CATION PARTITIONING BETWEEN MINERALS OF THE TRIPHYLITE ± GRAFTONITE ± SARCOPSIDE ASSOCIATION IN GRANITIC PEGMATITES

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Key words: graftonite, triphylite, sarcopside, textures, cation partitioning

Introduction

Phosphates of the graftonite-beusite $(Fe^{2+},Mn^{2+},Ca)_3(PO_4)_2$, and the triphylite-lithiophilite $Li(Fe^{2+},Mn^{2+})PO_4$ solid-solution series, as well as sarcopside $(Fe^{2+},Mn^{2+},Mg)_3(PO_4)_2$, are primary phases that frequently occur together in intimate intergrowths in some granitic pegmatites. These and other phosphates generally appear in the intermediate zones and/or core margin of the pegmatites, mainly in nodules that vary widely in size range, from a few millimeters up to ~ 2m in diameter. Most commonly, silicates are absent or scarce inside these nodules, with quartz, muscovite and plagioclase the most commonly observed. Nevertheless, it is not unusual to observe some Fe-Mn-Mg-rich silicates, such as tourmaline, biotite and/or garnet, in close contact with these phosphates.

Despite studies on this phosphate association, which are relatively numerous, genetic relationships between these minerals are not fully understood. Consequently, phosphate assemblages from 11 pegmatites - Cañada, Pereña, La Fregeneda (Spain); Nossa Senhora de la Assunçao (Portugal); Cema, Santa Ana, La Empleada (Argentina); Boavista (Brasil); Palermo#1 (USA); and Tsaobismund, Abbabis (Namibia) - have been tested for cation partitioning of Fe-Mn-Mg by electron microprobe techniques, in order to determine some evidence for their genetic relationships, and for a discussion of pegmatite evolution in general. In this study we present the petrographic results and the preliminary data on partitioning of Fe-Mn-Mg between these phases.

Selected materials

The different localities where the studied phosphates occur and their main petrographic features are listed in Table 1. The Fe/(Fe+Mn) ratio of triphylite-lithiophilite (or its topotactic replacement product, ferrisicklerite-sicklerite) is given as well. A broad range for this ratio is presented by the studied samples, from Mn-rich members (Fe/(Fe+Mn) = 0.25 in La Empleada), to Fe-rich terms (Fe/(Fe+Mn) = 0.89 in Palermo #1). The Fe/(Fe+Mn) ratio in phosphates indicates the degree of fractionation of the initial pegmatitic melt as well as the evolutionary stage of pegmatite formation (e.g., Fransolet *et al.* 1986, Keller *et al.* 1994). This way, the phosphates with the lowest Fe/(Fe+Mn) ratios would have crystallized from the most evolved pegmatitic melt fractions. However, in some cases this ratio seems to be anomalously lower than expected, which is interpreted as a result of an impoverishment in Fe of the pegmatitic melt due to the previous crystallization of other Fe-rich phases, such as schörl or almandine (Roda-Robles *et al.* 2009). This could be the case in some of the studied samples, such as Cema, Santa Ana and La Empleada pegmatites. Anyway, the important differences in this ratio between the different samples, allow us to check if cation partitioning is influenced by changes in the Fe-Mn proportions.

TABLE 1. List of selected samples with coexisting members of the triphylite-lithiophilite and graftonite-beusite series and sarcopside, and main features of the hosting pegmatites.

