Stability of genthelvite, $Zn_4(BeSiO_4)_3S$: An exercise in chalcophilicity using exchange operators

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Abstract

Despite differences in ionic radii and chemical affinities, Be and Zn have somewhat similar crystal chemical tendencies, although they rarely occur together in minerals. The only silicate in which they do so is genthelvite, a rare accessory in alkaline to peralkaline granites, syenites, and related pegmatites and greisens. The formula of genthelvite, $Zn_4(BeSiO_4)_3S$, can be expressed as a mixture of phenakite, willemite, and sphalerite. This fact, plus the fact that Zn is much more chalcophile than Be, allows the prediction of a series of seven sulfide-silicate reactions that involve SO_{-1} (the "acid anhydride" of H_2S) and the seven phases sphalerite, bromellite, zincite, phenakite, willemite, genthelvite, and quartz. When Al_2O_3 and F_2O_{-1} (the "acid anhydride" of HF) are added to the model system (in the additional phases corundum, gahnite, chrysoberyl, beryl, andalusite, and topaz), the resulting quartz-saturated $\mu_{F_2O_{-1}} - \mu_{SO_{-1}}$ diagram shows that genthelvite might be incompatible with beryl (or, at best, shares a narrow stability field with it). In addition, the rare assemblage genthelvite-topaz is stable only at low H_2S and very high HF fugacities, whereas the pegmatite assemblage gahnite-quartz sulfidizes and fluorinates to the greisen assemblage sphalerite-topaz with increases in the fugacity of both H_2S and HF. Because the order of chalcophilicity—i.e., the tendency to chalcophile behavior—is Zn > Fe > Mn, genthelvite is stable only at lower H_2S fugacities than either danalite or helvite, and it is therefore unlikely to occur in solid solution with helvite.

Introduction

Genthelvite, $Zn_4(BeSiO_4)_3S$, is the rarest of the sulfosilicates in the helvite group, which also contains helvite, $Mn_4(BeSiO_4)_3S$, and danalite, $Fe_4(BeSiO_4)_3S$. Genthelvite and helvite were synthesized by Mel'nikov et al. (1971) and all three (including danalite) by Fursenko and Klyakhin (1981) and Fursenko (1982); no further experimental studies on genthelvite appear to have been published. This paper represents a first attempt to delineate some phase relations involving genthelvite using physical-chemical principles (particularly the concept of exchange operators) and natural occurrences.

Natural occurrences of genthelvite, reviewed by Haapala and Ojanpera (1972), Dunn (1976), and Zubkov et al. (1976), are mainly restricted to highly fractionated alkaline to peralkaline granites and syenites or to their associated pegmatites, although genthelvite also occurs in greisens, or rarely, skarns. Genthelvite is commonly found in solid solution with danalite, but not with helvite (Dunn, 1976). Interesting questions regarding genthelvite thus are why it is so rare compared to beryl or to other members of the helvite group, why its occurrences are essentially restricted to one rock type (alkaline granite), and what its stability has to say about the comparative crystal chemistry of Be and Zn, on the one hand, and of Zn, Fe, and Mn, on the other.

Even though Zn is less abundant in the crust than Fe or Mn, it is relatively common in sphalerite (or gahnite, in some environments); also danalite is rarer than helvite, despite the fact that Fe is more abundant than Mn. Furthermore, Zn, Fe, and Mn are all concentrated relative to Mg by fractional crystallization. In other words, the geochemical rarity of Zn alone is insufficient to explain the rarity of genthelvite.

Although Zn (Shannon, 1976) has a divalent octahedral radius (0.74 Å) that is comparable to that of Mg (0.72), Fe (0.78), or Mn (0.83), it commonly occurs in fourfold, rather than sixfold coordination with oxygen, and in that respect (and some others) seems to have as much in common with the much smaller Be (tetrahedral radius 0.27 Å: Shannon, 1976) as with Mg, Fe, or Mn (Newmann, 1949; Plakhov, 1982; cf. Ross, 1964; Hormann, 1974; Brehler, 1969; Wedepohl, 1972; Robert and Gasperin, 1985). That is—although Zn is in sixfold coordination in its fluoride, carbonates (smithsonite and minrecordite: Garavelli et al., 1982), sulfate (zinkosite), and tungstate (sanmartinite: Dunn, 1978) and when in solid solution in most rock-forming silicates (e.g., mica, pyroxene, and amphibole)—it is in fourfold coordination (with average radius 0.60 Å: Shannon, 1976) in staurolite (e.g., Griffen, 1981) and in most of its simple compounds. Familiar examples include its sulfides (sphalerite and wurtzite), oxide (zincite), normal spinel (gahnite), and silicates (willemite, hemimorphite, hardystonite, and larsenite). Many

