Mineralogical Magazine, December 2018, Vol. 82(6), pp. 1301–1306

Classification of the minerals of the graftonite group

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[*Received 5 September 2017; Accepted 11 November 2017; Associate Editor: Stuart Mills*]

ABSTRACT

A classification and nomenclature scheme has been approved by the International Mineralogical Association Commission on New Minerals, Nomenclature and Classification for the minerals of the graftonite group. The crystal structures of these minerals have three distinct sites that are occupied by Fe^{2+}, Mn^{2+} and Ca^{2+}. These sites have coordination numbers [8], [5] and [6], and these differences lead to very strong order of Fe^{2+}, Mn^{2+} and Ca^{2+} over these sites. As a result of this strong order, the following compositions have been identified as distinct species: graftonite: $FeFe_2(PO_4)_2$; graftonite-(Ca): $CaFe_2(PO_4)_2$; graftonite-(Mn): $MnFe_2(PO_4)_2$; beusite: $MnMn_2(PO_4)_2$; and beusite-(Ca): $CaMn_2(PO_4)_2$.

Keywords: graftonite group, classification, nomenclature, beusite.

Introduction

Graftonite, ideally $Fe^{2+}_3(PO_4)_2$, was described from a granitic pegmatite in New Hampshire by Penfield (1900). Beus (1950) and Brooks and Shipway (1960) reported a graftonite-like mineral with Mn^{2+} dominant over Fe^{2+}, and beusite, ideally $Mn^{2+}_3(PO_4)_2$, was formally described as a distinct species from the pegmatites of the San Luis area, Argentina, by Hurlbut and Aristarain (1968). Graftonite and beusite form a solid-solution series and are common as late-stage accessory minerals in complex granite pegmatites (e.g. Fransolet, 1977; Fransolet *et al.*, 1986; Lahti, 1981; Wise and Černý, 1990; Wise *et al.*, 1990; Černý *et al.*, 1998; Smeds *et al.*, 1998; Pieczka, 2007; Guastoni *et al.*, 2007; Vignola *et al.*, 2008; Galliski *et al.*, 2009; Ercit *et al.*, 2010). They also occur as constituents of phosphate-oxide inclusions in IIIAB iron meteorites (Bild, 1974; Steele *et al.*, 1991; Olsen *et al.*, 1999), and Stalder and Rozendaal (2002) reported graftonite as a primary phase in a P-rich iron formation. The chemical composition of the graftonite series is written as $(Fe^{2+}, Mn^{2+}, Ca)_3(PO_4)_2$, and although previously considered a minor constituent, Ca plays an important role in the structure of these minerals.

The crystal structures of graftonite and beusite were solved by Calvo (1968) and Hurlbut and Aristarain (1968), respectively. Steele *et al.* (1991) and Wise *et al.* (1990) refined the structures of Ca-free and Ca-rich beusite, respectively. Nord (1982) and Nord and Ericsson (1982*a*) looked at solid solution and Fe–Mn order in synthetic phases along the join graftonite–beusite, and Nord and Ericsson (1982*b*) looked at Fe^{2+}–(Ca^{2+}, Mg^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}) order in synthetic graftonite-structure phases by Mössbauer spectroscopy.

Structural considerations

The structure of graftonite–beusite is a dense framework of polyhedra, with extensive edge- and corner-sharing (Hawthorne, 1998; Huminicki and Hawthorne, 2002) between phosphate tetrahedra and [5]- to [8]-coordinated divalent-metal-oxide polyhedra. There has been extensive discussion as to the coordination numbers of the $M(1)$, $M(2)$ and $M(3)$ sites in the graftonite–beusite structure; detailed examination of the issue by Tait *et al.* (2013) led to the following conclusion: $M(1) = [8]$,

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https://doi.org/10.1180/minmag.2017.081.092

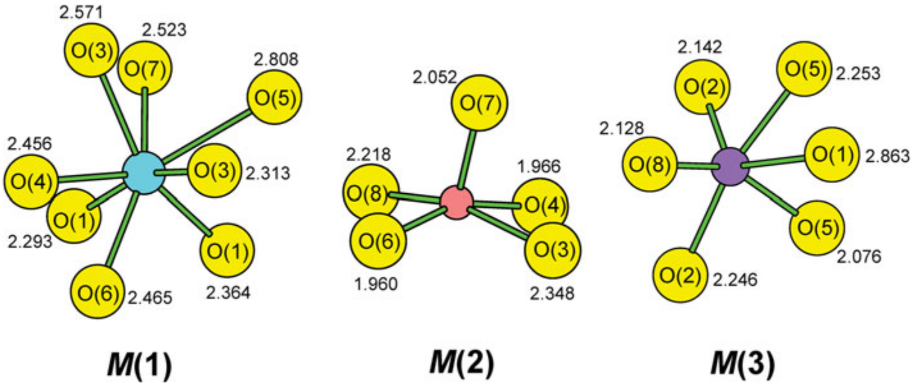

FIG. 1. The $M(1)$, $M(2)$ and $M(3)$ sites in the graftonite–beusite structure; distances are from beusite-(Ca) (Hawthorne *et al.*, 2018).

