

SHORT COMMUNICATIONS

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Crystal chemistry of danalite from Daba Shabeli Complex (N Somalia)

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DANALITE is the Fe^{2+} end-member of the minerals of the helvite group, which have the general formula $M_8(\text{BeSiO}_4)_6\text{S}_2$, with $M = (\text{Mn}, \text{Fe}^{2+}, \text{Zn})$. These minerals are relatively uncommon, although limited amounts are known at many localities round the world (e.g. Ragu, 1994; Larsen, 1988; Kwak and Jackson, 1986, and references therein). Their typical host rocks are skarns, but occurrences in mineralized veins pegmatites, and altered alkali granites have also been reported. Danalite is rarer than helvite (Mn end-member) and genthelvite (Zn end-member) and, unlike the other two end-members, has never been found nor synthesized as a pure mineral (Mel'nikov *et al.*, 1968). Hassan and Grundy (1985) demonstrated that there is no crystal-chemical reason for pure danalite not being stable and that complete miscibility should exist between the Mn, Fe, and Zn end-members. The apparently restricted stability of danalite in natural environments is probably controlled by sulphur and oxygen fugacities, danalite being replaced by pyrite- or pyrrhotite-bearing assemblages at high f_{S_2} , and by magnetite-bearing assemblages at high f_{O_2} (Burt, 1980; Kwak and Jackson, 1986). It follows that the association of danalite with magnetite, quartz, fayalite and/or pyrite (or pyrrhotite) may help to constrain petrogenetic conditions.

Several works have addressed the chemical and physical properties of danalite (e.g. Kwak and Jackson, 1986, and references therein), but few crystal-chemical data have so far been produced.

Pauling (1930) first recognized helvite-group minerals to be isotypic with sodalite, the (Mn,Fe,Zn), Be, and S atoms of helvite corresponding to the Na, Al, and Cl atoms of sodalite, respectively. Holloway *et al.* (1972) were the first to refine the structure of a helvite crystal. More recently, Hassan and Grundy (1985) reported structural data for six members of the helvite group, including two danalite samples from Western Australia and New Hampshire. In the present work we report the first finding of danalite from the Daba Shabeli Complex, Somalia, and provide new crystal-chemical data on a $\text{Fe}_{65}\text{Mn}_{23}\text{Zn}_{12}$ danalite sample from this locality.

Geological and petrological relationships

An E–W gabbro–syenite belt occurs in the crystalline basement of N Somalia, consisting of multipulse bodies with an age of *ca.* 690 Ma. Among these bodies, the Daba Shabeli Complex (about 70 km SSE of Berbera) is notable for the occurrence of danalite-bearing alkali-feldspar leucogranites, representing the evolved members of mantle-derived magmas which differentiated in deeper chambers. These granites occur as coarse-grained, often porphyric dykes with a rapakivi texture. Mafic minerals are scarce and consist of poikilitic biotite ($mg = 0.24\text{--}0.39$ and Cl up to 1%), amphibole (Fedenite with Fe-actinolic hornblende rims and Cl up to 1.7%), magnetite ilmenite and large (up to 30 mm) reddish-brown rounded danalite crystals

(Visonà, 1993). It appears that danalite is the latest phase which crystallizes from a magnetite-series (Ishihara, 1977) granitic magma with relatively low f_{S_2} and f_{O_2} , as indicated by the narrow stability field of the magnetite + quartz + danalite assemblage in the $\log f_{S_2}/\log f_{O_2}$ plot of Burt (1980) for $P = 0.2\text{--}2$ kbar and $T = 300\text{--}500^\circ\text{C}$. The danalite₆₅ composition studied here is consistent with a f_{S_2} lower than that of the pyrite-magnetite and pyrrotite-magnetite buffers, but not so low as to determine its oxidation into a mixture of magnetite, quartz and phenakite.

