RARE EARTH ELEMENTS GEOCHEMISTRY OF FLUORITE FROM THE MATO PRETO CARBONATITE COMPLEX, SOUTHERN BRAZIL

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RESUMO GEOQUÍMICA DE ELEMENTOS TERRAS RARAS DE FLUORITAS DO COMPLEXO CARBONATÍTICO DE MATO PRETO, PARANÁ Depósitos de fluorita no sul do Brasil associam-se em geral a rochas graníticas e sedimentares carbonáticas. O depósito de fluorita de Mato Preto constitui uma exceção uma vez que as encaixantes são carbonatitos e rochas alcalinas silicáticas. Este trabalho discute a origem das fluoritas de Mato Preto e mostra que elas apresentam um amplo espectro de razões $(La/Lu)_n$: fluoritas com alta razão $(La/Lu)_n$ são relacionadas ao magmatismo alcalino; enquanto fluoritas com baixa razão $(La/Lu)_n$ são relacionadas a contaminação por rochas encaixantes. Dados de isótopos de oxigênio, carbono e estrôncio mostram também que os carbonatitos de Mato Preto foram significativamente contaminados pelas rochas encaixantes.

Palavras-chaves: carbonatito, elementos terras raras, Mato Preto

ABSTRACT Fluorite deposits in Southern Brazil are usually associated to limestone and granitic rocks. The Mato Preto deposit fluorite is an exception because it occurs associated to carbonatite and alkaline silicate rocks. We discuss the origin of this deposit based on rare earth element (REE) geochemistry and show that fluorite from Mato Preto has an REE spectrum ranging from high to low $(La/Lu)_n$ ratios. We suggest that fluorite with high $(La/Lu)_n$ are related to the alkaline magmatism, whereas fluorite with intermediate to low $(La/Lu)_n$ did not derive from alkaline magmatism, but probably from the country rocks. This interpretation is supported by oxygen, carbon and strontium isotopes that show that the carbonatites are significantly contaminated by their country rocks.

Keywords: carbonatite, rare earth element, Mato Preto

INTRODUCTION Carbonatites have high concentration of REE, with values usually higher than 15000 ppm (Cullers & Medaris 1977). They also present high normalized La/Lu ratios, indicating an enrichment of the LREE relative to the HREE (Balaskov & Pozharitskaya 1965, Eby 1975, Cullers & Medaris 1983, Hogarth *et al.* 1985). Fluorine enrichment have been described in the late stages of carbonatite evolution and, in particular, in shallow seated complexes (LeBas 1977, Jago & Gittins 1991). Besides fluorite (CaF_2), fluorine is also hosted by apatite and biotite which may have up to 3% F (Deer *et al.* 1992). Large concentrations of fluorite associated with carbonatites were described in Amba Donga, India (Deans *et al.* 1973), and Okurusu (Van Zijl 1962). Similar to Mato Preto complex, these complexes exhibit strong potassic fenitization and potash-feldspar-bearing fenites.

Southern Brazil has several fluorite deposits, among which the most important are Mato Preto, Barra do Itaipirapuã, Braz, Mato Dentro, Volta Grande, Lageado Grande and Sete Barras. Except for Mato Preto and Barra do Itaipirapuã, these deposits are interpreted as related to either sedimentary-hydrothermal (Volta Grande and Lageado Grande) or hydrothermal (Lages) in origin. Mato Preto and Barra do Itaipirapuã are related to alkaline carbonatite complexes.

This paper discusses the REE, oxygen and carbon isotope data of fluorite and country rocks from the Mato Preto fluorite deposit and aims to better understand the relationship the fluorite deposit and the alkaline magmatism.

GEOLOGY OF THE MATO PRETO COMPLEX

The Mato Preto complex is part of the Arco de Ponta Grossa alkaline province (Almeida 1983) (Fig. 1). The complex is emplaced along the Morro Agudo Fault Zone, which marks the contact between the Açungui metasedimentary rocks and the Três Córregos granite (Fig. 2). The Morro Agudo fault zone, together with other regional structures, had an important role in the emplacement of the complex and the fluorite deposit.

The complex has approximately 24 km² and consists of four circular structures, each measuring 1 km in diameter. The

dominant rocks include fenitized syenites, phonolites, and carbonatites. K-Ar dating of phonolite dikes from the complex gave an age of 65 m.y. (Cordani & Hasui 1969). The Mato Preto complex displays strong potassic fenitization in which the main products are potassic feldspar fenites derived from the syenites and country rocks, and glimmerites from the phonolites and mafic rocks.

