UNIVERSIDADE FEDERAL DO PARANÁ
SETOR DE CIÊNCIAS DA TERRA
CURSO DE GEOLOGIA

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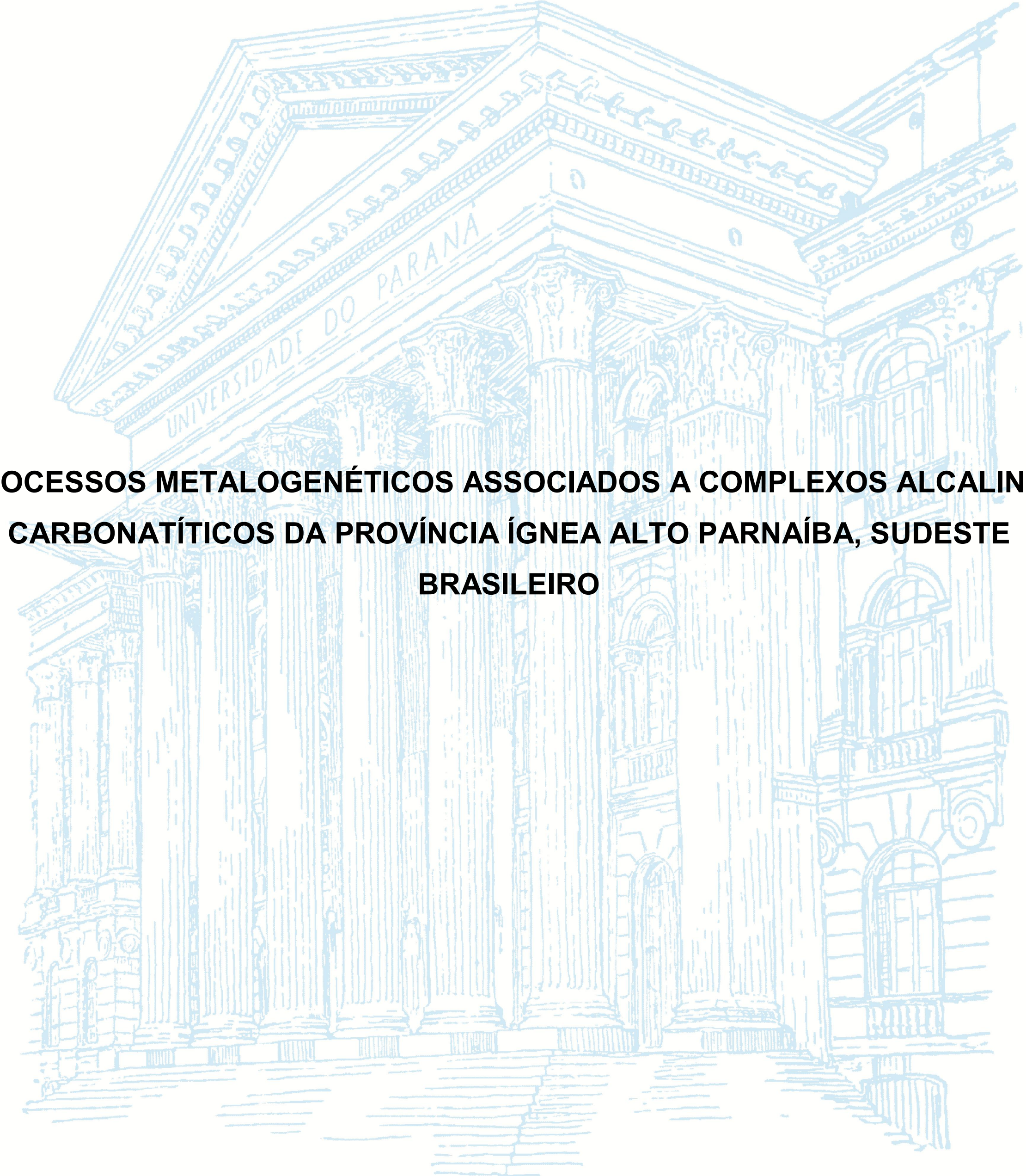

PROCESSOS METALOGENÉTICOS ASSOCIADOS A COMPLEXOS ALCALINO-CARBONATÍTICOS DA PROVÍNCIA ÍGNEA ALTO PARNAÍBA, SUDESTE BRASILEIRO

CURITIBA
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Trabalho de Conclusão de Curso apresentado como requisito parcial à obtenção do grau de geóloga no curso de Bacharelado em Geologia, Departamento de Geologia, Setor de Ciências da Terra, Universidade Federal do Paraná.

Orientador: Prof.º Dr.º Pedro Filipe de Oliveira Cordeiro

CURITIBA
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“Não sou pedra mas posso endurecer.”
Francisco, El Hombre - Calor da rua

“*Solo allí, en lo más alto de nosotros mismos,*
en lo más profundo de nuestras inquietudes,
podremos separar los brazos, y volar.”
Dulce Chacón - La construcción de un sueño

"Sunflower still grows at night.
Waiting for a minute until the sun is seen through my eyes.”
Rex Orange County - Sunflower

RESUMO

Carbonatitos são mundialmente conhecidos como importantes hospedeiros de depósitos de Elementos Terras Raras (ETR), nióbio e fosfato. Estas *commodities* possuem interesse especial para economia global, já que estão intrinsecamente ligadas ao avanço das tecnologias modernas e à produção de fertilizantes para a indústria agropecuária. Seguindo esta premissa, a Província Ígnea Alto Parnaíba (APIP) se destaca em meio as outras, devido a singularidade das características metalogenéticas envolvidas na formação do minério em suas rochas carbonatíticas. A APIP relaciona-se geneticamente a rochas ultramáficas e ultrapotássicas, a exemplo de kamafugitos, lamproitos e kimberlitos, além de hospedar grandes complexos alcalino-carbonatíticos (Araxá, Catalão I and II, Salitre, Serra Negra e Tapira). Apesar de possuirem uma origem claramente mantélica estabelecida através de dados químicos e isotópicos, muitos detalhes sobre este sistema continuam em debate. Por esta razão, este trabalho busca revisar e discutir aspectos gerais sobre os complexos alcalino-carbonatíticos da APIP, incluindo petrogenese, geometria dos corpos de minério e processos de enriquecimento que podem levar ao grau de minério. Assim, concluiu-se que as três séries petrogenéticas que compõem os complexos da APIP (bebedourítica, foscorítica e carbonatítica) sugerem uma origem dominantemente ígnea, com assimilação-cristalização fracionada (AFC), desgaseificação, metassomatismo e intemperismo como processos chave na formação do minério. A série bebedourítica é volumetricamente predominante na maioria dos depósitos, mas os minerais de minério costumam concentrar-se em rochas e perfis de intemperismo relacionados à série foscorítica. As imiscibilidades entre líquidos carbonático-silicático, carbonático-fosfático e fosfático-silicático são amplamente sugeridas na tentativa de explicar a formação destas rochas hospedeiradas de nióbio, mas até agora apenas o processo de AFC foi comprovado com participante ativo na petrogênese de foscoritos. De outra forma, isótopos estáveis de C-O indicam também que alguns foscoritos foram afetados por fluídos de baixa temperatura, ricos em CO_2, enquanto o intemperismo se mostra essencial na concentração residual de minerais de minérios para atingir o grau de enriquecimento necessário e possibilitar a exploração de nióbio e fosfato.

Palavras Chave: Província Ígnea Alto Parnaíba, Complexos Carbonatíticos

ABSTRACT

Carbonatites are known as important hosts for Rare Earth Elements (REE), Niobium and phosphate deposits worldwide. These commodities are of special interest for the global economy, since they are intrinsically connected to the advance of modern technologies and the production of fertilizers for the agricultural industry. Following this premise, the Alto Parnaíba Igneous Province (APIP) stands out among others for the uniqueness of the metallogenic features within ore formation in its carbonatitic rocks. The APIP is genetically linked to ultramafic and ultrapotassic rocks, such as kamafugites, lamproites and kimberlites, and hosts large alkaline-carbonatitic complexes (Araxá, Catalão I and II, Salitre, Serra Negra and Tapira). Although their origin is clearly linked to mantle processes, as established through isotopic and chemical data, this system is still under debate. For this reason, this work aims to review and discuss general aspects of alkaline-carbonatitic complexes from the APIP, including petrogenesis, orebody geometry and enrichment processes that might drive to ore grades. Therefore, the three petrogenetic series that comprise the APIP complexes, the bebedourite, phoscorite and carbonatite series, suggest a dominant igneous origin with assimilation-fractional-crystallization (AFC), degassing, metasomatism and weathering as key ore-formation processes. The bebedourite series predominate volumetrically in most complexes, but ore minerals dominantly concentrate in rocks and weathering profiles related to the phoscorite series. Immiscibility between carbonate-silicate, carbonate-phosphate and silicate-phosphate liquids are widely suggested to explain the formation of these pyrochlore-bearing rocks, but so far only AFC was proven to participate actively in phoscorites petrogenesis. Similarly, C-O isotope data indicate that some phoscorites have been affected by CO_2-rich low temperature fluids. Regarding weathering, the residual concentration processes are imperative in order to reach ore-grade and enable Nb and phosphate explotation.

Key-words: Alto Parnaíba Igneous Province, Carbonatite Complexes

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1 INTRODUÇÃO

Os complexos alcalino-carbonatíticos são formados por magmas raros e consistem nas mais importantes fontes de nióbio (Nb) e elementos terras raras ETR) do mundo, ambos metais essenciais para o avanço tecnológico global. Estas rochas abrigam ainda importantes jazidas de fosfato, barita, magnetita, anatásio, vermiculita, bauxita e fluorita. A quantidade de estudos dedicados a estes complexos é grande e continua crescendo: São teses, dissertações, capítulos de livros e artigos contendo estudos petrológicos, geoquímicos, isotópicos, de química mineral e de petrologia experimental, que vêm sendo usados há décadas na tentativa de compreender a evolução e origem destas rochas (Barker, 1989; Eggler, 1989; Eriksson, 1989; Woolley, 1989; Woolley & Kempe, 1989; Gomes *et al.*, 1990; Dalton & Wood, 1993; Gibson *et al.*, 1995; Harmer & Gittins, 1998; Lee & Wyllie, 1998; Brod, 1999; Brod *et al.*, 2000; Junqueira-Brod *et al.*, 2000; Brod *et al.*, 2004; Krasnova *et al.*, 2004a,b; Comin-Chiaramonti *et al.*, 2005; Ribeiro *et al.*, 2005; Comin-Chiaramonti *et al.*, 2007; Melluso *et al.*, 2008; Ribeiro, 2008; Woolley & Kjarsgaard, 2008; Barbosa, 2009; Cordeiro, 2009; Cordeiro *et al.*, 2010; Grasso, 2010; Cordeiro *et al.*, 2011a,b; Barbosa, 2012a,b; Brod *et al.*, 2013; entre outros).

No Brasil, a maior parte das ocorrências carbonatíticas e rochas alcalinas associadas concentra-se na borda da Bacia Sedimentar do Paraná, em províncias alcalinas que possuem idades entre o Cretáceo Inferior e o Cretáceo Superior. Com exceção da mineração de fosfato Morro da Mina em Cajati, onde explota-se o carbonatito de Jacupiranga (Província Ponta Grossa), as únicas ocorrências carbonatíticas exploradas no Brasil pertencem aos complexos alcalino-carbonatíticos da Província Ígnea Alto Parnaíba (APIP), nos estados de Minas Gerais e Goiás. Na região de Araxá (Minas Gerais), a Companhia Brasileira de Metalurgia e Mineração (CBMM) produz ferronióbio, óxidos de nióbio e ligas metálicas com esta *commodity* desde a década de 50 (CBMM, 2018). Também na região, a chinesa CMOC (*China Molybdenum*) comprou as operações de nióbio e fosfato da *Anglo American* no Brasil, em 2016, hoje produzindo em Catalão I e II, Goiás (CMOC, 2018). Já em 2018, a Mosaic Fertilizantes completou a aquisição da Vale Fertilizantes (Mosaic, 2018a), sendo atualmente a empresa que detém o maior número de minas em carbonatitos no Brasil, explotando fosfato em Tapira, Patos de Minas, Araxá (Minas Gerais), Catalão (Goiás) e Cajati (São Paulo) (Mosaic, 2018b).

O interesse mineral na região é nítido e está diretamente relacionado às grandes reservas de nióbio e fosfato da APIP, concentradas em espessos perfis intempéricos através de processos de enriquecimento supergênico. Apesar de explorada há décadas, faltam estudos que compilem dados e busquem esclarecer a gênese das mineralizações na província. Portanto, este tipo de estudo beneficiaria não somente a continuidade das operações de mineração atuais como também a descoberta e exploração de futuros prospectos.

1.1 OBJETIVOS

Pretende-se agregar ao conhecimento sobre a origem e evolução dos carbonatitos e rochas alcalinas associados aos complexos alcalino-carbonatíticos da Província Ígnea Alto Parnaíba, sudeste do Brasil, bem como aos modelos propostos de gênese da mineralização, utilizando-se de dados petrográficos, mineralógicos, geoquímicos e isotópicos anteriormente publicados e visando produzir um trabalho de revisão de tais dados.

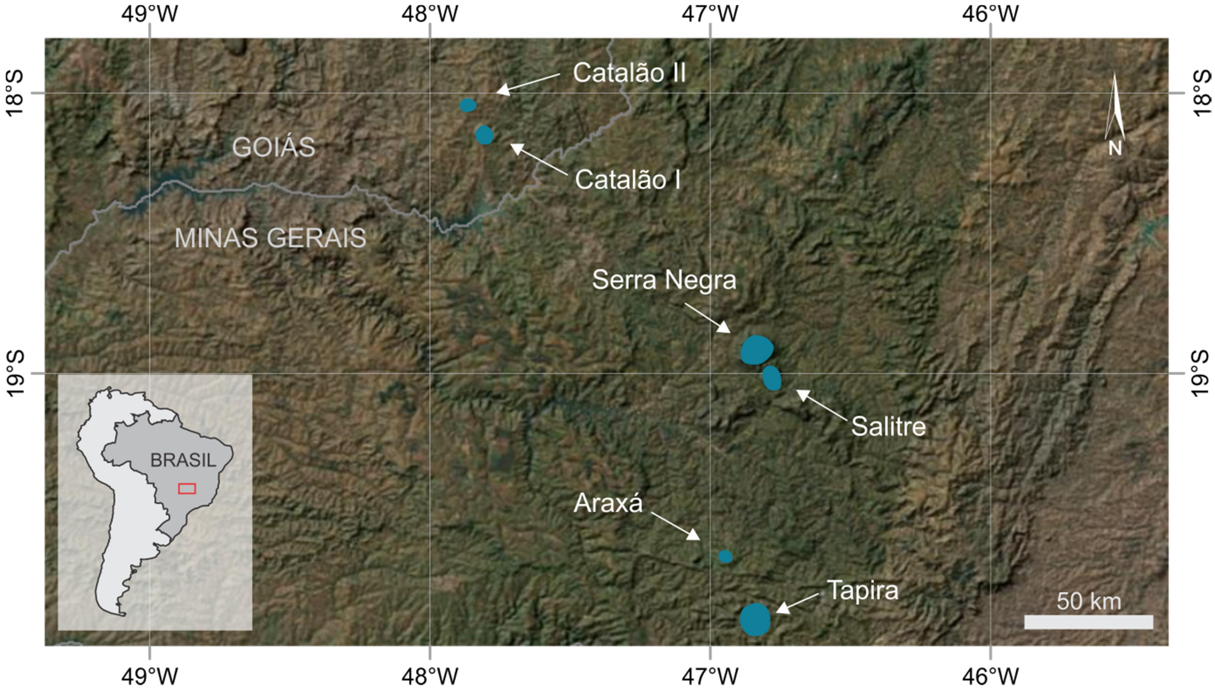
1.1.1 Objetivos Especificos

I. Investigar a distribuição dos diferentes litotipos e séries petrogenéticas nos complexos;
II. Compilar dados de caracterização petrográfica das rochas das diferentes séries petrogenéticas que ocorrem nestes complexos;
III. Compilar dados de geometria dos corpos de minério;
IV. Observar as diferentes propostas de sequências de diferenciação para cada complexo com base em critérios de química mineral;
V. Investigar modelos de origem e evolução dos complexos;
VI. Investigar modelos de origem das mineralizações associadas;
VII. Estabelecer um modelo de evolução generalizado para os complexos da Província Ígnea Alto Parnaíba.

2.2 LOCALIZAÇÃO

Os complexos alcalino-carbonatíticos abordados no âmbito desta monografia localizam-se nos limites dos estados de Minas Gerais (Tapira, Araxá, Salitre, Serra Negra) e Goiás (Catalão I e II), conforme representa a Figura 1.

FIgura 1 - Figura de Localização dos Complexos Carbonatíticos da APIP



Fonte: USGS, NASA and ESRI Inc. (2018)

2 ESTADO DA ARTE

2.1 SÉRIES PETROGENÉTICAS EM COMPLEXOS ALCALINO-CARBONATÍTICOS

Mundialmente, são conhecidos três principais tipos de magma formadores dos complexos alcalino-carbonatíticos: silicático, carbonático e fosfático. Estes magmas não necessariamente ocorrem juntos e suas relações são extremamente complexas, envolvendo processos petrogenéticos diversos, como cristalização fracionada, imiscibilidade de líquidos, desgaseificação e metassomatismo. Durante a evolução de cada um destes tipos de magma, ocorre a geração de produtos diferentes, definindo séries petrogenéticas distintas (Woolley & Kjaarsgard, 2008; Grasso, 2015; entre outros).

Dentre os magmas silicáticos, a série petrogenética a ocorrer depende fundamentalmente da afiliação geoquímica. Na Província Ponta Grossa, por exemplo, ocorrem rochas do Cretáceo Inferior (Comin-Chiaramonti *et al.*, 2007), com afinidade sódica e associação de litotipos das séries carbonatítica e ijolítica (Gomes *et al.* 1990). Por outro lado, a Província Ígnea Alto Parnaíba é caracterizada por rochas do Cretáceo Superior (Gomes *et al.* 1990) que possuem afinidade potássica, estando presentes as séries bebedourítica, foscorítica e carbonatítica (Brod *et al.*, 2004). A série ijolítica é uma das mais comuns nos complexos carbonatíticos pelo mundo e corresponde às rochas plutônicas derivadas da diferenciação de magmas parentais nefeliníticos. Enquanto isso, um número mais restrito de ocorrências está associado à série bebedourítica, que representa o equivalente plutônico de rochas formadas por magmas alcalinos ultrapotássicos, como kamafugitos (Grasso, 2015).

2.1.1 Série Ijolítica

As rochas da série ijolítica (jacupiranguito-melteigito-ijolito-urtito) provém de magmas silicáticos e são essencialmente compostas por nefelina e clinopiroxênio, e classificadas em função das variações modais entre estes constituintes (Figura 2). Apesar de ser importante nos complexos carbonatíticos da Província de Ponta Grossa, os membros desta série não foram, até então, reconhecidos na Província Ígnea do Alto Parnaíba (Grasso, 2015).

Figura 2 - Classificação da Série Ijolítica

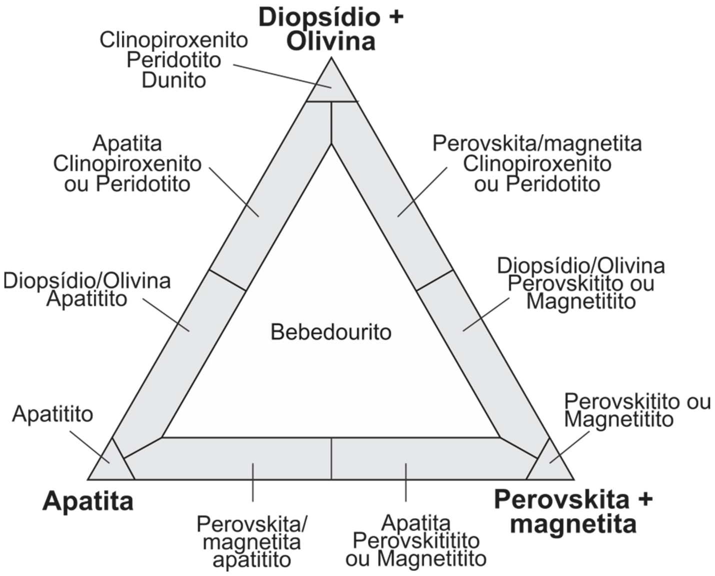
Adaptado de Le Maitre (2002)

2.1.2 Série Bebedourítica

Resultado de sua afinidade potássica, na APIP as rochas silicáticas são representadas pela série bebedourítica. O bebedourito foi definido por Tröger (1928) como um clinopiroxenito rico em perovskita, com aproximadamente 54% de diopsídio, 21% de flogopita, 14% de perovskita e 10% de minerais opacos, com apatita, feldspato potássico e olivina como minerais acessórios. Entretanto, alguns estudos relacionados aos bebedouritos da APIP (Brod, 1999; Brod *et al.* 2004, Ribeiro, 2008; Barbosa, 2009; Grasso, 2010; Palmieri, 2011; Barbosa *et al.*, 2012a) constataram que muitas das variações petrográficas da série bebedourítica envolvem uma mineralogia variada, com nenhum mineral atingindo mais de 50% modal, o que se esperaria para o diopsídio. Além disso, sabe-se também que em diversos bebedouritos de Salitre e Tapira, apatita é uma fase essencial, e não acessória (Grasso, 2015). Desta forma, alguns autores descrevem os bebedouritos como cumulados com ampla variação modal de seus constituintes: olivina, clinopiroxênio, flogopita, perovskita (± melanita, titanita) e apatita (Brod *et al.*, 2004; Barbosa *et al.*, 2012a; Palmieri, 2011). Para representar essas rochas, Brod *et al.* (2004) sugeriram um diagrama para classificação de bebedouritos da APIP (Fig. 3).

A série bebedourítica pode incluir dunitos, clinopiroxenitos e bebedouritos, além de sienitos como termo mais diferenciado. Os termos mais primitivos, representados pelas rochas ultramáficas da série, são precoces na história de evolução dos complexos alcalinos da APIP, encontrando-se geralmente intrudidos por *stockworks* de carbonatito e foscorito. Enquanto isso, os sienitos tendem a ser mais tardios e associam-se frequentemente a carbonatitos, podendo representar produtos de imiscibilidade de líquidos (Brod, 1999). Estas rochas costumam ainda ser afetadas por um metassomatismo potássico de intensidade variável, tendo-se flogopititos como produto da alteração ocasionada pela intrusão de corpos foscoríticos e carbonatíticos (Palmieri, 2011).

Figura 3 - Classificação da Série Bebedourítica

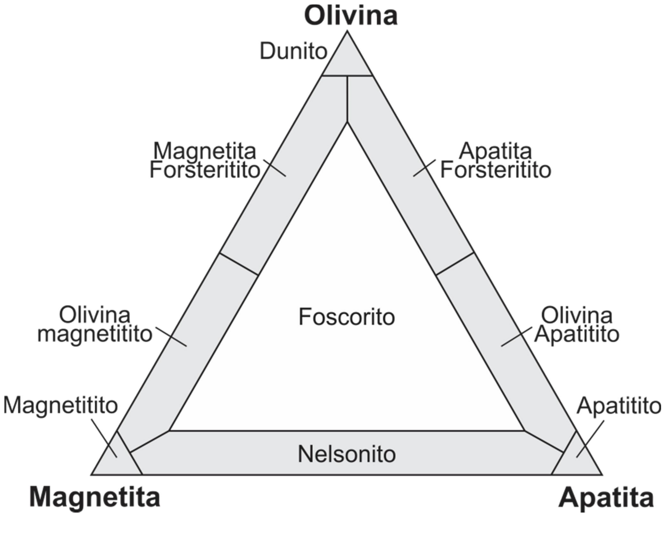


Adaptado de Brod *et al.* (2004).

2.1.3 Série Foscorítica

Yegorov (1993) define foscorito como uma rocha ígnea composta essencialmente por apatita, magnetita e olivina, bem como Le Maitre (2002) usa uma definição similar, acrescentando apenas a comum associação deste litotipo com rochas carbonatíticas. Krasnova *et al.* (2004a), através da compilação da informação já disponível, adicionaram que a nomenclatura “foscorito” poderia ser utilizada também para rochas contendo outros silicatos magnesianos, como diopsídio e flogopita, que deveriam ser somados ou substituir a olivina. Entretanto, neste caso Cordeiro *et al.* (2010) destacam que, para as rochas de Catalão I (e aqui extende-se a afirmação para todos os Complexos da APIP), a fase silicática possui importância essencial para identificação do estágio evolucionário da rocha dentro da série foscorítica. Assim, os autores propuseram uma adaptação da classificação de Yerogov (Figura 4). Além dos foscoritos *sensu strictu*, Cordeiro *et al.* (2010) também descrevem foscoritos sem olivina e ricos em magnetita ou apatita, tendo a tetra-ferriflogopita como principal silicato. Na classificação de Yegorov (1993), estas rochas podem ser nomeadas como nelsonitos.

Figura 4 - Classificação da Série Foscorítica



Adaptado de Yegorov (1993) e Cordeiro *et al.* (2010).

2.1.4 Série Carbonatítica

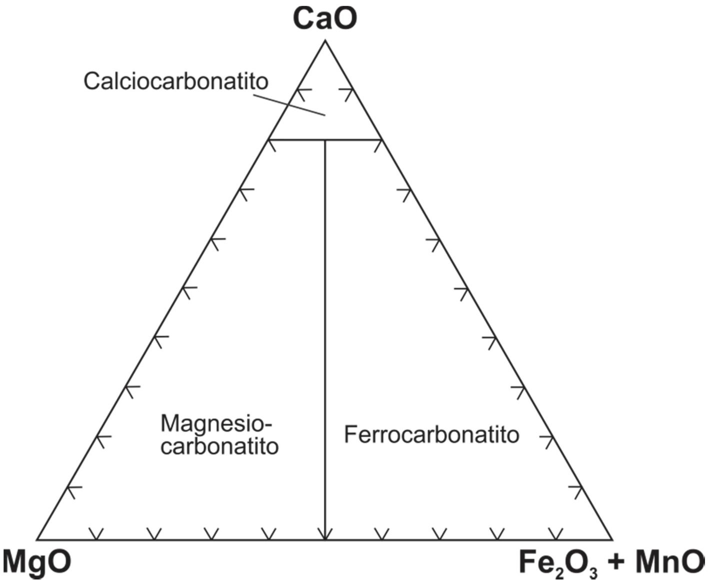
Por definição, carbonatitos são tidos como rochas ígneas, intrusivas ou extrusivas, que contenham mais de 50% em volume de carbonatos (Streckeisen, 1980). Estas rochas são classificadas com base em seu carbonato predominante (Le Maitre, 2002), entretanto, na impossibilidade de identificar o carbonato, Woolley & Kempe (1989) recomendam a utilização de critérios químicos para classificar os carbonatitos (Tab. 1; Figura 5). Contudo, a nomenclatura química pode não refletir diretamente a composição mineralógica da rocha. É possível, por exemplo, que um ferrocarbonatito seja rico em oxidos de ferro, em vez de carbonatos de ferro. Considerando a composição variada dos carbonatitos, é possível destacar apatita (fósforo e ETR), pirocloro (nióbio), anatásio (titânio) e vermiculita como os principais minerais de minério nos complexos brasileiros (Gomes *et al.*, 1990).

Tabela 1 – Classificação de carbonatitos

Carbonato principal	**Nomenclatura**	**Nomenclatura química**
Calcita	Calcita-carbonatito	CaO: Caciocarbonatito
Dolomita	Dolomita-carbonatito	MgO: Magnesiocarbonatito
Ankerita, Siderita	Ferrocarbonatito	FeO + Fe2O3 + MnO: Ferrocarbonatito
Carbonatos de Na, K e Ca	Natrocarbonatito	-

Fonte: Streckeisen (1980); Brod *et al.* (2004).

Figura 5 - Classificação Química da Série Carbonatítica



Adaptado de Woolley & Kempe (1989).

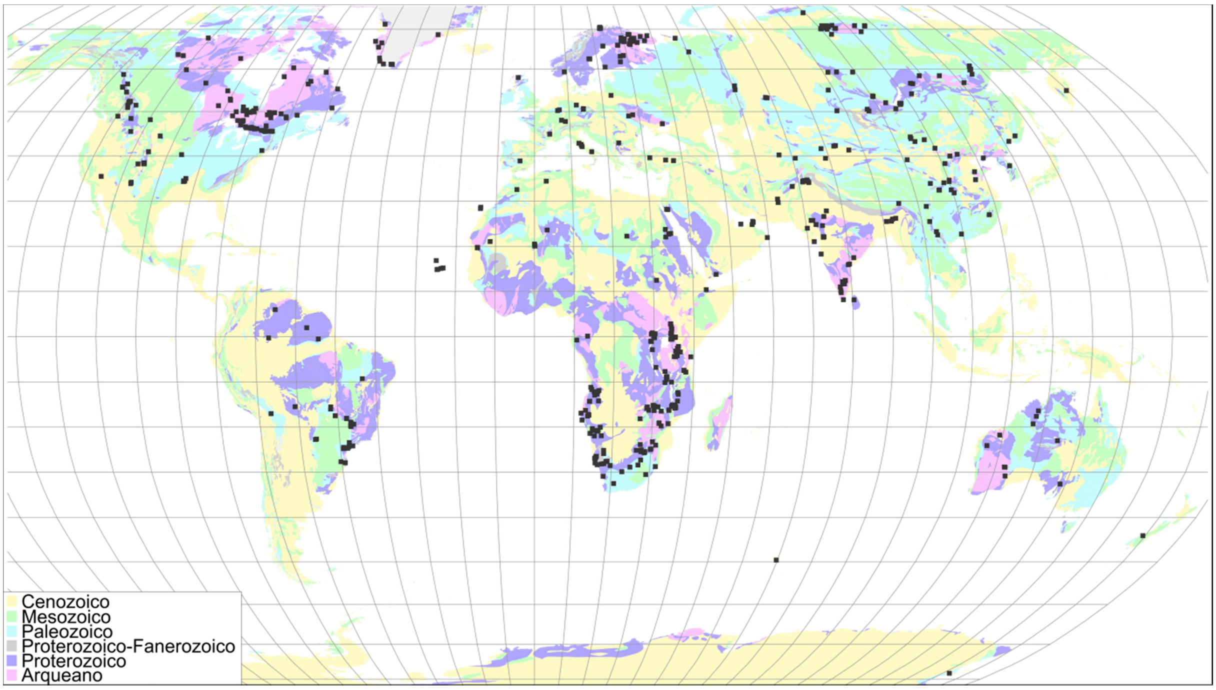
Essas rochas podem ser formadas por três diferentes processos, sendo eles: Fusão parcial do manto; cristalização fracionada; e imiscibilidade de líquidos. Carbonatitos com origem apenas na fusão do manto são considerados “carbonatitos primários” e não possuem necessariamente associação com rochas alcalinas silicáticas. Entretanto, casos de carbonatitos associados à estas rochas silicáticas são muito mais comuns (Woolley e Kjarsgaard, 2008), dando abertura para a sugestão de que a geração destas rochas por cristalização fracionada ou imiscibilidade de líquidos a partir de um magma silicático rico em CO_2 seja mais usual.

Assim, devido à sua derivação de fontes mantélicas e processos genéticos associados, os carbonatitos ocorrem, em muitos casos, associados à rochas alcalino-silicáticas, em grandes províncias alcalinas, a exemplo da Província Alto Parnaíba (Brod *et al*., 2004).

2.2 OCORRÊNCIAS CARBONATÍTICAS BRASILEIRAS

São conhecidas no mundo cerca de 527 ocorrências carbonatíticas, listadas por Woolley & Kjarsgaard (2008; Figura 6), e que localizam-se predominantemente em ambiente intraplaca relativamente estável, podendo ser encontradas também próximas à margens de placas tectônicas, relacionadas à atividade orogênica ou de separação de placas (Wooley, 1989).