Experimental

A danalite crystal from Daba Shabeli was mechanically formed into a sphere ($r = 0.13$ mm) and investigated by means of single-crystal X-ray diffractometry (XRD). XRD data were collected using a STOE AED four-circle automated diffractometer with Mo- $K\alpha$ radiation monochromatized with a flat graphite crystal. Unit-cell parameters were determined by means of least-squares refinement of 48 reflections with $20^\circ < 2\theta < 30^\circ$. The intensities of 5166 reflections with $-13 < hk < 13$ and $0 < l < 13$ were measured up to $2\theta \leq 70^\circ$ using the ω -scan mode, and equivalent reflections were averaged. Structural refinement was carried out in space group $P\bar{4}3n$ without chemical constraints, using the STRUCSY package (STOE, Germany). Starting atom coordinates were those of helvite (Holloway *et al.*, 1972). Reflections with $I \geq 3\sigma(I)$ were considered as observed and were given unit weight. All structural sites were considered as fully occupied. Atomic scattering curves were taken from the *International Tables for X-ray Crystallography* (1974) and Tokonami (1965); neutral factor curves were adopted for S, while fully or partially ionized

factors were used for Fe (Fe^{2+}), Be (Be^{2+}), Si ($\text{Si}^{2.5+}$) and O ($\text{O}^{1.5-}$). This scheme yielded the smallest differences between observed and calculated structure factors, especially in the low- θ region. Scale factor, secondary extinction parameter (Zachariasen, 1963), Fe and O coordinates and displacement parameters, and Fe occupancies were allowed to vary in four isotropic and three anisotropic least-squares minimization cycles to $R = 2.13\%$. A verification of Si-Be ordering was then attempted by refining Si against Be in both *TA* and *TB* sites. Since Si_{TA} occupancy remained virtually unchanged, it was fixed again at 1.0. A slightly better fit was obtained by allowing for a small Si contribution on the *TB* site, yielding a final $R = 2.11\%$. Selected structural refinement data are given in Table 1.

The same crystal studied by XRD was subsequently mounted on a glass slide and polished for WDS electron microprobe (EMP) and ion microprobe analyses (SIMS; for Be). EMP analysis was carried out with a CAMECA/CAMEBAX system, operating at 15 kV and 15 nA with a count time of 5 s for major and 10 s for minor elements. The CAMECA-PAP program was used to convert elemental X-ray counts into weight % oxides. The following synthetic compounds were used as standards: pure oxides (for Mg, Al, Cr and Fe), MnTi oxide (for Mn and Ti), wollastonite (for Si and Ca), sphalerite (for Zn and S), and jadeite (for Na). Analyses are believed to be precise to *ca.* $\pm 1\text{--}2$ relative % for major and *ca.* ± 5 relative % for minor elements. The crystal was analysed at fourteen spots. No significant zoning was detected, except for a mild variation in Fe and Zn contents (Fe/Zn atomic ratio range: 3.8–5.1). SIMS analysis of Be was carried out with a CAMECA IMS 4f ion microprobe at CSCC, Pavia, following the same procedures as those

TABLE 1. Selected structural refinement data (estimated standard deviations in brackets)

a (Å)	8.2127(8)				
obs. non-eq. refl.	339				
$R\%$	2.11				
	occ.	x/a	y/b	z/c	Beq(Å ²)
S	1.000	0	0	0	0.984
Si(<i>TA</i>)	1.000	0	½	¼	0.530
Be(<i>TB</i>)	0.983(9)	½	0	¼	0.780
Si(<i>TB</i>)	0.017(9)	"	"	"	"
Fe(<i>M</i>)	1.003(7)	0.1689(0)	0.1689(0)	0.1689(0)	0.742
O	1.000	0.1408(2)	0.1394(2)	0.4121(3)	0.755
<i>TA</i> –O (Å)	1.623(2)				
<i>TB</i> –O	1.638(2)				
<i>M</i> –S	2.402(0)				
<i>M</i> –O	2.026(2)				
S–O	3.755(3)				

described by Ottolini *et al.* (1993). Chemical analysis and site partitioning are given in Table 2. The measured content of BeO is close to the ideal value of 13.43 wt.% of a pure danalite. The sum of *M* cations calculated on the basis of 26(O + S) is fairly close to the ideal value of 8 atoms in the formula $M_8(\text{BeSiO}_4)_6\text{S}_2$ (hereafter apfu), and the sum of Si and Be approaches the value of 12 apfu. A small overestimate of FeO with EMP (less than 2 relative %) may account for the observed residuals. Calculated (EMP + SIMS) and observed (XRD) site mean electron densities agree within $0.13 e^-$ for the *TB* site and within $0.09 e^-$ for the *M* site.

