

## Perovskite-group minerals from the Rio Apa and Amambay regions, NE Paraguay

*Minerais do grupo da perovskita das regiões do Rio Apa e Amambay, NE Paraguai*

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### Abstract

Perovskite-group minerals of alkaline-carbonatitic rocks from the Rio Apa and Amambay regions in Eastern Paraguay are members of the perovskite-lueshite-loparite-latrappite solid-solution series. Strontian-loparite is prevailing in the fenitized trachytic rocks and defines an evolutionary trend represented by an increase of Sr and LREE. The crystallization of the perovskite-group minerals resulted probably from metasomatic processes caused by fluids derived from cognate alkaline or carbonatitic sources, at relatively low temperatures (e.g. 400-700°C).

**Keywords:** Perovskite; Alkaline rocks; Carbonatites; Eastern Paraguay.

### Resumo

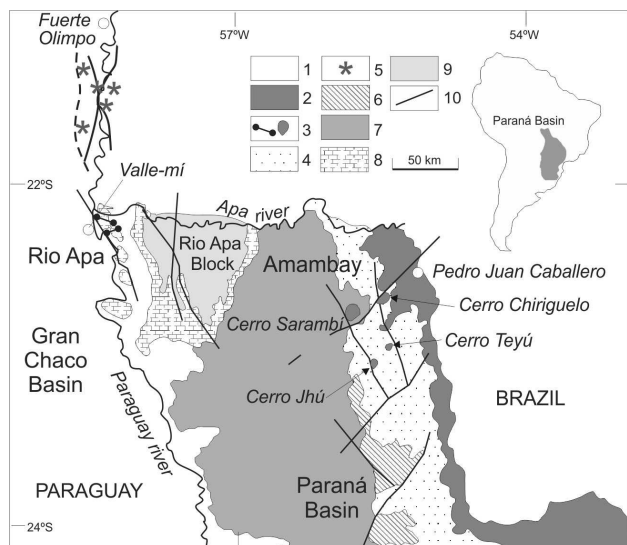
Minerais do grupo da perovskita de rochas alcalino-carbonatíticas das regiões do Rio Apa e Amambay no Paraguai Oriental são membros da série de solução sólida perovskita-lueshita-loparita-latrappita. Loparita rica em Sr é predominante nas rochas traquíticas fenitizadas e define uma tendência evolutiva representada pelo aumento de Sr e ETRL. A cristalização dos minerais do grupo da perovskita resultou provavelmente de processos metassomáticos causados por fluidos derivados de fontes comuns alcalina ou carbonatítica, a temperaturas relativamente baixas (p.e. 400-700°C).

**Palavras-chave:** Perovskita; Rochas alcalinas; Carbonatitos; Paraguai Oriental.

## INTRODUCTION

This paper results from a systematic research program aiming to characterize rare minerals of usually complex composition occurring as accessory phases in alkaline and alkaline-carbonatitic associations. It follows the recently concluded contribution on eudyalite-group minerals from the Monte de Trigo Island, SE Brazil (Enrich et al., submitted).

Perovskite-group of minerals is a common association in the Brazilian kamafugitic-kimberlitic rocks (Junqueira-Brod et al., 2000; Sgarbi et al., 2000, 2004; Araújo et al., 2001; Brod et al., 2005; Melluso et al., 2008; Guarino et al., 2013) and mica-bearing pyroxenites (bebedourites) (Morbidelli et al., 1997; Brod, 1999; Barbosa et al., 2012), being investigated to some extent and different aspects in various occurrences from the Goiás and Alto Paranaíba Provinces. It is also found associated with alkaline and alkaline-carbonatitic rocks, as indicated by studies in a few complexes such as Araxá (Traversa et al., 2001), Banhadão (Ruberti et al., 2012), Jacupiranga (Menezes Jr. and Martins, 1984) and Lages (Traversa et al., 2004). Furthermore perovskite is a typical accessory mineral in K-alkaline-carbonatitic lithotypes (138-139 Ma) from the Rio Apa (Valle-mí) and Amambay regions at north Eastern Paraguay, predating the tholeiitic basalts (133 Ma) of the Paraná Basin (Comin-Chiaramonti et al., 2007; Gomes and Comin-Chiaramonti, 2013). This alkaline-carbonatitic magmatism is intruding a Cambro-Ordovician carbonatic platform and Precambrian metamorphic rocks along with Permo-Carboniferous sediments (Figure 1).



**Figure 1.** Geological map of northern regions of Eastern Paraguay (modified after Comin-Chiaramonti et al., 1997, 1999, 2007, 2014). 1, Recent sedimentary cover; 2, Early Cretaceous tholeiites of the Paraná Basin; 3, Early

Cretaceous potassic alkaline rocks (pre-tholeiites, Rio Apa and Amambay Provinces); 4, Cretaceous sedimentary rocks (Misiones Formation); 5, Permo-Triassic alkaline rocks (Alto Paraguay Province); 6, Permian sedimentary rocks (Independencia Group); 7, Permo-Carboniferous sedimentary rocks (Coronel Oviedo Group) (4 to 7 formations belong to the Paraná Basin); 8, Cambro-Ordovician rocks (metaterrigenous and metacarbonatic sediments of the Itacupumí Group); 9, Paleoproterozoic to Neoproterozoic crystalline basement (Rio Apa complex, Centurion suite and San Luis Group); 10, major tectonic lineaments and faults.

