectra

were collected, according to the orientation of the crystallographic axes of the analyzed crystals in relation to the Raman laser beam.

Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectroscopy can help distinguishing between natural and synthetic emeralds, as well as assisting in the separation of specimens from different localities.

The samples were prepared as KBr pellets, by compressing 0.006 g of powdered emerald on the 200-mesh fraction mixed with 0.3 g of KBr powder, under 10 tons of hydraulic pump pressure for 2 minutes. The KBr pellets were used to minimize the polarization effects.

Infrared spectroscopy analyses were carried out using a Bruker Spectrometer (Vertex 70), in the spectral range between 400 and 6000 cm^{-1} , with an average of 72 scans per sample, and 4 cm^{-1} resolution. The data obtained were produced using OriginPro 9.0[®] software.

Ultraviolet-visible-near infrared Absorption Spectroscopy (UV-Vis-NIR)

Spectroscopy in the ultraviolet to near infrared range is one of the most effective techniques to identifying the causes of color in minerals. Schist-hosted emeralds generally have much higher Fe content than hydrothermal/metamorphic emeralds and this chemical distinction is most easily seen using UV-Vis-NIR spectroscopy (Saeseaw, et al., 2019).

Spectroscopy analysis in the ultraviolet-visible light region did not require prior sample preparation, since samples with at least one well-defined face were used, and no polishing was necessary.

The Shimadzu UV-Vis UV-2600 spectrometer was used for analyses since its source of electromagnetic radiation is a tungsten lamp that covers the visible spectral range and a deuterium lamp the ultraviolet range. The spectral range selected for the study of beryl is 300-850 nm. This region covers all the visible light (Vis 370-750 nm), part of the ultraviolet region (UV 300-370 nm) and part of the near infrared region (NIR 750-850 nm). The data were acquired between 200 and 1400 nm. The spectra were produced using OriginPro 9.0[®] software. The spectrum baseline was determined using LabSpec[®] software.

Results and Discussions

Raman Spectroscopy

When possible, Raman spectra from the Monte Santo emerald were acquired on different directions, with the laser beam perpendicular to the **c**-axis (dashed spectra) and parallel to the **a**-axis. The results are shown in Figure 1, ranging from 150 to 1700 cm^{-1} (left-side graphs) and from 3900 to 4400 cm^{-1} (right-side graphs).

Despite the orientation dependence of its Raman peaks, beryl can be accurately identified by the spectrum of a randomly oriented sample, because some Raman bands are always seen, although their relative intensity can vary. These bands are the so-called main emerald Raman bands (Jasinevicius, 2009).

In all the emerald samples analyzed, strong luminescence effects caused by the presence of Cr^{3+} were observed at 4095 cm^{-1} (680 nm) and 4170 cm^{-1} (685 nm), where the luminescence peaks exceeded the Raman peaks and the limit of the equipment signal. In order to minimize this effect and to prevent saturation, the laser intensity had to be reduced. The luminescence features are very useful in emerald identification when chemical analyses are not available.

The 1200 cm^{-1} peaks correspond to the main Raman vibrations of the beryls, where those between 321 to 325 cm^{-1} represent the ring vibrations; 325 to 395 cm^{-1} to the deformation mode of the tetrahedral ring; the peak at 686 cm^{-1} to the signatures of the Be-O stretching bond ring; 1002 to 1010 cm^{-1} to the Si-O bond stretching; as for 1070 cm^{-1} there are controversies about whether the peaks are attributed to Be-O or Si-O stretching of beryl vibration. Previous studies attributed the Raman peak at 1070 cm^{-1} to either Si-O (Adams & Gardner, 1974); (Charoy, et al., 1996) or Be-O stretching in the beryl structure (Kim, et al., 1995); (Moroz, et al., 2000). However, correlation diagrams of chemical data in recent investigations have shown Raman band positions and Raman band width-FWHM (full width at half maximum) where the band broadened and shifted to a higher wavenumber when the silicon content decreased. The same relationships were not found between these bands and Be concentration (Houng 2010; 2013).

According to Houng et al. (2010), the position of these bands in synthetic emeralds (high silicon and low alkali contents) was around 1067-1068 cm^{-1} and the FWHM varied from 11 to 14 cm^{-1} . In natural low-alkali content emeralds, the Raman shift was around 1068-1070 cm^{-1} and the FWHM varied from 12 to 15 cm^{-1} , while in natural high-alkali content emeralds the Raman shift was about 1069-1072 cm^{-1} and the FWHM from 17 to 26 cm^{-1} .

In our investigation, the maximum position of this Raman band varied from 1069 to 1072 cm^{-1} . This is probably a result of chemical substitution, where ions such as Al^{3+} , Be^{2+} and Li^{+} replace silicon in the beryl crystal structure with charge-compensating alkali ions such as Na^{+} , K^{+} , Cs^{+} in the structural channels.

Control over the dominant presence of the type of H_2O molecules in the channels along the **c**-axis into the beryl structure is a strong indicator of the presence of alkaline elements in the system where they were generated. The well-defined peaks centered at 1630 cm^{-1} and 3595 cm^{-1} represent the vibration of type II molecular water

(water molecules bound to alkaline ions), while those at 1598 cm^{-1} and 3605 cm^{-1} represent vibrations of type I molecular water (water molecules without the presence of alkaline ions). In our investigation, both molecular types of water were detected in the analyzed samples, but the type II water is dominant over type I. The H_2O deformation band, which appears around 610 cm^{-1} , was also detected.

The elevations near $1230\text{--}1240\text{ cm}^{-1}$, at 1284 cm^{-1} and at $1385\text{--}1387\text{ cm}^{-1}$ indicate CO_2 vibrations (Charoy, et al., 1996). These elevations are very slight in some samples and more pronounced in others. These peaks are seen for both crystallographic orientations, when E is normal to the *c*-axis and parallel to the *c*-axis.

An additional small peak at 2328 cm^{-1} was observed in some of our samples, assigned to N_2 , probably due to fluid inclusions in the emerald samples. This peak is also found in Colombian emeralds (Giuliani, et al., 1993) and it was earlier documented in gems by (Dele-Dubois, et al., 1980).

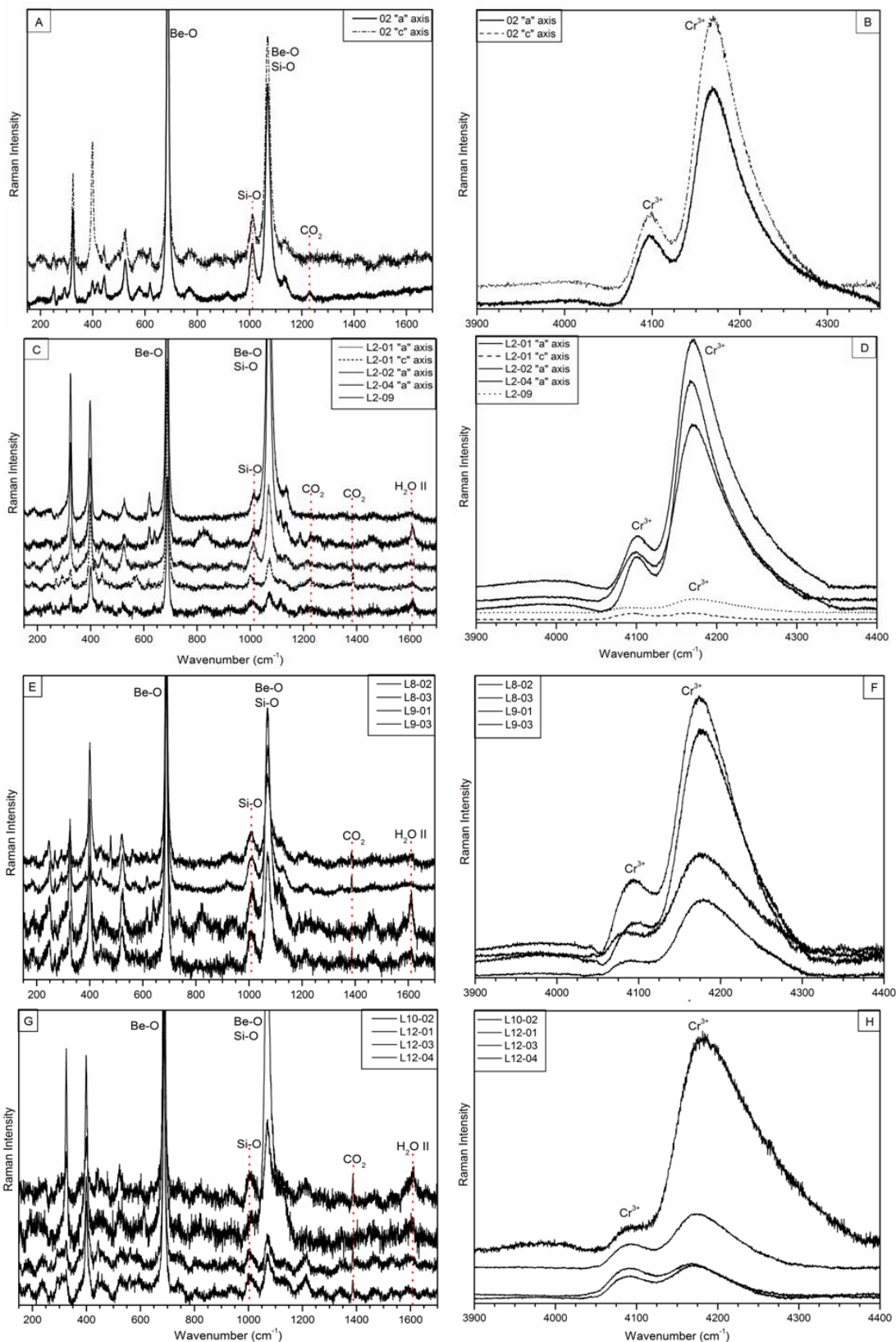


Fig. 4. Raman spectra of emerald samples from the Monte Santo deposit, from 150 to 1700 cm^{-1} (left-side graphs) and 3900 to 4400 cm^{-1} (right-side graphs).

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR absorption bands between 400 and 1500 cm^{-1}

For beryls, several bands are observed between 400 and 1500 cm^{-1} . Despite the fact that the bands in this range have been investigated in several studies, the origin of some of these vibration modes remains controversial. Monte Santo emerald FTIR spectra ranging between 400 to 1400 cm^{-1} are displayed in the Figure 5A.

According to Tarte (1965), the bands between 400 and 600 cm^{-1} correspond to LiO_4 vibrations. However, according to Gervais & Piriou (1972), two bands at 500 cm^{-1} and 525 cm^{-1} belong to SiO_4 tetrahedrons vibrations, and according to Plyusina & Surzhanskaya (1967), these bands are correlated with Si-O-Al stretching.

The weak shoulder at 560 cm^{-1} is due to the substitution of Li in Be tetrahedra (Auricchio, et al., 1994). It appears initially as a shoulder and absorbance increases progressively with the entry of $^{\text{IV}}\text{Li}$ into the $^{\text{IV}}\text{Be}$ site. This weak shoulder is also visible in alkali-rich beryl, which has another weak shoulder at 450 cm^{-1} and 413 cm^{-1} , unreported to date, and possibly due to the M-O vibration, where M is the cation substituted in the Si tetrahedron (Parameshwaran, 2016).

The bands appearing at 680, 750 and 810 cm^{-1} were ascribed to the Be-O cluster by Hofmeister et al. (1987) and to Al-O coordination by Plyusina & Surzhanskaya (1967). According to Auricchio et al. (1994), the band at 808 cm^{-1} is assigned to the Be-O bond.

FTIR Absorption Band around 1200 cm^{-1}

Many authors have assigned the bands in the 800-1300 cm^{-1} range either to the internal Si-O vibrations (Adams & Gardner, 1974); (Hofmeister, et al., 1987); (Auricchio, et al., 1994), or the vibrations of the BeO_4 tetrahedral coordination (Plyusina, 1964); (Plyusina & Surzhanskaya, 1967). According to Houn, et al. (2010, 2014), by correlating diagrams of chemical data and these infrared band positions, the 1200 cm^{-1} IR band is clearly related to the Si concentrations in the emerald crystal structure.

Some investigations of infrared spectra of beryls demonstrate that the band around 1200 cm^{-1} varies between 1171-1207 cm^{-1} . Low-alkali natural and synthetic emeralds show this band with an apparent maximum between 1200 and 1207 cm^{-1} , while high-alkali natural emeralds show it between 1171 and 1203 cm^{-1} . In addition, all high-alkali and low-silicon content emeralds ("schist type") exhibit a shoulder at around 1140 cm^{-1} . In low-alkali and high-silicon content ("non-schist type") samples, this shoulder was observed in Colombian (Chivor) and Chinese but not Nigerian emeralds or in synthetic samples (Huong, et al., 2014).

All the Monte Santo emerald IR spectra displayed the 1200 cm^{-1} band with an apparent maximum varying between 1170 and 1186 cm^{-1} , indicating that they are high-alkali emeralds. Furthermore, all the samples showed an additional shoulder at 1140 cm^{-1} , confirming their high-alkali content and suggesting a magmatic-related "schist type" nature (Fig. 5A).

Water Molecules

Two types of water molecule arrangements in the structural channels of beryl are widely accepted and can be identified by infrared absorption spectroscopy: type I, which represents the vibrations of the H-H vector parallel to the *c*-axis of the crystal; and type II with the H-H vector perpendicular to the *c*-axis and bonded to alkali elements. Water molecule vibrations are investigated in the ranges from 1500 to 1700 cm^{-1} (Fig. 5B) and from 3500 to 3800 cm^{-1} (Fig. 5C, D).

Type-I water is represented by the centered peaks near 1598, 3606 and 3696 cm^{-1} , while type-II water is attributed to centered peaks near 1636 and 3592 cm^{-1} and a less expressive centered peak at 3661 cm^{-1} present in some samples, as suggested by Wood & Nassau (1967, 1968) and several other authors.

Flux synthetic "emeralds" show no water absorption bands. This occurs because of the lack of water in the crystal growth process itself. In hydrothermal synthetic "emeralds", only type-I water bands are observed, because the growing process is free of alkali ions, while in natural emeralds, both type-I and type-II water bands are found.

All the samples exhibit the presence of both water types I and II, with type I represented by the peaks at 1600-1607 cm^{-1} and at 3694-3698 cm^{-1} and type II assigned by the peaks at 1617-1625 cm^{-1} ; 1637 cm^{-1} ; 3591-3593 cm^{-1} and 3654-3658 cm^{-1} .

Although both types of water molecules (I and II) are present in the structural channels of the Monte Santo emerald, the type II water absorption band predominates over its type I counterpart in the spectrum of all the samples in our investigation, thus demonstrating a high concentration of charge compensating alkali ions, suggesting that these samples were formed in the presence of fluids with high alkali content.

Type II water molecules can be subdivided into type II_d, doubly bound to alkali ions ($\text{H}_2\text{O}-\text{Na}-\text{OH}_2$) and type II_s, singly bound ($\text{H}_2\text{O}-\text{Na}-\square$ vacancy) (Fukuda & Shinoda, 2008); (Fridrichová, et al., 2016). The band at 3694 cm^{-1} (referred to as A) is assigned to type-I water molecules not bound to alkali ions, at 3592 cm^{-1} (referred to as B) to type-II_d water molecules, and at 3655 cm^{-1} (referred to as C) to type-II_s water molecules.

According to the classification of natural and synthetic emeralds determined by the IR spectroscopic features in the 3500 to 3800 cm^{-1} range (Schmetzer & Kiefert, 1990), when B band intensities are greater than those of their C band counterparts, which are higher than those of A bands, it is believed that the alkali ion content

in these samples is about 1.6 to 1.8 wt%. According to Huong (2008), they are found in samples from many localities in Brazil (Santa Terezinha, Itabira, Socotó, Capoeirana, Carnaíba), Russia (the Urals) and South Africa (Transvaal).

The absorption band at about 3240 cm^{-1} is linked to the $[\text{Fe}_2(\text{OH})_4]^{2+}$ poly ion, occupying the 2a position, and polymerized by hydrolyzed Fe^{3+} , because Fe^{3+} in the channel has very high electronegativity and easily combines with the O–H of H_2O (Li, et al., 1998); (Qi, et al., 2001). This band has been related to H_2O II (Qiao, et al., 2019).

It is believed that the set of absorption bands almost overlapping in the range between 3200 and 3800 cm^{-1} , seen in this study, is due to the many ions and molecules in the channel that can easily bond with the O–H of H_2O . A similar set of overlapping bands in this region were also seen by Qiao et al. (2019). According to Houng (2008), the band between 3430 and 3470 cm^{-1} is a result of water absorbed in KBr powder, which is difficult to prevent.

CO_2

The band located at 2358 cm^{-1} is attributed to CO_2 molecules in the c channel, and vibrations linked to the presence of ^{13}C and ^{18}O isotopes (Fig. 5B) (Rondeau, et al., 2008); (Charoy, et al., 1996). According to (Wood & Nassau, 1967), CO_2 bands are more pronounced along the ordinary-ray.

The ν_2 and ν_1 vibrational overtones of CO_2 can interact to form two strong lines at 1388 and 1286 cm^{-1} (Nakamoto, 1963), (Parameshwaran, 2016).

A short and a sharp band at ~ 1384 and 2358 cm^{-1} , respectively, with weak shoulders at about 2290 , 2341 and 2377 cm^{-1} are linked to CO_2 molecules in the c channel and were detected in almost all emerald samples analyzed in this study, representing an important signature of the Monte Santo emeralds (Fig. 5B).

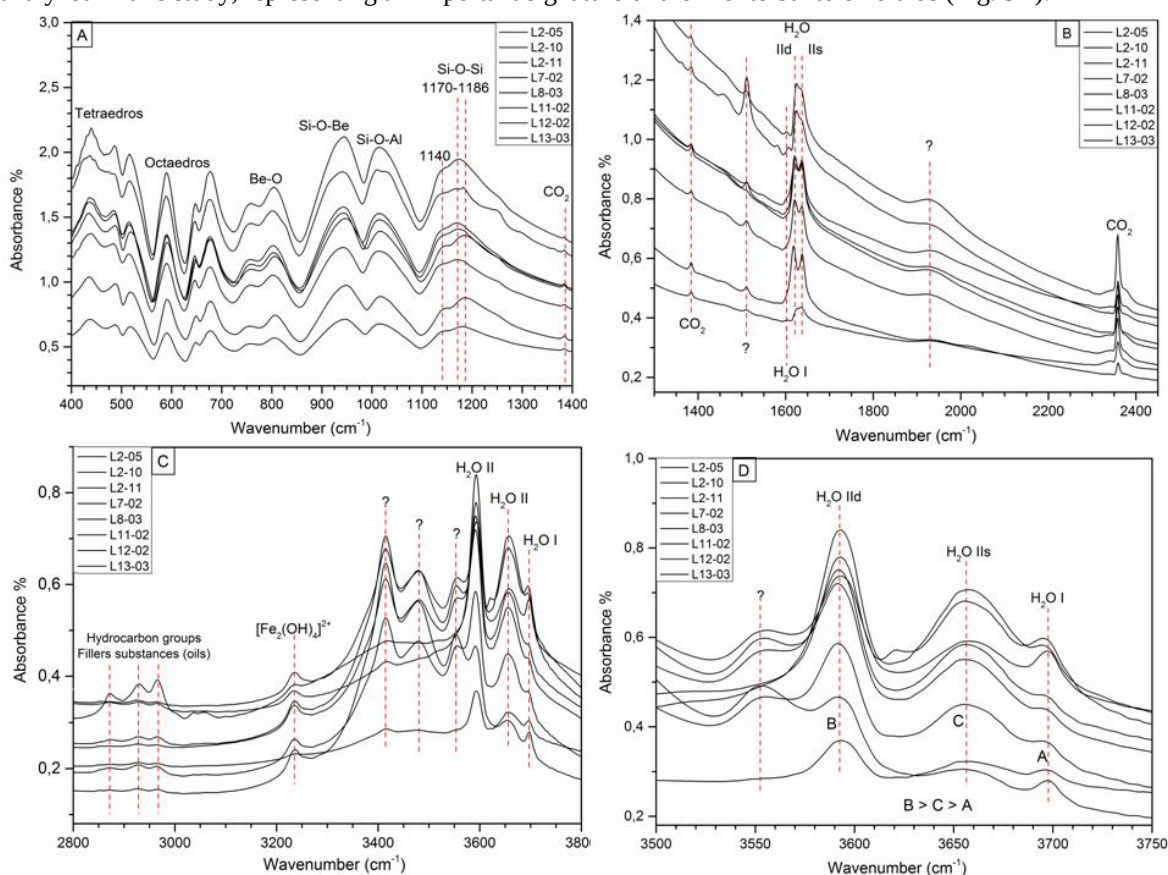


Fig. 5. Infrared spectra of emerald samples from the Monte Santo deposit, ranging from: (A) 400 to 1400 cm^{-1} ; (B) 1300 to 2500 cm^{-1} ; (C) 2800 to 3800 cm^{-1} ; and (D) 3500 to 3750 cm^{-1} .

Filler Substances

Emerald clarity is usually affected and reduced by the presence of inclusions, structural features, healing fissures, internal cavities and open fissures. In order to improve clarity, most emeralds are “filled” with a material that has a refractive index similar to that of emerald (oils, resins, waxes or others). The filler material reduces the visibility of the fissures and, sometimes, the cavities. FTIR spectroscopy is very helpful in identifying these fillers.

Disregarding any human impact, such as explosive use during mining, fissure formation in emerald is related to tectonic events affecting the mother rock. The developing emerald is subjected to significant mechanical

strain, resulting in fissures and fractures throughout the stone, even in high-end specimens. Thus, natural emeralds, regardless of their origins, always contain fissures that may affect the transparency, appearance and durability of the final polished stone. Fissure filling is standard practice, enhancing the visual appearance of emeralds, often dramatically, and it is now generally accepted as being necessary due to their nature (Kan-Nyunt & Kwok, 2019).

The most important spectral region for identifying treated stones is the 2800 to 3100 cm^{-1} range. Peaks in this region generally correspond to C-H bonds from organic compounds. The bands at 2870, 2928 and 2965 cm^{-1} observed in this investigation are attributed to the hydrocarbon groups $-\text{CH}_3$, $-\text{O}-\text{CH}_3$ and $-\text{CH}_3$, respectively (Kiefert, et al., 1999), from filler substances used to improve the clarity of the emerald crystals from the Monte Santo deposit, Brazil (Fig. 5C).

Unknown Peaks

Some peaks were seen in all samples, but they could not be correlated with their respective causes, such as those between 1507 and 1512 cm^{-1} and the centered band from 1922 to 1929 cm^{-1} .

Ultraviolet-visible-near infrared absorption spectroscopy (UV-Vis-NIR)

In order to observe the relationship between the color of emerald samples and UV-Vis spectroscopic analysis results, the sample batch was separated according to a color scale ranging from the lightest (L 1) to the darkest (L 13) green, as depicted in Figure 6A.

It should be noted that the intensity of certain bands is influenced by differences in the thickness of the samples. Except for the two euhedral samples (Figure 3C), all the analyzed samples from the batch have similar thicknesses.

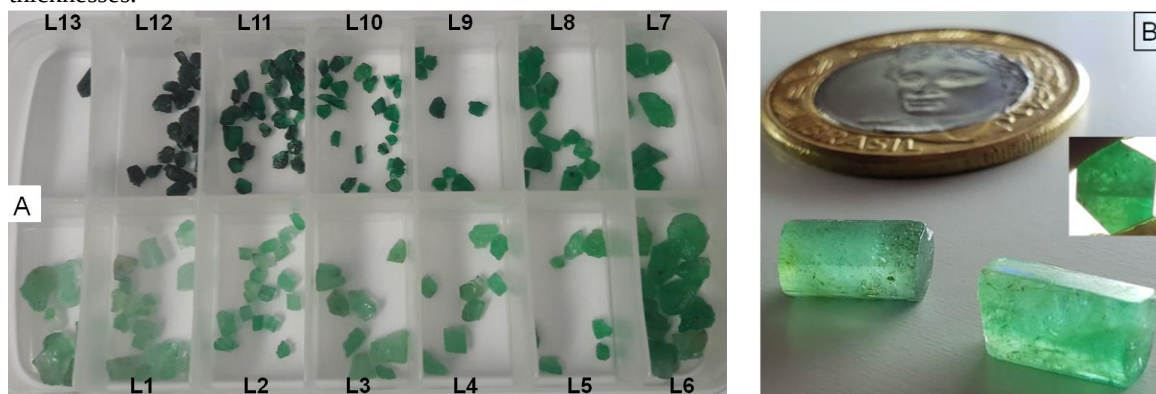


Fig. 6. (A) Emerald samples separated according to a color scale, showing the relationship between color and UV-Vis spectroscopic analysis result; (B) the two euhedral emerald crystals exhibiting a light green-bluish color.

Representative UV-Vis-NIR spectra of the Monte Santo emerald samples ranging from 350 to 1000 nm are shown in Figure 7. They are mostly dominated by broad absorption bands in the 400-500, 600-700 and 800-1000 nm ranges, with parts of these absorption bands splitting into different maxima, showing various shoulders.

The broad bands centered at approximately 420-430 nm and 600 nm correspond to spin-allowed electronic transitions d-d of Cr^{3+} at the Al position. Absorption peaks at ~ 630 , ~ 660 and ~ 680 nm are assigned to the spin-forbidden electronic transitions of Cr^{3+} . According to Wood & Nassau (1968), these three absorption peaks are absent in pure vanadium emerald spectra (chromium-free).

The spectrum of trivalent vanadium in beryl consists of strong absorption bands in the visible range at approximately 645, 605, 430 and 395 nm, assigned to V^{3+} in octahedral aluminium sites. The assignment of an additional shoulder at 680 nm, which is seen in the spectra of various natural and synthetic vanadium-bearing samples (Wood and Nassau, 1968; Schmetzer, 1978, 1982) is rather uncertain. This shoulder might be due to vanadium cations, which are not in the trivalent state (Schmetzer, et al., 2006).

Natural emerald from most sources reveals traces of both vanadium and chromium, with the ratio V/Cr varying considerably. Because the absorption bands of these two trace elements are found in the same spectral range, vanadium- and chromium-related absorptions are superimposed in the spectra of emeralds containing both trace elements. As a result, the different vanadium and chromium maxima are not shown individually (Schmetzer, 2014).

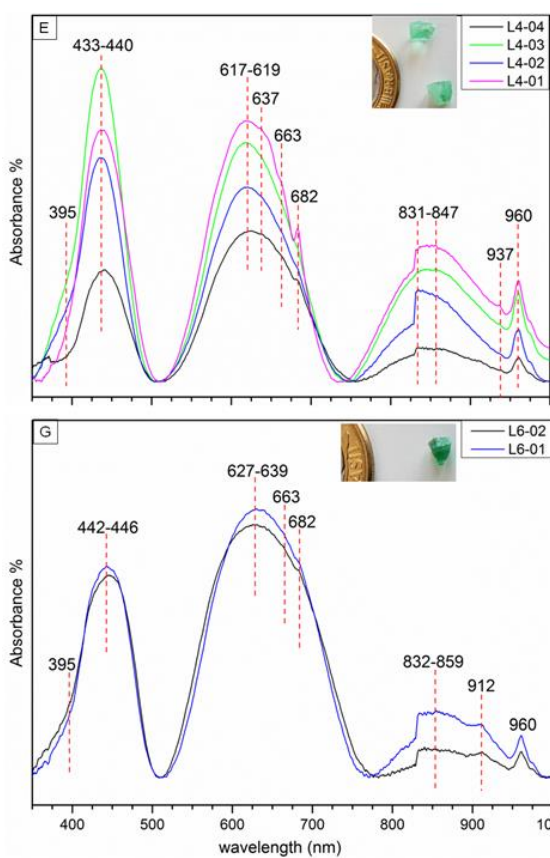
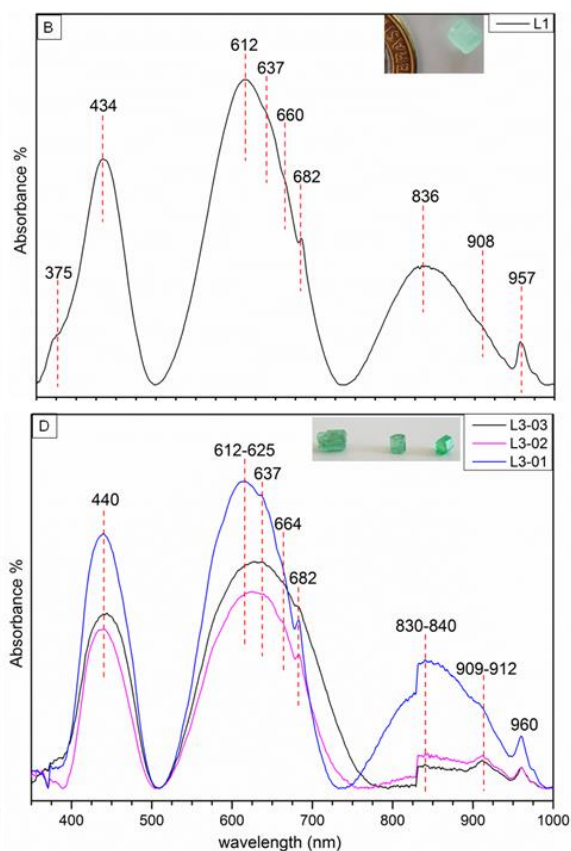
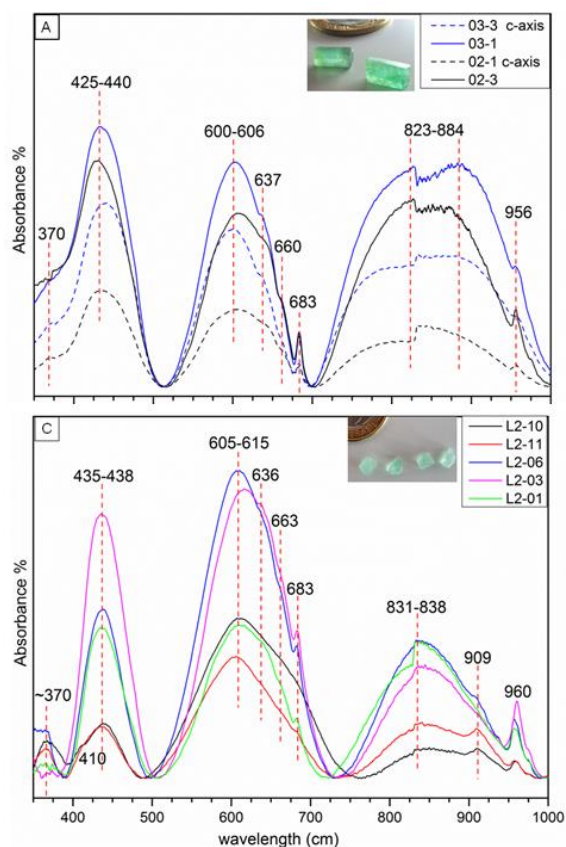
Tetrahedral Fe^{2+} causes a crystal field band in the optical absorption spectrum at 820 nm. The 820 nm absorptions are outside the visible region and contribute no color (Andersson, 2019). Although it does not contribute to the color, it is a key feature in separating emeralds from different localities.