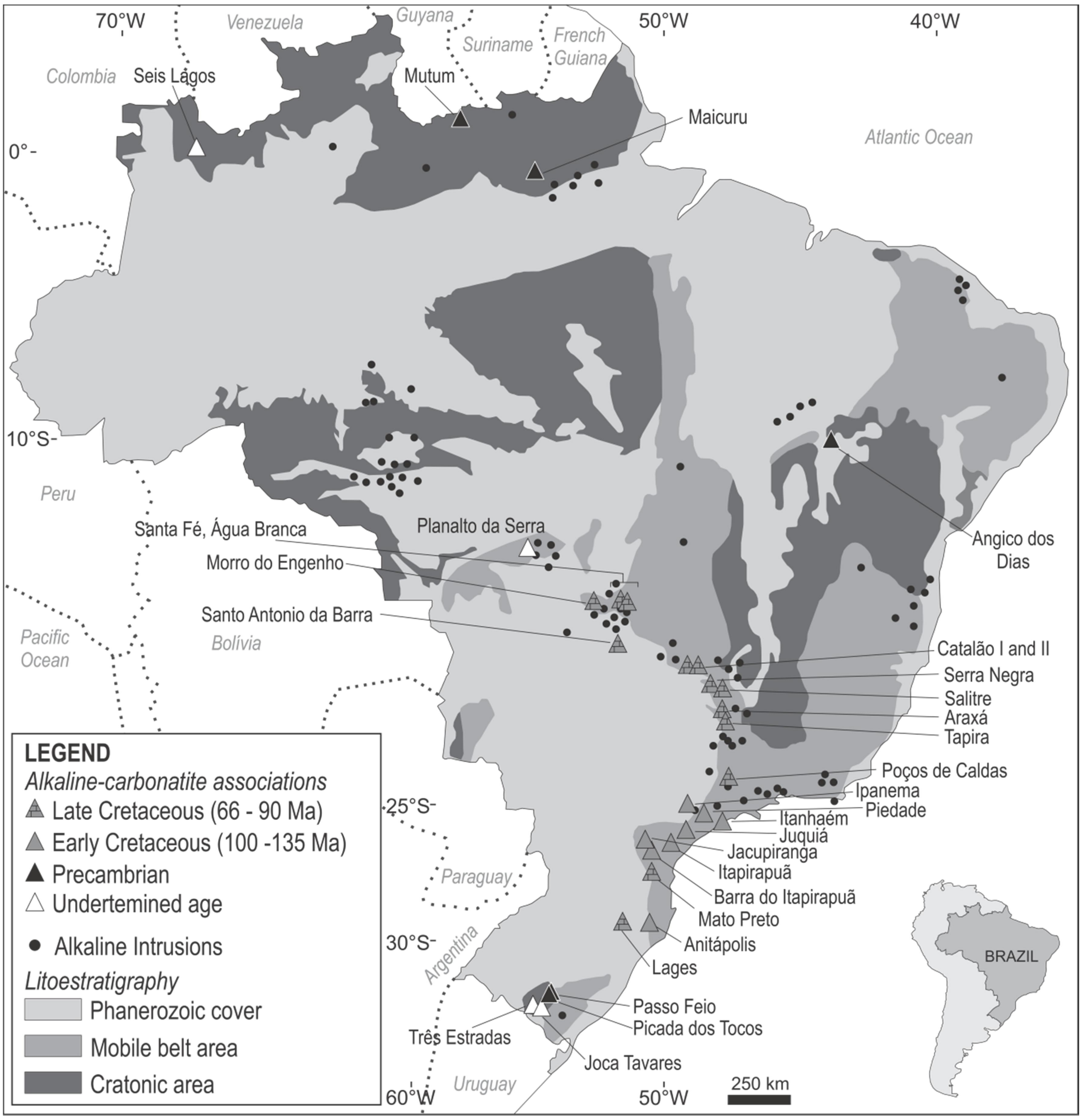
Figura 6 - Mapa de distribuição das ocorrências carbonatíticas pelo mundo



Adaptado e traduzido de Woolley & Kjarsgaard (2008).

Através da compilação de diversos trabalhos (Gomes *et al.,* 1990; Woolley & Kjarsgaard, 2008; Cerva-Alves *et al.*, 2017; Gomes *et al.,* 2018; entre outros), chegou-se a contagem de 32 ocorrências carbonatíticas brasileiras (Figura 7). Os complexos carbonatíticos brasileiros geralmente estão associados à províncias ígneas, como as províncias de Ponta Grossa (e.g. Jacupiranga, Juquiá, Ipanema, Mato Preto, Barra do Itapirapuã; Gomes *et al.*, 1990), do Alto Parnaíba (Araxá, Catalão I e II, Salitre,Serra Negra e Tapira; Brod, 1999; Brod *et al.*, 2004) e de Goiás (Caiapó, Morro do Engenho, Santo Antônio da Barra, Santa fé e Água Branca; Gomes *et al*., 2018).

Figura 7 - Mapa das ocorrências carbonatíticas brasileiras



Adaptado de Cerva-Alves *et al.* (2017)

Este complexos representam predominantemente corpos intrusivos e hipabissais, subcirculares ou ovais, indicativos de alta energia de colocação. Neles, os carbonatitos são encontrados principalmente como *stocks*, *plugs,* diques, enxames de diques e veios ou *stockworks*. Os carbonatitos brasileiros e suas rochas alcalinas associadas encontram-se alojados em grupos pré-cambrianos (e.g., Açungui, Araxá, Canastra, etc.) e têm quartzitos, xistos, granitos e gnaisses como suas principais rochas encaixantes (Gomes *et al.*, 2018).

No Brasil, a atuação extensa de processos intempéricos é característica das ocorrências alcalino-carbonatíticas, dando origem a camadas lateríticas que podem atingir até 300 m de espessura (Brod *et al.*, 2004; Gomes *et al.*, 2018). Solos residuais originam-se principalmente da alteração de rochas ultramáficas e da dissolução de carbonatos. Como resultado, formam-se grandes depósitos supergênicos e residuais de apatita, pirocloro, vermiculita, anatasio, dentre outros.

2.3 PROVÍNCIA ÍGNEA ALTO PARNAÍBA (APIP)

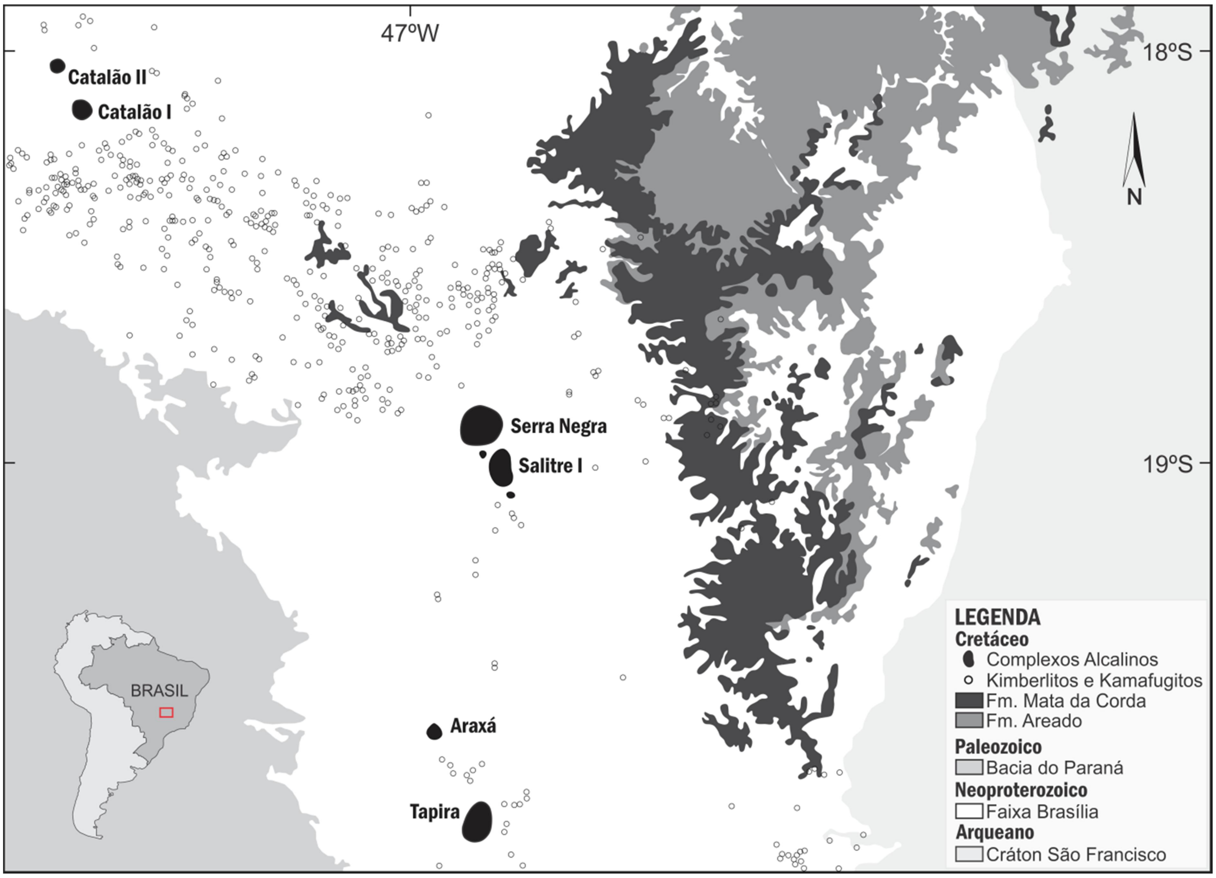
Localizada entre os estados de Goiás e Minas Gerais, a APIP demonstra a singularidade das características metalogenéticas dentro da formação de minério em rochas carbonatíticas. Hospedando a maior reserva de nióbio conhecida no mundo, com cerca de 4.100 milhões de toneladas (Mt) (USGS, 2018), esta província é o resultado de um evento magmático alcalino com idades entre 80 e 90 Ma e que é representado por uma grande diversidade de formas ígneas, como fluxos de lava, diques, *pipes*, diatremas, depósitos piroclásticos e grandes complexos plutônicos que abrangem rochas carbonatíticas (Gibson *et al.*, 1995).

A APIP possui afinidade potássica e está geneticamente ligada a rochas ultramáficas e ultrapotássicas, como kamafugitos e kimberlitos, além dos próprios carbonatitos (Figura 8). Os Complexos Carbonatíticos da APIP constituem, no geral, intrusões circulares ou dômicas, compostas por núcleos de carbonatitos cercados de rochas das séries bebedourítica (rochas silicáticas incluindo dunitos, clinopiroxenitos e bebedouritos) e foscorítica (foscoritos, nelsonitos, magnetititos e apatititos; Gibson *et al.*, 1995, Brod *et al.*, 2004).

Com excessão de Serra Negra, estes complexos apresentam metassomatismo moderado a intenso de suas rochas ultramáficas, gerando flogopititos, além da fenitização das rochas encaixantes (geralmente xistos e quartzitos), nas quais há a formação de minerais como ortoclásio e anfibólios alcalinos (Brod *et al.*, 2004).

Estas características transformaram a província em foco de explorações de Nióbio e Fosfato, além de alvo de estudos para prospecção de ETR. Este fato implica em uma grande importância econômica dos carbonatitos para o país, o que faz com que os estudos relacionados à gênese do minério sejam ainda mais relevantes.

Figura 8 - Mapa Geológico da Província Ígnea Alto Parnaíba.



Após Oliveira *et al.* (2004).

3 MATERIAIS E MÉTODOS

Existem dois tipos principais de revisões de literatura, sendo elas a Revisão de Literatura Sistemática (RLS) e a Revisão de Literatura Narrativa (RLN). A Revisão de Literatura Sistemática utiliza de critérios específicos, pré-selecionados, para a definição das obras que virão a ser analisadas, produzindo uma avaliação extremamente quantitativa dos trabalhos. Embora tenham sido estabelecidos critérios para a seleção dos artigos aqui referenciados, acredita-se que uma avaliação qualitativa é a mais ideal na interpretação de dados geológicos. Assim, confere-se um caráter de Revisão de Literatura Narrativa a esta monografia.

Entretanto, a fim potencializar os resultados obtidos através deste trabalho, optou-se por seguir a lógica dos sete passos sugeridos pela *Cochrane Collaboration* (órgão altamente referenciado em trabalhos de revisão na área da ciência médica; 2011), para Revisões de Literatura Sistemáticas. Estes passos são passíveis de aplicação, ao menos parcialmente, também à produção de uma RLN. São eles:

1. Definir o questionamento: Para o inicio de um Revisão de Literatura, é necessário estabelecer um questionamento claro a ser respondido durante o desenvolvimento do trabalho. Nesta monografia, procura-se responder “quais são e como atuam os principais processos metalogenéticos envolvendo carbonatitos da Província Ígnea Alto Parnaíba?”;
2. Localizar estudos: Buscar e arquivar artigos publicados em periódicos, publicações em anais de congressos, bancos de dados disponibilizados *online*, livros, entre outros;
3. Avaliação crítica dos estudos: Aqui, aplicam-se os critérios para seleção dos artigos que serão investigados. Para este trabalho, foram selecionados estudos com foco na petrogênese, geoquímica, metalogênese e geometria de minério dos depósitos carbonatíticos;
4. Coleta de Dados: Para uma RSL, esta fase representa a descrição da abordagem metodológica de cada estudo analisado (variáveis, amostragem, medidas e análise de dados) que permitem a comparação entre os estudos selecionados. Entretanto, o foco de uma RNL não é comparar metodologias e sim compilar resultados e interpretações. Para tal, na fase de coleta de dados, foram elaborados tópicos para facilitar a coleta seletiva de dados a partir das obras escolhidas, sendo ele: Petrografia e química mineral; Geoquímica de Rocha total; Geometria dos corpos de minério; Metalogênese e intemperismo;
5. Análise de Dados: Para uma RSL, este passo consiste na análise estatística e síntese dos resultados (meta-análise). Aqui, a análise dos dados é feita apenas no sentindo de compilação das informações extraídas dos trabalhos estudados, através de tabelas, gráficos e figuras;
6. Interpretação dos dados: Apresentação das interpretações feitas a partir dos dados analisados;

7. Aprimoramento e atualização da revisão: consiste na atualização do trabalho de revisão, visando incluir sugestões e corrigir pontos criticados. Este passo não se aplica ao escopo desta monografia.

Durante a leitura dos trabalhos selecionados, também optou-se por seguir uma hierarquização, partindo dos trabalhos mais abrangentes (e.g. ocorrências carbonatíticas brasileiras e Província Ígnea Alto Parnaíba) e avançando até os trabalhos mais específicos (direcionados à petrogênese, geoquímica, metalogênese e geometrias dos complexos Araxá, Catalão I e II, Salitre, Serra Negra e Tapira). Por fim, o número e classificação das obras consultadas durante esta pesquisa constam na Tabela 2.

Tabela 2 - Quantidade de obras consultadas no escopo da monografia

Tipo de obra	**Quantidade**	**Anos de publicação**
Artigo de periódico ou livro	73	1977 – 2018
Dissertação (mestrado)	8	2001 – 2015
Tese (doutorado)	6	1999 – 2015

4 RESULTADOS

Niobium, Rare earth elements and Phosphate-bearing Alkaline-Carbonatite Complexes of Alto Parnaíba Igneous Province, Central Brazil: A Review

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Abstract

Carbonatites are known as important hosts for Rare Earth Elements (REE), Niobium and phosphate deposits worldwide. These commodities are of special interest for the global economy, since they are intrinsically connected to the advance of modern technologies and the production of fertilizers for the agricultural industry. Following this premise, the Alto Parnaíba Igneous Province (APIP) stands out among others for the uniqueness of the metallogenic features within ore formation in its carbonatitic rocks. The APIP is genetically linked to ultramafic and ultrapotassic rocks, such as kamafugites, lamproites and kimberlites, and hosts large alkaline-carbonatitic complexes (Araxá, Catalão I and II, Salitre, Serra Negra and Tapira). Although their origin is clearly linked to mantle processes, as established through isotopic and chemical data, this system is still under debate. For this reason, this paper aims to review and discuss general aspects of alkaline-carbonatitic complexes from the APIP, including petrogenesis, ore body geometry and enrichment processes that might drive to ore-grades. Therefore, the three petrogenetic series that comprise the APIP complexes, the bebedourite, phoscorite and carbonatite series, suggest a dominant igneous origin with assimilation-fractional-crystallization (AFC), degassing, metasomatism and weathering as key ore-formation processes. The bebedourite series predominate volumetrically in most complexes, but ore minerals dominantly concentrate in rocks and weathering profiles related to the phoscorite series. Immiscibility between carbonate-silicate, carbonate-phosphate and silicate-phosphate liquids are widely suggested to explain the formation of these pyrochlore-bearing rocks, but so far only AFC was proven to participate actively in phoscorites petrogenesis. Similarly, C-O isotope data indicate that some phoscorites have been affected by CO_2-rich low temperature fluids. Regarding weathering, the residual concentration processes are imperative in order to reach ore-grade and enable Nb and phosphate explotation.

Key-words: Alto Parnaíba Igneous Province, Alkaline-carbonatitic Complexes, Brazilian Carbonatites

1. Introduction

Carbonatites can be important sources of economically strategic mineral deposits of Nb, U, Th, Ti, Ba, Sr, rare earth elements (REE) and industrial minerals such as apatite and magnetite (Hogarth, 1989; Mariano, 1989), which is the main reason leading to attempts to explain the genesis and evolution of alkaline-carbonatitic complexes around the world (Barker, 1989; Eggler, 1989; Eriksson, 1989; Woolley, 1989; Woolley & Kempe, 1989; Gomes et al., 1990; Dalton & Wood, 1993; Gibson et al., 1995; Harmer & Gittins, 1998; Lee & Wyllie, 1998; Brod, 1999; Brod et al., 2000; Junqueira-Brod et al., 2000; Brod et al., 2004; Krasnova et al., 2004a,b; Comin-Chiaramonti et al., 2005; Ribeiro et al., 2005; Comin-Chiaramonti et al., 2007; Melluso et al., 2008; Ribeiro, 2008; Woolley & Kjarsgaard, 2008; Barbosa, 2009; Cordeiro, 2009; Cordeiro et al., 2010; Grasso, 2010; Cordeiro et al., 2011a,b; Barbosa et al., 2012a,b; Brod et al., 2013; among others). There are approximately 527 known carbonatite occurrences in the world, as listed by Woolley & Kjarsgaard (2008). Among these, 32 are Brazilian occurrences (Fig. 1).

The Alto Parnaíba Igneous Province, in Central-Southeastern Brazil, hosts the largest reserves of Nb in the world, along with great phosphate and REE deposits, and has long been a reason of interest for the Brazilian and international geological community. APIP is part of a history of alkaline magmatism that formed several ultramafic-alkaline provinces in the margin of Paraná Sedimentary Basin and includes a large diversity of igneous forms, such as lava flows (Mata da Corda Formation), dikes, pipes, diatremes, pyroclastic deposits and large plutonic complexes (Gibson et al., 1995).

APIP dates from Upper Cretaceous and has an unusual potassic filiation that results in the association of bebedouritic, phoscoritic and carbonatitic petrogenetic series within its large intrusive alkaline complexes (Araxá, Catalão I and II, Salitre, Serra Negra and Tapira).

The alkaline-carbonatitic complexes from the APIP have been mineral exploration and prospecting targets for decades, but many details about their ore genesis are still under debate. Liquid immiscibility and crystal settling are believed to be the main mechanisms to generate carbonatites. Otherwise, ore mineralization is more complicated and also directly linked to supergenic enrichment processes.

2. Intrusion Geometry

The APIP Carbonatitic Complexes represent relatively shallow multiphase intrusions, with circular or oval geometry. These large intrusions are hosted in Neoproterozoic quartzites and phyllites (Ibiá, Araxá and Canastra Groups) from the Brasilia Belt. The high energy emplacement of these bodies resulted in doming of the country rocks (Gomes et al., 2018), frequently expressed on surface as a dome-shaped topographic high.

The various lithotypes comprising the alkaline-carbonatitic complexes are usually arranged in a certain pattern (Fig. 2). Generally, the fenitized country rocks are in contact with outer ultramafic cumulates from the bebedouritic series. In most of APIP's complexes this is the dominant petrogenetic series and often shows metasomatic alteration to phlogopitites (also formerly called glimmerites). Phoscorite and carbonatite series rocks are concentrated in the center of the complexes, where both phoscorites and carbonatites can be found as stocks, plugs, dikes, swarms of dikes and veins or stockworks (Brod et al., 2004; Cordeiro et al., 2010).

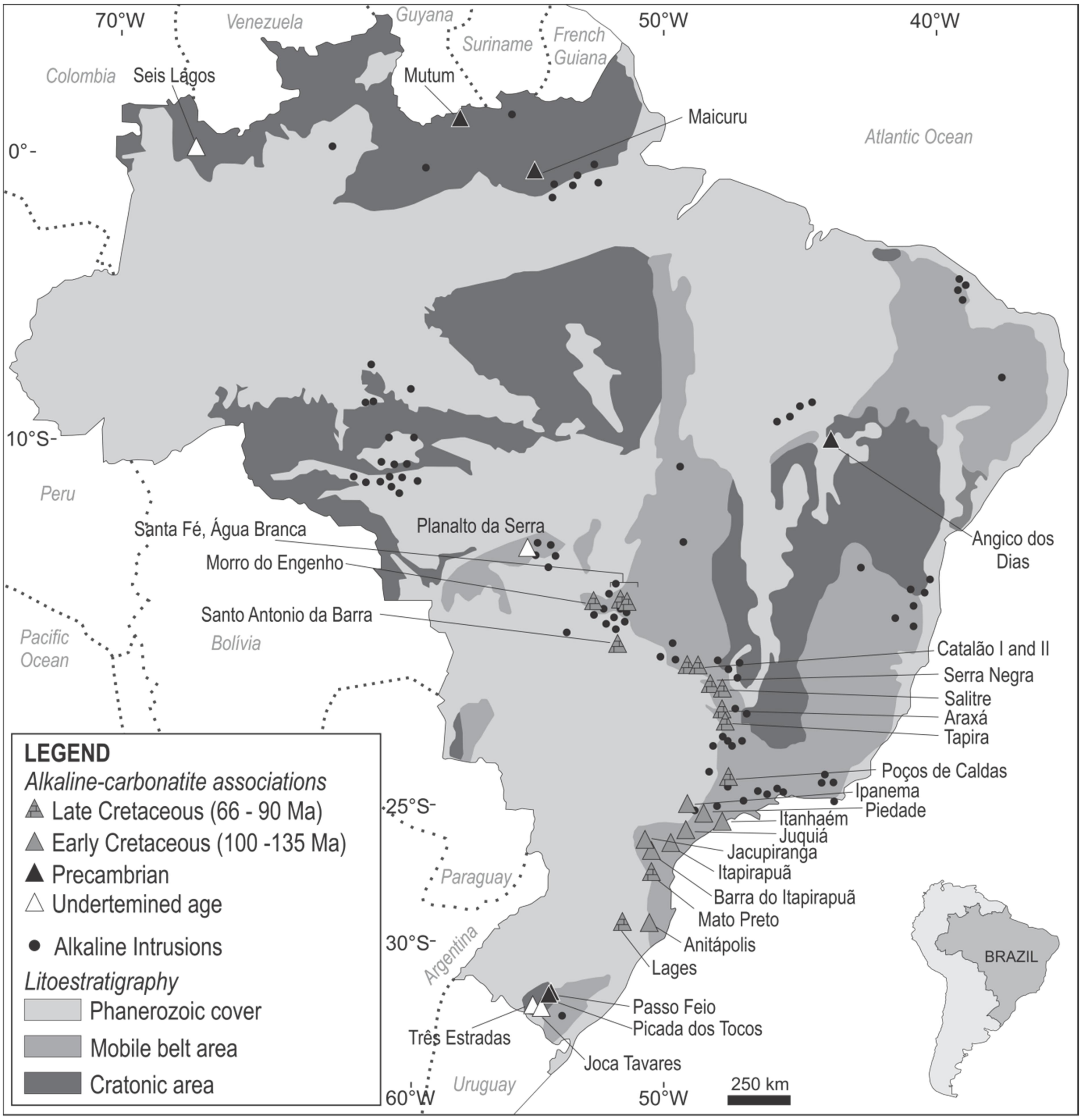

Fig. 1 - Brazilian carbonatite occurrences. Adapted from Cerva-Alves et al. (2017).

The patterns observed in geological maps and sketches reflect intrusions arranged in a vertical envelope, similar to what is interpreted for Sokli and Palaborwa complexes (O'brien & Hyvönen, 2015; Dixon, 1979). On the other hand, based on the description of magmatic banding in carbonatites from APIP complexes (e.g. Barbosa, 2009; Grasso, 2015), the occurrence of phoscorite and carbonatite as horizontal layers within the intrusion envelope, besides only dike-like bodies and dike-swarms, is also feasible. Therefore, figure 3 is an attempt to represent a possible geometry model for the APIP alkaline-carbonatite complexes intrusions. Ultramafic rocks tend to compose the magmatic chamber, composing a volumetrically significant horizontal body, often displaying magmatic bedding and cumulate texture. Meanwhile, early phoscorites can also display horizontal geometry, although generally carbonatites and phoscorites tend to form transgressive intrusions with variable thickness. Cumulates of apatite, magnetite and olivine (nelsonites) might be present, besides carbonatites with magmatic bedding.

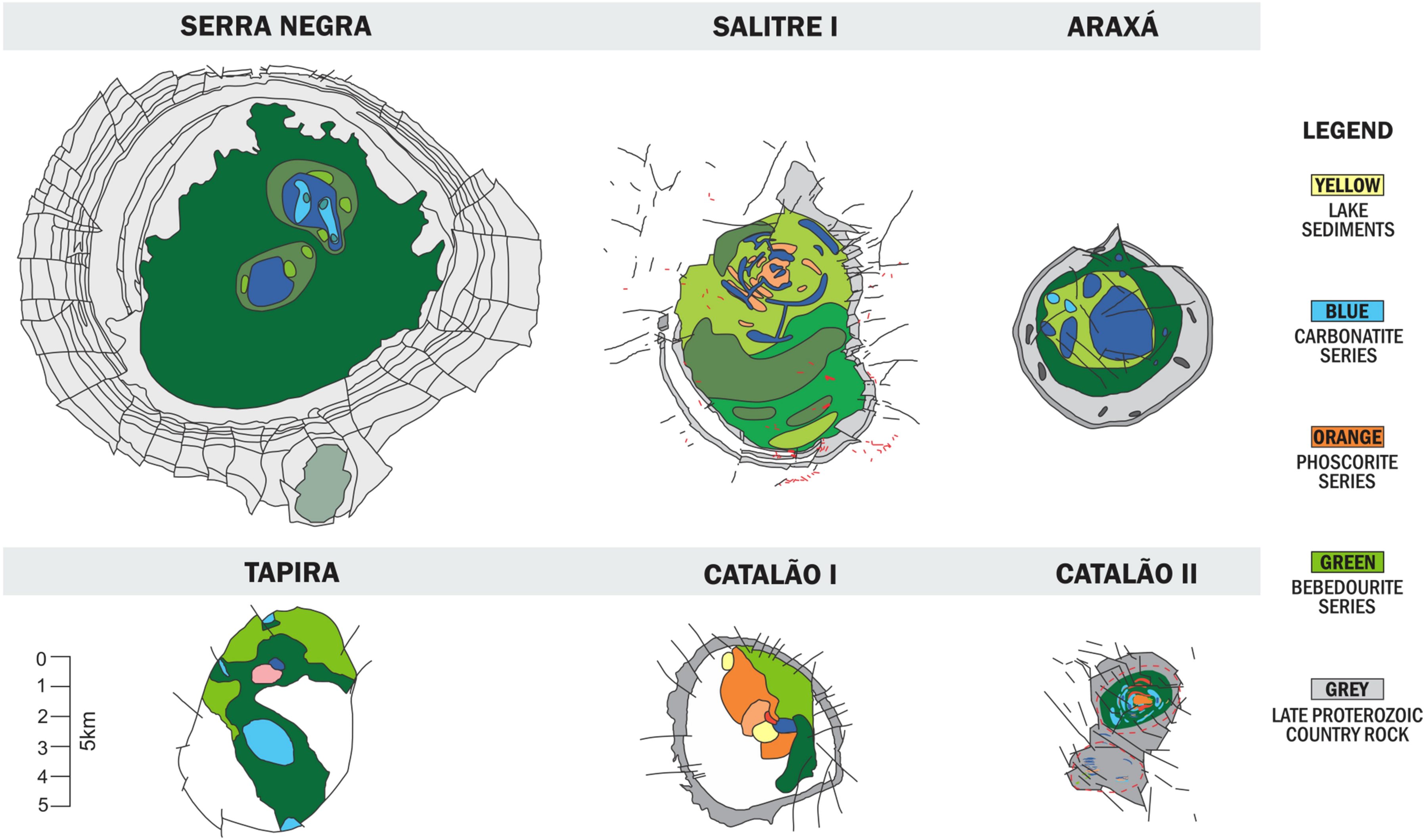

Fig. 2 - Comparative geometry and sizes of Alkaline-Carbonatitic complexes from APIP. Geological sketches based on: Grasso (2010) – Serra Negra; Barbosa (2009) – Salitre; Grasso (2015) – Araxá; Brod et al., (2013) – Tapira; Cordeiro et al., (2010) – Catalão I; and Palmieri (2011) – Catalão II.

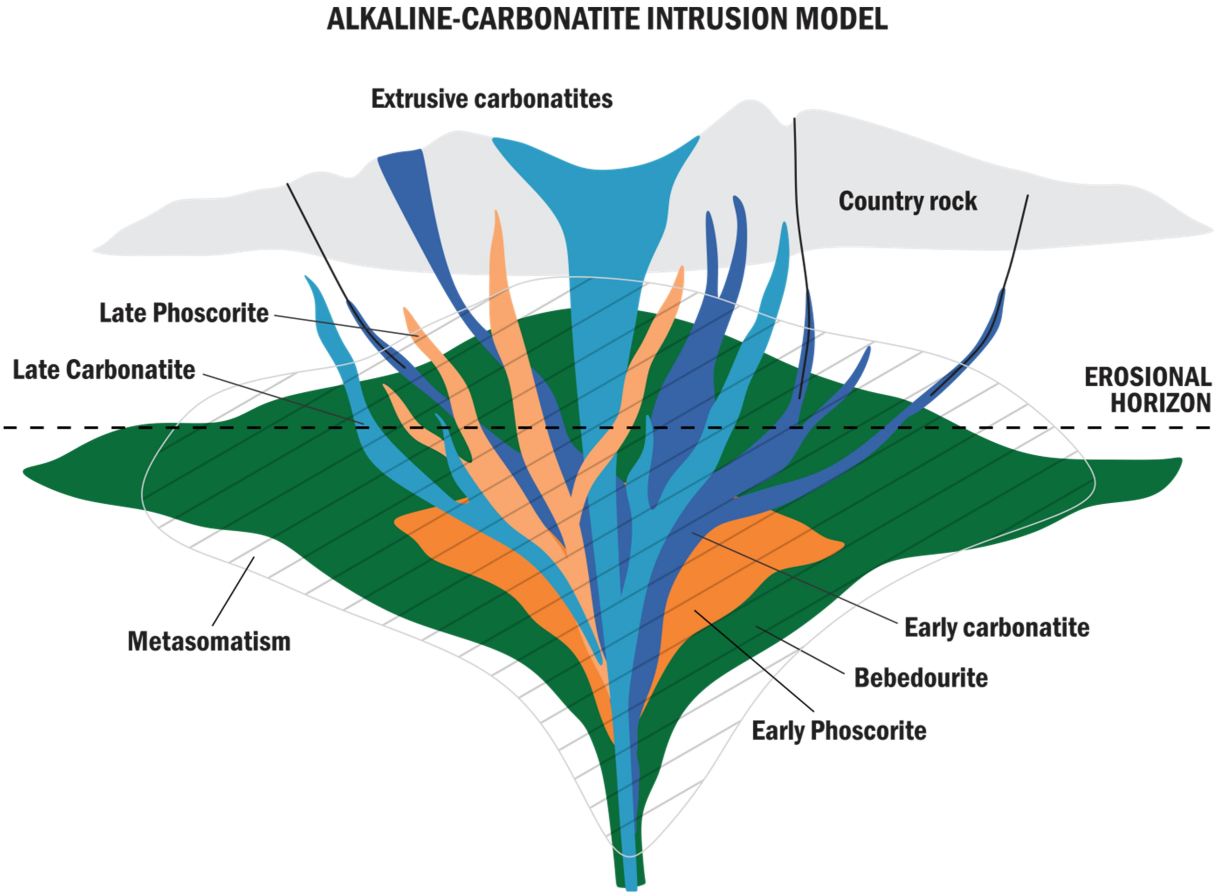

Fig. 3 - General schematic model for bebedourite-phoscorite-carbonatite intrusions in the Alto Parnaíba Igneous Province.

Late stage carbonatite and phoscorites are often related and can reach shallower depths. Carbonatites in this geological setting also present an extrusive form that is not observed in APIP complexes due to the current erosional horizon.

3. Araxá Complex

The region of Araxá, Minas Gerais, Brazil, has been an object of mineral prospecting since the eighteenth century, with deposits being currently exploited by the Brazilian CBMM (Companhia Brasileira de Metalurgia e Mineração) and the north american Mosaic Company. The Araxá Complex, also known as Barreiro, is located about 6 kilometers near its homonymous city, at the coordinates 19°38'S, 46°56'W, and bears the greatest niobium reserve in the world, as well as highly relevant phosphate deposits and REE ores.

The Araxá Complex is a small (4.5 km of diameter), roughly circular, intrusive body. Host rocks are represented by deformed and fenitized schists and quartzites from the Ibiá Group Seer (1999). Based in K-Ar isotopes, Sonoki & Garda (1988) proposed ages between 77 and 97 Ma for this complex. At last, the fenitization rim takes its place, hosting the intrusion and reaching up until a 2.5 km distance from the contact (Brod et al., 2004; Fig. 4).

The complex outer ring is composed of phlogopitites formed by the metasomatism of ultramafic rocks. Metamasomatic phlogopitites represent altered rocks from bebedouritic series and are volumetrically very significant in the complex. Locally, it's possible to find relicts from pyroxene and olivine grains, besides rare preserved remains of the primary ultramafic rocks (Brod et al., 2004).

The complex core contains a central carbonatite and phoscorite plug, with other additional and less expressive carbonatite intrusions. The predominant type of carbonatite is dolomitic, with typical calcite carbonatites presented only in the NW portion of the complex (Silva, 1986).

The Araxá Complex hosts supergene phosphate and niobium deposits developed by a process of residual concentration during intense weathering, particularly of phoscoritic and carbonatitic rocks, in which the primary concentrations of apatite and pyrochlore are higher. In the Araxá complex, this weathering profile can reach 250 meters of thickness (Brod et al., 2004). Therefore, Araxá can be considered an example for dolomite carbonatite predominance, intensity of metasomatic alteration and weathering, besides hosting of great niobium and phosphate reserves.

