The dumortierite supergroup. I. A new nomenclature for the dumortierite and holtite groups

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ABSTRACT

Although the distinction between magnesiodumortieite and dumortierite, i.e. Mg *vs.* Al dominance at the partially vacant octahedral Al1 site, had met current criteria of the IMA Commission on New Minerals, Nomenclature and Classification (CNMNC) for distinguishing mineral species, the distinction between holtite and dumortierite had not, since Al and Si are dominant over Ta and (Sb,As) at the Al1 and two Si sites, respectively, in both minerals. Recent studies have revealed extensive solid solution between Al, Ti, Ta and Nb at Al1 and between Si, As and Sb at the two Si sites or nearly coincident (As,Sb) sites in dumortierite and holtite, further blurring the distinction between the two minerals.

This situation necessitated revision in the nomenclature of the dumortierite group. The newly constituted dumortierite supergroup, space group *Pnma* (no. 62), comprises two groups and six minerals, one of which is the first member of a potential third group, all isostructural with dumortierite. The supergroup, which has been approved by the CNMNC, is based on more specific end-member compositions for dumortierite and holtite, in which occupancy of the Al1 site is critical.

(1) Dumortierite group, with Al1 = Al^{3+}, Mg^{2+} and $\square$, where $\square$ denotes cation vacancy. Charge balance is provided by OH substitution for O at the O2, O7 and O10 sites. In addition to dumortierite, endmember composition $AlAl_6BSi_3O_{18}$, and magnesiodumortierite, endmember composition $MgAl_6BSi_3O_{17}(OH)$, plus three endmembers, "hydroxydumortierite", $\square Al_6BSi_3O_{15}(OH)_3$ and two Mg-Ti analogues of dumortierite, $(Mg_{0.5}Ti_{0.5})Al_6BSi_3O_{18}$ and $(Mg_{0.5}Ti_{0.5})Mg_2Al_4BSi_3O_{16}(OH)_2$, none of which correspond to mineral species. Three more hypothetical endmembers are derived by homovalent substitutions of Fe^{3+} for Al and Fe^{2+} for Mg.

(2) Holtite group, with Al1 = Ta^{5+}, Nb^{5+}, Ti^{4+} and $\square$. In contrast to the dumortierite group, vacancies serve not only to balance the extra charge introduced by the incorporation of pentavalent and quadrivalent cations for trivalent cations at Al1, but also to reduce repulsion between the highly charged cations. This group includes holtite, endmember composition $(Ta_{0.6}\square_{0.4})Al_6BSi_3O_{18}$, nioboholite (2012-68), endmember composition $(Nb_{0.6}\square_{0.4})Al_6BSi_3O_{18}$, and titanoholtite (2012-69), endmember composition $(Ti_{0.75}\square_{0.25})Al_6BSi_3O_{18}$.

(3) Szklaryite (2012-70) with Al1 = $\square$ and an endmember formula $\square Al_6BAs_3^{3+}O_{15}$. Vacancies at Al1 are caused by loss of O at O2 and O7, which coordinate the Al1 with the Si sites, due to

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replacement of Si^{4+} by As^{3+} and Sb^{3+}, and thus this mineral does not belong in either the dumortierite or the holtite group. Although szklaryite is distinguished by the mechanism introducing vacancies at the Al1 site, the primary criterion for identifying it is based on occupancy of the Si/As,Sb sites: $(As^{3+} + Sb^{3+}) > Si^{4+}$ consistent with the dominant-valency rule. A Sb^{3+} analogue to szklaryite is possible.

Introduction

As presently constituted, the dumortierite group comprises three minerals: dumortierite, $(Al,\square)Al_6BSi_3O_{16}(O,OH)_2$, magnesiodumortierite, $(Mg,\square)Al_6BSi_3O_{16}(O,OH)_2$, and holtite, $(Al,Ta,\square)Al_6B(Si,Sb,As)_{\Sigma3}O_{15}(O,OH,\square)_{\Sigma3}$, where $\square$ denotes cation or anion vacancy. Dumortierite is second only to tourmaline-supergroup minerals as the most abundant B-bearing phase in metamorphosed pelitic and psammitic rocks, aluminous metasomatic rocks and granitic plutonic rocks (Grew, 2002). It was first reported in 1880 from pegmatitic veins near Lyon, France (Bertrand, 1880; Gonnard, 1881), and named for the French palaeontologist Eugène Dumortier. It took many years for the full complexity of dumortierite chemistry to be revealed, e.g. that it contains essential B (Schaller, 1905), and that its cation and OH contents are non-stoichiometric (Golovastikov, 1965; Moore and Araki, 1978). Until about 1995, P_2O_5, MgO, TiO_2, Fe_2O_3 and FeO were thought to be the most abundant constituents other than H_2O, B_2O_3, Al_2O_3 and SiO_2 (Grew, 2002), but more recent work has shown that As_2O_3, Sb_2O_3, Ta_2O_5 and Nb_2O_5 are also present in substantial quantities, and a few samples contain Bi, presumably as Bi^{3+} (e.g. Groat *et al.*, 2001, 2012; Cempírek and Novák, 2005; Borghi *et al.*, 2004; Vaggelli *et al.*, 2004; Cempírek *et al.*, 2010; Pieczka *et al.*, 2011).

Magnesiodumortierite was reported as the Mg-dominant analogue of dumortierite from ultra-high-pressure rocks at Dora Maira in the Italian Alps (Chopin *et al.*, 1995; Ferraris *et al.*, 1995). The most magnesian compositions reported by Visser and Senior (1991 and unpublished data) and by Kihle (1989 and unpublished data) in dumortierite from the Bamble Sector, Norway, might also qualify as magnesiodumortierite (Chopin *et al.*, 1995; Grew, 2002), but to date no other occurrence has been reported.

Holtite was first described from alluvial deposits formed from pegmatite at Greenbushes, Western Australia (Pryce, 1971) and named for Harold E. Holt, Prime Minister of Australia from 1966 to 1967, and its crystal structure refined by Hoskins *et al.* (1989). It is known only from complex granitic pegmatites, having been reported from three other localities: Voron'i Tundry, Kola Peninsula, Russia (Voloshin *et al.*, 1977; 1987; Voloshin and Pakhomovskiy, 1988); Szklary, Lower Silesia, Poland (Pieczka and Marszałek, 1996; Pieczka *et al.*, 2011), and Virorco, San Luis range, Argentina (Galliski *et al.*, 2012). In contrast to the situation for many new minerals described in the last 50 years, none of the four constituents that distinguish holtite from dumortierite is dominant at a specific crystallographic site, e.g. Si is dominant over Sb^{3+} and As^{3+} at the two tetrahedral sites and Al is dominant over Ta, Nb and vacancy at the Al1 site in both minerals. Voloshin *et al.* (1977, 1987) introduced the terms "holtite I" and "holtite II" for clusters of holtite compositions differing in (As+Sb) content, but compositions from other localities, particularly the Szklary pegmatite, filled the apparent gap between the two compositions (Pieczka *et al.*, 2011). Groat *et al.* (2009) suggested the clustering could be an artifact resulting from there being two generations of holtite formed in different chemical environments at Voron'i Tundry, rather than from a crystallographic control. Moreover, the compositional range in holtite from the Szklary pegmatite extended to higher (Sb+As) contents than the high (Sb+As) composition of "holtite II" (Pieczka *et al.*, 2011).