343 A broad band related to tetrahedral Fe^{2+} absorption can be observed at about 830 nm in almost all samples.
344 However, the intensity of this broad band is variable, going from almost absent in the darkest samples (Fig. 7L-N)
345 to weak in most of the sample (graphs 3 F-K) and even moderate in some of the samples (Fig. 7A-E).

346 It is important to notice that for all analyzed samples ranging from L1 to L13 of the sample batch, the
347 relative intensity of the iron related band at ~830 nm is weaker than the chromium and vanadium related bands.
348 This feature ($\text{Fe} < \text{Cr}$ and/or V) is just seen in few emerald specimens, like those from Colombia, Afghanistan,
349 China (Saeseaw, et al., 2019); (Karampelas, et al., 2019); (Hu & Lu, 2019); (Krzemnicki, et al., 2021) and,
350 therefore, it is a very important feature for a primary separation or an "origin opinion".

351 For the two additional euhedral samples (n. 02 and 03), the intensity of the iron related band is clearly
352 stronger when compared to the other samples, but still weaker when compared to the chromium and vanadium
353 related bands. This phenomenon can be explained by the thickness of the mentioned samples combined with their
354 distinctly light green-bluish color (Figure 6B).

355 Additionally, some of the samples displayed a slight absorption band at ~370 nm. This weak absorption
356 band is caused by forbidden transitions of octahedral Fe^{3+} (Andersson, 2019), and tend to be more prominent in
357 higher-iron emeralds than in hydrothermal/metamorphic ones.



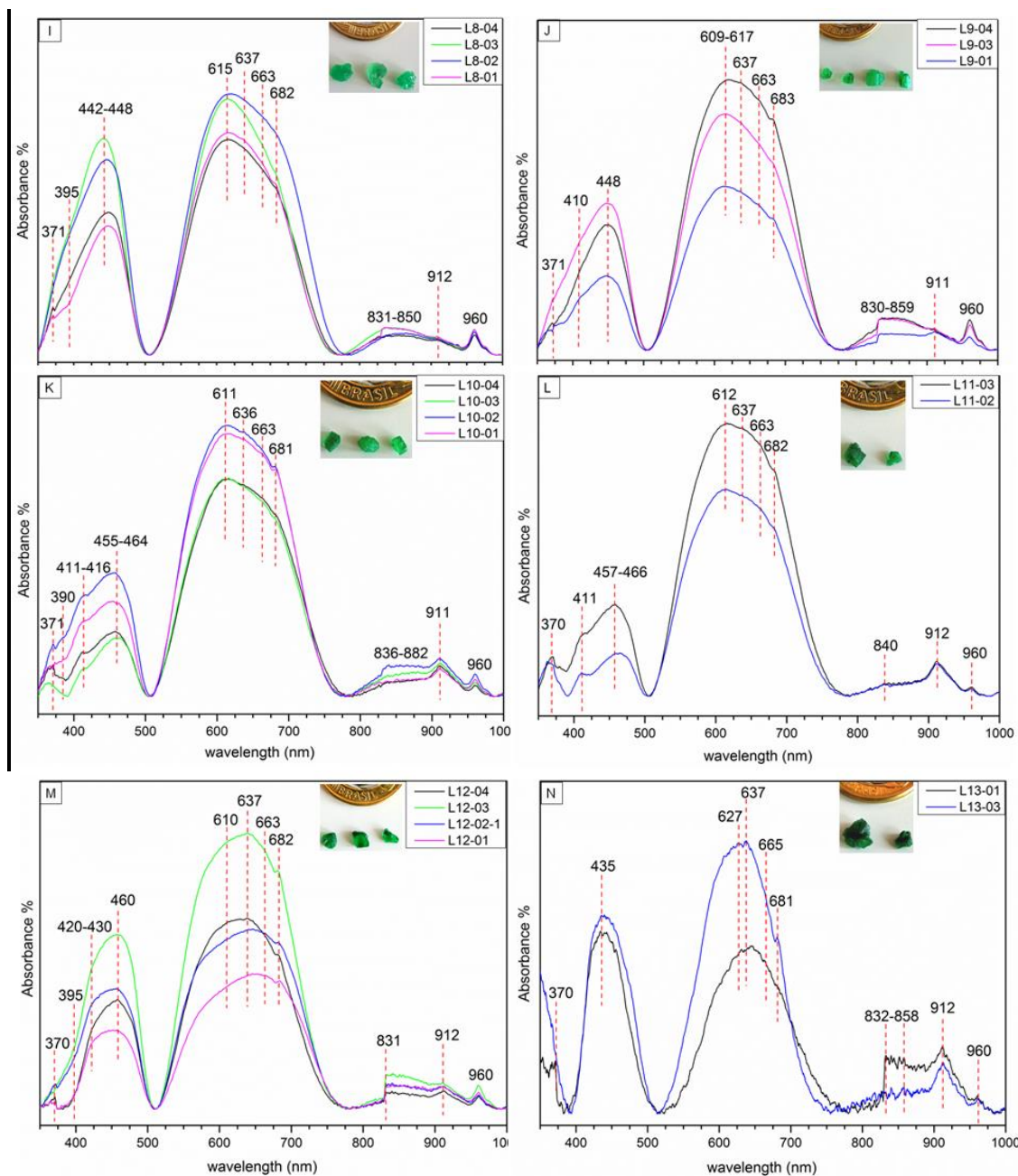


Fig. 7. Absorption spectra in the ultraviolet-visible-near-infrared range of emerald samples from the Monte Santo deposit, ranging from 350 to 1000 nm.

In the spectra obtained, there is a significant presence of V and Cr^{3+} in all the samples analyzed. A relationship is observed between Cr^{3+} , V and Fe^{2+} absorption, where peak and broadband intensity relative to Fe^{2+} are visibly more pronounced in lighter colored samples, while intensity decreases substantially in their darker counterparts. This relationship is in contrast to Cr^{3+} and V^{3+} absorptions, where their intensities increase in medium-to-dark green samples.

The UV-Vis results clearly demonstrate differences for each color group, showing the need to obtain a representative sampling field for each emerald occurrence, with a large number of samples systematically collected from different portions of their source deposit, in order to create a reliable statistical universe that can be used for comparison with provenance determination purposes.

Conclusions

In our investigation, the position of the 1070 cm^{-1} Raman band had an apparent maximum varying from 1069 to 1072 cm^{-1} . This variation is likely a result of chemical substitution, where ions such as Al^{3+} , Be^{2+} and Li^{+} replace silicon in the beryl crystal structure with charge compensating alkali ions such as Na^{+} , K^{+} , Cs^{+} and Rb^{+} in the structural channels. Its position indicates a natural emerald with high-alkali contents.

The presence of CO₂ vibrations was detected in all samples. An additional small peak assigned to N₂ was observed in some of our samples, probably due to fluid inclusions in the emerald samples. This peak is also seen in Colombian emeralds. The luminescence centers of Cr³⁺ exceed the fundamental Raman peaks in most of the spectra obtained, due to the presence of this element in all samples.

Infrared spectroscopy revealed similar features. All the Monte Santo samples displayed a 1200 cm⁻¹ IR band with an apparent maximum varying between 1170 and 1186 cm⁻¹, demonstrating that they are alkali-rich emeralds. Furthermore, all the samples showed an additional shoulder at 1140 cm⁻¹, supporting the high-alkali content hypothesis.

In regard to water content, both types of water molecules (I and II) are present in the structural channels of the Monte Santo emerald, but the type II water absorption band dominates over type I in the spectrum of all the samples. The presence of the doubly coordinating water (type II_d) suggests a highly hydrated alkali-rich environment with Na as the dominant cation coordinated by type II water.

IR spectroscopy peaks attributed to hydrocarbon groups -CH₃, -O-CH₃ and -CH₃ were detected in all samples, due to filler substances, such as oils, used to improve the clarity of the Monte Santo emeralds.

Given the degree of mineral deposit heterogeneity observed in the color, alkali content, fluid and solid inclusions of the emeralds, and other compositional and structural differences between samples from the same deposit, it is necessary to obtain a representative sampling field, with a large number of samples systematically collected from different portions of their source deposit, in order to create a statistical universe. Based on UV-Vis spectroscopy, we demonstrated how these results can change according to visible differences such as color tones.

UV-Vis spectra help distinguishing between the various geographic origins of emeralds by indicating differences such as the influence of their iron content, since type IA emeralds contain high-intensity iron-related bands while the type II presents low-intensity iron-related bands. A typical Monte Santo UV-Vis-NIR spectrum is characterized by very low to moderate-intensity iron-related features, which can separate them from the majority of the type I-tectonic magmatic-related emerald members. More challenging, however, is the separation between Monte Santo emerald and the type II-hydrothermal/metamorphic members (Afghanistan, China and Fe-rich Colombian), as they present some overlapping in the UV-Vis spectra.

The band at ~830nm, attributed to Fe, does not contribute to color, but is an important fingerprint that helps distinguish the Monte Santo emerald from some others.

The proportion between Cr³⁺, V and Fe²⁺ absorption is observed, where peak and broad band intensities of Fe²⁺ are visibly more pronounced in lighter colored samples, whereas intensity decreases substantially in their darker counterparts. This relationship is in contrast to Cr³⁺ and V³⁺ absorptions, where intensities increase for darker samples.

While Raman and infrared spectral features lead the Monte Santo emeralds to a tectonic magmatic-related nature due to their high alkali-contents, the absorption spectra suggest a tectonic metamorphic-related origin due to their low-to-moderate iron concentration. A distinctive combination of high V and Cr, and moderate to low Fe, as well as high alkali contents displayed by the spectral features, helps to separate Monte Santo emerald from other deposits.

This study further shows that an accurate separation between emeralds of various geographic origins cannot be achieved using analytical techniques individually, but the combination of these methods allows to separate emeralds from certain localities. However, in order to establish more accurate signatures that identify their exact origin, complementary advanced analytical methods, such as chemical characteristics (major, minor and trace elements), isotope analysis and microscopic features are needed.

Chemical analysis aiming to obtain major, minor and trace elements profile measurements are being performed, as well as the study of the emeralds inclusions. The results will help to establish a more precise separation, as well as for a better understanding on some genetic uncertainties.

Acknowledgements

The authors would like to thank the Instituto Nacional de Ciência e Tecnologia de Estudos Tectônicos (INCTET - UnB), for all the support that made the project possible; the Optical Spectroscopy Laboratory of the Physics Institute of the Universidade de Brasília (UnB), for the analyses and training; to the Geosciences Institute of the Universidade de Brasília (UnB) and to Dr. Lina Ester for providing the samples used in this research. This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001. RAF thanks CNPq for research fellowship.

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Dear Editor,

Please find attached our original manuscript entitled: "**Emerald Fingerprinting by Spectroscopic Analysis: Monte Santo Emeralds from Tocantins State, Brazil**" which we wish to be considered for publication in **Mineralogical Magazine**.

In this study, an approach is proposed to establish a spectroscopic fingerprint of the Monte Santo emeralds, from Tocantins State, Brazil, making it possible to compare and distinguish them from other important emerald deposits worldwide. Provenance is an important economic and societal issue inherent to the gems industry. Consumers increasingly aim to know the origin of their gems to ensure that their purchase does not support inhumane working conditions, cause legal problems, and to distinguish between natural, treated, and synthesized stones. For this purpose, spectroscopic methods were used, such as Raman spectroscopy, ultraviolet-visible-near-infrared spectroscopy (UV-Vis-NIR) and Fourier transform infrared spectroscopy (FTIR), in order to identify the presence of the fluid components, as well as data to determine the chromophore elements, their ionic charge and probable position in the emerald crystalline structure. In sum, this investigation provided, for the very first time, spectroscopic data on the Monte Santo emerald deposit, in addition to establishing its spectroscopic fingerprint.

Thank you in advance for considering this manuscript for publication in **Mineralogical Magazine**.

We will be pleased to apply any corrections suggested by the reviewers or editors that can make this manuscript better suited to the journal expectations.

Compliance with ethical standards:

Conflict of interest: The authors declare that they have no conflict of interest. Authors disclose all relationships or interests that could have direct or potential influence or impart bias on the work.

Participation of each author:

We declare that each of the authors participated effectively in the study:

Vibrational Spectroscopy

RAMAN SPECTROSCOPY OF EMERALDS: CHALLENGING ANALYTICAL PROBLEMS WITH Cr-FLUORESCENCE

--Manuscript Draft--

Manuscript Number:	
Article Type:	Research Paper
Keywords:	Raman Spectroscopy; Emerald; Cr-luminescence; Mineralogy; Gemology.
Corresponding Author:	Débora Ezequiel Cavalcanti, Ph.D. Universidade de Brasília Brasília, Distrito Federal BRAZIL
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Abstract:	Raman spectroscopy, is a non-destructive technique used to interpret atomic vibrations which has become a popular tool for its rapid identification of materials. Raman spectra produce unique vibrational fingerprints useful in identifying a multitude of materials. With the advent of numerous gem treatments and a variety of methods available for mineral synthesis, Raman spectroscopy is particularly useful in identifying and characterizing gemstones and their micro-inclusions, providing evidence of mineral genesis and geologic origin. Luminescence features attributed to chromophoric ions and trace elements have been observed in Raman spectra, revealing important information about their crystallochemical. Analysis and interpretation of these features help distinguishing between natural, treated, and synthesized gems. However, luminescence can easily dominate the spectra making it very difficult to obtain the Raman scatter experimentally. This paper presents the results of experiments on the luminescence of emeralds containing Cr and demonstrates a solution to the characterization of Cr-emeralds and potentially other gems. About sixty emerald samples from the Monte Santo deposit, Tocantins State, Brazil, were analyzed by Raman spectroscopy, aimed at characterization of fluid components (H₂O types I, II, III and CO₂,) present in the crystalline structure of the mineral, and defining the chromophor elements. The samples were examined in a whole range of settings and using different laser excitations, in order to provide solutions to a host of interesting and challenging analytical problems as fluorescence, due to the chromium, a major element in emerald crystals. The presence of the fluid components H₂O types I, II and CO₂, were evidenced, as well as data for determination of the chromophor elements, their ionic charge and probable position in the crystalline structure.
Suggested Reviewers:	Stefanos Karampelas Stefanos.Karampelas@danat.bh Emmanuel Fritsch Emmanuel.FRITSCH@univ-nantes.fr Vincent Pardieu vince@fieldgemology.org

Dear Editor,

Please find attached our original manuscript entitled: "**Raman Spectroscopy of Emeralds: Challenging Analytical Problems With Cr-Fluorescence**" which we wish to be considered for publication in **Vibrational Spectroscopy**.

In this research, an approach is proposed to make a scientific contribution by presenting solutions for challenging analytical problems of Raman Spectroscopy analysis in emeralds, due to the fluorescence caused by the Cr, a major element in the composition of this gem mineral.

Raman spectroscopy is particularly useful in identifying and characterizing gemstones. Analysis and interpretation of Raman spectra help distinguishing between natural, treated, and synthesized gems, in addition to providing evidence of mineral genesis and geologic origin. However, luminescence can easily dominate the spectra making it very difficult to obtain the Raman scatter experimentally.

The development of databases and interpretation of emeralds and other gems at the Raman spectra is required. However, due to the presence of elements that cause interference in the Raman spectra by their fluorescence, this technique has still been challenging. Additionally, this study presents a characterization of the fluid components, as well as the chromophore elements of the Monte Santo emeralds, Tocantins, Brazil.

Thank you in advance for considering this manuscript for publication in **Vibrational Spectroscopy**.

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Conflict of interest: The authors declare that they have no conflict of interest. Authors disclose all relationships or interests that could have direct or potential influence or impart bias on the work.

Participation of each author:

We declare that each of the authors participated effectively in the study:

RAMAN SPECTROSCOPY OF EMERALDS: CHALLENGING ANALYTICAL PROBLEMS WITH Cr-FLUORESCENCE

Débora Ezequiel Cavalcanti ^{*1}; Valmir da Silva Souza¹; Paola Ferreira Barbosa¹; Alexandre Silva Santos²; Ísis Oliveira Szlachetka²; José de Araújo Nogueira Neto³; Sebastião William da Silva²; Reinhardt Adolfo Fuck¹; Martha Noélia Lima³.

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ABSTRACT

Raman spectroscopy, is a non-destructive technique used to interpret atomic vibrations which has become a popular tool for its rapid identification of materials. Raman spectra produce unique vibrational fingerprints useful in identifying a multitude of materials. With the advent of numerous gem treatments and a variety of methods available for mineral synthesis, Raman spectroscopy is particularly useful in identifying and characterizing gemstones and their micro-inclusions, providing evidence of mineral genesis and geologic origin. Luminescence features attributed to chromophoric ions and trace elements have been observed in Raman spectra, revealing important information about their crystallochemical. Analysis and interpretation of these features help distinguishing between natural, treated, and synthesized gems. However, luminescence can easily dominate the spectra making it very difficult to obtain the Raman scatter experimentally. This paper presents the results of experiments on the luminescence of emeralds containing Cr and demonstrates a solution to the characterization of Cr-emeralds and potentially other gems. About sixty emerald samples from the Monte Santo deposit, Tocantins State, Brazil, were analyzed by Raman spectroscopy, aimed at characterization of fluid components (H₂O types I, II, III and CO₂,) present in the crystalline structure of the mineral, and defining the chromophor elements. The samples were examined in a whole range of settings and using different laser excitations, in order to provide solutions to a host of interesting and challenging analytical problems as fluorescence, due to the chromium, a major element in emerald crystals. The presence of the fluid components H₂O types I, II and CO₂, were evidenced, as well as data for determination of the chromophor elements, their ionic charge and probable position in the crystalline structure.

Keywords: Raman Spectroscopy; Emerald; Cr-luminescence; Mineralogy; Gemology.

1. INTRODUCTION

Emerald is the green chromium-vanadium-bearing gem variety of the beryl minerals. It is one of the "precious gems" (diamonds, rubies, emeralds and sapphires) and generally the most valuable after the diamonds and rubies. Although considered rare, emerald is found on all five continents of the world. The main producers are Colombia, Zambia, Brazil, Russia, Canada, China, Pakistan and Zimbabwe (Groat, et al., 2008), (Giuliani, et al., 2019). In general, each emerald occurrence around the world has a specific spectroscopic, isotopic, and geochemical signature, which can be important diagnoses as to the origin of this gemstone.

The beryl (ideal chemical formulae $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$) shows a great variety of colors, which is mainly related to oxidation state and/or charge transfers effects of impurities in the form of transition metal ions (so-called chromophore elements, such as Fe, Mn, Cr, V, Cu), in specific lattice positions, or in the interstitial channels of the crystalline structure. Variations in the chemical composition of beryl, particularly the content of alkalis and fluids such as H_2O , are closely correlated to the geochemical and paragenetic characteristics of the geological systems where beryl varieties are generated (Beus, 1966).

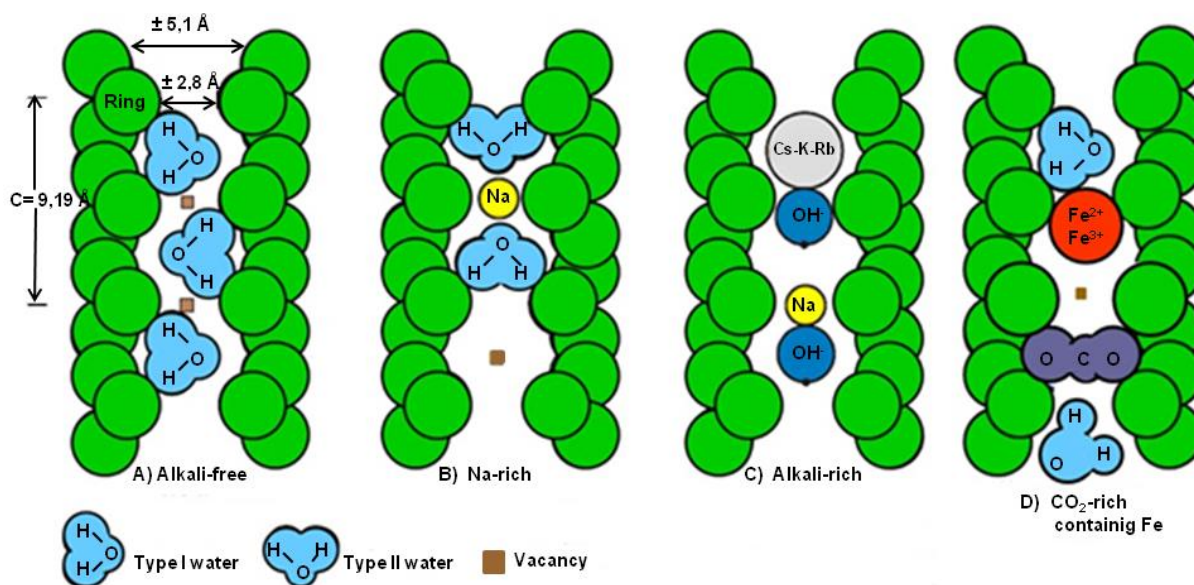
Raman spectroscopy is an extremely powerful tool for characterizing the physical and chemical properties of minerals. The Cr^{3+} properties in natural beryl samples have been studied by photoluminescence techniques as a function of Cr content (50–11370 ppm) as well as impurities, such as Fe and V. The most serious problem associated with conventional continuous wave Raman spectroscopy is the minuteness of the effect. Even in the most favorable cases, only on the order of 10^{-6} of the incident intensity is converted into signal.

For most analytical techniques that aim to establish the chemical composition, such as the electron microprobe (EPMA), the OH^- and H_2O molecules contents can be difficult to detect, so their contents are obtained indirectly through molecular calculations, not measured. OH^- and H_2O molecules can be detected by X-ray or neutron diffraction. However, Raman and infrared spectroscopies, can be both simpler and faster, methods for detecting OH^- and H_2O in a sample, and on top of that, non-destructive.

Two possible types of arrangements for water molecules in the structural channels of beryl, identified by infrared absorption spectroscopy (Wood & Nassau, 1967; Aurisicchio, et al., 1994) have been widely accepted. In the first arrangement, for water Type I, the molecules of the H-H axis are positioned parallel to the c-axis of the beryl. In the second arrangement, in water Type II, the H-H axis are perpendicular to the c -axis, as can be seen in figure 1. This last arrangement is due the presence of alkalis as impurity in the structurals channels,

producing the electrostatic attraction that causes the rotation of the water molecule, so that the O^{2-} ion is next to the alkaline element, usually Na.

Figure 1 – Lateral projection of the structure of beryl, parallel to the *c* axis, showing both spatial orientations of the H₂O molecules (type I and II) as well as the position of alkalis and fluids. A) Alkali-free beryl, with type I H₂O and vacancies; B) Sodium-rich beryl, with type II H₂O; C) Alkali-rich beryl, stimulating OH⁻ groups; D) Beryl substituted by Fe²⁺, Fe³⁺, with unbound CO₂ and H₂O molecules.



Source: Modified from (Wood & Nassau, 1967), (Wood & Nassau, 1968), (Aines & Rossman, 1984), (Aurischio, et al., 1994) and (Mathew, et al., 1998).

Additionally, a third type of water (Type III) was proposed by (Mashkovtsev & Lebedev, 1992). Type III water is associated with heavy alkaline cations filling the channel, and the H-H axis molecules are oriented parallel to the *b*-axis of the beryl, just like Type I water, however, the cations are located at a greater distance from the water molecules, producing active bands in the spectral region of the infrared field.

The development of databases and interpretation of emeralds at the Raman spectra is required. However, due to the presence of elements that cause interference in the Raman spectra by their fluorescence, this technique has still been challenging. This study presents a characterization of the vibrational and electronic characteristics present in the Raman spectra from the Monte Santo emerald and the associated interpretation of their spectral characteristics.

After numerous tests and comparisons with different laser excitations and adjustments to the equipment settings, it was possible to successfully define the position of certain Raman bands and features in the spectra obtained, establishing a fingerprint of the Monte Santo

emeralds, and demonstrating that even with the interference of the luminescence caused by the presence of Cr in emeralds, Raman spectroscopy is still one of the most powerful tools to characterize this mineral.

As it has been demonstrated, in Raman spectroscopy, choosing the laser excitation is one of the most important decisions to be done, because despite the Raman signature of any material is related to the material's unique chemical structure, so the molecular fingerprint will be the same regardless of the laser excitation (Zhou, 2015). However, the wavelength chosen will impact many factors such as Raman intensity, background fluorescence, spatial resolution and acquisition time, for instance.

In order to obtain a Raman spectra despite the fluorescence, the options would be or to decrease the excitation intensity or to move to a higher laser wavelengths. Plus, to optimize the measurement parameters individually for each sample was needed very often. Spatial filters in the optical receive end can also help (confocal microscopy). Time-resolved Raman spectroscopy with fast pulsed lasers also can be used to filter out fluorescence, which may occur in the ~ 500 nano-second time scale and longer.

Fluorescence leads us toward to the 785 nm laser in order to get away from it. But on the other side, a laser that provides a lower energy to bombard the sample, takes the longest amount of time to get adequate levels of signal to analyze, while having a higher probability of overheating the sample and even burning it, and so this happened while using the 785 nm laser. Experiments were also made by using the 633 nm laser, but the photoluminescence was enough to overwhelm the Raman signal. So the alternative was to use the 532 nm laser, but lowering its power to a minimum excitation intensity (between 10 and 0.1%) and so it worked out.

2. MATERIAL AND EXPERIMENTAL METHODS

2.1. Samples and Preparation

Care was taken to use the samples where at least one face of the crystal could be identified, between subhedral to euhedral, in order to obtain a representative sample space. The samples collected were catalogued and separated according to a color scale, showing the relationship between the color and the results of the analysis. About 60 emerald samples were selected, prepared and analyzed. The samples were georeferenced with the point of the extraction in situ at the "garimpo (G4)" (mining site), followed by the numbering used for sample cataloguing.

2.2. Raman spectroscopy

Raman analyzes were performed at the Optical Spectroscopy Laboratory of the Physics Institute-IF of the University of Brasília-UnB. The Raman signatures of the samples were collected at room temperature ($\pm 20^\circ \text{C}$), using the Horiba LabRAM HR Evolution Raman spectroscopy equipment, which performs measurements with a Raman confocal microscope coupled to a CCD (Charge Coupled Device) using a diode laser. semiconductor with a grid of 1800 lines/mm.

Lasers with three different excitation sources were used: 785 nm (near infrared), 633 nm (red radiation) and 532 nm (visible range), which allowed analyzing the entire range between 150 and 5620 cm^{-1} , and evaluating the photoluminescence effects ($>1500 \text{ cm}^{-1}$) and the Raman effect.

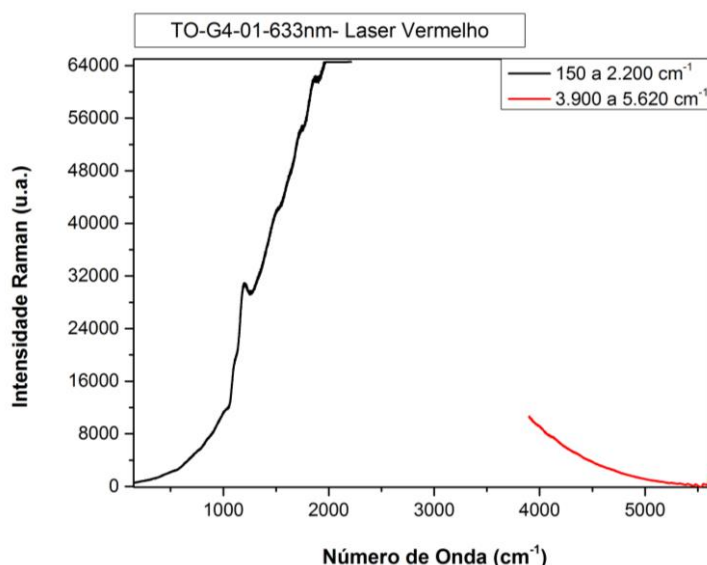
The data obtained were saved in X and Y files and their background was not corrected. Raman spectra were generated in OriginPro 9.0 software (©OriginLab, s.d.) and the spectra were baselined in LabSpec® software (Horiba, s.d.). For some samples, two distinct Raman spectra were collected, according to the orientation of the crystallographic axes of the analyzed crystals in relation to the Raman laser beam, for comparison.

3. RESULTS AND DISCUSSIONS

3.1. Luminescence Features in this Study

For emeralds samples, the luminescence features appear in the extended range ($>1500 \text{ cm}^{-1}$) of the Raman spectra. An example of the luminescence features in Raman spectra of emeralds can be observed on the graph below (Figure 2). In many cases like that, the luminescence features are so intense that you can no longer see the Raman peaks associated with the atomic vibrations of the mineral. Notice that the luminescence features overwhelm the intensity of the Raman spectra for the emeralds samples by pulsing the red laser (633 nm).

Figure 2: Raman spectra of emerald samples acquired with a 633 nm laser, exhibiting photoluminescence that overwhelm the Raman signal, ranging from 150 to 2200 cm^{-1} (black spectra) and from 3900 to 5620 cm^{-1} (red spectra).



The Raman spectra acquired with a 785 nm laser, also exhibit fluorescence that overwhelms the Raman signal. In natural Cr-free beryl, fluorescence generated by the 785 nm incidente beam is minimal, making this optical phenomenon diagnostic of Cr-emeralds, showing that the presence of Cr^{3+} is likely the cause of this fluorescence.

As a solution to a host of interesting and challenging analytical luminescence problem caused by the presence of Cr^{3+} , it is demonstrated in this work that the Raman spectra of Cr-green-colored beryls collected using a laser of a higher energy, such as 532 nm, but with a minimum excitation intensity (between 10 and 0.1%), minimizes this effect, together with adjustments in the equipment configuration to perform the analyses, which led to the reduction of noise in the spectra (Figure 3).

Due to the photoluminescence effects caused by Cr^{3+} , where the luminescence peaks exceed the Raman peaks, "bursting" the signal limit of the equipment, it was necessary to analyze, separately, the regions from 150 to 3900 cm^{-1} and from 3500 at 5400 cm^{-1} . This measure was adopted so that the Raman spectra of the region from 150 to 1700 cm^{-1} could be recorded, with the main Raman vibrations of the beryls and some of their fluid components, without interference from the luminescence caused by Cr, which occurs in the region of approximately 4000 cm^{-1} .