PEGMATITE	Country Rock	Main minerals	Phosphate association	Phosphate textures	trph(fsck) Fe/(Fe+Mn)
Cañada (border) (Salamanca, Spain)	leucogranite & gabbro	Qtz, Pl, Kfs, Ms, tur, phos±Bt±Grt	fsck, grft, mgtr, jhsm, Mn-apt, xnt, allu, stnk	granoblastic texture an- to subhedral habit	0.74-0.78
Cañada(core margin) (Salamanca, Spain)	leucogranite & gabbro	Qtz, Pl, Kfs, Ms tur, phos	trph, srcp, fsck, grft, wolf, mtbr	srcp lamellae inside granoblastic trph granoblastic grft	0.80-0.83
Pereña (Salamanca, Spain)	leucogranite	Qtz, Pl, Kfs, Ms, brl, Bt, py, phos	fsck, het, srcp, grft, allu, stnk	srcp lamellae inside granoblastic fsck/het granoblastic grft	0.84-0.88
La Fregeneda (Salamanca, Spain)	micaschists	Qtz, Pl, Kfs, Ms	fsck, het, srcp, grft, allu, wyll-rsm, Mm-apt	srcp lamellae inside granobl. Fsck and grft	0.77-0.78
N^{a}S^a de Assunçao (Aguiar, Portugal)	two-mica granite	Qtz, Pl, Kfs, Ms, Bt, brl, phos	trpl, trph, srcp, isok, apt	srcp lamellae inside granoblastic trph	0.50-0.53
Cema (San Luis, Argentina)	schists	Qtz, Pl, Kfs, Ms, tur, Grt, brl, phos, spd	sck, beus, var, qng, apt, joos	granoblastic sck and beus	0.46-0.48
Santa Ana (San Luis, Argentina)	micaschists	Qtz, Pl,Kfs, Ms, tur, Grt, brl, phos, crd	ltph, sck, beus, qng, apt,	ltph/sck lamellae inside beus	0.35-0.40
La Empleada (San Luis, Argentina)	micaschists	Qtz, Pl, Kfs, Ms, tur, Grt, brl, phos, crd	ltph, sck, srcp, beus, qng, var	srcp lamellae inside ltph/sck	0.25-0.28
Tsaobismund (Karibib, Namibia)	Kfs-bearing quartzites	Qtz, Pl, Kfs, Ms, tur, brl, col, phos	trph, fsck, het, trpl, srcp, apt, allu, beus	srcp and beus irregular grains or srcp lamellae inside trph/fsck	0.63-0.64
Abbabis I (Karibib, Namibia)	micaschists	Qtz, Pl, Ms, brl, col, phos	fsck, het, srcp, arroj, Fe-wyll	srcp lamellae inside granoblastic trph	0.84
Palermo#1 (New Hampshire, USA)	schists	Qtz, Pl, Kfs, Ms, brl, phos±tur	grft, trph, fsck,	trph/fsck lamellae inside grft. granoblastic grft and trph/fsck	0.74-0.82
Palermo#1 (New Hampshire, USA)	schists	Qtz, Pl, Kfs, Ms, brl, phos±tur	grft, trph, fsck, srcp,	trph/fsck lamellae inside grft. srcp lamellae inside trph	0.89
Boavista (Galiléia, Brasil)	schists	Qtz, Pl, Kfs, Ms, brl, spd, phos	trph, srcp	srcp lamellae inside granoblastic trph	0.79-0.80

Symbols of rock-forming minerals taken from Kretz (1983)

Members of the triphylite-lithiophilite series (or ferrisicklerite-sicklerite) are present in all the studied pegmatites. However, members of the graftonite-beusite series and sarcopside are only present in some of them (Table 1). By this way, three different associations have been distinguished: 1) trph/fsck + grft + srcp, where the three phases are present; 2) trph/fsck + grft, where sarcopside has not been identified; and 3) trph/fsck + srcp, where members of the graftonite-beusite series are absent. Textures in every association may be different. In associations 1 and 2 the most common is that triphylite-lithiophilite and graftonite-beusite members appear together in discrete grains of granoblastic texture (Cañada border, Cañada core margin, Pereña, La Fregeneda, Cema, Tsaobismund, and Palermo#1), whereas an intergrowth of graftonite containing coarse lamellae of triphylite-lithiophilite, or its topotactic replacement products ferrisicklerite-sicklerite, is less frequently observed (Palermo#1, Santa Ana and La Empleada). In this case most lamellae are platy and form a single set that share a quite uniform optical orientation, enclosed in monocrystalline graftonite, giving rise to a laminated parallel intergrowth. In associations 1 and 3, the triphylite hosts lamellae of sarcopside. These lamellae usually show two preferential crystallographic orientations, and are restricted just to the triphylite, usually inside it (Cañada core margin, Pereña, La Fregeneda, Nossa Senhora de la Assunçao, La Empleada, Tsaobismund, Abbabis, Palermo#1 and Boavista) and, more rarely, as a rim between triphylite and graftonite (Cañada core margin and Palermo#1). Sarcopside lamellae are usually lenticular, expanding inward and pinching out at the boundary of triphylite with graftonite in association 1.

ANALYTICAL METHODS

Representative phosphates were collected from the 11 pegmatites listed in Table 1. Mineral identification was carried out by a combination of petrographic, powder XRD, and EPM techniques. Close to 850 chemical analyses were performed at the LMTG (Laboratoire des Mécanismes et Transferts en Géologie, Toulouse, France), with a Camebax SX 50 electron microprobe. The analytical conditions were an operating voltage of 15 kV and a beam current of 20 nA. Standards used for the phosphates were: CaF_2 for F, albite for Na, orthoclase for K, corundum for Al, andradite for Fe, Ca and Si, graftonite for Mn and P, titanite for Ti, olivine for Mg, and ZnS for Zn.

TABLE 2. Representative KD and Fe/(Fe+Mn) ratios from the studied phosphates. Associations: 1 = trph/fsck + grft + srcp; 2 = trph + grft; 3 = trph + srcp.