In the absence of a rigorous definition, the term holtite was being applied indiscriminately to an ever-widening compositional range, while dumortierite was found to contain substantial amounts of the elements that supposedly distinguish holtite from dumortierite. The end result is that distinction between holtite and dumortierite has become blurred, and consequently, we are recommending a new classification of the dumortierite group in which the minerals are distinguished on the basis of crystal chemistry and consistently with current CNMNC practice.

Crystal structure of dumortierite and related minerals

The crystal structure of dumortierite (Fig. 1), space group *Pnma* (no. 62), was described by Golovastikov (1965) and Moore and Araki (1978) as a design on the semi-regular planar net {6·4·3·4}, which Moore and Araki (1978) showed can be broken down into four regions: (1) [AlO$_3$] chains of face-sharing octahedra (the Al1 sites) with circumjacent "pinwheels" of six SiO$_4$ tetrahedra, two Si1 and four Si2 sites; (2) [Al$_4$O$_{12}$] cubic close-packed chains parallel to the [100] direction, containing the Al2 and Al3 octahedral sites, that are joined to equivalent chains by reflection at the O1 corners of the Al2 octahedra to form [Al$_4$O$_{11}$] sheets oriented parallel to (001); (3) [Al$_4$O$_{12}$] double-chains parallel to the [100] direction containing the Al4 octahedral sites with some face-sharing; and (4) BO$_3$ triangles. The Al1−Al1 distance is ~2.35 Å, which is unusually short for face-sharing octahedra, and the Al1 site is on average 75% occupied by Al (e.g. Moore and Araki, 1978). The Al1 face-sharing chains are disor-

dered, which results in an average chain length that can be adjusted to fit the repeat distance of the remaining octahedral framework in the structure (Moore and Araki, 1978). Evans *et al.* (2012) reported that when there is minor substitution for Al at Al1, three distinct sub-sites of Al1 could be distinguished depending on which adjacent Al1 sites were occupied; each sub-site was found to be ~¼ occupied. Such ordering would not be expected in compositions with more substitution at Al1. Although Al cations in individual face-sharing Al1 octahedral chains are ordered, cations from chain to chain are disordered, preserving *Pnma* symmetry.

Groat *et al.* (2012) reported splitting of the two (As, Sb) sites into four distinct As1, Sb1, As2 and Sb2 positions, and the single Al1 site split into three Al1a, Al1 and Al1b positions whose occupancies refined to Al1 > Al1a > Al1b in dumortierite containing a significant amount of As and Sb, but relatively little Ta and Nb. The unequal occupancies suggest that the hexagonal tunnels contain a disordered mix of face-sharing octahedral dimers, trimers and longer units separated by vacancies. The splitting does not
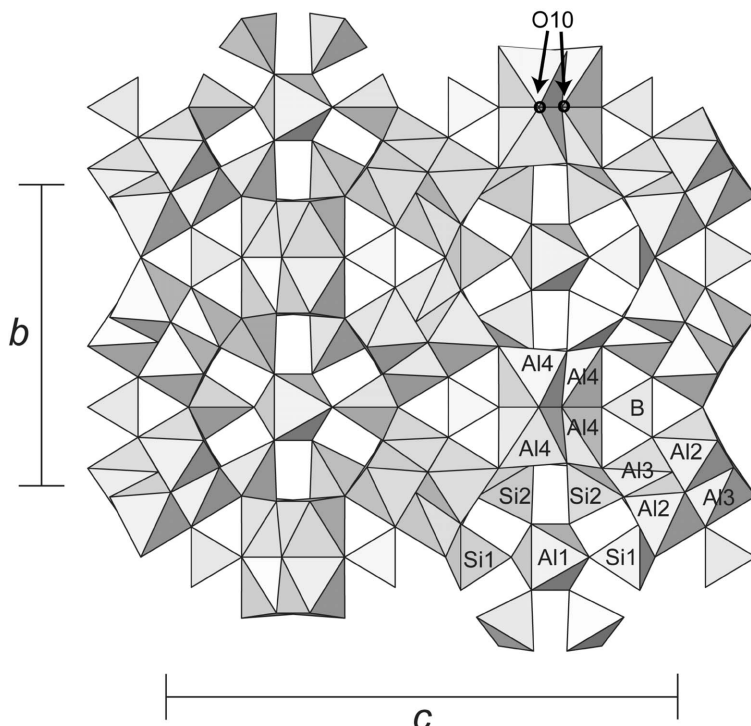

FIG. 1. The crystal structure of dumortierite viewed down the *a* axis. *Pnma* setting (from Groat *et al.*, 2009, 2012).

result in a superstructure, which was reported in a dumortierite-like mineral found as fibres in rose quartz (Applin and Hicks, 1987; Goreva *et al.*, 2001; Ma *et al.*, 2002). This mineral differs from dumortierite in having a superstructure with the *b* and *c* dimensions doubled (*Pnma* orientation), which Ma *et al.* (2002) attributed to ordering of Ti and Fe at "Type II" Al1 sites and Al at "Type I" Al1 sites with "Type I" and "Type II" having a regular distribution in (100). Ma *et al.* (2002) reported that (Fe + Ti) ranged from 0.28 to 0.34 a.p.f.u. (18 O basis), which is above average, but within the reported range for dumortierite (Grew, 2002). Thus, the ordering could be related to the relatively low temperatures of exsolution of the fibres from quartz as Ma *et al.* (2002) suggested, and not to composition.

In magnesiodumortierite, Mg substitutes for Al at the Al1 and Al4 sites, but Mg > Al only at Al1 (Chopin *et al.*, 1995; Ferraris *et al.*, 1995). Hydroxyl in dumortierite and magnesiodumortierite is thought to occur at the O2 and O7 positions (e.g. Moore and Araki, 1978; Alexander *et al.*, 1986; Cempírek and Novák, 2005; Fuchs *et al.*, 2005), and at the four-coordinate O10 site (Ferraris *et al.*, 1995; Farges *et al.*, 2004).

Hoskins *et al.* (1989) showed that the crystal structure of holtite is closely related to that of dumortierite, but differs in several important respects, all of which lie within six-sided