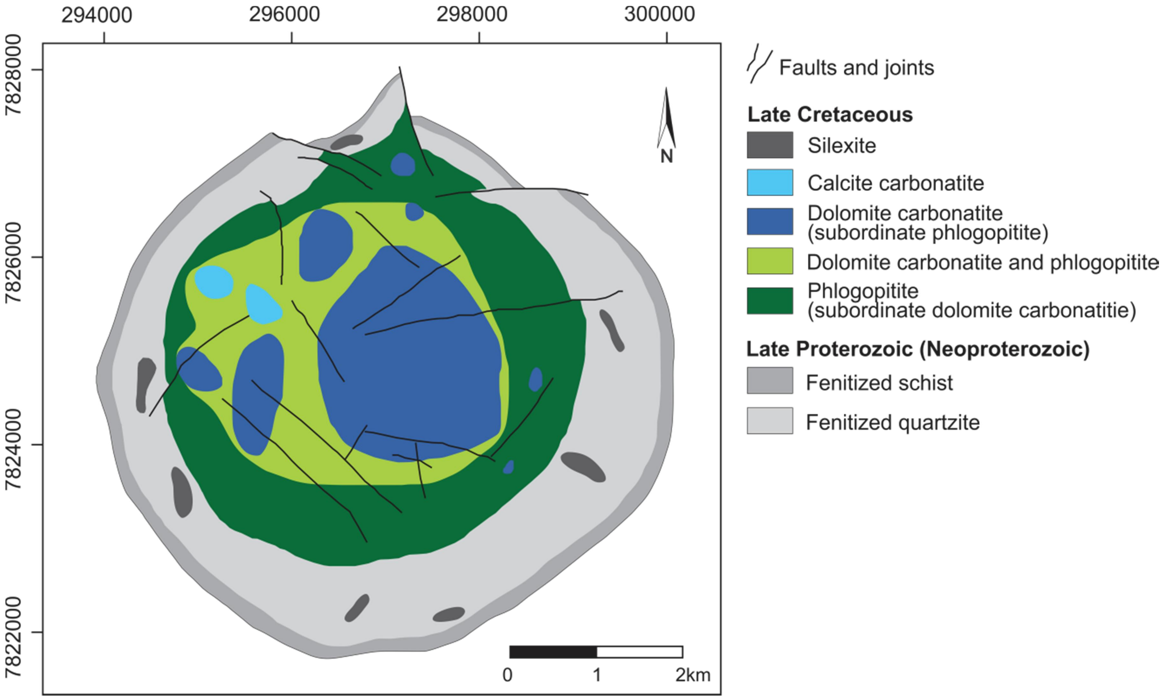

Fig. 4 - Geological sketch from Araxá Complex. Adapted after Grasso (2015).

3.1 Petrography

3.1.1 Bebedourite Series

Bebedourite series phases are very important and predominate in most of APIP complexes. Rocks from this series are usually phlogopitized in variable intensities. In the Barreiro mine, Grasso (2015) describes lithotypes with wide modal variation of apatite, olivine, diopside, phlogopite, magnetite, perovskite and carbonate, besides accessory titanite. Tetra-ferriphlogopite, anatase, amphibole, serpentine and chlorite are also present and compose products of metasomatism. Based on composition features, the author characterizes two distinctive bebedourite types: bebedourites and amphibole bebedourites. Torres (2008) also mentions the remarkable presence of phlogopitites, as expected due to the influence of metasomatic alteration processes. The presence of Tetra-ferriphlogopite in APIP complexes is explained through the substitution of the main tetrahedral cations Si^{4+} and Al^{3+} by the cation Fe^{3+} in alkaline rocks, generating the tetra-ferriphlogopite/tetra-ferriannite series $K(Mg,Fe^{2+})_3(Al,Fe^{3+})Si_3O_{10}(OH)_2$ (Cordeiro et al., 2010).

Bebedourite

Bebedourites occur as gray to dark-brown rocks with unequigranular texture varying from medium to coarse-grained. Olivine generally appears in the cumulus phase, sparse or forming irregular banding and is transformed to phlogopite in variable intensities, often showing an alteration rim when in contact with carbonatite. Diopside occurs as cumulus phase, in euhedral crystals also metasomatized to phlogopite. Meanwhile, phlogopite crystals can occur in two ways: (a) primary, coarse-grained, cumulatic and euhedral phlogopite, with alteration rims to tetraferri-phlogopite; or (b) fine crystals of red tetra-ferriphlogopite replacing regular phlogopite, mainly in the contact between bebedourite and carbonatite. Apatite occurs as cumulus crystal, euhedral, fine- to coarse-grained and disseminated or forming pockets. It can also occur in veins. Perovskite appears in very similar ways, composing rare pockets or disseminated. In these rocks, carbonate is predominantly interstitial and disseminated. It also typically occurs in veins and gives brecciated aspect to the rock. Magnetite, ilmenite, Ti-garnet, pyrite, chlorite, anatase and serpentine are also present (Grasso, 2015).

Amphibole bebedourite

The presence of amphibole gives a greenish aspect to the rock, which is normally fine to coarse-grained and cross-cut by thin carbonate veins or locally carbonatitic dikes. Besides the distinctive presence of amphibole, this type of bebedourite is distinguished by the lack of olivine and perovskite (Grasso, 2015).

Diopside is a cumulus phase and has frequent alteration brims to amphibole. Phlogopite tends to appear in fine grains with intercumulus character. Titanite is also usual and, the same way apatite does, it occurs in cumulatic euhedral crystals. Apatite though also composes pockets and associates with carbonate or phlogopite veins. For these rocks, carbonate is interstitial or fills veins. Magnetite is also present (Grasso, 2015).

The amphibole is described by Grasso (2015) as richterite and represents the metasomatic alteration of diopside. Although this is a very common mineral in Barreiro pit mine, this is an unusual mineral phase for other APIP complexes.

3.1.2 Phoscorite Series

Phoscorites occur mainly in the northeast region of the Barreiro mine and consist of dikes hosted predominantly by carbonatites and, in a subordinate way, in bebedourites (Grasso, 2015). In the region, Grasso (2015) describes rocks with wide modal variation of apatite, olivine, phlogopite and magnetite, besides interstitial carbonate. Tetra-ferriphlogopite and chlorite appear as products of metasomatism, meanwhile pyrochlore, pyrite and perovskite can be found as accessory phases (Grasso, 2015; Torres, 2008). Therefore, Grasso (2015) distinguished three rock groups, priming for parameters of genetic evolution: (a) Olive-rich Phoscorites (P1); (b) Olivine-poor Phoscorites (P2); and (c) Nelsonites (P3). According to the author, this would also be their evolutional sequence.

In these three rocks, olivine and aluminum-phlogopite can be preserved or transformed to tetra-ferriphlogopite. Apatite occurs as fine inclusions and prismatic crystals, but also forming sub-millimeter veins. Magnetite is sparse and carbonate is usually interstitial or composes small veins. Pyrochlore reaches up to 10% in a nelsonite sample and appears as euhedral disseminated crystals associated to magnetite and tetra-ferriphlogopite. Chlorite and serpentine are usual metasomatic products (Grasso, 2015).

Phoscorites in Araxá are vein-like and cross-cut both carbonatites and ultramafic rocks (Torres, 2008). In the complex, this rock type is affected by intense metasomatism, as reported by Grasso (2015).

3.1.3 Carbonatite Series

Carbonatites take place as dikes of centimetric to decametric thickness or less expressive plugs, hosted by bebedourites. Traversa et al. (2001) classifies the rocks in Magnesiocarbonatites, Calciocarbonatites and Ferrocarbonatites, according to the chemical classification of Woolley (1982) e Woolley & Kempe (1989). Elseways, Grasso (2015) distinguish two groups: Dolomite carbonatites (DC) and Calcite Carbonatite (CC), following the mineral classification of Le Maitre (2002). For simplification purposes, here we describe the rocks with both chemical and mineralogical classifications.

Dolomite Carbonatite or Magnesiocarbonatite (DC)

Magnesiocarbonatites or Dolomite-carbonatites are the most abundant carbonatite type in Araxá (Traversa et al., 2001; Torres, 2008; Grasso, 2015). It occurs in dikes emplaced in bebedourites and phoscorites, with fine to coarse-grained texture and sometimes presenting magmatic banding. Metasomatic rims in the contact between carbonatites and the wall-rock are common (Grasso, 2015). For Traversa et al. (2001), Magnesiocarbonatites are equigranular, fine-grained and allotriomorphic in texture. Carbonate phases consist mainly of dolomite with subordinate calcite. Tetra-ferriphlogopite, apatite and magnetite are also present. Pyrochlore, pyrite, rutile, monazite, baritocalcite, huanghoite, tainiolite and norsethite are described as accessory phases (Traversa et al., 2001; Grasso, 2015). Secondary phases include barite, quartz and celadonite (Traversa et al., 2001).

Calcite Carbonatite or Calciocarbonatites (CC)

Calcite-carbonatites occurs as dikes hosted by bebedourites, mainly in the northwest-western region of the complex (Grasso, 2015). Calciocarbonatites, according to Traversa et al. (2001), are texturally equigranular, hypidiomorphic to allotriomorphic and have grain size averaging 1-5 mm. Magmatic banding defined by magnetite is also describe in these rocks, coming to form nelsonite cumulates (Grasso, 2015). Calcite and dolomite, present in variable amounts, make up the principal carbonate minerals. Other constituents are tetra-ferriphlogopite, apatite, magnetite and arfvedsonite. Monazite, ilmenite, spinel, pyrochlore, rutile, zircon and ore minerals (pyrite and chalcopyrite) are found as accessories (Traversa et al., 2001; Grasso, 2015). Again, barite, quartz and celadonite constitute the principal secondary phases (Traversa et al., 2001).

Ferrocarbonatite (FeC)

Ferrocarbonatites are described by Traversa et al. (2001) and are clearly subordinate to the previous types. They show similarities in texture, except for the presence in a few samples of large magnetite grains and celadonite-phlogopite aggregates pseudomorphically formed after olivine and pyroxene crystals thereby giving the rocks a porphyritic character. Here, dolomite is the major carbonate phase (this way, the rock would be classified also as a dolomite-carbonatite), while strontianite, siderite, burbankite and ankerite are subordinate. Phlogopite is practically absent, whereas apatite is commonly found. Monazite, ilmenite, pyrite, chalcopyrite, sphalerite and galena are described found as accessories.

3.2 Mineral Chemistry

3.2.1 Olivine

Olivine is an important phase to be observed in silicate rocks from APIP complexes. Generally, its composition can be described in terms of the end-members forsterite (Mg_2SiO_4), fayalite (Fe_2SiO_4) and tephroite (Mn_2SiO_4). (Deer et al. 1992). In Araxá, fresh olivine crystals are restricted to the phlogopite-olivine-pyroxenites and have forsterite content between 86 and 92% mol. In comparison, Tapira phlogopite picrites, suggested to correspond to a primitive magma composition, have olivines with Fo_{84-90} (Brod, 1999). In parallel with interpretations made by Barbosa (2009), this feature migh indicate that Araxá's pyroxenites are more evolved if compared to phlogopite picrites, what is evidenced by a trend of Mg-Fe substitution during the evolution of silicate rocks.

According to Barbosa et al. (2012b), forsterite contents cannot be used to compare bebedourites and phoscorites/carbonatites, since the factors controlling the partition coefficient of MgO and FeO in olivine from phoscorites and carbonatites magmas are different from those active in silica magmas.

3.2.2 Phlogopite

For micas, the most common cations in the interlayer site are Na and K, although Ba, Cs, NH_4, Rb and Ca are also possible alternatives. Additionally, Ti is also a common element in phlogopite of carbonatite-related rocks (Lee et al., 2003). In this context, the phlogopite-annite series is basically defined by the substitution of Fe^{2+} for Mg^{2+} in the octahedral site. The main tetrahedral cations are Si^{4+} and Al^{3+}, but Fe^{3+} often substitutes for tetrahedral Al^{3+} in alkaline rocks, therefore generating the tetra-ferriphlogopite/tetra-ferriannite series. The tetra-ferriphlogopite can be present as both igneous and metasomatic varieties in all the APIP carbonatitic complexes and the crystal origin can be determined mainly by textural evidences (Cordeiro et al., 2010).

In Araxá, mica is represented by both phlogopite and tetra-ferriphlogopite. The latter can occur as an intercumulus primary phase, but is mainly found as small secondary aggregates. In general, early phlogopite, a high Al_2O_3 and low FeO phase, can be found grading progressively into tetra-ferriphlogopite as a result of Al-deficiency during the magmatic crystallization or as product of secondary alteration, (Traversa et al, 2001) meaning that Mg-Fe substitution can also be an evolutionary indicator in phlogopite.

3.2.3 Carbonates

Calcite in Araxá usually shows a homogeneous and limited composition. It is, in general, low in MgO and FeO. The SrO content is higher than 1%, whereas MnO is practically absent. However, dolomites display a wider compositional field, ranging from pure Mg-carbonate to more iron-enriched compositions (and even grading to ankerite (Traversa et al., 2001).

3.2.4 Apatite

Apatite ($Ca_{10}(PO_4)_6(OH,F,Cl,CO_3)_2$) is generally the main phosphate bearer in the APIP, and is the only phosphate ore mineral in worldwide magmatic phosphate deposits (Araújo, 2015). It is an early crystallizing phase in alkaline magmas and may persist up to the late stages of magmatic evolution (Hogarth, 1989). Primary phosphate mineralization in the APIP complexes may occur as apatite-rich bebedourite cumulates, as phoscorite dikes and as apatite rich cumulates derived from phoscorite and/or carbonatite magma (Brod et al 2004; Ribeiro 2008, Grasso, 2010; Grasso, 2015; Cordeiro et. al, 2010; Barbosa 2012a,b; Ribeiro et al., 2014; Araújo, 2015).

In the apatite's A site, expected substitutes of Ca are chiefly Sr, Ba, REE, U and Th, with Fe, Mg and Na occurring in smaller but variable concentrations. Meanwhile, the phosphate ideally occupies the X site, substituted more frequently by CO_3 especially in late-stage apatites (Hogarth, 1989). The increase in Ba and Sr in apatite structure is also pointed to happen towards late stages of carbonatite evolution (Kasputin, 1980). During magmatic evolution, SrO, Na_2O, F and REE_2O_3 contents might equally increase (Lee et al., 2004; Krasnova et al. 2004; Karchevsky & Moutte, 2004).

As expected, apatite is also the most common and important phosphate mineral in Araxá rocks (Traversa et al., 2001). This mineral is found in carbonatites, phoscorites and also bebedourites, besides tardi-magmatic apatite veins (Grasso, 2015; Torres & Gaspar, 1995b). According to Traversa et al. (2001), apatite chemical composition is regular, with large amounts of P_2O_5 and CaO. The SrO content remains in the range of 3 – 5%, but can reach up to 10% in some cases, forming more evolved Sr-enriched apatites.

3.2.5 Monazite

Monazite is the main rare earth bearing mineral in APIP and occurs in variable proportions both in the fresh rock and in the lateritic profile. Along with bastnaesite, this mineral represents the mean ore mineral in worldwide REE economic deposits (Araújo, 2015). Monazite group minerals consist of the general formula A_BO_4 where the A site is normally occupied by Bi^{3+}, Ca^{2+}, Ce^{3+}, La^{3+}, Nd^{3+}, Th^{4+} and U^{4+}, while the B site is occupied by As^{5+}, P^{5+} or Si^{4+} (Fleischer et al, 1990). In most minerals in this group, the B site is dominated by P^{5+}, with variable proportions of REE in the A site (Araújo, 2015). In carbonatite complexes, REE concentrations in the primary igneous rocks are rare, but mineralization associated with metasomatic alteration is abundant (Wall & Mariano, 1996).

In the Araxá complex, REEs are predominantly carried by monazite (over 70%; Neumann & Medeiros, 2015) and analyses obtained by Traversa et al. (2001) indicate Ce_2O_3 as the most abundant Rare Earth Element, with the concentration going up to 37% in ultramafic rocks.

3.2.6 Pyrochlore

Pyrochlore consists in a widespread accessory mineral of Araxá rocks and is the main Nb-bearing mineral in the APIP. The pyrochlore general formula is $A_{2-m}B_2X_{6-w}Y_{1-n}\cdot pH_2O$ (Lumpkin and Ewing, 1995). The A site is occupied by large ions such as As, Ba, Bi, Ca, Cs, K, Mg, Mn, Na, Pb, REE, Sb, Sr, Th, U and Y. This site is more likely to be occupied by Ca, Sr, Ba and Ce, but these elements vary considerably in concentration and may not necessarily be present in the same crystal (Traversa et al., 2001). Meanwhile, the B site comprises smaller and highly charged cations such as Nb, Ta, Ti, Zr, Fe^{3+}, Al and Si (Zurevinski and Mitchell, 2004) and rarely W^{5+} (Caprilli et al., 2006). The Y and X anions can be O, OH and F.

The Ba-rich pyrochlore (or bariopyrochlore) represents the most important mineral of pyrochlore group at Araxá (Hogarth 1977). Equally important is establishing that High Ba concentration in pyrochlore is believed to be an indicative evidence of its secondary origin (Heinrich 1980, Mariano 1989) and, in fact, Araxá's bariopyrochlore is interpreted by Heinrich (1980) as a product of hydrothermal activities. In Araxá, Issa Filho et al. (2013) and Mariano et al. (1997) also have demonstrated that magmatic early-formed Ba-bearing pyrochlore can be replaced along fractures by hydrothermal bariopyrochlore in the primary ores. In other words, Ca and Na are "leached" from the A site and replaced by Ba (Mariano et al., 1997). Similar patterns of alteration are evident in the primary pyrochlores of most Nb deposits (Lumpkin and Ewing, 1995; Mitchell, 2015) and have been attributed to deuteric/hydrothermal alteration in several localities (Lee et al., 2006; Nasraou and Bilal, 2000; Zurevinski and Mitchell, 2004).

3.3 Whole-rock Chemistry

3.3.1 Major elements

Traversa et al. (2001) analyzed carbonatites and "mica-rich rocks" (compatible with the description of bebedourite series rocks).

The mica-rich rocks are quite homogeneous in composition and contain high contents of Cr and Ni, showing their proximity to a less differenciated magmatic spectrum. They have also been sub-divided by Traversa et al. (2001) into mica-bearing rocks with olivine-clinopyroxene pseudomorphs (P; probably equivalent to metasomatic phlogopitites) and mica-olivine pyroxenites (MOP; or phlogopite-olivine pyroxenites). CO_2 content varies within the two rock-types, the average values being 9% and 15.5% for MOP and P, respectively (Traversa et al., 2001). The highest value for metasomatic phlogopitites (P) could be explained through the action of CO_2 rich fluids.

3.3.2 REE and other trace elements

Generally, all the rock-types in Araxá are strongly enriched in REE, the highest values found in some magnesiocarbonatite samples (Fig. 5).

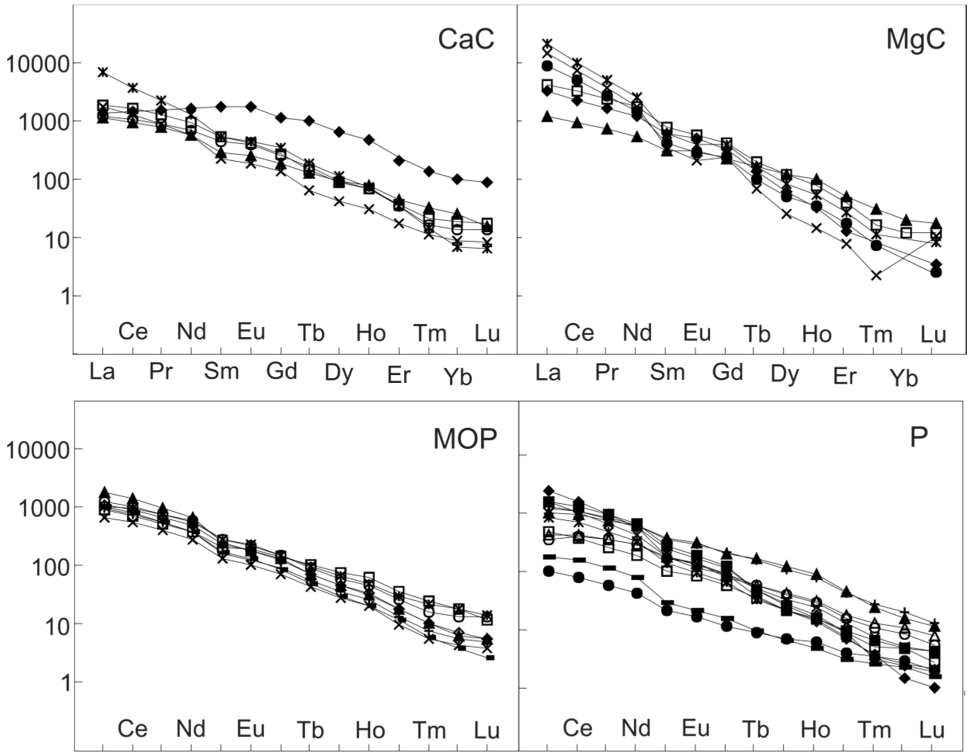

Fig. 5 - Chondrite normalized (Boyton, 1984) REE patterns for carbonatites and mica-rich rocks from Araxá Complex. Initials correspond as the following: CaC – Calciocarbonatites; MgC –

Magnesiocarbonatites; MOP – Phlogopite/Mica-Olivine pyroxenites; and P – Phlogopitites. Adapted from Traversa et al. (2001).

REE distribution in MOP rocks is very uniform and characterized by slight LREE/HREE fractionation, the maximum (La/Lu)N value being 389.7. Meanwhile, rocks from the P group exhibit an irregular pattern with variable enrichment degree for LREE (La and Ce values ranging from 100 up to 3000 times chondrite) and also variable LREE/HREE fractionation (Traversa et al., 2001). The LREE/HREE is a common feature in the rocks from APIP and the decreasing REE pattern is strongly correlated to the pattern observed in phlogopite picrites (Brod, 1999; Brod, 2000), what is an indicator of cogeneticity.

Although Nb-pyrochlore is one of the main ore minerals in Araxá, the carbonatites showed significantly lower Nb contents in relation to the numbers listed in literature (Woolley & Kempe, 1989): 127 vs. 1204 ppm for Calciocarbonatite; 334 vs. 569 ppm for Magnesiocarbonatite; and 194 vs. 1292 ppm for Ferrocarbonatite.

4. Catalão I Complex

The Catalão I Complex is located at the coordinates 18°08'S, 47°48'W, about 20 kilometers from the city of Catalão. It is a multiphase and multi-intrusion body, with circular setting and a 6-km diameter in surface. With a K-Ar age between 85 ± 6.9 Ma reported by Sonoki and Garda (1988) in phlogopites, the complex intrudes upon quartzites, schists, and phyllites from the Late Proterozoic Araxá Group. Its lithological types include dunite, clinopyroxenite, bebedourite (IUGS classification for perovskite-rich pyroxenite), carbonatite and phoscorite, in addition to abundant metasomatic phlogopitites (Brod et al., 2004). Similarly to Araxá, this complex has a center dominated by a carbonatite body, where the dolomite variety predominates over the calcite-bearing type. The outer portion is, in the same way, composed by ultramafic rock, here converted into phlogopitite (Fig. 6).

The phlogopitite rock, which is a result from the interaction of the primary ultramafic alkaline rocks with intrusive carbonatites (Brod et al., 2001), is the dominant petrographic type in the complex, what demonstrates the intense self-metasomatism that affected Catalão I (Cordeiro, 2010). Meanwhile, phoscorite and carbonatite occur as dike swarms, rather than massive intrusions, and become increasingly common towards the center of the complex (Cordeiro, 2010), fact that can be also observed in other complexes from Alto Parnaíba province.

The emplacement of carbonatite bodies, together with the intense weathering and metassomatism that affect the Catalão I complex, difficults the production of a precise geological map. For similar reasons, sometimes the geological representation in these complexes corresponds to the predominance of a certain lithotype (Fig.6) and other geological features described, such as dikes or pipes, can not be represented in the map scale.

Catalão I bears a great diversity of mineralizations, including apatite, pyrochlore, monazite, anatase, barite, magnetite, and vermiculite (Gibson et al., 1995; Ribeiro, 2008). Currently, the weathering profile over phoscorite-series rocks is mined for phosphate, niobium and barite (as by-product).

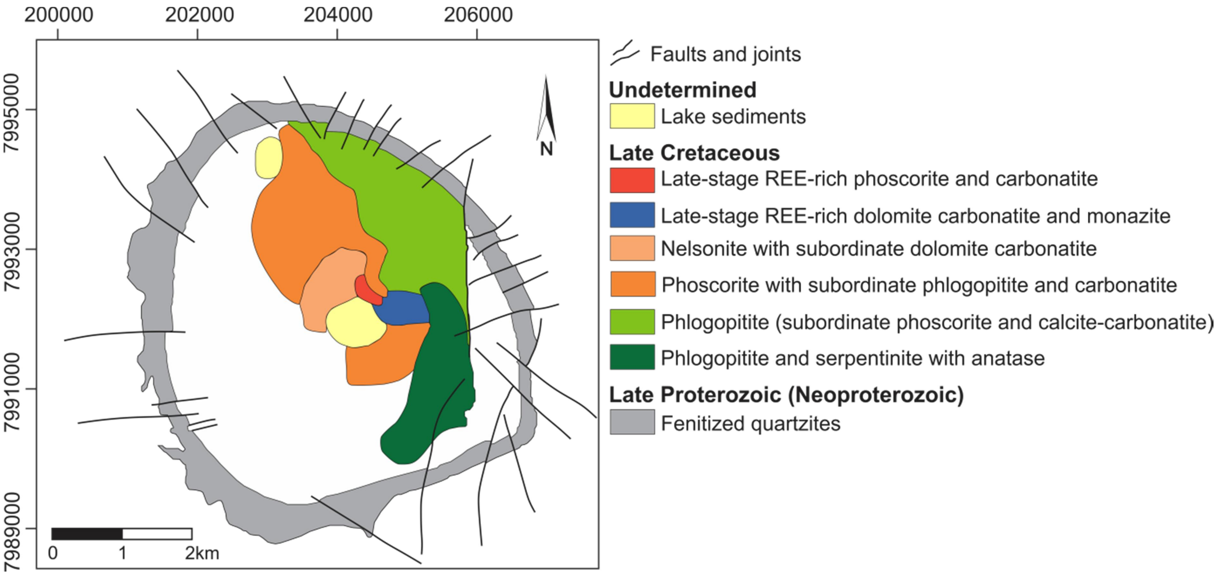

Fig. 6 - Geological scketch from the Catalão I carbonatite complex. Adapted after Cordeiro et al. (2010; 2011a,b).

4.1 Petrography

4.1.1 Bebedourite Series

Likewise other APIP complexes, the bebedourite-series predominates in Catalão I. Following Ribeiro's (2008) petrographic descriptions of the complex, it is possible to distinguish four different subgroups for this series: a) pyroxenites and dunites; b) magmatic phlogopitites; c) metasomatic phlogopitites; and d) magmatic breccias.

Pyroxenites and dunites

These rocks are composed by phlogopite, magnetite, ilmenite, perovskite, anatase, apatite, pyroxene, olivine and serpentine. The serpentine predominates, probably derived from pyroxene and olivine. Similarly, anatase and phlogopite are inferred to be a result from the alteration of perovskite and olivine/pyroxene, respectively. At last, tetra-ferriphlogopite can occur in alteration brims of primary phlogopite. These features suggest that this lithotypes can be thus interpreted as cumulates that went through intense metasomatism (Ribeiro, 2008).

This kind of rock, according to the mentioned author, occurs more often in the east-southern portion of the complex, taking place randomly in its border and being probably masked by the intense metasomatism that tends to transform ultramafic rocks in phlogopitites. With rare exceptions, it is still possible to identify primary olivine and pyroxene in preserved cores within intense phlogopitization zones.

Magmatic and Metasomatic Phlogopitites

Together, magmatic and metasomatic phlogopitites are the most abundant lithotype in the complex. The main phases in both cases are phlogopite, magnetite and dolomite, though apatite, amphibole, diopside, sodic clinopyroxene, anatase and perovskite are common minerals. Magnetite appears in fine grains, always related to carbonate and apatite, suggesting a co-genetic relation. Dolomite, in turn, can occur interstitially or in micro-veins (Ribeiro, 2008). Lee et al. (2004) and Krasnova et al. (2004b) describe similar phlogopitites in Sokli (Finland) and Kovdor (Russia).

There are some suggested features that indicate that both, magmatic and metasomatic phlogopitites, are present in Catalão I. For the metasomatic case, Ribeiro (2008) mentions the presence of phlogopite ± oxides ± carbonate ± serpentine forming olive pseudomorphs, as well as Reliquiar minerals (diopside and amphibole), occasionally with reaction brims or substituted for phlogopite. The author also mentions heterogeneous and unequigranular texture, along with the presence of a magnetite and ilmenite exsolution and the substitution of magnetite for carbonate. The suggested magmatic features include homogeneous and equigranular texture, flow texture, euhedral phlogopite and interstitial carbonate and fine oxides.

Magmatic Breccias

These rocks represent a late event and crosscut phlogopitites, phoscorites and carbonatites, excepting late stage carbonatites. Breccias' bodies have variable sizes and are characterized by a phlogopitic or carbonatitic fabric sustaining xenoliths from carbonatite, phoscorite, phlogopitite and dunite (Ribeiro, 2008).

In the Lagoa Seca region, where lake sediments were detected, Ribeiro et al. (2001; 2005) describe five different geometries for pipe-like bodies, emplaced in Catalão I igneous rocks and filled with breccias (Fig. 7).

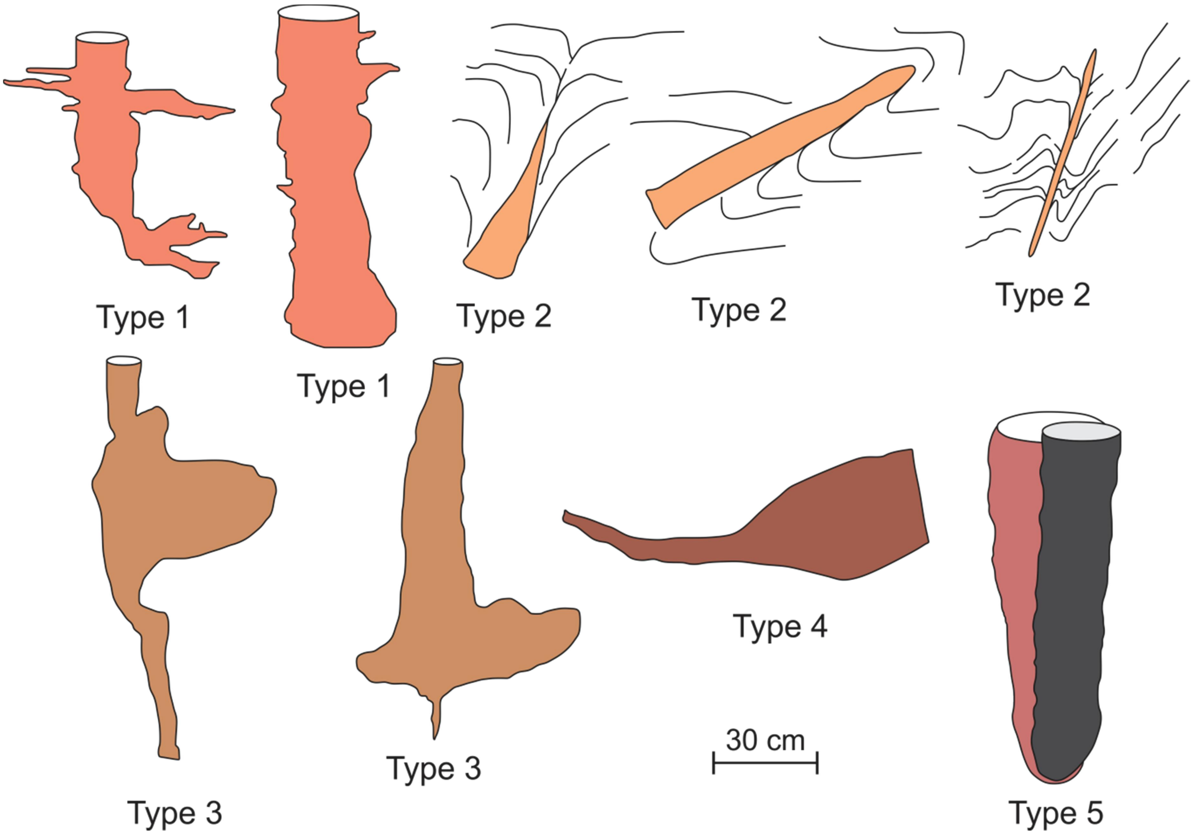

Fig. 7 - Classification of pipe types in the Lagoa Seca area of the Catalão I complex (Modified from Ribeiro et al., 2001). Type 1: these pipes are cylindrical conduits filled with breccia that range in diameter from 20 to 50 cm and in length from 1 to 2 m. They do not appear to cause any hydraulic fragmentation of the host rock; Type 2: represent elliptical conduits with small diameters (near 10 cm) that are distinguished from other types by the deformation caused in the host rock during pipe intrusion, which resulted in structures that resemble drag folds; Type 3: elliptical conduits usually divided into three internal portions (basal, intermediate and upper sections) with slightly different breccia fillings. Diameters are normally decametric; Type 4: characterized by the horizontal direction of mass movement. It is distinguished from Type 3 by the lack of graded, cross-, and parallel bedding. This type of pipe has irregular dimensions and is approximately 10 m long, with diameters ranging

from 15 to 60 cm; Type 5: Represented by vertical cylindrical conduits filled entirely by a matrix-supported breccia. The pipes are 40-50 cm in diameter and up to 2 m long. The contact with the host rock is linear and well defined, and there is no visible deformation of the host rock (Ribeiro et al., 2005)

4.1.2 Phoscorite Series

The Phoscorite-series is also quite expressive in Catalão. This series was divided by Cordeiro et al. (2010) into four different stages, considering their modal mineralogy and paragenetic sequence. This way, there are the Phoscorites (P1), the Apatite Nelsonites (P2), the Magnetite Nelsonites (P3) and finally the Dolomite Carbonatite (DC).