The main rock-types, all characterized by the presence of primary carbonates, range from basanite-tephrite to trachyphonolite-trachyte (and intrusive equivalents) to carbonatite, as shown on the La vs. La/Yb diagram (Figure 2A, cf. Castorina et al., 1997; Comin-Chiaramonti et al., 2005). Glimmeritic and pyroxenitic veins may be also present.

Field evidences support the formation of almost pure  $\text{CaCO}_3$  immiscible liquids from carbonated silicate liquids. Previous papers on the carbonatitic rocks (e.g., Castorina et al., 1997) show that O-C isotopic compositions of the carbonates vary from values typical of continental lithospheric mantle up to values typical of hydrothermal environment: the isotopic exchanges (Figure 2B) implies temperatures ranging from 1200°C to < 400°C, involving fluids with  $\text{CO}_2/\text{H}_2\text{O}$  ratios between 0.8 and 1.0, and are suggestive of an increase of the carbonate volumes in the silicate liquids.

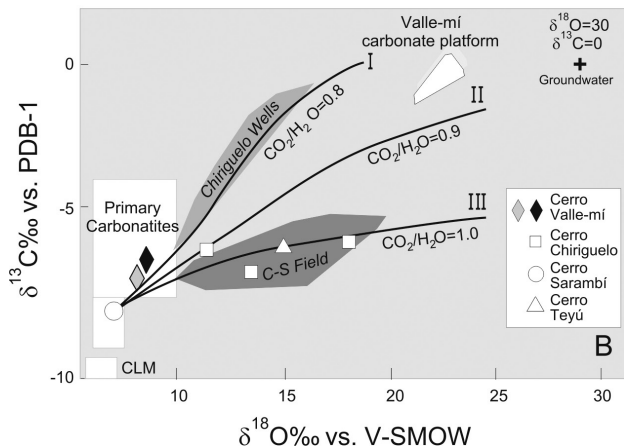
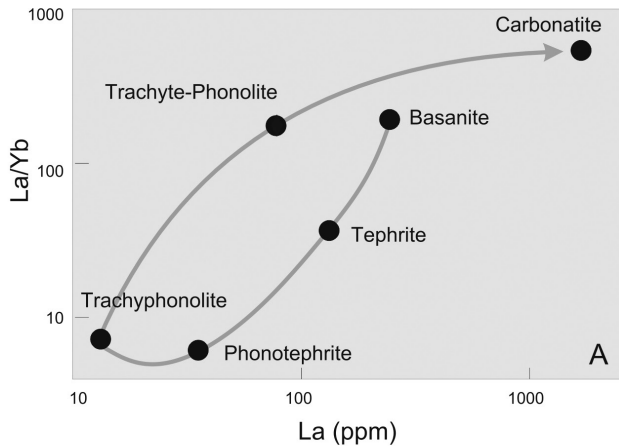
Perovskite-group minerals are ubiquitous accessory phases in the alkaline-carbonatitic associations (Haggerty and Mariano, 1983; Comin-Chiaramonti et al., 2014) forming euhedral to subhedral crystals that occur as microphenocrystals or members of the groundmass and range in size from 0.9 mm to 0.02 mm, respectively.

## CLASSIFICATION AND PETROGRAPHIC OUTLINES

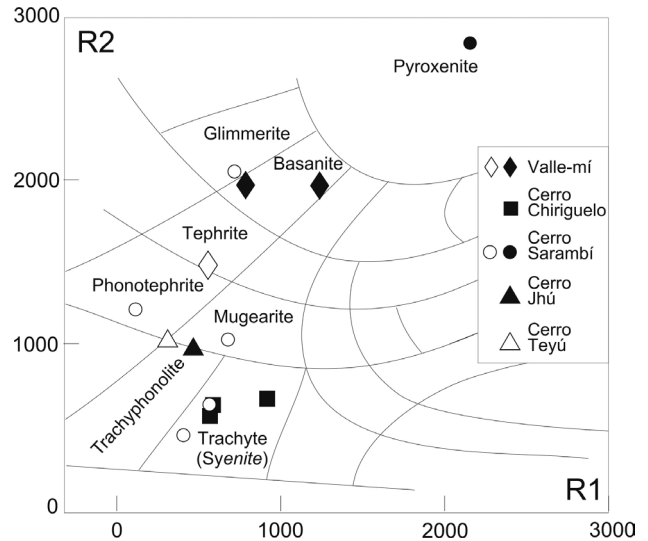
Selected samples include the main rock-types from the Rio Apa (Valle-mí) and Amambay regions (Cerro Chirigué, Cerro Jhú, Cerro Sarambí and Cerro Teyú, cf. Comin-Chiaramonti et al., 1999, 2014). The classification of the whole-rocks bearing perovskite is based on the De La Roche et al. (1980) and on the data listed in the papers by Censi et al. (1989) and Comin-Chiaramonti et al. (2014). A complete list of analyses is available on request to the authors. Chemical data for the various alkaline rocks occurring in the whole Amambay area are also found in Gomes et al. (2011). Figure 3 shows the

plot of the perovskitic rocks in the R1-R2 diagram (De La Roche et al., 1980).

