

The stability of danalite, $\text{Fe}_4\text{Be}_3(\text{SiO}_4)_3\text{S}$

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Abstract

End-member danalite is compositionally equivalent to a mixture of pyrrhotite, phenakite, and fayalite, but danalite's natural occurrences with pyrite, magnetite, and quartz suggest that it is stable under somewhat more sulfidizing conditions than pyrrhotite and more oxidizing conditions than fayalite. Danalite tends not to occur with hematite. These facts can be used to construct a tentative $\log f_{\text{S}_2}$ - $\log f_{\text{O}_2}$ diagram for the stability of the end member. The diagram shows that danalite, if it is stable at all, has an extremely narrow stability field centered near the pyrrhotite/magnetite field boundary. Outside this field, phenakite (or, at low temperatures, bertrandite) is stable with magnetite, pyrrhotite (or pyrite), and quartz. A natural example of these equilibria apparently occurs at Iron Mountain, Bartlett, New Hampshire, where zoned danalite-helvite solid solutions occur as overgrowths on phenakite with magnetite, pyrite, and quartz.

Danalite is the only end member of the helvite group that is appreciably sensitive to hypogene oxidation. The Mn and Zn end members helvite and genthelvite are instead sensitive only to S-O exchange (variation in $\log f_{\text{S}_2}/f_{\text{O}_2}$).

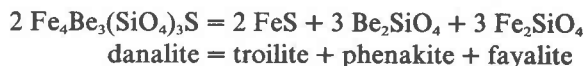
Introduction

Danalite, $\text{Fe}_4\text{Be}_3(\text{SiO}_4)_3\text{S}$, is a rare beryllium ore mineral in iron-rich skarns, greisens, and related metasomatic rocks (Glass *et al.*, 1944; Beus, 1966; Dunn, 1976). It typically contains considerable helvite, $\text{Mn}_4\text{Be}_3(\text{SiO}_4)_3\text{S}$, or genthelvite, $\text{Zn}_4\text{Be}_3(\text{SiO}_4)_3\text{S}$, in solid solution, and crystals may be distinctly zoned. The closest approach to "danalite" in analyzed natural specimens is 87 mole percent of the Fe end member (Dunn, 1976). In a laboratory study (Mel'nikov *et al.*, 1968), danalite was the only end member of the helvite group that could not be synthesized.

The above data might suggest that end-member danalite is unstable. This question cannot be answered without further experimental work; my objective is merely to examine the reason for the rarity of danalite-rich solutions in nature. The stabilities of helvite and genthelvite will be considered in later contributions.

Phases

Compositionally, end-member danalite is equivalent to a mixture of troilite, phenakite, and fayalite, as shown by the following equation:



Troilite (Tr) is not a common terrestrial phase; for the purposes of this discussion it can be replaced by pyrrhotite, Fe_{1-x}S . The non-stoichiometry of pyrrhotite has been neglected for convenience in balancing reactions.

The compositional relation expressed by the equation is also shown in Figure 1, a tentative depiction of mineral compatibilities in the reciprocal ternary system /Fe,Be/ /SiO₄,S/ [or Fe_2SiO_4 - $2\text{BeFe}_{1-x}\text{S}_2(\text{SiO}_4)_{-1}$ in the "exchange operator" notation of Burt, 1974]. This system is a subsystem of the four-component system FeO-BeO-SiO₂-SO₋₁, itself a subsystem of the five-component system Fe-Be-Si-O-S. Eight minerals in this system are listed in Table 1.

Incompatibilities

The phase rule implies that not all eight of the phases in Table 1 can be compatible at a given pressure and temperature. Well-known incompatibilities (unstable assemblages) in the Be-free subsystem Fe-Si-O-S include pyrrhotite-hematite, pyrite-fayalite,