3.2. Spectral Features Related to Chromophores and Other Ions

Distiguishing between an emerald and a green beryl is a controversial issue in gemology. The presence of Cr^{3+} substituting for Al^{3+} in a deep green-colored beryl was the original defining characteristic of an emerald. However, V^{3+} substituting for Al^{3+} can also produce deep green-colored beryl (Gaft, et al., 2005). Whether or not a gemstone is marketed as an emerald or simply a green beryl can greatly affect the gemstone's value. Chromium is the only emerald chromophore that exhibits photoluminescence (PL); vanadium does not cause PL in emerald. Luminescence studies reported by Gaft et al. (2005) attribute two distinct luminescence centers located at 680 and 685 nm in emerald due to octahedrally coordinated Cr^{3+} .

The peaks observed in the Raman spectra associated with Cr^{3+} luminescence centers centered in the region of 4095 cm^{-1} (680 nm) and 4170 cm^{-1} (685 nm) (Gaft et al., 2005) exceed the fundamental Raman peaks in most of the spectra obtained, strongly indicating the presence of this element in all samples.

3.3. Spectral Features Related to Main Raman Bands of Beryls

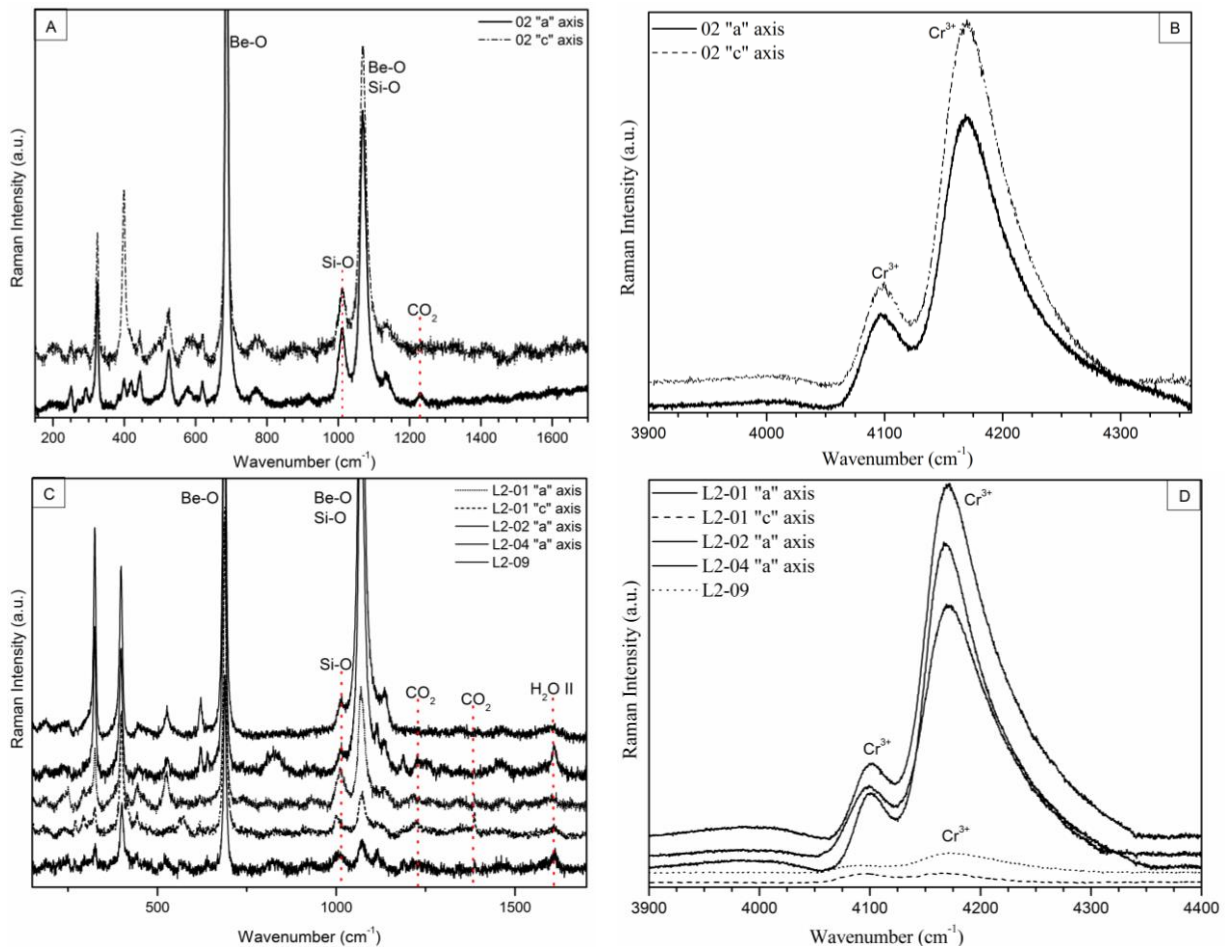
When the beryl is oriented with the a-axis parallel to the incident laser beam (the cross-section of the optical indicator is an ellipse), the peak intensities change with rotation due to a change in the atomic vibration degree of freedom. When the sample is oriented with the c-axis parallel to the laser (the cross section of the optical indicatrix is a circle), there is no perceptible change in peak intensities due to an equal distribution of atomic vibration in all directions. In order for this phenomenon to be observed and no information could escape the analysis, some samples were analyzed in both orientations of their crystallographic axes, for comparison.

Regardless the crystallographic orientation is, beryl can be accurately identified by the spectrum of a randomly oriented sample, as some Raman bands are always seen, although their relative intensity can change. These bands are known as main Raman bands of beryl, and they can be seen in the range up to 1200 cm^{-1} .

The peaks present in the region from $321\text{ to }325\text{ cm}^{-1}$; $325 - 395\text{ cm}^{-1}$, and $683\text{-}688\text{ cm}^{-1}$ have been assigned to ring vibrations (Moroz, et al., 2000), (Adams & Gardner, 1974), (Charoy, et al., 1996); the bands around $1002 - 1010\text{ cm}^{-1}$ are linked to the stretching of the Si-O bond; and at 1070 cm^{-1} there are still controversies about whether the peaks are attributed to Be-O or Si-O stretching of beryl vibration, although the latest studies demonstrate that it is more likely to be related to Si-O bonding vibration (Huong, et al., 2010); (Huong, et al., 2014).

In our investigation, the position of the 1070 cm^{-1} Raman band has an apparent maximum varying from 1069 to 1072 cm^{-1} . This variation in the Raman band in beryl is interpreted as a result of chemical substitution, where ions such as Al^{3+} , Be^{2+} and Li^+ replace silicon in the beryl crystal structure with charge compensating alkali ions such as Na^+ , K^+ , Cs^+ and Rb^+ in the structural channels. According to some studies (Huong, et al., 2010); (Huong, et al., 2014), this Raman-shift occurs in natural alkali-rich emeralds and therefore leads us to classify it as such.

Figure 3: Raman spectra of emerald samples from the Monte Santo deposit, ranging from 150 to 1700 cm^{-1} (left-side graph A and C) and 3900 to 4400 cm^{-1} (right-side graph B and D).



3.4. Spectral Features Related to Fluid Components and Alkali Content

Control over the dominant presence of one type of H_2O molecules in the channels along the c-axis in the beryl structure is a strong indicator of the presence of alkaline elements in their crystal structure and in the system where they were generated. The well-defined peak centered at approximately 3595cm^{-1} represents type II molecular water vibration (water molecules bound to alkaline ions), while the peak at 3605cm^{-1} represents type I molecular

water vibrations (water molecules without the presence of alkaline ions) (Wood & Nassau, 1967) e (Auricchio, *et al.*, 1994). Both molecular types of water were detected in the analyzed samples. It was also detected the band of deformations of H₂O, which appears in the region around 1610 cm⁻¹ (Figure 3C).

Elevations in the vicinity of 1230 to 1240 cm⁻¹ and at 1385 cm⁻¹ indicate CO₂ vibrations (Figures 3 A and C). These elevations are very subtle in some samples and more pronounced in others. For samples analyzed according to crystallographic orientation, with the exception of one sample, these peaks are generally seen when E is normal to the c-axis (Figure 3 A). According to Charoy *et al.* (1996) these bands are generated by the vibration of CO₂ molecules existing in the channels of the crystal structure. The disappearance of these peaks when E is parallel to the c-axis supports the fact that the CO₂ molecule is oriented normally to the c-axis (Figure 3 A). However, the reason for the disappearance of the band at 1385-1387 cm⁻¹ in some origins is not explained by this.

4. CONCLUSIONS

In all analyzed samples, photoluminescence effects caused by the presence of Cr³⁺ were observed, where the luminescence peaks exceed the Raman peaks, often bursting the signal limit of the equipment. Raman spectra collected with both, a 785 nm laser and a 633 nm laser have been shown to exhibit fluorescence that exceeds the Raman signal. However, using a higher energy laser, such as 532 nm (green laser), but with a minimum excitation intensity (between 10 and 0.1%), together with adjustments in the equipment configuration to perform the analyses, it is possible to minimize the luminescence effect, which led to the reduction of noise in the spectra, making it possible to obtain the Raman spectra for Cr-emeralds and potentially for other minerals that present luminescence.

ACKNOWLEDGEMENTS

We would like to thank to the National Science and Technology Institute of Geotechnical Studies (INCTET - UnB), for all the support that made this research possible; the Optical Spectroscopy Laboratory of the Physics Institute of the University of Brasilia (UnB), for the analyses and teachings. We are also grateful to Coordination for the Improvement of Higher Education Personnel (CAPES) for the research grant, the Geosciences Institute of the University of Brasilia (UnB) and to Dr. Lina Encarnação for providing the samples from the Monte Santo deposit used in this research.

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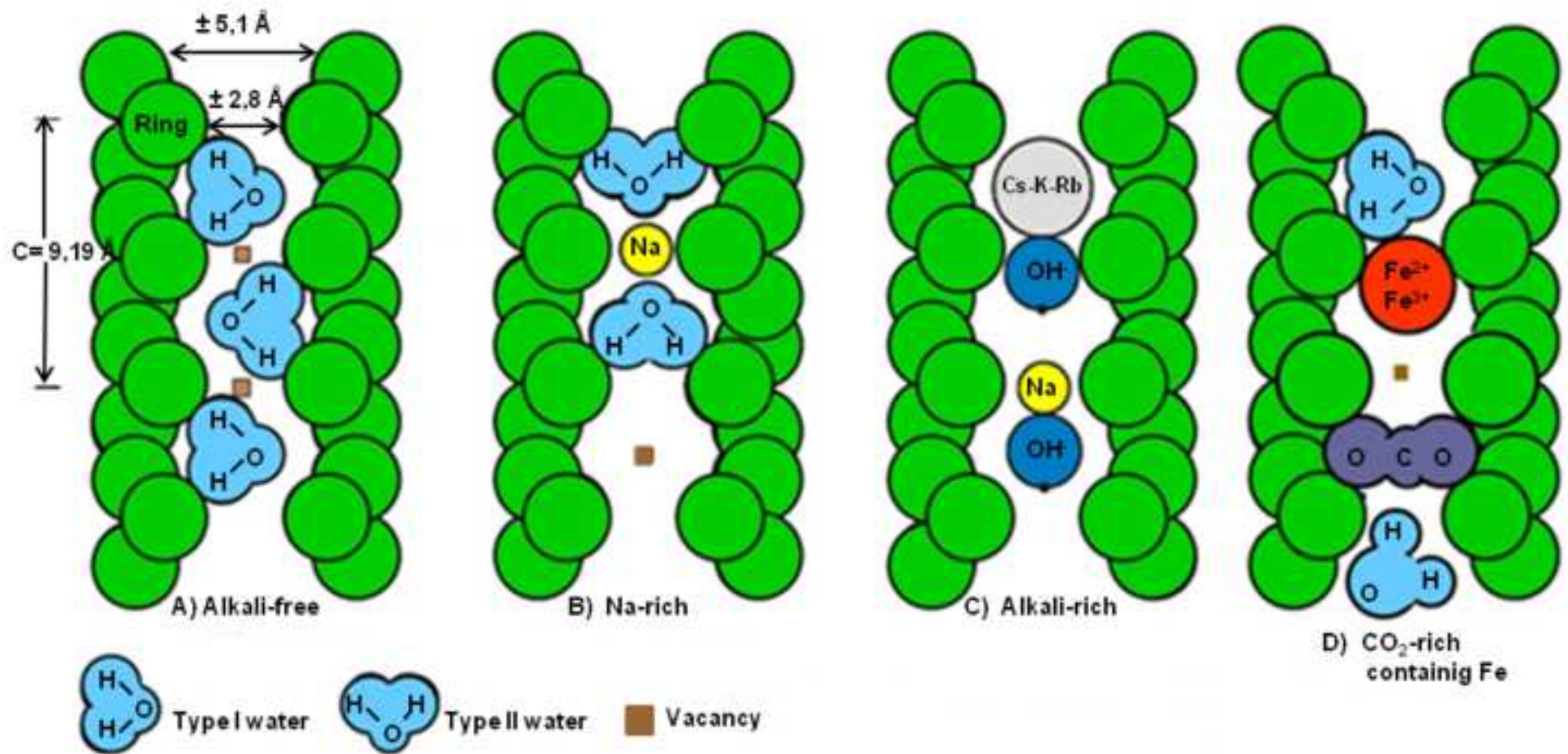
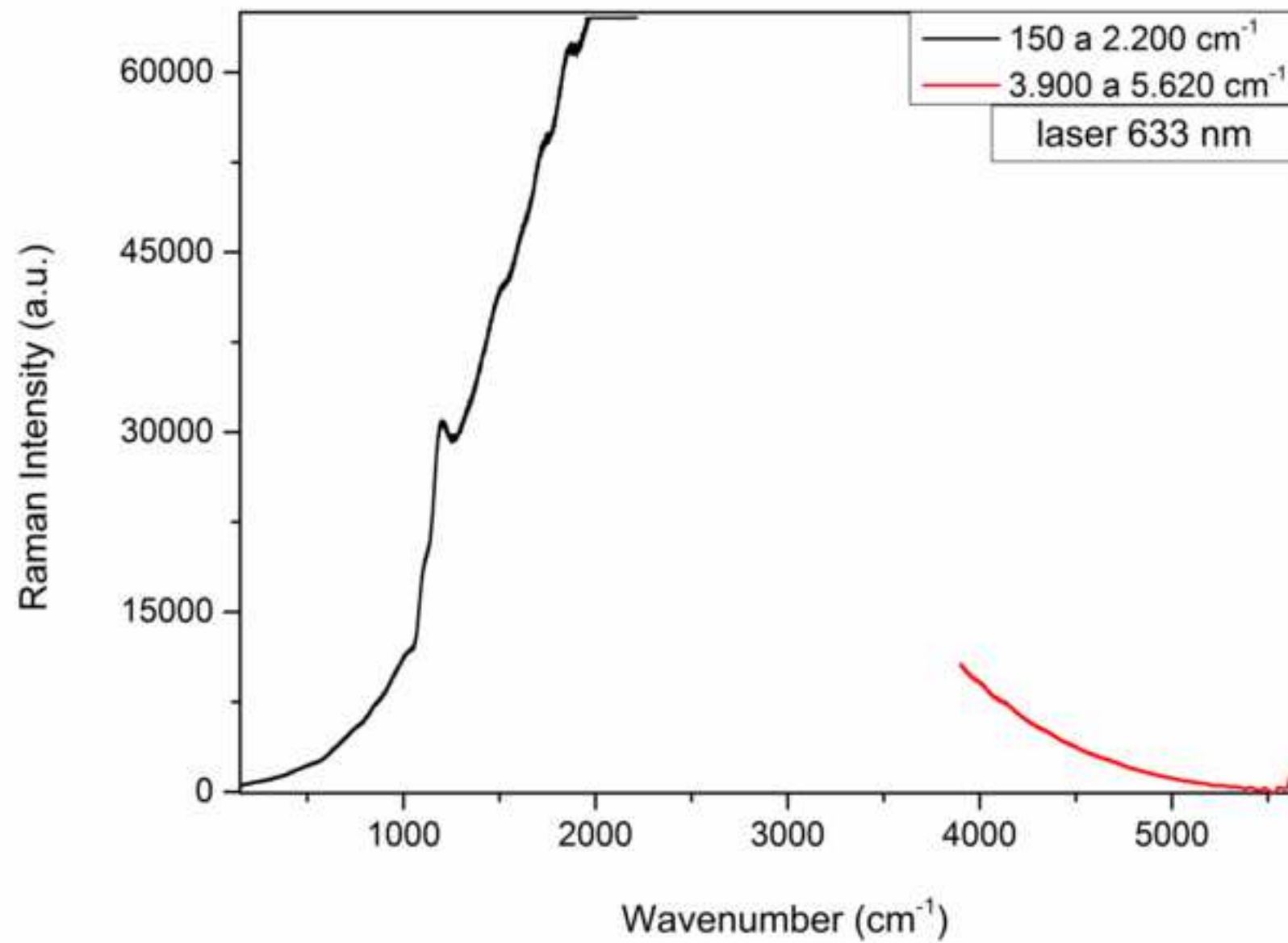
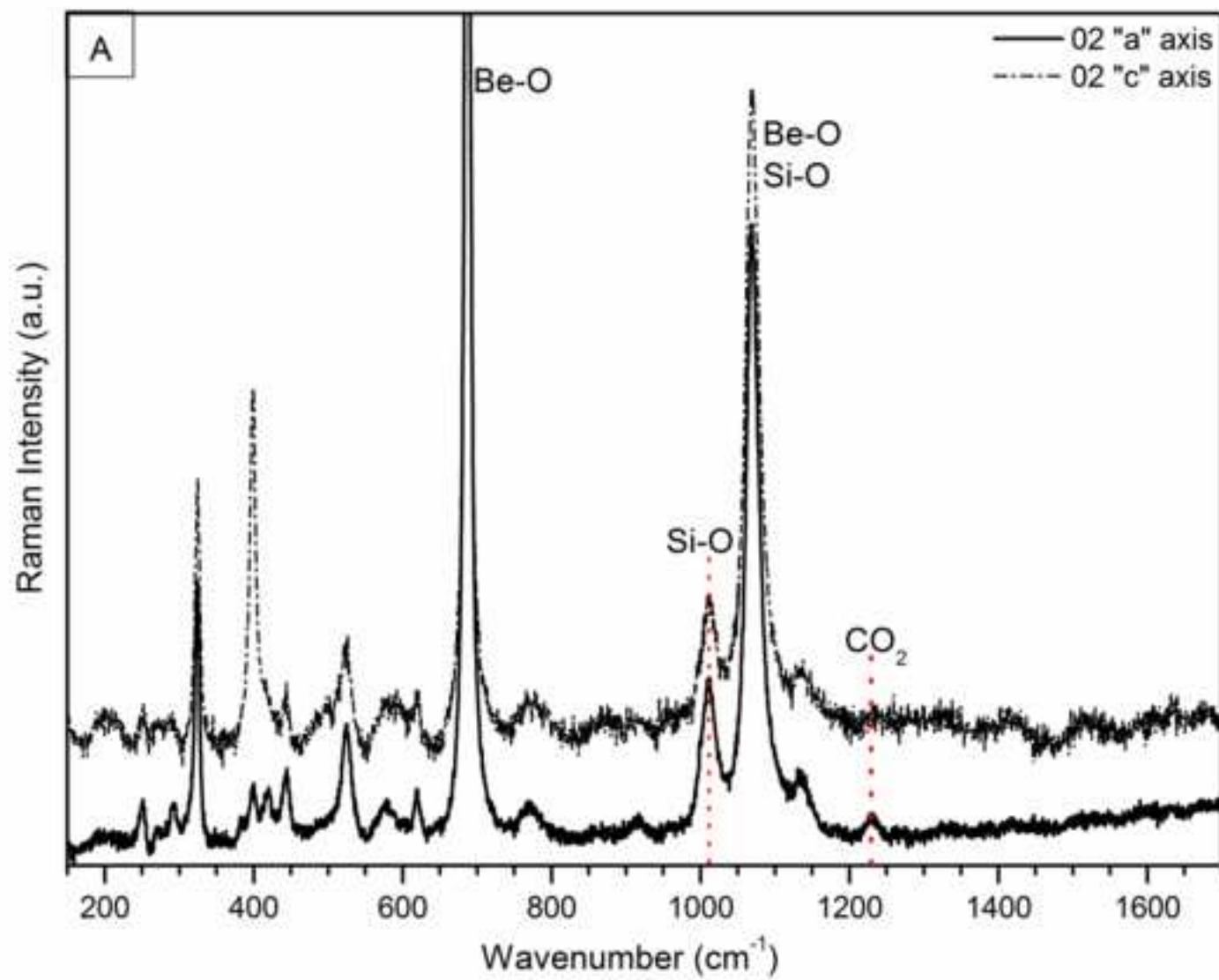
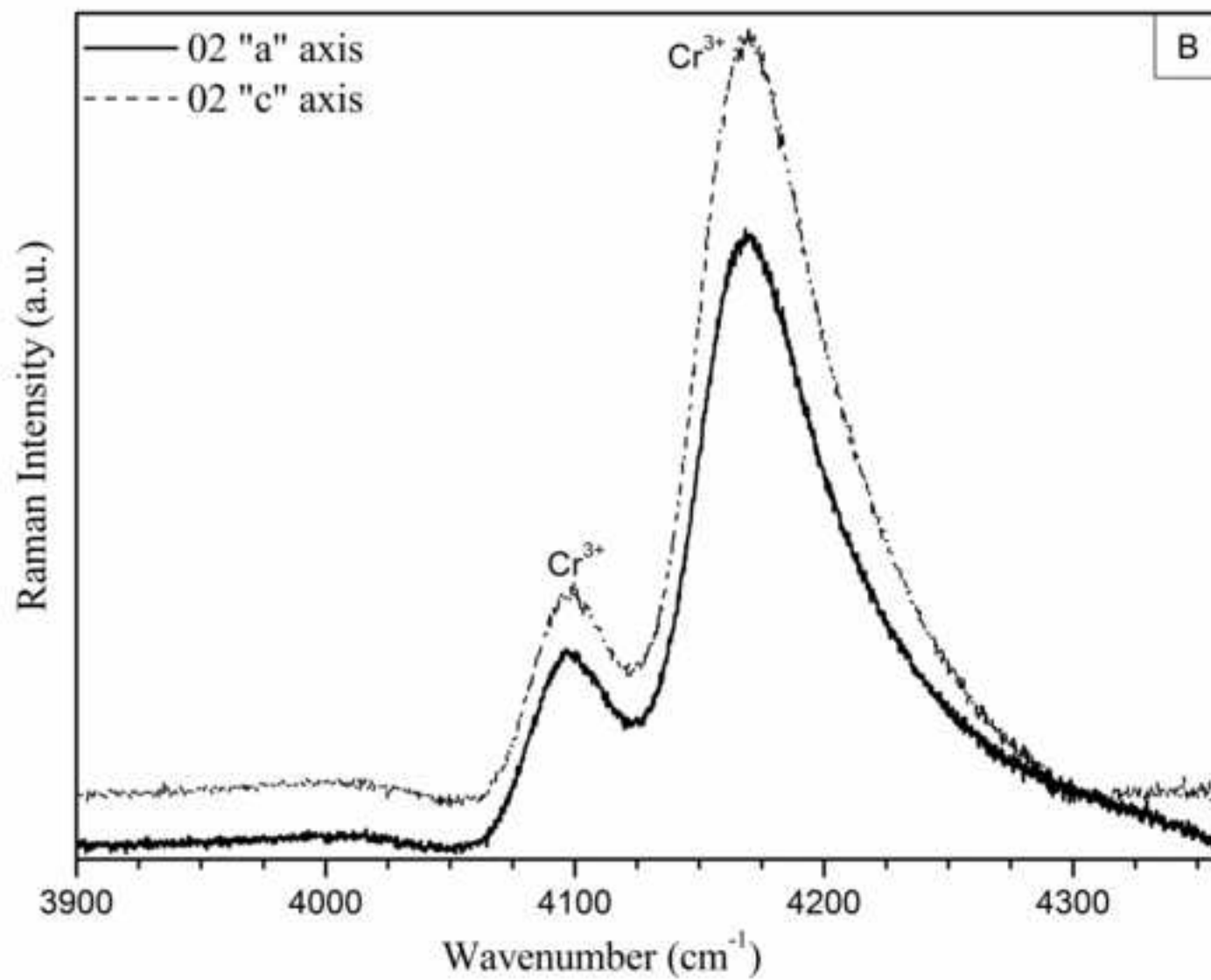
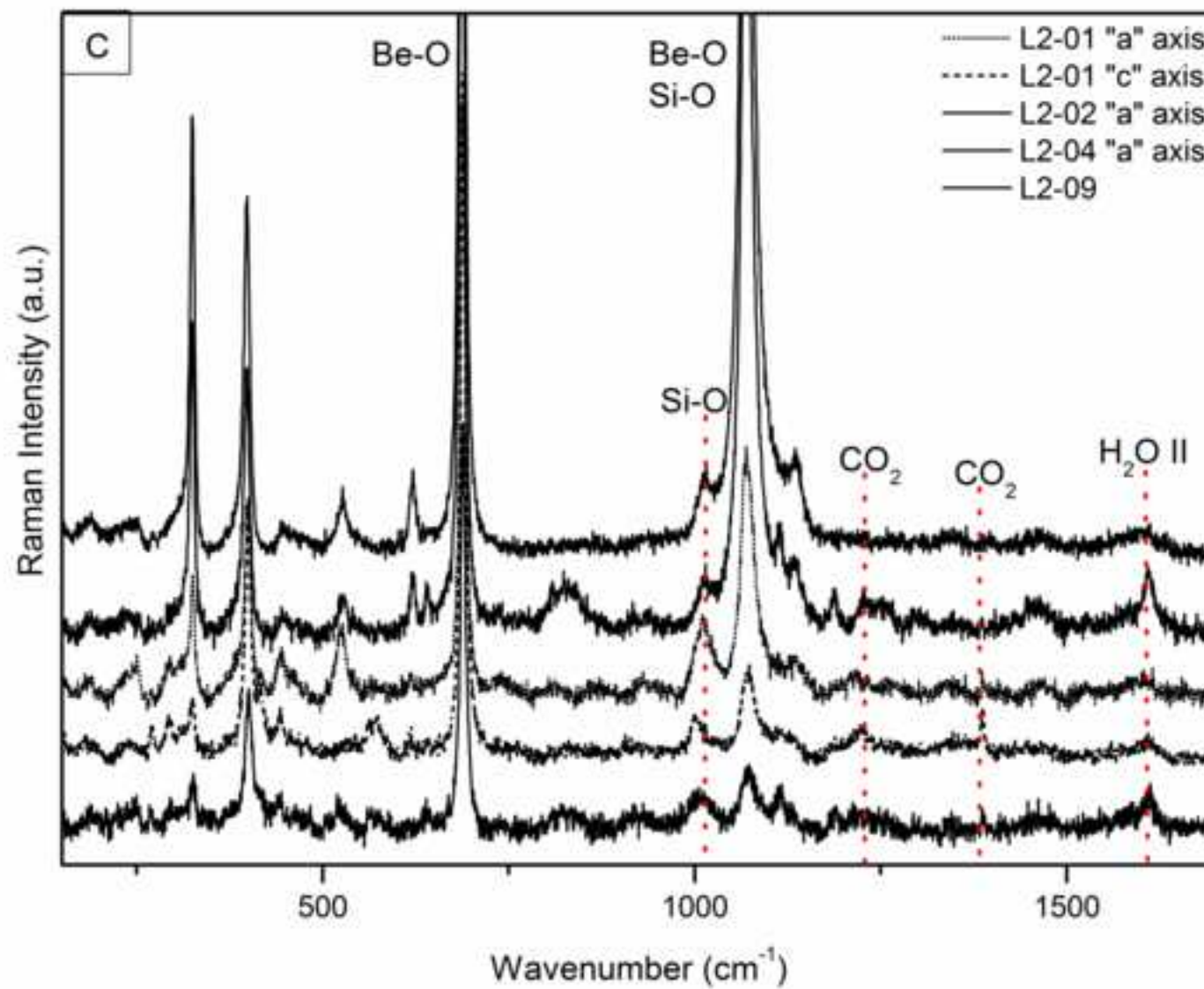


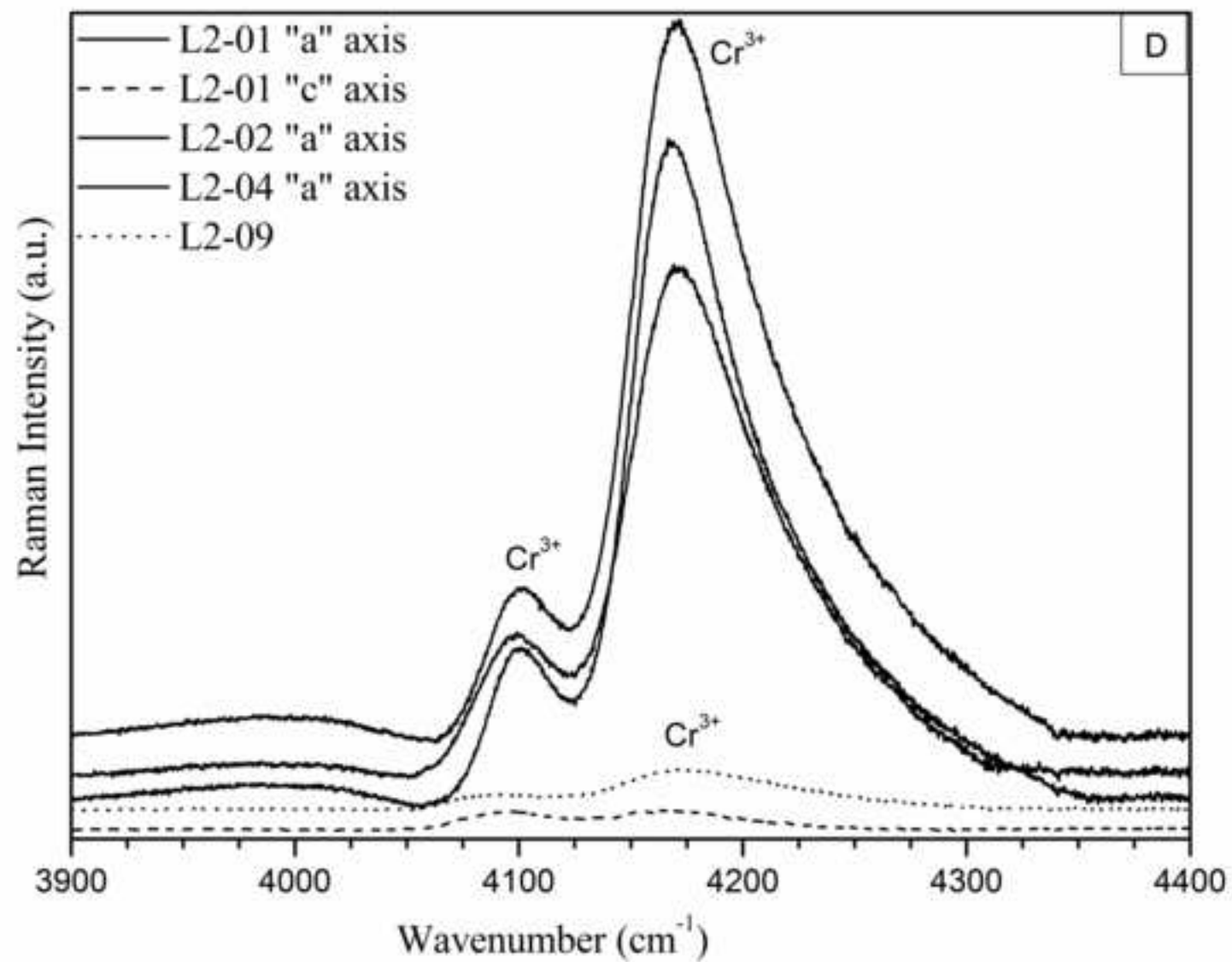
Figure 2











Declaration of interests

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



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SCIENTIFIC MANUSCRIPT

For review only.