Carbonatites from Mato Preto occur as dikes, plugs or as the matrix of feldspathic breccias both of which intruded fenitized syenites and country rocks (Loureiro & Tavares 1982, Jenkins 1987, Santos 1988, Santos & Dardenne 1988, Santos *et al.* 1990). Santos (1988) described two main carbonatite generations: a) dolomite- to ankerite-bearing carbonatites commonly associated to feldspar clasts; and b) calcite-bearing carbonatites of the matrix of carbonatite breccias. These two carbonatite generations occur in the Clugger deposit and may not be recognizable in other parts of the complex.

Fluorite in Mato Preto occurs in four subparallel N50-60° E lenses dipping 80-85°NW. The lenses measure 250x80m and are enveloped by hydrothermally altered phonolite and tinguaitite dikes, both of which intrude the carbonatite and breccias (Jenkins 1987). Santos (1988) and Santos & Dardenne (1988) described four main fluorite generations in the Mato Preto complex: black-purple fluorite, purple fluorite, colorless-microcrystalline fluorite, and remobilized fluorite. Among these generations, the black-purple is the only so far not described in the Clugger deposit.

METHODS AND RESULTS

Carbonatite samples were defined as consisting of more than 50 wt% carbonate and having magmatic banding, magmatic flow structures and country rock xenoliths. They were collected in outcrops and drill cores of the fluorite mine. In general, they are medium- to coarse-grained. Metasomatic rocks usually occur close to the carbonatites and may or not preserve the original protolith texture.

REE and trace element data were obtained by plasma spectrometry at Geosol Laboratory, Belo Horizonte. Fluorite samples were selected according to their generations de-

Figure 1 - Location of alkaline complexes in Central and Southern Brazil. From Ulbrich & Gomes (1981).
 Figura 1 - Localização dos complexos alcalinos no sul e centro do Brasil. Extraído de Ulbrich & Gomes (1981).

scribed by Santos & Dardenne (1988), i.e. black-purple, purple, colorless microcrystalline, and remobilized, from which the mineral was concentrated by means Franz magnetic separator and dense liquids.

The REE patterns of two carbonatites, a fenitized syenite, a phonolite, and a fenitized porphyritic granite of the Mato Preto complex show a remarkable enrichment of light REE (LREE) relative to heavy REE (HREE), and normalized ratio La/Lu ranging between 2.52 and 3.66 (Table 1). The total content of REE increases in the following order: fenitized granite - phonolite - fenitized syenite - carbonatite.

The fenitized porphyritic granite has a turbid potassic feldspar which replaces both quartz and older phases of feldspar. The REE pattern does not show Eu anomaly and has one of the largest La/Lu ratio among the analyzed samples (Fig. 3). The phonolite and the fenitized syenite present total REE contents slight higher than the granite. The fenitized syenite is an equigranular rock which may be a more evolved fenitization product of the granite. The carbonatites have the highest concentration of total REE, with values ranging between 630 and 3007 ppm. The normalized La/Lu ratio ranges between

Figure 2 - Geologic map of the Mato Preto complex from Santos (1988).
 Figura 2 - Mapa geológico do complexo de Mato Preto (Santos 1988).

2.38 and 3.66 (Table I), which is close to those observed in the previous rocks.

The REE data of the carbonatites are similar to those of the purple and the colorless microcrystalline fluorites (Fig. 4). The purple fluorite occurs as veinlets in the carbonatite and presents high contents of REE and high normalized La/Lu ratios (2.01 to 2.52). Contrasting to the purple fluorite, textural evidence shows that the colorless microcrystalline fluorite replaces both the carbonate of the carbonatite and the purple fluorite. Its La/Lu ratio ranges from 2.13 to 3.66 (Table 2). The remobilized fluorite generations present a wide spectrum of REE patterns in which normalized La/Lu ratios are usually lower than those of older fluorite generations (0.78 to 2.93). One of the samples of remobilized fluorite presents a strong negative Ce anomaly and HREE enrichment.