A more detailed description of the different rock-types is mainly based on the studies of Comin-Chiaramonti et al. (2014) and also of Gomes et al. (2011) regarding the Amambay rocks.



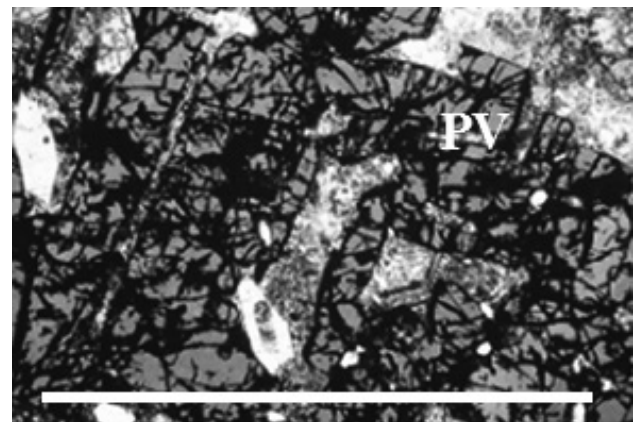
**Figure 2.** A. La (ppm) vs. La/Yb ratios for silicate rocks and carbonatites from the Rio Apa (Valle-mí) and Amambay regions (cf. Comin-Chiaramonti et al., 2005, modified after Castorina et al., 1997). B. Plot of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  for the primary carbonates from north Eastern Paraguay and the evolution of the O-C isotope compositions from magmatic (i.e. carbonatite box) to hydrothermal conditions (I, II, III lines) at variable  $\text{CO}_2/\text{H}_2\text{O}$  ratios. Cerro Chiriguano wells and C-S (Cerro Chiriguano-Cerro Sarambí complexes) main fields as in Comin-Chiaramonti et al. (2005); whole rock chemical analyses after Censi et al. (1989) and Comin-Chiaramonti et al., 2014; data source for Valle-mí carbonate platform and groundwater as in Castorina et al. (1996, 1997). Primary carbonatite box after Taylor et al. (1967); CLM, continental lithospheric mantle (Kyser, 1990). Arbitrary starting compositions of groundwater:  $\delta^{13}\text{C} = 0\text{‰}$ ;  $\delta^{18}\text{O} = 30\text{‰}$  (after Taylor, 1978; Usdowski 1982).



**Figure 3.** Classification diagram after De La Roche et al. (1980). R1 and R2 (atoms x 1000):  $\text{R1} = 4 \text{Si} - 11^*(\text{Na} + \text{K}) - 2^*(\text{Fe} + \text{Ti})$ ;  $\text{R2} = 6\text{Ca} + 2\text{Mg} + \text{Al}$ .

### Rio Apa (Valle-mí)

*Basanitic* dykes are only found intruding a Cambro-Ordovician carbonatic platform in the Rio Apa region near the Valle-mí town. They are characterized by chilled margins, less than 1.0 mm thick, and contain microcrystalline carbonates in the composition. The rocks, mesocratic, are fine- to medium-grained and porphyritic in texture with up to 30 vol% phenocrysts and microphenocrysts of euhedral to subhedral of clinopyroxene ( $\text{Wo}_{45-48}\text{En}_{42-47}\text{Fs}_{8-12}$ ), olivine ( $\text{Fo}_{84-86}$ ) and tetra-ferrilphlogopite ( $\text{mg}\#$  up to 0.74). The microcrystalline groundmass consists of clinopyroxene, primary carbonates (up to 20 vol%) forming globules (*ocelli*) and patches, alkali feldspar, feldspathoids and magnetite. Accessory phases include apatite, titanite and perovskite, the latter mineral occurring in the interior of the carbonate patches (Figure 4).



**Figure 4.** Skeletal perovskite grains (PV) and magnetite microlites (white) in a carbonatic patch from Valle-mí basanite. Transmitted light, bar 1 mm.

*Tephritic* dykes are fine-grained and porphyritic in texture with phenocrysts and microphenocrysts mostly of clinopyroxene ( $Wo_{44-49}En_{40-48}Fs_{9-14}$ ) and olivine ( $Fo_{72-79}$ ). Pseudoleucite and rare zoned plagioclase ( $An_{20-70}$ ) are also present. The groundmass is microcrystalline showing microlites of clinopyroxene ( $Wo_{47-48}En_{38-40}Fs_{12-15}$ ), primary calcite (up to 10 vol%), perovskite, plagioclase ( $An_{14-20}$ ), alkali feldspar ( $Or_{65-70}$ ), Ti-magnetite, olivine ( $Fo_{70-72}$ ), pseudoleucite, biotite (mg# 0.65), pargasite, apatite and titanite.