tunnels bounded by the two regions composed of $[Al_4O_{12}]$ chains (Fig. 1). Both SiO_4 tetrahedra are replaced partially by $Sb^{3+}O_3$ triangular pyramids (As^{3+} is dominant at this site in szklaryite, Fig. 2) with no evidence of preference of Sb for one of the Si sites, and Ta replaces Al at the Al1 position. As a result, there are vacancies at the coordinating anion sites (O2 and O7) as well as at the Al1 site. Relative to the Si positions, the Sb^{3+} sites are shifted ~0.5 Å closer to the Al1 position to accommodate the longer Sb^{3+}-anion bonds (average ~1.9 Å). When the Sb sites are occupied, O2 (for Si1) and O7 (for Si2) positions are vacant. Hoskins *et al.* (1989) obtained the formula $(Si_{2.25}Sb_{0.75})B[Al_6(Al_{0.43}Ta_{0.27}\square_{0.30})O_{15}(O,OH)_{2.25}]$ ($Z = 4$) from their crystal-structure study. Even for zero OH content, this formula has an excess positive charge of +0.39. Kazantsev *et al.* (2005, 2006) refined the crystal structure of an As-bearing "holtite I" crystal from Voron'i Tundry to $R = 0.046$. They reported that As^{3+} is incorporated into the crystal structure in $(Sb,As)O_3$ pyramids substituting for SiO_4 tetrahedra just as SbO_3 pyramids substitute for SiO_4 tetrahedra in holtite from Greenbushes, and there was no preference for one of the two Si positions. In their refinement of four holtite crystals, Groat *et al.* (2009) reported that charge-balance calculations suggest that essentially no water is present, but that Fourier transform infrared
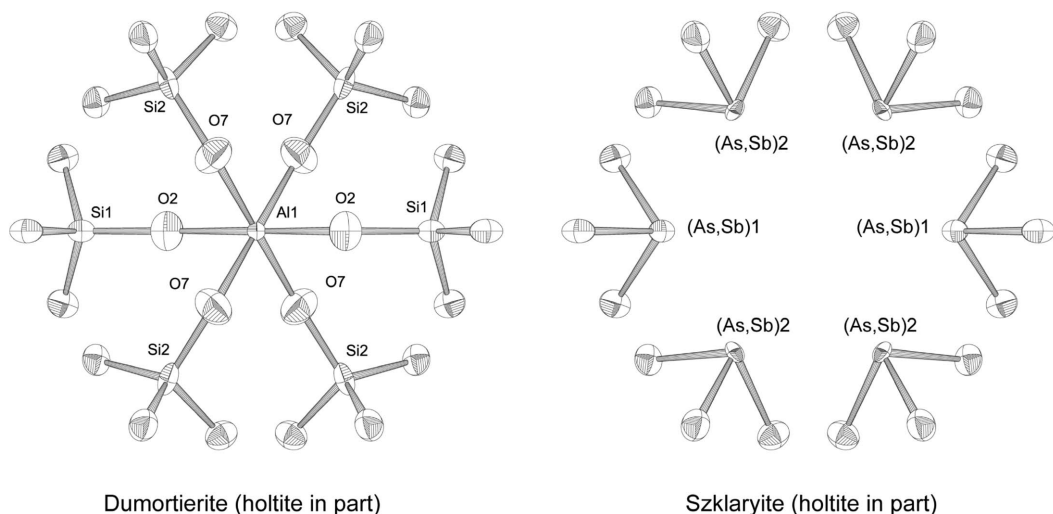

FIG. 2. The six-sided tunnels (region 1 of Moore and Araki, 1978) filled with Al1 octahedra and SiO_4 tetrahedra in dumortierite, $(As,Sb)O_3$ groups in the new mineral szklaryite, or a mixture of $(Sb,As)O_3$ groups and SiO_4 tetrahedra in holtite (after Hoskins *et al.*, 1989; Groat *et al.*, 2009, 2012). Al1 is largely vacant in szklaryite.

spectra confirm that some OH is present at the O2 and O7 positions. Their proposed general formula for holtite is $Al_{7-[5x+y+z]/3}(Ta,Nb)_x\square_{[2x+y+z]/3}B$ $Si_{3-y}(Sb,As)_yO_{18-y-z}(OH)_z$, where x is the total number of pentavalent cations, y is the total amount of Sb + As and $z \leqslant y$ is the total amount of OH. The splitting of (Sb, As) and Al1 sites observed in dumortierite has not been found in holtite (Groat et al., 2012).

In crystallographic studies of dumortierite, magnesiodumortierite and holtite, B has been reported to occupy only the trigonal site, which is confirmed by study of B K-edge spectra (Garvie et al., 1995; Fleet and Muthupari, 2000). No evidence for deviation from stoichiometry been reported for B in the crystal structure refinements, which is consistent with B contents reported in synthetic dumortierite by Werding and Schreyer (1990; cf. Ono 1981). Chemical determination of B content is difficult both by wet methods, because dumortierite supergroup minerals are often finely fibrous and impure, and by electron or ion microprobe because of problems with matrix correction and standardization. Thus, it is not surprising that a wide range of B contents has been reported, e.g. the non-stoichiometric B content obtained by wet chemical analysis in type holtite, 1.82 wt.% B_2O_3 (Pryce, 1971), which was later shown to be in error by single-crystal refinement (Hoskins et al., 1989). In other cases, B contents less deviant from stoichiometry, or even approaching it, were reported using wet chemical (e.g. Claringbull and Hey, 1952; Voloshin et al., 1977; Chopin et al., 1995), ion microprobe (Willner and Schreyer, 1991), and electron microprobe analyses (Vrána, 1979; Chopin et al., 1995; Fuchs et al., 2005; Pieczka et al., 2013), but the precision was too low to properly assess whether the observed deviations are significant.

Relationship to ellenbergerite, phosphoellenbergerite and ekatite

Dumortierite supergroup minerals have a strong structural affinity with the isotypic hexagonal species ellenbergerite, phosphoellenbergerite and ekatite. Moore and Araki (1978) implied that transformation of the orthorhombic dumortierite into a hexagonal dimorph might be relatively simple in principle. However, as pointed out by Ferraris et al. (1995) (and later by Keller, 2001, and Evans and Groat, 2012), transformation of dumortierite into an ellenbergerite-type hexagonal

polymorph "would be far from straightforward," and thus including these three minerals in the dumortierite supergroup is not warranted. Evans and Groat (2012) grouped the dumortierite supergroup, ellenbergerite, phosphoellenbergerite, ekatite and a host of synthetic compounds together as "dumortierite-like materials."

We agree with Ferraris et al. (1995) and Keller (2001) that the differences are significant enough that ellenbergerite, phosphoellenbergerite and ekatite should remain separate from the dumortierite supergroup. Ferraris et al. (1995) emphasized that the difference in the two structures involves more than simply replacing Al2−Al3 chains in dumortierite with copies of the Al4 chains. The tetrahedral groups in each hexagonal channel give the channel a defined orientation. Ferraris et al. (1995) described how both the dumortierite and ellenbergerite structures can be decomposed into slabs parallel to the $[Al_4O_{11}]$ sheets. In the hexagonal structure, hexagonal channels have the same orientation in every slab, whereas in the orthorhombic structure, the hexagonal channels reverse orientations every other slab. The Al2−Al3-type chains show similar alternating orientations. Ferraris et al. (1995) argued that this made an orthorhombic-to-hexagonal transition in dumortierite unlikely, as such a transition would involve inverting half the structure. There is also a significant difference in the triangular channels. The triangular channel in all the dumortierite supergroup minerals contains only trigonal-planar borate groups, whereas the minerals related to ellenbergerite each contain multiple tetrahedral or pyramidal groups: silicate and phosphate in ellenbergerite (Chopin et al., 1986); phosphate and (trigonal planar) carbonate in phosphoellenbergerite (Raade et al., 1998); and silicate and arsenite in ekatite (Keller, 2001). The lack of any known substitution at the B site in dumortierite minerals is very distinctive and might be related to the other differences between the dumortierite and ellenbergerite structures, the latter of which appears to incorporate negligible B: Ferraris et al. (1995) considered it significant that ellenbergerite found in contact with magnesiodumortierite contains only 10 ppm B.

Nomenclature of the dumortierite supergroup

The new classification for the dumortierite group has been approved by the IMA Commission on

TABLE 1. A classification of the dumortierite supergroup.