Monday 08 May 2023

Category: *research papers*

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Crystallochemical Characterization of Brazilian Emeralds from Monte Santo-Tocantins.

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Synopsis In this study, an approach is proposed to study the crystallographic reticulum of emeralds from Monte Santo deposit in Tocantins State, Brazil, in order to classify them and elucidating the origin and evolution of its deposits.

Abstract Brazil is an important producer of emeralds, with many occurrences located in the center-southeast and northeast of the country. Important emerald mineralization occurs in the municipality of Paraíso do Tocantins, a mid-western portion of the State of Tocantins, where samples were collected for this research. We present the crystallochemical characterization of the Monte Santo emerald, an important occurrence from this region. Emerald is the green gem variety of the beryl mineral, which has the ideal formula of $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ and whose elements V^{3+} , Cr^{3+} are its chromophores. It is considered a “precious gem” and one of the most valuable after the diamond. Beryls are cyclosilicates composed of hexagonal Si_6O_{18} rings connected by Be atoms to tetrahedral sites, and Al atoms to octahedral sites. The pairing of Si_6O_{18} rings creates a channel parallel to the c-axis, that may be empty or occupied by alkali cations, water, and other molecules and/or elements. Several different replacements occur in the octahedral and tetrahedral sites, leading to beryl varieties such as emerald, ruby, and aquamarine. Cation substitutions predominantly occur in the octahedral Al site, substituting Al^{3+} with divalent metals such as Fe^{2+} and Mg^{2+} , or trivalent transition metals such as Fe^{3+} , Cr^{3+} , V^{3+} , among others. In the case of divalent substitutions, alkali cations (most commonly Na^+) enter the channel sites to maintain a balanced charge by coupled substitution. About sixty emerald samples were analysed, using single-crystal X-ray diffraction (XRD), and electron microprobe analysis

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(EMPA), aimed at studying its crystallographic structure, axial parameters and unit cells, as well as the presence and nature of impurities and substitutions in its structure, and its chemical composition. Data were supplied to determine the polytypes of beryl, according to their crystallographic substitutions, chemical composition and position of the elements in the crystalline structure. Analysis of beryl chemical composition revealed the alkaline elements such as Na, K and Cs in the channels. The presence of V, Cr and Sc as chromophore elements in the beryl structure, results in its green colour. The Monte Santo deposit was classified into octahedral type.

Keywords: Emerald. X-Ray Diffraction. Crystallography. Crystallochemical. Mineralogy.

1. Introduction

Monte Santo emeralds occur in the Araguaia Belt geological domain, State of Tocantins, central Brazil. The deposit was discovered in 1996 and is becoming an important source of emeralds, since they are typically of excellent quality, compared to some of the finest emeralds worldwide.

Despite being an important region, from both an economic and scientific standpoint, there are no studies that contain crystallochemical and mineralogical data of Monte Santo emerald. Thus, the main aim of this research was to contribute scientifically using crystallographic and chemical data of samples from Monte Santo emerald.

The ideal chemical formula of beryl is $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$, with the common presence of fluids and other volatiles, as well as alkalis and metal elements.

The basic structure of beryl (Figure 1) consists of hexagonal rings with six Si–O tetrahedra (Deer, *et al.*, 1966), composed of continuous channels or canaliculi, parallel to the *c*-axis of the crystal, that may be empty or filled with ions (Aurisicchio, *et al.*, 1994) and/or molecules (water, for example). According to Deer *et al.* (1966), in each 6n-ring of SiO_4 , two oxygen atoms are shared by two other adjacent SiO_4 tetrahedra, such that the radical of the rings is represented by $[\text{Si}_6\text{O}_{18}]^{12-}$, with an Si:O ratio of 1:3. The aluminium (Al^{3+}) and beryllium (Be^{2+}) atoms are placed alternately between the rings, with each aluminium atom coordinated by an octahedral group of six oxygen atoms $[\text{AlO}_6]^{9-}$ and each beryllium atom coordinated by four oxygen atoms $[\text{BeO}_4]^{6-}$, forming a distorted tetrahedron. The oxygen of the neighbouring rings $[\text{Si}_6\text{O}_{18}]^{12-}$ is united laterally and vertically by the aluminium and beryllium.

Its theoretical composition contains approximate Be values $\cong 14\%$, $\text{Al}_2\text{O}_3 \cong 19\%$ and $\text{SiO}_2 \cong 67\%$ (Deer *et al.* 1966). The typical impurities that make up a substantial part of most beryl varieties are alkalis (Na, Li, Cs, Rb, K), and to a lesser extent H_2O , Ca, Mg, Mn, Fe^{2+} , Fe^{3+} , Cr, CO_2 , He and Ar

(Beus, 1966). Alkalis of up to 11% and H₂O up to 4% are common, in addition to trace elements of Fe, Mg, Mn, Ti, V, Cr, P, Ba, Zr, Sr, Sc, Zn, Ca (Deer, *et al.*, 1966), among others.

While water content in beryl is difficult to measure, its link to Na₂O concentration means it can be calculated using certain equations.

The wide variety of colors in beryl is related primarily to the presence of impurities in the form of transition metals (chromophore elements), in the interstices of the crystalline structure of the mineral, along with its position in the crystalline reticulum, its oxidation state and charge transfer.

Variations in the chemical composition of beryl show a strong correlation with geochemical and paragenetic characteristics of the geological environment where they were originated. Thus the elemental distribution in beryl can be used as an important tool to classify its deposits and elucidate its origin and evolution.

The crystallochemical formula of beryl can be expressed by [A]X₃Y₂T₆O₁₈, associating the various isomorphic substitutions in the mineral structure and alkaline elements in the form of mono and bivalent ions. Thus, **A** represents the ions and/or molecules that occupy the vacancies and channels, such as H₂O, OH⁻, Na⁺, Ca²⁺, Fe²⁺, K⁺, Cs⁺, Rb⁺, and Li⁺; **X** the tetrahedral sites of Be²⁺, Al³⁺, Li⁺, and Si⁴⁺; **Y** the octahedral sites of Al³⁺, Fe²⁺, Mg²⁺, Fe³⁺, Ca²⁺, Mn²⁺, Cr³⁺, V⁵⁺, Te⁴⁺, and Sc³⁺; and **T** the tetrahedral sites of Si⁴⁺.

Three types of substitutions are distinguished: **1)** octahedral substitution of Al³⁺, **2)** tetrahedral substitution of Be²⁺ and **3)** limited substitution of Be²⁺ and octahedral substitution of Al³⁺. Octahedral Al³⁺ deficiency is common, with bivalent substitutions, resulting in occupation of site **A** by charge compensation. Beryl with a high Al³⁺ content tends to exhibit significant Be²⁺ substitution by Li⁺, while low Al³⁺ content tends to display site **X** completely occupied by Be²⁺. In the event of excessive Al³⁺, its amphoteric nature means it enters the tetrahedra, substituting Be²⁺ and Si⁴⁺, while an excess of Si⁴⁺ can substitute Be²⁺ in the tetrahedron [BeO₄]⁶⁻.

Analyses demonstrate that Li⁺ → Be²⁺ substitution strongly favours alkali entry in the crystalline network channels parallel to the crystallographic *c* axis (Deer *et al.* 1966).

(Bragg & West, 1926) were the first to determine the axial parameters for beryl, with *a*₀ values = 9.21 Å and *c*₀ = 9.17 Å. According to Deer *et al.* (1992), unit cell constants for beryl are *a*₀ = 9.21 Å, and *c*₀ = 9.20 Å. According to (Aines & Rossman, 1984) and (Aurischio, *et al.*, 1994), as well as several other authors, the axial parameters for beryl are *a*₀ = 9.21 Å and *c*₀ = 9.19 Å, and will be the standard values in the present study.

Authors such as (Frank-Kamenetskii & Sosedko, 1958), (Schaller, *et al.*, 1962), (Radeliffe & Campbell, 1966) and (Bakakin, *et al.*, 1970) suggest that changes in axial parameters occurred when there are substitutions at crystallographic sites, as well as in the positioning of ions in the channels.

The c/a ratio is normally used to indicate the sites where substitutions occur and classify them into polytypes according to these substitutions.

Some authors, such as (Deer, et al., 1992) and (Sampaio Filho, *et al.*, 1973), suggest that the a_o parameter increases with the entry of other chemical elements (Fe, Mn, and Mg, among other alkalis) into the beryl structure, while c_o remains constant.

(Bakakin, *et al.*, 1967) and (Gandini, 1999) suggest that the entry of alkali and water into the beryl structure results in an increase in the c_o parameter, while a_o remains constant or rises slightly.

Bakakin *et al.*, (1967) concluded that partial substitution of Be with Li is accompanied by an increase in a and c parameters, the latter increasing more. On the other hand, partial substitution of Al with Li in the beryl structure, maintaining Be constant, promotes a rise in the a parameter. The same authors emphasize that due to the large ionic radius of the Cs (1.67 Å), this element would enter the structural channel as a charge neutralizing ion, causing an increase in the cell unit towards the a crystallographic axis.

Although it is not considered a rule, and despite the lack of consensus on the variations of a and c parameters as a function of the chemical impurities in the beryl structure of pegmatitic origin, the c axis value of beryl can vary with the number of alkalis in the structural channels. Thus, c axis deformation will be higher or lower depending on the type of beryl (more or less rich in alkalis).

Bakakin *et al.* (1970) and Aurisicchio *et al.* (1988, 1994) separated beryl into 5 polytypes: octahedral [$O = (Na, Cs, Rb, K) AlMe_2+Be_3Si_6O_{18}.nH_2O$ and c/a between 0.991 and 0.996], transition between the octahedral and normal ($O-N$), “normal” ($N = Al_2Be_3Si_6O_{18}.nH_2O$ and c/a between 0.997 and 0.998), transition between the normal and tetrahedral ($N-T$) and tetrahedral type [$T = (Na, Cs, Rb, K)Al_2Be_2LiSi_6O_{18}.nH_2O$ and c/a between 0.999 and 1.003].

According to (Aurisicchio, et al., 1988), “normal” beryl (N) exhibits both tetrahedral and octahedral substitutions, without any type of cationic substitution, approximating its theoretical formula.

In type T , beryllium is partially substituted by lithium and sometimes, silicon, in the tetrahedral site, which results in the entry of alkaline elements into the channel. In type O , Al is partially substituted by Fe, Mg, Sc, and Mn among other elements, in the octahedral site.

1.1. Geological Context

The Monte Santo emerald deposit is inserted within an important regional geotectonic unit named Tocantis Province, central Brazil (Almeida et al. 1976), which was formed during the large Neoproterozoic orogenic event (900-600 Ma) called Brasiliano-Pan Africano, result of the convergence and collision of the Amazonian, São Francisco-Congo and Parapanema continental blocks (Brito Neves et al. 2014, Fuck et al. 2017).

The Monte Santo emerald deposit is located in the southern portion of the Araguaia fold/thrust belt domain, which present elongated shape at north-south trend and put together psammict and pelitic metamorphic rocks, as well as carbonate, mafic-ultramafic and granitic rocks (Alvarenga et al. 2000). The Monte Santo emerald deposit occurs in the contact zone between syntectonic granitoids with pods-type shape and amphibolites/metavolcano-sedimentary lithologies related to the Neoproterozoic Estrondo Group (CPRM 1997).

2. Experimental and Analytical Methods

2.1. Samples and Preparation

A batch of emerald crystals of assorted quality, color and size, was donated during a field trip to the mine, so that this research could be carried out. Care was taken to use the samples that at least one face of the crystal could be identified, between subhedral to euhedral and based on their apparent homogeneities. The samples were catalogued and separated according to a color scale ranging from light to dark green, where the relationship of the color with the results of the analysis could be observed. A total of 60 emerald samples were selected, prepared, and analyzed in the present study. The samples were georeferenced with the point of the extraction in situ at the "garimpo (G4)", followed by the numbering used for cataloguing the samples. All the sample preparations were performed in the Laboratory of Petrography of the University of Brasília-UnB, Brazil.

2.2. X Ray Diffraction (XRD)

2.2.1. Single-Crystal X-Ray Diffraction

In single-crystal X-ray diffraction analysis, 16 emerald samples were analyzed. The samples were prepared to reach a particle size of approximately 1 mm, required to perform XRD analysis using the single-crystal method.

The data from the 8 crystals analyzed were collected in a Bruker Kappa APEX II DUO diffractometer, using Mo- $K\alpha$ radiation ($\lambda = 0.71073$), at ambient temperature. Analyses were conducted at the Single-crystal X-ray Structural Crystallography Laboratory of the Department of Physics of the Universidade Federal do Ceará (UFC).

The crystallographic structures were obtained using the Vesta crystallographic program.

2.3. Electron Microprobe Analysis (EMPA)

Electron microprobe analysis were used for measuring major, minor and trace elements in about 20 samples with a total of 260 spot analysis of the Monte Santo emeralds.

Wavelength dispersive spectrometry (WDS) was carried out using a JEOL JXA-8230 microprobe and five WDS detectors with LDE1, LDE2, TAP, PET/L-H and LIF-L/H crystals. A JEOL energy-

dispersive spectrometer (EDS) coupled to a microscope was also used for control. Analyses were performed under acceleration voltage of 15 kV, current of 20 nA and bandwidth of 5 μm . Analysis time varied from 20 to 80 seconds per element, according to the expected abundance in the mineral.

For analysis, the samples were coated with conductor material (carbon) in a JEOL-JEE-420 vacuum evaporator. EMPA was conducted at the Centro Regional para Desenvolvimento Tecnológico e Inovação (CRTI) of the Universidade Federal de Goiás (UFG).

3. Results and Discussions

3.1. Single-Crystal X-Ray Diffraction

The results of XRD analyses using the single crystal method are presented in table 1 below. The acquired results were used to plot the graphs relating the samples and the values of their crystallographic axes "a" and "c", in addition to determining the ratio between the axes c/a .

Table 1 Single-crystal X-ray diffraction data collection.

Sample	a_0 (Å)	c_0 (Å)	c_0/a_0
TO_G4_01	9,2904	9,2143	0,9918
TO_G4_03	9,2635	9,2054	0,9937
TO_G4_L02_01	9,2438	9,2078	0,9961
TO_G4_L02_02	9,2843	9,2167	0,9927
TO_G4_L02_03	9,2852	9,2127	0,9922
TO_G4_L02_04	9,2537	9,2070	0,9950
TO_G4_L02_06	9,2660	9,2262	0,9957
TO_G4_L07_01	9,2789	9,2262	0,9943
TO_G4_L07_05	9,2778	9,2283	0,9947
TO_G4_L08_02	9,2988	9,2340	0,9930
TO_G4_L09_03	9,2719	9,2102	0,9933
TO_G4_L11_03	9,2819	9,2105	0,9923
TO_G4_L12_01	9,2661	9,2291	0,9960
TO_G4_L12_02	9,2902	9,2253	0,9930
TO_G4_L12_03	9,3027	9,2376	0,9930
TO_G4_L12_04	9,2815	9,1831	0,9894

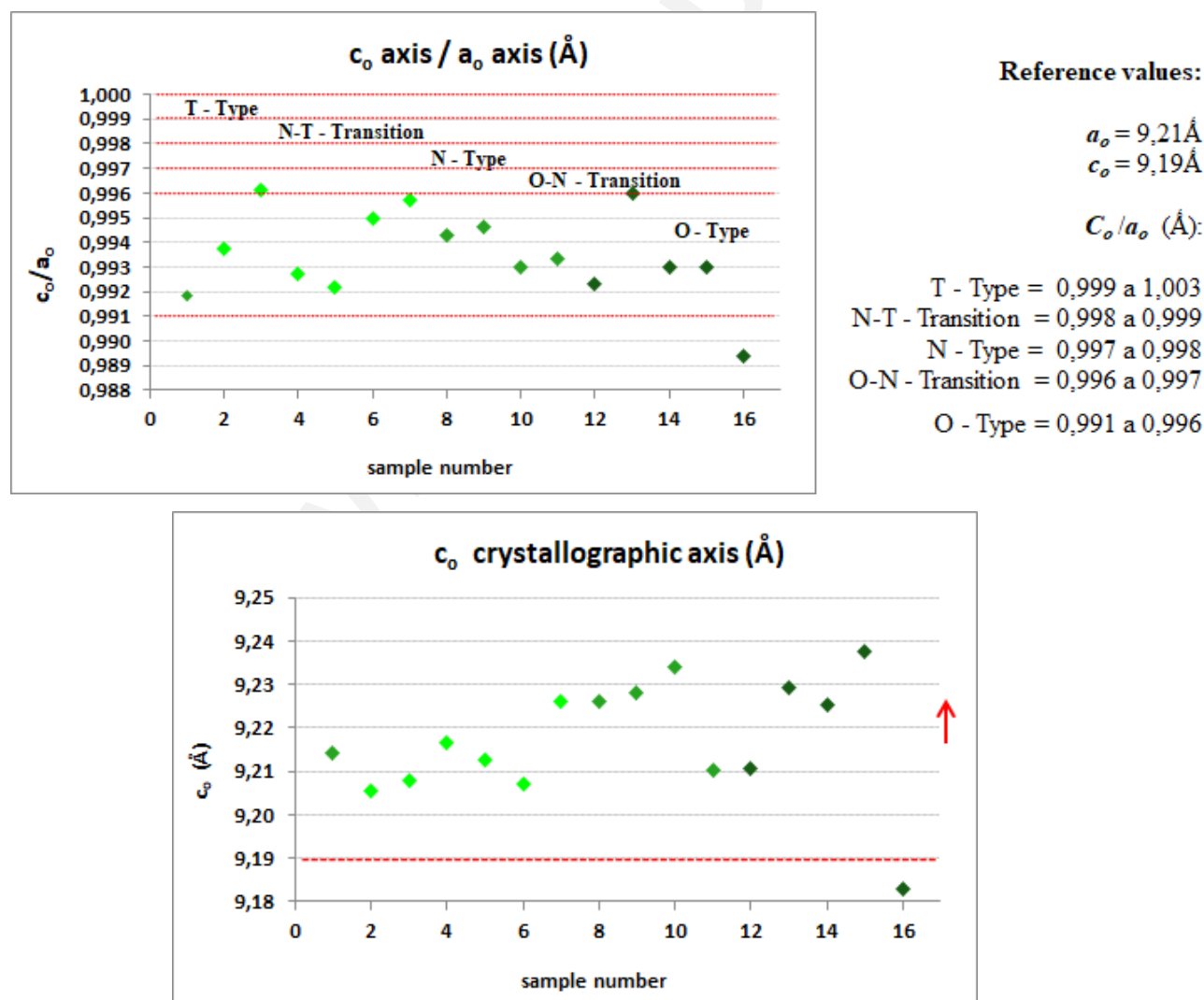
The variations in the axis values are related both to the presence of alkali in the mineral's structure and to chemical substitutions in the tetrahedral and octahedral sites. These substitutions result in changes in the axial parameters and represent distortions in the crystallographic axes, which can be observed based on the ideal values for each one of the axes.

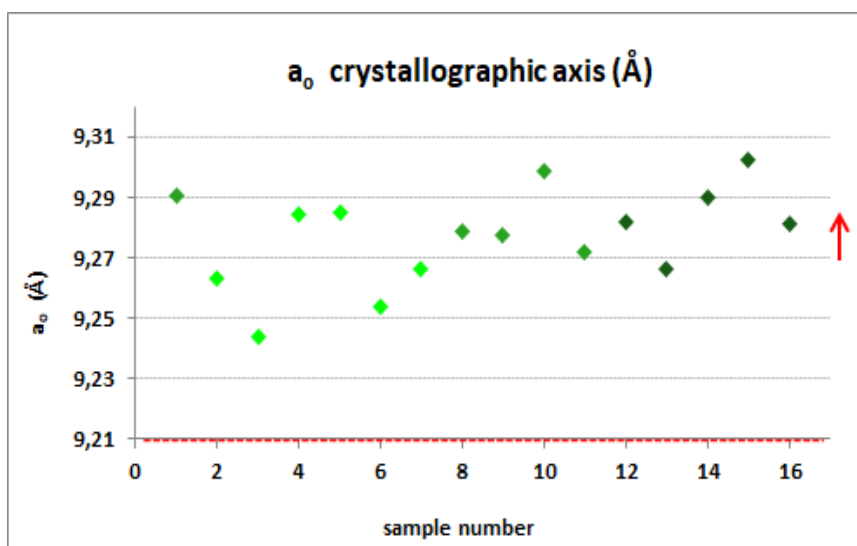
In the analyzed samples the c axis increases to above-ideal values, ranging from 9.1831-9.2376 Å. This increment is related to the content of alkalis present in the mineral structure.

The **a**-axis also increases to above-ideal values, ranging from 9.2438-9.3027 Å. According to Deer *et al.* (1992) and Sampaio Filho *et al.* (1973), this result is due to the entry of metal transition elements (and alkalis) into the beryl structure. The **a**-axis increases nearly twice than the increment reported by the **c**-axis.

Based on the calculation of the "**c/a**" ratio, it is possible to determine the crystallographic site where the substitutions occur, allowing a classification of the beryl into polytypes. According to the acquired results and their subsequent plotting in graph 3, about 93.8% of the samples analyzed were classified as O-type, indicating that the substitutions occur mainly in octahedral sites.

Figure 1 Axial parameters for the Monte Santo beryl unit cell, presenting the **c_o/a_o** ratio, **c_o** axis and **a_o** axis, respectively. The red line represents reference values, according to Aines & Rossman, 1984, Aurisicchio, et al., 1994 and others. Reference Values for **a** and **c** crystallographic axes: **a_o** = 9,21 Å; **c_o** = 9,19 Å. Reference Values for **c_o/a_o** ratio (Å): 0,999 to 1,003 = T-type; 0,998 to 0,999 = N-T-transition type; 0,997 to 0,998 = N-type; 0,996 to 0,997 = O-N-transition type; 0,991 to 0,996 = O-type;

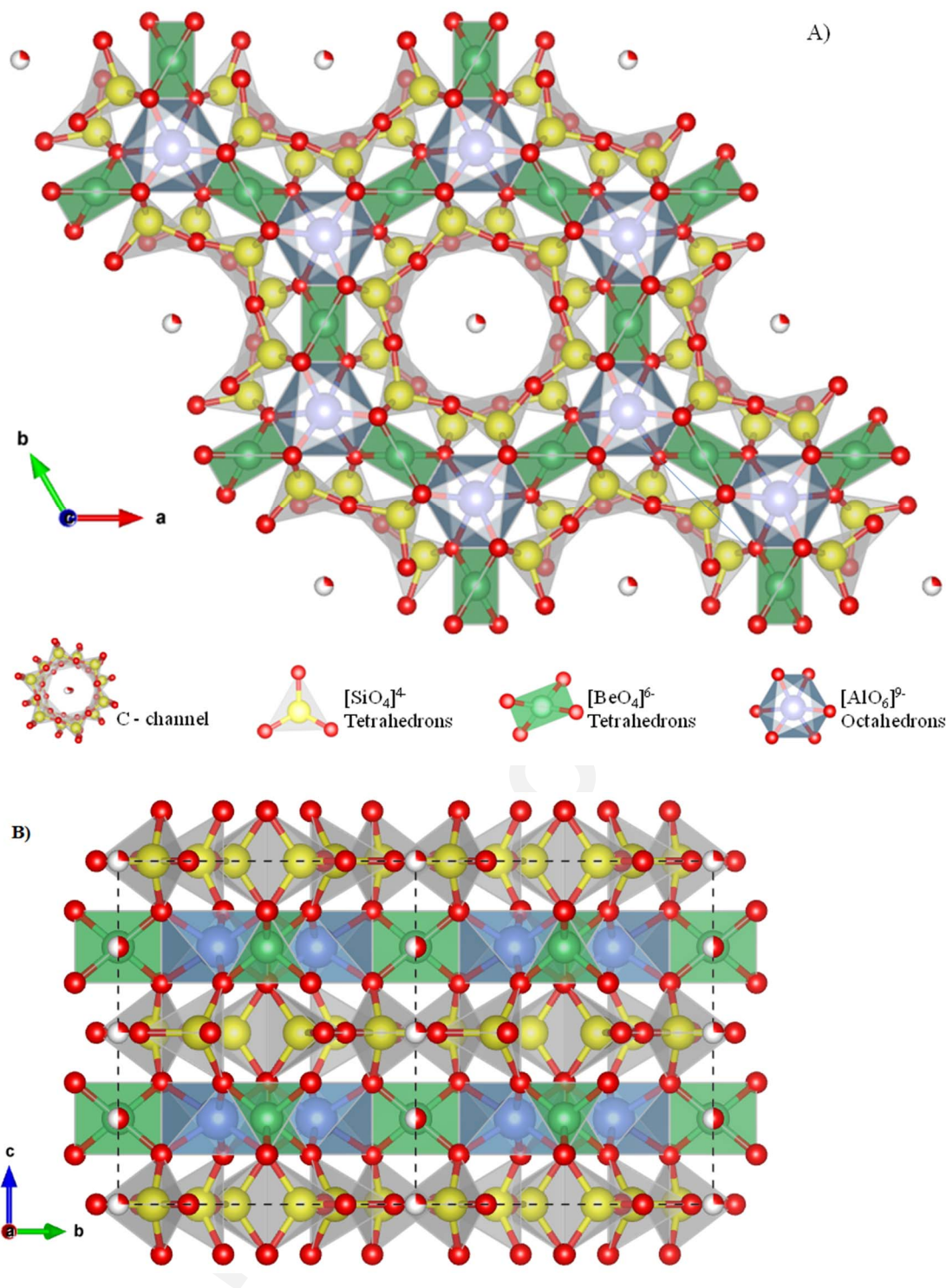




Data obtained from XRD analysis in single crystals were also used to create crystallographic models for the Monte Santo emerald samples analyzed (Figure 2). The crystallographic models were built using the Vesta software (Momma & Izumi, 2011).

In the structure obtained for the beryl samples, hexagonal rings were formed by six Si-O tetrahedra, where these rings are linked and reticulated by Al^{3+} atoms in octahedral coordination and by Be^{2+} atoms in tetrahedral coordination (Figure 2), in the basal plane projection (a). These hexagonal rings are reticulated along the c axis, according to the lateral projection (b).

Figure 2 Beryl structure analyzed, obtained from refined XRD data using the single-crystal method and Vesta software. A) Basal plane projection; B) Lateral plane projection.



Source: the author, using Vesta software.

3.2. Electron Microprobe Analysis (EMPA)

The results obtained in electron microprobe analysis are equal to the theoretical percentage of elements that can be measured by the equipment (86% for beryl), illustrated in Table 2 below. The

water content is often difficult to measure directly, but due to its link to the Na content, it was possible to calculate by applying the equation proposed by Marshall *et al.* (2016).

Table 2 Average compositions of emerald samples.

Element	Min - Max	Average	Element	Average
SiO ₂ (wt%)	62.746 - 66.373	64.267	Si ⁴⁺ (apfu)	6.0357
Al ₂ O ₃	12.457 - 17.331	13.996	Ti ⁴⁺	0.0004
MgO	0.836 - 3.883	2.812	Al ³⁺	1.5531
V ₂ O ₃	0.013 - 1.340	0.432	Sc ³⁺	0.0200
Cr ₂ O ₃	0.012 - 1.115	0.263	V ³⁺	0.0285
FeO (total)	0.047 - 0.507	0.204	Cr ³⁺	0.0192
Na ₂ O	0.550 - 2.152	1.686	Mg ²⁺	0.3945
K ₂ O	0.008 - 0.492	0.196	Ca ²⁺	0.0047
Cs ₂ O	bdl - 0.042	0.008	Fe ²⁺	0.0164
Sc ₂ O ₃	0.012 - 1.327	0.286	Ba ²⁺	0.0014
SrO	0.193 - 0.349	0.278	Mn ²⁺	0.0005
CaO	0.001 - 0.221	0.045	Sr ²⁺	0.0152
BaO	bdl - 0.217	0.044	Na ⁺	0.3070
CuO	bdl - 0.075	0.019	K ⁺	0.0007
CoO	bdl - 0.034	0.006	Cs ⁺	0.0003
Bi ₂ O ₃	bdl - 0.059	0.007	H ₂ O	
TiO ₂	bdl - 0.088	0.008		
ZrO ₂	bdl - 0.118	0.011		
Ga ₂ O ₃	bdl - 0.011	0.0001		
ZnO	bdl - 0.063	0.007		
MnO	bdl - 0.035	0.006		
UO ₂	bdl - 0.048	0.006		
PbO	bdl - 0.068	0.011		
ThO ₂	bdl - 0.041	0.005		
Gd ₂ O ₃	bdl - 0.157	0.023		
Ce ₂ O ₃	bdl - 0.064	0.014		
La ₂ O ₃	bdl - 0.015	0.001		
Cl	bdl - 0.020	0.004		
*BeO	12.65 - 14.06	13.28		
**H ₂ O	1.96 - 2.94	2.66		

*BeO assumed as 3 apfu, and 8 Si + M site cations for normalization; ** H₂O content calculated from the equation $H_2O \text{ (in wt\%)} = [0.6097 \times Na_2O \text{ (wt\%)}] + 1.6290$ (Henry, et al., 2021).

