

Composition of priderite in phlogopitites from the Catalão I carbonatite complex, Brazil

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Abstract

Magnetite grains with exsolved ilmenite lamellae may be replaced by pyrite or carbonate in phlogopitites of the Catalão I carbonatite complex, Goiás State, Brazil. The ilmenite is transformed in part to priderite and sometimes to rutile. Priderite occurs as small anhedral grains (<0.2mm) or composite crystals associated with ilmenite and rutile. Chalcopyrite, magnetite, monazite, and pyrochlore also occur inside the area of original magnetite grains. The priderite belongs to the $K_2FeTi_7O_{16}$ - $BaFeTi_7O_{16}$ series with $K/(K + Ba)$ ranging from 1.0 to 0.53. The highest contents for other elements are: V_2O_5 2.65, Cr_2O_3 4.1, and Nb_2O_5 1.98 wt.%. Priderites associated with magnetite have the highest V, Cr, and Nb contents whereas others have the highest Ba content. Zoning characterized by K-Ba substitution is patchy but always present. V- and Cr-poor priderites are similar in composition to priderites from lamproites, and the V- and Cr-rich ones are compositionally similar to hollandite-group minerals found in kimberlites.

KEYWORDS: priderite, carbonatite, phlogopite, ilmenite, Brazil.

Introduction

PRIDERITE, as a member of the hollandite structural group, has been reported as a typical constituent mineral of lamproites (Mitchell, 1985, Jaques *et al.*, 1986). Hollandites, including priderites, have been found in some South African kimberlites: DeBruyn (Mitchell and Haggerty, 1986); Star Mine and New Elands (Mitchell and Meyer, 1989); Benfontein, and Wesselton (Mitchell, 1991). Ba-rich hollandite, incorrectly termed priderite (Mitchell and Meyer, 1989), has been reported in the Kovdor carbonatite, Kola Peninsula (Zhuravleva *et al.*, 1978, in Mitchell, 1991). Gierth and Leonardos (1989) briefly noted the occurrence of priderite in the Catalão I carbonatite complex in Brazil. In this paper we present further details regarding the nature of the occurrence and composition of priderite in the Catalão I carbonatite.

The Catalão I Complex is located 15 km northeast of the town of Catalão, Goiás State, Brazil. K/Ar studies indicate an intrusive age of 82.9 ± 4.2 m.y. (Hasui and Cordani, 1968). The complex is mainly composed of phlogopitites intruded by several stages of carbonatite plugs,

dykes, and veins. The phlogopitites are the result of extensive reaction of previous dunites and clinopyroxenites with later carbonatites. Several authors have described the geological and petrographic features of the complex (Carvalho, 1974; Gaspar and Adusumilli, 1976; Baecker, 1983; Gierth *et al.*, 1985; Danni *et al.*, 1991)

Occurrence

Priderite occurs in phlogopitites; these are medium to coarse grained, essentially composed of mica of the phlogopite-tetraferriphlogopite series. The phlogopite also contains apatite, calcite, diopside, and arfvedsonite, plus numerous accessory minerals; the most common are perovskite, magnetite, ilmenite, pyrite, and pyrochlore. The phlogopitites are usually extensively crosscut by millimetre to metre wide veins and dykes of carbonatite.

Magnetite in the phlogopitites commonly contains trellis-type ilmenite lamellae. Furthermore, magnetite itself is commonly replaced by pyrite or carbonate, leaving the ilmenite lamellae as relics in these later minerals. In such cases, parts of the ilmenite are transformed