Phoscorites P1

Composed by olivine, phlogopite and magnetite, with baddeleyite, ilmenite, clino-humite, rutile, dolomite and magnesite as accessory minerals, the Phoscorite P1 occurs in small plugs or dikes near to the core of the complex, sometimes intruding carbonatites and bebedourites of metasomatic phlogopitite wallrock. It’s important to observe that this rock is well affected by metasomatism, what is demonstrated by the transformation of olivine into tetra-ferriphlogopite crystals and clino-humite (Cordeiro et al., 2010).

Apatite Nelsonite P2 (apatite/magnetite > 0.8)

With an apatite/magnetite rate above 0.8, the Apatite Nelsonite P2 is also characterized by the lack of olive and by tetra-ferriphlogopite as essential silicate phase. Pyrochlore can be an accessory or compose till 50 vol. % of the rock. Other important accessories are dolomite, barite, norsethite, pyrite, sphalerite and chalcopyrite (Cordeiro et al., 2010).

Magnetite Nelsonite P3 (apatite/magnetite < 0.8)

With an apatite/magnetite rate below 0.8, the Apatite Nelsonite P3 is also characterized by the lack of olive, with tetra-ferriphlogopite being the only silicate. Pyrochlore can be an important mineral for both nelsonite stages, composing till 50 vol. % in most enriched rocks. Again, dolomite, barite, norsethite, pyrite, sphalerite and chalcopyrite appear as accessories (Cordeiro et al., 2010).

Dolomite Carbonatite DC

Associated and coeval to the nelsonites, Dolomite Carbonatites occur as small plugs (up to 15 m wide) and dikes (up to 2 m). The dikes crosscut both the phoscorite-series rocks and their wallrocks, being up to 20 cm thick and composed of dolomite, ilmenite, tetra-ferriphlogopite, apatite, norsethite, barite, pyrochlore, and magnetite, and they are interpreted as carbonatites extracted either from a phoscorite or nelsonite magma or cumulate pile (Cordeiro *et al.*, 2010).

Also, the dolomite carbonatite occurs as round to irregularly-shaped pockets of varied sizes within nelsonites. These pockets are often composed of a central zone of dolomite with subordinate barite, norsethite, pyrite and chalcopyrite, and a rim at the contact with the host nelsonite, composed of magnetite aggregates, subhedral pyrochlore, radial prismatic apatite, tetra-ferriphlogopite, and ilmenite. Crystals in the rim zone are often elongated toward the center of the pocket, resembling a comb-layered texture (Cordeiro *et al.*, 2010).

4.2 Mineral Chemistry

4.2.1 Olivine

Pseudomorphs of the original olivine are often found in Catalão I rocks, indicating that primary olivine was euhedral and medium-grained. However, metasomatic alteration resulted in the replacement of olivine in phoscorites (particularly P1, the most affected phoscorite) and earlier silicate rocks by clino-humite, magnesite and tetra-ferriphlogopite (Cordeiro et al., 2010). Araújo (1996) reported olivine compositions from Catalão I phoscorites ranging between Fo 84 – 94 mol%, with MnO varying from 0.34 to 0.63 wt.%.

4.2.2 Phlogopite

Generally, all of micas from the Catalão I phoscorites, nelsonites and dolomite carbonatites plot as members of the phlogopite-tetra-ferriphlogopite series. In P1 phoscorites, magmatic Al-phlogopite predominates, occurring with rims of tetra-ferriphlogopite. In P2 and P3 nelsonites, the tetra-ferriphlogopite is the predominant phase and may contain Al-rich cores. Regarding DC pockets, the crystals of tetra-ferriphlogopite may occur perpendicularly to the DC pocket contacts in an inward-growing (Cordeiro et al., 2010).

4.2.3 Magnetite

There is a wide overlap in the chemical compositions between magnetite from different rock units (P1, P2, P3 and DC) in Catalão I. TiO_2 content in the phoscorite-series magnetite generally averages from 1 to 3 wt.%, whereas the Al_2O_3 content is very low (mostly <0.1 wt.%). Together with Al_2O_3 and MnO, the MgO values decrease towards the later-stage facies. All the describe aspects consist in good features to indicate magma evolution in the series (Cordeiro et al., 2010).

4.2.4 Carbonate

Dolomite is the essential carbonate phase in the phoscorite series of Catalão I. In P1, it occurs as an interstitial phase, but it can also be present in pockets of variable sizes (centimetric to metric) within P2 and P3 nelsonites, what might represent carbonatitic segregations from the cooling magma. Primary carbonates are usually coarse- to medium-grained, with a clear aspect in thin section, whereas secondary carbonates are anhedral and develop a turbid aspect (Cordeiro, 2009).

4.2.5 Apatite

In P1 phoscorite, apatite tends to typically form aggregates of subhedral crystals. Meanwhile, in P2 apatite occurs as fine-grained euhedral crystals, often presenting flow texture. P3 apatite is also fine-grained and occurs within homogenous magnetite aggregates or apatite-monomineralic aggregates with poorly defined outlines. In DC pockets and dikes, the crystals are often perpendicular to the walls, growing toward the center of either the pocket or dike, like the tetra-ferriphlogopite crystals (Cordeiro et al., 2010).

Because carbonatite magmas are Sr- and REE-rich, apatite crystallized from them is expected to reflect this enrichment (Cordeiro et al, 2010). Strontium incorporation in apatite altered by deuteric fluids is described by Chakhmouradian et al. (2002) in crystals of Lovozero and Murun complexes and in magmatic apatite of kimberlite in Lac de Gras. The REE substitution is usually coupled with Na or Si in apatite structures (Toledo & Pereira, 2001; Chakhmouradian et al., 2002). The presence of Si is also common and the most evoked substitution to explain all os these aspects is the britholite-type: $Ca^{2+} + P^{5+} = Si^{4+} + REE^{3+}$ (Hogarth, 1989; Chakhmouradian et al., 2002).

This is important because in the Ca-Sr and Ca+P-Si+REE diagrams (Fig. 8) for phoscorite-series rocks of Catalão I, it is clear that Ca decreases and Sr increases in the apatite from the complex. P1 apatite evolution is therefore controlled by the britholite substitution, whereas apatite shows a wider Sr range in more evolved nelsonites, indicating evolution by Sr enrichment (Cordeiro et al., 2010). The clear decrease in Ca and increase in Sr are also true for the Kola Province complexes in Russia (Karchevsky and Moutte, 2004; Krasnova et al., 2004b; Lee et al., 2004), suggesting that Sr content in apatite is indeed a reliable index of magma evolution in the carbonatite and phoscorite series (Cordeiro et al., 2010).

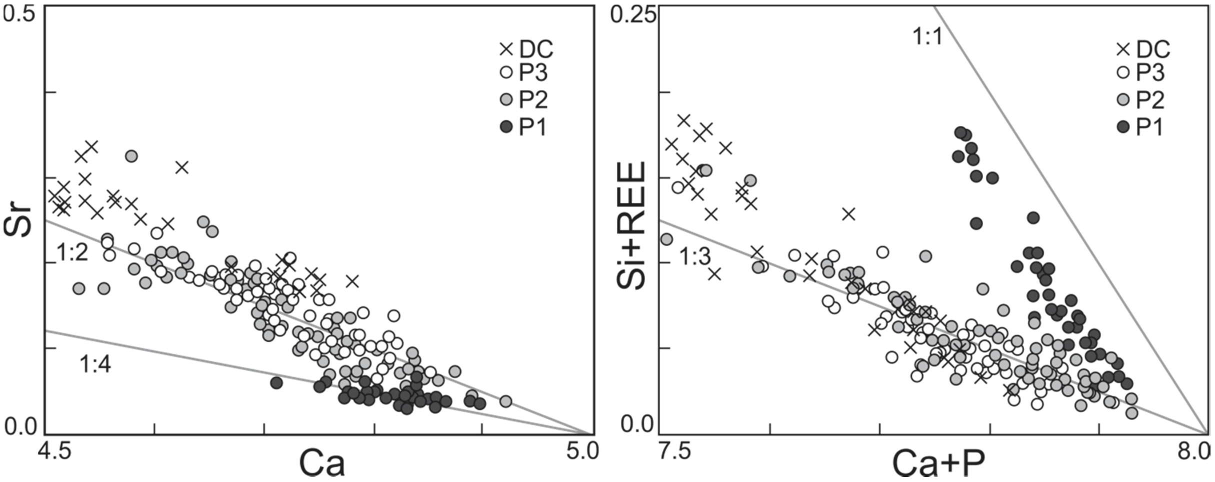

Fig. 8 - Apatite substitution schemes showing Sr enrichment from P1 to DC. Note that the Si+REE substitution scheme varies from 1:1 in P1 to 1:3 in P2/P3/DC. All variables represent cations per formula uni. Adapted from Cordeiro et al. (2010).

4.2.6 Pyrochlore

Nelsonites are the main host for Niobium mineralization in Catalão I. Similarly to Araxá, here Ba is one of the most common substitutes for both Na and Ca in the A site, with the BaO content reaching up to 18 wt. %. In what concerns to Nb mineralization, the Nb_2O_5 content varies from 50 to 70 wt. %. (Cordeiro et al., 2011a)

In their work, Cordeiro et al. (2011a) indicate several authors that tried to explain the evolution of pyrochlore composition throughout magmatic evolution (Chakhmouradian and Williams, 2004; Hogarth et al., 2000; Knudsen, 1989). It is believed that during the early stages of carbonatite magmatism Nb and Ta are probably transported as phosphate and fluorine complexes, which might explain the common correlation between the occurrence of apatite and pyrochlore (Hogarth et al., 2000; Knudsen, 1989). Knudsen (1989) affirmed that during the carbonatitic magmatism, Niobium is more soluble than Tantalum, which could explain the occurrence of Ta-rich pyrochlore in primitive magmas and Nb-rich in late stage ones. This way, Hogarth et al. (2000) concluded that the normal path of evolution of pyrochlore in carbonatites is one of progressive enrichment in Na, Ca and Nb and depletion in Ta, Th, REE, Ti and U. Pyrochlore from the Catalão I fresh rock deposit seems to fit well into the proposed scheme, but without Ta–Th–U enriched pyrochlore phase. Thus, Cordeiro et al. (2011a) concludes that Ca–Na pyrochlore in P2 and P3 nelsonites and related DC dolomite carbonatites can be interpreted as belonging to a more evolved phase.

In what concerns pyrochlore from residual deposit, notable differences occur in the B and A sites. Similar to what it is possible to find in several secondary Nb carbonatitic ores (e.g. Mitchell, 2015), Ba-enriched pyrochlores are found in Catalão I. However, fresh rock and residual Ba-rich pyrochlores are different from each other. Usually, fresh rock crystals show a negative Sr–Ca correlation that leads toward Sr-enrichment. The same correlation is also observed in the residual deposit pyrochlore crystal cores (Fava, 2001), but the majority of pyrochlore in the residual deposit lack a negative Sr–Ca correlation (Cordeiro et al., 2011a). For Cordeiro et al. (2011a), these chemical features suggest that different processes originated the fresh rock and the residual pyrochlore deposits, suggesting fresh-rock deposit pyrochlores had interaction with low-temperature fluids that carried Sr, while residual deposit would be originated by depleting pyrochlore from Ca and Na, due to the interaction with weathering-related fluids.

4.3 Whole-rock Chemistry

4.3.1 Major elements

Here, we intend to picture mainly the chemical composition of phoscorite-series rocks, since it reflects a different magmatic evolution if compared to carbonatites and silicate rocks. A carbon and oxygen stable isotope study on carbonates for phoscorite-series rocks (Cordeiro, 2009; Cordeiro, et al. 2011b) established that they are of primary (magmatic) origin, with pervasive interaction with low temperature H_2O-rich fluids, probably of meteoric origin. However, the textural properties of the samples analyzed by Cordeiro et al. (2010) and the mineral chemistry results suggest that alteration during this event was mostly restricted to carbonates (Cordeiro et al., 2010).

Regarding major elements, the phoscorite-series rocks studied by Cordeiro (2009) are very silica-poor. P1 phoscorite varies from 12 to 25 wt. % SiO_2, while all P2 and P3 stay below 13 wt. % SiO_2. A positive Si-Mg correlation is also observed in these rocks, meaning that the early fractionation of olivine drives the magma towards SiO_2 decrease with evolution, as well as towards a MgO decrease (Cordeiro, 2009).

4.3.2 REE and other trace elements

Phoscorite-series rocks, including carbonatites, have highly fractionated REE patterns with the LREE enriched two to three orders of magnitude relative to the HREE. In comparation with REE with primitive magmas of the APIP complexes (phlogopite picrites, Brod et al., 2000; Fig. 9), the phoscorites and nelsonites show very similar REE pattern, only more fractionated (Cordeiro et al., 2010). Also important is to say that Cordeiro et al. (2010) could find no significant chemical discrepancies terms of trace-elements between nelsonites and coexisting DC pockets, which suggests that the two domains may be crystallized in equilibrium. Therefore, the authors believe that the referred dolomite–carbonatites from Catalão I are the result of squeezing of a residual (rather than immiscible) carbonatite liquid after originating as a nelsonitic crystal mush. The squeezed carbonatite liquid could eventually coalesce into larger bodies and, in turn, supply suitable volumes of carbonatite magma to form the DC dikes and plugs (Cordeiro et al., 2010).

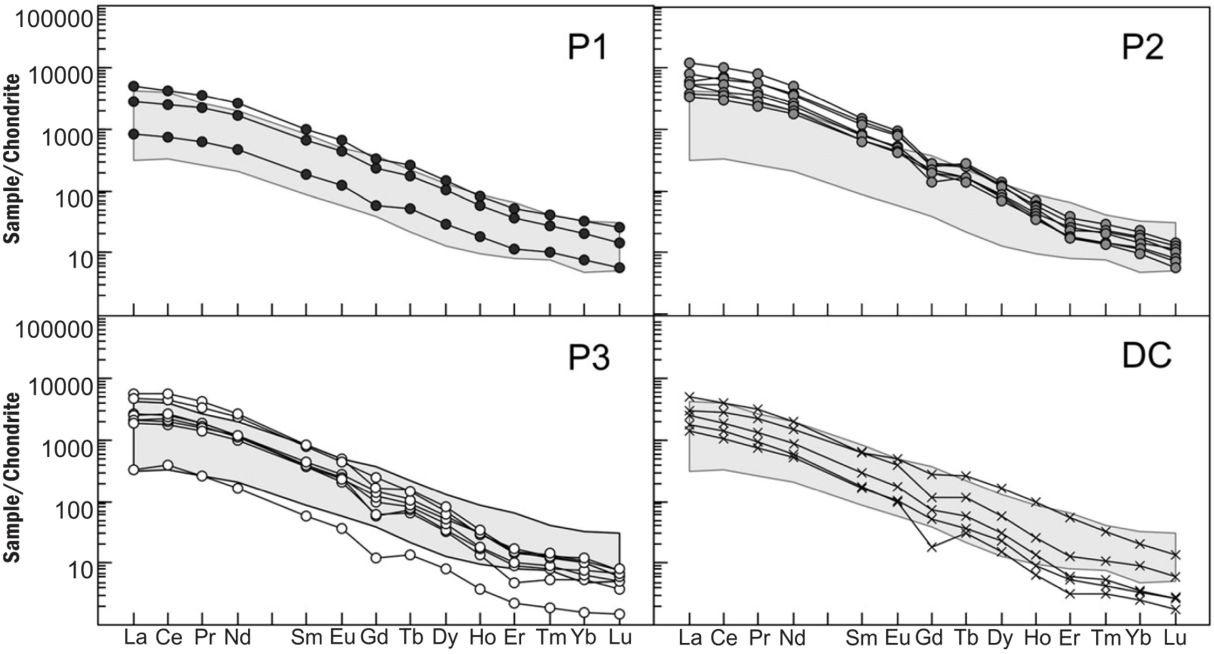

Fig. 9 - REE patterns for the phoscorite series rocks. The grey field represents the REE composition of phlogopite picrites in Catalão I (Cordeiro, 2009). Chondrite normalization values from McDonough and Sun (1995). Figure adapted from Cordeiro et al., 2010.

5. Catalão II Complex

Placed north of Catalão I, at the coordinates 18º 01'S and 47º 51'W, the Catalão II is smaller and geomorphologically less evident than its sibling. The multi-phase body intrusion induced fenitization of the Late Proterozoic Araxá Group wallrocks, with also very widespread brecciation (Brod et al, 2004). In situ U-Pb ages on perovskite for Catalão II phlogopite picrites suggest ages between 82 ± 3 Ma, 83 ± 4 Ma and 90 ± 4 Ma (Guarino et al., 2013). Here, the alkaline magmatic rocks are only partially exposed, preferably in the north of the complex. According to Palmieri (2011), the northern area is characterized by a succession of alkaline silicate rocks (pyroxenites and bebedourites), phoscorites, and carbonatites and contains a important phosphate deposit within phoscorite-series rocks (Coqueiros). On the other hand, smaller occurrences found in the south consist of dike swarms of nelsonites, and carbonatites, with subordinate alkaline silicate rocks (phlogopite picrites and bebedourites), intruding fenitized Late Proterozoic phyllites and amphibolites from Brasília Belt, and contain most of the niobium mineralization. The alkaline rocks in the northern and southern portions of the complex show remarkable differences in composition and mode of emplacement, which are the reasons why the same author suggests the presence of two distinct magma chambers (Fig 10).

Therefore, similarly to Catalão I, this complex also bears several mineral deposits, with important highlight to niobium and phosphate. Likewise other APIP complexes, this one in interpreted as one or more shallow magmatic chambers with multiphasic evolution and presence of distinguishable petrogenetic series.

5.1.1 Alkaline-silicatic rocks (Bebedourite Series)

No papers describe a bebedourite-series for Catalão II. However, we believe some silicatic-alkaline rocks characterized by several authors (Machado Junior, 1991; Rocha et al., 2001; Palmieri 2011; Guarino et al., 2016) were not classified but still correspond to this series.

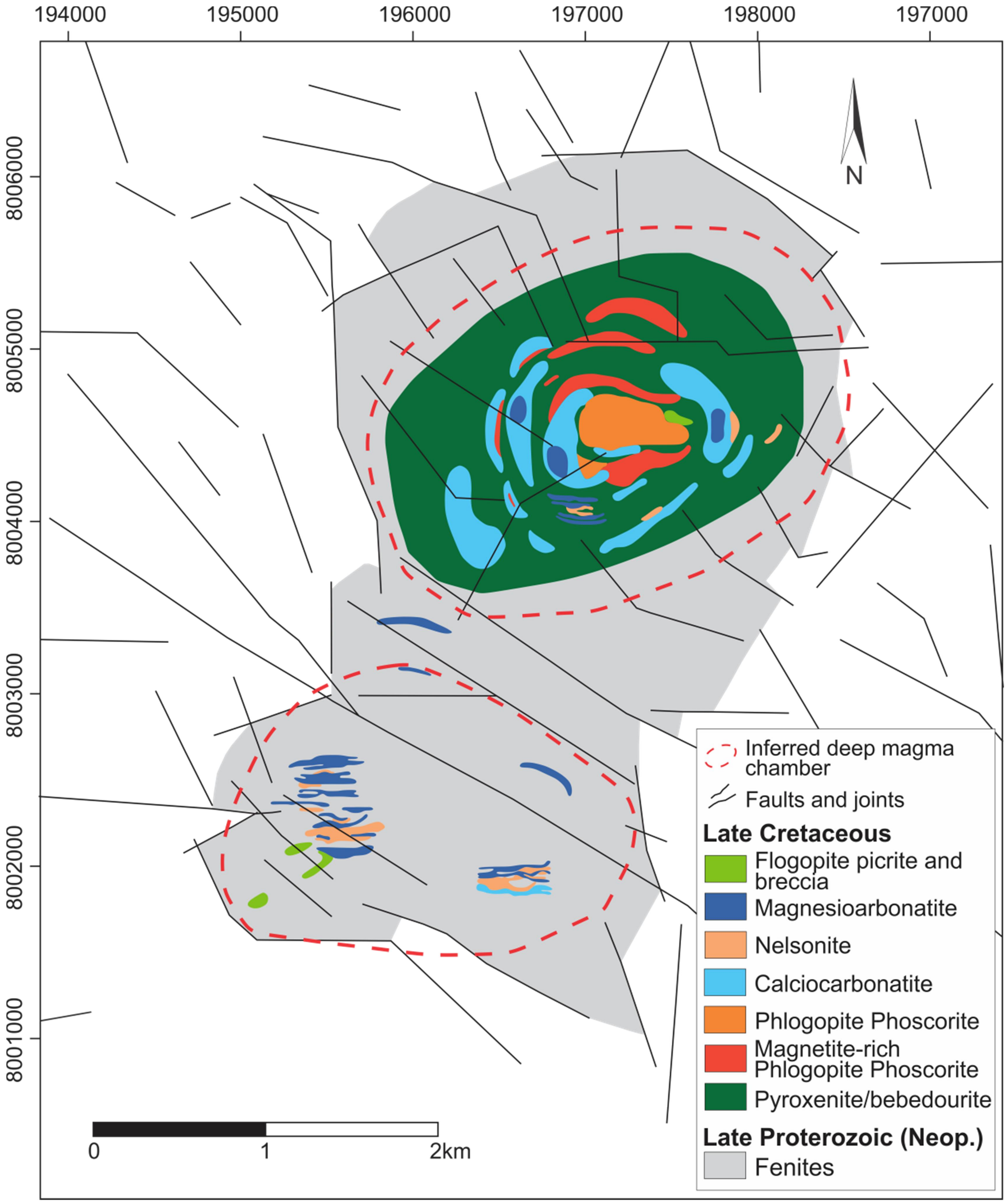

Fig. 10 - Geological scketch from the Catalão II carbonatite complex. Adapted after Palmieri (2011).

Pyroxenite or bebedourite

These rocks have been encountered mainly in the northern part of the complex and at various depths. They are massive or brecciated and have a medium to coarse-grained texture. Two types can be distinguished: biotite-pyroxenites, of dark green color and magnetite and apatite pyroxenites, of light green color. The first type consists mainly of sodium augite, associated with the following minerals: biotite, sodium amphibole, apatite and potassic feldspar. Primary calcite, titanite and magnetite are the accessory minerals of this first type. The second type consists of augite, apatite, magnetite, titanite and zircon; Sodium amphibole is rare. In some cases, magnetite is accompanied by ilmenite and sulphides (pyrrhotite, pyrite, chalcopyrite, and bornite). This second type may have a coarse or pegmatitic texture (Rocha et al., 2001). The pyroxenites are frequently fractured and metasomatized into phlogopitites in contact with the carbonatites dikes (Rocha et al., 2001; Guarino et al., 2016). Furthermore, Palmieri (2011) refers to these pyroxenites also as bebedourites.

Phlogopitite

Also mentioned as glimmerite, the phlogopitites have phlogopite as the dominant phase and contain minor magnetite, pyrochlore and apatite, and rare accessory carbonates. They can also be cross-cutted by calciocarbonatite bodies, showing embayed zircon crystals with corroded and altered rims (Guarino et al., 2016).

Phlogopite picrites

Phlogopite picrites are reported by Palmieri (2011) and Guarino et al. (2016) and display a porphyritic texture, with olivine and phlogopite phenocrysts in a pseudo-fluidal groundmass rich in phlogopite laths and made up also of olivine, spinel, apatite, perovskite, calcite and rare garnet and rutile (Guarino et al., 2016). Rocha et al. (2001) described this rocks as lamprophyre are dikes that cross-cut all previous lithotypes.

5.1.2 Phoscorite (Phoscorite Series)

Located on the north pipe only, where they make up 10% of the rocks encountered in the holes, phoscorites are medium to coarse grained and very rich in apatite, which can represent 50% of total mineral assemblage. Calcite, olivine, phlogopite, pyrochlore, zircon and magnetite are also present. A large part of the phlogopites comes from the transformation of olivine due to metasomatic processes (Rocha et al., 2001).

Otherwise, Palmieri (2011) describes the occurrence of nelsonites dykes in the southern pipe, while Guarino et al. (2016) characterize magnetitites and apatitites in the complex (north pipe) – which could be considerate varieties of magnetite- and apatite-rich nelsonites.

To sum up, at least two types of nelsonites are recognized by Palmieri (2011), and Jácomo (2010), who produced models of Morro do Padre (MP) ore bodies in Catalão II. One type of nelsonite (N1) is typically apatite-rich, finer-grained, and often displays a homogeneous granular texture. It occurs in rare dikes at the ore deposit intermediate zone, becoming more abundant with depth. Carbonate pockets in this type of nelsonite tend to be rare, small and mostly calcitic, but no genetic links of this unit with a particular variety of carbonatite has been established. This nelsonite type is rich in P, Sr, REE, Zr, and Th, and their modal composition varies between apatitite and apatite-nelsonite (Palmieri, 2011). The other nelsonite type (N2), also referred as “pseudonelsonite”, is generally more abundant, coarse-grained, phlogopite- magnetite- and pyrochlore-rich. It contains variable amounts of chalcopyrite, and dominates the deposit’s upper portion. If compared to N1, the N2 nelsonite is richer in Si, Fe, Mg, K, Ba, Nb, S, and Cu. It also tends to be apatite-poor and either phlogopite- or magnetite-rich. In addition, carbonate can occur as an interstitial constituent or as centimeter to decimeter-sized carbonate pockets (Palmieri, 2011).

In comparison to Catalão I nelsonites (Cordeito et al., 2010), Jácomo (2010) describes N1 as an equivalent for P2 (apatite nelsonite) and N2 as correspondent to P3 (magnetite nelsonite).

5.1.3 Carbonatite (Carbonatite or Phoscorite Series)

Carbonatites in Catalão II are considered a more evolved phase of phoscoritic-series, according to Rocha et al. (2001). However, since the textural and spatial relationship between phoscorites and carbonatites were not detailed, we present carbonatites and phoscorites in distinct topics.

Mineralogical classification

Considering mineralogical and texture features, Rocha et al. (2001) classified carbonatites into five types (C1, C2, C3, C4 and C5). C1 is the first carbonatite and has an intermediate mineralogical composition between the phoscorites and calcite-carbonatites; these dikes width range from centimeters to meters and they are recognizable in surface. It is a coarse-grained rock, very rich in magnetite, accompanied by apatite, phlogopite, pyrochlore, calcite and ilmenite. Sulphides are frequent. Locally, apatite can account for nearly 50 wt. %. Magnetite and ilmenite can also form important clusters. C1 is considered to be the richest in pyrochlore. This mineral displays in octahedral, millimetric to centimetric crystals and can constitute up to 20% of the total rock volume (Rocha et al., 2001).

C2 is a silico-calcite-carbonatite with 50 wt. % calcite and wt. 5% dolomite. It contains apatite, augite aegirine, magnetite, phlogopite and, rarely, pyrochlore. Pyroxenites are frequently transformed into phlogopitite in contact with these bodies.

C3 constitutes a fine-grained calcite-carbonatite, mainly composed of white calcite (95% of rock volume) and containing sulphides, dolomite, baryte and phlogopite as accessory minerals. C4 is also a calcite-carbonatite, of brownish color, occurring in dykes. Calcite accounts for 50-65 wt. % and is accompanied by ankerite, dolomite, baryte, quartz, and REE-bearing carbonates. Finally, C5 corresponds to centimetric veinlet-like bodies of calcite-carbonatite (fine-grained) and of dolomite-carbonatite (Rocha et al., 2001).

In a more simple description in the Morro do Padre deposit (MP), Palmieri (2011) limits the carbonatites into C1 and C2 types. C1 corresponds to early-stage calciocarbonatites and can be divided into two sub-types, based on drill-core observations and whole-rock chemical compositions: C1a is a P-, Nb-, Th-, and Zr-rich carbonatite and can be found only in MP Lower Zone. C1b seems to be more differentiated and occurs in the intermediate zone, forming a stockwork of dikes in the southern portion of MP. In this zone, carbonatite frequently contains fenite xenoliths which develop a thin aureole of metasomatic phlogopitite. The dolomite accounts for subordinate amounts in the calciocarbonatites. Apatite may reach up to 14 % in C1a, and rarely up to 4% in C1b, whereas the main accessory minerals are phlogopite and magnetite, with less ilmenite and pyrochlore, and rare monazite (Palmieri, 2011).

C2 are late-stage magnesiocarbonatites enriched in Fe, Ba, Mn, Nb, REE, S, Th, and Cu. These magnesiocarbonatites form most of the centrimetric- to metric-sized carbonate-rich pockets in N2, also occurring as a dike swarm that crosscut the rocks of that unit. They are widespread at MP deposit and occur at all depth zones, but are particularly abundant in the northern part of the intermediate zone, demonstrating close spatial association with N2. C2, similarly to C1, can be divided into C2a and C2b. C2a is strongly enriched in Ba, REE, U, Th, Cu, Pb, Zn, and slightly enriched in P_2O_5, $Fe_2O_{3(t)}$, and S relatively to C2b (Palmieri, 2011)

The geochemical characteristics of the two magnesiocarbonatite types, and the close spatial and genetic relationships of these rocks with the N2 pseudonelsonites suggest that C2b represents the depleted residue of mineral crystallization such as apatite, phlogopite, magnetite, and pyrochlore from C2a to form the N2 pseudonelsonites (Palmieri, 2011). Taking into account the pyrochlore distribution and characteristics in this deposit, Palmieri (2011) affirms this is probably the chief Nb ore-forming process in place. The author also believes that the N1 nelsonites evolved to the C1 calciocarbonatites by fractional crystallization processes, in agreement with Rocha et al. (2001), and states that N2 seems to be formed as cumulates on the walls of C2 dikes. In other words, Palmieri (2011) aims that a phoscorite/nelsonite magma generated N1 + C1, whereas a magnesiocarbonatite magma generated the N2 + C2 association.

Chemical classification

According to chemical classification (Woolley & Kempe, 1989), carbonatites from Catalão II are calciocarbonatites and ferrocarbonatites (Guarino et al., 2016). This carbonatites are characterized by medium- to coarse-grained anhedral carbonates, and minor amounts of macro- and microcrysts of zoned phlogopite, apatite, magnetite, pyrochlore, rutile, rare clinopyroxene and amphibole.

It is important to notice that, in contrast to Catalão I, calcite-carbonatite or calciocarbonatite predominates in Catalão II.

5.2 Mineral Chemistry

5.2.1 Phlogopite

Phlogopite picrites, ferrocarbonatites and phlogopitites of Catalão II bear phlogopite and tetra-ferriphlogopite. In phlogopite picrites, $Mg/(Mg+Fe^{2+})$ ratios are higher, reaching up to 0.87, while in phlogopitites they reach up to 0.77 (Guarino et al., 2016). These data show the Mg decrease related to Mg-Fe substitution, confirming phlogopitites as a more evolved term when compared to phlogopite picrites.

5.2.2 Pyrochlore

Pyrochlore composition in several rock types from Morro do Padre deposit have been analyzed by Palmieri (2011). According to the author, subtle chemical variations with magma evolution in pyrochlore from N1+C1 to N2+C2 in this case may comprehend decreasing FeO and CaO and increasing BaO, SrO and Na_2O. As said before, magmatic pyrochlore forming in carbonatite complexes normally evolves by progressive enrichment in Na, Ca, and Nb, and depletion in Ta, Th, REE, Ti and U (Hogarth et al., 2000; Knudsen, 1989; Lee et al., 2004; 2006; Cordeiro et al., 2011a). Considering only the MP pyrochlore and assuming that its chemistry is a direct result of magma evolution from N1+C1 to N2+C2, pyrochlore seems to evolve towards lower REE, titanium, tantalum and zirconium contents (Palmieri, 2011), consistently with the observed evolutionary patterns.

Regarding the effects of weathering in pyrochlores, Catalão II presents the already discussed substitution from Ca-Na-pyrochlore to Ba-pyrochlore (Palmieri, 2011), what seems to be a pattern for pyrochlore in APIP weathering profiles. However, Cordeiro et al. (2011a) argue that Ba-pyrochlore may also be formed by interaction with low temperature fluids, what is possible to distinguish in Catalão I due to a negative Ca-Sr correlation, leading to Sr-enriched of hydrothermal Ba-pyrochlore but absent in the weathering-related variety.

Although Ba-pyrochlore is the dominant type in the Catalão II weathered cover and very common in fresh-rock of the MP deposit, the fresh rock pyrochlore does not show the strong Sr enrichment observed in Catalão I (Palmieri, 2011).

However, Palmieri (2011) shows that high Ba contents can occur in pyrochlore even at the great depths of the "Lower Zone" of the MP deposit (over 10 wt. % BaO in pyrochlore from samples deeper than 750 m), confirming that, as suggested by Cordeiro et al. (2011a), Ba-pyrochlore formation is not necessarily restricted to weathering processes.