ASSOC LOCALITY	1 Cañada Core m.	1 Pereña	1 Fregen.	1 Emplea.	1 Tsaob.	1 Pal.#1	2 Cañada border	2 Cema	2 S. Ana	2 Pal.#1	3 Cañada Core m.	3 NSAss.	3 Abbabis	3 Boavista
Fe/(Fe+Mn)	0.83	0.79	0.77	0.25	0.64	0.89	0.77	0.46	0.37	0.79	0.80	0.52	0.84	0.79
$KD_{Fe\ grft/trph}$	0.79	0.75	0.76	-	-	0.88	0.90	0.80	0.80	0.83	-	-	-	-
$KD_{Mn\ grft/trph}$	2.33	1.95	1.85	-	-	2.51	2.44	1.27	1.32	1.91	-	-	-	-
$KD_{Mg\ grft/trph}$	0.24	0.18	0.17	-	-	0.29	0.25	0.28	0.30	0.31	-	-	-	-
$KD_{Fe\ grft/srcp}$	0.78	0.78	0.78	-	-	0.85	-	-	-	-	-	-	-	-
$KD_{Mn\ grft/srcp}$	2.10	1.70	1.69	-	-	2.30	-	-	-	-	-	-	-	-
$KD_{Mg\ grft/srcp}$	0.39	0.25	0.27	-	-	0.50	-	-	-	-	-	-	-	-
$KD_{Fe\ srcp/trph}$	1.01	0.96	0.98	1.43	1.04	1.03	-	-	-	-	1.01	1.02	1.13	1.04
$KD_{Mn\ srcp/trph}$	1.11	1.15	1.09	0.91	0.98	1.09	-	-	-	-	1.06	0.98	1.19	1.08
$KD_{Mg\ srcp/trph}$	0.61	0.75	0.65	0.49	0.54	0.58	-	-	-	-	0.57	0.54	0.56	0.53

FE-MN-MG PARTITIONING AND DISCUSSION

Correlated pairs of data have been used to calculate empirical partition coefficients on molar basis (KD). For associations 2 and 3 the analyses used in these calculations were made on common interfaces between two phosphates (trph(fsck)/grft and trh(fsck)/srcp respectively). In association 1, this was done in the same way for these pairs of phosphates. However, sarcopside and graftonite do not exhibit common interfaces. In that case, to calculate the K_D we used pairs of data from the same sample. No chemical zoning has been observed in any of the studied samples, permitting us to use these data in such a way.

The evaluated mole fractions are X_{Fe} = Fe/(Fe+Mn+Mg), X_{Mn} = Mn/(Fe+Mn+Mg) and X_{Mg} = Mg/(Fe+Mn+Mg). The partition coefficients are defined as follows: $KD_{M\ A/B} = X_A/X_B$, where M = Fe, Mn or Mg; A = graftonite or sarcopside, and B = triphylite or sarcopside (Table 2). Plots of the mole fractions (Fig. 1) let us draw some conclusions in relation to the distribution of Fe, Mn and Mg among coexisting phases. In all the cases, the crystal structure of graftonite shows a strong preference for Mn. This preference seems to decrease as the Fe/(Fe+Mn) decreases. This way, in the samples from Santa Ana and Cema, where the phosphates correspond to the Mn-rich terms, the $KD_{Mn\ grft/trph}$ are in the range 1.27-1.32, whereas for the rest of the occurrences, which are Fe-richer, $KD_{Mn\ grft/trph}$ values are significantly higher, ranging from 1.75 to 2.57. Fe is preferentially partitioned into triphylite-lithiophilite and sarcopside over graftonite, with $KD_{Fe\ grft/trph}$ in the range 0.75-0.88 and $KD_{Fe\ grft/srcp}$ in the range 0.77-0.93. For the pairs trph-srcp there is not a clear tendency for the distribution of Fe and Mn as, in general, KD are quite close to unity. However, mainly in the association 1, where the three phases coexist, there is a tendency to increase the $KD_{Mn\ srcp/trph}$ with increasing Fe/(Fe+Mn) (R^2 = 0.640), whereas the $KD_{Fe\ srcp/trph}$ tends to decrease (R^2 = 0.857). Finally, Mg is clearly partitioned preferentially into triphylite, with graftonite the Mg-poorest of the three phases, with $KD_{Mg\ grft/trph}$ in the range 0.17-0.35, $KD_{Mg\ grft/srcp}$. in the range 0.25-0.53 and $KD_{Mg\ srcp/trph}$ in the range 0.17-0.77.