Mineral	Endmember formula	Relationship with dumortierite
		——— Dumortierite group ———
Dumortierite	$AlAl_6BSi_3O_{18}$	
Fe^{3+} analogue of dumortierite	$Fe^{3+}Al_6BSi_3O_{18}$	$^{AII}Fe^{3+} \rightarrow\ ^{AII}Al$
Mg-Ti analogue of dumortierite	$(Mg_{0.5}Ti_{0.5})Al_6BSi_3O_{18}$	$^{AII}Mg +\ ^{AII}Ti \rightarrow 2^{AII}Al$
Fe^{2+}-Ti analogue of dumortierite	$(Fe^{2+}_{0.5}Ti_{0.5})Al_6BSi_3O_{18}$	$^{AII}Fe^{2+} +\ ^{AII}Ti \rightarrow 2^{AII}Al$
"Titano-magnesiodumortierite"[#]	$(Mg_{0.5}Ti_{0.5})Mg_2Al_4BSi_3O_{13}(OH)_2$	$^{AII}Mg +\ ^{AII}Ti \rightarrow 2^{AII}Al;\ ^{AI4}Mg + OH \rightarrow\ ^{AI4}Al$
Magnesiodumortierite	$MgAl_6BSi_3O_{17}(OH)$	$^{AII}Mg + OH \rightarrow\ ^{AII}Al + O$
Fe^{2+} analogue of magnesiodumortierite	$Fe^{2+}Al_6BSi_3O_{17}(OH)$	$^{AII}Fe^{2+} + OH \rightarrow\ ^{AII}Al + O$
"Hydroxydumortierite"	$\square Al_6BSi_3O_{15}(OH)_3$	$^{AII}\square + 3OH \rightarrow\ ^{AII}Al + 3O$
		——— Holtite group ———
Holtite	$(Ta_{0.6}\square_{0.4})Al_6BSi_3O_{18}$	$0.6^{AII}Ta + 0.4^{AII}\square \rightarrow\ ^{AII}Al$
Nioboholtite	$(Nb_{0.6}\square_{0.4})Al_6BSi_3O_{18}$	$0.6^{AII}Nb + 0.4^{AII}\square \rightarrow\ ^{AII}Al$
Titanoholtite	$(Ti_{0.75}\square_{0.25})Al_6BSi_3O_{18}$	$0.75^{AII}Ti + 0.25^{AII}\square \rightarrow\ ^{AII}Al$
		——— Potential group ———
Szklaryite	$\square Al_6BAs_3^{3+}O_{15}$	$^{AII}\square + 3As^{3+} \rightarrow\ ^{AII}Al + 3Si^{4+}$
Sb analogue of szklaryite	$\square Al_6BSb_3^{3+}O_{15}$	$^{AII}\square + 3Sb^{3+} \rightarrow\ ^{AII}Al + 3Si^{4+}$

Bold – Mineral approved by the IMA Commission. [#]A major constituent of magnesiodumortierite.

New Minerals, Nomenclature and Classification (CNMNC proposal 12-C, November 6, 2012). The group is now considered a supergroup as it can be subdivided into three groups (one is potential as only one representative has been found to date) on the basis of the differences in the substitution mechanisms that decrease occupancy at the Al1 site, which is the basis of the classification (Table 1, Fig. 3). It is important to note that up to 5% vacancies have been reported at the other three octahedral Al sites, which are generally believed to be real (e.g. Fuchs *et al.*, 2005; Groat *et al.*, 2012), although Moore and Araki (1978) and Alexander *et al.* (1986) inferred that vacancies at these sites resulted from correlation between the site occupancies and atomic displacement parameters. In addition, Mg substitution for Al at Al4 is reported for magnesiodumortierite, $^{Al4}Mg + OH \rightarrow {}^{Al4}Al + O$ (Chopin *et al.*, 1995; Ferraris *et al.*, 1995). However, for the purposes of the classification we only consider the Al1 site because Al is overwhelmingly dominant at the other Al sites, excepting the ~50% Al at Al4 in Ti-rich magnesiodumortierite (Chopin *et al.*, 1995; Ferraris *et al.*, 1995).

We have identified three distinct mechanisms for introducing vacancies at Al1, which gives us two groups and a potential group:

(1) **Dumortierite group**: Charge-balance for vacancies at Al1 is provided by OH substitution for O at the O2, O7 and O10 sites.

(2) **Holtite group**: Vacancies serve not only to balance the extra charge introduced by the incorporation of pentavalent and quadrivalent cations for trivalent cations at Al1, but also to reduce repulsion between the highly charged cations.

(3) **Potential group including szklaryite**. Vacancies at Al1 are caused by loss of O2 and O7, which coordinate the Al1 with the Si sites, due to replacement of Si^{4+} by As^{3+} and Sb^{3+}, and thus this mineral does not belong in either the dumortierite or the holtite group. An Sb^{3+} analogue to szklaryite is possible.

Dumortierite group

The dumortierite group includes eight endmembers (Table 1), two of which are major constituents of naturally occurring minerals: dumortierite, endmember composition $AlAl_6BSi_3O_{18}$, and magnesiodumortierite, endmember composition $MgAl_6BSi_3O_{17}(OH)$ (Fig. 4). In general, classification of the dumortierite group follows the dominant-valency rule (Hatert and Burke, 2008) as the formulae given for three corners of the tetrahedron represent different valences at the Al1 site, i.e. 0 ($\square$), 2 (Mg, Fe^{2+}) and 3 (Al, Fe^{3+}), whereas the fourth corner $(Mg,Fe^{2+})_{0.5}Ti_{0.5}$ can be considered a case of valency-imposed double site-occupancy.

The Al1 site has not been reported to be fully occupied by Al, the maximum occupancy being
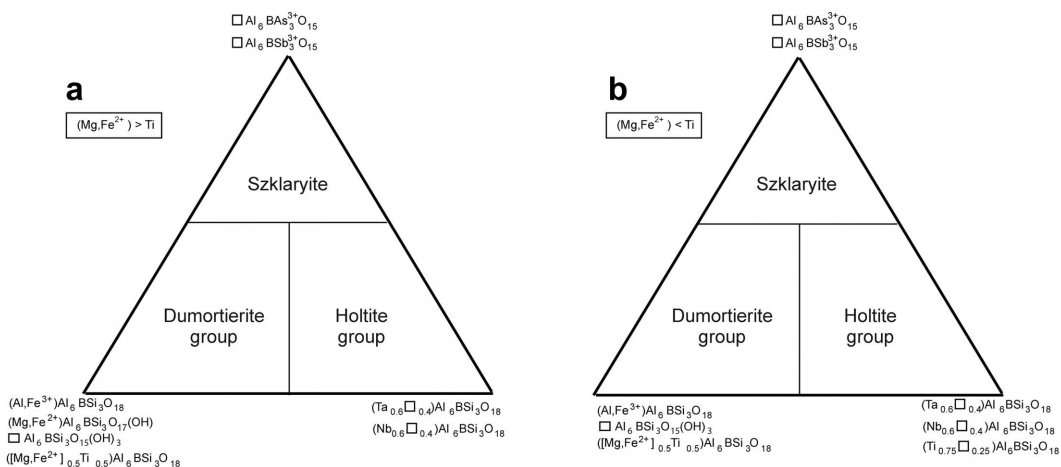

FIG. 3. Subdivision of the dumortierite supergroup into two groups and one potential group on the basis of Al1 occupancy. Fe^{3+} is added to Al and Fe^{2+} to Mg. Ti is considered a constituent of dumortierite only if coupled with Mg and Fe^{2+}.
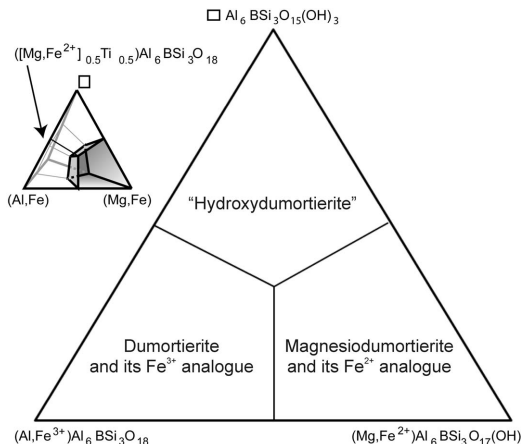
FIG. 4. By combining Fe with Al and Mg, the dumortierite group can be represented by a four-component system (inset) with most compositional variation in the Ti-free system (triangle), where two recognized minerals and one hypothetical component are recognized on the basis of Al1 occupancy.