5.3 Geochemistry

5.3.1 Major elements

Chemically, phlogopite picrites are ultrabasic, ultrapotassic and ultramafic rocks, with moderately CaO-rich contents (Guarino et al., 2016), corresponding to primitive magmatic compositions, similarly to those of APIP kamafugites and kimberlites (Gomes et al., 1990; Gibson et al. 1995; Brod et al. 2000). Phlogopite picrites present up to 18.7 wt% MgO, while phlogopitites have slightly lower values (17.7 wt. % MgO) (Guarino et al., 2016).

5.3.2 REE and other trace elements

The Catalão II phlogopite picrites have high and variable Cr (270 – 1040 ppm) and Ni (160 – 360 ppm) concentrations, indicating their primitive nature In contrast, magnetitites, apatitites and carbonatites display generally low concentrations of Cr (<20 ppm) and Ni (<50 ppm; Guarino et al., 2016), what can be related to a later evolutionary stage. Generally, the Catalão II rocks also exhibit highly fractionated REE patterns (Guarino et al., 2016), similar to those of other APIP complexes.

6. Salitre Complex

The Salitre alkaline-carbonatite-phoscorite complex belongs to Late-Cretaceous Alto Parnaíba Igneous Province and consists of three separate bodies positioned south of Serra Negra Complex, nearby Patrocínio city, all hosted by fenitezed rocks from Late Proterozoic Canastra Group. The main body, Salitre I, is located at the coordinates 19º03'S; 46º47ºW. Salitre I has distorted oval settings (kidney-shaped body) and an approximated diameter of 7 km. It is composed dominantly of bebedourites, with swarms of ring dikes of carbonatites and phoscorites. Meanwhile, Salitre II represents a small plug located between Salitre I and Serra Negra Complexes; and Salitre III constitutes another small plug south Salitre I. These last two are both bebedourite-dominated smaller intrusions (Brod et al., 2004; Barbosa, 2009; Barbosa et al., 2012b; Fig. 11).

Therefore, the complex is composed mainly of bebedourite, with lesser amounts of carbonatite and phoscorite in central-north portion of the main body. According to Barbosa et al. (2012a), Salitre I, as a multi-intrusion complex, hosts two different bebedourite intrusions that represent at least five bebedouritic units with distinct petrographic characteristics. Carbonatites and phoscorites occur in ring-like to radial interconnected dikes. Barbosa (2009) has identified two phoscoritic unities and at least five carbonatitic phases (magnesiocarbonatites, calciocarbonatites and nelsonitic cumulates).

K/Ar geochronological data in phlogopites from bebedourites suggest an age of 86.3 ± 5.7 Ma (Sonoki & Garda, 1988). Furthermore, Sr and Nd isotopic data indicate that bebedourites parental magmas from Salitre complex were originated in a metasomatized sub-continental lithospheric mantle similar to that related to the origin of the rest of the APIP (Barbosa et al., 2012b). As well as other complexes in

APIP, Salitre is a multiphasic and multi-intrusion body involved in a complicated multi-stage evolution, with fractional crystallization and liquid immiscibility as possible generation mechanisms.

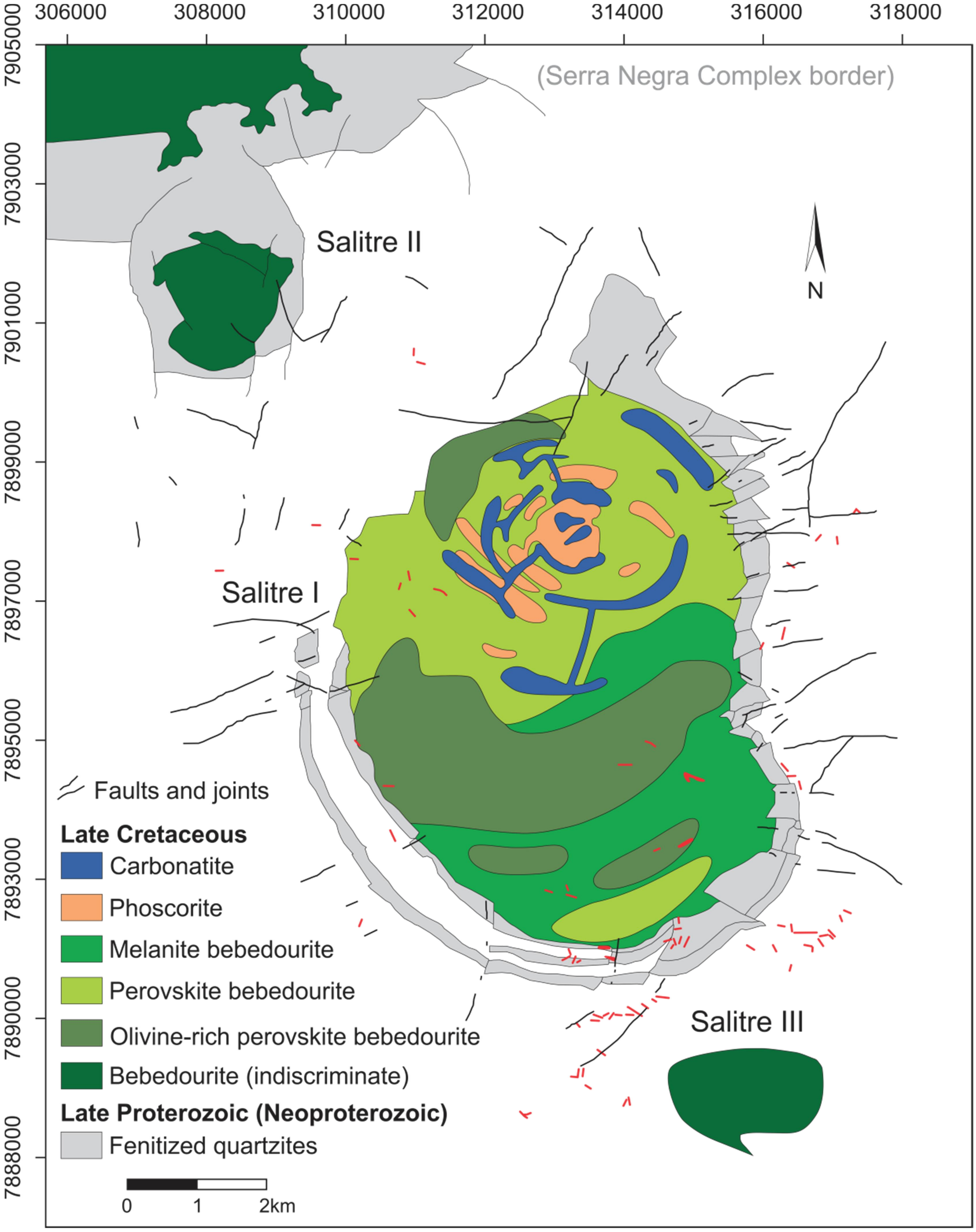

Fig. 11 - Geological sketch from Salitre Complex. Adapted from Barbosa (2009).

6.1 Petrography

6.1.1 Bebedourite Series

Analysing a total of 62 Salitre bebedourite samples, Barbosa (2009) and Barbosa et al. (2012a) concluded that these rocks vary from fine- to coarse-grained, rarely pegmatoidal, and may occur both as cumulates and dikes intruding other alkaline rocks. Likewise other APIP complexes, relevant modal variations occur, including bebedourite facies rich in olivine, phlogopite, perovskite, and apatite, in addition to typical bebedourite. According to their petrographic features, Barbosa et al. (2012a) classified these rocks into two bebedouritic intrusions: B1 and B2.

B1 Intrusion

The B1 intrusion can be divided into B1a and B1b bebedourites that are, respectively, olivine-bearing (B1a) and olivine-lacking (B1b) rocks, where perovskite is the only Ca-Ti phase present, except for the very rare occurrence of titanite as accessory in a few samples (Barbosa et al., 2012a). The bebedourites in this intrusion are typically medium- to coarse-grained, green, and show brown or black patches formed, respectively, by phlogopite or magnetite+perovskite concentrations. This intrusion occupies the northern section of the complex and the crescent shape of the areas occupied by B1a rocks and their occurrence as a segmented ring around the B1b bebedourites suggest that these two rock types are part of a cumulate pile (Barbosa et al., 2012a).

In the B1a bebedourites (perovskite-rich dunites and pyroxenites of Morbidelli et al., 1997), mapped as “olivine-rich perovskite bebedourite”, the olivine and perovskite occur as subhedral to anhedral cumulus grains with variable amounts of intercumulus diopside, magnetite, phlogopite, and rare apatite. Olivine is locally serpentinized and magnetite is variably oxidized. Perovskite is usually well preserved and optically zoned, associated with magnetite and ilmenite, and often rimmed by magnetite (Barbosa et al., 2012a; Araújo, 2015). In addition, rims of dark-orange metasomatic tetra-ferriphlogopite are often observed on large crystals of Al-rich magmatic phlogopite. Perovskite also may be converted into metasomatic anatase, forming a rim near the contact of carbonates veins with the bebedourite (Araújo, 2015). This bebedourite type is interpreted as product of crystal accumulation (Barbosa et al., 2012a).

In the B1b bebedourites, diopside and subordinate perovskite are the main cumulus phases, but perovskite can also occur as small crystals in the intercumulus material. Here, the cumulus perovskite varies in size and may also be optically zoned. Phlogopite is subhedral, often displaying slightly deformed lamellae whose borders appear to be locally recrystallized. The magnetite is present in the intercumulus as anhedral crystals and may contain ilmenite exsolution lamellaes. The apatite is also anhedral and interstitial (Barbosa et al., 2012a).

The presence of perovskite and the lack of Ca–Ti silicates in the B1 bebedourites is an indicator of the strong degree of silica undersaturation in the magmas from which they crystallized (Barbosa et al., 2012a).

B2 intrusion

The B2 intrusion can be subdivided into three groups, based on their petrographic features and the dominant Ca-Ti mineral present: B2a, B2b, B2c. While B2a group comprises rocks containing perovskite+titanite+Ti-garnet, the B2b bebedourites are characterized by the Ti-garnet (melanite) presence only, and the B2c group corresponds to the most evolved members of the bebedourite, being perovskite-free and containing either titanite or titanite+Ti-garnet as Ca-Ti phases (Barbosa et al., 2012a). Because B2a and B2c subtypes occur mostly as dikes that cross-cut the B1 intrusion (Barbosa et al., 2012a), they are not representable at the scale of figure 11.

The B2a bebedourites are relatively rare medium-grained rocks and are generally brown in color with green diopside patches. There are two distinct generations of pyroxene and phlogopite present: one consists of larger, subhedral phenocrysts, and the other of small, anhedral groundmass crystals. Perovskite is anhedral, not optically zoned, often surrounded by a titanite rim, which may in turn be coated in Ti-garnet (Barbosa et al., 2012a). This textural feature suggests destabilization of the initially formed Ca-Ti phases progressively replaced by more silica-rich equivalents. The replacement or overgrowth of titanite by Ti-garnet is accompanied by an iron increase and a concomitant titanium decrease in the latter, but not necessarily in silica, as reported by Barbosa et al. (2012a). These settings may indicate a two-step replacement, initially by SiO_2 increase (perovskite to titanite or Ti-garnet) and then by Fe_2O_3 increase (titanite to Ti-garnet). Alternatively, this iron content differences observerd in titanite and Ti-garnet may be due to crystal-chemistry constraints. Also in this bebedourite subtype, well-preserved perovskite crystals are found only as inclusions in pyroxene phenocrysts, whereas perovskite included in phlogopite phenocrysts is coated by titanite. In a similar way, individual titanite crystals from the groundmass are coated with Ti-garnet, while the titanite inclusions in phlogopite phenocrysts are not. These features indicate that the transformation/overgrowth of perovskite into/by Ca–Ti silicates is a product of a middle- to late-stage increase in silica activity and that the order of overlapping crystallization of the relevant phases is perovskite–diopside–titanite–phlogopite–Ti-garnet. Aside from coating perovskite, the most common titanite occurrence in B2a is as subhedral to anhedral individual crystals. Most Ti-garnet crystals form coatings on titanite, although the melanite may rarely occur as isolated grains in the groundmass (Barbosa et al., 2012a).

Meanwhile, the B2b bebedourites are medium- to coarse-grained and vary in color from green when diopside-rich to brown when Ti-garnet-rich. Among other bebedourite types, this is the only one that contains significant interstitial carbonate amounts. Here, the Ti-garnet is a relatively late-stage phase, occurring as large, interstitial anhedral grains, often poikilitic, with irregular shapes and borders. Titanite is subordinate and is always coated in Ti-garnet, indicating preference for garnet crystallization due to higher silica activity (Barbosa et al., 2012a).

The B2c rocks are perovskite-free and contain either titanite or titanite+Ti-garnet as Ca–Ti minerals. The titanite-only bebedourite kind is relatively rare and occurs mainly as thin, fine-grained dikes with a dark green to black color. Flow texture is locally well marked by the orientation of subhedral phlogopite and diopside. In this context, subhedral titanite, anhedral apatite and magnetite are also oriented by flow. The B2c titanite and Ti-garnet-bearing bebedourites happen to be fine to medium-grained and greenish brown rocks. Here, titanite is subhedral or anhedral, with the latter usually surrounded by a rim of also anhedral Ti-garnet. Melanite is often interstitial and poikilitic, resembling an atoll texture. Some individual Ti-garnet crystals may occur in isolation, but there is no clarity if whether they are primary or the result of a complete replacement of the previous titanite (Barbosa et al., 2012a).

Syenites

Salitre syenite dikes are fine-grained rocks composed mainly by tabular K-feldspar and prismatic aegirine, with euhedral fine-grained titanite crystals and the essential accessory phase. Syenites can present trachytic or, in some cases, porphyritic textures, with pyroxene and K-feldspar phenocrysts (until 1 cm). These rocks represent the most evolved terms of bebedouritic-series and are generally associated to melanite bebedourites (B2b). (Barbosa et al., 2012a).

The syenites occur mostly as dikes (Barbosa et al., 2012a), but Morbidelli et al. (1997) also reported their presence at the top of the ultramafic cumulate sequence, therefore suggesting that these rocks are the evolved endmembers of the bebedourite series. This interpretation is in good agreement with the presence, although rare, of K-feldspar in some evolved bebedourites from the Tapira complex in the APIP (Brod, 1999; Brod et al., 2005).

6.1.2 Phoscorite Series

Phoscorite-series is a subordinate constituent in Salitre Complex, restricted to its northern portion, along with B1 (bebedourite domain). These rocks mainly occur as an interface between bebedourites and carbonatites, or are only carbonatite-related, with frequent magmatic flow textures. As general characteristics, they are coarse-grained, and composed essentially by apatite, olivine, and magnetite. Phlogopite, carbonates (calcite and dolomite) and pyrochlore are qualifying accessories, with some minor sulfide presence. Barbosa (2009) divided Salitre phoscorites into P1 and P2 units. P1 is composed by olivine, Al-phlogopite, apatite, magnetite and rare perovskite relicts. Although P2 phoscorites are composed by olivine, apatite, magnetite, with pyrochlore, (rare) phlogopite with tetra-ferriphlogopite rims as important accessory phases (Barbosa 2009; Barbosa et al., 2012b).

P1 Phoscorite

P1 phoscorites are spatially related to olivine-rich perovskite bebedourites (B1a), and carbonatite venules often mark the contact between these two rock types (Araújo, 2015).

These rocks are essentially composed by apatite and olivine (locally turned into clino-humite), with considerable and variable amounts of phlogopite. Magnetite plays its role as an accessory mineral, along with minor carbonates. Locally, the presence of sulfides such as pyrite, pyrrhotite, and chalcopyrite can be observed. Rare perovskite is also described, occurring in fine-grained crystals commonly oxidized (Barbosa, 2009).

According to Barbosa et al. (2012b), olivine has two textural varieties: first, occurs as subhedral to anhedral coarse-grained crystals (until 0.5 cm), with opaque inclusions (probably magnetite) that delimit crystalgrowth lines. The second variety comprehends fine-grained anhedral olivine crystals with almost no inclusions. P1 phlogopites occur as well-developed euhedral lamellaes reaching up centimeters, with dark-green to orange pleochroism, similar to those phlogopites described in Salitre bebedourites. Locally, zoned phlogopite with red brims are deformed, indicating magma chamber movement during its crystallization. Magnetite presents exsolution lamellae with ilmenite. Sulfides are anhedral and disseminated (Barbosa, 2009).

P2 Phoscorite

P2 phoscorites are fine- to coarse-grained and locally exbihit microporphyritic textures. They are mainly composed by proportional amounts of olivine, apatite and magnetite, as well as expressive carbonate amounts. Phlogopite and pyrochlore are main accessory phases (Barbosa, 2009).

Barbosa et al. (2012b) report these rocks containing olivine, magnetite and apatite microphenocrysts in a fine-grained groundmass, composed by olivine, magnetite, apatite, pyrochlore and rare phlogopite. Olivine microphenocrysts (2-3mm) tipically have fluid inclusions, often contain apatite inclusions, and locally show reaction rims, as well some poikilitic magnetite grains, that can reach up to 1cm and frequently coat all mineral phases. Apatite prisms tend to appear as clear euhedral crystals and pyrochlore is disseminated as fine euhedral reddish grains. Phlogopite is rare and constitute small anhedral lamellaes with light- to dark-orange pleochroism and tetra-ferriphlogopite brims (Barbosa, 2009). Carbonate occurs as centimetric irregular pockets, and rarely as intersticial disseminated grains. These carbonate pockets have similar comb-layering features such as Cordeiro et al. (2011) described for Catalão I nelsonites.

6.1.3 Carbonatite Series

Salitre I carbonatites range from white to grayish, fine- to coarse-grained rocks. They occur mainly as dikes, with millimetric (venules) and centimetric thickness. Larger bodies of metric sizes were distinguished by drill core information, but it is not clear if they represent larger dikes or layered intrusions. Centimetric dikes are composed almost exclusively of carbonates (calcite and dolomite, also strontianite and ancyllite), with poor phlogopite and sulfides (mainly pyrite and pyrrhotite, with minor chalcopyrite). When in larger bodies, carbonatite varies from fine to coarse-grained and often grind of pure carbonatite, until carbonatites with magnetite-, phlogopite-, apatite-, olivine- and pyrochlore-richer portions. These minerals may be disseminated or concentrated in bands, setting a magmatic bedding, described as a crystal mush, where crystals often were deformed and rupted due to magmatic chamber movements (Barbosa et al., 2012b; Araújo, 2015).

Based on field relations and petrographic characteristics, five units (C1, C2, C3, C3a and D4) have been distinguished by Barbosa (2009). According to its classification, C1 and C2 correspond to magnesiocarbonatites, C3 represents calciocarbonatites, C3a are nelsonitic cumulates and D4 comprehends late magnesiocarbonatite dikes. Likely other APIP complexes, carbonatite bodies that cross-cut bebedouritic series rocks often result in the formation of metasomatic phlogopitites.

Magnesiocarbonatites (C1)

C1 are fine- to coarse-grained rocks composed by carbonate and containing important and minor variable amounts of apatite, phlogopite, olivine and magnetite (with exceptional 10%). Other mineral phases include pyrochlore and sulfides (pyrite, chalcopyrite and pyrrhotite). Apatite is find typically in prismatic aggregates within irregular to intersticial discontinuous pockets. Magnetite is often amoeboid and locally encompasses apatite crystals. Phlogopite is euhedral with localized tetra-ferriphlogopite rims. Olivine is anhedral and its presence is very restricted. Pyrochlore ranges from orange euhedral crystals to reddish anhedral grains (Barbosa, 2009).

Magnesiocarbonatite (C2)

C2 is composed chiefly by practically pure carbonates, with up to 5% apatite and 1% phlogopite, magnetite and sulfides (chalcopyrite and pyrrhotite). Apatite forms subhedral prisms and phlogopite, when present, occurs as anhedral tetra-ferriphlogopite —flakes (Barbosa, 2009).

Calciocarbonatites (C3)

According to Barbosa (2209), C3 calciocarbonatites can vary significantly: from olivine-calciocarbonatites, olivine-pyrochlore-calciocarbonatites, pyrochlore-carbonatites, until pure calciocarbonatites, which represent the more evolved terms (Barbosa, 2009).

This author reports that olivine-carbonatites represent the less evolved rocks of C3 unit, with carbonate, olivine, apatite and magnetite as essential phases. Main accessories are phlogopite, pyrrhotite and pyrite. Olivine-pyrochlore carbonatites evolve from the latter by gradual decrease of olivine and appearance of pyrochlore, followed by pyrochlore calciocarbonatites, where pyrochlore and phlogopite content increase meanwhile olivine lacks. Here, apatite, magnetite, and sulfides, as pyrrhotite, chalcopyrite and pyrite are accessories (Barbosa, 2009). Araújo (2015) also describes thin intercumulus monazite lamellae associated with calcite in C3 rocks.

For this unit, Barbosa (2012b) observed olivine grains occurring as fine-grained anhedral or larger euhedral crystals, frequently zoned. In pyrochlore-bearing samples, olivine presents reaction rims and is substituted for phlogopite, suggesting a non-balanced system. Locally rounded olivine xenocrysts were observed, and was related to a possibly magma reabsorption feature. Apatite appears in disseminated subhedral prisms and rare aggregates. Phlogopite and tetra-ferriphlogopite occur in variable proportions as euhedral to subhedral crystals, with frequent zonation (phlogopite core and tetra-ferriphlogopite brim). Pyrochlore is euhedral to anhedral, yellow to red colored and can show color zonation. Carbonates tend to form anhedral medium- to coarse-grained crystals with local flow texture (Barbosa, 2009).

Barbosa (2009) highlights that is common to observe segregation layered patches of apatite, magnetite, olivine and pyrochlore suggesting phoscoritic and nelsonitic accumulation. These layers are frequently deformed and discontinuous, indicating magmatic chamber movements.

Nelsonitic Cumulates (C3a)

C3a represent nelsonitic cumulates that occur in the interface between olivine -bearing or -lacking calciocarbonatites, and may vary widely in composition. It consists into essential apatite, magnetite, with interstiticial carbonate and phlogopite, and minor amounts of pyrochlore. Within nelsonitic cumulates, the layers vary between magnetitites and nelsonites, with carbonate and phlogopite contents increasing towards the nelsonitic composition (Barbosa, 2009).

Segregation of pure apatite patches (apatitites) occurs in late stages, which apatite forms irregular shaped pockets. This feature, according to Barbosa (2009), suggests a genesis by the immiscibility between phosphate and carbonatite liquids or, alternatively, layers of cumulus apatite grains, that were rupted and remobilized by magma movement. Anyhow, these rocks represent accumulation of sacaroidal apatite with intersticial carbonate (Barbosa, 2009).

Magnesiocarbonatites D4

D4 corresponds to late magnesiocarbonatite thin dikes. They represent a more evolved phase, where carbonates (calcite and dolomite) are the main phases, with minor apatite, and rare pyrrhotite and pyrite. Intercumulus barite and monazite are present, and associated with metasomatized anatase (Araújo, 2015; Barbosa, 2009). Apatite associated with late stage D4 magnesiocarbonatite dikes may form aggregates of euhedral crystals carbonatite cavities, frequently associated with dolomite and monazite. Bebedourites metasomatized by D4 carbonatite contains apatite crystals overgrown by banded apatite with characteristic high birefringence and high Sr and REE contents (Araújo, 2015).

6.2 Mineral Chemistry

6.2.1 Olivine

Olivine is a relatively rare constituent in of B1a bebedourites of Salitre I (Barbosa et. al, 2012). However, the mineral is abundant in the Salitre II body (Morbidelli et al., 1997) and in other Salitre rock types, such as phoscorites and carbonatites (Barbosa et al., 2012b). The forsterite content in the olivines from B1a ranges from 83 to 87 mol%, what is consistent with olivine samples from Salitre II (Fo_{82-87}, Morbidelli et al., 1997) and Tapira (Brod, 1999) bebedourites. However, it is noteworthy that the B1a olivine forsterite content is slightly lower than that of olivine in primitive phlogopite picrites from Tapira (Fo_{84-90}, Brod, 1999), suggesting that the magma from which the Salitre and Tapira bebedourites accumulated is more evolved than the typical phlogopite picrite, although still ultramafic in composition. This magma may represent the evolution of a phlogopite picrite liquid, after some degree of fractionation of dunitic cumulates (Barbosa et al., 2012a).

6.2.2 Phlogopite

The analyzed mica from bebedourite belongs to the phlogopite–annite series, with a slight Fe^{3+} enrichment. (Barbosa et al., 2012a). Regarding the occurrence of phlogopite–tetra-ferriphlogopite solid solution, this is a common primary (magmatic) feature of carbonatites (e.g., Brod, 1999; Brod et al., 2001) and carbonatite–phoscorite associations (e.g., Brod et al., 2001), but its presence in the accompanying of silicate rocks may be the result of different causes, such as carbonatitic metasomatism or the reaction of early-formed aluminous phlogopites with a carbonated residual magma (Barbosa, 2009).

Phlogopite from Salitre I is, therefore, an essential phase in P1 and accessory in P2 phoscorite. It shows an increase in Fe^{3+} and a decrease in Al_2O_3 contents towards its rim, what has been interpreted as a typical feature of phoscoritic-carbonatitic magmas (Brod et al., 2001; Barbosa, 2009). Al_2O_3 contents in P2 phlogopites, for example, are about 9 – 11.7% in its core and 0.1 – 4.5% in its rim (Barbosa, 2009).

6.2.3 Apatite

Igneous apatite from B1a and B1b bebedourites is often intercumulus, prismatic and commonly associated with perovskite and magnetite. Additionally, low Sr and REE values indicate that apatite from the B1 bebedourite sample is less evolved than that from other bebedourite types found in the complex (Barbosa et al., 2012a). Relevant cation substitutions occur mostly on apatite from the carbonatite series and Araújo (2015) has reported substitutions of the britholite-type, as observed by Cordeiro et al. (2010) in Catalão I, and belovite-type ($2Ca^{2+} = Na^{+} + REE^{3+}$) as described by Hogarth (1989). The Sr-Ca substitution occurs in apatite from metasomatic origins, but is less expressive in igneous and supergenic apatite. (Araújo, 2015; Barbosa et al., 2012).

6.2.4 Monazite

As said before, monazite is the main rare earth bearing mineral in APIP and occurs in variable proportions both in the fresh rock and in the lateritic profiles. In the Salitre carbonatite complex, the unaltered igneous rocks contain monazite in small proportions, usually as a late-stage phase (intercumulus or hydrothermal). As expected, monazites from Salitre are enriched in LREE, with elements heavier than Dy not detected or close to the detection limits (Araújo, 2015).

6.2.5 Pyrochlore

In Salitre, pyrochlore occurs in P2 phoscorites, C1/C2 magnesiocarbonatites, C3 calciocarbonatites and C3a nelsonitic cumulates. Ba-rich pyrochlore (untill 8.09% BaO) occurs only as irregular cores in a few magnesiocarbonatite (C1, C2) crystals. This feature suggests that Ba-rich pyrochlore formation may be related to early-stages of magmatic evolution and not only weathering or hydrothermal processes (Barbosa, 2009), what is consistent to data from Catalão II (Palmieri, 2011).

6.3 Whole-rock Chemistry

6.3.1 Major Elements

Discussing whole rock geochemistry and differentiation processes for bebedouritic rocks is complicated, considering they are cumulate rocks and one must be careful, considering the distribution of many elements may be strongly controlled by the distribution of specific minerals (Barbosa et al., 2012a). The data obtained by Barbosa et al. (2012a) shows that SiO_2 increases, whereas both MgO and TiO_2 decrease from B1 to B2 bebedourites, reflecting olivine and perovskite fractionation in the early stages of magmatic evolution. This progression also drives CaO and P_2O_5 to increase, leading to the crystallization of plenteous diopside and apatite in B1b and then in B2 bebedourite (Barbosa et al., 2012a). According to the same authors, the more evolved B2 magmas then become enriched in alkalis and Al_2O_3, what results in the crystallization of more abundant phlogopite, initially as an intercumulus phase and later as well-formed lamellae. In Salitre, P1 phoscorite presents slightly higher contents of MgO than the P2 type. This feature is consistent to Krasnova et al. (2004a) observations for Kola Province, suggesting MgO values decrease towards magmatic evolution of phoscoritic phases. It is noteworthy that from a certain evolutionary moment, bebedouritic and phoscoritic series follow distinctive magmatic differentiation paths, producing a bifurcated trend (Fig. 12; Barbosa, 2009).

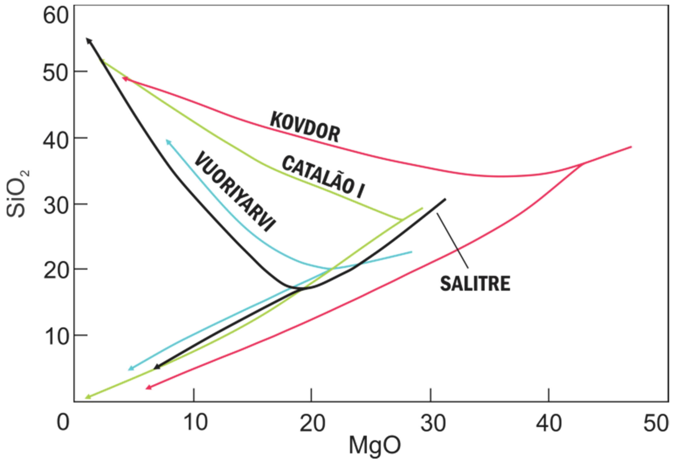

Fig. 12 - Patterns of evolution of Salitre Complex. In comparision, we present patterns of Catalão I (Cordeiro, 2009), in APIP, and Kovdor and Vuoriyarvi Complexes (Krasnova et al., 2004, and additional data available at http://www.emse.fr/~moutte/), in Kola Province. It is noteworthy that in all cases, there is a bifurcated pattern that separates the silicate series from the phoscorite series, suggesting liquid immiscibility. The bifurcation occurs at distinct stages of evolution for each complex. Adapted from Barbosa (2009).

6.3.2 REE and other trace elements

Regarding REE, diagrams produced by Barbosa (2009) show that normalized to chondrite patterns indicates a LREE enrichment in relation to HREE for all of Salitre Complex rocks, a typical feature from APIP and alkaline rocks (Fig. 13).

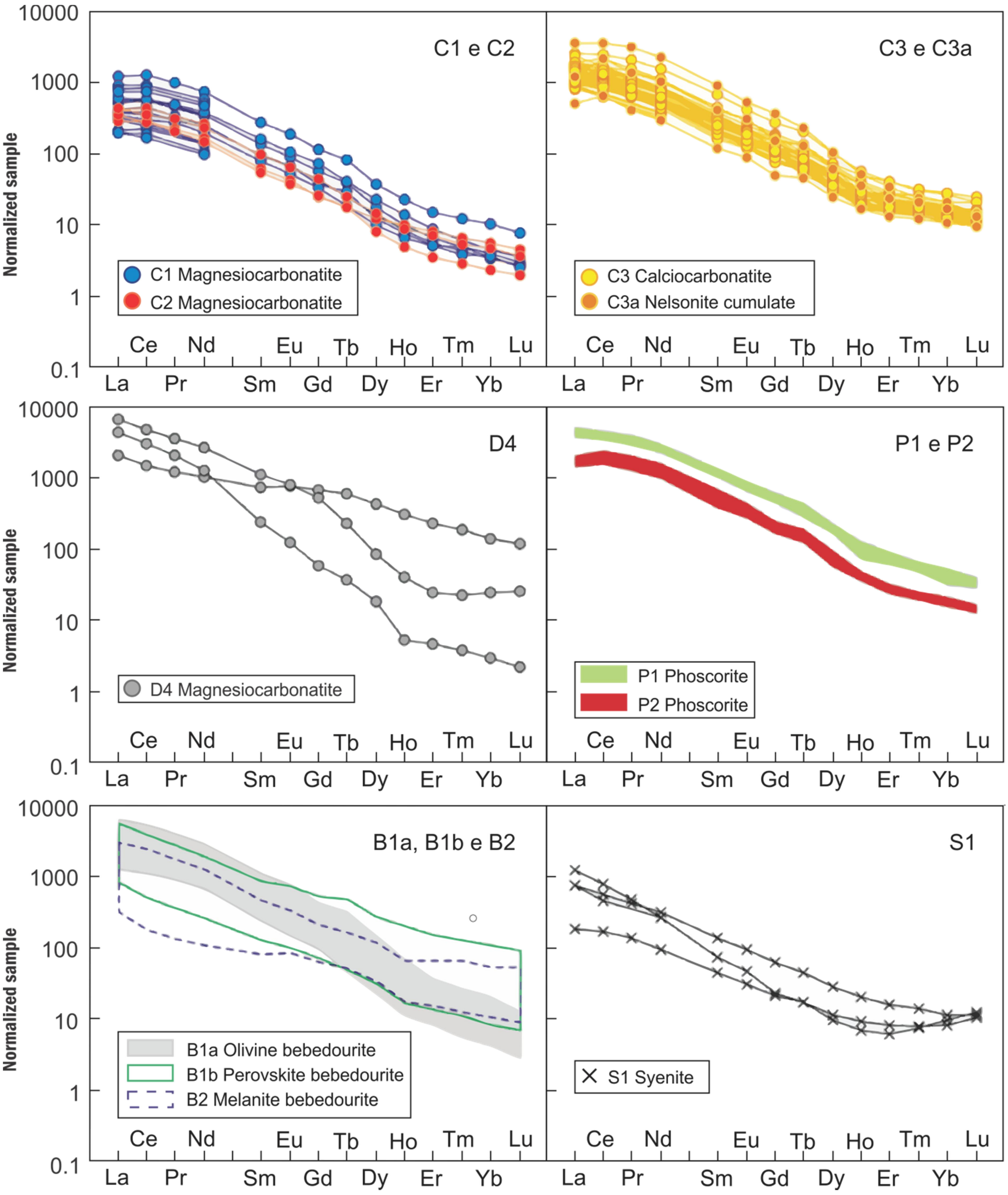

Fig. 13 - REE normalized to the chondrite (Boynton, 1984) diagrams for Salitre carbonatites (C1, C2, C3a, C3 e D4), phoscorites (P1 and P2), bebedourites (B1a, B1b and B2) and syenites (S1). Adapted from Barbosa (2009).

