The Complete Phlogopite-Tetraferriphlogopite Series in the Catalão-I and -II Carbonatite Complexes, Brazil

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Introduction

Phlogopite from the Catalão-I and -II Carbonatite Complexes shows a wide range in Al_2O_3 (0.01 to 14.5%; 0.0 to 2.5 a.p.f.u) and FeO (5.0 and 32.3%) contents and also normal and reverse pleochroism, what has suggested the occurrence of. the phlogopite-tetraferriphlogopite series (Araújo and Gaspar, 1993). Therefore, in order to verify the existence of the $Fe^{3+(IV)} \leftrightarrow Al^{3+(IV)}$ substitution three samples were analyzed in a Mössbauer spectrometer and the results were compared to their average chemical composition. The presence of tetrahedral ferric iron has been confirmed in phlogopite and biotite through Mössbauer spectroscopy (e.g. Dyar, 1987; Rancourt *et al*, 1992, Cruciani *et al*, 1995).

Geological Setting

The Catalão-I and -II Carbonatite Complexes are located in the southeast part of the Goiás State, central Brazil. They belong to the Cretaceous Alto Paranaíba Magmatic Province which comprises several alkaline occurrences as kimberlitic rocks (Bizzi *et al*, 1991; Bizzi, 1993), kamafugites (Sgarbi and Valença, 1991) and other carbonatites along a NW regional trend (AZ 125).The complexes are intruded in metasedimentary rocks (Araxá Group) of the Neoproterozoic Brasília Fold Belt which occurs in the southwestern border of the São Francisco Craton. The Catalão-I Complex is 10 Km far away from Catalão-II. They are interpreted as cogenetic bodies comprising an ultramafic phase represented by dunite and clinopyroxenite and several carbonatite phases. The carbonatites had interacted with the primary ultramafic rocks forming carbonate-, phlogopite- and clinopyroxene-bearing rocks. Phoscorites also occur and are associated to the carbonatite. In the Catalão-I Complex a breccia with a phlogopite- and olivine- rich matrix cut the former rocks and contains fragments of the rock intrusion.

Chemical results

The phlogopites were analyzed in a CAMECA SX-50 microprobe (15kv and 25nA) at the University of Brasília. 96 analysis represent phlogopites from the clinopyroxenite, carbonatite, phoscorite, phlogopitite, and the breccia. The chemical analysis were normalized to 22 oxygen and the tetrahedral site (T site) is fulfilled with Fe^{3+} until the sum of Si, Al and Fe^{3+} equals 8.0 p.f.u., yielding the stequiometric $Fe^{3+(IV)}$ ($Fe^{3+(IV)*}$; in Table 1). Fe^{3+} does not enter in the octahedral site. The plots of $Fe^{3+(IV)*}$ *versus* $Al^{3+(IV)}$ and $Si^{4+(IV)}$ *versus* $Al^{3+(IV)}$ presented in figures 1 and 2 clearly exhibit a possible phlogopite-tetraferriphlogopite series where the normal and reverse crystals are shown. The phlogopites can be divided in two groups according to their pleochroism and chemical composition: (1) high Al-, Ti- and low Si-, Mg- and Fe_t- phlogopites with normal pleochroism, and (2) high Fe_t- and Si- and low Al- and Ti- tetraferriphlogopites with reverse pleochroism. Si plays an important role in cationic substitutions of the normal phlogopites. As shown in Figure 2 there is a clear break in the series for $Al^{IV} > 1.5$ a.p.f.u., coincident with pleochroism change, when it is observed an inverse correlation between Si^{IV} and Al^{IV}. The high Al^{IV} content is accompanied by high Ti^{VI} and low Mg^{VI}. The most important coupled substitution for the high Al members of the series could be $Ti^{4+(VI)} + 2Al^{3+(IV)} \leftrightarrow Mg^{2+(VI)} + 2Si^{4+(IV)}$. Conversely, the reverse tetraferriphlogopites show a smooth inverse correlation between Si^{IV} and Al^{IV} but Fe^{IV} and Al^{IV} are strongly antipathetic, which does not happen in normal or high Al- phlogopites (Figure 1). The $Fe^{2+(VI)}$-$Mg^{2+(VI)}$ substitution is more pronounced in

tetraferriphlogopites. The coupled substitution $Fe^{3+(IV)} + Fe^{2+(IV)} \leftrightarrow Mg^{2+(VI)} + Al^{3+(IV)}$ is proposed for the high $Fe^{3+(IV*)}$ series members (Araújo, 1996).

Mössbauer results

Three phlogopite samples were analyzed in the Mössbauer spectrometer at the University of Espirito Santo, Brazil. The samples were submitted to γ-Ray absorption using a $^{57}CO/Rh$ source and pattern transmission geometry. The Fe^{2+}/Fe^{3+} Mössbauer ratio is shown in Table 1.