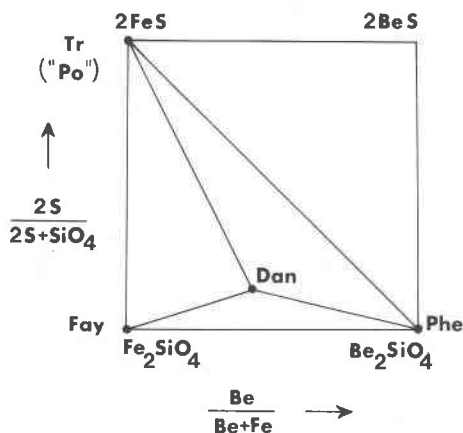


Fig. 1. Assumed mineral compatibilities in the reciprocal ternary system $\text{Fe}_2\text{SiO}_4\text{-Be}_2\text{SiO}_4\text{-2FeS-2BeS}$ (or $\text{Fe,Be//SiO}_4\text{,S}$). The phases shown are probably compatible with quartz in the system $\text{FeO-BeO-SiO}_2\text{-SO}_{-1}$. Abbreviations are given in Table 1 and the text.

and hematite-fayalite. Figure 1 implies that, if danalite is stable, pyrrhotite-fayalite-phenakite must also be an unstable assemblage. (Strictly speaking, due to the non-stoichiometry of pyrrhotite, this conclusion does not follow directly from Figure 1. Nevertheless, it can easily be shown that non-stoichiometric pyrrhotite plus fayalite plus phenakite is compositionally equivalent to the presumably more stable assemblage magnetite-danalite-quartz.)

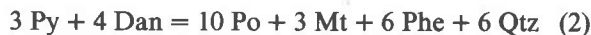
The phases in Table 1, and the incompatibilities mentioned above, can be used as input for computer program REACTION (Finger and Burt, 1972), in order to determine if there are other incompatibilities. Two reactions that are printed out are:



Table 1. Eight phases in the system Fe-Be-Si-O-S

Name	Abbreviation	Composition
Pyrrhotite	Po	Fe_{1-x}S
Pyrite	Py	FeS_2
Magnetite	Mt	Fe_3O_4
Hematite	Hm	Fe_2O_3
Fayalite	Fay	Fe_2SiO_4
Phenakite	Phe	Be_2SiO_4
Danalite	Dan	$\text{Fe}_4\text{Be}_3(\text{SiO}_4)_3\text{S}$
Quartz	Qtz	SiO_2

and



Hematite-danalite is not a well-documented assemblage, and the alternative assemblage apparently occurs (Barton and Goldsmith, 1968, p. 59). Analogies with other systems also suggest that an FeO-rich mineral such as danalite will be incompatible with hematite. Reaction (1) has therefore been assumed to go to the right. Note, however, that Zubkov *et al.* (1972, p. 362-363) have reported a danalite with 51 atomic percent Fe end member being altered by hematite, but it is not known if this represents an equilibrium assemblage.

Reaction (2) is still more of a problem. The left assemblage, pyrite-danalite, is relatively common, whereas the right assemblage apparently has not yet been reported. On the other hand, the danalite stability field in nature is undoubtedly extended by solid solution of other components, and pyrrhotite-bearing assemblages are rarely reported. Without experimental data, then, the stable assemblage in this reaction cannot be determined.

Stability diagrams

Given the above data and assumptions, danalite has five possible breakdown reactions involving O_2 , S_2 , and the phases in Table 1. These reactions are listed in Table 2 and are depicted on Figure 2, a schematic isobaric, isothermal $\log f_{\text{S}_2}\text{-}\log f_{\text{O}_2}$ diagram. In view of the lack of thermochemical and experimental data on the Be-bearing phases, the diagram is drawn at an arbitrary (moderate or low) pressure and temperature. The slopes of the lines on this diagram are fixed by compositional restrictions, and the topology should remain the same over a range of pressures and temperatures (in the vicinity of 0.2-2.0 kbar, 300-500°C).

The reactions involving the Be-free subsystem Fe-Si-O-S on Figure 2 are too well known to require comment (Holland, 1965). Superimposed on these is a hypothetical danalite stability field, outlined with dark lines. The danalite stability field is seen to be restricted to the vicinity of the pyrrhotite/magnetite field boundary. The assemblage danalite-quartz is stable over the same area as danalite alone, except at the lower left corner of the diagram. Danalite's compatibility with pyrite is, as mentioned, uncertain, and the danalite stability field could be considerably smaller than Figure 2 implies. (As mentioned in the introduction, end-member danalite could be unstable.)