TABLE 2. Average chemical analysis (standard deviations on 14 points in brackets) and site partitioning

BeO*	13.5(1)
Na ₂ O	0.14(6)
MgO	0.02(2)
Al ₂ O ₃	n.d.
SiO ₂	32.6(1)
S	5.9(1)
CaO	0.01(1)
K ₂ O	n.d.
TiO ₂	0.01(1)
Cr ₂ O ₃	0.02(3)
MnO	11.6(3)
FeO	33.8(7)
ZnO	7.2(5)
Total	104.80
Total less O=S	101.68
Atoms on basis of 26(O + S)	
Fe	5.21
Mn	1.81
Zn	0.97
Na	0.05
Mg	0.01
Ca	0.00
Ti	0.00
Cr	0.00
Σ	8.05
Si	6.00
Be	5.97
Σ	11.97
S	2.05
O	23.95
Σ	26.00

n.d.: content below detection limit.

*: analysed by ion probe.

Crystal chemistry

Danalite is a cubic ($P\bar{4}3m$) beryllosilicate; alternating SiO_4 (*TA*) and BeO_4 (*TB*) tetrahedra are arranged in a three-dimensional framework, formed by the join of four- and six-membered rings (Fig. 1). The framework is not rigid, so that the tetrahedra may rotate about the two-fold axes depending on the size of the interframework cations (Fe, Mn and Zn). Since these are relatively small, the framework is in a partially collapsed state (Pauling, 1930). It follows that the proportions of Fe, Mn, and Zn have no effect on the volumes and geometries of the framework tetrahedra (Hassan and Grundy, 1985).

Our data essentially confirm previous results. As observed in other helvite-group members (Holloway *et al.*, 1972; Hassan and Grundy, 1985), Be is confined to *TB* sites. Structural refinement suggests that small fractions of Si (0.10 apfu) may substitute for Be in *TB*, as found in helvite by Holloway *et al.* (1972). Nevertheless, the observed Si_{TB} occupancy is quite low compared with measurement precision (Table 1); moreover, any change in *TB*-O distance due to the presence of these small Si fractions would be negligible, due to the similarity of Be-O and Si-O bond lengths. We therefore conclude that Si-Be ordering is complete within analytical uncertainty.

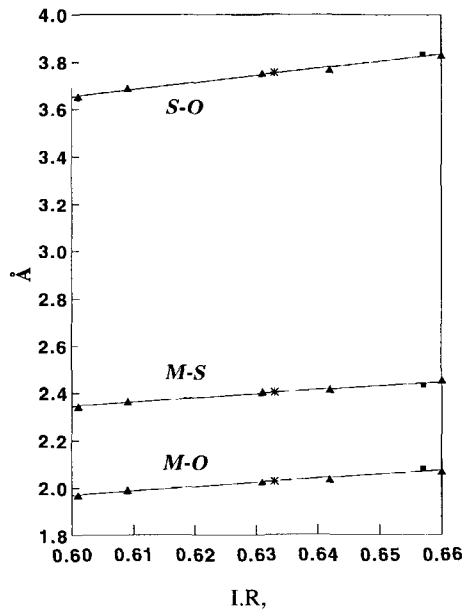


FIG. 2. *M*-O and *M*-S and *S*-O distances vs. mean ionic radius of *M* cations. Star: this work; square: data after Holloway *et al.* (1972); triangles: data after Hassan and Grundy (1985).