DISCUSSION Fluorite from Mato Preto shows a general decrease in the total REE content from the earlier to

the younger generation suggesting that the F-bearing solutions became progressively depleted in REE (Fig. 4). Similar feature was observed in fluorites from other localities (Strong *et al.* 1984), and in particular, in Volta Grande and Sete Barras (Ronchi & Dardenne 1987).

The REE patterns of the purple microcrystalline fluorite from Mato Preto suggest that this generation is probably related to late magmatic fluids, as also suggested by petrographic studies and the association of this fluorite with REE minerals. The colorless microcrystalline fluorite occurs associated to strong hydrothermal alteration in which phonolite dikes and potassic-feldspar clasts within the carbonatite are transformed into clay mineral-bearing rocks. Thin section studies reveals that this fluorite replaces both the carbonates of the carbonatite and the purple fluorite, suggesting that its REE patterns is probably inherited. This fluorite presents a wide range of La/Lu ratio indicating a larger degree of remobilization if compared to the purple fluorite. The remobilized

Tabela 1: REE data from alkaline and country rocks from the Mato Preto Complex.

Tabela 1: Terras Raras das rochas alcalinas e encaixantes do Complexo de Mato Preto.

	Carbonatite			Phonolite	Fenitized syenite	
	10DB46	7DB46	P95B	P26B	SR501	P78
La	187	935.3	333.5	101.5	154.7	73.3
Ce	278.1	1392	544.9	161.8	229.5	141.3
Nd	107.6	496.5	218.9	52.3	75.1	41.6
Sm	15.9	79.6	39.8	7.2	13.2	7.3
Eu	3.8	20.2	11.3	2	4.1	1.9
Gd	10.1	51.1	30.5	5.5	11.8	5.8
Dy	8.1	20.4	21.8	3.6	7.4	3.4
Ho	1.8	3.3	4	0.65	1.3	0.48
Er	4.8	6.4	9.4	2	3.7	1.6
Yb	2.7	2	4	1.95	1.9	1.1
Lu	0.3	0.25	0.4	0.3	0.21	0.14
Y	96	168	260	24		
(La/Lu) _n	2.52	3.66	2.38	2.63	2.87	3.42

Figure 3. REE patterns of carbonatite and alkaline silicate rocks from Mato Preto normalized to chondrite values of Evensen et al. (1978).

Figura 3: Padrão de Terras Raras dos carbonatitos e rochas silicáticas de Mato Preto normalizados a conduto, valores de Evensen et al. (1978).

Table 2: REE data offluorites from Mato Preto.

Tabela 2: Terras Raras das fluoritas de Mato Preto.

	Purple fluorite						Colorless fluorite			Remobilized fluorite		
	P81B	29DB34	P30A	P34B	P70B	TH2	GAL 01	P34C	P71C	71DB60	P71D	T1C
La	15113	2881	699	1670.1	761.8	832.6	126.3	2122	501.3	55.1	3501	15.8
Ce	18869	3017	1178	2121	1241	1573	183.1	2522	841.5	79.8	21.9	28.1
Nd	4416	550.2	411.8	670.4	407.6	707.8	65.4	421.4	349.3	32.4	50.1	26.1
Sm	453.1	59.3	67.5	96.9	69	121.3	10.2	35.8	50.2	6.8	9.5	7.9
Eu	94.3	14.4	17.3	24.6	21.3	32	2.7	6.9	14.2	2.5	3	3.3
Gd	241.4	49.8	43.8	66.6	71.6	70.7	7.2	24.6	31.52	9.1	8.5	11.7
Dy	81.5	38.7	27	29.6	47.2	33	6.4	8.9	14.1	13	8.9	25.5
Ho	17.4	6.8	4.8	5.1	6.9	6.3	1.3	1.92	2.6	2.7	1.9	6.5
Er	38.7	16.6	12.3	11.9	13.7	15.9	3.9	4.7	5.4	7.8	5.7	24.2
Yb	15.4	12	9.6	7.3	6.6	9.7	3.5	2.5	2.4	7.9	5.3	22.7
Lu	1.7	1.5	1.2	0.85	0.79	1.09	0.43	0.43	0.29	1.02	0.72	2.7
Y	3360	520	440	392	520	840	168	164	200	280	368	164
(La/Lu) _n	2.52	2.26	2.01	2.43	2.26	2.05	2.13	3.66	3.09	1.39	2.93	0.78

fluorite displays a more heterogeneous REE patterns and an enrichment of HREE relative to LREE if compared to other fluorite generations. For instance, the remobilized white fluorite displayed in Figure 4 presents a negative Ce anomaly that was not observed in other fluorites, indicating that it formed under more oxidizing conditions than other fluorite generations.