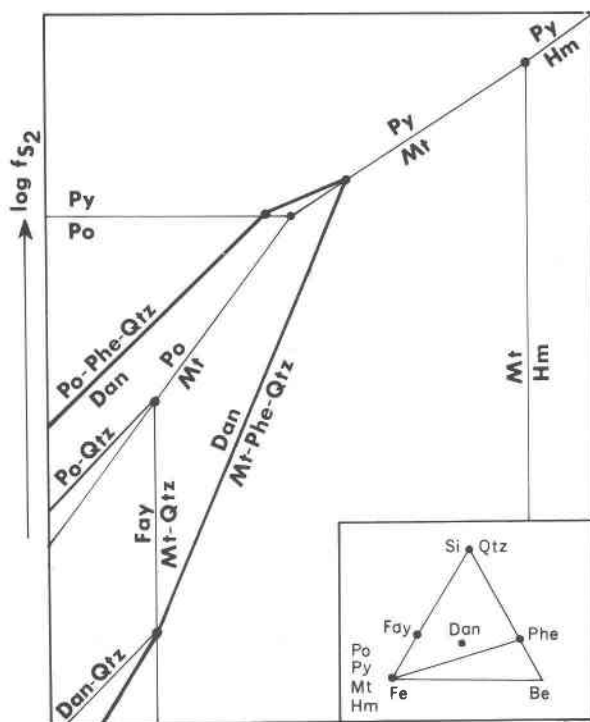


Fig. 2. Hypothetical $\log f_{S_2}$ - $\log f_{O_2}$ diagram for danalite stability in the system Fe-Be-Si-O-S. The inset shows mineral compositions projected onto the composition plane Fe-Be-Si. The thicker lines outline the danalite stability field; the reactions involving danalite are listed in Table 2. Mineral abbreviations are given in Table 1.

Danalite-rich solid solutions are common enough in nature, however, and their stabilities can similarly be depicted (Fig. 3). Figure 3 is analogous to Figure 2, except that a small fugacity of CO_2 allows the graphite line to eclipse the fayalite stability field (*cf.* Holland, 1965). By analogy with other systems, solid solution of, *e.g.*, helvite is shown as allowing the end-member danalite field (here shown as not touching pyrite) to expand considerably. Again due to the lack of data on danalite, the fields and numbers shown on this diagram are purely hypothetical. Minor substitution of Mn in magnetite has been neglected.

The superposition of a stability field for siderite (Sid) on Figure 3 has also been neglected. At low temperatures, with increasing CO_2 fugacity, siderite would gradually replace the magnetite field (and part of the pyrrhotite field). The lines of equal danalite content in helvite solid solutions would be deflected upwards as they entered the siderite field (to a slope of +1, instead of +7/3 as in the magnetite field). Eventually, increasing CO_2 fugacities would lead to the destruction of danalite, by reactions such as the following:

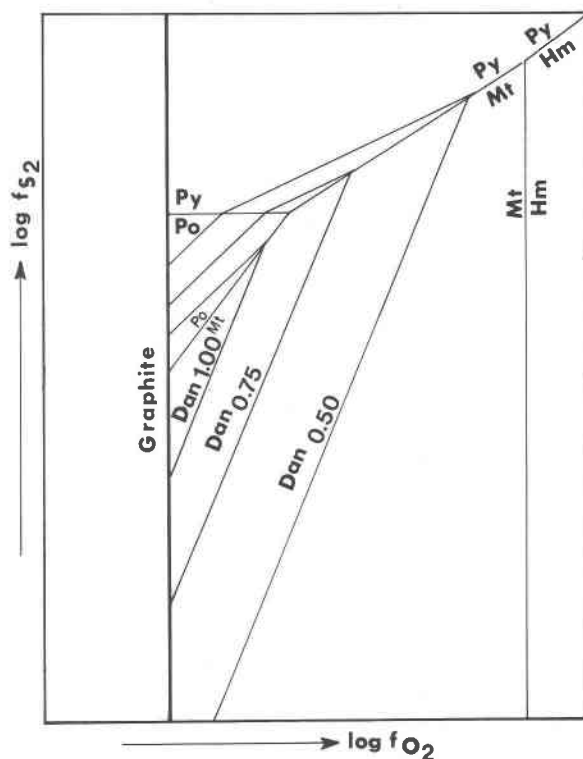
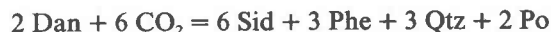