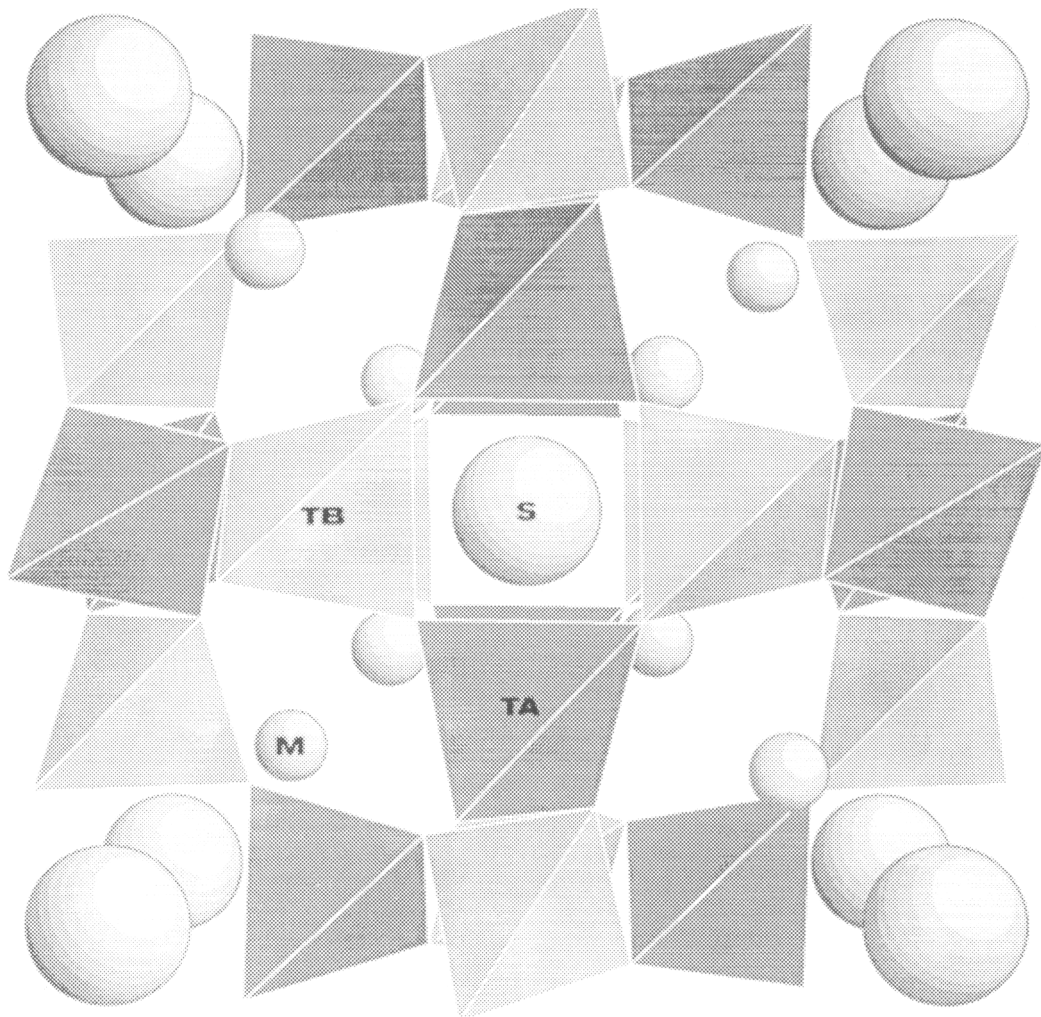


FIG. 1. Perspective view of danalite structure perpendicular to (100) plane, with site nomenclature used in the text.

Polyhedron geometries (Table 1) closely resemble those of the other helvite-group members studied by Hassan and Grundy (1985) and Holloway *et al.* (1972). $M-S$, $M-O$ and $S-O$ bond lengths reflect the proportions of M cations (Fig. 2). Hassan and Grundy (1985) attributed these variations to differences in the effective ionic radii of the interframework cations ($Mn^{2+} = 0.66 \text{ \AA}$; $Fe^{2+} = 0.63$; $Zn^{2+} = 0.60 \text{ \AA}$; Shannon, 1976) and the consequent change in the rotation angles of the framework tetrahedra. Our data confirm their model. Minor differences concern the lengths of $Si-O$ and $Be-O$ distances, which are, respectively, lower and higher than the average values proposed by Hassan and Grundy (1985; $Si-O = 1.629 \text{ \AA}$; $Be-O = 1.634 \text{ \AA}$), but identical

to those reported for helvite by Holloway *et al.* (1972). These differences are, respectively, triple and double the estimated standard deviations (σ) of the corresponding interatomic distances (Table 1) and are not related to chemical changes. Since the σ 's reported by Hassan and Grundy (1985) for their refinement data are higher than ours (about double), we suggest 1.623 and 1.638 \AA as the best estimates for $Si-O$ and $Be-O$ bond lengths, respectively, in helvite-group minerals.

On the whole, our data support the hypothesis that the nature of the interframework cations has no influence on the dimensions of beryllosilicate tetrahedra, and further confirm the model of a partially collapsed state for the structure of danalite.

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Subsilicic sodium gedrite in leptite of quartz keratophyric origin, Nordmark (Sweden)

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THE Mg–Fe orthoamphibole series $\square(\text{Mg, Fe})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$ – $\text{Na}(\text{Mg, Fe})_5\text{Al}_2\text{Si}_5\text{Al}_3\text{O}_{22}(\text{OH})_2$ has an open end in the sense that

the Si_5 end member has not been found in nature; tiny domains of near end-member composition in intricately zoned crystals (Schumacher, 1980;