TABLE 1. Priderite compositions

	1a	1b	2a	2b	3a	3b	3c	3d	4a
Nb ₂ O ₅	0.17	0.30	0.11	0.04	0.12	0.13	0.07	0.12	0.10
SiO ₂	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
TiO ₂	79.36	75.94	71.73	77.59	77.67	72.90	71.60	77.75	68.79
ZrO ₂	0.00	0.03	0.13	0.11	0.09	0.09	0.12	0.09	0.13
Al ₂ O ₃	0.06	0.07	0.06	0.04	0.04	0.10	0.05	0.03	0.07
V ₂ O ₃	0.52	0.57	1.14	0.39	0.50	1.50	1.51	0.42	1.44
Cr ₂ O ₃	0.08	0.09	0.38	0.01	0.01	0.23	0.27	0.02	0.76
MgO	0.27	0.23	0.24	0.25	0.22	0.25	0.20	0.28	0.21
CaO	0.15	0.13	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MnO	0.00	0.02	0.00	0.01	0.00	0.00	0.05	0.00	0.01
FeO*	8.36	9.82	10.28	9.43	9.34	10.62	10.91	9.53	10.84
SrO	0.01	0.04	0.03	0.02	0.00	0.00	0.03	0.00	0.05
BaO	1.95	5.23	9.46	3.02	3.04	6.73	6.59	2.76	12.02
Na ₂ O	0.10	0.04	0.03	0.01	0.03	0.04	0.03	0.03	0.04
K ₂ O	9.26	7.73	6.15	8.89	8.24	7.30	7.23	8.66	4.80
Total	100.30	100.24	99.74	99.80	99.31	99.89	98.67	99.68	99.26
Nb	0.009	0.017	0.007	0.002	0.007	0.007	0.004	0.007	0.006
Si	-	-	-	-	-	0.001	-	-	-
Ti	7.088	6.961	6.812	7.044	7.061	6.814	6.793	7.047	6.692
Zr	-	0.002	0.008	0.006	0.005	0.005	0.007	0.005	0.008
Al	0.009	0.011	0.008	0.005	0.006	0.015	0.007	0.004	0.010
V	0.049	0.055	0.116	0.038	0.049	0.149	0.152	0.041	0.149
Cr	0.008	0.009	0.038	0.001	0.001	0.023	0.027	0.002	0.077
Mg	0.047	0.042	0.046	0.044	0.040	0.047	0.038	0.051	0.041
Ca	0.020	0.017	-	-	-	-	-	-	-
Mn	-	0.002	-	0.001	-	-	0.006	-	0.001
Fe	0.831	1.001	1.086	0.952	0.944	1.104	1.151	0.960	1.173
Sr	0.000	0.003	0.002	0.002	-	-	0.002	-	0.004
Ba	0.091	0.250	0.468	0.143	0.144	0.328	0.326	0.130	0.609
Na	0.024	0.011	0.008	0.002	0.007	0.009	0.009	0.006	0.010
K	1.404	1.201	0.991	1.369	1.270	1.158	1.163	1.332	0.792
Total**	9.579	9.581	9.589	9.610	9.534	9.659	9.686	9.584	9.573

to priderite and rutile. It is possible to recognize all of the stages in this replacement process and the resulting different mineral associations. In detail, the associations of priderite so far recognized are: (a) pyrite; (b) pyrite and ilmenite; (c) ilmenite, chalcopyrite, monazite, and pyrochlore; (d) ilmenite, rutile, chalcopyrite, ancyllite, and monazite; (e) ilmenite, magnetite, serpentine, and monazite. Composite crystals of priderite and ilmenite are frequent and priderite, ilmenite and rutile are less common. Isolated priderite crystals are anhedral and very fine grained (<0.2mm).

Composition

Analyses were performed using a wave-length dispersive CAMECA SX50 electron microprobe

operated at 15kV and 20nA using synthetic and natural standards. The accuracy of the analyses is $\pm 5\%$ of the amount present for concentrations up to 2 wt.% and $\pm 2\%$ of the amount present for major elements.