Fig. 3. Diagram similar to Figure 2, but in the presence of a constant fugacity of CO_2 , and showing hypothetical (schematic) stability limits for danalite solid solutions of 75 and 50 atomic % Fe. This diagram assumes that the end-member danalite field (Dan_{100}) is more restricted than that indicated on Figure 2. Siderite stability is not considered.



In this regard, Palache (1907) reports the alteration of danalite in a granite cavity from Cape Ann, Massachusetts to a mixture of siderite, phenakite, quartz, pyrite, and sphalerite, all coated by later kaolinite and hematite.

Table 2. Five breakdown reactions of danalite*

1. $6 \text{ Dan} + 4 \text{ O}_2 = 2 \text{ Mt} + 9 \text{ Fay} + 9 \text{ Phe} + 3 \text{ S}_2$
2. $2 \text{ Dan} + \text{ Qtz} + \text{ O}_2 = 4 \text{ Fay} + 3 \text{ Phe} + \text{ S}_2$
3. $6 \text{ Dan} + 7 \text{ O}_2 = 8 \text{ Mt} + 9 \text{ Phe} + 9 \text{ Qtz} + 3 \text{ S}_2$
4. $2 \text{ Dan} + 8 \text{ S}_2 = 8 \text{ Py} + 3 \text{ Phe} + 6 \text{ Qtz} + 4 \text{ O}_2$
5. $2 \text{ Dan} + 4 \text{ S}_2 = 8 \text{ Po} + 3 \text{ Phe} + 6 \text{ Qtz} + 4 \text{ O}_2$

* Abbreviations are as in Table 1.

Table 3. Selected associations of danalite

<u>Locality</u>	<u>Association</u>	<u>References</u>
Cape Ann, Massachusetts	Cavities in granite. Danalite altered to siderite, phenakite, quartz, pyrite, sphalerite.	Cooke, 1866 Palache, 1907 Pough, 1936
Iron Mountain, Bartlett New Hampshire	Metasomatically replaced granite. Danalite-helvite solid solutions overgrowing phenakite, with magnetite, pyrite, sphalerite, quartz, galena, fluorite, hematite, and pyroxene.	Wadsworth, 1880 Glass et al., 1944 Warner et al., 1959 Barton and Goldsmith 1968 Dunn, 1976 Author's visits, 1976, 1977
North End Peak, Iron Mountain New Mexico	"Ribbon rock" banded skarn replacing limestone. Danalite with fluorite, magnetite, grossularite, chlorite, and biotite.	Glass et al., 1944 Jahns and Glass, 1944
Needlepoint Mt., McDame area, B.C., Canada	Skarn in limestone. Danalite with magnetite, quartz, chlorite, fluorite, and native bismuth.	Thompson, 1957
Redruth, Cornwall, England	Purchased specimen. Danalite with quartz, arsenopyrite, sphalerite, chalcopyrite, and chlorite.	Miers and Prior, 1892
New Tolgus shaft, Redruth, Cornwall, England Levant Mine, St. Just, Cornwall, England Tretoil Mine, Lanivet, Cornwall, England Wheal Maudlin, Lanlivery Cornwall, England	All are skarn-related veins in greenstone. Danalite with chlorite, arsenopyrite, pyrite, chalcopyrite, and sphalerite; at individual localities with calcite, fluorite, and garnet.	Kingsbury, 1961
Mihara Mine, Hiroshima Prefecture, Japan	Danalite with phenakite in monzonite near skarn contact. Phenakite in adjacent feldspar-fluorite-biotite-scheelite skarn.	Aoki and Hida, 1974
Unspecified, U.S.S.R.	Pegmatites. Danalite replaces beryl; is in turn replaced by bertrandite, phenakite, pyrite, and hematite.	Orlov et al., 1961 Cerny, 1970
Precambrian Russian platform, U.S.S.R.	Quartz veins in altered granite and diabase. Danalite (51 at. % Fe) altered by hematite. Helvite, phenakite, muscovite, calcite, magnetite, acmite, and other minerals occur in related rocks.	Zubkov et al., 1972
Far East, U.S.S.R.	Complex tin-rare metal deposits. Danalite in plagioclase-clinopyroxene skarns in marble with cassiterite, scheelite, garnet, fluorite, and arsenopyrite. Also, danalite in diopside-magnetite skarns with chrysoberyl, phlogopite, idocrase, epidote, garnet, hastingsite, fluorite, cassiterite, and chalcopyrite.	Marshukova and Pavlovskii, 1969