88% (Alexander *et al.*, 1986, not including their 0.95 empirical correction; Groat *et al.*, 2012), and it appears that the dumortierite endmember $AlAl_6BSi_3O_{18}$ is unattainable due to face-sharing in the chain of Al1 octahedra. Instead, all naturally occurring dumortierite is a mixture of this composition with others, most commonly, the "h y d r o x y d u m o r t i e r i t e" c o m p o n e n t, $\square Al_6BSi_3O_{15}(OH)_3$ (Moore and Araki, 1978), which Werding and Schreyer (1990) cited as constituting up to 33% of dumortierite synthesized at pressures from 3 to 20 kbar in the Al_2O_3–SiO_2–B_2O_3–H_2O system. Natural dumortierite with relatively few impurities is estimated to contain <30% $\square Al_6BSi_3O_{15}(OH)_3$ (Moore and Araki, 1978; Alexander *et al.*, 1986; Cempírek and Novák, 2005; Fuchs *et al.*, 2005).

Except for magnesiodumortierite from the type locality, Dora Maira, the maximum MgO content of 3.42 wt.% was reported by Visser and Senior (1991) in a dumortierite from the Bamble Sector, Norway. Assuming OH = 0.75 per 18 O, the composition of this dumortierite gives an Al1 occupancy corresponding in endmembers to 45% magnesiodumortierite, 37% dumortierite, 5% $(Mg_{0.5}Ti_{0.5})Al_6BSi_3O_{18}$, 5% of an Fe endmember and 7% $\square Al_6BSi_3O_{15}(OH)_3$, i.e. magnesiodumortierite is dominant whether Fe is ferrous or ferric. However, the calculated proportions are sensitive to the assumed OH content, e.g. for OH

= 0.6 per 18 O and Fe assumed to be Fe^{3+} and added to dumortierite (dominant-valency rule), the magnesiodumortierite endmember is no longer dominant. Several other dumortierite samples from the Bamble Sector contain >3 wt.% MgO (Visser and Senior, 1991 and unpublished data; Kihle, 1989 and unpublished data), and formulae give nearly equal proportions of the magnesiodumortierite and dumortierite endmembers. As compositions straddle the boundary between the two minerals, determining whether any dumortierite from the Bamble Sector is magnesiodumortierite would require precise measurements of water content and iron valence.

Iron contents of dumortierite-group minerals range from 0 to 5.94 wt.% Fe as Fe_2O_3 (Claringbull and Hey, 1958; Grew, 2002; Groat and Evans, unpublished data), but determining its valence requires wet chemistry (titrations) or a spectroscopic method. Platonov *et al.* (2000) attributed the marked blue, violet and red coloration and pleochroism to Fe^{2+}-Ti^{4+} inter-valence charge transfer with little, if any, contribution from Fe^{2+}-Fe^{3+} charge transfer, whereas Goreva and Rossman (2000) found evidence that pink and blue colours were due to Fe^{2+}-Ti^{4+} intervalence charge transfer and Fe^{2+}-Fe^{3+} intervalence charge transfer, respectively, in nano-inclusions of a dumortierite-like phase in quartz, consistent with the findings that Fe^{3+} is also involved in coloring dumortierite (Alexander *et al.*, 1986; Farges *et al.*, 2004; Fuchs *et al.*, 2004). Mössbauer spectroscopy also shows that both Fe^{2+} and Fe^{3+} are present in dumortierite (Farges *et al.*, 2004). Thus, three endmembers involving homovalent substitutions of Fe^{3+} and Fe^{2+} for ^{AI1}Al and ^{AI1}Mg, respectively, are theoretically possible (Table 1), although the Fe contents of natural material are never sufficient for an Fe analogue to be dominant.

The TiO_2 contents range from 0 to >4 wt.%, i.e. reaching 4.3 and 4.6 wt.% in dumortierite from an unspecified locality in Mozambique and Rogaland, Norway, respectively (Borghi *et al.*, 2004; Huijsmans *et al.*, 1982), but Visser (unpublished data) obtained up to 5.10 and 5.24 wt.% (corresponding to 0.37−0.38 Ti p.f.u.) in two samples from Estima, Mozambique (Grew, 2002). There are two mechanisms for incorporation of Ti in the dumortierite group. In dumortierite containing <0.06 $(Mg + Fe^{2+})$ per formula unit, incorporation of Ti fits an empirical relationship $0.5Ti \rightarrow {}^{[6]}Al$ (Grew, 2002), which suggests that the substitution

inferred for incorporation of Ti in the holtite group, $0.75Ti + 0.25\square \rightarrow Al$ at Al1 to form the Ti analogue of holtite (Table 1; Fig. 5), could also contribute to Ti incorporation in the dumortierite group, i.e. incorporation of the Ti analogue of holtite in dumortierite if $Ti > (Mg+Fe^{2+})$ (Fig. 3b). However, it is doubtful that this substitution would be relevant for dumortierite containing more Mg and Fe^{2+}. In this case, incorporation of $Ti + (Mg, Fe^{2+})$ for $2Al$ at the Al1 site (Table 1, Fig. 3a) is more plausible; this substitution was cited to explain the large Ti contents in magnesiodumortierite, which reach 4.28 wt.% TiO_2 or 0.30 Ti p.f.u. (Chopin et al., 1995; Ferraris et al., 1995). This Ti-rich magnesiodumortierite is one of the few examples of a dumortierite-supergroup mineral in which constituents other than Al have also been reported at the Al2, Al3 or Al4 sites. Magnesium is interpreted to be incorporated at the Al4 site by the substitution $^{Al4}Mg + OH \rightarrow {}^{Al4}Al + O$, reaching about 50% replacement of Al. The structural formula deduced by these authors, $(Mg_{1/3}Ti_{1/3}\square_{1/3})(Al_{0.5}Mg_{0.5})_2Al_4BSi_3O_{16}(OH)_2$, is not a valid endmember because more than one site has multiple occupancy (Hawthorne, 2002). It can be split into three endmembers: 16.7% $(Mg_{0.5}Ti_{0.5})Al_6BSi_3O_{18}$, 33.3% $\square Al_6BSi_3O_{15}(OH)_3$ and 50% $(Mg_{0.5}Ti_{0.5})Mg_2Al_4BSi_3O_{16}(OH)_2$, where the last is a "titano-

magnesiodumortierite" component with Mg at the Al4 site unique to the Dora Maira locality.