In addition, trace element contents in Salitre bebedourites may highlight some important differences between the olivine-bearing and olivine-lacking rocks. The olivine-rich bebedourites (B1a) contain significant amounts of Cr (up to 1122 ppm) and Ni (up to 1291 ppm), suggesting that they derive from a relatively "primitive" magma, while in olivine-lacking bebedourites (B1b; both dikes and cumulates), the Cr content is below 100 ppm and the Ni content below 115 ppm (Barbosa et al, 2012a).

Regarding phoscorites, the main differences observed between P1 and P2 are related to geochemical pairs Nb-Ta and Zr-Hf. In most petrologic processes, this pairs present a constant ratio, what is not observed is this case. Decoupling between Nb and Ta and between Zr and Hf has been recently recognized in strongly alkaline magmatic systems (Barbosa, 2009) and studies involving High Field Strength Elements (HFSE) like Nb, Ta, Zr or Hf in the context of silicatic-carbonatic liquid immiscibility show that these elements prefer silicatic liquids (Hamilton et al., 1989, Veksler et al., 1998). In addition, studies from Veksler et al. (1998) indicate that Zr and Hf have a stronger trend to stay in silicatic liquid than Nb and Ta, but the fractionation of Zr/Hf ratio is much smaller than the Nb/Ta one. According to the authors, Zr- and Nb-rich carbonatites are originated from residual liquids formed through fractional crystallization and not a product of immiscibility (Barbosa, 2009).

7. Serra Negra Complex

Serra Negra alkaline-carbonatitic complex (SN) is situated east of Patrocínio city (Minas Gerais), approximately 600 km from Brasília (Federal district), and north of Salitre Complex. With about 10 km in diameter, this is the largest and, until then, least known complex of the Alto Parnaíba Igneous Province (APIP). Likewise its siblings, Serra Negra intrudes neoproterozoic schists and quartzites from Canastra Group, Brasília Mobile Belt. This intrusion has a circular format and originated and exceptional example of domic morphology (Brod et al., 2004; Grasso, 2010). In the complex, Amaral et al. (1967) obtained ages between 83.7 e 83.4 Ma, in biotites from ultramafic rocks.

The complex is composed by about 70% of dunites, which are part of the bebedouritic series rocks and occur from the external contact with the country rock to near the center of the dome (Fig. 14). Additionally, two magnesiocarbonatite bodies intrude the central and northern portions of the complex, causing brecciation of the previously formed dunites. Within the northern intrusion, there are two small regions with predominance of calciocarbonatite veins and dikes. In this areas, phoscorite cumulates occur grading of calciocarbonatites or associated to the northern magnesiocarbonatite intrusion. There are also perovskite bebedourites spatially associated with both the northern and central magnesiocarbonatites intrusions (Grasso, 2010).

Within Serra Negra is also possible to find phlogopite picrites and trachyte dikes cross-cutting the other rock types. These phlogopite picrites have similar geochemical affinity to other phlogopite picrites and kamafugites from APIP. Several authors suggest a parental magma with phlogopite-picritic composition for APIP rocks (Brod, 2000; Grasso, 2010). Following this path, Grasso (2010) claims fractional crystallization and liquid immiscibility play an important role in these rocks petrogenesis.

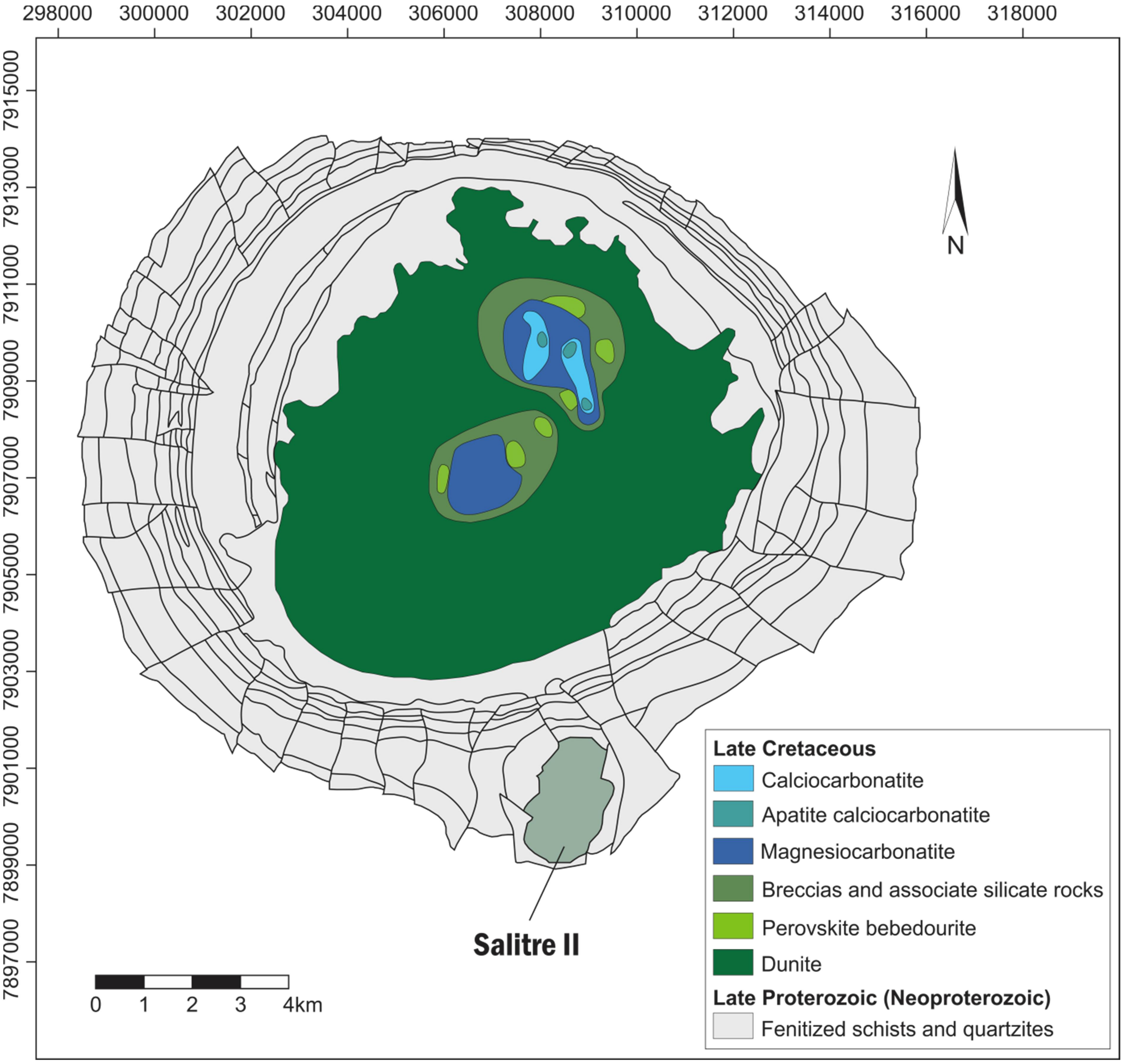

Fig. 14 - Geological sketch from Serra Negra Complex. Adapted from Grasso (2010).

7.1 Petrography

7.1.1 Phlogopite picrites

In Serra Negra, the phlogopite picrites are constituted by millimetric olivine and phlogopite phenocrysts set in a dark-gray groundmass composed of phlogopite, carbonates, perovskite and opaque minerals. These rocks are structurally massive, but in some dikes the phenocrysts are concentrated toward the center, suggesting the occurrence of flow-differentiation. The typical modal composition is ca. 20% of phlogopite and olivine phenocrysts, in a groundmass composed of 50% phlogopite, 20% of carbonate globules, 5% perovskite, 5% opaque minerals, and interstitial carbonate. The olivine phenocrysts (1 mm) are euhedral and usually serpentinized. Phlogopite phenocrysts (1 mm) are euhedral to subhedral, usually with tetra-ferriphlogopite rims, similarly to what is described in other APIP complexes. The groundmass is formed by fine-grained phlogopite (0.1 – 0.25 mm), carbonate globules, opaque minerals, perovskite (0.1 – 0.25 mm), and interstitial carbonate (0.2 mm). It is common to find serpentine filling fractures of the phlogopite picrites, as a typical supergenic alteration feature (Grasso, 2010).

7.1.2 Bebedourite Series

Serra Negra bebedourite-series comprises mostly dunites, perovskite-rich cumulates, and a more evolved group of trachytes/syenites (Grasso, 2010). When compared with Salitre and Tapira bebedourites, these rocks are modally similar to the early-stage perovskite bebedourites (Brod, 1999; Barbosa et al., 2012a) in those complexes (Grasso, 2010).

Dunites

Serra Negra dunites are dark-gray fine-grained rocks displaying cumulate structures due to modal variations in olivine, magnetite and phlogopite. Secondary minerals comprise serpentine and clino-humite. Carbonate in small amounts is found as intercumulus phase. Olivine and magnetite are cumulus phases, with crystal-sizes of 0.05 to 2 mm and 0.25 mm, respectively. Magnetite can also occur as inclusions in olivine and, in some cases, be late cumulus to intercumulus. Phlogopite represents an intercumulus phases, occurring as subhedral to anhedral fine-grained crystals (0.25 mm). It generally forms rims on magnetite, possibly through reaction of the magnetite with a potassium-rich residual liquid. Carbonate is fine-grained, intercumulus. Serpentine and clino-humite form rims around olivine, representing alteration products (Grasso, 2010).

Bebedourite

The bebedourites are dark-gray coarse-grained (locally pegmatoidal) rocks with a mosaic texture and massive structure, composed mostly of perovskite and less expressive phlogopite and magnetite. Euhedral olivine is a typical cumulus phase. Perovskite occurs as a euhedral cumulus phase (0.15 to >3 mm) and also as fine-grained inclusions in magnetite. Magnetite is intercumulus (0.1 – 2 mm), subhedral to anhedral. Phlogopite is an intercumulus phase, in subhedral (0.2 – 1 mm) but also as thin rims on perovskite (Grasso, 2010).

Syenite/Trachyte

In Serra Negra, there are descriptions of an altered, fine-grained porphyritic trachyte dike, formed by submilimetric K-feldspar and biotite phenocrysts set in a very fine-grained groundmass rich in biotite and magnetite. The modal composition is ca. 83% K-feldspar, 15% biotite and 2% magnetite (Grasso, 2010). This lithotype probably represents a more evolved member of the bebedouritic-series rocks, similarly to what observed in other APIP complexes.

7.1.3 Carbonatite Series

According to Woolley & Kempe (1989) classification, Serra Negra carbonatites correspond to the calico- and magnesiocarbonatite types. It is noteworthy that the SN carbonatites are fairly restricted in composition compared with carbonatites from the Araxá, Tapira, Salitre and Catalão I complexes. It is also important to establish that APIP carbonatites plotting in the ferrocarbonatite field, the high iron content is not due to the presence of iron carbonate, but a result from the presence of other minerals, such as Fe-oxides (Grasso, 2010).

Here, carbonatites vary from homogeneous to distinctively banded, with layers evidenced by modal variations in carbonate, apatite, oxides, and olivine. This feature is usually interpreted as product of segregation of selected minerals from the carbonatite magma. Apatite and magnetite-rich layers resembling phoscorite-series are produced probably due to the magma segregation process (Grasso, 2010).These last rock types can be described as phoscorite cumulates, similarly to C3a cumulatic nelsonites from Salitre complex (e.g. Barbosa 2009; Barbosa et al., 2012b)

Calciocarbonatites

Grasso (2010) divides calciocarbonatites into two types: the calciocarbonatite and the apatite-rich calciocarbonatite. Apatite calciocarbonatites are grayish white, typically fine- to medium-grained rocks, composed by carbonates, apatite and magnetite, with less phlogopite amounts. They may or not contain olivine. Sulfides (pyrite and pyrrhotite) and pyrochlore are common accessories. Carbonate occurs as subhedral grains (0.5 – 2 mm), and forms a granular, mosaic-like groundmass. Apatite (0.1 - 2 mm) is often oriented along rock's banding, and may contain abundant melt (carbonate-rich) inclusions. Solid inclusions are mostly of phlogopite and opaque minerals. Magnetite (2.5 mm) appears preferably within coarser-grained bands, with inclusions of phlogopite and apatite. Phlogopite crystals vary from euhedral to nearly anhedral (2.5 mm in size), but the mineral also occurs as fine-grained "flakes" (0.1 mm). Phlogopite also presents tetra-ferriphlogopite rims, as described for the other APIP complexes. More rarely, not only thee brim but the whole lamella is tetra-ferriphlogopite. Olivine occurs as subhedral crystals (1.25 mm), usually associated with apatite-rich bands. Pyrochlore occurs as small (0.25 mm) euhedral grains dispersed in the rock. Clino-humite is a common alteration product at the rims of olivine crystals, in rare cases replacing the whole grains (Grasso, 2010).

The "Calciocarbonatite" type represents white, medium-grained rocks which may correspond to residues of the fractionation of apatite, magnetite and olivine, from the apatite-calciocarbonatites. They occur both as carbonatitic bands in cumulates or as fine-grained dikes cross cutting other rocks from the complex. These carbonatites have minor amounts of apatite, phlogopite, magnetite, and accessory pyrochlore. The carbonates are subhedral to anhedral (0.15 – 0.75 mm), making a granular texture. Mica phase is represented by euhedral to subhedral tetra-ferriphlogopite. Magnetite is fine to coarse-grained (0.15 mm), nearly euhedral, normally concentrated in bands, together with phlogopite and apatite. Apatite (0.25 – 0.5 mm) is typically subhedral to euhedral, prismatic, usually forming millimetric to centimetric pockets and may also contain tetra-ferriphlogopite. Locally, apatite is rich in opaque inclusions. Pyrochlore is euhedral (0.6 mm) and concentrically zoned, occurring always within or in closely associated with apatite-rich pockets (Grasso, 2010).

Magnesiocarbonatites

Magnesiocarbonatites are white, fine to locally very coarse-grained, with barite, sulfides and pyrochlore accessories. Dolomite is subhedral (1.75 mm). Tetra-ferriphlogopite occurs as small (0.2 mm), euhedral and subhedral lamellae, usually associated with barite. It also occurs as inclusions in dolomite and apatite. Apatite is very rare, euhedral, prismatic, up to 0.15 mm, usually associated with magnetite. Magnetite is subhedral (0.4 – 1.8 mm), usually associated or forming inclusions in phlogopite. Barite (0.1 – 0.6 mm) is subhedral and disseminated in the rock. Pyrochlore is often subhedral (0.25 mm). The presence of turbid carbonate suggest that some samples from the central intrusion may be slightly altered by late-stage metasomatism or weathering (Grasso, 2010).

Phoscorite Cumulates

As mentioned before, phoscorite cumulates occur as apatite and magnetite-rich layers in calciocarbonatites and, more rarely, in magnesiocarbonatites. Their textural properties and drill core relationships suggest that they are cumulates separated from the carbonatite magma. These rocks are coarse-grained and have pronounced magmatic banding apatite and magnetite-rich layers. Magmatic flow texture is also present in some samples (Grasso, 2010).

Phoscorites modal composition is widely variable in terms of the essential constituents, with pyrochlore and sulfides as accessories. Apatite is euhedral and prismatic (0.25 – 1.2 mm). Magnetite (0.2 – 2 mm) is subhedral to anhedral and may contain apatite inclusions. Tetra-ferriphlogopite varies from euhedral to anhedral, often developing late-stage, poikilitic tetra-ferriphlogopite rims. Carbonates (0.2 – 1.5 mm) are anhedral and intercumulus, composing bands and irregular, millimetric to centimetric pockets, similar to those of Catalão I (e.g. Cordeiro et al., 2011a) Pyrochlore (1.5 mm) is often concentrically zoned (Grasso, 2010).

7.2 Mineral Chemistry

7.2.1 Olivine

Forsterite content varies between 87 and 90 mol % in dunites, 88 and 91 mol % in perovskite bebedourites and from 96 to 97 mol % in apatite calciocarbonatites. Meanwhile, NiO is highest in dunites (up to 0.29%), considerably lower in perovskite bebedourites (averaging 0.07%) and lowest (reaching 0.01%) in apatite calciocarbonatite (Grasso, 2010). Like observed by Barbosa et al. (2012b), forsterite content in olivine can not be used to compare silicatic to phoscoritic/carbonatitic rocks in terms of magmatic evolution, since the factors controlling the partition coefficient of MgO and FeO between olivine in phoscorite or carbonatite magmas are different from those operating in silicate magmas (Grasso, 2010). However, the MgO/(MgO+FeO) contents of Serra Negra olivines are higher than those from Salitre I (Barbosa, 2009; Barbosa et al., 2012b) and lower than most olivines from Catalão I (Araújo, 1996). In addition, when compared with other APIP complexes, NiO values for olivine from Serra Negra dunites are intermediate between that of olivine in similar rocks from Salitre I (Barbosa, 2009; Barbosa et al., 2012b) and Catalão I (Araújo, 1996). These features could suggest, according to Grasso (2010), a progressively more evolved silicate magma composition in the sequence Catalão I – Serra Negra – Salitre I.

7.2.2 Phlogopite

Phlogopite is present in all rock-types and is the most frequent silicate in the Serra Negra. The phlogopites of bebedourite-series rocks show a trend of increasing Fe^{2+} and decreasing Mg^{2+} with magmatic evolution (phlogopite-annite substitution). The presence of tetra-ferriphlogopites can be explained by metasomatism resulting from carbonatite intrusions which locally affected the composition of some phlogopites (Grasso 2010).

7.2.3 Magnetite

The general magnetite evolution trend in the APIP silicate ultramafic rocks may be gauged by the Mg/(Mg+Fe2+) ratio and the Cr content, both decreasing with magma evolution. This affirmation considers that Cr^{3+} substitution for Fe^{3+} is relevant only in magnetites from primitive silicate rocks. Therefore, magnetites from dunites are the only ones with significant Cr_2O_3 contents (2.7 to 21.6 wt. %; Grasso, 2010).

The magnetite from Serra Negra dunites is relatively less evolved than magnetite from dunites in other APIP complexes, and more evolved than magnetite from Tapira phlogopite picrites. Magnetite from SN bebedourite is similar in composition to those in bebedourites from Tapira and Salitre I, and clearly more evolved than those from SN dunites (Grasso, 2010).

7.3 Whole-rock Chemistry

To Grasso (2010), most of Serra Negra rocks are the product of crystal accumulation, and therefore not representative of a magmatic liquid. On the other hand, fine-grained dikes of phlogopite picrites, some fine-grained carbonatites and the trachyte may represent or approximate the composition of some magmatic liquid (Grasso 2010).

7.3.1 Major Elements

Serra Negra fresh rock phlogopite picrites are strongly unsaturated in silica, have high CO_2 contents, are very K-rich, with also high MgO, CaO and TiO_2, but low Al_2O_3. Therefore, the phlogopite picrites have been classified as ultrapotassic and peralkaline (Grasso 2010). In counterpart, the trachyte from Serra Negra (the more evolved member of present silicate rocks) has relatively low SiO_2, high K_2O and low Na_2O, classifying as alkaline and ultrapotassic (Grasso 2010). Serra Negra carbonatites and phoscorites, as expected, have low values of SiO_2, Al_2O_3 and TiO_2 (Grasso 2010).

7.3.2 REE and other trace elements

Serra Negra phlogopite picrites have moderate contents of Cr (68 – 582 ppm) and Ni (37 – 399 ppm), but they are rich in incompatible elements such as Ba (1180 – 2410 ppm), Sr (1196 – 3291 ppm) and LREE (Fig. 15; Grasso, 2010). As evidenced before, high concentrations of incompatible trace elements are a characteristic of the APIP rock associations (Gibson et al., 1995; Brod, 1999). Serra Negra phlogopite picrites are very similar to those described by Brod et al. (2000) in the Tapira complex and also have strong chemical affinity with kamafugites and phlogopite picrites from other APIP complexes, reasons why Grasso (2010) interpret these rocks as representative of the parental magma of the Serra Negra Complex, in accordance with the interpretation of Brod et al. (2000) for the Tapira complex. Cr and Ni contents decrease from phlogopite picrites to dunites and from dunites to perovskite bebedourites, what is consistent with magmatic evolutionary patterns. The REE contents are lower in dunites than they are in phlogopite picrites and perovskite bebedourites, due the absence or low concentrations of REE mineral hosts that crystallize in dunites, like apatite and perovskite (Grasso, 2010).

Although the already mentioned common decreasing LREE-HREE pattern present in almost all APIP rocks, carbonatites show the strongest LREE/HREE fractionation among Serra Negra rocks. Both the calciocarbonatites and the phoscorites are enriched in REE compared with phlogopite picrites. The magnesiocarbonatites, however, have lower REE contents compared with phlogopite picrites, with exception of two samples that show petrographic evidence (altered, turbid carbonate) of metasomatic or weathering alteration, explaining REE anomaly (Grasso, 2010).

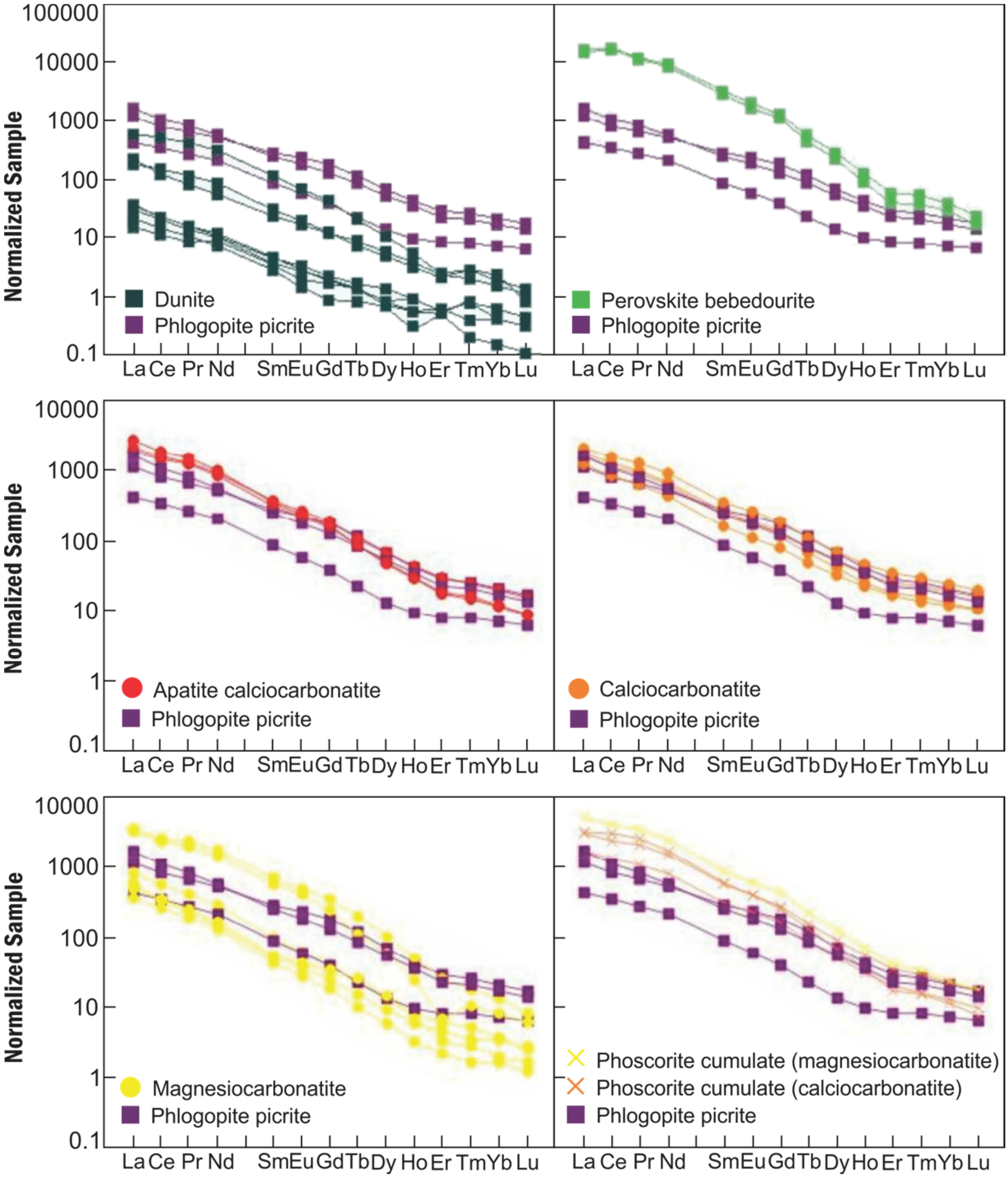

Fig. 15 - REE patterns for Serra Negra bebedourite diagram and carbonatite series rocks normalized to chondrite (Sun and McDonough, 1989). The composition of SN phlogopite picrites is shown for comparison. Adapted from Grasso (2010).

8. Tapira Complex

Tapira, located at coordinates 19º53'S; 46º50'W, is the southernmost of the APIP alkaline-carbonatite complexes, placed approximately 30 km southeast of Araxá city, Minas Gerais State. It intrudes Late proterozoic metasedimentary rocks of the Brasília Belt (Canastra Group), which are deformed into a dome structure, as well as slightly fenitized. This complex has elliptical settings and has a 8 km diameter, being approximately 35 km^2 in area (Fig. 16). It consists dominantly of bebedourite, with subordinate serpentinized dunite, carbonatite, syenite, melilitolite (uncompahgrite), ultramafic potassic dikes, and metasomatic phlogopitite (Brod et al., 2013). Ultramafic rocks from the bebedouritic series are commonly in contact with the fenitized country rock and are cross cut by smaller carbonatite and late stage syenite bodies, generally concentrated in the center of the complex. For Tapira rocks, K/Ar dating of mica yielded ages of 85.6 and 87.2 Ma (Sonoki & Garda, 1988).

Along with the other complexes, Tapira constitutes a multi-intrusion and multiphasic body with a unique and complicated evolution story. For this matter, Brod et al. (2013) present data to propose Tapira's petrogenesis is linked to a phlogopite picrite parental magma and, again, fractional crystallization and liquid immiscibility are pointed to play important roles in the complex formation and mineralization.

Tapira bears meaningful deposits of phosphate, titanium, niobium, REE and vermiculite, all formed by residual concentration in the weathering mantle. Currently, the North American Mosaic Fertilizers Company explores phosphate in the region.

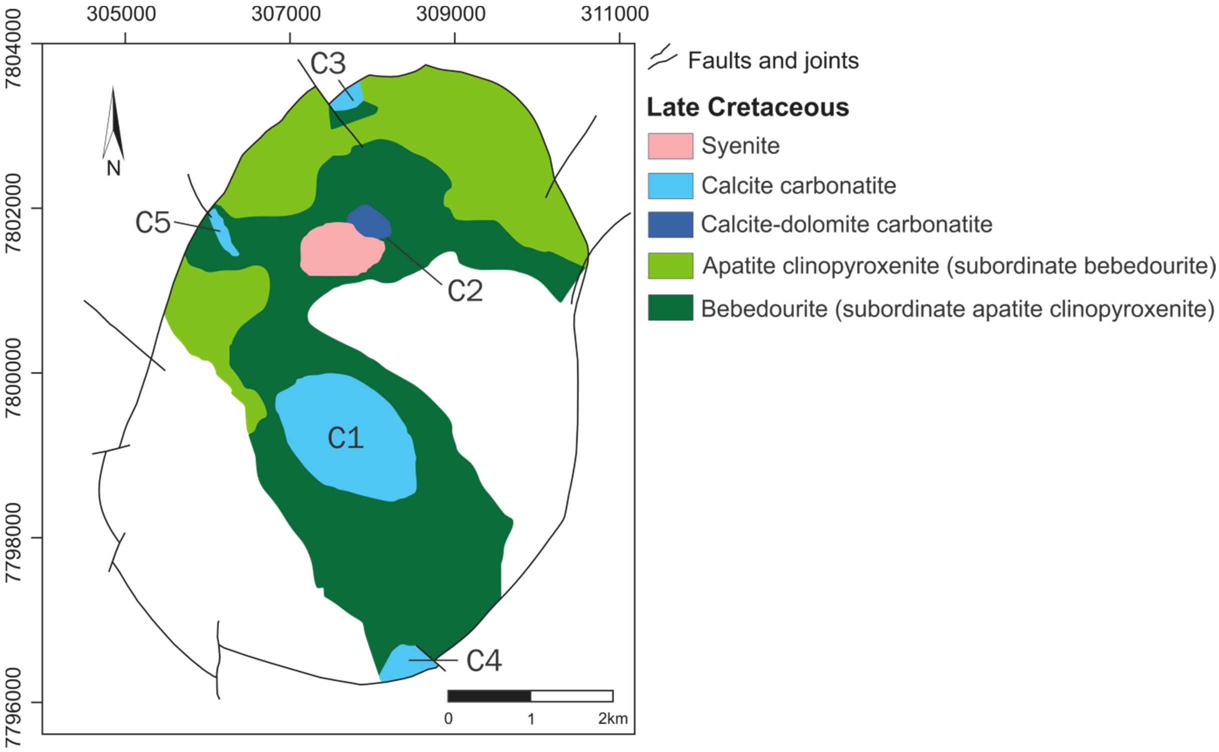

Fig. 16 - Geological sketch from Tapira Complex. After Brod et al. (2013).

8.1 Petrography

8.1.1 Bebedourite Series

Several authors described dunites, wehrlites, bebedourites and syenites from Tapira Complex as part of so called Silicate Plutonic Series (SPS), rather than a "bebedourite-series" (Brod, 1999; Brod et al., 2005; Brod et al. 2013; Eberhardt, 2014). For nomenclature proposes only, in this work the series will be referred as "bebedourite-series". Nevertheless, the ultramafic rocks present in this silicatic series consist dominantly of bebedourites that can be sub-divided into the B1 and B2 units. Because of their restricted occurrence, dunites, wehrlites, and modal variations in the proportions of perovskite, magnetite and/or apatite, once reported by Brod (1999) as part of B1, were latter reclassified and are now preferably not individualized within B1 and B2, besides also not representable at map scale (Fig. 16; Brod et al., 2013).

It is noteworthy that modal variations in bebedourites of Tapira may produce facies rich in olivine (dunites, wehrlites), perovskite-magnetite or apatite. Whilst this is primarily the result of magmatic layering, some of the apatite- or perovskite-magnetite-rich rocks may occur as discordant bodies. Such features indicate the remobilization of pockets of crystal-mush and, together with the lack of fenitization effects in country rocks, may indicate that the intrusion was partially consolidated during emplacement (Brod et al., 2013).

B1 bebedourites

The bebedourites from B1 unit comprise clinopyroxene-rich rocks containing essential perovskite, apatite, phlogopite and opaque minerals. Melanite (Ti-garnet) and carbonate can occur as accessory phases, while olive and Cr-magnetite are absent in the bebedourites lithotype. These rocks are medium- to corse-grained, locally pegmatitic, with the possibility of strongly orientated fabric. Modal variations can produce facies rich in olivine (dunites, wehrlites), perovskite-magnetite or apatite related to these rocks (Brod, 1999; Brod et al., 2005; Brod et al., 2013). Apatite occurs in small prismatic rounded grains, as solitary crystals or inclusions. Perovskite is euhedral to subhedral. Ti-Garnet may be present as rare discrete crystals or, more typically, forming rims in perovskite crystals. Clinopyroxene (diopside) usually occurs as coarse-grained prismatic crystals. Phlogopite forms large anhedral crystals with diopside, apatite, perovskite and melanite inclusions (Brod, 1999).

B2 bebedourites

Bebedourites of B2 unit are usually finer-grained and have higher pyroxene content than those of B1. Apaptite, perovskite, melanite and titanite are subordinate phases (Brod, 1999; Brod et al., 2005). B2 unit rocks typically formed under higher SiO_2 activity than B1, which is supported by: a) the presence of primary Ti-garnet (melanite) and titanite in B2 wehrlites and bebedourites; b) absence or very low modal content of perovskite; c) disequilibrium features of the existing perovskite, which is invariably replaced by Ti-rich silicate minerals, d) intercumulus K-feldspar in the B2 most evolved, perovskite-free bebedourites (Brod et al., 2005).

Syenites

Syenites occur as small independent intrusions or as fragments in carbonatite-syenite breccias. Besides K-feldspar, they may contain significant phlogopite and/or aegerine, zircon and titanite as accessory phases. Carbonate globules and irregular patches are locally present, indicating the coexistence with immiscible carbonatite liquid (Brod et al., 2013).