Analytical data are presented in Tables 1 and 2. The association of priderites with pyrite and Fe₂O₃-poor ilmenites (Table 2) suggests that a significant Fe²⁺/Fe³⁺ ratio may be present in these hollandites. Despite the fact that this is not an important point we have decided to calculate Fe as FeO (Table 1). The priderites from Catalão I belong to the K₂FeTi₇O₁₆-BaFeTi₇O₁₆ series with relatively low contents of V- and Cr-end members. In a broader classification these titanates belong to the hollandite-group minerals (e.g. Mitchell and Meyer, 1989). The lowest K/(K + Ba) observed is

TABLE 1. *Contd.*

	4b	4c	4d	5a	5b	5c	6a	7a
Nb ₂ O ₅	0.00	0.04	0.56	0.39	1.98	1.89	0.47	0.24
SiO ₂	0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.00
TiO ₂	76.55	71.94	80.04	75.37	73.06	73.14	77.37	78.32
ZrO ₂	0.09	0.11	0.13	0.13	0.15	0.17	0.18	0.13
Al ₂ O ₃	0.04	0.05	0.04	0.08	0.56	0.57	0.06	0.07
V ₂ O ₃	0.41	1.42	1.36	2.65	1.88	1.98	2.30	2.47
Cr ₂ O ₃	0.04	0.47	0.07	4.10	0.73	0.23	3.55	2.19
MgO	0.28	0.15	0.02	0.56	0.22	0.16	0.75	0.79
CaO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MnO	0.01	0.00	0.00	0.03	0.00	0.00	0.00	0.00
FeO*	10.21	10.98	7.23	6.53	10.17	11.52	5.81	6.66
SrO	0.00	0.00	0.01	0.03	0.00	0.00	0.06	0.04
BaO	3.46	7.10	0.83	0.60	0.99	0.50	0.10	0.34
Na ₂ O	0.03	0.02	0.02	0.03	0.10	0.07	0.06	0.04
K ₂ O	8.68	6.96	8.77	9.10	8.31	8.40	8.84	8.94
Total	99.82	99.23	99.08	99.60	98.16	98.63	99.55	100.24
Nb	-	0.002	0.030	0.021	0.109	0.104	0.025	0.013
Si	-	-	0.001	0.000	0.001	0.000	-	-
Ti	6.992	6.797	7.136	6.741	6.709	6.694	6.850	6.902
Zr	0.005	0.007	0.008	0.007	0.009	0.010	0.010	0.008
Al	0.006	0.008	0.005	0.011	0.081	0.082	0.009	0.010
V	0.040	0.143	0.129	0.253	0.184	0.193	0.217	0.232
Cr	0.004	0.047	0.006	0.385	0.070	0.022	0.330	0.203
Mg	0.051	0.028	0.004	0.100	0.040	0.028	0.132	0.138
Ca	-	-	-	-	-	-	-	-
Mn	0.001	-	-	0.003	-	-	-	-
Fe	1.037	1.154	0.717	0.649	1.039	1.173	0.572	0.653
Sr	-	-	0.001	0.002	-	-	0.004	0.003
Ba	0.165	0.350	0.039	0.028	0.047	0.024	0.004	0.016
Na	0.007	0.005	0.004	0.007	0.024	0.018	0.013	0.009
K	1.345	1.116	1.326	1.381	1.295	1.305	1.327	1.337
Total**	9.654	9.654	9.405	9.589	9.608	9.653	9.494	9.522

* - Total iron as Fe²⁺.

** - Normalized to 16 oxygens.

a, b, a, ... - refer to different analyses in the same crystal.

1 to 4 - Associated with ilmenite and rutile.

5 to 7 - Associated with ilmenite and magnetite.

0.53 (Fig. 1). Two compositional populations are distinguished (Table 1 and Fig. 1): (a) high to low BaO (0.60 to 12.02%) and low V₂O₃ (0.41 to 1.51%), Cr₂O₃ (0.04 to 0.76%), and Nb₂O₅ (0.04 to 0.56%); (b) low BaO (0.1 to 0.99%) and high V₂O₃ (1.88 to 2.65%), Cr₂O₃ (0.23 to 4.1%), and Nb₂O₅ (0.24 to 1.98%). Despite these two populations it is possible to see in Fig. 1 that there is a fairly continuous compositional range. The high-Cr, -V, -Nb crystals are associated with magnetite. The Ba-rich group is not associated with magnetite. The Ba-rich priderites display a

relation between K/(K + Ba) and Fe/(Fe + Cr + V) indicating simultaneous variation of Ba and (Cr + V). This behaviour is not present in the magnetite-associated priderites (higher Cr and V contents) (Fig. 1)

Compositional zoning is present in all analysed crystals. The main variation is the substitution of K by Ba, although no regular zoning pattern could be identified. Fig. 2 is an example of zoning in priderite included in pyrite.