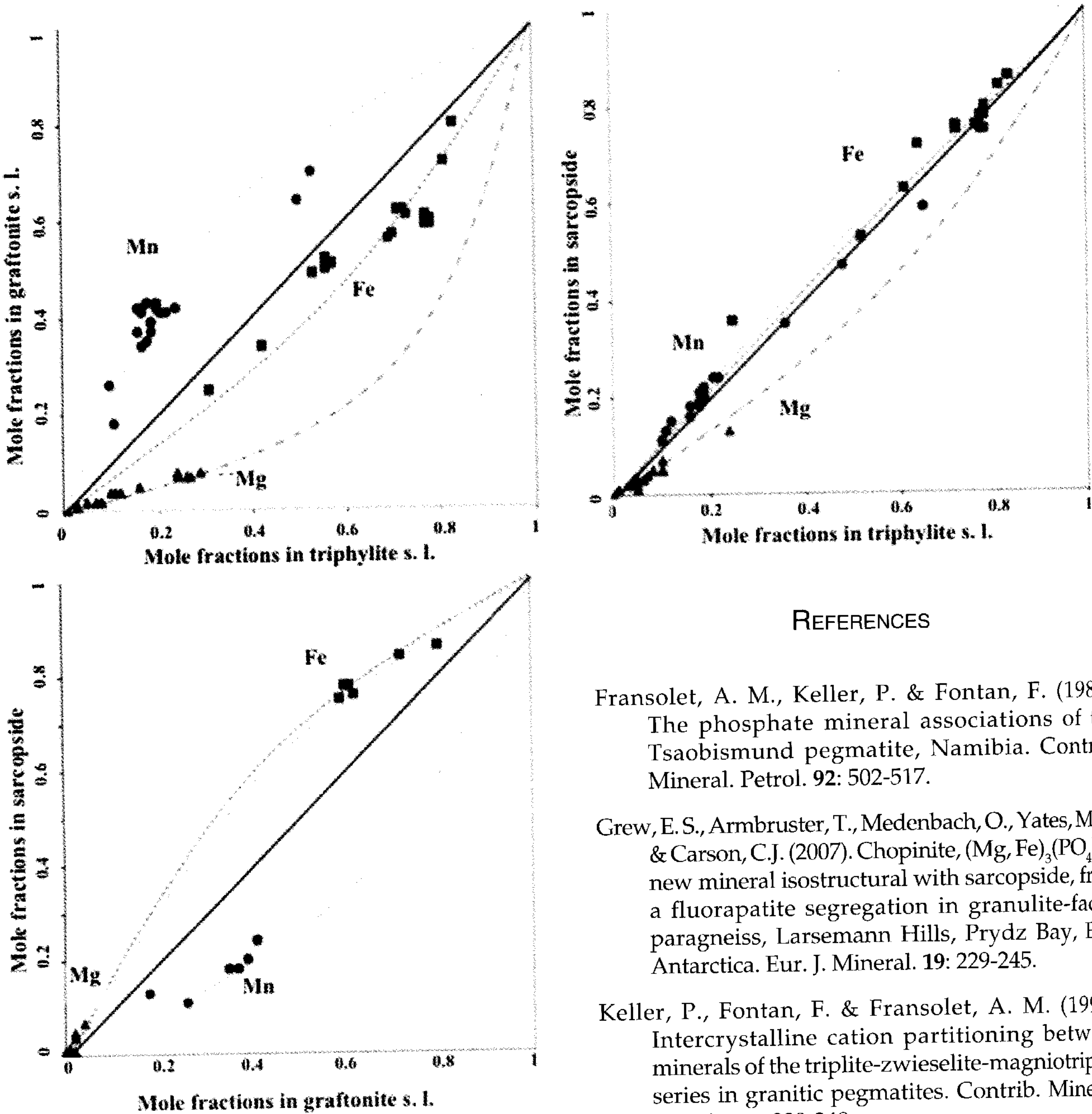

FIGURE 1. Partitioning of Fe, Mn and Mg between coexisting sarcopside and members of the triphylite and graftonite series. Legend: squares = Fe^{2+}; circles = Mn^{2+}; and triangles = Mg

The strong preference of minerals of the graftonite-beusite series for Mn was already reported in the literature (Smeds *et al.* 1998), and is certainly due to the presence of the large 7-coordinated *M*(1) site in the graftonite structure, which is able to contain significant amounts of Ca (Wise *et al.* 1990). On the other hand, the preference of the sarcopside structure for Mg, compared to graftonite, explains the recent discovery of chopinite, $Mg_3(PO_4)_2$, in granulite-facies rocks from East Antarctica (Grew *et al.* 2007).

AKNOWLEDGMENTS

This study has been carried out with the support of the UPV/EHU (project nº 08/02)

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