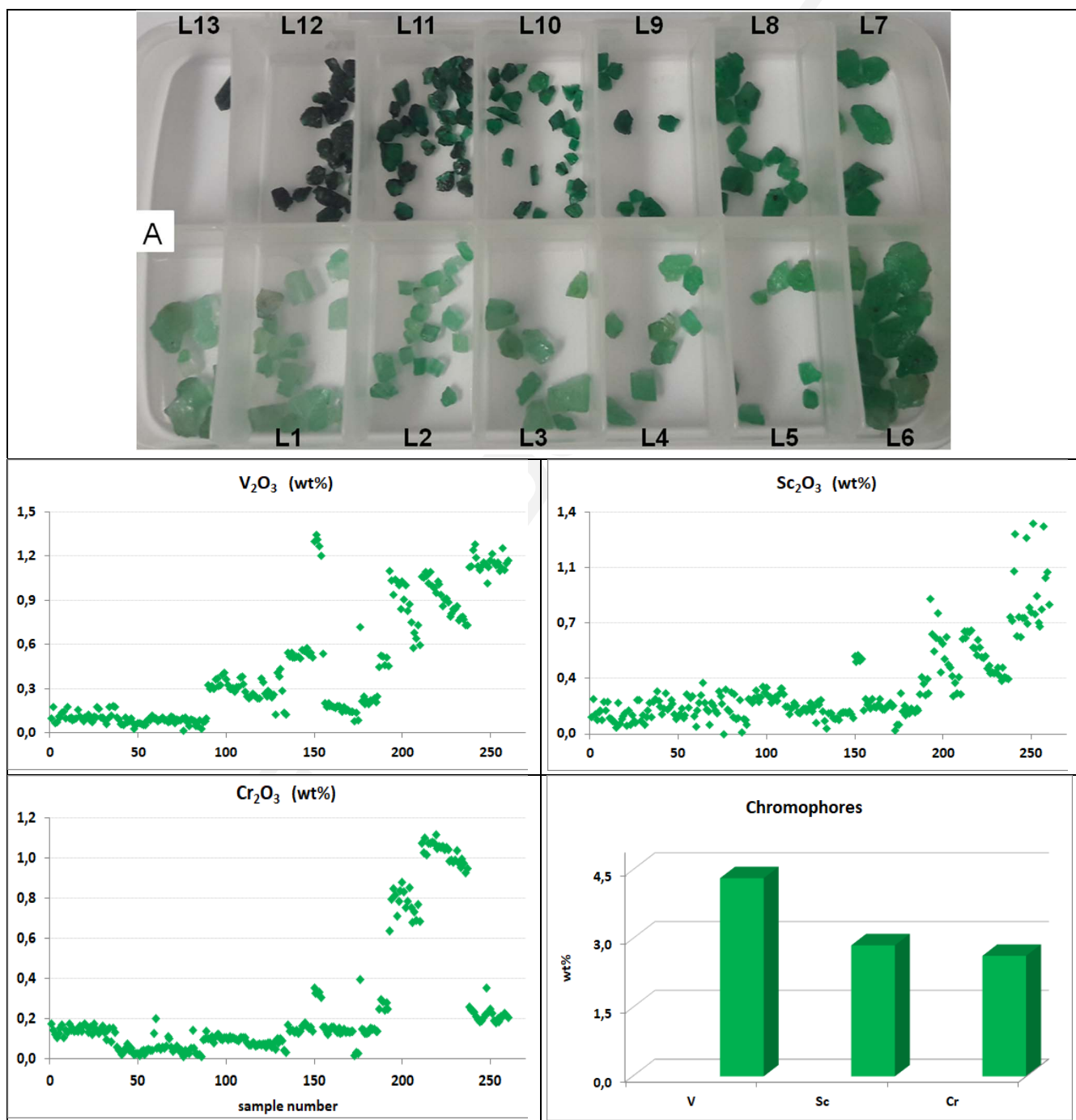
In order to establish trends for association between the chemical composition obtained for the different shades of green (figure 3A) variation graphs (figures 3B and 4) were created.

The main occupant of the octahedral site is Al, which ranges from 65,7% to 91,4% of the total site occupancy. Mg, Fe, V, Cr, Sc, Ca and Ba ions are the main substitutes for Al (Fig. X), in the order $Mg > V > Sc > Cr > Fe > Ca > Ba$. Sodium is the predominant cation in the channels and its content is mainly controlled by the octahedral site substitutions, for charge balancing (Fig. X).

The most important chromophore elements in the Monte Santo emerald are V (avg. 4322 ppm), followed by Sc (avg. 2858 ppm) and Cr (avg. 2628 ppm), as can be seen in the figure 3B. Although it is less common, Sc is also considered a coloring element, which may confer a pale green color to

minerals (Mellini et al., 1982). Fe (avg. 2045 ppm) may also contribute to the colour but to a lesser extent.

Figure 3 A) Emerald samples separated according to a color scale, showing the relationship between color and chemical analysis result; B) Graphics of the main chromophore elements content (average wt%) of emeralds from the Monte Santo deposit, obtained by electron microprobe analysis. Graphics of the correlations between the oxides percentage composition and the colours of the emerald samples, obtained by electron microprobe analysis.



The theoretical percentage of beryl is $\text{BeO} \cong 14\%$, $\text{Al}_2\text{O}_3 \cong 19\%$ and $\text{SiO}_2 \cong 67\%$ (Deer *et al.* 1966), and according to the procedures (Bakakin & Belov, 1962) apud (Gandini, 1999), summarized below, we can identify the possible positions of the different cations in the beryl structure:

Si⁴⁺ - occupying tetrahedra $[\text{SiO}_4]^{6-}$. In excess, it can substitute Be in the tetrahedron $[\text{BeO}_4]^{6-}$;

Al³⁺ - occupying octahedra $[\text{AlO}_6]^{9-}$. In excess, it enters the tetrahedra, due to its amphoteric nature, substituting Si and Be;

Be²⁺ - occupying tetrahedra $[\text{BeO}_4]^{6-}$ or jointly with Si in the tetrahedra $[\text{SiO}_4]^{4-}$. Under Si and Al deficiency, Al is preferentially substituted;

Cr³⁺, V³⁺, Sc³⁺, Fe^{2+/3+}, Mg²⁺, Mn²⁺, - substituting Al in the octahedra $[\text{AlO}_6]^{9-}$; **Fe²⁺** may also be present in the channels;

Na⁺, Ca⁺ - in the channels, associated with one or two H-O-H groups and rarely, in the spaces between the rings;

K⁺ - in positions similar to those of the H-O-H group in the channels, and sometimes in the positions occupied by Rb⁺;

Rb⁺ - in the channels between H-O-H and three oxygens of a ring, significantly deformed;

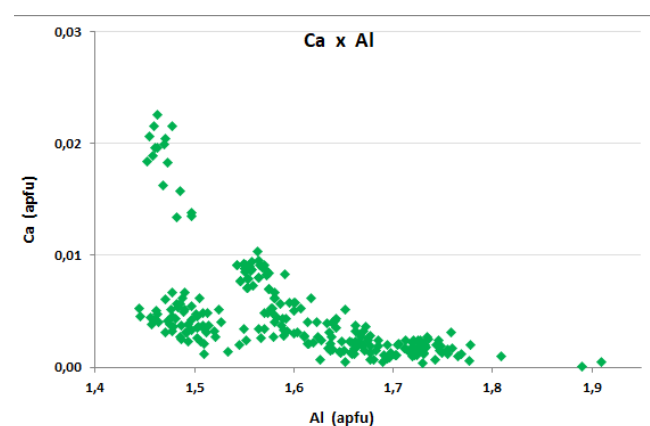
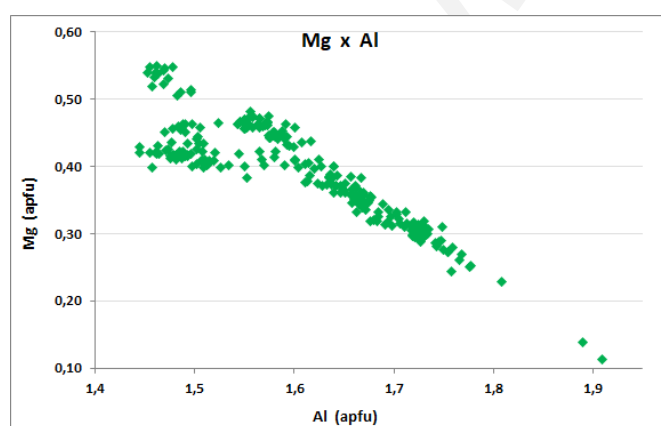
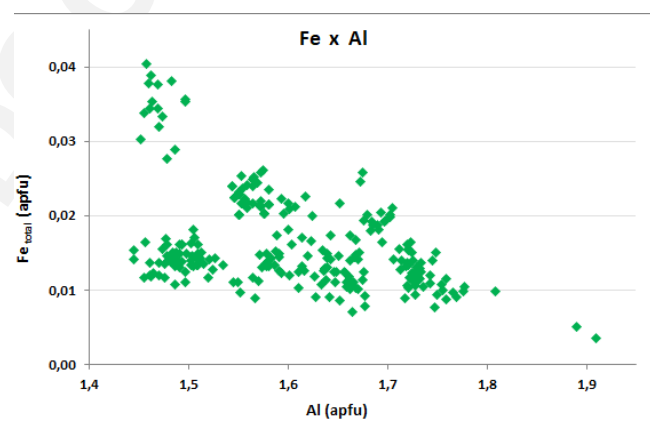
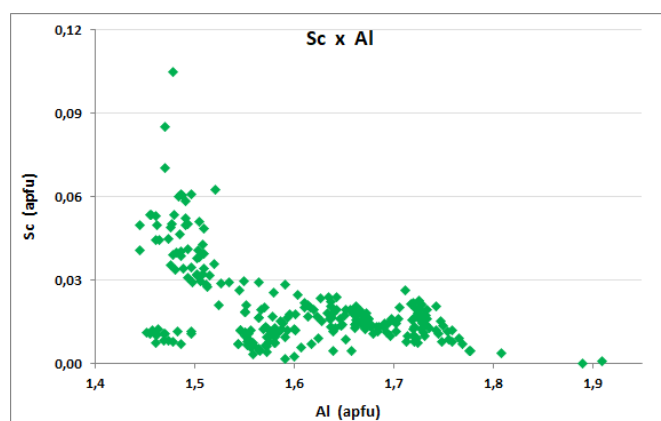
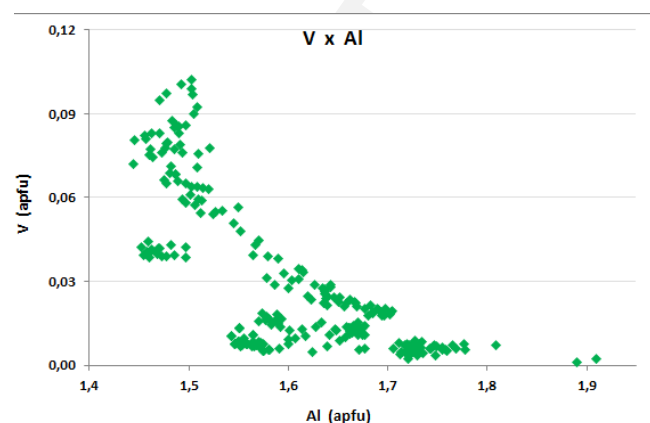
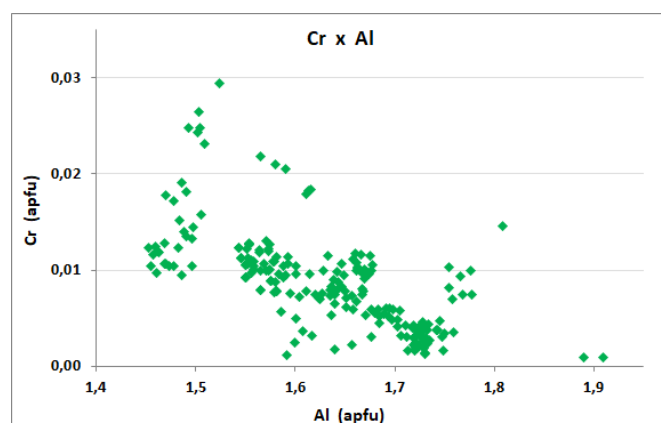
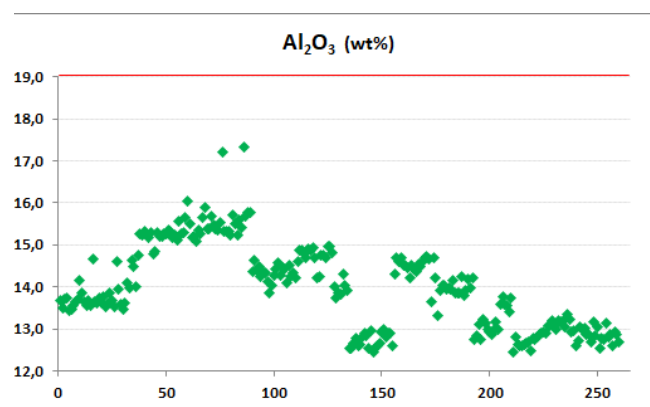
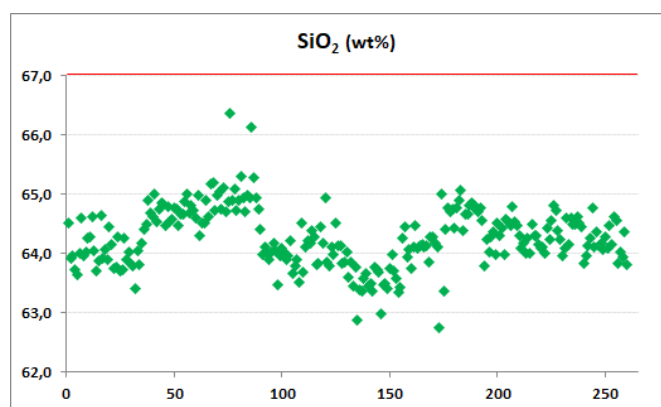
Cs⁺ - in the channels, analogous to the Rb⁺, but only with slight ring distortion;

Li⁺ - a) in the Al positions, not substituting it, but occupying voids when there is a deficiency of Al; b) in the Be positions; c) when there is an excess, it rarely enters the special positions in the spaces between the rings.

Considering the ideal amount of SiO_2 of approximately 67% for beryls, there is a clear trend towards Si deficiency for the analysed samples (~64.26 wt % on average). In the case of deficiency, this lack can be compensated by the entry of Al, substituting Si, or Be along with Si in the tetrahedra $[\text{SiO}_4]^{4-}$.

Regarding to the ideal amount of Al_2O_3 in beryls, which is around 19%, there is a remarkable decrease (~13.99 wt % on average) of this element in the octahedral site. This deficiency is clearly compensated, at least partially, by the entry of transition metal elements such as Mg, V, Sc, Cr and Fe into its crystallographic position. If Al deficiency is not compensated by the entry of those transition metal elements, Li⁺ may enter, not as a substitution for Al, but occupying voids to balance the deficiency. Al deficiency is clearly inversely proportional to Mg, V, Sc, Cr and Fe concentrations in the analyzed samples (figure 4).

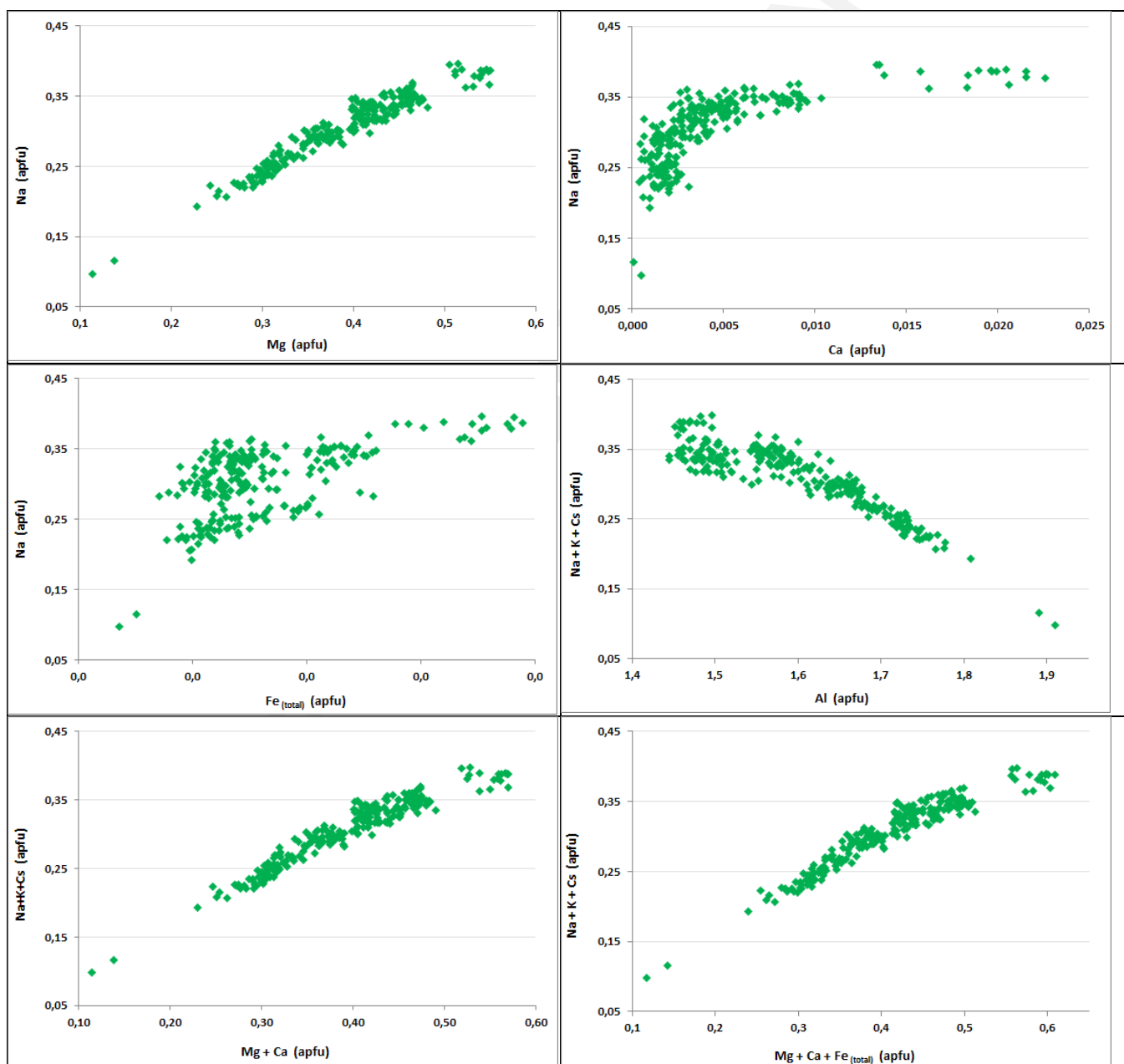
Figure 4 Graphics of the theoretical percentage of Al_2O_3 and SiO_2 , and the correlations between the main occupant of the octahedral site.



Schwarz (1994) suggested that a Na_2O content of emeralds <1 wt % is considered low, 1 wt % $<$ medium < 2 wt % and >2 wt % high. The analyzed samples feature a Na_2O content ranging from 0,55 to 2,15 wt%, which allows us to classify them as ranging from low to high Na_2O content.

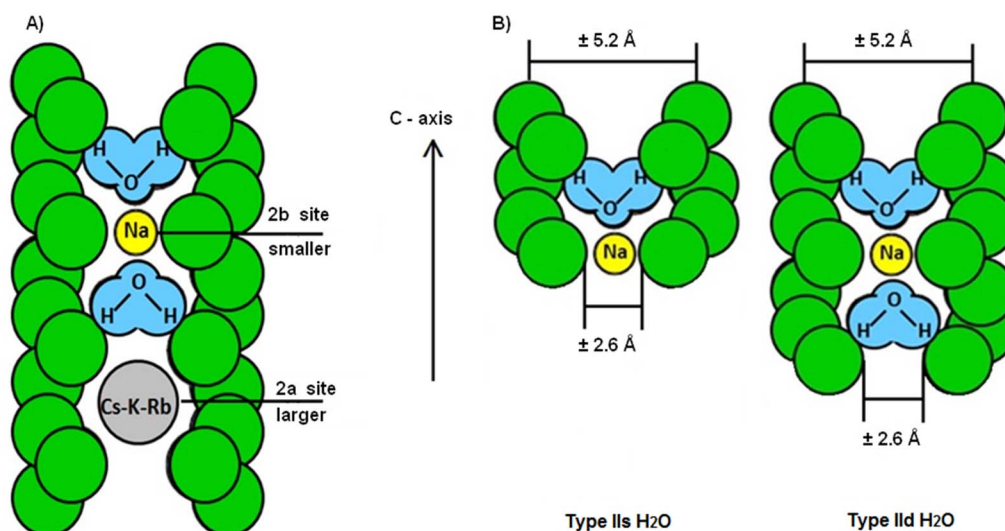
The sum content of the alkali metal ions Na (avg. 16865 ppm), K (avg. 1958 ppm), and Cs (avg. 78 ppm) in the structural channel of the Monte Santo emerald indicates that it is moderate to alkali-rich.

Figure 5 Correlation graphs between the occupant bivalent cations of the octahedral site and the predominant cations in the channels for charge balancing.



In natural beryls, the structural channels are generally partially filled by alkaline elements, such as Na, Rb, Cs and K, transition metal ions and small molecules such as H₂O, CO₂ and other impurities (Figure 6A). The alkaline elements in the structural channels play an important role in balancing deficient charges, which may occur due to heterovalent substitutions in the octahedral and tetrahedral sites of the beryl structure. Among the channels, Na⁺ is incorporated preferentially in the center of the Si rings in the smaller crystallographic sites (2b) (0,0,0), where it may be coordinated with a single type II water molecule, called “type IIs” or even coordinated with two type II water molecules, called “type IId” (Figure 6B), while Cs⁺, Rb⁺ and K⁺, because their ionic radii are larger, preferentially incorporate the larger 2a crystallographic site (0,0,1/4) between the rings.

Figure 6 Schematic diagram of beryl channels, where A) the larger (2a) and smaller (2b) crystallographic sites are demonstrated along the *C* axis, within the channels, with their possible occupations and water molecule types; and B) the different H₂O coordination (type IIs and IId) with the Na alkaline cation.



Source: Modified by the author from (Wood & Nassau, 1967), (Aurisicchio, *et al.*, 1988) and (Aurisicchio, *et al.*, 1994).

4. Conclusions

The beryl samples analysed display a range of green shades varying from light to dark green, and are often transparent and present good quality.

The presence of three elements as a chromophore in the Monte Santo samples is quite fascinating and unexpected. Scandium as a chromophore element in emerald and its concentration is an

unprecedented major result on this research, whereas only a few and rare specimens of emeralds worldwide have this element in their composition and, those that do, have a much lower concentration when compared to the results of the Monte Santo emerald.

Based on the greater content of V_2O_3 than Cr_2O_3 , the Monte Santo emerald is here classified as a vanadium-dominant emerald.

Chemical analyses detected alkaline elements such as K^+ , Cs^+ and Na^+ , present in the "c" channels, with the latter ranging from low to high concentration.

In addition, trace amount of the elements Sr, Mn, Zn, Zr, Cu, Ba, Gd, Ce, La, Th, U, Pb, among others, were also detected in the crystalline structure of the emeralds.

Based on the c_0/a_0 ratio, obtained by XRD analyses, the emerald samples were classified as O-type beryl, with the substitutions in the octahedral site predominating.

A statistically significant study requires a large number of samples from one locality (e. g. between 10 and 30 sample). Such a large number of samples is available from only a few of the known emerald localities. The large number of samples studied in this research allowed establishing correlations and variances between the chemical composition and the crystallographic characteristics of these emeralds, as well as providing reliable results, despite the inherent heterogeneities that a mineral deposit displays.

Acknowledgements The authors would like to thank the Instituto Nacional de Ciência e Tecnologia de Estudos Tectônicos (INCTET - UnB), for all the support that made the project possible; to the Single-Crystal X-ray Structural Crystallography Laboratory of the Universidade Federal do Ceará (UFC) Department of Physics, and the Centro Regional para o Desenvolvimento Tecnológico e Inovação (CRTI) of the Universidade Federal de Goiás (UFG), for their support in developing the present research. We also thank the Geosciences Institute of the Universidade de Brasília (UnB). This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001. RAF thanks CNPq for research fellowship.

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THE MONTE SANTO EMERALDS, FROM TOCANTINS STATE, BRAZIL: CHEMICAL AND FLUID INCLUSIONS ANALYSIS

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ABSTRACT

The Monte Santo Emerald, from Tocantins State, Central part of Brazil, has been studied to determine its chemical composition, depositional-fluid characteristics, pressure-temperature emplacement conditions, and formational model. The Monte Santo emerald is vanadium- dominant, with considerable amounts of Cr. Among significant known deposits, Monte Santo emerald has a very unique chemical composition in its combination of high V and Sc, moderate to high Cr, and low to moderate Fe concentrations. The relative chemical diversity of emeralds from worldwide deposits allows confidence in origin determination in most cases. A distinctly higher Sc concentration is the main criterion that separates the Monte Santo emerald from its worldwide counterparts.

Emerald is among the best hosts for fluid inclusions. The origin of the parental fluid and the crystallization process of the Monte Santo emerald is very complex and the study of fluid inclusions helps to understand its formation. The emerald deposit genesis is consistente with a multi-stage mineralizing episode derived from both metamorphic and magmatic contributions.

The petrographic description of fluid inclusions (FIs) allows their division into four distinct types and they represent aqueous, carbonic, and aquocarbonic fluids. The observed characteristics, such as distinct compositions, large variations of gaseous volume in the same group, widely varied salinities, and the spatial and temporal relationships of the types of FIs, allow a previous interpretation of their origin associated with an environment with mixture of fluids originating from distinct sources, common in a tectonometamorphic environment, which allow multi-stages of emerald formation linked to cyclic remobilization of fluids. Devolatilization during the metamorphic process is noted as the main source of CO₂ and CH₄ for carbonic and aquocarbon fluids. Evidence of boiling and carbonaceous phase separation are identified as processes during heterogeneous trapezoiding and post trapping features such as *leakage*, *necking down* e *stretching*. Four dominant fluid inclusions types are identified as follows:

two-phase (vapour+liquid) and three-phase (brine+-vapour+halite) fluid inclusions and these are interpreted to represent conjugate fluids of a boiling system. The emerald was precipitated from these saline fluids with approximate overall salinities on the order of XX mass per cent NaCl equivalent. Raman analyses indicate molar gas fractions for H₂O, CO₂, N₂, and CH₄. Formational temperatures and pressures of approximately X-X°C and below X bars were derived from fluid inclusion data and lithostatic pressure estimates from fluid inclusion studies.

Keywords: V-dominant Emerald; Geographic Origin Determination; Geochemistry; Mineralogy.

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1. INTRODUCCION

Emerald is one of the most commercially interesting gemological varieties of the mineral beryl. It is generally formed in geological environments involving metasomatism, marked by the introduction of fluids rich in Be, in contact with rocks or fluids rich in chromium (Cr^{3+}) and/or vanadium (V^{3+}), under specific conditions of temperature and pressure.

The genesis of emerald deposits is linked to the intense percolation of fluids, allowing for metasomatic (fluid-rock) exchange, whether in a magmatic or metamorphic environment. In general, magmatic environments tend towards saline aqueous fluids (H_2O -NaCl), with a smaller contribution of aqueous carbonic fluids (H_2O - CO_2 -NaCl). On the other hand, metamorphic environments tend toward a mixture of H_2O -NaCl and H_2O - CO_2 - CH_4 -NaCl fluids with high salinities.

Emerald deposits are commonly subdivided into three main models (Giuliani et al., 2015) apud (Marshall, et al., 2017): a) The most common occurs in granitic and pegmatitic intrusions in contact with ultramafic and mafic rocks or shales, rich in Cr ($\pm\text{V}$), promoting strong metasomatism (Loughrey et al., 2013); b) The second model involves a similar process of Be-rich fluids derived from metamorphism of granitic and sedimentary quartz-feldspathic rocks, concentrated along major faults, fractures, or shear zones; and c) The third model still involves a similar mixture of Be and Cr ($\pm\text{V}$) chemistry, but occurs at relatively low temperatures, usually in the range of 250 to 350°C, and depends on fluid reduction (Ottaway et al., 1994, Hewton et al., 2013).

Studies report that emerald deposits in the world without evidence of magmatic activity, such as the Colombian emeralds, are associated with saline fluids of evaporitic or metamorphic origin (Keith et al., 2002, Franz & Morteani, 2002). The variations in the chemical composition of the beryl, particularly the content in fluids, alkalis and H_2O , are intimately correlated with the geochemical and paragenetic characteristics of the geological systems where the varieties of beryl are generated (Beus, 1966).

Although considered rare, emerald is found in all five continents of the world. Brazil is one of the most important producers of emeralds, with many occurrences located in the center-southeast and northeast parts of the country.

The emerald occurrences studied are located in the central portion of the Tocantins State, in the geological context of the Araguaia Belt. The discovery of emeralds in the Tocantins State, Brazil, occurred in 1996. Its dissemination resulted in a large flow of "garimpeiros" to the area, leading to the creation of the "Cooperativa de Garimpeiros de Monte Santo - COOPERGEMAS" (CPRM, 1997).. The mining area is located at the south part of the Monte Santo village, and Paraíso do Tocantins is the closest municipality.

The mineralized zone is in tectonic contact between mafic schists, paragneisses and albitite lenses, with emerald crystals occurring mainly in biotite lenses/pockets. The crystals are generally euhedral, weakly to moderately fractured, sometimes zoned, and range in color from moss green to

bluish green. The emeralds occur in pockets, like scattered crystals in biotite, and associated with aggregates of quartz, tremolite, flogopite and biotite. It was suggested by CPRM (1997), according to the Schwarz's classification (1987), that these are type I occurrences, characterized by the association of mafic-ultramafic rocks or their metamorphic derivatives, supplying Cr, V, Fe, and of pegmatites supplying Be, from the interaction of their fluids.

We present results from a detailed study of fluid inclusions and chemical composition to characterize the emeralds from Monte Santo. Our findings can provide insights that can be used for both, understanding the genesis of the emeralds in this deposit, and also shedding light on the geographic origin separation of this emerald deposit from its counterparts.

1.1 Contexto Geológico Regional

The emerald occurrences studied here are located in the central portion of Tocantins state, in the geological context of the Araguaia Belt. Emeralds were discovered in Tocantins in 1996. Their dissemination resulted in a large flow of prospectors ("garimpeiros" in Portuguese) to the area, leading to the creation of the "Cooperativa de Garimpeiros de Monte Santo - COOPERGEMAS" (CPRM, 1997). The mining area is located in the southern part of Monte Santo city, and Paraíso do Tocantins is the closest municipality.