Except for the priderite richest in V and Cr, the majority of priderites from Catalão I are similar in

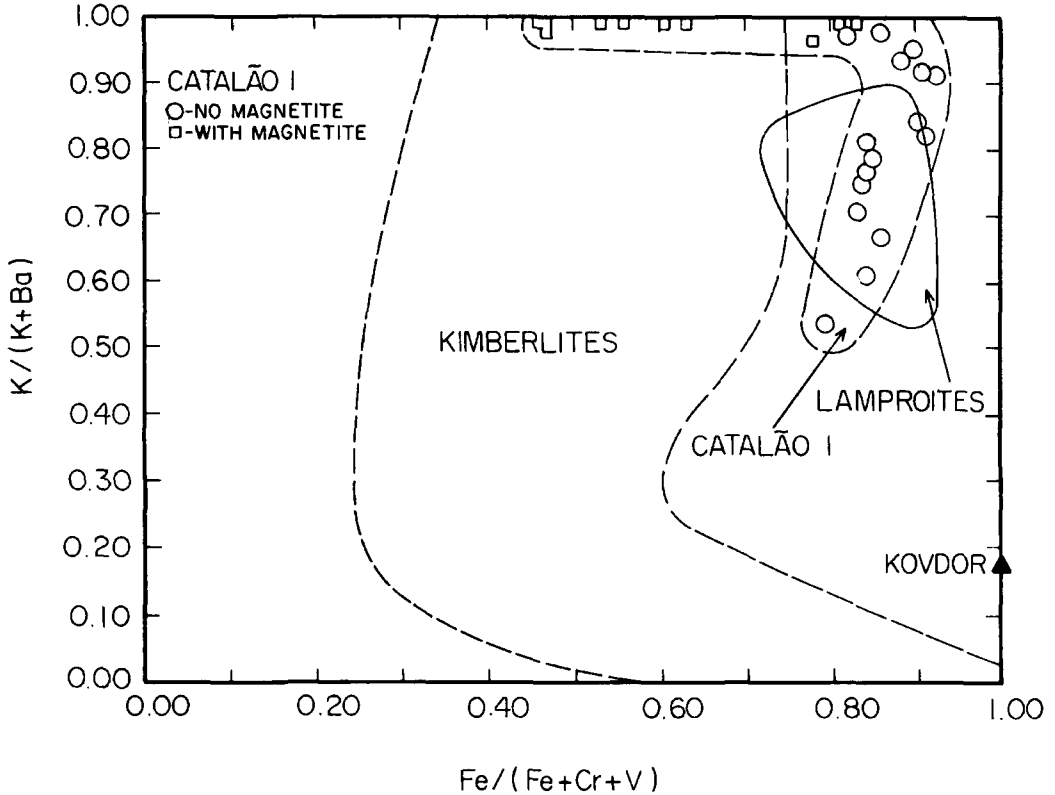


FIG. 1. Compositional variation of hollandite-group minerals (including priderites) from lamproites (Mitchell, 1985; Jaques *et al.*, 1986), kimberlites (Mitchell and Haggerty, 1986; Mitchell and Meyer, 1989; Mitchell, 1991), and carbonatites (Kovdor: Zhuravleva *et al.*, 1978, in Mitchell, 1991; Catalão I: this work).