8.1.2 Carbonatite Series

Several carbonatite bodies intrude, brecciate and metasomatize the silicatic rocks from the bebedouritic series. They have been sub-divided (Brod, 1999; Brod et al., 2005) into five units (C1 to C5) according to location and petrographic or compositional features (Fig. 16). Carbonatite bodies from Tapira can display different geometries, ranging from massive carbonatite plugs through dikes to even small veinlets. (Brod et al., 2013).

As seen in all APIP complexes, carbonatite intrusion in the ultramafic rocks often results in the development of a metasomatic phlogopitite. Brecciation of silicate rocks due to carbonatite intrusion is also a common feature. In the northwest portion of the complex, C2 carbonatites intrude both the B1 bebedourites and the syenites. In the Tapira mine area, a more explosive style of C2 carbonatite intrusion resulted in the local development of small diatremes filled with polymitic breccias, containing angular blocks of several petrographic varieties of bebedourite-series rocks, in addition to less frequent xenoliths of county rock (Brod et al., 2013).

In addition, some fine-grained carbonatite dikes may contain silicate globules, indicating coexistence with immiscible silicate magmas. In the five sub-units, three compositional variaties of carbonatite were recognized: C1, C3 and C4 bodies correspond to calciocarbonatites, whereas dolomite-bearing calciocarbonatites can occur in C1 and C2. C5 is represented by magnesiocarbonatites. Calciocarbonatites and dolomite-bearing calciocarbonatites occur as massive bodies and dikes, while magnesiocarbonaties corresponds to a dike swarm C5 area (Fig. 16) and also as late-stage dikes and veinlets scattered throughout the complex. Main accessory phases in these rocks are pyrochlore (in calciocarbonatites and dolomite calciocarbonatites), apatite, phlogopite, magnetite, pyrite and barite (Brod et al., 2013)

8.1.3 Ultramafic dikes

Numerous ultramafic dikes cross-cut Tapira's rocks. They are usually a few centimetres or decameters thick, rarely exceeding 1 m thick. They are often porphyritic, containing euhedral olivine (less frequently phlogopite, apatite, clinopyroxene or perovskite) phenocrysts set in a carbonate- and phlogopite-rich fine-grained to aphanitic groundmass with subordinate apatite and magnetite (Brod et al., 2013). Brod et al. (2013) refer to these dikes as phlogopite picrites, based on their high olivine and phlogopite contents and consequently very high MgO values (up to 21 wt. %). Flow textures are marked by the orientation of olivine and phlogopite phenocrysts as well as of groundmass phlogopite. Globules or irregularly-shaped pockets of carbonate in the phlogopite picrites have been observed and may suggest the onset of liquid immiscibility at a very early stage during the petrological evolution of the Tapira complex (Brod et al., 2013).

Another type of ultramafic dike occurs at Tapira. This one corresponds to bebedouritic dikes, with very fine-grained character and emplacement in fractures. Bebedouritic dikes contain rare phenocrysts of phlogopite, clinopyroxene, and/or apatite, set in a groundmass of the same mineral phases in addition to magnetite and carbonate. They are characterized by the absence of olivine and chromite, and interpreted as a more evolved counterpart of the phlogopite picrites. Immiscible carbonate globules or irregular patches are again locally present (Brod et al., 2013).

8.2 Mineral chemistry

8.2.1 Olivine

Present in dunites, wehrlites and phlogopite picrites, olivine from Tapira has forsterite contents that vary from 84.2 to 86.9 mol % in wehrlites and 81.6 to 89.8 mol % in phlogopite picrites (Brod, 1999). Data from Brod (1999) suggest that in olivines from phlogopite picrites the forsterite contents are the range of mantle olivines and that they crystallized in equilibrium with a liquid that is compositionally equivalent to Tapira phlogopite picrite dikes. Clearly, wehrlite's olivines cannot be interpreted in the same way, since these rocks are cumulates and therefore do not represent magmatic liquids. However, their high forsterite contents still suggest that they crystalized in equilibrium with a primitive ultramafic liquid (Brod, 1999).

8.2.2 Phlogopite

Primary phlogopites from carbonatites and silicate rocks in Tapira seem to evolve independently and follow divergent trends. In the silicate plutonic rocks (bebedourite-series), mica evolves from high-Mg phlogopite in the least differentiated wehrlites to biotite in the more evolved syenites. This variation follows a continuous trend of Fe decreasing and Mg increasing. Ti and Mn also increase with differentiation (Brod, 1999).

Regarding phlogopite picrite and bebedourite dykes, phlogopites from the two types of dykes have generally low Cr_2O_3. Apparently, Cr_2O_3 decreases from core to rim, following a Cr depletion trend (Brod, 1999).

In carbonatites, tetra-ferriphlogopite is a more important member and, summarizing, the only micas with clear textural evidence for magmatic crystallization from a carbonatite magma are the euhedral, zoned crystals of tetra-ferriphlogopite in C1 carbonatite. Meanwhile, tetra-ferriphlogopite in silicate rocks is interpreted as a product of metasomatism (Brod, 1999).

8.2.3 Perovskite

It also occurs in the phlogopite picrite dykes and, rarely, in carbonatites. Perovskite is the main primary Ti mineral in this complex and an important host for the REE in the ultramafic cumulate rocks, having a major effect on the distribution of Ti and REE during magma evolution. In wehrlites and bebedourites perovskite occurs as a cumulus phase, accompanying olivine and clinopyroxene. In the phlogopite picrite dykes it may be present as rare phenocrysts, discrete crystals in the groundmass or rings of discrete grains coating olivine phenocrysts (Brod, 1999).

8.2.4 Magnetite

Besides magnetites, chromite and ilmenite also occur in Tapira, like in other APIP complexes (e.g. Traversa et al., 2001). An increase in the Fe/(Fe+Mg) ratio with progression of differentiation can be observed in the Tapira Complex. Similarly, minor element contents of Tapira magnetites are also consistent with magmatic evolution of the host rock. Thus, magnetites from phlogopite picrites have the highest TiO_2, Al_2O_3, MnO and MgO, whilst magnetites in the more evolved silicate rocks and carbonatites become progressively poorer in all minor elements (Brod, 1999).

8.2.5 Carbonates

Tapira's early calcite typically consists of crystals with a clear appearance, and contains significantly high amounts of SrO and MgO. These carbonates can show a consistent chemical progression towards purer $CaCO_3$ from C1 to C5. All trace-elements decrease in this direction, but Fe and Mn increase in C5 (late-stage dykes and veins). Summarizing, C1 can be interpreted as the earliest and C5 as the latest carbonatite intrusion, at least based on calcite chemistry (Brod, 1999).

8.2.6 Apatite

Tapira apatites have a considerable variable composition, but generally, a trend to Sr enrichment has been observed according to magmatic evolution, in both silicate and carbonatite series of rocks (Eberhardt, 2014).

8.3 Whole-rock Chemistry

8.3.1 Major Elements

Tapira phlogopite picrite dikes are extremely silica undersaturated, CO_2 carbonate-rich and strongly potassic. They also present high TiO_2, and typically low Al_2O_3. The high MgO contents positively correlate with high Cr and Ni, evidencing their unevolved character. Meanwhile, the bebedourite dikes comprise rocks mineralogically more evolved than the phlogopite picrites and can be distinguished from phlogopite picrites by their lower MgO contents. Bebedourite's chemical composition is more variable than that of phlogopite picrites, and it is possible that rocks within this group had more than one origin or evolved along different paths (Brod et al., 2013).

Similar patterns can be observed within the Bebedourite units (B1 and B2). In terms of major elements, B1 bebedourites have higher TiO_2 and tend to have slightly higher MgO, while bebedourites from B2 have higher SiO_2 values and MnO and tend to a lesser extent of CaO (Brod et al., 2013).

Except for some dikes and breccias associated with the C2 unit, all other carbonatites are expected to have less than 10 wt. % SiO_2, and the majority of samples have less than 5 wt. % SiO_2 and the concentrations of TiO_2 and Al_2O_3 are usually below 1 wt. %. MgO are also usually below 10 wt. % (Brod et al., 2013).

8.3.2 REE and other trace elements

As mentioned before, the high Cr (134 – 1012 ppm) and Ni (82 – 932 ppm) contents in phlogopite picrites are consistent with the ultramafic character of these rocks, suggesting that the least evolved members of the phlogopite picrite series can be considered as mantle-derived primary magmas. They also show enrichment of LREE relatively to the HREE, reflected into the chondrite-normalized patterns (Fig. 17; Brod et al., 2013).

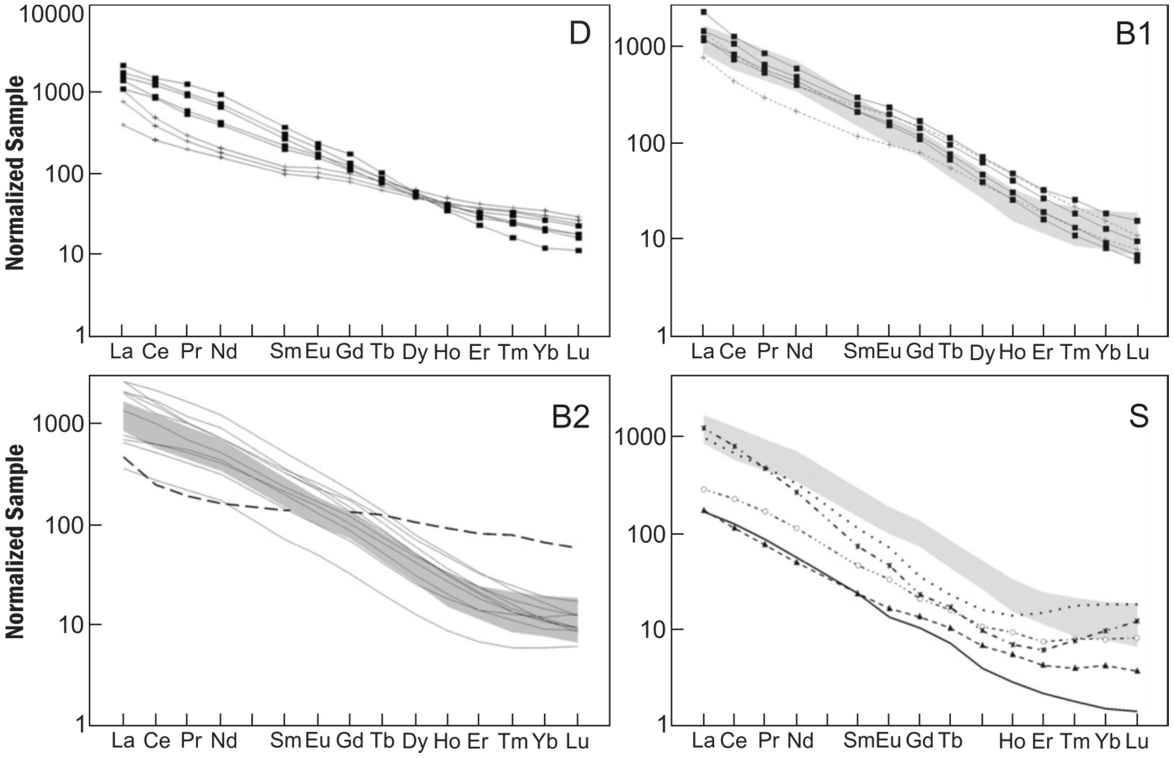

Fig. 17 - REE chondrite normalized patterns for Tapira rocks. D – Bebedourite dikes; B1 – Bebedourite from B1 unit; B2 – Bebedourite from B2 unit. Dashed line represents a high-Zr and low-Th bebedourite sample; S – Syenite. Normalization factors from Boynton (1984). Adapted from Brod et al., 2013.

Trace elements and REE patterns for bebedourite dikes show a good approximation to the phlogopite picrites patterns. However, in a group of samples, trace-elements depart significantly from the primitive pattern. The first group produces normalized REE patterns that are parallel to those of phlogopite picrites, whereas the anomalous bebedouritic dikes' REE patterns "cross over" those of the first group at Dy (Fig 17), these two groups of bebedourite dikes have contrasting REE behaviour. It is clear from these features that, although the phlogopite picrites may evolve to the bebedouritic dikes through crystal fractionation, the latter group encompasses rocks with more than one origin, or which underwent distinct differentiation processes (Brod et al., 2013).

Regarding the REE patterns for B1 and B2 bebedourites (Fig . 17), most B2 bebedourites have chondrite-normalized $La_{(N)}/Lu_{(N)}$ ratios similar to those of the phlogopite picrites. A few samples of B2 bebedourite present a REE crossover pattern that resembles that of some of the bebedouritic dikes (Brod et al., 2013).

In Tapira Syenites it is noteworthy the relatively low total sum of REE and the variable Nb/Ta ratios when compared with those of the phlogopite picrites, what can be seen from chondrite-normalized REE diagrams (Fig 17; Brod et al., 2013).

9. Ore body geometry

In order to better understand ore body geometries of APIP complexes, primary (fresh-rock or hypogene) and secondary (supergenic) ores need to be treated separately since they require such distinctive mining and ore processing techniques. Hypogene ores usually present themselves as vertical envelopes, as in Catalão I and II niobium deposits (Cordeiro, 2009; Palmieri, 2011). Supergene deposits occur as horizontal sheets of residually concentrated ore minerals in all of APIP complexes.

9.1 Vertical ore bodies

Catalão I and II are the best understood examples of carbonatite-related orebody geometries in the APIP. The Catalão I complex intruded quartzites and schists of the Late Proterozoic Araxá Group as a vertical pipe with a diameter of nearly 6 km at surface, creating a dome like structure (Cordeiro, 2011a). As mentioned before, the complex can be divided into an outer zone dominated by phlogopitite and an inner zone composed mostly of dolomite carbonatites and phoscorite-series rocks. In other words, the inner zone is therefore composed of magnetite-apatite-rich rocks and with carbonatites, bearing important niobium deposits associated to pyrochlore. Following this path and intending to better characterize Catalão I fresh rock ore, the deposit has been divided into Mine II and East Area ore bodies (Fig. 18; Cordeiro et. al, 2011a).

According to the mentioned authors, Mine II is a roughly oval, pipe-like phoscoritic body, 200 m long and 100 m wide, hosted mainly by dolomite carbonatite. Meanwhile, the East Area is an L-shaped ore body, 400 m long, 200 m wide, hosted by phlogopitite. Both ore bodies are open at depth and deep drilling confirmed their extension at until a depth of at least 800 m. East Area and Mine II ore bodies have a general pipe-like geometry but, despite their shape, the ore bodies do not represent single, homogeneous pyrochlore-bearing phoscorite, but rather dike swarms up to 2 m wide and plugs up to 10 m wide (Cordeiro et al., 2011a).

Besides pyrochlore modal content, ore grades are also controlled by frequency and width of nelsonite dikes and can be broadly reduced by barren wall rocks (Cordeiro et al., 2011a). The nelsonites P2 and P3 described by Cordeiro et al. (2010; 2011a,b) represent the bulk of the fresh rock niobium mineralization in the complex. According to Cordeiro et al. (2011a), this nelsonites can be distinguished

from early-stage phoscorites by a) emplacement as dikes and small plugs; b) occurrence of internal pockets of dolomite carbonatite; c) no visible evidence of carbohydrothermal alteration; d) absence of olivine; e) abundant pyrochlore, reaching up to 50 vol.% in some samples.

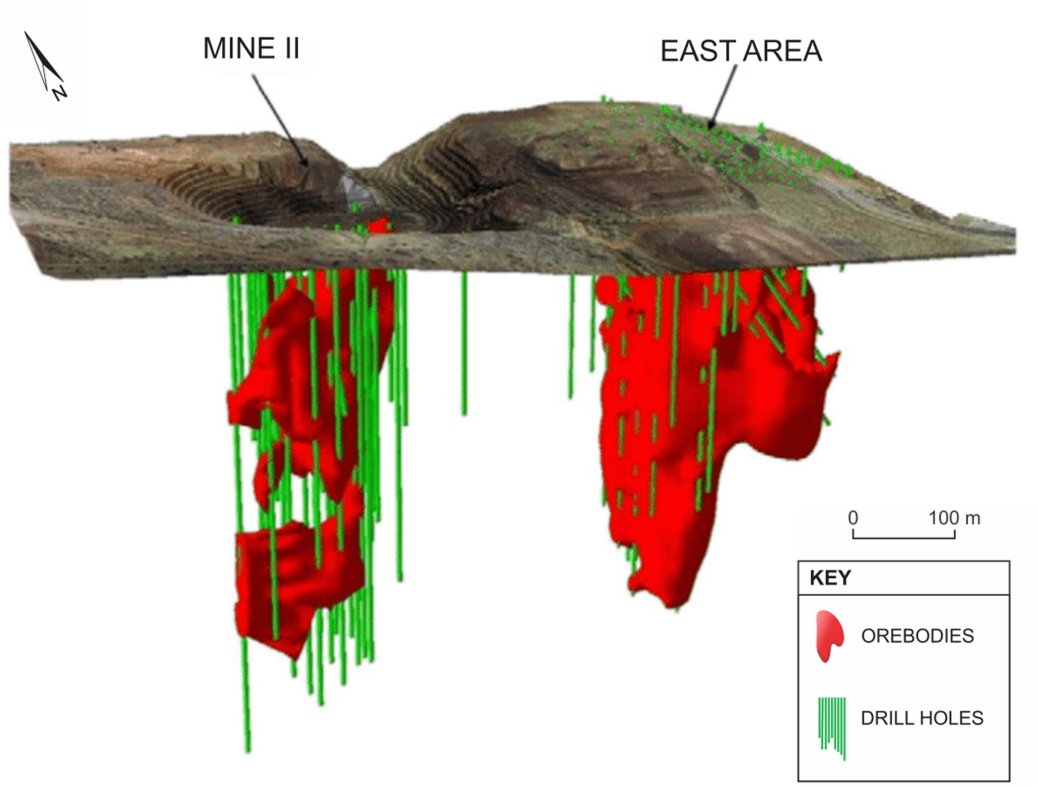

Fig. 18 - Combination of an Ikonos image showing the roughly circular Mine II open pit and a 3-D model of the Mine II and East Area orebodies. Modified from Cordeiro et al. (2011a).

Besides pyrochlore modal content, ore grades are also controlled by frequency and width of nelsonite dikes and can be broadly reduced by barren wall rocks (Cordeiro et al., 2011a). The nelsonites P2 and P3 described by Cordeiro et al. (2010; 2011a,b) represent the bulk of the fresh rock niobium mineralization in the complex. According to Cordeiro et al. (2011a), this nelsonites can be distinguished from early-stage phoscorites by a) emplacement as dikes and small plugs; b) occurrence of internal pockets of dolomite carbonatite; c) no visible evidence of carbohydrothermal alteration; d) absence of olivine; e) abundant pyrochlore, reaching up to 50 vol.% in some samples.

Dolomite carbonatite is abundant, but up to 15 m wide plugs and up to 2 m wide dikes of calcite carbonatite occur. Carbonatites, particularly dolomite carbonatites, dikes and plugs are widespread in Catalão I and are especially abundant within P1, in which metasomatic alteration by carbohydrothermal fluids can be noticed trough widespread transformation of olive to tetra-ferriphlogopite. Nelsonites do not present signs of metasomatic alteration, but are intimately related to phoscoritic-series DC, which may occur within P2 and P3 as centimetric to metric pockets as well as dikes and plugs. DC can be easily discriminated from earlier generations of dolomite carbonatites by the absence of olivine and presence of pyrochlore and ilmenite (Cordeiro et al., 2010; 2011a,b). The relationship between different rocks in Catalão I is showed in Fig. 19.

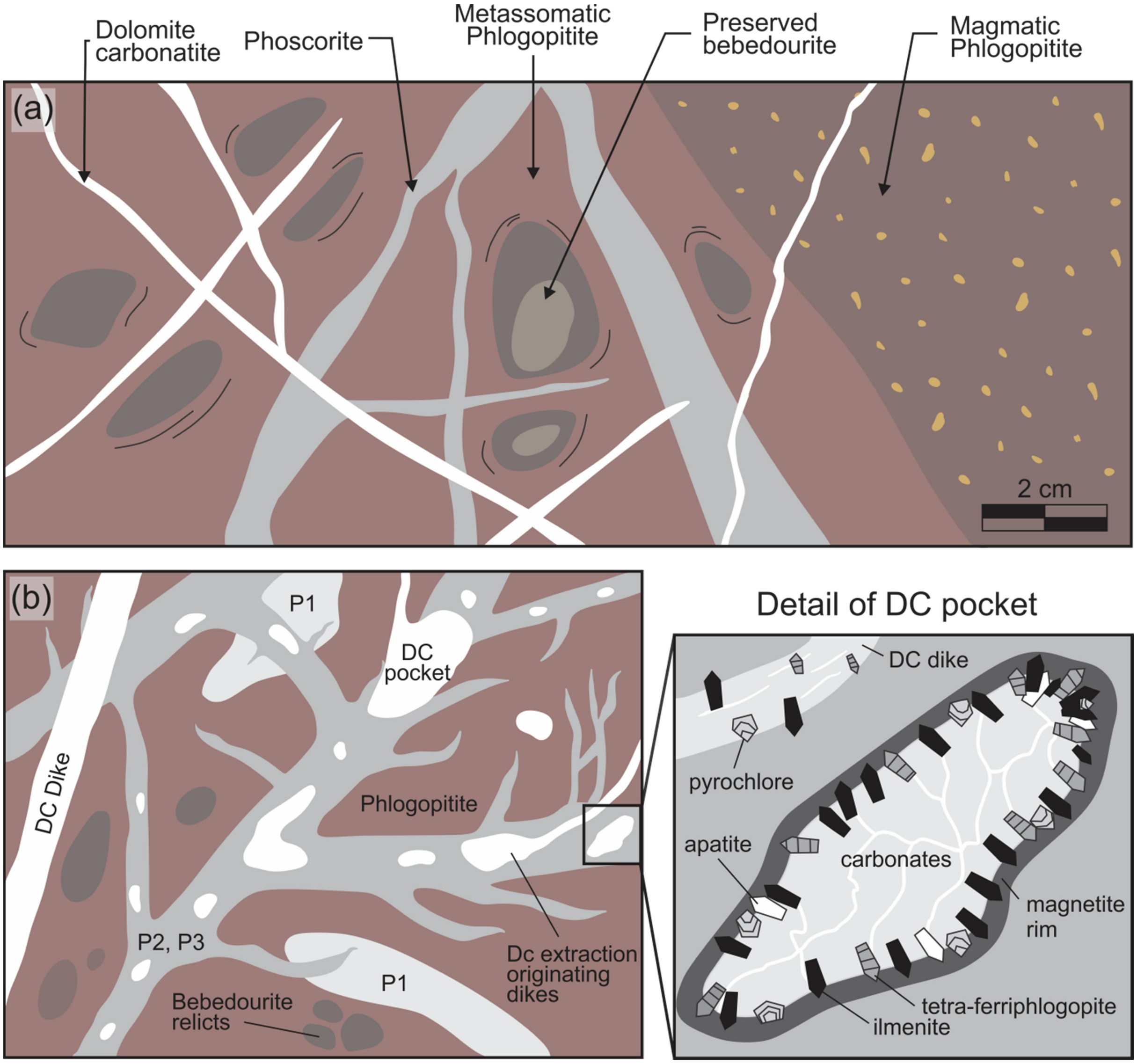

Fig. 19 - Schemes representing the relationship between different intrusion phases in Catalão I. (a) Sketch based on a picture by Ribeiro (2008), showing the interaction between magmatic phlogopitites, metasomatic phlogopitites, phoscorite and dolomite carbonatite. Notice the preserved bebedourite cores within metasomatic phlogopitite; (b) Schematic model of the fresh rock niobium ore, where apatite nelsonite P2, magnetite nelsonite P3, and dolomite carbonatite DC crosscut phlogopitite. The detail shows the common textural feature of DC pockets, demonstrating how crystals are often perpendicular to the walls, growing toward the center of DC pockets. Adapted from Cordeiro et al. (2011a).

Regarding Catalão II, the primary mineralization is formed mainly by nelsonite and carbonatite, with the occurrence of subordinate phoscorite, pyroxenite, phlogopite picrite, syenite, metasomatic phlogopitite and fenite (Rocha et al., 2001; Palmieri, 2011; Guarino 2016). For modeling purposes, Palmieri (2011) has divided the Morro do Padre Niobium ore in Catalão II into three distinct sections: 1) an Upper Zone, that is relatively thin (up to 80m); 2) an Intermediate Zone, extending to an average depth of 460 m; and 3) a Lower Zone that has between 460 and 600 m, on average (Fig. 20).

The Catalão II intermediate zone is an important example of vertical pipe-like ore body. Here, the fresh rock is represented by nelsonites and carbonatites, with minor phlogopite picrite, and rare pyroxenite, intruding and fenitizing phyllites and amphibolites. All igneous lithotypes in this zone occur as dike swarms and the dikes are usually a few centimeters thick. This feature is consistent with the very low viscosity expected for these magmas, particularly carbonatitic and nelsonitic ones (e.g. Treiman, 1989; Dobson et al., 1996). Because of the extremely low-SiO_2, these liquids are incapable of forcing their intrusion and forming large massive igneous bodies. Instead, they show a rather "runny" behavior, seeping through existing weak zones such as fractures (Palmieri, 2011).

Regarding other complexes, in Araxá the pyrochlore is frequently associated to phoscorite series rocks. Of all studied lithotypes, phoscorites from the center of the complex, similarly to Catalão I, have shown the highest concentrations of Nb (Issa Filho, 1984), therefore corresponding to an important facies of primary ore. This facies consist in brecciated fine to coarse-grained dike-like intrusions. Carbonatite and phoscorite series rocks are often described as centimetric to metric-thickness transgressive intrusions and all APIP complexes, including Salitre, Serra Negra and Tapira. For this reason, we believe that, like Catalão I and II, Araxá, Salitre, Serra Negra and Tapira ore bodies might also correspond to heterogeneous pipe-like oval bodies, composed of swarms of dike-like structures.

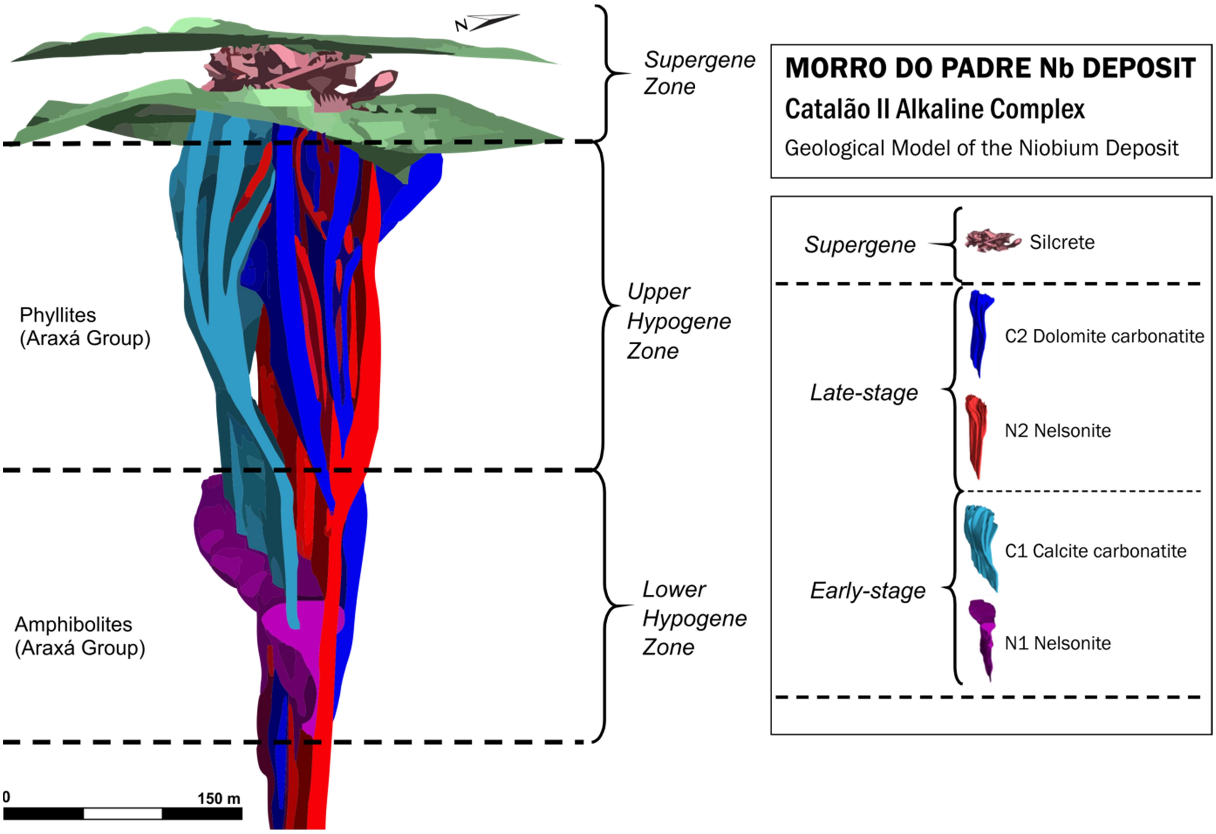

Fig. 20 - Modeled ore envelope and the limits between the Upper, Intermediate and Lowerzones. Adapted from Palmieri (2011).

9.2 Horizontal ore bodies

9.2.1 Fresh-rock ore

Catalão II Lower zone (on the other words, the deepest zone; Fig.20), is located between 460 and 600m and is dominated by several sets of rhythmic layers of apatite-nelsonite, pegmatoidal nelsonite, and carbonatite, interpreted as the result of the infilling of a small chamber or sill underneath the deposit, also to be described as horizontal ore bodies. Composed mainly by N1 and N2 nelsonites and carbonatites and despite the fact that the zone was reached by a single exploratory drilling in Palmieri's (2011) research and its lateral extension remains to be determined, it is believed that this zone represents a region where N1-type nelsonite magmas ponded and underwent several stages of differentiation and recharge, this way producing horizontal cyclic units. Although these rocks are intruded by many dikes of magnesiocarbonatite and N2-type nelsonite, their original horizontal layered units are still recognizable (Palmieri, 2011).

9.2.2 Supergene ore

In Catalão II upper mineralization zone, weathering is responsible for the leaching of soluble components of more susceptible minerals, such as carbonates and mica. This results in the residual enrichment of weather-resistant phases, like apatite, pyrochlore and monazite. Besides increasing the ore grade, this process also provides a certain homogenization of the ore, a feature that quickly disappears towards the primary (fresh-rock) mineralization (Palmieri, 2011).

As shown by figure 21, it is notable that silcrete lenses coincide with the presence of nelsonite-rich zones underneath the soil cover. The silcretes occurring in this setting may be very rich in Nb_2O_5, but their mechanical characteristics represent severe difficulties for the ore processing, in contrast with the softer and easier-mining ores above and below silcrete levels. Also note the irregular shape of the limit between the soil and fresh rock. Notice that where silcretes are not present, this limit is considerably lower over the carbonatite- and nelsonite-rich zones than in the adjacent areas, suggesting that these particular rock-types are more easily weathered than the others (Palmieri, 2011).

From top to bottom, the Upper Zone is divided into a clay-rich section (kalonite-oxide ore), up to ca. 40m deep, followed by a micaceous ore, from ca. 40m to ca. 90m. Silcretes are mostly confined to the limit between these two domains, extending further down into de micaceous ore, besides a second silcrete level that occurs between 70 and 76 m (Palmieri, 2011).

The upper, kaolinite-oxide ore is composed kaolinite, oxides and hydroxides (goethite, hematite, ilmenite, magnetite), various secondary phosphates of Al, Ca, Ba (more rarely of REE and Th), and pyrochlore. The hallmark of this zone is the absence of apatite, phlogopite, vermiculite and interstratified phylossilicates. Similarly to other APIP complexes (Araxá, Catalão I), this part of the soil profile in Catalão II is barren for phosphate ore, but still a viable niobium ore, as pyrochlore persists even in the extreme weathering conditions (Palmieri, 2011).

Otherwise, the micaceous ore is characterized, according to Palmieri (2011), by the presence phlogopite, vermiculite, apatite, magnetite, ilmenite, quartz, carbonate and pyrochlore. This horizon is also marked by the partial destruction of phlogopite, which is converted into an interstratified phyllosilicate. Carbonate is limited to the lower parts of the micaceous ore, adjacent to the fresh rock, and its presence defines the "altered rock" level. Within this ore, the Ba-pyrochlore is more homogeneous, although still compositionally variable, and shows the preservation of variable amounts of remnant Ca from the primary Ca-Pyrochlore (Palmieri, 2011).

The concentration of silcrete levels above the nelsonitic ore body comes from the idea that nelsonites constitute a preferred channel for groundwater percolation, resulting in faster and more effective weathering than in the other rocks and that groundwater enriched in dissolved silica from the break-up of micas and other minerals in the kaolinite-oxide ore section is then able to percolate the weathered nelsonite and precipitate its silica content at the top of the water-saturated zone

(Palmieri, 2011). The silcrete ore is therefore composed by quartz, magnetite, ilmenite, crandallite-group, REE phosphates, goethite, phlogopite, barite, and Ba-pyrochlore (Palmieri, 2011).

Similar layered horizons are present in other APIP complexes, like Catalão I and Araxá, corresponding to phosphate ore bodies. The phosphate is concentrated in apatite grains and tends to reach higher contents within the micaceous ores. In Araxá, for instance, P_2O_5 content can go from nearly from 6% in the alterated rock to over 15% in the top of the micaceous ore bed.