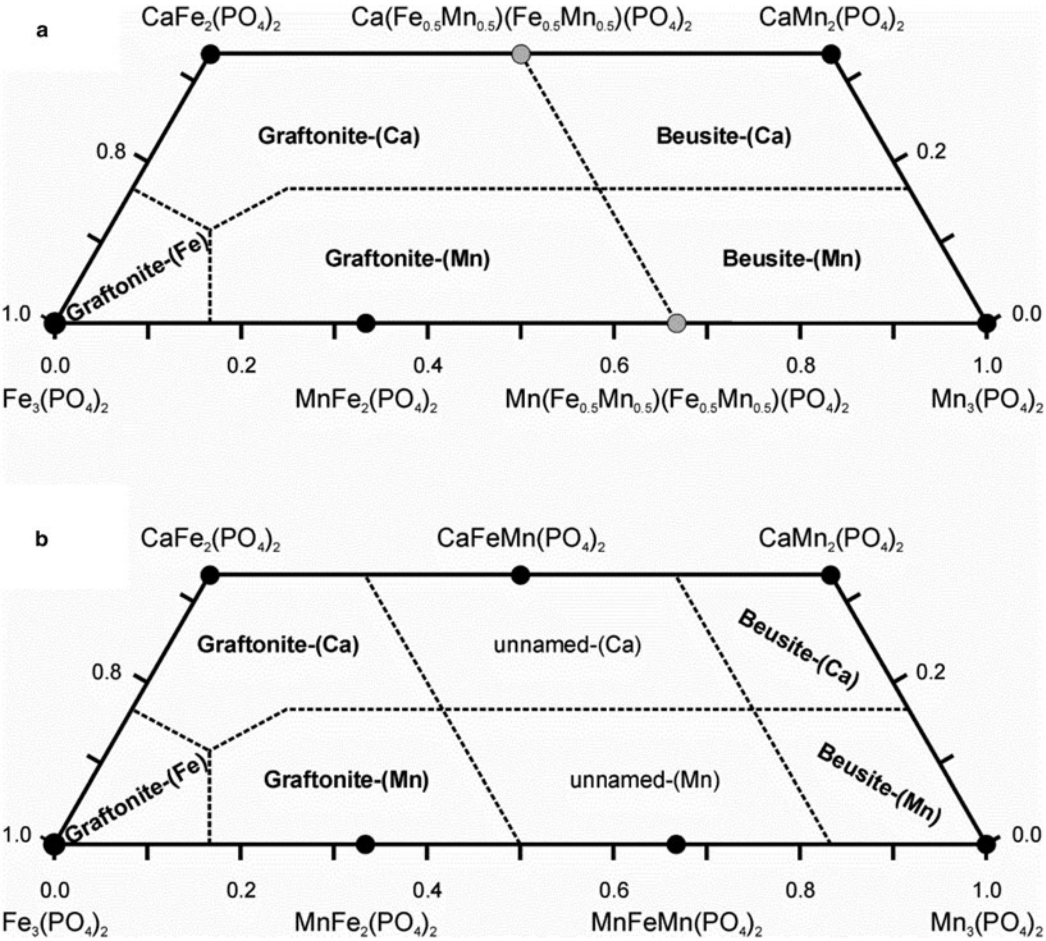

FIG. 2. (*a*) Classification based on (Fe,Mn) disorder over $M(2)$ and $M(3)$; (*b*) classification based on (Fe,Mn) order over $M(2)$ and $M(3)$.