The only substitutions reported at the Si sites (except As and Sb, see below) involve Al^{3+} and P^{5+}, reaching 0.17 Al and 0.09 P per formula unit (Grew, 2002; Fuchs et al., 2005), much less than the 0.49–0.51Al reported in dumortierite synthesized at 3−5 kbar via the substitution $^{Si1,2}Al + H \rightarrow {}^{Si1,2}Si$ (Werding and Schreyer, 1990). However, incorporation of Al and P at the Si sites could involve other constituents in natural dumortierite.

Dumortierite-group minerals commonly contain Ta, Nb, As and Sb, and locally, Bi, all of which represent solid solution with holtite-group minerals and szklaryite. Thus, calculation of the proportion of vacancies at the Al1 site attributed to "hydroxydumortierite" must be corrected for vacancies contributed by these four constituents, as well as by Ti not associated with Mg and Fe^{2+} in the component $([Mg,Fe^{2+}]_{0.5}Ti_{0.5})Al_6BSi_3O_{18}$. The role of Bi, presumed to be Bi^{3+}, remains unclear because it may be too large for the (As, Sb)-like sites, and could instead substitute for Al^{3+} at the Al1 site (Groat et al., 2012).

No other constituent has been reported in amounts of >0.1 wt.% and usually mostly well below, e.g. Be, F, Na, K, Ca, Cr, Mn and Zr (Grew, 2002; Fuchs et al., 2005; Groat et al., 2012).
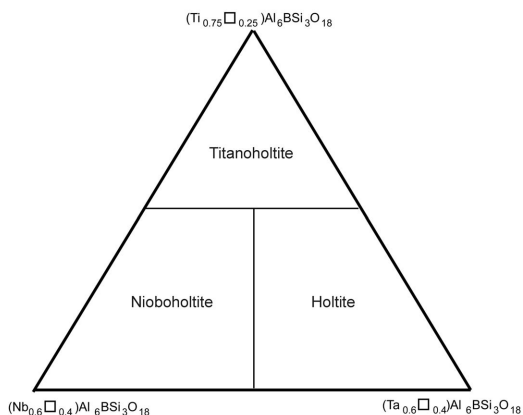

FIG. 5. Subdivision of the holtite group into one recognized mineral, holtite, and two new minerals, nioboholtite (2012-68) and titanoholtite (2012-69), on the basis of Al1 occupancy. $Ti = (Mg,Fe^{2+})$ is deducted from total Ti to obtain the amount of Ti in the holtite group.

Holtite group

There are now three minerals in the holtite group, holtite, endmember composition $(Ta_{0.6}\square_{0.4})Al_6BSi_3O_{18}$, nioboholtite (IMA 2012-68), endmember composition $(Nb_{0.6}\square_{0.4})Al_6BSi_3O_{18}$, and titanoholtite (IMA 2012-69), endmember composition $(Ti_{0.75}\square_{0.25})Al_6BSi_3O_{18}$ (Fig. 5); the latter two minerals are described in Pieczka et al. (2013). Figure 3 shows that the basis for recognizing the holtite group is valency-imposed double site-occupancy in which Ta^{5+}, Nb^{5+} and Ti^{4+} are paired with $\square$ in proportions to give a total valence of 3, whereas Fig. 5 shows that division within the group is based on the dominant-valency rule.

Iron contents are generally small, not exceeding 0.77 wt.% FeO in dumortierite-supergroup minerals at Szklary (Pieczka et al., 2011) and generally less, whereas MgO contents are negligible. Thus, the most abundant component in dumortierite-group minerals would be

$AlAl_6BSi_3O_{18}$, with subordinate $\square Al_6BSi_3O_{15}(OH)_3$ contributing the OH found in holtite-group minerals. Compositions containing Sb^{3+} and As^{3+} are relatively abundant, and for this reason, Sb^{3+} and As^{3+} have previously been considered essential for distinguishing holtite from dumortierite. There is some crystallographic basis for this inference. In the absence of Sb^{3+} (and As^{3+}) substitution for Si, the Al1−Al1 distance is too short to allow Ta^{5+} or Nb^{5+} (or Ti^{4+}) at adjacent Al1 positions, i.e. Al1 positions containing Ta^{5+} or Nb^{5+} (or Ti^{4+}) must be preceded and followed by vacant Al1 sites (Groat *et al.*, 2009). These authors suggested that in holtite the vacancies due to $Sb^{3+} \rightarrow$ Si substitution may provide enough separation between Ta^{5+} or Nb^{5+} (or Ti^{4+}) to stabilize the channel without introducing additional vacancies. However, compositions of holtite (Groat *et al.*, 2009; Pieczka *et al.*, 2011; Galliski *et al.*, 2012) show only crude correlation between Ta^{5+} or Nb^{5+} (or Ti^{4+}) on the one hand and Sb^{3+} and As^{3+} on the other. Because this correlation is not well defined, we recommend distinguishing vacancies introduced without $(Sb,As)^{3+} \rightarrow$ Si from vacancies introduced with $(Sb,As)^{3+} \rightarrow$ Si by recognizing a new group in the new classification.

Szklaryite – a new mineral from Szklary and a potential group

Szklaryite (IMA 2012-70), endmember formula $\square Al_6BAs_3^{3+}O_{15}$, is the first mineral isostructural with dumortierite to contain more $(Sb^{3+}$ and $As^{3+})$ than Si (Pieczka *et al.*, 2011, 2013), and, according to the dominant-valency rule, qualifies as a distinct mineral (Hatert and Burke, 2008). An Sb^{3+} analogue to the new mineral has not yet been discovered. However, many minerals called holtite contain more Sb^{3+} than As^{3+} (Pryce, 1971; Voloshin *et al.*, 1987; Groat *et al.*, 2009; Pieczka *et al.*, 2011), and thus the component $\square Al_6BSb_3^{3+}O_{15}$ plays a major role in the dumortierite supergroup, and has been listed in Table 1 and included in Fig. 3.

Although the potential new group is distinguished by the mechanism introducing vacancies at the Al1 site, the primary criterion for identifying minerals in the potential group is based on occupancy of the Si/As,Sb sites: $(As^{3+} + Sb^{3+}) >$ Si^{4+} consistent with the dominant-valency rule. That is, vacancies introduced by the substitutions $^{Al1}\square + 3(As,Sb)^{3+} \rightarrow$ $^{Al1}Al +$

$3Si^{4+}$ can be dominant at Al1 in some compositions for which $(As^{3+} + Sb^{3+}) < Si^{4+}$.

Szklaryite is also noteworthy for its small content of $(Ta^{5+} + Nb^{5+} + Ti^{4+})$, which underscores the observation noted above that $(Ta^{5+} + Nb^{5+} + Ti^{4+})$ and $(Sb^{3+} + As^{3+})$ are poorly correlated. Indeed, in cases where Si is nearly entirely replaced by Sb^{3+} and As^{3+}, Al1 should be nearly vacant, and very little Ta^{5+}, Nb^{5+} or Ti^{4+} could be accommodated. Conversely, if occupancy of Al1 by $(Ta^{5+} + Nb^{5+})$ approaches 60% (or 75% if Ti^{4+} were dominant), then very little substitution of Si is possible. For these reasons, a separate grouping is needed to account for the compositional variations in the dumortierite supergroup.