Discussion

In reducing, ore-depositing fluids, H_2S is a much more abundant species than either S_2 or O_2 (Holland, 1965). On Figures 2 and 3, in the presence of water, lines of equal H_2S fugacity would have a slope of +1, more-or-less parallel to the direction of elongation of

the danalite field. (On Figure 2, reactions 2 and 5 of Table 2 also have slopes of +1.) If sulfate species are ignored, the stability of danalite on Figures 2 and 3 could therefore be summarized by stating that at low H_2S fugacities, danalite oxidizes to a mixture of magnetite, phenakite, and quartz (or fayalite). At high H_2S fugacities, it sulfidizes to a mixture of pyrrhotite

(or pyrite), phenakite, and quartz. Danalite solid solutions are stable over a narrow intermediate range of H_2S fugacities that pinches out with increasing fugacities of S_2 and O_2 (or SO_2).

At low temperatures, in hydrous systems, bertrandite, $Be_4Si_2O_7(OH)_2$, presumably replaces phenakite in the above equilibria (Burt, 1978). If CO_2 is added to the system, siderite can replace the iron oxides, as mentioned.

Numerous examples of these equilibria are given in Table 3. This table only includes danalite occurrences for which fairly complete mineral associations have been described; for other occurrences consult, e.g., Glass *et al.* (1944); Beus (1966); Gorman (1975); and Dunn (1976).

One of the more interesting associations of minerals in Table 3 occurs in the Fe–Be deposits at Iron Mountain, Bartlett, New Hampshire. Here danalite–helvite solid solutions, in places growing on phenakite, are also associated with magnetite, quartz, pyrite, sphalerite, galena, and fluorite (Barton and Goldsmith, 1968). The danalite crystals are zoned, with helvite cores and danalite rims (with up to 86 mole percent Fe end member, according to Dunn, 1977). The deposit appears to be a local hydrothermal replacement of the Conway granite.

At some deposits not listed in Table 3, danalite-equivalent assemblages occur alone. For example, Hügi and Rowe (1970) summarize numerous hematite–phenakite–quartz occurrences and a hematite–bertrandite–quartz occurrence in the Alps. Nearly Fe-free helvite occurs with hematite and quartz at an unspecified locality in the USSR; bertrandite is also present with hematite (Pavlova *et al.*, 1966; Pavlova, 1970). Numerous other examples could be cited (*cf.* Pough, 1936; Egorov, 1967; Chukhrov, 1972).

As the above assemblages with hematite imply, the unique feature of danalite, as compared with Zn and Mn end members of the helvite group, is its sensitivity to oxidation. The reactions that determine genthelvite and helvite stabilities in nature are apparently sensitive only to the chemical potential of the component SO_{-1} (or to the fugacity ratios f_{S_2}/f_{O_2} and f_{H_2S}/f_{H_2O} ; *cf.* reactions 2 and 5 of Table 2). This potential can be related to the chalcophile–lithophile tendencies of the elements (Burt, 1974). The chalcophile tendencies of the helvite group elements can be expressed as the inequality $Zn \gg Fe > Mn$ (Marakushev and Bezmen, 1969). This concept explains the tendency for genthelvite to occur in distinctly alkaline, sulfur-poor igneous environments (Burt, 1977), and also explains the otherwise puzzling gap between

the Zn and Mn ends of the helvite series noted by Dunn (1976).

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