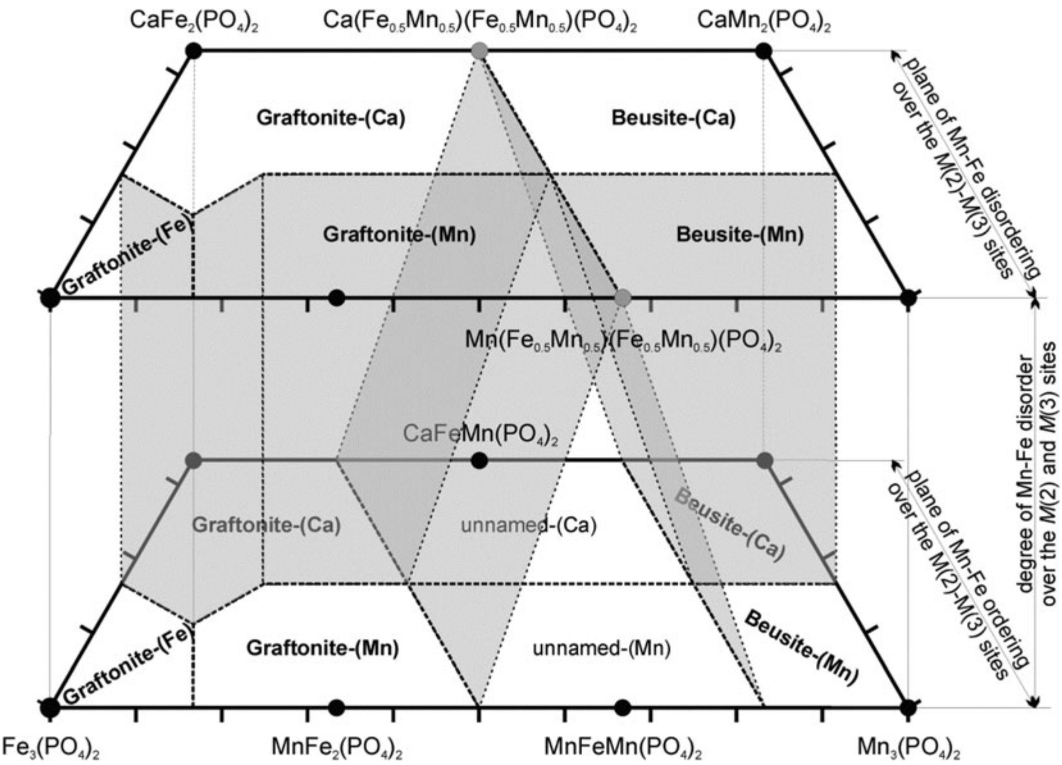

FIG. 3. Classification based on (Fe,Mn) order–disorder over *M*(2) and *M*(3).

M(2) = [5] and *M*(3) = [6] (Fig. 1). All authors who have worked on the structures of graftonite–beusite minerals and their synthetic analogues have noted very strong ordering of cations over the *M*(1), *M*(2) and *M*(3) sites. In particular, in the Ca-rich beusite of Wise *et al*. (1990), all Ca was completely ordered at the *M*(1) site and the site was dominated by Ca^{2+}: $Ca_{0.98}Mn_{0.02}$, which warrants recognition as new species: $Ca(Mn,Fe)_2(PO_4)_2$. However, inspection of all crystallographic work on these structures shows strong order of Mn^{2+} and Fe^{2+} over the *M* sites, indicating that other distinct species are also possible. Mössbauer spectroscopy shows that Mn–Fe ordering over the *M*(1) and *M*(3) sites is not complete, and we may recognize two different schemes of order for Ca^{2+} completely ordered at *M*(1): [1] Mn^{2+} enters *M*(1), and Mn^{2+} and Fe^{2+} are disordered over the *M*(2) and *M*(3) sites; and [2] Mn^{2+} fills the sites in the order *M*(1) > *M*(3) > *M*(2) with Fe^{2+} making up the difference. These two schemes are illustrated in Figs 2*a* and 2*b*. The two schemes shown in Fig. 2 are end-members of an order–disorder series. This is illustrated in Fig. 3, which incorporates a third axis as representing the degree of disorder of Mn^{2+} and Fe^{2+} over the *M*(2) and *M*(3) sites.

Classification

It is desirable to develop a classification scheme that is useful to petrology as well as mineralogy, and thus a classification scheme should not involve details of cation order that depend on techniques (such as Mössbauer spectroscopy) that are not very widespread in the mineralogy community. Thus we have based the classification of graftonite-group minerals on Fig. 2*a*, in which the mineral formula is based on 8 O^{2-} anions per formula unit and: (1) Ca^{2+} is assigned completely to the *M*(1) site, and any deficiency at *M*(1) is filled first with Mn^{2+} and then with Fe^{2+}; and (2) Mn^{2+} and Fe^{2+} are considered as disordered over the *M*(2) and *M*(3) sites.

The resulting divisions of the compositional field are shown in Fig. 4*a*.