TABLE 2. Ilmenite, rutile and magnetite

	1	2	3	4	5	6
Nb ₂ O ₅	0.88	0.56	2.82	3.30	0.00	0.00
SiO ₂	0.01	0.89	0.19	0.36	0.05	0.08
TiO ₂	54.75	53.46	93.66	92.64	0.86	0.98
ZrO ₂	0.14	0.09	0.13	0.16	0.22	0.16
Al ₂ O ₃	0.04	0.04	0.04	0.04	0.03	0.30
V ₂ O ₃	Nd	Nd	Nd	Nd	0.29	0.17
Cr ₂ O ₃	0.01	0.03	0.00	0.03	0.94	0.47
MgO	9.10	0.42	0.01	0.06	0.73	0.76
MnO	3.69	1.04	0.00	0.02	0.07	0.06
FeO	30.84	42.93	2.21	2.27	65.93	64.92
Fe ₂ O ₃ *	0.00	0.00	0.00	0.00	30.42	30.13
BaO	0.25	0.32	0.44	0.48	0.00	0.12
K ₂ O	0.01	0.11	0.20	0.24	0.03	0.10
Total	100.26	100.20	100.32	100.23	99.62	98.50

* - Calculated according to stoichiometry

1 and 2 - Ilmenite

5 and 6 - Magnetite

3 and 4 - Rutile

Nd - Not determined

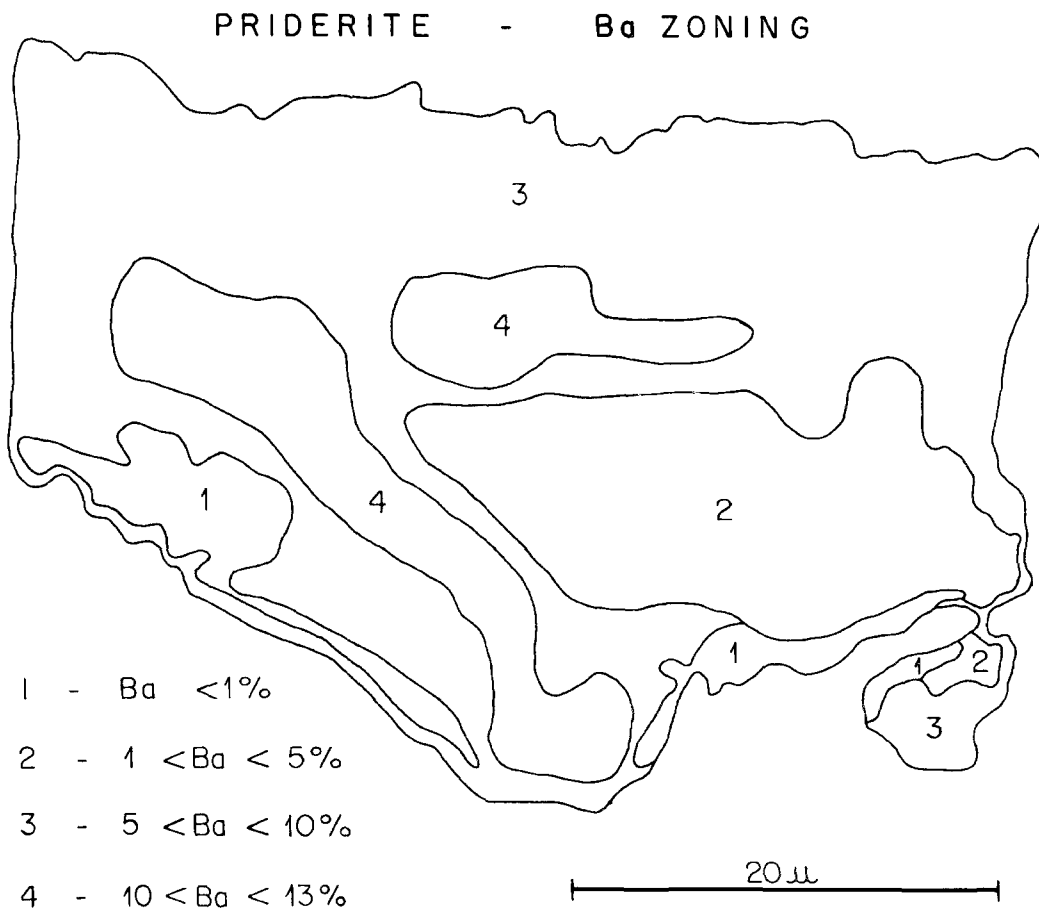


FIG. 2. Patchy zoning in a priderite crystal included in a pyrite grain. Figure based on backscattered electron image.