The Araguaia Belt (CA) is a Neoproterozoic to Cambrian orogenic belt, located in the northern portion of Tocantins Province (Figure 1), formed during the Neoproterozoic in the Brasiliano/Pan-African) Orogeny (Almeida *et al.*, 1976) (Hasui *et al.*, 1977) (Alvarenga *et al.*, 2000). It is about 1200 km long in the N-S and 110 km wide in the E-W direction, bordered to the north and east by the Parnaíba Basin, to the west by the Amazon Craton, to the southwest by the Bananal Basin and to the south and southeast by the Transbrasilian Lineament. It is composed of Archean and Paleoproterozoic basement rocks, Neoproterozoic supracrustal rocks and syn- to post-collisional granitic rocks of the Ediacaran/Cambrian interface. In this geological context, emerald crystals occur near or inside the contact zone between small bodies of albite granite and amphibolites/shales (Figure 2).

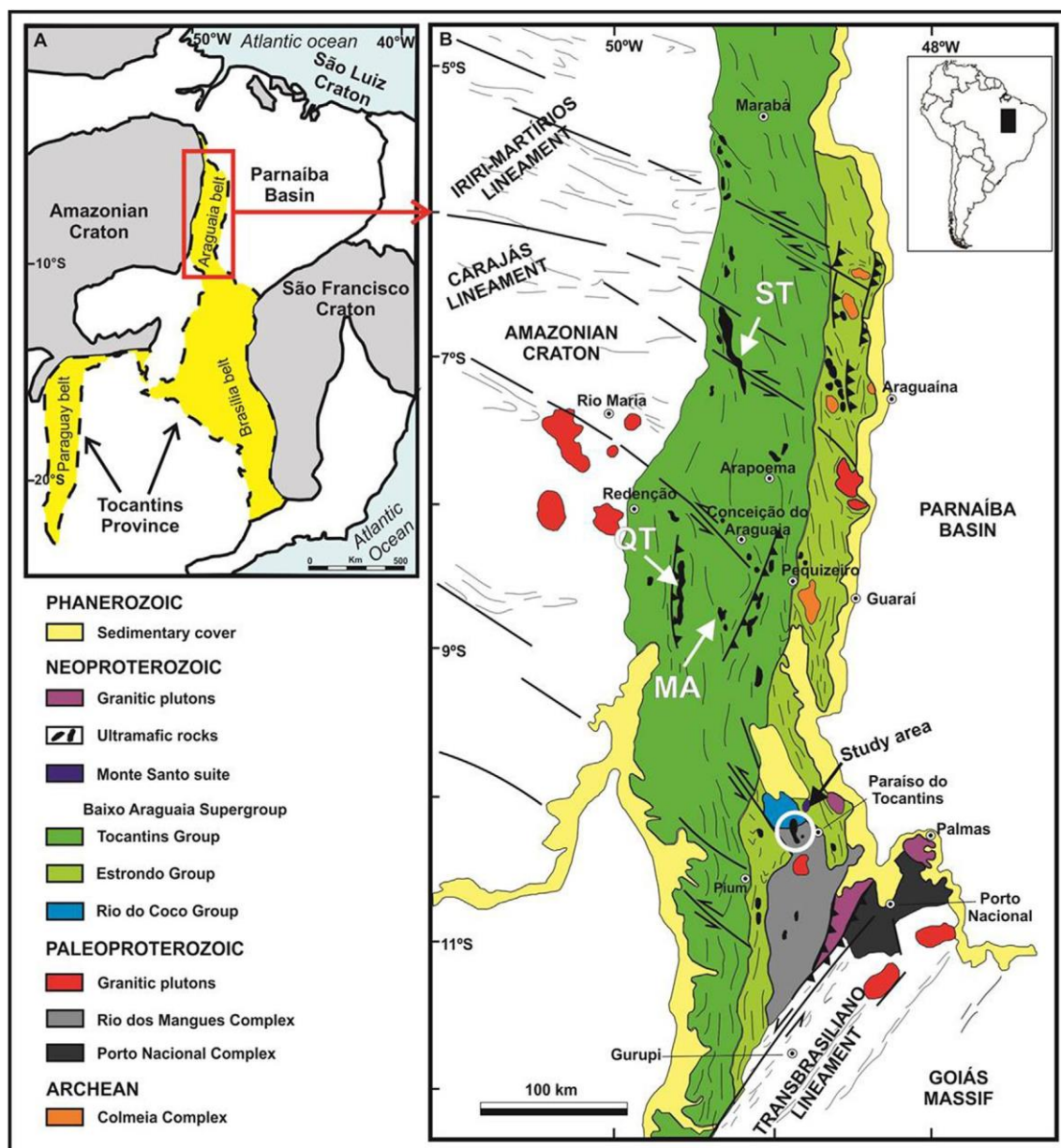


Figure 1: A) Schematic tectonic map of Central Brazil, with the Tocantins Structural Province and the Araguaia Belt highlighted. Adapted from Delgado and Pedreira (1995). (B) Geological map of the Araguaia Belt highlighting the study area. adapted from Alvarenga et al. (2000) and Souza et al. (2019).

Emeralds occur in pockets, as scattered crystals in biotite, and are associated with aggregates of quartz, tremolite, flogopite and biotite (Figure 2). According to Schwarz's classification (Schwarz, 1987), the CPRM (1997) suggested that these are type I occurrences, characterized by the association of mafic-ultramafic rocks or their metamorphic derivatives (amphibolites and shales), supplying Cr, V, Fe, and pegmatites supplying Be, via the interaction of their fluids.



Figure 2: A) Prospect G5 gallery, highlighting the "frizo" (brazilian term prospectors use for the portion of rock where mineralization occurs); B) Emerald crystals contained in the schist; C) Emerald crystals embedded in the contact between the albitized granite and the schist; D) batch of emerald samples from Monte Santo; E) hexagonal euhedral emerald samples; F) green bluish emerald samples; G) zoned emerald sample.

2. MATERIALS AND METHODS

2.1 Samples and Preparation

A batch of emerald crystals of assorted quality, color and size, was donated during a field trip to the mine, so that this research could be carried out. Care was taken to use the samples that at least one face of the crystal could be identified, between subhedral to euhedral and also based on their apparent homogeneities. The samples were catalogued and separated according to a color scale ranging from light to dark green, where the relationship of the color with the results of the analysis could be observed (Figure 3). About 60 emerald samples were selected, prepared and analyzed. The samples were georeferenced with the point of the extraction in situ at the "garimpo (G4)", followed by the numbering used for cataloguing the samples.

All the sample preparations were performed in the Laboratory of Petrography of the University of Brasília-UnB, Brazil.

2.2 Electron Microprobe Analysis (EMPA)

Electron microprobe analysis were used for measuring major, minor and trace elements in 260 spots of the Monte Santo emerald samples. These analyses can determine the geochemical fingerprints in order to help discriminate the geographic origin.

Wavelength dispersive spectrometry (WDS) was performed using a JEOL JXA-8230 electron microprobe, with five WDS detectors with the LDE1, LDE2, TAP, PET/L-H and LIF-L/H crystals. A JEOL energy dispersive spectrometer (EDS) coupled to the microscope was also used for control. The analyses were performed under accelerating voltage of 15 kV, 20 nA current and beam aperture of 5 μm . The analysis time varied from 20 to 80 seconds per element according to the expected abundance in the mineral. For the analysis, the samples were coated with conductive material (carbon) in a JEOL-JEE-420 vacuum evaporator.

The samples preparation was carried out at the Laboratory of Petrography of the Institute of Geosciences -IG of the University of Brasília-UnB, Brazil. The Electron Microprobe Analysis (EMPA) were performed at the Centro Regional para o Desenvolvimento Tecnológico e Inovação-CRTI of the Federal University of Goiás -UFG, Brazil.

2.3 Fluid Inclusions

The fluid inclusion investigations were performed on five samples in bipolished thin sections with a thickness of around 0.2 mm and cut in parallel and perpendicular directions to the *c*-axis of emerald crystals. The samples were then subjected to petrographic, microthermometric, and micro-Raman spectroscopy investigations.

The petrographic study of the fluid inclusions was performed under a transmitted and reflected light petrographic microscope at room temperature (± 25 °C). The fluid inclusion groups were divided and described based on their mode of occurrence, spatial and temporal relationships, morphology, number of phases, phase ratio, and nature of fluids.

The samples preparation was carried out at the Laboratory of Petrography of the Institute of Geosciences -IG of the University of Brasilia-UnB, Brazil. The Electron Microprobe Analysis (EMPA) were performed at the Centro Regional para o Desenvolvimento Tecnológico e Inovação-CRTI of the Federal University of Goiás -UFG, Brazil.

Raman spectra were recorded using a Horiba-Jobin Yvon (Labram type) Raman microspectrometer at the Unicamp laboratory, State University of Campinas, São Paulo. The Raman microspectrometer is equipped with an Edge filter, a holographic grating with 1800 grooves per millimeter, and a liquid nitrogen-cooled CCD detector. The excitation radiation at 514.5 nm was provided by an ionized Argon laser (Spectra physics); the laser was focused on the sample using an 803 objective (Olympus) for these analyses. Raman spectra were measured in the host crystal close to the inclusions in order to check for the possible contribution of atmospheric N₂ using the method outlined by Dubessy et al. (1989). The measurements were carried out at room temperature.

2.4 Raman microscopy measurements

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3. RESULTS

Through the performed analyses, it is possible to notice that the color of emeralds is represented by a set of mechanisms, such as the presence of chromophore elements in the form of transition metals such as V, Cr and Fe, where the V and Cr presents the greatest contribution to the more accentuated color of green, and Fe contribute minimally. The color cause of emeralds is also related to the effects of "ligand-to-metal charge transfer" (LMCT) and "intervalence charge transfer" (IVCT). These are the color causes observed through the analyses performed, besides effects that could not be observed, such as selective light absorption, color centers and other effects.



Figure 3: Acquired emerald samples, separated according to a color scale.

3.1 Chemical Analysis

The minor and trace elements of an emerald are a powerful indicator for both, understanding its formers processes and establishing its geographic provenance, even though the number of studies is still limited. In order to stablish a chemical fingerprint for the Monte Santo emeralds, here we the behaviors of its major, minor and trace elements, never investigated before.

The EPMA compositions are reported in Table 1 as both oxide weight percentages and calculated atoms per formula unit.

Tabela 1: Average compositions of emerald samples.

Element	Min - Max	Average	Element	Average
SiO ₂ (wt%)	62,746 - 66,373	64,267	Si ⁴⁺ (apfu)	6,0357
Al ₂ O ₃	12,457 - 17,331	13,996	Ti ⁴⁺	0,0004
MgO	0,836 - 3,883	2,812	Al ³⁺	1,5531
V ₂ O ₃	0,013 - 1,340	0,432	Sc ³⁺	0,0200
Cr ₂ O ₃	0,012 - 1,115	0,263	V ³⁺	0,0285
FeO (total)	0,047 - 0,507	0,204	Cr ³⁺	0,0192
Na ₂ O	0,550 - 2,152	1,686	Mg ²⁺	0,3945
K ₂ O	0,008 - 0,492	0,196	Ca ²⁺	0,0047
Cs ₂ O	bdl - 0,042	0,008	Fe ²⁺	0,0164
Sc ₂ O ₃	0,012 - 1,327	0,286	Ba ²⁺	0,0014
SrO	0,193 - 0,349	0,278	Mn ²⁺	0,0005
CaO	0,001 - 0,221	0,045	Sr ²⁺	0,0152
BaO	bdl - 0,217	0,044	Na ⁺	0,3070
CuO	bdl - 0,075	0,019	K ⁺	0,0007
CoO	bdl - 0,034	0,006	Cs ⁺	0,0003
Bi ₂ O ₃	bdl - 0,059	0,007	H ₂ O	
TiO ₂	bdl - 0,088	0,008		
ZrO ₂	bdl - 0,118	0,011		
Ga ₂ O ₃	bdl - 0,011	0,0001		
ZnO	bdl - 0,063	0,007		
MnO	bdl - 0,035	0,006		
UO ₂	bdl - 0,048	0,006		
PbO	bdl - 0,068	0,011		
ThO ₂	bdl - 0,041	0,005		

Gd ₂ O ₃	bdl - 0,157	0,023
Ce ₂ O ₃	bdl - 0,064	0,014
La ₂ O ₃	bdl - 0,015	0,001
Cl	bdl - 0,020	0,004
*BeO	12,65 – 14,06	13,28
**H ₂ O	1,96 - 2,94	2,66

bdl = below detection limit (commonly a few ppb for heavy elements to hundreds of ppb for light elements).

*BeO assumed as 3 apfu, and 8 Si + M site cations for normalization; ** H₂O content calculated using the equation $H_2O \text{ (in wt\%)} = [0.6097 \times Na_2O \text{ (wt\%)}] + 1.6290$ (Henry, et al., 2021).

The most important chromophores in the Monte Santo emerald are V (avg. 4322 ppm), followed by Sc (avg. 2858 ppm), Cr (avg. 2628 ppm) and, in a lesser extent, Fe (avg. 2045 ppm). Based on the greater content of V₂O₃ than Cr₂O₃, the Monte Santo emerald is here classified as a vanadium-dominant emerald, together with some of its counterparts from Salininha/Bahia (Brazil), Eidsvoll (Norway), Mohmand/Gandao (Pakistan), La Pita, Muzo and Coscuez (Colombia), Davdar and Dayakou/Malipo (China), Lened (Canada) and others (Graphic x).

Sc (avg. 2858 ppm) is also considered a coloring element, which may confer a pale green color to minerals (Mellini et al., 1982) apud Correia Neves (1984).

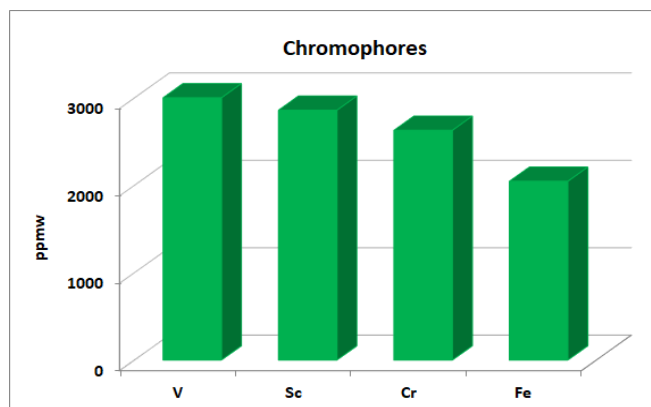
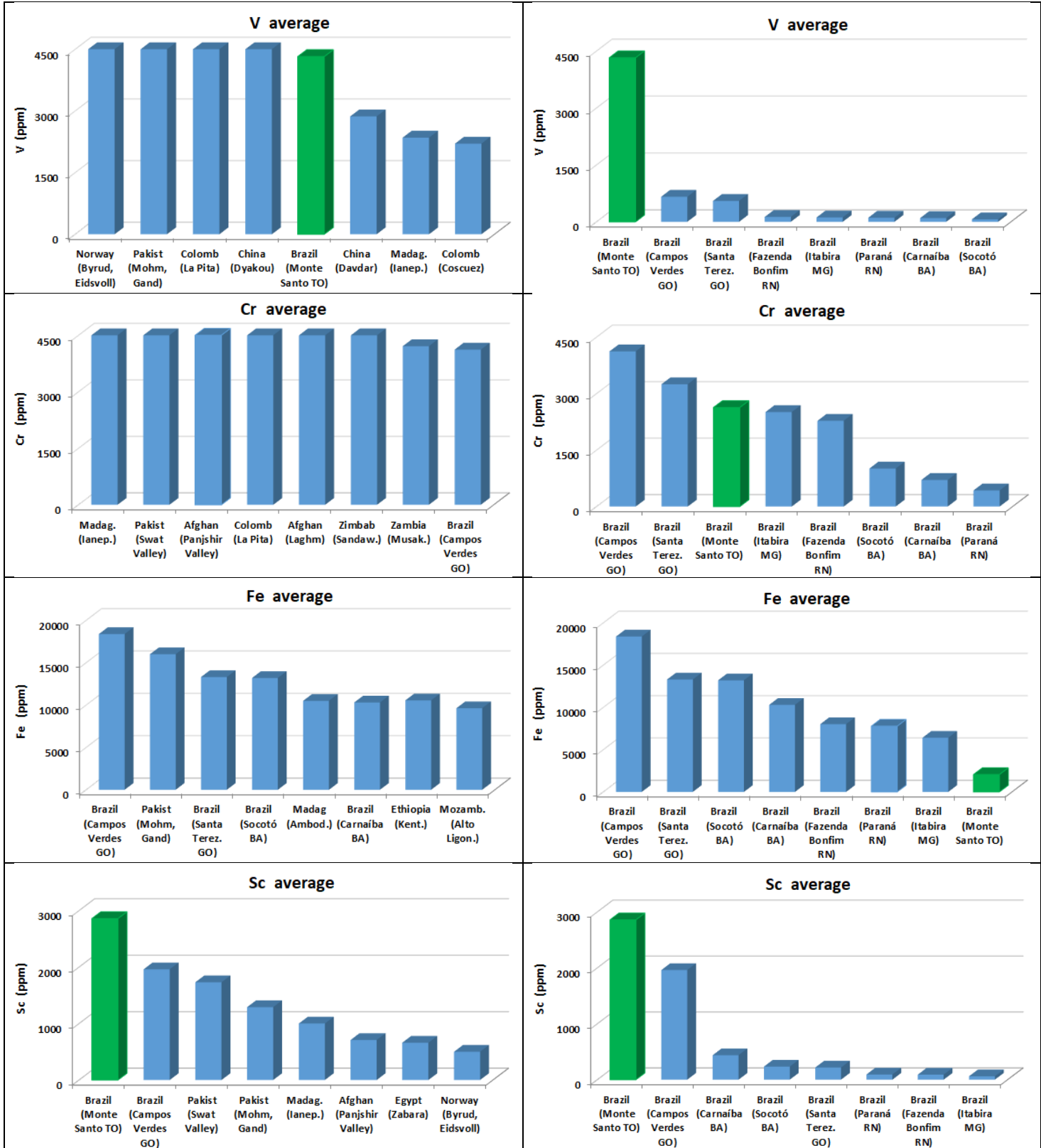


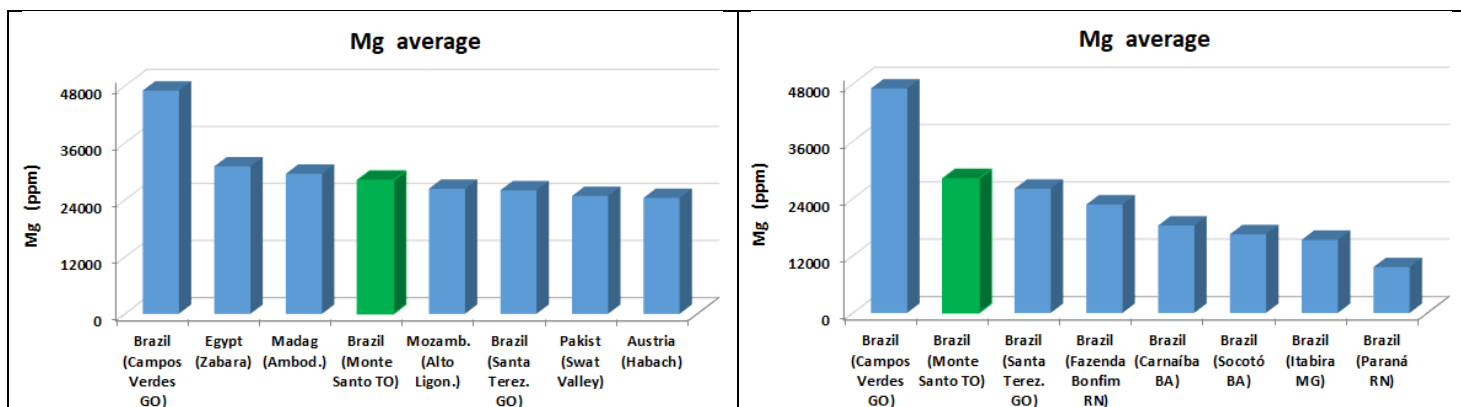
Figura 1: Concentration of the main chromophores occupant of the octahedral site (V, Sc, Cr and Fe).

The sum of the contents of Na (avg. 16865 ppm), K (avg. 1958 ppm), and Cs (avg. 78 ppm) ions as alkali metal ions in the structural channel with the concentration decreasing accordingly, indicating that the Monte Santo emerald are alkali-rich. Rb could not be measured. Schwarz (1994) suggested that a Na₂O content of emeralds <1 wt % is considered low, 1 wt % < medium < 2 wt % and >2 wt % high. The analyzed samples feature a Na₂O content ranging from 0,55 to 2,15 wt%, which allows us to classify them as ranging from low to high Na₂O content.

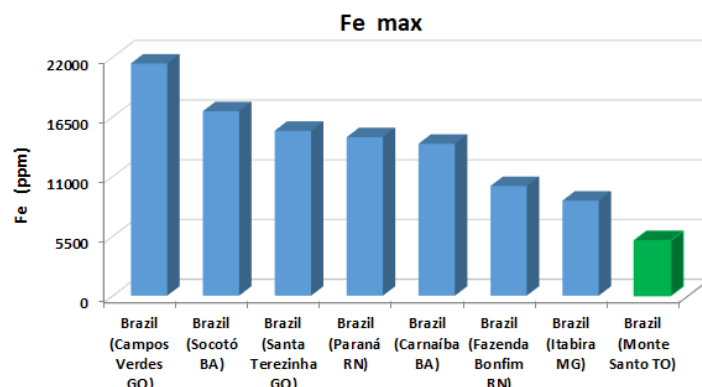
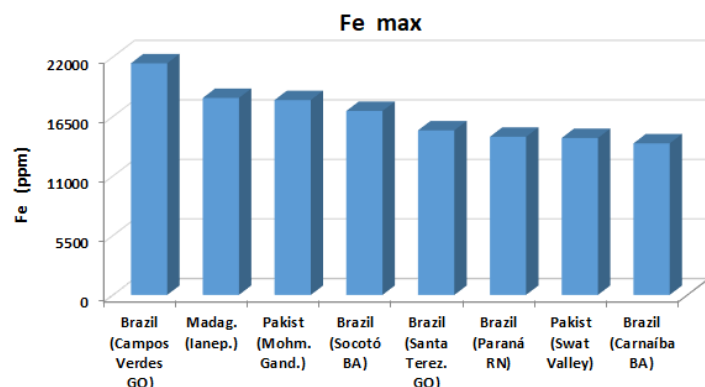
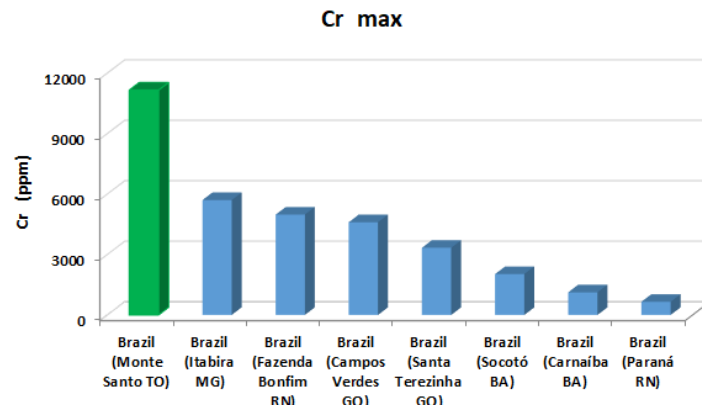
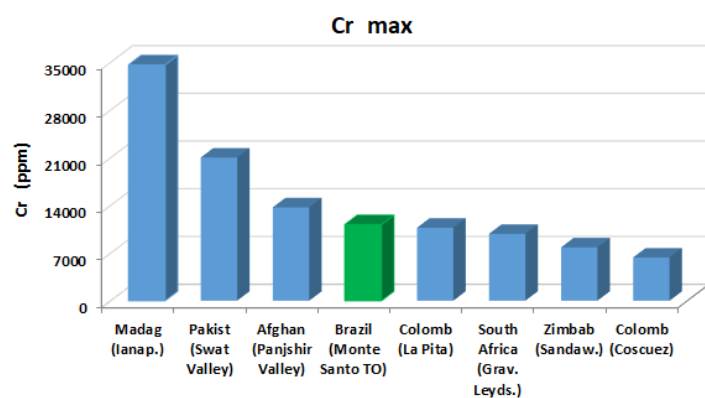
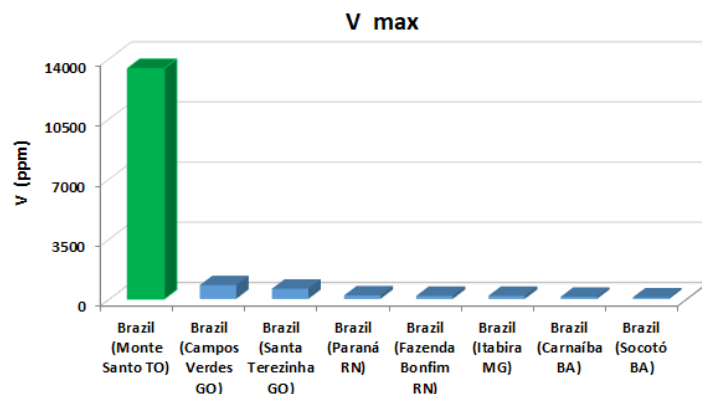
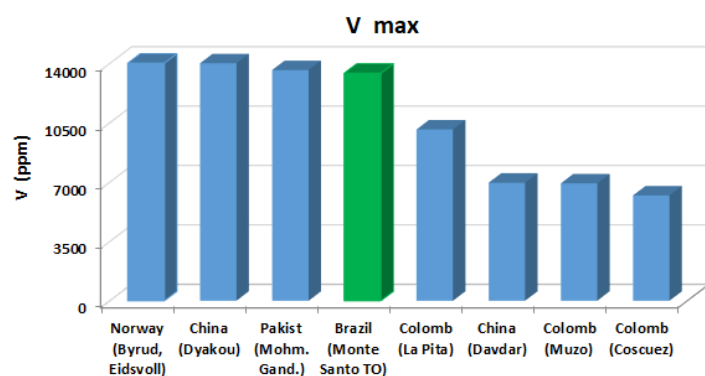
The vanadium content helps separating the Monte Santo emeralds from most of the other occurrences. So far, the most important chemical fingerprint observed for the Monte Santo emerald is the Sc content, because it is the highest Sc content compared to any other emerald deposit in the world, as we can observe in the graphic bellow. Therefore, the plot of Sc contents clearly separates the Monte Santo emeralds from all the other occurrences of emeralds worldwide.

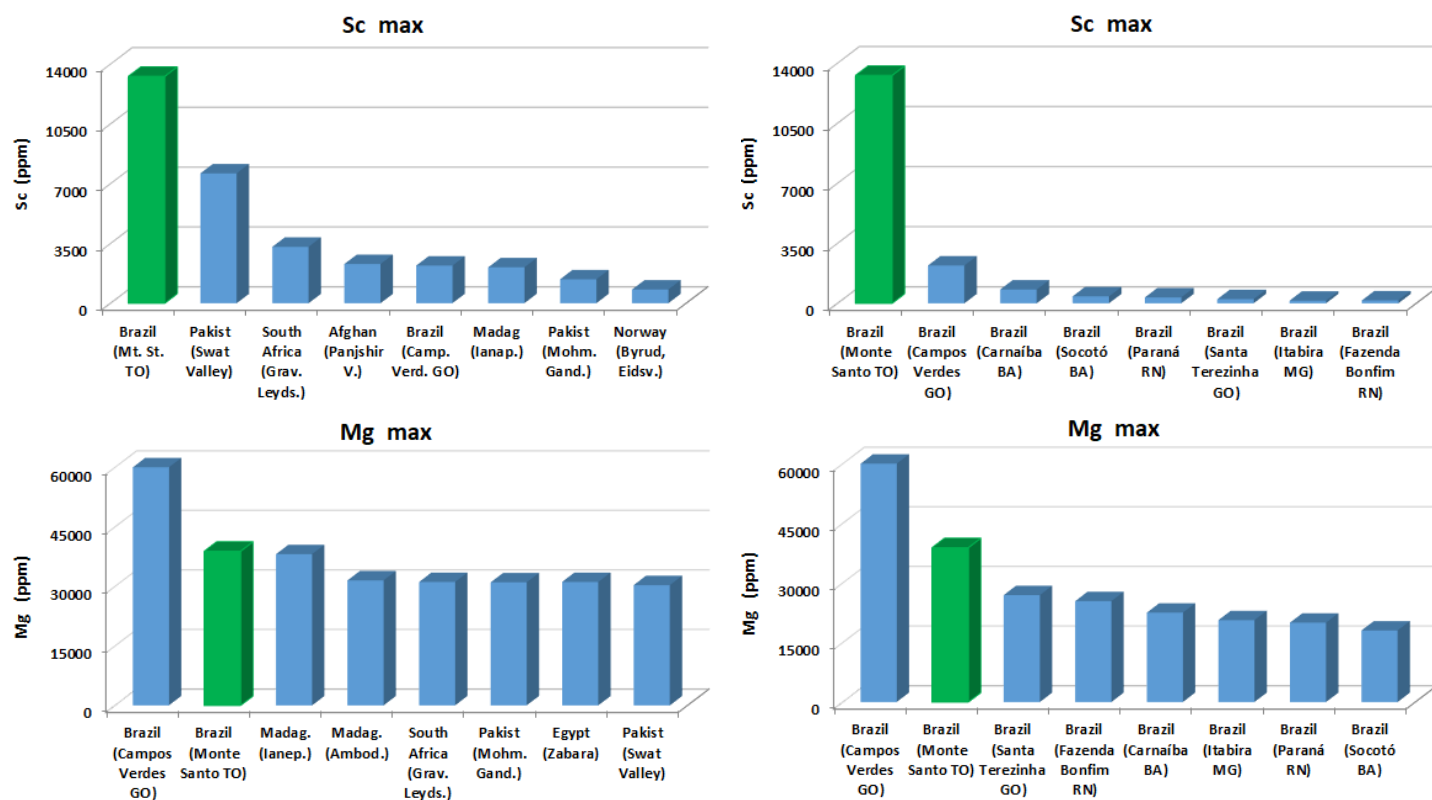
Source: (Loughrey, et al., 2012), (Auriscchio, et al., 2018), (Lum, et al., 2016), (Pardieu, et al., 2020), (Saeseaw, et al., 2014), (Zwaan, et al., 2012), (Krzemnicki, et al., 2021), (Kazmi & Snee, 1989), (Zwaan, et al., 1997), (Rondeau, et al., 2008), (Auriscchio, et al., 2018), (Karampelas, et al., 2019), (Hu & Lu, 2019), (Zheng, et al., 2019), (Pulz, et al., 1998), (Capovilla, 1995), (Araújo Neto, et al., 2019), (Schollenbruch, et al., 2017), (Vertriest, et al., 2019).