### Cerro Chiriguelo

Massive *trachytic* rocks surround a central *søvitic* core and appear to be strongly fenitized (Censi et al., 1989). The massive fenites (rheomorphic fenites according to Haggerty and Mariano 1983) exhibit porphyritic texture with phenocrysts of sanidine ( $Or_{94-97}$ ) and microphenocrysts of sanidine, aegirinic clinopyroxene ( $Ae_{45}Wo_{24}En_{12}Fs_{19}$ ), biotite (mg# 0.70), occasional garnet (andradite up to 81 mol%) and magnetite set in a groundmass consisting of the same phases, plus glass and goethite-limonite secondary patches. Apatite is a common accessory. Uranpyrochlore, strontian-loparite and strontio-chevkinite may be occasionally present (Haggerty and Mariano, 1983). The fenitic dykes are also trachytic in texture and show a weakly porphyritic texture with pheno- and microphenocrysts of sanidine set in a groundmass made of glass, sanidine, aegirine and as accessories apatite, opaques and perovskite. Rheomorphic fenite dykes with accessory strontian-loparite are cutting the country rocks metasediments and the massive fenites in the northwest area of the complex (Haggerty and Mariano, 1983).

The *carbonatites*, mainly forming an elliptical, NE-SW-trending, body occupying the central parts of the Cerro Chiriguelo complex, are *søvite* (C1 stage, according to the nomenclature of Le Bas, 1981) having on the whole a subhedral-granular texture, medium- to coarse-grained. However, fine-grained, “aplitic” textures are scattered as veins through the *søvites* (C2 stage). Quartz, phlogopite, barite, sanidine, apatite, dolomite, uranpyrochlore, magnetite, aegirine, zircon, strontianite, synchysite, haematite, goethite, perovskite and pyrite may be present. A third stage of emplacement of carbonatitic rocks (C3 ferrocarnatites) is also distinguished by Censi et al. (1989).

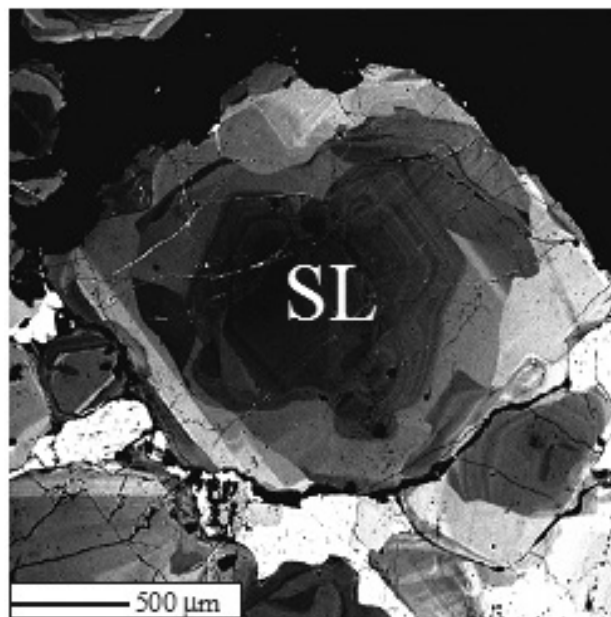
### Cerro Sarambí

The main rock-types are syenitic crosscut by phonotephritic, *søvitic* and silico-*søvitic* dykes, as well by glimmeritic and pyroxenitic veins. Trachytic-trachyphonolitic satellite plugs are noticeable (Gomes et al., 1996, 2011; Castorina et al., 1996, 1997), the largest one represented by Cerro Apuá, lying a few kilometers from the NW border of the complex.

*Syenites* are medium to coarse-grained, allotriomorphic to porphyritic in texture with alkali feldspar ( $\sim Or_{73}Ab_{27}$ ) and clinopyroxene phenocrysts ( $Wo_{48-49}En_{36-40}Fs_{11-14}$ ) set in a groundmass having alkali feldspar (Or up to 82 mol%), clinopyroxene (augite with aegirinic component up to 20 mol%), nepheline (kalsilite component around 20 mol%), mica (phlogopite-andrite series with mg# 0.68), occasional garnet (andradite rich up to 86 mol%), amphibole and accessory apatite, titanite, opaques, zircon and perovskite (Comin-Chiaramonti et al., 2014).

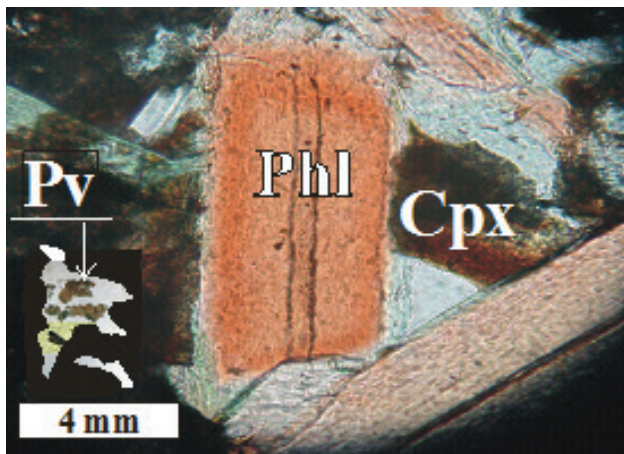
*Phonotephritic* dykes are porphyritic in texture, similarly to the tephritic dykes from Rio Apa, and consist of pheno- and microphenocrysts of clinopyroxene, biotite and plagioclase set in a hypocrySTALLINE groundmass with alkali feldspar, clinopyroxene, biotite, feldspathoids (nepheline, analcime) and accessory apatite, zircon and titanite and perovskite.