composition to those from lamproites (Fig. 1). Lamproitic priderites, however, are compositionally homogeneous within a given province and show no or very minor zoning (Mitchell and Lewis, 1983; Mitchell, 1985; Jaques *et al.*, 1986; Mitchell and Bergman, 1991). Hollandite from the Kovdor carbonatite is compositionally distinct from that of Catalão I; it contains no Cr or V and has a higher Ba content (Fig. 1). Barium and potassium titanates from kimberlites have a wide compositional field and little overlap with priderite from Catalão I and lamproites (Fig. 1). Cr- and V-rich priderite from Catalão I overlaps the Ba-poor composition field of kimberlite hollandites. Barium enrichment towards the margins of some of the kimberlite hollandites has been described previously (Mitchell and Meyer, 1989).

The compositions of ilmenite, rutile, and magnetite associated with priderite are presented in Table 2. Magnetite is almost pure, but ilmenite may contain up to 9.1% MgO, 3.69% MnO, and 0.88% Nb₂O₅. Rutile contains up to 5.1% Nb₂O₅, 2.66% FeO, 0.63% BaO, and 0.31% K₂O. The compositional variation of ilmenite, magnetite, phlogopite, and carbonates from the phlogopitites and carbonatites has been described elsewhere (Araújo and Gaspar, 1992, 1993).

Discussion

The nature of the occurrence and mineral association of priderite in Catalão I clearly indicates that it results from late-stage reactions. Its formation is related to the multi-stage

transformation of early formed dunites and clinopyroxenites into phlogopites. Priderite formation appears to be related to the last stages of this transformation, i.e. transformation of ilmenite lamellae when the magnetite host is replaced by pyrite or carbonate. In the case where magnetite is not present, priderite contains less Cr and V, and more Ba (Table 1). The absence of magnetite indicates more extensive reaction which may account for these chemical differences. The Ba content of priderite is certainly related to Ba-enrichment in late-stage fluids related to the carbonatite activity. A similar conclusion was drawn by Zhuravleva *et al.*, (1978; in Mitchell, 1991) regarding the origin of priderite in the Kovdor carbonatite. The priderite crystallization was the result of reaction of late-stage carbonate-rich magmas with early formed Ti-minerals.

Hollandite has been described by R. G. Platt from the Schryburt Lake carbonatite complex, Ontario, in a perovskite-spinel cumulate derived from an ultramafic lamprophyre (R. H. Mitchell, personal communication). Platt considers the mineral to be a primary phase. It is probable that priderite will be found in other carbonatite complexes. If hollandite-group minerals in carbonatite rock themselves are mostly derived from reactions related to late-stage liquids or fluids, one should expect that carbonatite titanates will display variable compositions. Hollandite-group minerals in kimberlites are late-stage groundmass minerals (Mitchell and Haggerty, 1986; Mitchell and Meyer, 1989; Mitchell, 1991) while priderite in lamproites are considered to be a primary phase that crystallized prior to most groundmass minerals (Mitchell, 1985; Jaques *et al.*, 1986; Mitchell and Bergman, 1991).

Acknowledgments

We thank Mineração Catalão de Goiás Ltda and Goiásfértil for access and sampling of mine pits and drill-hole cores; Henry O. A. Meyer and Maria S. Adusumilli for reviewing an initial draft of the manuscript; Roger H. Mitchell for a detailed and important revision of the manuscript, and the University of Brasília for financial support.

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