Applying the classification

Table 2 and Fig. 6 give the set of the compositional variables, including vacancy, which we recommend using to identify the group and species to which a particular mineral belongs. However, application of this classification requires firm knowledge of the occupancy of the cation and anion sites, particularly the Al1 site, which necessitates single-crystal structure refinement (SREF), supplemented by spectroscopic data on iron valence and H_2O content. Even with a complete dataset, full characterization of dumortierite-supergroup minerals is a challenge. Only B is present in a stoichiometric amount, whereas total octahedral cations, total anions and hydroxyl content are all non-stoichiometric. Complicating interpretation of site occupancy from SREF is the presence of several cations at the partially occupied Al1 site, i.e. Ta, Nb, Ti and Al, which are impossible to distinguish unless SREF is combined with electron probe microanalysis.

Unfortunately, in most cases neither the necessary instrumentation nor suitable material is available for complete characterization, and thus in order to apply the classification, simplifying assumptions will have to be made. The present recommendations are for users with only electron microprobe data at hand. The simpler case is dumortierite containing little Ta, Nb, As, Sb and Bi. Hydroxyl content must be assumed, e.g. 0.75 OH p.f.u. (Moore and Araki, 1978) or 0.40 p.f.u. (Alexander *et al.*, 1986) for Mg-poor dumortierite, but more OH for Mg-bearing dumortierite, i.e. one OH for each Mg (OH was assumed to be absent in dumortierite

TABLE 2. Compositional variables used for plotting.

Mineral	$Ti > (Mg + Fe^{2+})$	$Ti < (Mg + Fe^{2+})$
	Dumortierite group	
Dumortierite	^{Al1}Al	^{Al1}Al
Fe^{3+} analogue of dumortierite	Fe^{3+}	Fe^{3+}
Magnesiodumortierite	———	$Mg-Ti*[Mg/(Mg + Fe^{2+}]$
Fe^{2+} analogue of dumortierite	———	$Fe^{2+}-Ti*[Fe^{2+}/(Mg + Fe^{2+}]$
Mg-Ti analogue of dumortierite	$2Mg$	$2Ti*[Mg/(Mg + Fe^{2+})]$
Fe^{2+}-Ti analogue of dumortierite	$2Fe^{2+}$	$2Ti*[Fe^{2+}/(Mg + Fe^{2+})]$
"Hydroxydumortierite"[§]	$⅓(OH)^{†}$	$⅓(OH-[Mg+Fe^{2+}-Ti])^{†}$
	Holtite group[‡]	
Holtite	$⅔Ta$	$⅔Ta$
Nioboholtite	$⅔Nb$	$⅔Nb$
Titanoholtite	$⅔(Ti-Mg-Fe^{2+})$	———
	Potential group[†]	
Szklaryite	$⅓As^{3+}$	$⅓As^{3+}$
Sb analogue of szklaryite	$⅓Sb^{3+}$	$⅓Sb^{3+}$

Bold − Mineral approved by the IMA Commission. [§] OH was assumed to be absent in the compositions plotted in Fig. 7. [†] Amount of vacancy introduced at Al1 by the addition of these constituents. [‡] Vacancy introduced at Al1 is included in the quantities of these constituents.

compositions plotted in Fig. 7a). A second simplifying assumption is that the difference between total cations and the maximum possible, 11 p.f.u., gives the vacancy at Al1; other sites are presumed to be fully occupied. In the absence of spectroscopic information, Fe valence must be assumed, but associated minerals could provide guidance, e.g. association with minerals containing only Fe^{2+} is strong reason to presume Fe is Fe^{2+} in dumortierite (Pieczka, 2010; Pieczka et al., 2011).

In the cases of minerals in the dumortierite supergroup containing substantial Ta, Nb, As, Sb and/or Bi, the situation is more complex. We recommend a modification of the approach adopted by Pieczka et al. (2011) based on a simplified version of the formula derived by Groat et al. (2009). Assuming 1.000 B p.f.u. and the
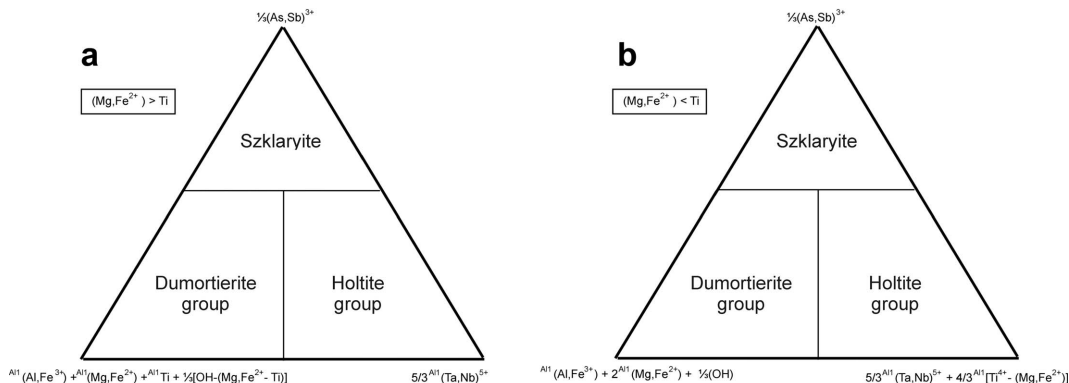

FIG. 6. Diagram of the dumortierite-supergroup showing the constituents used to plot compositions for determining group and species.
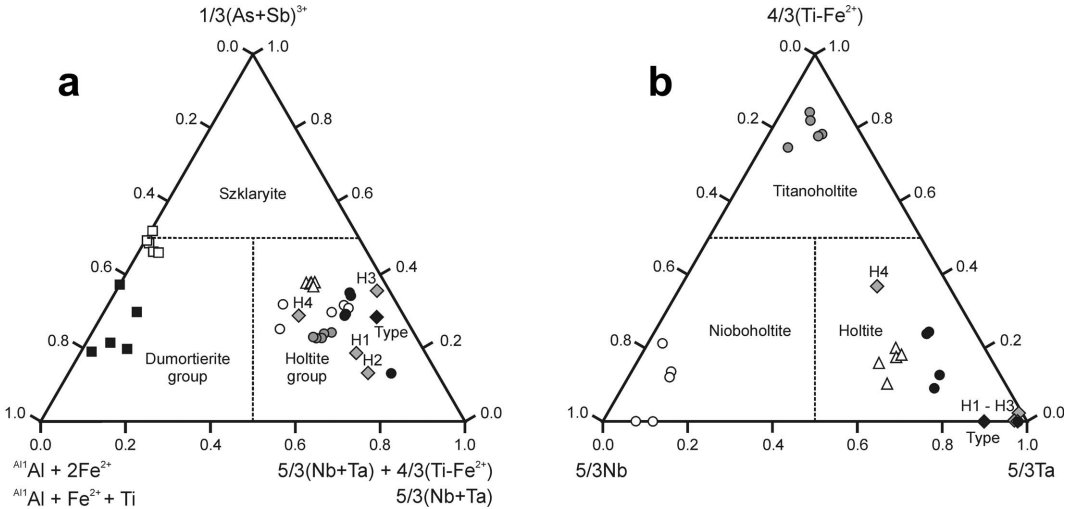
FIG. 7. Plots of selected dumortierite-supergroup minerals from the Szklary pegmatite (Pieczka *et al.*, 2011) in the ternary system for the three groups in the dumortierite supergroup (*a*); and in the ternary system for the holtite group (*b*). The dumortierite-group component with $Fe^{2+}_{0.5}Ti_{0.5}$ is deducted from total Ti to get the amount of Ti present as titanoholtite. Symbols: ■ − (As+Sb)-bearing dumortierite; □ − szklaryite and dumortierite approaching szklaryite in composition; ●,○ and ◕ holtite, nioboholtite and titanoholtite, respectively; △ − the Sb-richest holtite; ◆ − type holtite (Pryce, 1971); ◆ − holtite H1, H2, H3 and H4 from Groat *et al.* (2009).