*Trachytes* and *trachyphonolites*, exhibiting together with some syenites clear evidence of fenitization, show occasionally mafic bands of prismatic aegirinic clinopyroxene ( $Ae_{50}Wo_{21}En_{11}Fs_{18}$ ). The rock-types display aphyric to porphyritic textures with alkali feldspar ( $Or_{85-88}$ ), feldspathoids (mainly kalsilite nepheline-rich), clinopyroxene ( $Wo_{48-49}En_{26-39}Fs_{13-25}$ ) and biotite (mg# 0.60-0.65) as pheno- to microphenocrysts, set in a hypohyaline groundmass formed by the same minerals plus glass. Accessory phases include apatite, strontian-loparite (Figure 5) associated with lamprophyllite and strontio-chevkinite (Haggerty and Mariano, 1983). In the trachyphonolitic variants primary calcite may be an important phase (up to 7-10 vol%).



**Figure 5.** BSE image showing idiomorphic crystal of strontian-loparite (SL) in fenitized trachyte from the Cerro Sarambí complex. The rims are mainly of Fe-Ti oxides.

*Glimmeritic* veins are inequigranular rocks with prevailing phlogopite/tetraferriphlogopite (up to 60 vol% with mg# 0.70-0.80), subordinate calcite (up to 25 vol%) and diopsidic clinopyroxene (about 5%, mg# ~0.80). Accessory minerals are magnetite, apatite, fluorocarbonates, titanite and perovskite (Figure 6). Notably, the glimmerite is characterized by the presence of ocelli textures.



**Figure 6.** Perovskite (Pv) associated with phlogopite (Phl) and clinopyroxene (Cpx) in glimmeritic vein from the Cerro Sarambí complex. Transmitted light.

*Pyroxenitic* veins are essentially medium-grained cumulates of diopside (mg# 0.75-0.80) with interstitial phlogopite, alkali feldspar, magnetite, carbonates, titanite, perovskite and apatite.

### Cerro Jhú and Cerro Teyú occurrences

These intrusions are geologically poorly known and found not so far from the Cerro Chirigué complex. Trachyphonolites and analcime phonolites form an impressive plug in Cerro Jhú, whereas partially altered trachyphonolites occur as probable dykes in Cerro Teyú (also referred to as Colônia Indígena Itaipaúsú by Paula, 2004) associated with reddish sandstones (Gomes et al., 2011).

## CHEMICAL COMPOSITION OF PEROVSKITES

### Analytical methods

Quantitative analyses were performed by WDS (Wavelength Detector System) at the Padova University (Italy, Geosciences and Georesources, CNR, Institute) on carbon-coated thin sections, employing accelerating voltage and beam current ranging between 15-20 kV and 10-20 nA, respectively.

X-ray counts were converted into oxide mass percentage by means of a PAP correction program provided by Cameca.

Special care was taken in the selection of peak and background positioning to eliminate peak overlap. Counting times for analyses were 10-20 s for light elements (F, Na, Mg, Al, Si, P, Cl, S, K, Ca, Fe, Mn, and Ti) and 60 s for other elements. The following well-characterized mineral and synthetic standards were used: TiO<sub>2</sub> (TiKa), Nb (NbLa), plagioclase An<sub>50</sub> (AlKa), synthetic Ca-Al-silicate glasses (LaLa, CeLa, PrLβ, NdLa, SmLa), Mn-hornblende (FeKa), diopside (MgKa), wollastonite (CaKa) and Amelia albite (NaKa).