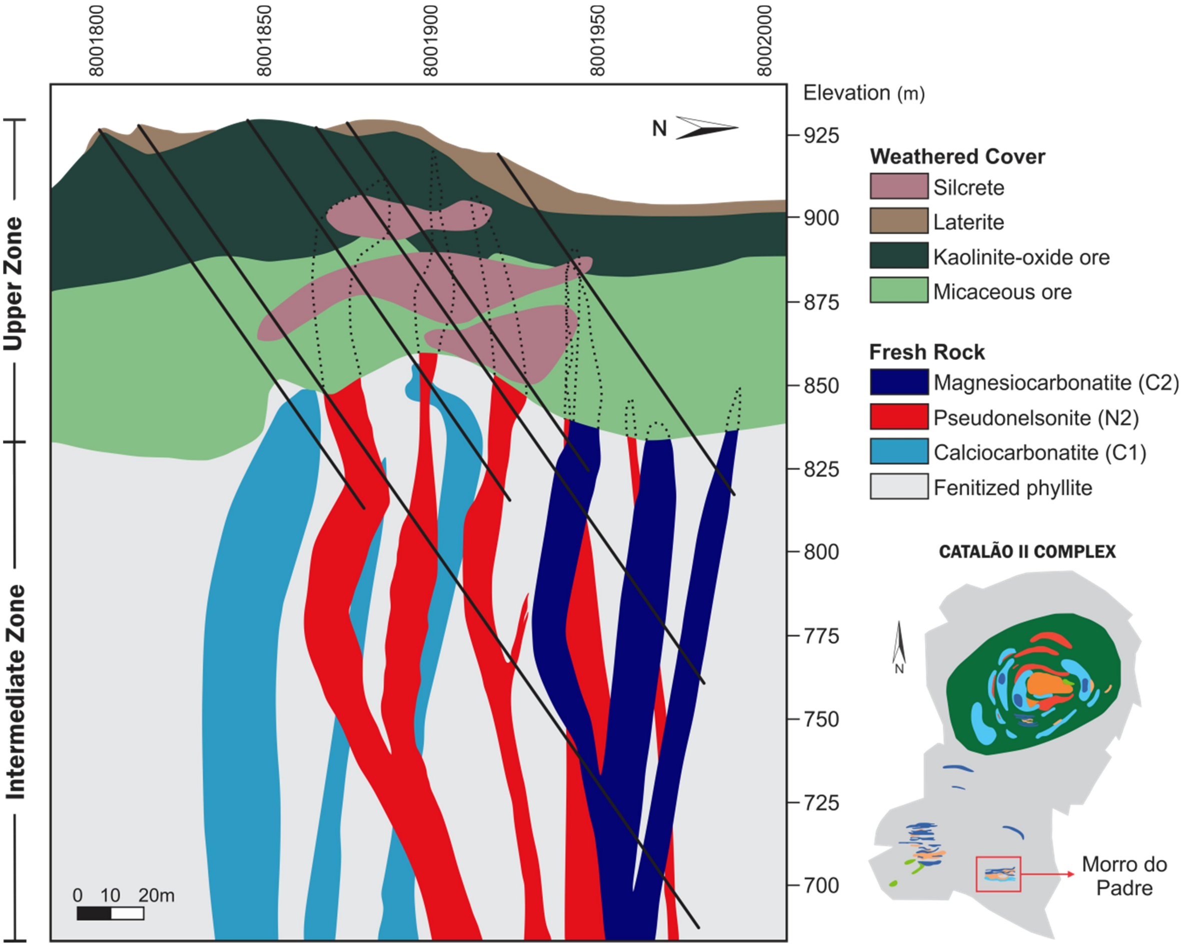

Fig. 21 - Geological section showing the model for ore types distribution in the Upper and Itermediate Zones of the Morro do Padre deposit, in Catalão II. Adapted from Palmieri (2011).

10. Considerations about REE mineralization

Despite the abundance of rare earth elements-bearing carbonatites, REEs have been produced from just a few deposits, like the Mountain Pass, United States, and the Bayan Obo, China. These elements are of special interest to the global economic settings and are essential for a wide range of applications, since they are part of the production of popular technology such as smartphones, batteries and LCD displays, getting even to catalytic converters and wind turbines (Neumann & Medeiros, 2015).

In an experimental study surrounding REE partitioning between immiscible carbonate and silicate liquids and CO_2 vapor, Wendlant & Harrison (1979) reached the conclusion that the vapor phase is enriched in light REE relative to both carbonate and silicate melts at 20 kbar and enriched in all REE, especially the light elements, at 5 kbar. From this results emerges the propose that mantle metasomatism by a CO_2-rich vapor enriched in light REE, occurring as a precursor to magma genesis, might explain the enhanced REE contents and light REE enrichment of carbonatites, alkali-rich silicate melts, and kimberlites. The APIP alkaline-complexes follow that pattern, as demonstrated, being LREE enriched and HREE depleted.

Regarding ore-minerals, the main mineral phases carrying REE are monazite, apatite and, eventually, perovskite. Perovskites from Tapira bebedourites concentrate REE, but cannot be exploited due to lack of appropriate metallurgy. Neumann & Medeiros (2015) have indeed produced a study of mineralogical and technological characterization in the Araxá complex, where REE are predominantly carried by monazite (over 70%), and pointed out that considering the large REE reserves (6.37 Mt proved, and additional 21.94 Mt inferred), its 6.8% TREE grade and the already available infrastructure, Araxá certainly is a very interesting prospect for REE-bearing minerals.

11. Considerations about Niobium mineralization

Most commercial niobium in the world is from carbonatite-related sources. Although there are several carbonatite-related niobium deposits worldwide, comprising residual and/or fresh rock resources, only the Boa Vista (Catalão II), CBMM (Araxá) and Niobec (Saint Honoré) deposits are currently in production (Cordeiro et al., 2011a). However, Brazilian supergene deposits account for about 92% of the total worldwide production of Nb, with the primary St. Honoré carbonatite and other sources accounting for only for 7 and 1%, respectively (Mitchell, 2015).

Experimental data presented by Mitchell & Kjarsgaard (2004) for the solubility of $NaNbO_3$ in the ternary system calcite–fluorite–lueshite (a kind of perovskite), or $CaCO_3$–CaF_2–$NaNbO_3$, over the temperature range 500 – 1,000ºC at 0.1 GPa pressure, show that in fluorine-bearing anhydrous system, pyrochlore is the principal Nb-hosting supra-solidus phase, in contrast to fluorine-free hydrous melts from which perovskite-structured compounds crystallize and bear Nb. This way, Mitchell & Kjarsgaard (2004) conclude that the crystallization of pyrochlore and/or perovskite-structured compounds from simple carbonatite liquids is thus considered to be dependent upon the F/OH ratio of the melt. In comparison, APIP petrographic and mineralogical data demonstrate that pyrochlore is the main Nb-bearing phase, as expected, generating Nb-ores.

The early precipitation of pyrochlore, as suggested by Mitchell & Kjarsgaard (2004) experiments, also indicates that in natural systems pyrochlore can be concentrated by differentiation processes. Therefore, economic deposits of Nb-pyrochlore might result from the rheological or gravitational concentration of this mineral. Further, accumulations of pyrochlore in magma chambers can also be redistributed by the introduction of subsequent batches of carbonatite magma (Mitchell & Kjarsgaard, 2004). Such processes, coupled with mixing of pyrochlore derived from each of these different magmas, would lead to the co-existence of diverse compositional varieties of pyrochlore at the scale of a hand sample, as observed in many carbonatites e.g. the Bond Zone, Niocan and St. Lawrence Nb-occurrences at Oka and Prairie Lake calcite carbonatites (Zurevinski & Mitchell 2004). However, in APIP, no divergent pyrochlore varieties have been identified.

12. Ore formation processes

Multiple ore formation processes occurred in the APIP carbonatite complexes to generate its current mineral deposits. These processes can be divided into: a) Magmatic; b) Metasomatic; c) Supergene.

12.1 Magmatic Processes

Dike-like geometry, abrupt contacts and textural aspects, along with isotopic data indicating a mantle-like composition for phoscorites and carbonatites in APIP (e.g. Barbosa, 2009; Cordeiro et al., 2011b), correspond to strong evidence for the igneous origin of these rocks. At the same time, geochemical information shows that carbonatites/phoscorites and silicate rocks seem to evolve independently and follow divergent trends. This becomes evident when considered that in the silicate rocks of APIP complexes, mica evolves from high-Mg phlogopite in the least differentiated rocks to biotite in the more evolved syenites (Brod et al, 2001), but the same Mg-Fe substitution trend cannot be interpreted on the same premise in carbonatites and phoscorites, where tetra-ferriphlogopite tends to predominate. In a different way, the evolution of phoscorite series in Catalão I is evidenced based on Ca-Sr substitution and consequent Sr enrichment observed in apatite crystals (Cordeiro et al., 2010). The clear decrease in Ca and increase in Sr are also true for the Kola Province complexes in Russia (Karchevsky & Moutte, 2004; Krasnova et al., 2004b; Lee et al., 2004), suggesting that Sr content in apatite is a reliable index of magma evolution in the carbonatite and phoscorite series (Cordeiro et al., 2010). Comparing element patterns, several authors not only attribute a mantle-linked origin to APIP rocks series, but also propose that the parental magma to generate silicate-carbonatite-phosphate liquids would correspond to the phlogopite picrite composition (e.g. Brod, 1999; Ribeiro, 2008; Barbosa, 2009; Cordeiro, 2009; Brod et al., 2013; and others).

Previous studies have argued that the petrogenesis of phoscorite involves assimilation-fractional-crystallization (AFC) and/or liquid immiscibility (Krasnova et al. 2004a), and the same can be applied to the other rock series within APIP complexes. Summarizing, phoscorites may be generated trough liquid immiscibility processes or accumulation of olivine, apatite and magnetite from a carbonatite or silicate magma. However, the origin of these rocks is still debatable. This is because, in most cases, it is not clear which liquid (carbonatite or silicate) underwent immiscibility to generate the phosphate liquid. Regarding this issue, in a more detailed study Barbosa (2009) was able to identify two groups of phoscorite rocks in the Salitre Complex: P1 Phoscorite, which is suggested to be originated trough immiscibility between silicate and phosphate liquids; and P2 Phoscorite, a possible result of immiscibility processes between carbonatite and phosphate. Results, as interpretated, are ambiguous and show that phoscorite series rocks can derive from both silicate and carbonatite magmas, as demonstrate by figure 12. Conversely, Cordeiro et al. (2010; 2011b) suggests that the Catalão I phoscorites and nelsonites probably formed by the accumulation of magnetite, apatite, phlogopite, and pyrochlore at the walls of dykes filled with a phosphate-rich carbonatite magma. Both hypothesis are not exclusive and might happen in the same complex, but the possibilities of liquid immiscibility in the phoscorite series are still under debate.

The petrogenetic evolution of the APIP can develop through multiple paths and figure 22 summarizes observed paths in Catalão I, II, Salitre, Serra Negra and Tapira in a general evolutionary scheme. Therefore, not all depicted paths will necessarily occur in every complex.

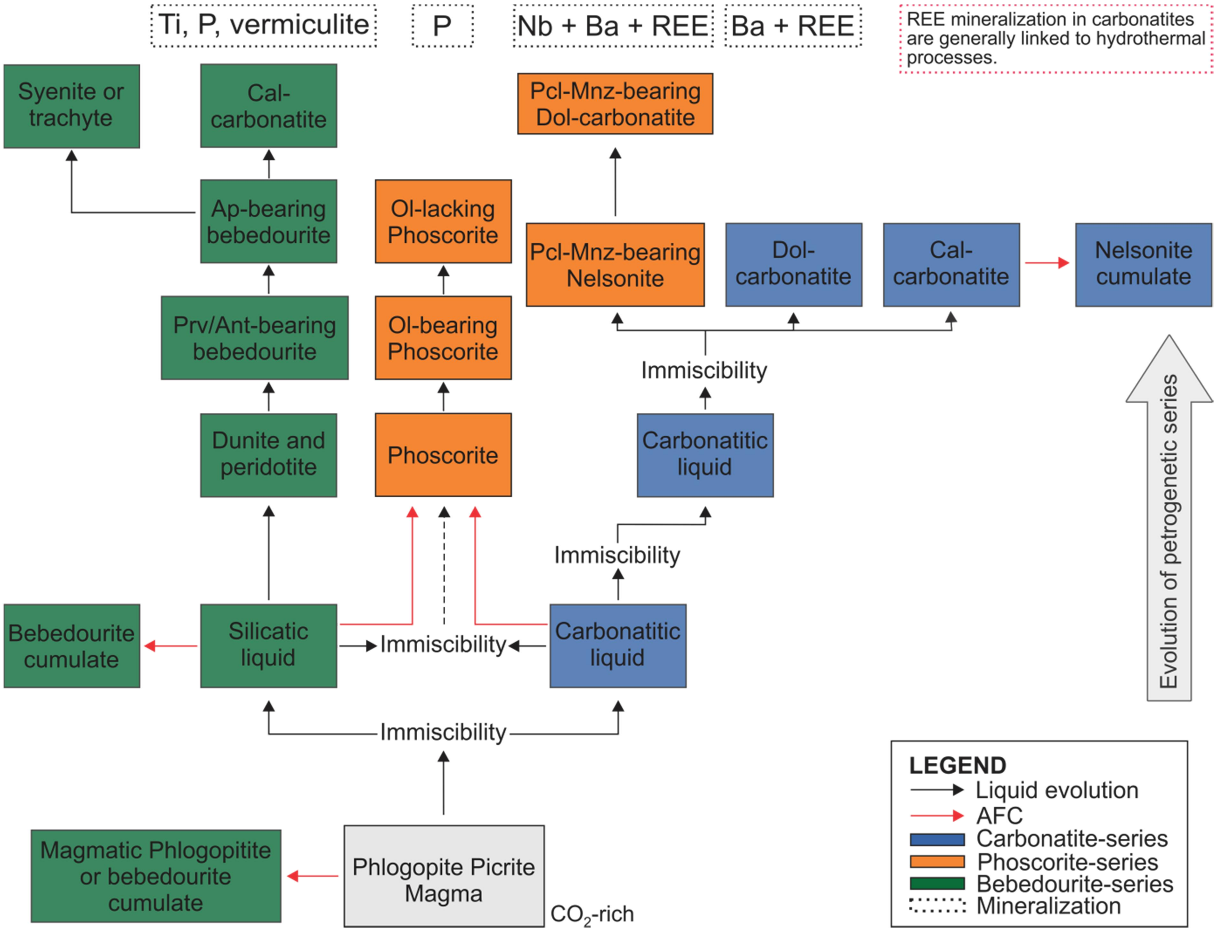

Fig. 22 – Proposed Scheme of Petrogenetic Evolution for APIP magmatic series, based on proposes by Ribeiro (2008), Barbosa (2009) and Grasso (2015). Notice that the dashe arrow referring to phoscorite-series immiscibility corresponds to the uncertainty of the presence of this process.

12.2 Metasomatism

Although magmatic processes are important in primary mineral concentration, metasomatism is also very relevant in the formation of APIP ores. Anatase (titanium) and REE deposits (Catalão I, Ribeiro, 2008; Tapira, Brod, 1999), for example, depend first on the actuation of hydrothermal processes, before becoming supergenic. To form a Ti-rich ore, perovskite from bebedourite series rocks must be converted into anatase due to the interaction with carbohydrotermal fluids, to only further be concentrated in supergenic ores (e.g. Ribeiro, 2008 and Brod, 1999). In the case of REE, the protolytes can be metasomatic phlogopitites or carbonatites enriched in REE (usually by also hydrothermal processes). Niobium and phosphate ores, however, doesn't depend on metasomatic enrichment (e.g. Araxá, Grasso, 2015; Catalão I, Cordeiro et al., 2009).

Stable isotopes (C, O) of carbonates might be in hand when trying to understand magmatic and post-magmatic processes in carbonatite complexes. The isotopic composition of carbonatites can be affected by distinct processes during magmatic (degassing and AFC) or post-magmatic evolution. Isotopic composition of carbonatites can be affected by wall rock assimilation or by the influence of high- or low-temperature fluids, for instance. In APIP, carbonatite samples may present high values of $\delta^{18}O$, whereas $\delta^{13}C$ values are compatible with those of primary carbonatites, suggesting that they were affected by interactions with water-rich fluids (e.g. Comin-Chiaramonti et al., 2005).

When analyzing carbonatite samples from Salitre Complex, Barbosa (2009) obtained results compatible only with primary carbonatites ($\delta^{13}{}_{CPDB}$ between -4‰ and -8‰; $\delta^{18}O_{SMOW}$ between 6‰ and 10‰; Taylor et al., 1967; Deines, 1989, Demény et al., 2004). On the other hand, considering that the phoscorites isotopic trend is similar to that of carbonatites, the author observed that these rocks have systematically lower $\delta^{13}C$ (PDB) and slightly higher $\delta^{18}O$ (SMOW) than those of carbonatites, suggesting that they interacted with low temperature fluids, during hydrothermal or weathering events.

In comparison, at least two events of magmatic fractionation (Rayleigh and degassing) and three fluid fractionation (fluid degassing, H_2O percolation, and CO_2–H_2O fluid percolation) have been identified by Cordeiro et al. (2011b) in Catalão I, based on isotopic data. Although of igneous origin, nelsonites and phoscorites (P1, P2, and P3) were subsequently affected by several post-magmatic events, which sometimes overprinted entirely the original magmatic features in the Complex. That drives us to deep discussions surrounding mineralization. The phoscorite series rocks represent the main ore hosts in APIP (e.g. Catalão I, Catalão II) and present textural, mineralogical and isotopic evidence of alteration by CO_2-rich fluids. Similarly, the presence of perovskite in Tapira has become economic significant, since perovskite ($CaTiO_3$) is instable in the presence of CO_2-rich fluids and is transformed to anatase (TiO_2), as earlier mentioned.

Summarizing, metasomatic processes are responsible to either transform minerals (perovskite to anatase, by instance) or leach the valuable substances from the original rocks, concentrating them in a new lithotype that will further originate mineral ores. Nonetheless, there is not much information available on characterizing the actuation of metasomatism and its influence in final ore grades and this is an aspect that deserves proper attention.

12.3 Supergene alteration

Supergenic alteration is widespread in APIP complexes and overlaps all other magmatic or metasomatic features, thus consisting in the most important process to generate ore graded bodies. Worldwide, the supergene Nb deposits are developed in laterites formed from primary carbonatites and phoscorites, with the process resulting in the physical concentration of resistant primary pyrochlores and removal of soluble more phases (Mitchell, 2015). All currently explored deposits in the APIP are indeed residual ores of not only pyrochlore, but also apatite (phosphate) and by-products such as anatase, barite and vermiculite.

In apatite (phosphate) and pyrochlore (niobium) deposits, weathering has the main role of residual concentration (e.g. Araxá, Grasso, 2015; Catalão I, Ribeiro, 2008), besides generating Ba-rich pyrochlore. On the other hand, anatase (titanium) and REE minerals depend first on the actuation of hydrothermal processes to only further be concentrated in supergenic ores.

The fact that phoscorites compose most of protolytes for APIP ore formation might be linked to weathering susceptibility. Textural aspects and stable isotopes data show that, phoscorites from Salitre, for example, in comparison with carbonatites, present higher susceptibility to weathering alteration, based chiefly on variations observed in terms of $\delta^{18}O$ (Barbosa, 2009). This information is also consistent to the ore body geometry model for Mina do Padre deposit (Catalão II), where the phoscorite body is more susceptible to groundwater percolation, what results in more effective weathering and consequent formation of silcretes (Palmieri, 2011).

In APIP complexes, deposits can be generally represented by a weathering profile that encompass, from bottom to top, the Fresh rock, Alterated rock, Isalterite micaceous ore, Isalterite oxide ore, Alloterite and, finally, a weathering cover (Fig. 23; Oliveira & Imbernon, 1998; Palmieri, 2011; Grasso, 2015). Generally, in alterated rocks levels there is the preservation of sulfides and carbonates, besides magmatic (like perovskite) and metasomatic minerals. The main trend is for carbonates and perovskite disappear upwards the profile, in the isalterites, and the phlogopite to be eventually entirely leached. The occurrence of neoformed phosphates and concentration of apatite is characteristic for isalterite levels. The oxide ore is also characterized by the lack of any mica kind. In the alloterite, apatite is not present. Anatase, however, might resist and be present even in the weathering cover.

Silcretes (Catalão II, Palmieri, 2011) and silico-carbonatated levels (Catalão I, Ribeiro,2008) may also occur above or with the alterated rock. One of the most feasible hypotheses to explain these levels is de silica remobilization from more susceptible rocks. Although these zones may be ore-graded, their explotation is more complicated than that of other weathering layers.

Although weathering processes are essential to propitiate high niobium, phosphate or titanium concentrations in the lateritic cover and to change ore geometallurgic proprieties, making exploitation feasible, there are practically no studies involving the age and evolution of the lateritic profiles. Every level in the weathering profile requires distinctive benefiting approaches and the same is applied to fresh rock ores. Therefore, better understanding their genesis is indispensable in terms of exploration.

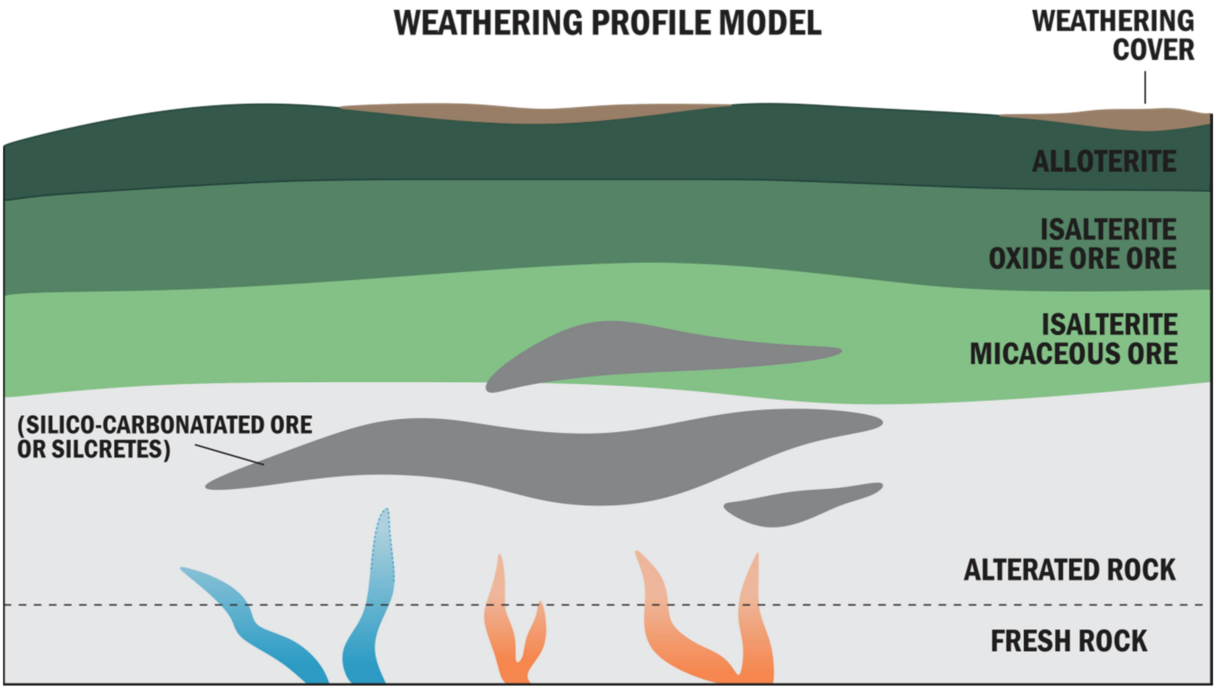

Fig. 23 - Schematic weathering profile suggested for APIP complexes. Based on models by Oliveira & Imbernon (1998), Palmieri (2011) and Grasso (2015).

13. Conclusions

In this paper, we have come to the following conclusions:

a) The alkaline and ultrapotassic magmatic event that generated the Alto Parnaíba Igneous Province (APIP), responsible for the intrusion of silicate-carbonatite complexes in the region of Minas Gerais and Goiás States (Brazil), is also responsible for magmatic and hydrothermal processes that originated niobium, phosphate and rare earth elements (REE) ores. The occurrence of these intrusions and their metasomatized products allowed a later overprinted by supergene enrichment processes.

b) The intrusion styles of the APIP complexes, such as dikes and small to large-scale intrusive bodies, and their lithological variation suggest that they represent multi-intrusive complexes. Domic structures originated during intrusion suggest that, although carbonatitic magmas are known for low viscosity (with low SiO_2 contents), in the APIP they were capable of deforming the country rock. To Brod (1999), this unexpected aspect suggests that the intrusions occurred as a crystal mush, rather than a fluid magma, therefore presenting higher viscosity.

c) The widespread presence of phlogopite picrite dikes in the APIP and their geochemical similarities to lithologies from carbonatite complexes suggest a genetic relation between them. Trace-element and REE patterns of phlogopite picrites and kamafugites from APIP, the high MgO, Cr and Ni contents and undifferentiated REE patterns (from Brod, 1999 and Brod et al., 2000), indicate both a common mantle-linked source and that phlogopite picrites represent the composition of primitive liquids. It is also argued that, based on the bulk-rock chemistry and REE patterns, other APIP rocks may have derived from phlogopite picrites trough assimilation-fractional-crystallization (AFC) and liquid immiscibility.

d) Geochemical data from Salitre phoscorite series rocks (Barbosa, 2009) argue in favour of an oxide-phosphate melt generated by liquid immiscibility, but the evidence are ambiguous and could also be supporting AFC. Geochemical data of phoscorites from Catalão I, Catalão II and Serra Negra have indicated a genesis as cumulates from carbonatite magmas.

e) The intrusive bodies from APIP complexes are predominantly emplaced as dykes and plugs (as observed in figures 18 to 21). This aspect has direct correlation with the predominance of vertical niobium ore bodies in Catalão I and II, although other magmatic processes such crystal settling can generate deeper bodies with a horizontal concentration of ore minerals, as in the deep zone of the Morro do Padre deposit, in Catalão II. The same level of detail is still not available for phosphate-rich phoscorites and bebedourites that compose the hypogenic ores of Araxá, Tapira, Serra Negra and Salitre complexes.

f) Despite the abundance of metasomatism in APIP, this process has only an indirect role in the generation of Nb and phosphate deposits by altering the host rocks into phlogopitites. In REE and Titanium (Ti) deposits, however, metasomatism plays the important role of redistributing REE concentrations and transforming perovskite into anatase (TiO_2). Nonetheless, little is known about processes involved in the generation of REE high-grade ores that are currently being prospected in Catalão I with CMOC and in Araxá with CBMM.

g) Supergenic processes, on the other hand, are important in reworking the primary mineralogical assemblage into various horizontal weathering beds that are mineralogically very distinct from hypogene equivalents (figure 22). This mineralogical variation indicates that processes like carbonate dissolution, leaching of elements and neoformation of phosphate are responsible for enriching the rock original contents to ore grade. In Araxá, for instance, P_2O_5 contents vary from 6% in alterated rock to over 15% in the micaceous isalterite ore, due to leaching of gangue minerals and consequent residual and/or supergenic concentration of apatite.

h) At least in Catalão I and Catalão II, phoscorite series rocks show a direct relation with phosphate supergenic mineralization. High phosphate contents in the lateritic profile present a spatial relation with the hypogenic phoscorite bodies, suggesting that phoscorite series rocks are the main source for supergenic ores. However, bebedourites can also nurture phosphate supergenic ores, as evidenced in Tapira and Araxá (Brod, 1999; Grasso, 2010). These features indicate that both bebedourite and phoscorite series rocks might generate secondary phosphate deposits.

i) The occurrence of supergenic ores superimposed to all the other types of mineralization indicates that these processes were the last to occur in the APIP complexes and were also responsible residually concentrating minerals, rather than inducing neoformed crystallization.

j) Along with the need for better comprehending the origin of phoscorite series rocks, the absence of studies on REE and Ti deposits genesis and the lack of understanding about geochronology of the evolution of supergene processes emphasize the need for new studies regarding alkaline-carbonatite complexes.

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5 CONCLUSÕES

No âmbito desta monografia, chegou-se às seguintes conclusões:

a) O evento alcalino e ultrapotássico que gerou a Província Ígnea Alto Parnaíba (APIP), responsável pela intrusão de complexos alcalino-carbonatíticos nas regiões de Minas Gerais e Goiás, é também responsável por por processos magmáticos e hidrotermais que deram origem a depósitos de nióbio (Nb), fosfato e elementos terras raras (ETR). A ocorrências destas intrusões e seus produtos metassomáticos permitiram a sobreposição posterior por processos de enriquecimento supergênico.

b) Os estilos instrusivos dos complexos da APIP, como diques e outras intrusões de pequeno a grande porte, e sua variação litológica sugerem que eles representam complexos multi-intrusivos. Estruturas dômicas originadas durante a intrusão sugerem que, embora os magmas carbonatíticos sejam conhecidos pela baixa viscosidade (com baixo teor de SiO_2), na APIP eles foram capazes de deformar a rocha encaixante. Para Brod (1999), estas circunstâncias sugerem que as intrusões teriam ocorrido na forma de crystal mush (uma “pasta de cristais”) em vez de um magma fluido, apresentando, portanto, uma maior viscosidade.

c) A presença disseminada de diques de flogopita picrito na APIP e suas similaridades geoquímicas com as litologias de complexos carbonatíticos sugerem uma relação genética entre eles. Os padrões de elemento traço e ETR de flogopita picritos e kamafugitos da APIP, os altos teores de MgO, Cr e Ni e padrões de ETR indiferenciados (de Brod, 1999 e Brod et al., 2000), indicam tanto uma fonte mantélica comum aos dois litotipos, quanto que flogopita picritos representam a composição de líquidos primitivos. Argumenta-se também que, com base na química de rocha e nos padrões de ETR, outras rochas APIP podem ter sido derivadas de flogopita picritos através de assimilação-cristalização-fracionada (AFC) e imiscibilidade de líquido.

d) Dados geoquímicos de rochas da série foscorítica em Salitre (Barbosa, 2009) argumentam a favor de um melt óxido-fosfatado gerado por imiscibilidade de líquidos, mas as evidências são ambíguas e também poderiam estar apoiando a atuação da AFC. Dados geoquímicos de foscoritos de Catalão I, Catalão II e Serra Negra indicaram uma gênese cumulática a partir de magmas carbonatíticos.

e) Os corpos intrusivos dos complexos da APIP apresentam-se alojados predominantemente na forma de diques e plugs (conforme observado nas Fig. 18 a 21). Este aspecto tem correlação direta com a predominância de corpos verticais de minério de nióbio em Catalão I e II, embora outros processos magmáticos, como decantação magmática, possam gerar corpos mais profundos, com concentração horizontal dos minerais de minério, como é o caso das intrusões da zona profunda no depósito Morro do Padre, em Catalão II. Entretanto, o mesmo nível de detalhamento ainda não está disponível para os foscoritos e bebedouritos ricos em fosfato que compõem os minérios hipogênicos dos complexos de Araxá, Tapira, Serra Negra e Salitre.

f) Apesar da abundância de evidências de metassomatismo na APIP, este processo tem apenas um papel indireto na geração de depósitos de Nb e fosfato, alterando as rochas hospedeiras em flogopititos. Nos depósitos de REE e Titânio (Ti), no entanto, o metassomatismo desempenha o importante papel de redistribuir as concentrações de ETR e transformar a perovskita em anatásio (TiO_2). Contudo, pouco se sabe sobre os processos envolvidos na geração de minério de alto teor de ETR que estão sendo prospectados em Catalão I e em Araxá com as atuais empresas encarregadas.

g) Processos supergênicos, por outro lado, são importantes no retrabalhamento da assembléia mineralógica primária em diversas camadas intempéricas horizontais que são mineralogicamente muito diferentes de seus equivalentes de hipogênicos (Fig. 22). Essa variação mineralógica indica que processos como dissolução de carbonato, lixiviação de elementos e neoformação de fosfato são responsáveis pelo enriquecimento do teor original da rocha até o grau de minério. Em Araxá, por exemplo, o conteúdo de P_2O_5 varia de 6% em rocha alterada a mais de 15% no minério de isalterita micáceo, devido à lixiviação de minerais de ganga e consequente concentração residual e/ou concentração supergênica de apatita.

h) Pelo menos em Catalão I e Catalão II, as rochas da série foscorítica apresentam relação direta com a mineralização supergênica de fosfato. Teores elevados da substância no perfil laterítico apresentam uma relação espacial com os corpos hipogênicos de foscoritos, sugerindo que as rochas da série dos foscoritos são a principal fonte de minérios supergênicos. No entanto, os bebedourites podem igualmente alimentar depósitos supergênicos de fosfato, como evidenciado em Tapira e Araxá (Brod, 1999; Grasso, 2010). Estas características indicam que tanto as rochas da série bebedourítica quanto as rochas da série foscorítica podem gerar depósitos secundários de fosfato.

i) A ocorrência de minérios supergênicos sobrepostos a todos os outros tipos de mineralização indica que esses processos foram os últimos a ocorrer nos complexos APIP e também foram responsáveis por concentrar residualmente os minerais, em vez de induzir a cristalização neoformada.

j) Por fim, juntamente com a necessidade de compreender melhor a origem das rochas da série foscorítica, a ausência de estudos sobre a gênese dos depósitos de REE e Ti e a falta de compreensão sobre a geocronologia da evolução dos processos supergênicos enfatizam a necessidade da produção de novos estudos acerca dos complexos alcalino-carbonatíticos.

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