Comparison between chemical and Mossbäuer results

The Mossbäuer Fe^{2+}/Fe^{3+} ratio was applied in the phlogopite chemical normalization in order to verify the iron distribution in the tetrahedral and octahedral sites. Table 1 presents the average chemical composition for each sample, their Fe^{2+}/Fe^{3+} ratio, and the normalization used as following: (1) determination of Fe^{2+} and Fe^{3+} amount according to the Mossbäuer Fe^{2+}/Fe^{3+} ratio for each sample; (2) fulfillment of the T site with Fe^{3+} until 8.0 a.p.f.u.. (3) fulfillment of the O site with the remaining Fe^{3+}. The O site became slightly vacant.

Discussion

The detection of Fe^{3+} in tetrahedral sites in the phlogopites of Catalão-I and -II through Mössbauer analysis confirms the existence of the tetraferriphlogopite member in these complexes. Considering also the large range of Al and Fe_t and due to the Al^{IV} variation from 0.0 to 2.5 a.p.f.u. (Figure 1) we report the first occurrence of a complete phlogopite-tetraferriphlogopite series.

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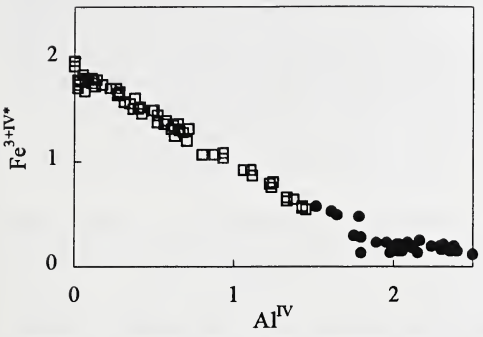

Figure 01 - Fe^{3+IV*} and Al^{IV} for phlogopites from Catalão-I and -II. Open squares: reverse pleochroism; filled circles: normal pleochroism.

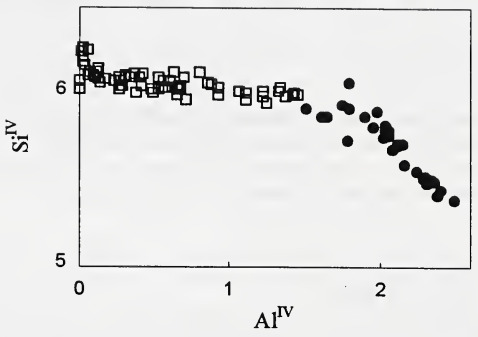

Figure 02 - Si^{IV} and Al^{IV} for phlogopites from Catalão-I and -II. Open squares: reverse pleochroism; filled circles: normal pleochroism.

Table 1 - Average Chemical Composition of Phlogopite.
Normalization based on Fe^{2+}/Fe^{3+} (see text).

	C61	C62	S/N
SiO_2	38,68	36,85	37,51
TiO_2	2,74	3,07	2,89
Al_2O_3	7,91	7,41	8,08
Cr_2O_3	0,01	0,01	0,02
Fe_2O_3	10,10	9,28	8,59
FeO	14,57	15,85	15,63
MnO	0,24	0,25	0,24
MgO	13,19	11,63	12,34
BaO	0,00	0,00	0,00
CaO	0,00	0,00	0,00
Na_2O	0,08	0,06	0,06
K_2O	9,64	9,52	9,52
H_2O	3,70	3,58	3,62
F	0,29	0,22	0,27
Cl	0,01	0,00	0,01
O=F	0,12	0,09	0,11
O=Cl	0,00	0,00	0,00
Total	101,29	97,81	98,89

	C61	C62	S/N
Si^{IV}	6,02	5,99	5,98
Al^{IV}	1,45	1,42	1,52
Fe^{3+IV*}	0,53	0,59	0,50
T Site	8,00	8,00	8,00
Al^{VI}	0,00	0,00	0,00
Ti^{VI}	0,32	0,38	0,35
Cr	0,00	0,00	0,00
Fe^{3+VI}	0,65	0,54	0,53
Fe^{2+VI}	1,90	2,15	2,08
Mn^{+2}	0,03	0,03	0,03
Mg	3,06	2,82	2,93
O Site	5,96	5,93	5,93
Ba	0,00	0,00	0,00
Ca	0,00	0,00	0,00
Na	0,02	0,02	0,02
K	1,91	1,97	1,94
A site	1,94	1,99	1,96
O	20,01	20,01	20,01
OH	3,84	3,88	3,85
F	0,14	0,11	0,13
Cl	0,00	0,00	0,00
Charge	0,00	0,00	0,00
Fe^{2+}/Fe^{3+} *	1.604	1.898	2.021

Fe^{2+}/Fe^{3+} * - Fe^{2+}/Fe^{3+} Mössbauer ratio