### Results

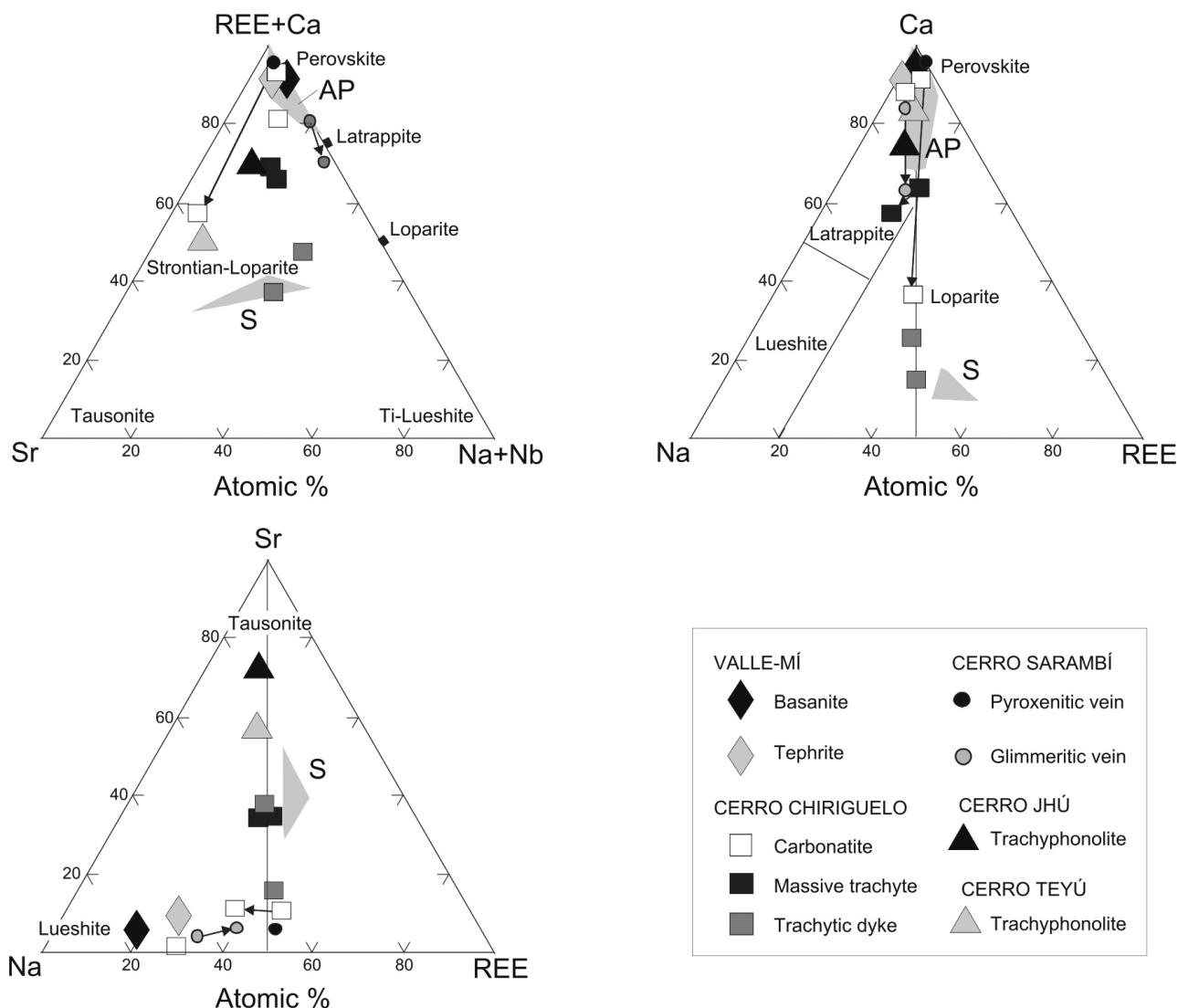
Perovskite microphenocrystals and microlites are ubiquitous and may be an important accessory phase (up to 2-3 vol%). Selected chemical analyses from various rock-types are reported in Table 1. The whole rock chemical analyses for major and trace elements are given in Censi et al. (1989) and Comin-Chiaromonte et al. (2014).

The perovskite-group minerals from the Valle-mí dykes and Amambay rocks is mainly represented by the end-member perovskite CaTiO<sub>3</sub> (Figure 7) similarly to the perovskites from the Alto Paranaíba kimberlites and kamafugites (Araújo et al., 2001; Melluso et al., 2008; Guarino et al., 2013) and the Salitre bebedourites (Morbidei et al., 1997; Barbosa et al., 2012). However, some specimens contain high amounts of Sr (10 to 28 wt%), particularly those from Cerro Jhú, Cerro Teyú and Cerro Chirigué fenitized trachytes (Table 1), being the perovskite member referred to as Sr-loparite following to Haggerty and Mariano (1983). In the latter minerals the sum of REE may reach up to 27.4 wt%. Notably, Nb<sub>2</sub>O<sub>5</sub> shows values around 8-9 wt% in pyroxenitic veins from the Cerro Sarambí and in the 3425 carbonatite from the Cerro Chirigué, whereas Na<sub>2</sub>O may be up to 6.35 wt% in the rim of a perovskite crystal from the 3422 carbonatite. These chemical features clearly distinguish the Paraguayan minerals from the Alto Paranaíba and Goiás perovskites, characterized in general by lower concentrations in REE, Sr and Nb.

Applying the oxygen barometer based on the Fe and Nb contents of CaTiO<sub>3</sub> perovskite to estimate the oxygen fugacity (*f*O<sub>2</sub>) during the crystallization and emplacement of the rock-types (ΔNNO after Bellis and Canil, 2007, relative to the nickel-nickel oxide buffer), the values range from -0.4 to -11.8. However, 60% of the ΔNNO values are within the -0.4 and -2.9 (basanite, tephrite, fenitized trachyte and trachyphonolite, glimmerite) interval, being the numbers very similar and corresponding to the *f*O<sub>2</sub> (ΔNNO) conditions reported by some authors (Chakhmouradian and Mitchell, 2001; Araújo et al., 2001; Canil and Bellis, 2007; Melluso et al., 2008) for kimberlites and kamafugites worldwide.