absence of OH, then these authors' formula simplifies to $Al_{7-(5x+4w+y)/3}(Ta,Nb)_xTi_w$ $\square_{(2x+w+y)/3}BSi_{(3-y)}(Sb,As)_yO_{18-y}$, i.e. analyses should be normalized on the basis of O = (18−As−Sb) a.p.f.u. Vacancies have not been reported at the Si or (As,Sb) sites, but normalizing formulae by assuming Si + P + As + Sb = 3 a.p.f.u. is not recommended despite the iteration involved, because [4]Al can substitute for Si not only in dumortierite, but also in some holtite (Groat *et al.*, 2009). Assuming OH is absent is a major simplification of holtite composition because FTIR spectra clearly show its presence in samples from Greenbushes, Australia and Szklary (Groat *et al.*, 2009), whereas Voloshin *et al.* (1977, 1987) reported infrared evidence for H_2O and OH in holtite from Voron'i Tundra, Russia. Moreover, incorporation of [IV]Al could require incorporation of OH for charge balance, as in the case of dumortierite (Werding and Schreyer, 1990), as would incorporation of (Mg,Fe^{2+}) in excess of Ti. Nonetheless, we think the assumption of negligible OH content is justified, because Groat *et al.* (2009) reported that charge-balance calculations based on their single-crystal structure refinements give results consistent with essentially no water being present. In other words, assuming holtite is anhydrous gives

formulae in good agreement with site populations determined in the structure refinements.

The recommended procedure for obtaining a formula of a dumortierite-supergroup mineral from an electron microprobe analysis is as follows:

(1) Calculate a formula on the basis of O = (18−As−Sb−Bi), if Bi^{3+} is present

(2) Assume B is stoichiometric at 1 B p.f.u.

(3) Ideally, Si+P+As+Sb = 3, filling the Si1 and Si2 sites or their As^{3+} and Sb^{+3} equivalents. In cases where the sum Si+P+As+Sb < 3 a.p.f.u., add Al to get Si+P+As+Sb+[IV]Al = 3 a.p.f.u.

(4) Assume Al2, Al3 and Al4 are fully occupied by Al, for a total of 6 Al p.f.u. Only in magnesiodumortierite has another cation been reported at these sites.

(5) Remaining Al, i.e. ΣAl-[IV]Al-6Al, is assigned to Al1, together with Mg, Ti, Fe, Nb and Ta

(6) If Nb and Ta are very subordinate at Al1, it is likely the mineral contains significant OH; the formula should recalculated on a different basis, e.g. O = (17.625−As−Sb) to allow for 0.75 OH p.f.u. (Moore and Araki, 1978).

(7) Iron valence could be estimated from context, e.g. valence of Fe in associated minerals

(8) If Fe is assumed to be trivalent, then it is present as the $Fe^{3+}Al_6BSi_3O_{18}$ endmember

(9) If Fe is assumed to be divalent and Ti $\leqslant$ (Fe^{2+} + Mg), combine the divalent components with Ti to form $(Fe_{0.5}^{2+}Ti_{0.5})Al_6BSi_3O_{18}$ and $(Mg_{0.5}Ti_{0.5})Al_6BSi_3O_{18}$ and the excess Mg and Fe^{2+} are present as $MgAl_6BSi_3O_{17}(OH)$ and $Fe^{2+}Al_6BSi_3O_{17}(OH)$, respectively. If significant amounts of these components are present, the formula should be calculated on a new O basis, allowing for additional OH with Mg and Fe^{2+}.

(10) If Ti $\geqslant$ (Fe^{2+} + Mg), then include Ti in excess of (Mg + Fe^{2+}) as $(Ti_{0.75}\square_{0.25})Al_6BSi_3O_{18}$

(11) Steps 5, 8, 9 and 10 will give the relative proportion of the endmembers, which can be used to plot in Fig. 3 or 6 to identify group, then in Fig. 4 or 5 to identify species.

Analysis 4, Sz34/54, from Pieczka *et al.* (2011) can serve as an example of this procedure. The calculated formula is:

$(\square_{0.37}Al_{0.24}Ti_{0.31}Nb_{0.04}Ta_{0.03}Fe_{0.01})_{\Sigma1.00}Al_6B$ $(Si_{2.29}Sb_{0.51}As_{0.19}Al_{0.01})_{\Sigma3.00}(O_{17.30}\square_{0.70})_{\Sigma18.00}$

Given the relatively large Ti and small Mg and Fe content, OH is assumed to be 0 and the formula was calculated for O = 18–Sb–As = 17.30. Si > (As + Sb), so the mineral is in the dumortierite or holtite group. Rearranging the contents at the Al1 in terms of the endmembers and assuming Fe is ferrous, we get in decreasing abundance: Al1 = $\{(Ti_{0.30}\square_{0.10})(Al_{0.24})(\square_{0.22})$ $(Nb_{0.04}\square_{0.03})(Ta_{0.03}\square_{0.02})(Fe_{0.01}^{2+}Ti_{0.01})\}_{\Sigma1.00}$

That is: 40% $(Ti_{0.75}\square_{0.25})Al_6BSi_3O_{18}$, 24% $AlAl_6BSi_3O_{18}$, 17% $\square Al_6BSb_3^{3+}O_{15}$, 6% $\square Al_6BAs_3^{3+}O_{15}$, 7% $(Nb_{0.6}\square_{0.4})Al_6BSi_3O_{18}$, 5% $(Ta_{0.6}\square_{0.4})Al_6BSi_3O_{18}$ and 2% $(Fe_{0.5}^{2+}Ti_{0.5})$ $Al_6BSi_3O_{18}$, Σ = 101%. Allowing for the dominant valency rule, whereby the two endmembers with $\square$ and R^{5+} at Al1 must be considered together (Hatert and Burke, 2008), the $(Ti_{0.75}\square_{0.25})Al_6BSi_3O_{18}$ component is dominant, and the mineral is titanoholtite.

Summary of conclusions and recommendations

We recommend a classification based on the octahedral Al1 site with three hierarchal levels: a dumortierite supergroup which comprises the dumortierite and holtite groups, plus a potential group not yet named, and six approved mineral species, dumortierite, magnesiodumortierite, holtite, nioboholtite, titanoholtite and szklaryite.

A new classification of the dumortierite group is necessitated by the blurring of the distinction between holtite and dumortierite, a situation arising from the term holtite being applied indiscriminately to an ever-widening compositional range, while dumortierite was found to contain substantial amounts of the elements that supposedly distinguish holtite from dumortierite.

Compositions of holtite show only crude correlation between Ta^{5+} or Nb^{5+} (or Ti^{4+}) on the one hand and Sb^{3+} and As^{3+} on the other. That this correlation is not well defined is a second rationale for recognizing a new group in the new classification, i.e. distinguishing vacancies at the Al1 site introduced without $(Sb,As)^{3+} \rightarrow$ Si (holtite group) and vacancies introduced with $(Sb,As)^{3+} \rightarrow$ Si (new group).

Thirteen endmembers are needed to account for variations in the major constituents in the minerals of the dumortierite supergroup.

Acknowledgements

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