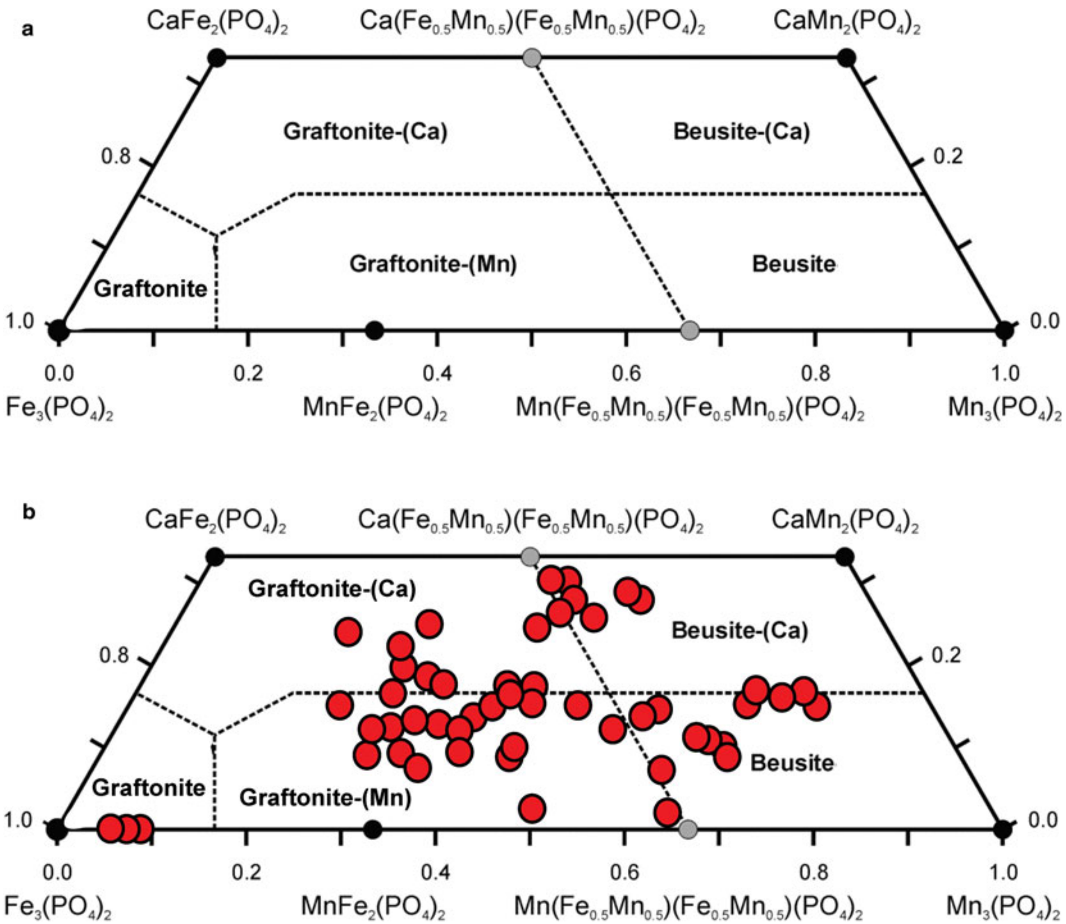

FIG. 4. (*a*) Approved classification of the minerals of the graftonite–beusite group; (*b*) compositions of graftonite-group minerals from Brooks and Shipway (1960), Hurlbut and Aristarain (1968), Olsen and Fredriksson (1966), Fransolet *et al*. (1986), Wise and Černý (1990), Wise *et al.* (1990), Staněk (1991), Černý *et al*. (1998), Smeds *et al*. (1998), Pieczka (2007) and Tait *et al*. (2013).

End-member compositions and mineral names

These are listed in Table 1. Graftonite was described by Penfield (1900) and beusite was described by Hurlbut and Aristarain (1968); thus in terms of a group name, graftonite has priority (Mills *et al.*, 2009). Moreover, the un-suffixed names graftonite and beusite are retained in accord with guidelines from the Commission on New Minerals, Nomenclature and Classification for the use of

TABLE 1. End-member formulae and names for the minerals of the graftonite group.

End-member formula	Name
$FeFe_2(PO_4)_2$	Graftonite
$CaFe_2(PO_4)_2$	Graftonite-(Ca)
$MnFe_2(PO_4)_2$	Graftonite-(Mn)
$MnMn_2(PO_4)_2$	Beusite
$CaMn_2(PO_4)_2$	Beusite-(Ca)

suffixes and prefixes in mineral nomenclature, and for the preservation of historical names (Hatert *et al*., 2013). The classification scheme proposed in Table 1 and Fig. 4*a* introduce three new mineral species: graftonite-(Ca), graftonite-(Mn) and beusite-(Ca). Figure 4*b* shows that compositional data for minerals from the literature occupy all five fields. This classification and nomenclature scheme has been approved by the International Mineralogical Association Commission on New Minerals, Nomenclature and Classification (memorandum 66–SM/17, Hålenius *et al.*, 2017).

Acknowledgements

This work was supported by a Canada Research Chair in Crystallography and Mineralogy, and Research Tools and Equipment, Major Facilities Access and Discovery Grants from the Natural Sciences and Engineering Research Council of Canada to FCH, and by a National Science Centre (Poland) grant 2015/17/B/ST10/03231 to AP.

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