On the other hand, according to Haggerty and Mariano (1983), the strontian-lopaprites of reomorphic phenites from Cerro Sarambí show  $\Delta NNO$  ranging from -5.8 to -8.6. Figure 7 makes evident the relationships among perovskite

[CaTiO<sub>3</sub>], latrappite [(CaNa)(NbTi)O<sub>3</sub>], tausonite [SrTiO<sub>3</sub>], loparite [(NaCa)(TiNb)O<sub>3</sub>] and lueshite [NaNbO<sub>3</sub>]. In particular, the Figure 7C is suggestive of a complete solution series between loparite and tausonite.



**Figure 7.** A. Plot of Sr-(REE+Ca)-(Na+Nb) for perovskite-group minerals. B. Loparite- and perovskite-groups as a function of Na-Ca-REE. C. Perovskite as a function of Na-Sr-REE. The line represents a probable solution series between tausonite and loparite. AP field, perovskite from Alto Paranaíba kimberlites and kamafugites (Melluso et al., 2008, and therein references); S field, strontian-lopaprite from Cerro Sarambí (Haggerty and Mariano, 1983).

Experimental data (Galasso, 1969; Mitchell, 1997; Peña and Fierro, 2001) also demonstrate extensive solid solubility among the components with perovskite-type structure (cf. Figure 7), and in particular suggest that solid solutions, especially

involving members enriched in REE, are probably stable at  $T = \sim 700^{\circ}\text{C}$ . Lower thermal stabilities, i.e.  $400\text{-}500^{\circ}\text{C}$ , are possible, as a function of the relatively high concentrations of Na<sub>2</sub>O (up to 6.35 wt%; cf. Table 1).

**Table 1.** Representative chemical compositions of perovskite-group minerals from the Valle-mí dykes. It also shows the structural formula on the basis of 3 oxygens and the calculated ANNO values after Bellis and Canil (2007).

Sample	Valle-mí		Cerro Chiriguelo					
	VM-1	VM-3	3422 core	3422 rim	3425	3427		
Wt%								
TiO <sub>2</sub>	55.91	55.46	53.85	44.30	43.98	42.45		
Al <sub>2</sub> O <sub>3</sub>	0.11		0.01		0.02	0.01		
FeO <sub>t</sub>	1.20	1.16	1.26	1.23	3.50	0.81		
CaO	37.31	37.63	35.62	12.34	32.23	7.53		
Na <sub>2</sub> O	1.63	1.14	0.99	6.35	1.75	5.69		
La <sub>2</sub> O <sub>3</sub>	0.59	0.79	1.69	7.48	1.22	7.86		
Ce <sub>2</sub> O <sub>3</sub>	1.28	1.33	3.21	12.20	3.85	12.21		
Pr <sub>2</sub> O <sub>3</sub>	0.18	0.15	0.23	1.02	1.02	1.64		
Nd <sub>2</sub> O <sub>3</sub>	0.20	0.30	0.99	3.78	1.60	3.65		
Nb <sub>2</sub> O <sub>5</sub>	0.26	0.63	1.00	7.09	9.70	5.51		
SrO	0.33	0.50	0.81	4.18	0.15	11.63		
<b>Sum</b>	99.00	99.09	99.66	100.01	99.02	98.99		
<b>Cations/3Oxygen</b>								
<b>A-site</b>								
Ca	0.913	0.933	0.905	0.379	0.864	0.234		
Na	0.074	0.052	0.045	0.334	0.085	0.308		
Sr	0.005	0.007	0.011	0.066	0.002	0.196		
La	0.005	0.007	0.015	0.075	0.006	0.082		
Ce	0.011	0.011	0.028	0.121	0.018	0.126		
Pr	0.001	0.001	0.002	0.010	0.005	0.017		
Nd	0.002	0.002	0.008	0.037	0.007	0.037		
<b>Sum</b>	1.011	1.006	1.014	1.022	0.987	1.000		
<b>B-site</b>								
Ti	0.960	0.976	0.971	0.914	0.828	0.905		
Fe	0.023	0.023	0.025	0.024	0.073	0.020		
Al	0.003	0.000						
Nb	0.003	0.007	0.011	0.055	0.110	0.075		
<b>Sum</b>	0.989	1.006	1.007	0.993	1.011	1.000		
<b>Rock-type</b>	Basanite	Tephrite	Carbonatite	Carbonatite	Carbonatite	Fenitized Trachytic dyke		
<b>ΔNNO</b>	-2.1	-2.6	-2.6	-8.3	-3.0	-11.8		
	<b>Cerro Chiriguelo</b>			<b>Cerro Sarambí</b>		<b>Cerro Jhú</b>	<b>Cerro Teyú</b>	
Sample	3431 core	3431 rim	T591G*	GL-SA	PS-56 core	PS-56 rim	SA-95b	P17
Wt%								
TiO <sub>2</sub>	46.99	47.68	40.60	54.02	49.92	44.15	42.84	47.44
Al <sub>2</sub> O <sub>3</sub>	0.08				0.18	0.31	0.10	
FeO <sub>t</sub>	1.10	1.04	0.86	1.39	2.24	1.40	0.88	1.50
CaO	19.21	19.85	2.71	36.10	32.51	22.91	16.96	26.50
Na <sub>2</sub> O	2.89	3.02	5.03	0.62	2.06	4.29	1.85	1.81
La <sub>2</sub> O <sub>3</sub>	4.66	4.57	8.25	1.29	1.31	3.10	1.47	1.79
Ce <sub>2</sub> O <sub>3</sub>	7.52	7.02	12.22	2.48	3.22	8.85	3.01	2.55
Pr <sub>2</sub> O <sub>3</sub>	1.56	1.31	2.22	0.54	0.30	1.26	0.72	0.70
Nd <sub>2</sub> O <sub>3</sub>	2.99	2.27	3.51	0.67	1.04	3.79	1.28	1.26
Nb <sub>2</sub> O <sub>5</sub>	2.36	2.40	3.93	1.54	9.04	7.06	2.00	2.29
SrO	10.01	9.86	19.08	0.36	0.32	1.53	28.27	13.89