Graphic 1: The left-side graphics represent vanadium, chromium, iron, scandium and magnesium average contents for emerald samples of the world (deposits with the highest concentrations of these element); The right-side graphics represent vanadium, chromium, iron, scandium and magnesium average contentes for emerald samples from Brazil. The green column represents the Monte Santo emerald samples.





Graphic 2: The left-side graphics represent vanadium, chromium, iron, scandium and magnesium maximum contents for emerald samples of the world (deposits with the highest concentrations of these element); The right-side graphics represent vanadium, chromium, iron, scandium and magnesium maximum contents for emerald samples from Brazil. The green column represents the Monte Santo emerald samples.

The concentration of Fe, Cr, and V as well as Fe, Mg and Cr have been plotted for comparison with emerald analyses worldwide (Figure 4).

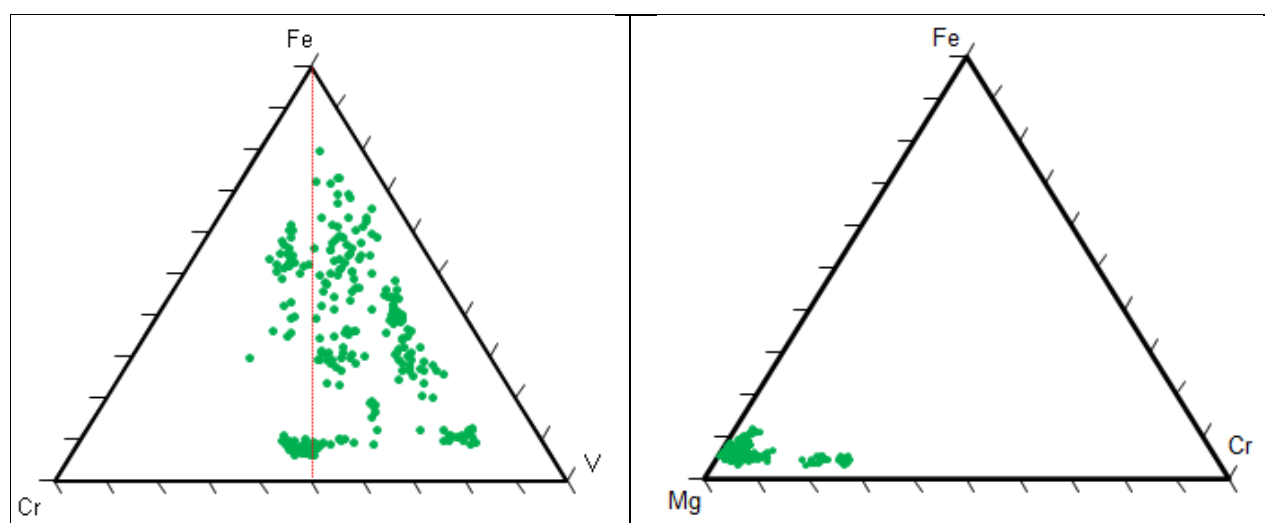
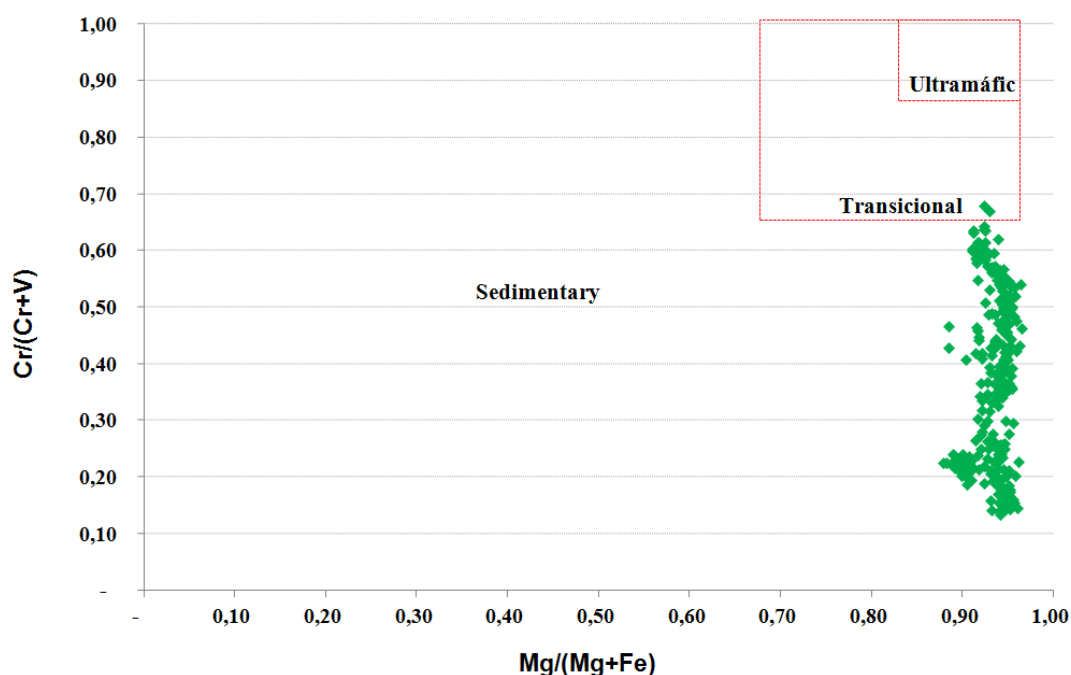


Figure 4: A) Ternary Fe–Cr–V (ppmw) plots of Monte Santo emerald compositions and B) Ternary Fe–Mg–Cr (ppmw) plots of Monte Santo emerald compositions.



Graphic 3: Characterization of the Monte Santo emerald deposits, based on $Cr\# = Cr/(Cr+V)$ vs. $Mg\# = Mg/(Mg+Fe)$. Many emerald deposits (24 out of 52) are characterized by high ratios between 0.8 and 0.9, which is the *ultramafic* schist type occurrence, where Cr as the coloring element is predominant, originating from metamorphosed mafic-ultramafic rocks. A small group (11 localities) is considered as *transitional*, where the sources for $Mg+Fe+Cr+V$ are both mafic-ultramafic rocks and metasediments. All other localities are considered as *sedimentary* with regard to their origin of highly variable $Cr\#$ and $Mg\#$. The Cordilleran-type occurrences from Colombia and Canada (Yukon, Mackenzie Mts., Lened) are typical examples, but also the Chinese deposits Davdar and Dyaku, Binntal (Switzerland), Pakistan (Sharbag-Swat, Gandao). (Franz, et al., 2020).

The main occupant of the octahedral site is Al, which ranges from 65,7% to 91,4% of the total site occupancy. Divalent and trivalent ions such as Mg, Fe, V, Cr, Sc, Ca and Ba are the main substitutes for Al (Fig. X), in the order $Mg > V > Sc > Cr > Fe > Ca > Ba$.

While only divalent substitutions are part of the coupled substitution that introduces Na^+ and H_2O into beryl, trivalent substitutions at the M site increase the molecular weight per formula unit, and therefore also change the relative weight percentages.

Sodium is the predominant alkali in the channels and its content is mainly controlled by the octahedral site substitutions, for charge balancing (Fig. X).

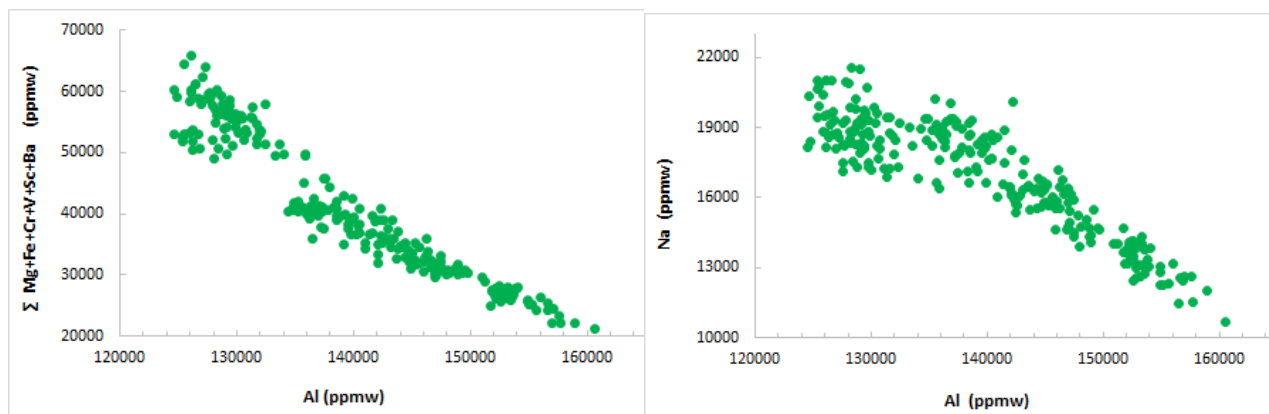


Figure 5: A) The main occupant of the octahedral site (Mg, V, Sc, Cr, Fe, Ba) versus Al (ppmw) and; B) Sodium in the channels versus the octahedral site substitutions from Al, for charge balancing.

3.2 Fluid Inclusions

The fluid inclusions studied occur in both aqueous and aqua carbonaceous systems, both of which are sometimes saturated, i.e., host one or more solid saturation phases (salts). The criterion adopted for group subdivision is based mainly on the number of phases and nature of the fluid, following the proposal of Van den Kerkhof and Hein (2001).

Fluid inclusions have three forms of occurrence, analyzed spatially and temporally. The primary inclusions occur alone or in small groups, are notably larger in size than the others, and in some domains follow the zonation or growth lines of the crystals. The pseudosecondary ones form small intracrystalline tracks, while the secondary ones fill fractures, probably posterior to crystal growth. In the latter two forms of occurrence the fluid inclusions are less than 5 μm in size. Some domains exhibit leakage, necking down and stretching features, typical of post-aperture deformation and fluid rebalancing with respect to surface pressure and temperature conditions.

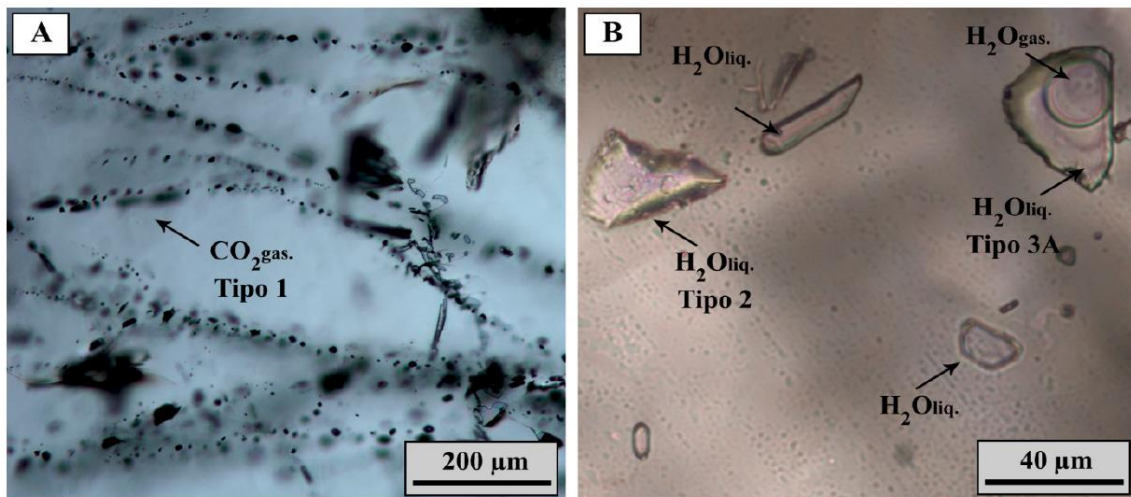
Petrografia

The petrographic observation at the room temperature (around 20° C) revealed that the emerald crystals host a varied set of fluid inclusion systems (carbonic, aqueous, and aqueous-carbonic), which have primary, pseudo-secondary, and secondary in nature with features from mono- to polyphasic in morphology (Table).

Primary fluid inclusions occur singly or in small groups, usually following zonation or lines of crystal growth. On the other hand, pseudo-secondary fluid inclusions form some intra-crystal trails, while the small secondary fluid inclusions occur distributed along microfracture lines formed after crystal growth. Occasionally, leakage, necking down, and stretching features are also observed, probably indicative some degree of post-trapping deformation or fluid rebalancing (Bodnar, 2003).

Based on the Van den Kerkhof and Hein (2001) proposal, we classify the fluid inclusion sets into four main types, whose compositional and morphological characteristics are summarized and illustrated in table 1:

- Type 1 (Fig. A) – composed by monophasic carbonic or CO₂-dominated fluid inclusions with a single gas phase. It has elongated and sub-rounded shapes and with sizes between 10 - 30 μm;
- Type 2 (Fig. B) - composed by monophasic aqueous fluid inclusions containing only a liquid or gas phase (H₂O). It has irregular, elongated, sub-rounded, and rounded in shapes, featuring a size ranging from 10 to 40 μm. This type commonly occurs along micro-fracture trails as secondary fluid inclusions;
- Type 3 - brings together biphasic and triphasic aqueous fluid inclusions. It was divided into the 3A and 3B subtypes, according to the presence of solid particles. The 3A subtype (Fig.) is biphasic (H₂O_{liq.} + H₂O_{gas.}) and show irregular, rounded and elongated in shape, with a size ranging from 20 to 90 μm. The volume of the gas phase (V_g) varies widely, occupying from 10 to 80 % of the total cavity volume. This type also occurs along micro-fracture trails as secondary fluid inclusions. On the other hand, the 3B subtype (Fig.) has similar morphology and size to 3A subtype, but may have one or more solid particles or phases saturation. In general, solid particles have cubic to sub-round in shape, low birefringence and with a size close to less than 10 μm, while the volume of the gas phase (V_g) varies from 40 to 60 % of the total cavity volume;
- Type 4 - this last type brings together triphasic and polyphasic aqueous-carbonic fluid inclusions, which also was divided into the 4A and 4B subtypes, according to the presence of solid particles. The 4A subtype (Fig.) is triphasic (H₂O_{liq.}+ CO_{2liq.}+ CO_{2gas.}) and present irregular, rounded and elongated in shape, with a size between 50 - 90 μm. The carbonic phases (CO_{2liq.}+ CO_{2gas.}) fill from 20 to 70% of the total cavity volume. The 4 B subtype (Fig.) has similar morphology and size to 4A subtype, however, it is polyphasic due to the presence of several solid particles or phases saturation. The solid particles are cubic to rarely irregular in shape, show low birefringence and less than 10 μm in size.



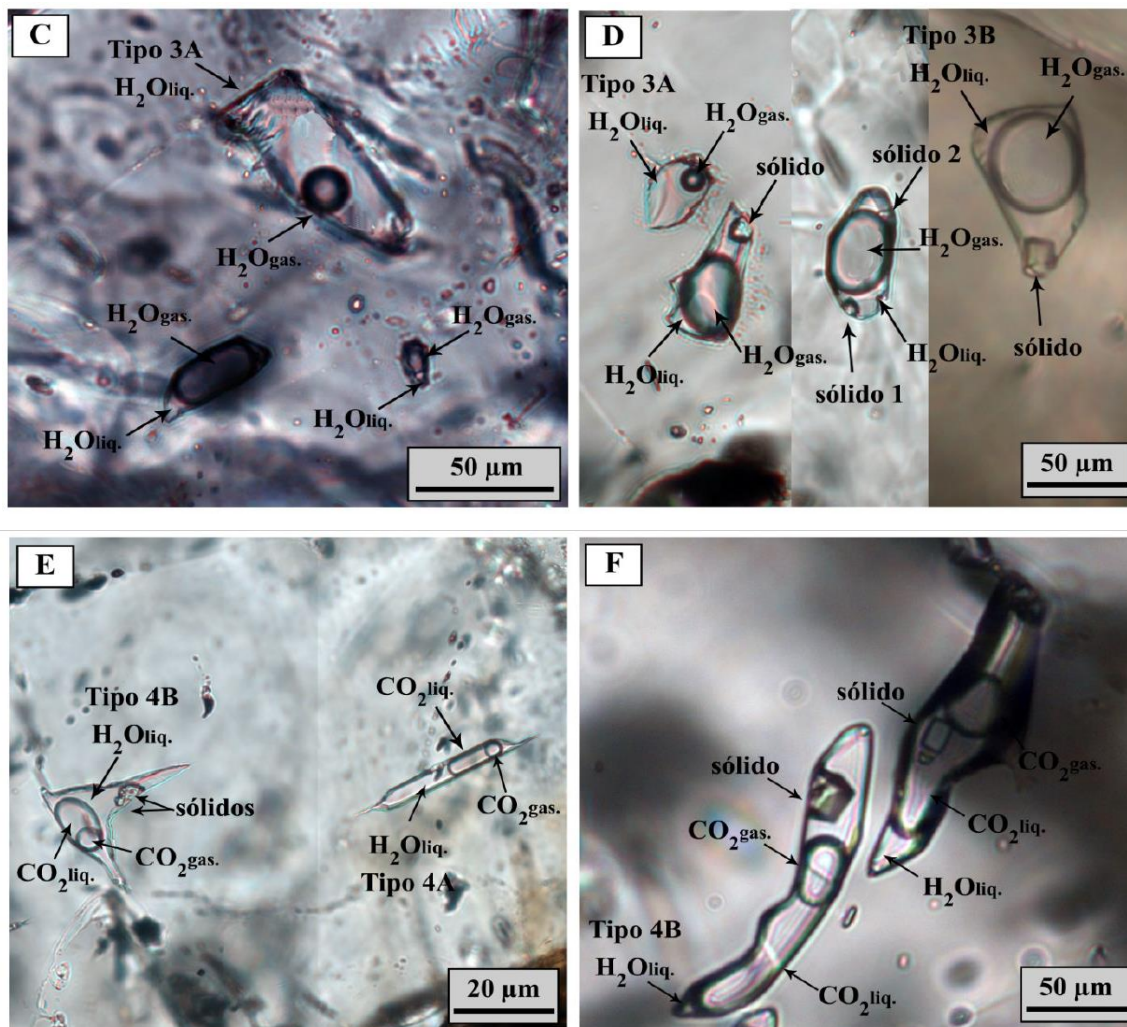


Figure 2: Types of fluid inclusions identified. A) Tracks of carbonaceous inclusions (Type 1). B) Association of types 2 and 3A. C) Type 3A inclusions, with notable gaseous volume variation. D) Three distinct fields containing saturated aqueous inclusions, subtype 3B, associated with subtype 3B. E and F) Unsaturated (subtype 4A) and saturated (subtype 4B) aqueous inclusions.

	Tipo e Subtipo	Descrição	Ilustração	
Carbônico	1	Monofásicas $\text{CO}_{2\text{gas}}$ ($V_g=100\%$) com morfologia variada, predominantemente alongada e arredondada. São primárias (10 a 30 μm), pseudosecundárias ou secundárias ($<5 \mu\text{m}$) e associam-se principalmente ao tipo 4.		
	2	Monofásicas $\text{H}_2\text{O}_{\text{liq}}$ ($V_g=0\%$) com morfologia variada, predominantemente alongada e arredondada. São primárias (10 a 40 μm) e pseudosecundárias ou secundárias ($<5 \mu\text{m}$) e associam-se principalmente ao tipo 3.		

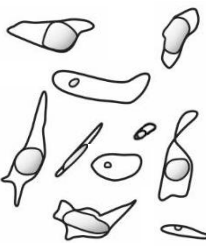
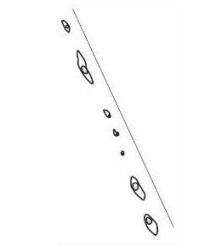
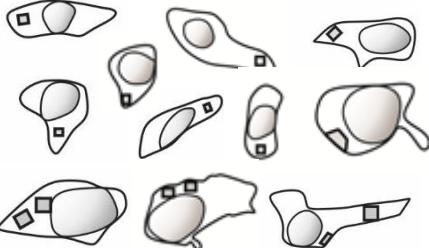
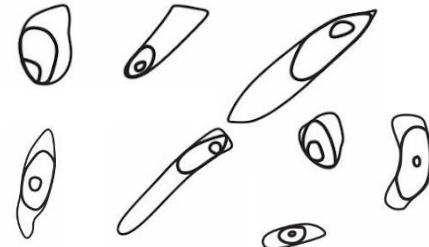
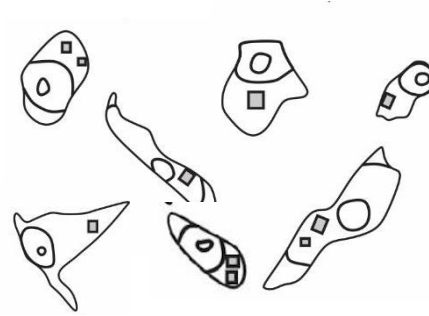
Aquocarbônico		A	Bifásicas ($H_2O_{liq} + H_2O_{vap}$) com Vg variando de 10 a 80%. São irregulares, alongadas, arredondadas e poligonais. Ocorrem como primárias (20 a $>100 \mu m$), secundárias e pseudosecundárias ($<5 \mu m$). Associadas aos tipos 2 e 4 e ao subtipo 3B.		
		B	Trifásicas ($H_2O_{liq} + H_2O_{vap} + Sólido$) a polifásicas ($H_2O_{liq} + H_2O_{vap} + Sólidos$), com Vg entre 30 e 60%. São irregulares, alongadas, arredondadas e poligonais. Ocorrem como primárias e variam de 20 a $>100 \mu m$. Estão associadas aos tipos 2 e 4 e ao subtipo 3A.		
		A	Trifásicas ($H_2O_{liq} + CO_{2liq} + CO_{2gas}$) com as fases carbônicas ocupando cerca de 20 a 70% do volume total. Possuem formas irregulares, com predomínio das alongadas e arredondadas. São primárias com tamanho entre 50 e $>100 \mu m$. Encontram-se associadas aos tipos 1, 2, 3 e subtipo 4B.		
		B	São multifásicas ($H_2O_{liq} + CO_{2liq} + CO_{2gas} + Sólidos$.) com presença de um ou mais sólidos. Apresentam morfologia variada, com formato geralmente alongado, arredondado, ovalar ou poligonal. São primárias e variam de 50 a $>100 \mu m$. Encontram-se associadas aos tipos 1, 2, 3 e subtipo 4A.		

Table 1. Main characteristics of the fluid inclusions present in emeralds accompanied by a schematic drawing of the representative FIs of each type and subtype. Note: The inclusions depicted refer to different fields of observation and have been grouped for better visualization of the type and/or subtype to which they belong. They are not in defined scale. (P=Primary; S=Secondary; PS=Pseudosecondary; Vg=Gaseous volume).

Microtermometria Fluid inclusion microthermometric measurements

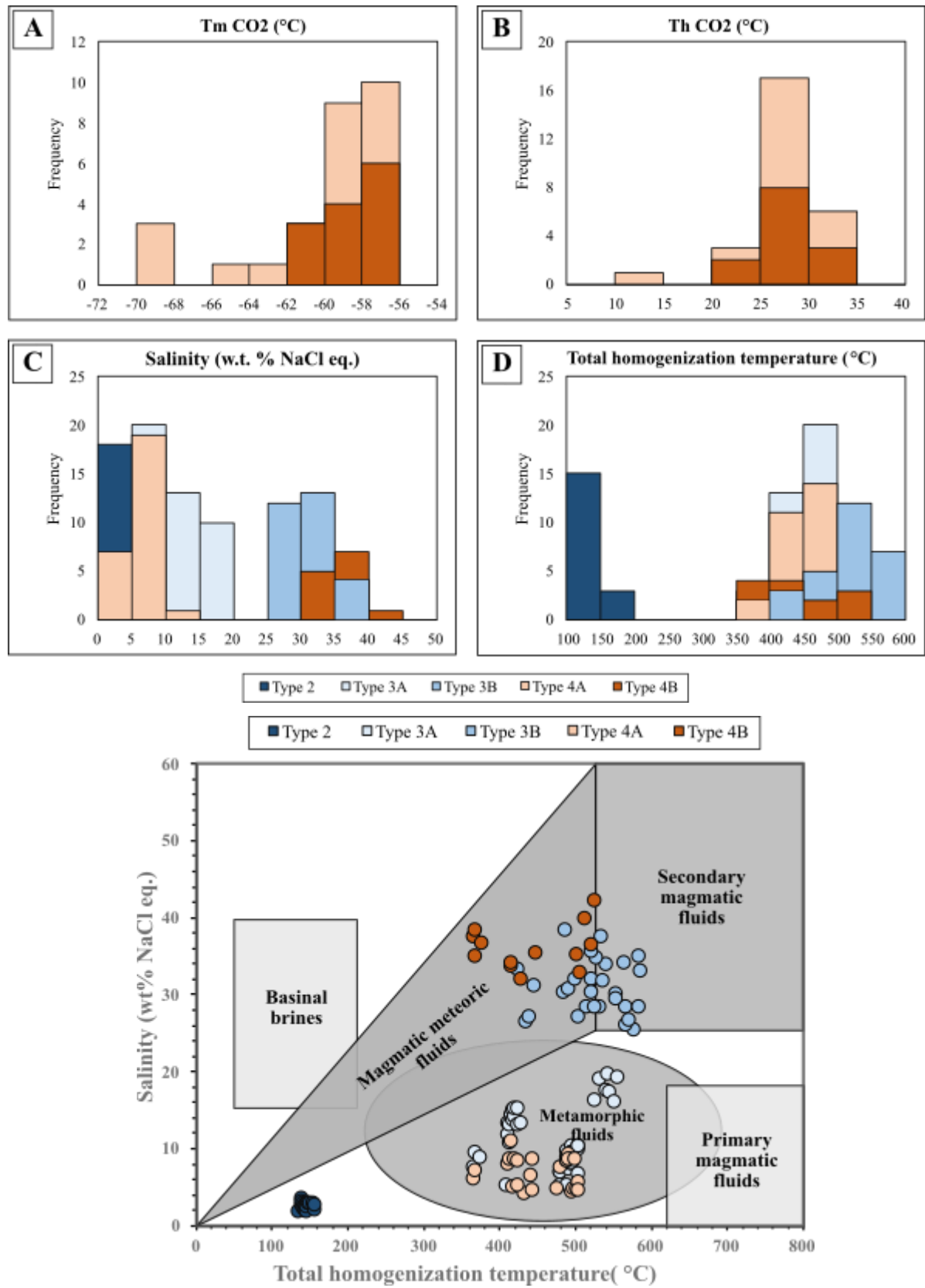
For this study, 112 primary and 18 secondary fluid inclusions hosted in emerald samples were targeted for microthermometric measurements. During the cooling step (up to $-100^\circ C$) the CO_2 melting, eutectic, ice melting and clathrate melting temperatures were obtained. Subsequently, during the heating step (up to $600^\circ C$), the homogenization of the carbonic phase ($CO_{2liq} + CO_{2gas}$), total homogenization systems, and dissolution of solid particles temperatures were obtained. The most important microthermometric features are summarized as follows:

- The primary monophasic carbonic fluid inclusions (Type 1) show a CO₂ melting temperature between -56.8° and -57.2° C, very close to pure CO₂ (-56.6° C) suggesting a few molecules of other dissolved/associated gases (*e.g.*, N₂, CH₄, according to Shepherd et al. 1985);

- The primary aqueous fluid inclusions (Type 2 and Type 3) show wide variation in eutectic temperature measurements ranging from -19.3° to -33.7° C, indicating the presence of the H₂O-NaCl fluid system, but with some content of KCl and MgCl₂ molecules (Shepherd, et al., 1985). The few ices melting temperature measured in Type 2 occurred between -3.3° and -6.5° C, indicating a calculated salinity varying from 5 to 20 wt.% NaCl eq., while for the subtype 3A fluid inclusions the ice melting temperature vary from -8.4° to -16.5° C, with a calculated salinity ranging from 5 to 20 wt.% NaCl eq. (applying the Bodnar 1993 equation). The subtype 3A revealed a total homogenization temperature of the system marked by gas phase contraction progressive towards the liquid phase (H₂O_{liq.} + H₂O_{gas} → H₂O_{liq.}) between 360.4° and 549.6° C (Fig.). On the other hand, the calculated salinity for the subtype 3B fluid inclusions were on base in the dissolution temperatures of some solid particles (phases saturation), which occur over a wide range between 102.4° and 322.6° C, allowed to determine a salinity calculated between 25 and 39 wt.% NaCl eq. (applying the Lecumberri-Sanchez et al. 2012 equation). However, some others solid particles did not show their dissolution temperatures up to the limit of 600° C, indicating probable minerals particles captured during the formation of fluid inclusion cavities;

- The primary aqueous-carbonic fluid inclusions (Type 4) showed wide variation in CO₂ melting temperature, which occurred between -56.7 a -69.2 °C (*i.e.*, very close to far below the melting temperature of pure CO₂ = -56.6° C), indicating variable molar content for other gases dissolved/associated together with the carbonic phase (*e.g.*, N₂, CH₄, according to Shepherd et al. 1985). These kinds of fluid inclusions also have a bimodal variation in the salinity content. The subtype 4A showed clathrate melting temperature between 3.7° e 7.8 °C, allowing to obtain a calculated salinity between 4.3 e 10.9 %wt. NaCl eq. (applying the). On the other hand, due to the presence of solid saturation phases in subtype 4B, its salinity was calculated on base in the solid phase dissolution temperature, which occur between 218.6° and 350.2° C, revealing a salinity between 32 e 43 %wt. NaCl eq. (Lecumberri-Sanchez, et al., 2012). In general, the CO₂ phases homogenization temperature (CO_{2liq.} + CO_{2gas} → CO_{2liq.}) occurred between 12.4° and 31.3° C, while that the liquid phases total homogenization temperature was marked by carbonic phase contraction progressive towards the aqueous phase (CO_{2liq.} + H₂O_{liq} → H₂O_{liq}) ranged from 360.5° to 520.3 °C. In this fluid inclusion type, some few solid particles also did not show their dissolution temperatures up to the limit of 600° C.

- Additionally, the secondary aqueous fluid inclusions (type 2 and subtype 3A) revealed an ice melting temperature between -1.1° and -2.3 °C, resulting in a calculated salinity between 2 - 4 %wt. NaCl eq. (Bodnar, 1993), while the subtype 3A showed total homogenization temperature towards the liquid phase ranged from 132.3° to 153.4 °C.



The heterogeneity of the fluids allows for classification into both types I and II of Giuliani's classification (Giuliani, et al., 2019).