Constraints on the nature of the fluorine mineralizing solutions The nature of the fluorine-rich solutions in Mato Preto is not well constrained, despite evidences that

both fluorine and carbonate complexes were important. Fluorine-rich solutions are usually accompanied by argillization and silicification, conspicuous during the formation of the colorless microcrystalline fluorite. Purple and remobilized fluorite have evidences, such as carbonate solid and fluid inclusions, that the REE were transported by solutions saturated in carbonate complexes (Santos 1988). In many instances, the fluid inclusions may have evolved from the solid inclusions.

Fluorine in Mato Preto may be related both to magmatic and non-magmatic fluids. The high REE concentration in

Figure. 4: REE patterns of fluorite from Mato Preto normalized to chondrite concentrations given by Evensen *et al.* (1978).
 Figura 4: Padrão de Terras Raras de fluorita de Mato Preto normalizados a valores de condrito de Evensen *et al.* (1978).

fluorite and in its host rocks (Fig. 3 and 4) supports a magmatic origin for at least the purple variety. Although the colorless microcrystalline fluorite has a REE patterns that is similar to the purple fluorite, field evidences suggest that it formed under hydrothermal conditions and by fluids that are not clearly related to the magmatism.

Carbon, oxygen and strontium isotope data indicate that carbonatites from Mato Preto underwent large-scale country rock contamination, suggesting that part of fluorine may derive from the country rocks. Oxygen and carbon isotope data from Santos *et al.* (1989) and Santos & Clayton (1995) indicate that, although country rock contamination played an important role in the evolution of the carbonatites, a better understanding of the process requires a detailed study of both carbonate and silicate rocks from this complex. Nevertheless, Figure 5 illustrates the effects of limestone contamination of alkaline melts through the oxygen and carbon data of the Mato Preto Complex. Despite the limited application of the model to Mato Preto, it shows that contamination by limestone from the country rock may have significantly affected the isotopic composition of its carbonatites.

Country rock contamination has also been invoked by Ronchi *et al.* (1993) to explain $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of two ore samples from Mato Preto. These samples present $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.70544 and 0.78394 indicating that the region of fluorite may also have been affected by crustal contamination. Among the deposits studied by the Authors, fluorite from Mato Preto presents the widest range in $^{87}\text{Sr}/^{86}\text{Sr}$ ratio.

Figure - 5. Diagram showing the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of samples

from Mato Preto, as well as a mixing line which models the contamination of a carbonatite-silicate melt by limestone, assuming that the uncontaminated magma consists of 70% silicates and has $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of 6.0‰ and -6.0‰,

respectively, and that the limestone has $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of 25.0‰ and 3.5‰, respectively. The numbers along the mixing line represent limestone fraction in the mixture. *Figura 5 - Diagrama de $\delta^{18}\text{O}$ versus $\delta^{13}\text{C}$ de amostras de carbonato dos carbonatitos de Mato Preto, mostrando curva de mistura entre magma silicático-carbonatítico contaminado por calcário. Para a construção da curva, assumiu-se que o magma silicático-carbonatítico consiste de 70% de silicatos e $\delta^{18}\text{O}$ e $\delta^{13}\text{C}$ iguais a 6,0‰ e -6,0‰, respectivamente. Para a composição isotópica do calcário assumiu-se valores de $\delta^{18}\text{O}$ e $\delta^{13}\text{C}$ de 25,0‰ e 3,5‰, respectivamente. Os números ao longo da curva representam a fração de calcário na mistura.*

CONCLUDING REMARKS The evolution of fluorite in Mato Preto complex has a close association with carbonatites, which in part explains its high REE contents. The earlier generation of fluorite has unique REE content and pattern, marked by a strong enrichment in LREE relative to HREE, as compared to fluorite not associated to carbonatite. However, younger fluorite generations are similar to fluorites from metasedimentary and hydrothermal deposits, suggesting that part of the fluorine in Mato Preto was not derived from the alkaline magmatism. In this regard, carbon, oxygen and strontium isotopes show that the carbonatites from Mato Preto were significantly contaminated by the country rocks.

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