(Cont.)

Table 1. Continued.

	Cerro Chiriguelo			Cerro Sarambí			Cerro Jhú	Cerro Teyú
<b>Sum</b>	99.37	99.02	98.41	99.01	102.14	98.65	99.38	99.73
<b>Cations/ 3Oxygen</b>								
<b>A-site</b>								
Ca	0.541	0.524	0.097	0.918	0.847	0.614	0.449	0.671
Na	0.147	0.164	0.293	0.029	0.103	0.208	0.089	0.083
Sr	0.153	0.164	0.333	0.005	0.005	0.022	0.404	0.192
La	0.045	0.048	0.091	0.011	0.012	0.029	0.013	0.016
Ce	0.072	0.073	0.135	0.022	0.029	0.081	0.028	0.022
Pr	0.015	0.013	0.024	0.005	0.003	0.012	0.006	0.007
Nd	0.028	0.022	0.038	0.006	0.009	0.033	0.010	0.010
<b>Sum</b>	1.001	1.008	1.011	0.996	1.008	0.999	0.999	1.001
<b>B-site</b>								
Ti	0.902	0.945	0.918	0.965	0.848	0.861	0.899	0.916
Fe	0.040	0.043	0.022	0.028	0.056	0.031	0.020	0.032
Al	0.002				0.003	0.005	0.005	
Nb	0.028	0.029	0.050	0.016	0.099	0.094	0.025	0.027
<b>Sum</b>	0.972	1.017	0.990	1.009	1.006	0.991	0.949	0.975
<b>Rock-type</b>	Fenitized trachyte	Fenitized trachyte	Fenitized trachytic dyke	Glimmeritic vein	Pyroxenitic vein	Pyroxenitic vein	Trachyphonolite	Trachyphonolite
<b>ΔNNO</b>	-1.0	-0.4	-8.2	-2.5	-5.9	-11.6	-5.6	-2.9

\*Sample T591G after Hagerty and Mariano (1983).

## CONCLUDING REMARKS

Perovskite compositions in the rock-types from the Rio Apa and Amambay regions may reflect a general tendency of the rare earth elements (REE) to accumulate in the more evolved or in the immiscible carbonate fractions of alkaline magmas. The highest concentrations of Sr are found mostly in the fenitized (rheomorphic) trachyte and trachyphonolite, forming the mineral strontian-loparite. The compositional changes are probably driven by H<sub>2</sub>O-CO<sub>2</sub> rich-fluids at temperatures between about 400 and 700°C, at a pressure of 1 Kbar (Mitchell, 1997): experiments have shown that perovskite is highly soluble (up 30%) in “haplocarbonatite” liquids and cristallizes as a “groundmass-microcrystal” phase. Other perovskite-group members appear unstable: lueshite and tausonite are not found as primary liquidus phases, with the data suggesting that both minerals will not crystallize from low temperature carbonatite melts and that Ti, REE and Nb will be preferentially concentrated in residual liquids from which calcian-loparite and diverse niobates can be formed. On the other hand, Figure 7 (cf. Table 1) shows that all the perovskite compounds are present in the Rio Apa and Amambay lithotypes, i.e. perovskite (CaOTiO<sub>3</sub>), loparite (NaCeTi<sub>2</sub>O<sub>6</sub>, with Na<sub>2</sub>O up to 6.35 wt% and LREE up to 24.48% in Cerro Chiriguelo carbonatite), tausonite (SrTiO<sub>3</sub>, with SrO up to

28,27 wt% in trachyphonolite from Cerro Jhú) and lueshite (NaNbO<sub>3</sub>, with Na<sub>2</sub>O = 1.75 wt% and Nb<sub>2</sub>O<sub>5</sub> = 9.70 wt % in Cerro Chiriguelo carbonatite).

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