Raman Spectroscopy

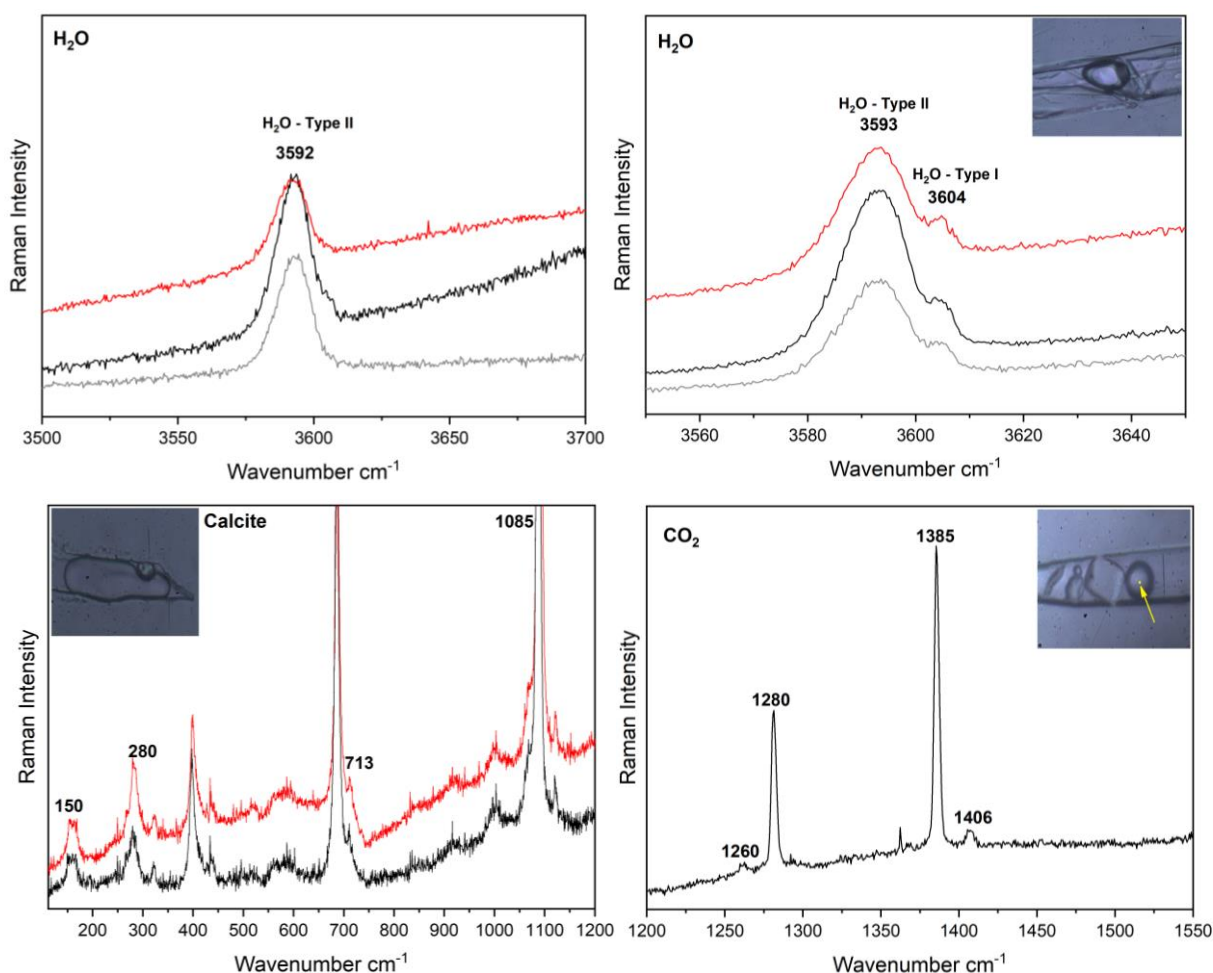
The micro-Raman spectroscopy investigation were carried out in the solid and gas phases present in the aqueous and aquo-carbonic fluid inclusions related to types 3B and 4B that had adequate sizes for the analysis.

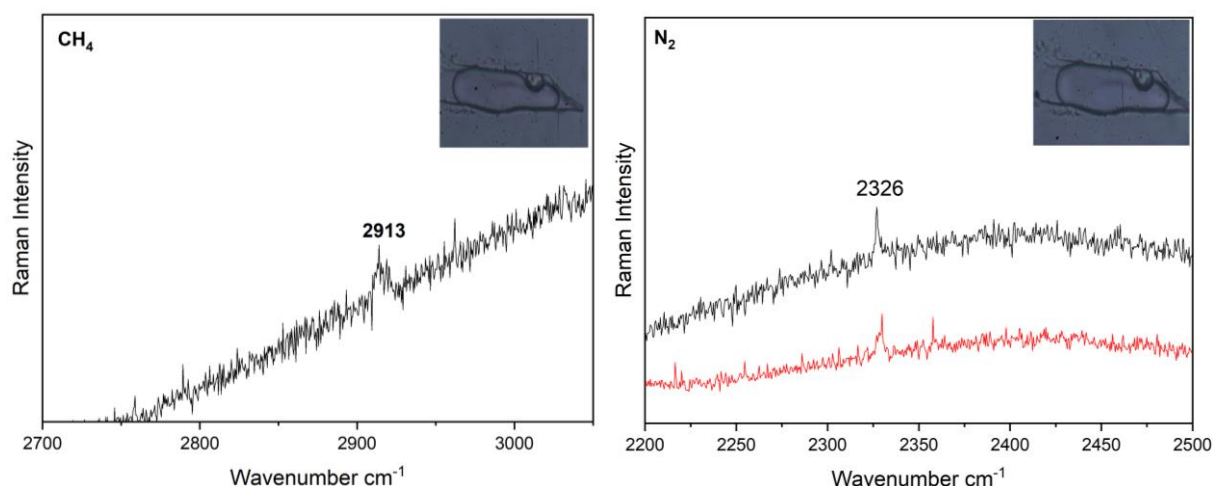
Some of the inclusions were identified by Raman spectroscopy (figures). The gas phases were identified as CO₂ (peaks at about 1260, 1280, 1385 and 1407cm⁻¹), N₂ (peaks at around 2325 cm⁻¹) and CH₄ (peaks at 2914 cm⁻¹).

Daughter crystals of solid inclusions were assigned to calcite, represented by the peaks at 152, 180, 280, 713 and 1087 cm⁻¹, as shown in figure X.

Fluid phases were identified as H₂O type I (not bonded to Na), represented by the peaks at around 3604 cm⁻¹, and H₂O type II (bonded to Na) or brine by the peaks in the range from 3591 to 3597 cm⁻¹ (fig. X).

Although both types of water (I and II) are present in the fluid inclusions of the Monte Santo emerald, the type II water absorption band predominates over its type I counterpart in the spectrum of all the samples in our investigation, thus demonstrating a high salinity and high concentration of charge compensating alkali ions, suggesting that these samples were formed in the presence of fluids with high alkali content and salinity.





4. DISCUSSÕES

Giuliani et al. (2019) propose the classification of emerald deposits based on the geological environment (magmatic or metamorphic), host rock type, degree of metamorphism, type of mineralization, type of fluids and their temperature, pressure and composition. In summary, deposits can be of either tectonomagmatic or tectonometamorphic types.

Magmatic environments tend to trap saline aqueous fluids (H₂O-NaCl), with a smaller contribution of aquocarbon fluids (H₂O-CO₂-NaCl). On the other hand, metamorphic environments tend toward a mixture of H₂O-NaCl and H₂O-CO₂-CH₄-NaCl fluids with high salinities. The fluids identified point to a generation from devolatilization during the metamorphism process, responsible for the release of volatiles such as CO₂ and CH₄. In addition, fluid supply with distinct salinity rates is evidenced, characterized by the absence or presence of one or more saturation solids in aqueous and aquocarbon inclusions for the primary inclusions, associated with exclusively low salinity secondary fluid inclusions.

Heterogeneous entrapment occurs due to fluid immiscibility either by decompression, hypersaturation in salts (trapped incidental solids) or by entrapment of fluids of distinct compositions (Pestilho and Monteiro, 2017; Roedder, 1984). Heterogeneous entrapment results in fluid inclusions with distinct compositions and salinities, as occurs in the boiling process (Van den Kerkhof and Hein, 2001). These processes are evidenced in the present work by the heterogeneous composition of the genetically coexisting fluids, as well as by the wide variation of the gaseous volume within the same type of fluid inclusion. The occurrence of single-phase carbonaceous inclusions (type 1) associated with aquocarbon (type 4) may also suggest separation of volatile phases during entrapment.

The data presented allow an interpretation about the possible genesis of the emerald gem-generating fluids of the Monte Santo deposit as a product of the mixture of fluids coming from distinct sources (magmatic + metamorphic), which allow multi-stages of emerald formation linked to cyclic remobilization of fluids. The release of volatiles during the metamorphism process acts as the main

source of CO₂ and CH₄. These relationships are based on the distinct composition of temporally and spatially coexisting fluids.

This hypothesis reinforces the strong shear zone conditioning of mineralization, since emeralds occur at the tectonic contact of biotite granite and, locally, of albitite granite with shales and amphibolites. Thus providing conditions conducive to fluid mixing and, consequently, heterogeneous trapping.

Moura (2005) studied the fluid inclusions present in the Monte Santo emeralds, identifying two types: 1) hypersaline aquocarbonic fluids (with more than one saturation solid) and 2) aquocarbonic.

The Cr-V-bearing beryl is relatively rare because its constituent elements have opposite affinities and behavior in the continental and oceanic lithospheres. Beryllium is a lithophile element, which has a strong affinity for oxygen producing, e.g., beryl and chrysoberyl at higher temperatures and at medium to low temperatures joins with silica to form silicate minerals, such as beryl and other minerals. These minerals have a relatively low-density and so they are concentrated in the crust whereas chromium and vanadium are high-density transition metals that generally concentrate in the core and the mantle of the earth. Although Cr and V show both lithophile and siderophile affinities, they tend to form solid solutions with iron (Fe) to form, e.g., chromite (FeCr₂O₄) at high temperatures.

Beryllium is present in crustal granites and associated dyke swarms of pegmatites, aplites, and quartz veins. The felsic rocks (FELSR), with more than 70% silica (SiO₂), are intrusive into the continental lithosphere. Chromium and vanadium are more highly concentrated in M-UMR of the oceanic lithosphere that contain less than 50% SiO₂. These rocks, which are generally termed peridotites, are often metamorphosed into serpentinites containing up to 14 wt.% H₂O, or into talc-chlorite-carbonate schists.

Chromium is dominantly sourced from chromite and vanadium is sourced from V-bearing magnetite or coulsonite (Fe₂+V₃+2O₄). Indeed, the weathering and erosion of M-UMR and FELSR on the continents delivers to the sea fine-grained clastic sediments composed of mud with Cr-V-Be-bearing grains and organic matter, as well as tiny fragments of quartz and calcite.

Metasediments represent another possible source for Cr and V, typically in the form of organic-rich rocks such as blackshales and impure limestones, as they are known organophiles (e.g., Tribovillard et al. 2006). Incorporation of these elements into minerals during metamorphism is well known for garnet and epidote (e.g., Bačík et al. 2017), and for oxide minerals (Di Cecco et al. 2018). In sediments, however, both elements are redox-sensitive, and can become enriched or depleted during diagenetic and metasomatic events, and can be coupled or decoupled, which results in highly variable Cr/(Cr+V). These localities are called “sedimentary,” referring to the sedimentary origin of Cr and V (Franz, et al., 2020).

On the basis of the amount of femag substitution, Mg/(Mg+Fe) (= Mg#), and their Cr/(Cr+V) (= Cr#) ratios, the critical element concentrations Mg, Fe, Cr, and V are controlled by ultramafic rocks at some localities, which are distinct from occurrences where (meta)sedimentary rocks provide the

source of Mg, Fe, Cr, and V, such as Monte Santo emerald deposit (Fig. X). At some localities (transitional), both types of rocks are present.

Scandium seems to be concentrated in beryls from less differentiated geological environments. In pegmatite beryls studied by Staatz et al. (1965) apud Correia Neves (1984), Sc rarely exceeds 5 ppm. However, Sc shows a tendency of higher concentration in beryls of the surrounding rocks immediately adjacent to the pegmatite, tends to concentrate more in the vein beryls, and the highest concentrations occur in granite beryls, beryls with higher Sc concentration are, as a rule, rich in Fe and Mg.

The high sodium concentration is justified by the existence of a marine environment prior to the formation of the emerald deposits, and its entry into the mineral's structure has a direct relationship to the charge balance needed to compensate for element substitutions in crystallographic sites.

5. CONCLUSÕES

The main occupant of the octahedral site is Al, which ranges from 65,7% to 91,4% of the total site occupancy. Mg, Fe, V, Cr and Sc ions are the main substitutes for Al, in the order $Mg > V > Sc > Cr > Fe$. Sodium is the predominant cation in the channels and its content is mainly controlled by the octahedral site substitutions, for charge balancing.

Based on the amount of femag substitution, $Mg/(Mg+Fe)$, and their $Cr/(Cr+V)$ ratios, it is believed that (meta)sedimentary rocks provide the source of Mg, Fe, Cr, and V, for the Monte Santo emerald deposit.

A distinctly high Sc concentration is the main criterion that separates the Monte Santo emeralds from all its others counterparts, since the average of Sc concentrations (2858 ppmw) in Monte Santo emeralds is the highest among worldwide sources, reaching a maximum concentration of up to 13274 ppmw, never reported so far.

It is interesting to learn that Sc is also considered a coloring element, which may confer a pale green color to minerals. Sc seems to be concentrated in less differentiated geological environments, but its source is not fully understood yet, which in my opinion renders them particularly interesting.

The Monte Santo emerald deposit shows many similarities with deposits from Colombia, Chinese (Davdar and Dyaku), Pakistan (Swat, Mohmand Gandao), Norway (Byrud Eidsvoll), Madagascar (Ianapera), Afghanistan (Panjshir Valley), Switzerland (Binntal) and others. Most of these localities are considered as (meta)sedimentary with regard to their origin of highly variable $Mg/(Mg+Fe)$ and $Cr/(Cr+V)$. They are also similar regarding to their vanadium and scandium contents.

The most probable hypothesis for the formation of these emeralds is the mixture of a hypersaline silicate fluid, with beryllium, at temperatures, in general, of $-500^{\circ} \pm 50^{\circ}\text{C}$, of probable magmatic origin, with metamorphic fluids rich in CO_2 and in Ca^+ , Mg^{2+} , Cr^{3+} , Y^{3+} . These ions would have been remobilized from the lithologies of the surrounding rocks, by the percolation of aquarmonic fluids generated in the lower levels.

The mixture of fluids from distinct sources demonstrates the complexity of the formation of this deposit, common in tectonometamorphic environments, revealing the multi-stages of emerald formation linked to the cyclic remobilization of fluids, with contributions from marine, ophiolitic, mafic-ultramafic sequences, Brasiliano granitic intrusions and sedimentary coverings, remobilized by compressive tectonics, folded and metamorphosed, followed by sinistral transcurrent tectonism.

The heterogeneity of the fluids allows for classification into both types I and II of Giuliani's classification (Giuliani, et al., 2019). The most likely deposit type is the sub-type IID, that includes: Tectonic Metamorphosed or Remobilized Type IA Deposits, Tectonic Hidden Granitic Intrusion-Related Emerald Deposits, and Some Unclassified Deposits (Egypt, Australia, perhaps also Brazil, Austria, Pakistan, Zambia)

Finally, the genesis of the Monte Santo emerald deposits can result from both metamorphic and magmatic contributions, with a multi-stage mineralizing episode proposed.

Acknowledgements

The authors would like to thank the National Science and Technology Institute of Geotechnical Studies (INCTET - UnB), for all the support that made the project possible; the Fluid Inclusions Laboratory of the University of Campinas (UNICAMP), for the fluid inclusion analyses; to the Geosciences Institute of the University of Brasilia (UnB) and to Dr. Lina Ester for providing the samples used in this research. This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001.

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6. PERSPECTIVAS FUTURAS

A exploração para além do século 21 pode exigir uma base de dados abrangente da tipologia de depósitos para entender porque somente poucas ocorrências de esmeralda são econômicas em termos de quantidade e qualidade. Esses esforços futuros melhorarão as diretrizes de exploração no campo.

Sejam por garimpeiros ou grandes empresas de mineração, mostrou-se uma tendência favorável à realização de parceria e fornecimento de amostras para a realização de pesquisa, haja visto que é do interesse de ambos uma completa caracterização de suas ocorrências e elucidação de questões técnico-científicas.

Os laboratórios das universidades e instituições de pesquisa mostram-se interessados a realizar análises, pois estes possuem interesse em realizar pesquisa com consequentes publicações.

Desta maneira, há perspectivas futuras para a realização de pesquisa, com suporte financeiro e apoio laboratorial.

6.1 - Banco de Dados Minerais

Com a continuação das pesquisas minerais e o consequente aumento da quantidade de dados armazenado, de maneira a representar um espaço amostral significativo, será possível a disponibilização do “Banco de Dados de Esmeraldas Brasileiras”, com livre acesso para consulta e comparação.

6.2 - Aquisição de Amostras para Pesquisas Futuras

Já dispomos de um universo amostral representativo de amostras de esmeralda dos depósitos de Carnaíba e Salininha-BA e Campos Verdes-GO, para a realização de pesquisas futuras, referente ao pós-doutorado de Débora Ezequiel Cavalcanti, dando continuidade à presente pesquisa.

7. - CONSIDERAÇÕES FINAIS

A demanda por determinação de origem da esmeralda foi inicialmente impulsionada pela proliferação de fontes com a descoberta de novas ocorrências mundiais. Esta expansão e diversificação das fontes de esmeralda e outras gemas, vem se tornando um grande desafio para laboratórios envolvidos na determinação da origem. O número de fontes cresce, assim como a sobreposição em suas características.

Consequentemente, cresce também o número e o nível de pesquisas que visam, ou caracterizar e estabelecer assinaturas cristal químicas para cada uma das ocorrências em particular (Lum *et al.*, 2016; Zheng *et al.*, 2019; Hu & Lu 2019; Guo *et al.*, 2020; Franz *et al.*, 2020; Krzemnicki *et al.*, 2021), ou mesmo realizar um estudo comparativo entre espécimes de diferentes origens (Yu *et al.*, 2000; Saeseaw *et al.*, 2014; Fridrichová, *et al.*, 2018; Aurisicchio, *et al.*, 2018; Saeseaw *et al.*, 2019; Karampelas *et al.*, 2019).

A determinação da origem geográfica é geralmente possível porque existe uma estreita relação entre o ambiente geológico de cristalização, especialmente a mineralogia e a composição química da rocha hospedeira, e as propriedades físico-químicas das gemas. A relativa diversidade química das esmeraldas de depósitos mundiais permite a confiança na determinação da origem na maioria dos casos (Groat *et al.*, 2019).

Essa determinação depende de uma combinação de técnicas analíticas minerais avançadas e, seu nível de confiança, utilizando os métodos analíticos disponíveis hoje em dia, pode ser obtido com diferentes graus de sucesso.

As inclusões e espectroscopias podem frequentemente ajudar a separar entre esmeraldas de diferentes origens, porém, algumas sobreposições podem ocorrer. Para a grande maioria das esmeraldas, análise química para determinar a concentração de elementos traços é necessário, além das informações espectroscópicas e de inclusões do cristal.

Os desafios apresentados pela síntese de gemas em laboratórios, novos tratamentos e sua identificação, multiplicação de novos depósitos de gemas, e o fato de que uma geração completa de gemólogos altamente qualificados estar se aposentando, começaram a preocupar muitos laboratórios, que estão agora começando a desenvolver Bancos de Dados e investindo em programas de campo de gemologia, como é o caso do *Asian Institute of Gemological Sciences-AIGS* em Bangkok, *Gübelin Lab* na Suíça e o *Gemological Institute of America-GIA*, nos Estados Unidos (Gübelin, 2006; Vertrieß *et al.*, 2019).

No Brasil, a Polícia Federal em parceria com a CPRM, idealizou o projeto intitulado "DNA do diamante", visando estabelecer assinaturas de diferentes depósitos diamantíferos brasileiros, objetivando a criação de um Banco de Dados para determinar a proveniência de pedras apreendidas.

A criação de um Banco de Dados é uma longa jornada que começa com uma referência confiável sobre a origem e coleta, catalogação adequada, aquisição e tratamento de dados, e finalmente, a criação de uma forma amigável para que esses dados sejam compartilhados.

Como qualquer Banco de Dados, seu elo mais fraco é a qualidade dos dados produzidos. Segundo John Emmett: *"Só há uma coisa pior do que nenhum dado: são dados ruins. Porque se dados ruins forem publicados, as pessoas os usarão"*. Os equipamentos de alta tecnologia e amostras são úteis, mas no final, sem gemólogos e mineralogistas qualificados e experientes para pesquisar, produzir, questionar, validar e utilizar os dados produzidos de forma sensata, o processo inteiro não é uma garantia de sucesso (Pardieu, 2020).

8. - CONCLUSÕES

As espectroscopias Raman e na região do infravermelho revelaram características similares. A posição das bandas espectrais sugere substituições químicas, onde íons como Al^{3+} , Be^{2+} e Li^{+} substituem o silício na estrutura do cristal de berilo, favorecendo a entrada de íons alcalinos compensadores de carga como Na^{+} , K^{+} , Cs^{+} e Rb^{+} nos canais estruturais. Os resultados revelam esmeraldas naturais, com elevado teor de elementos alcalinos, sugerindo origem com contribuição magmática. No entanto, uma separação clara entre as esmeraldas dos Tipos I e II não pode ser feita usando apenas os espectros Raman, devido à variação do conteúdo de elementos alcalinos nas amostras de diferentes ambientes geológicos, que podem se sobrepor.

Em relação ao teor de água, ambos os tipos de moléculas de água (I e II) estão presentes nos canais estruturais da esmeralda Monte Santo, mas a faixa de absorção de água tipo II domina sobre o tipo I no espectro de todas as amostras. A presença da água duplamente coordenada (tipo IId) sugere um ambiente altamente hidratado e rico em alcalinos, sendo o Na o cátion dominante coordenado pela água tipo II.

A presença das vibrações de CO_2 foi detectada em todas as amostras, além de um pico adicional sutil, atribuído ao N_2 , observado em algumas amostras, onde o último está provavelmente relacionado às inclusões fluidas nas esmeraldas.

A presença de hidrocarbonetos ($-\text{CH}_3$, $-\text{O}-\text{CH}_3$ e $-\text{CH}_3$) também foi detectada em todas as amostras, revelando a aplicação de "substâncias de preenchimento", geralmente óleos ou outro material com índice de refração semelhante ao da esmeralda, utilizadas para melhorar a claridade da gema, reduzindo a visibilidade das fissuras e, às vezes, das cavidades. Embora não desejado, esse procedimento é comumente utilizado e considerado aceitável no mercado de gemas.

Em todas as amostras analisadas, foram observados efeitos de fotoluminescência causados pela presença do Cr^{3+} , onde os picos de luminescência excedem o sinal Raman, frequentemente "estourando" o limite de sinal do equipamento. Através de metodologia própria, testada e estabelecida durante a pesquisa, foi possível minimizar o efeito de interferência da luminescência, o que levou à redução de ruídos nos espectros, tornando possível a obtenção dos espectros Raman para esmeraldas contendo Cr e, potencialmente, para outros minerais que apresentam luminescência.

Os espectros UV-Vis são úteis na separação entre esmeraldas dos tipos I e II, através da intensidade das bandas de absorção relacionadas ao ferro. A banda em $\sim 830\text{nm}$, atribuída ao

Fe, não contribui para a cor, mas é considerada uma assinatura importante, que ajuda a distinguir entre os dois grupos principais de esmeraldas. A grande variação na concentração dos elementos metálicos de transição nas esmeraldas Monte Santo resultou em sobreposições com outros depósitos, e sugere uma origem mista entre magmática e hidrotermal/metamórfica.

A proporção entre as absorções de Cr^{3+} , V e Fe^{2+} é claramente observada, onde a intensidade dos picos e da banda larga relacionados ao Fe^{2+} são visivelmente mais pronunciadas em amostras de cor mais clara, enquanto a intensidade diminui substancialmente em suas homólogas mais escuras, quase desaparecendo. Esta relação está em contraste com as absorções de Cr^{3+} e V^{3+} , onde as suas intensidades aumentam para as amostras mais escuras.

Os resultados da difração de raios-X em monocristal demonstraram significativas distorções cristalográficas, com acréscimo em ambos os eixos *c* e *a*, onde o primeiro é associado com a entrada de elementos alcalinos em sua estrutura, e o último sugere entrada de elementos de metais de transição (V, Cr, Sc, Fe, Mg e outros). A razão *c/a*, permite classificar as amostras em tipo tetraédrico **O**, onde as substituições ocorrem predominantemente nos sítios cristalográficos octaédricos.

O principal ocupante do sítio octaédrico é o Al, que varia de 65,7% a 91,4% da ocupação total deste sítio. Mg, Fe, V, Cr, Sc, Ca e Ba ions são os principais substitutos do Al, na seguinte ordem $\text{Mg} > \text{V} > \text{Sc} > \text{Cr} > \text{Fe} > \text{Ca} > \text{Ba}$.

O sódio é o cátion predominante nos canais *c*. A alta concentração de sódio é justificada pela existência de um ambiente marinho anterior à formação dos depósitos de esmeraldas, e sua entrada na estrutura do mineral possui uma relação direta ao balanço de cargas necessário para compensar as substituições dos elementos nos sítios cristalográficos.

Com base no maior conteúdo de V_2O_3 em relação ao Cr_2O_3 , a esmeralda Monte Santo é aqui classificada como uma esmeralda V-dominante, juntamente com algumas de suas homólogas de Eidsvoll (Noruega), Dayakou (China), Gandao (Paquistão), La Pita, Muzo e Coscuez (Colômbia), Davdar (China), Salininha (Bahia, Brasil) e possivelmente outras. Essa assinatura geoquímica ($\text{V} > \text{Cr}$) estabelece uma separação extremamente importante, com relação à maioria das outras ocorrências de esmeraldas ao redor do mundo, que são Cr-dominante.

Com base na quantidade de substituição e suas proporções de $\text{Mg}/(\text{Mg}+\text{Fe})$, $\text{Cr}/(\text{Cr}+\text{V})$, acredita-se que as rochas meta-sedimentares são a principal fonte de Mg e Fe e, principalmente Cr e V, para a esmeralda Monte Santo.

Fica aqui demonstrado que Sc também é um elemento cromóforo das esmeraldas, conferindo uma cor verde pálida a estes minerais. A presença de três elementos cromóforos (V, Sc e Cr) nas amostras de Monte Santo do Tocantins é bastante fascinante e inesperada. O escândio como elemento cromóforo em esmeralda e sua elevada concentração é um resultado de grande importância e sem precedentes nesta pesquisa, enquanto apenas alguns poucos e raros espécimes de esmeraldas do mundo inteiro têm este elemento em sua composição e, aqueles que têm, apresentam uma concentração muito inferior quando comparados aos resultados da esmeralda Monte Santo.

Sc parece estar concentrado em ambientes geológicos menos fracionados, mas sua fonte ainda não é totalmente compreendida, o que, em minha opinião, o torna particularmente interessante e responsável pela característica dessa ocorrência de esmeraldas que é tão peculiar e única dentre todas as outras ao redor do mundo.

Essa concentração distintamente alta de Sc é o principal critério que separa as esmeraldas Monte Santo de todas as suas análogas, sendo esta, a sua principal assinatura geoquímica, haja visto que nenhuma outra esmeralda do mundo apresenta concentrações tão elevadas deste elemento.

A classificação dos depósitos de esmeraldas é proposta com base no ambiente geológico (magmático ou metamórfico), tipo de rocha hospedeira, grau de metamorfismo, tipo de mineralização, tipo de fluidos e sua temperatura, pressão e composição. Em síntese, os depósitos podem ser dos tipos tectonomagmáticos ou tectonometamórficos.

Os ambientes magmáticos tendem a aprisionar fluidos aquosos salinos ($\text{H}_2\text{O}-\text{NaCl}$), com uma menor contribuição de fluidos aquocarbônicos ($\text{H}_2\text{O}-\text{CO}_2-\text{NaCl}$). Por outro lado, ambientes metamórficos tendem para uma mistura de fluidos $\text{H}_2\text{O}-\text{NaCl}$ e $\text{H}_2\text{O}-\text{CO}_2-\text{CH}_4-\text{NaCl}$ com elevadas salinidades.

Os fluidos identificados nesta pesquisa apontam para uma geração a partir da devolatilização durante o processo de metamorfismo, responsável pela liberação de voláteis tais como CO_2 e CH_4 . Além disso, evidencia-se o fornecimento de fluidos com taxas de salinidades distintas, caracterizadas pela ausência ou presença de um ou mais sólidos de saturação em inclusões aquosas e aquocarbônicas para as inclusões primárias, associados com inclusões fluidas secundárias exclusivamente de baixa salinidade.

O aprisionamento heterogêneo ocorre devido à imiscibilidade de fluidos seja por descompressão, por supersaturação em sais (sólidos acidentais aprisionados) ou pelo aprisionamento de fluidos de composições distintas. O trapeamento heterogêneo resulta em

inclusões fluidas com distintas composições e salinidades, assim como ocorre no processo de *boiling*. Estes processos são evidenciados no presente trabalho pela composição heterogênea dos fluidos coexistentes geneticamente, bem como pela ampla variação do volume gasoso dentro de um mesmo tipo de inclusão fluida.

Os dados apresentados permitem uma interpretação acerca da possível gênese dos fluidos geradores das gemas de esmeralda do depósito Monte Santo como produto da mistura de fluidos oriundos de fontes distintas (magmática + metamórfica), que permitem multi-estágios de formação de esmeralda ligados à remobilização cíclica de fluidos. A liberação de voláteis durante o processo de metamorfismo atua como principal fonte de CO₂ e CH₄. Estas relações estão baseadas na composição distinta de fluidos que coexistem temporal e espacialmente.

A heterogeneidade dos fluidos permite a classificação em ambos os tipos I e II da classificação de Giuliani (Giuliani *et al.*, 2019). O tipo de depósito mais provável é o subtipo IID, que inclui: depósitos tectônicos metamorfizados ou remobilizados tipo Ia, depósitos tectônicos com intrusão granítica oculta, e alguns depósitos não classificados (Egito, Austrália, talvez também Brasil, Áustria, Paquistão, Zâmbia).

Um estudo estatisticamente significativo requer um grande número de amostras de uma localidade. A grande quantidade de amostras estudadas nesta pesquisa (mais de 60 amostras) permitiu estabelecer correlações e variações entre a composição química e as demais técnicas analíticas utilizadas na pesquisa destas esmeraldas, além de proporcionar confiabilidade dos resultados, apesar das heterogeneidades inerentes que um depósito mineral exhibe.

Este estudo mostra, portanto, que uma separação precisa entre esmeraldas de várias origens geográficas não pode ser feita usando as técnicas analíticas individualmente, mas que é geralmente possível diferenciar as esmeraldas de diferentes localidades, com alta acurácia, com base na combinação desses métodos.

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