Mineral	Symbol	Formula
Sphalerite	Sl	ZnS
Beryllium sulfide		BeS
Silicon disulfide		SiS_2
Zincite	Znc	ZnO
Bromellite	Bro	BeO
Quartz	Qtz	SiO_2
Willemite	Wil	Zn_2SiO_4
Phenakite	Phe	Be_2SiO_4
Genthelvite	Gen	$Zn_4(BeSiO_4)_3S$

Fig. 1. Assumed mineral compatibilities in the reciprocal ternary system /Zn,Be//SiO$_4$,S/. For abbreviations, see Table 1. **(A)** The composition triangle Zn_2SiO_4-$2BeZn_{-1}$-$S_2(SiO_4)_{-1}$. **(B)** The square defined by the exchange operators Be_2Zn_{-2} (or $2BeZn_{-1}$) and $S_2(SiO_4)_{-1}$ as orthogonal vectors.

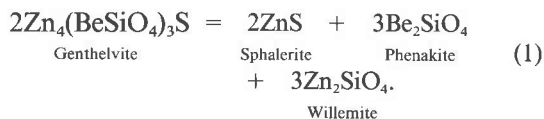of these have Be analogues (cf. Tables 1 and 3, also gugiaite for hardystonite: Grice and Robinson, 1984).

Genthelvite itself (Ross, 1964; Hassan and Grundy, 1985) is isostructural with sodalite, $Na_4(AlSiO_4)_3Cl$, with Na proxied by Zn, Al by Be, and Cl by S. BeO_4 tetrahedra are linked at all four corners to SiO_4 tetrahedra, and Zn is coordinated to 3 O and 1 S (i.e., Zn, is in fourfold coordination here as well).

Notwithstanding their crystal-chemical simlarities and tendency to be concentrated by fractional crystallization, Zn and Be rarely occur together in minerals (other than minor solid solution of, e.g., Be in willemite: Gurvich, 1965; Hahn and Eysel, 1970; Chatterjee and Ganguli, 1975). The only mineral other than genthelvite that contains both as essential constituents, according to listings in Wedepohl (1972) and Hormann (1974), is karpinskyite, which is discredited (Micheelsen and Petersen, 1971). More recently, Robinson et al. (1985) described the new calcium-beryllium-zinc phosphate hydrate ehrleite, the exception that proves the rule. In this phase, as in genthelvite, Be and Zn are both four-coordinated (Hawthorne and Grice, 1987).

The point of this discussion is that the anomalous tendency of Zn to seek four-coordination should, in anything, make genthelvite more common than helvite or danalite, in which the larger divalent Mn and Fe are "forced" into four-coordination. The correct explanation for the comparative rarity of genthelvite must be sought elsewhere, in the realm of comparative mineral stabilities.

Stability diagrams and exchange operators

The composition of genthelvite is equivalent to a mixture of sphalerite, phenakite, and willemite, according to the following relation (cf. Burt, 1980):

$$2Zn_4(BeSiO_4)_3S = 2ZnS + 3Be_2SiO_4$$
$$\text{Genthelvite} \quad\quad \text{Sphalerite} \quad \text{Phenakite}$$
$$+ 3Zn_2SiO_4. \quad\quad (1)$$
$$\text{Willemite}$$

This compositional relation is also shown in Figure 1, a depiction of mineral compatibilities in the reciprocal ternary system /Zn,Be//SiO$_4$,S/, which could also be expressed as Zn_2SiO_4-$2BeZn_{-1}$-$S_2(SiO_4)_{-1}$ in the exc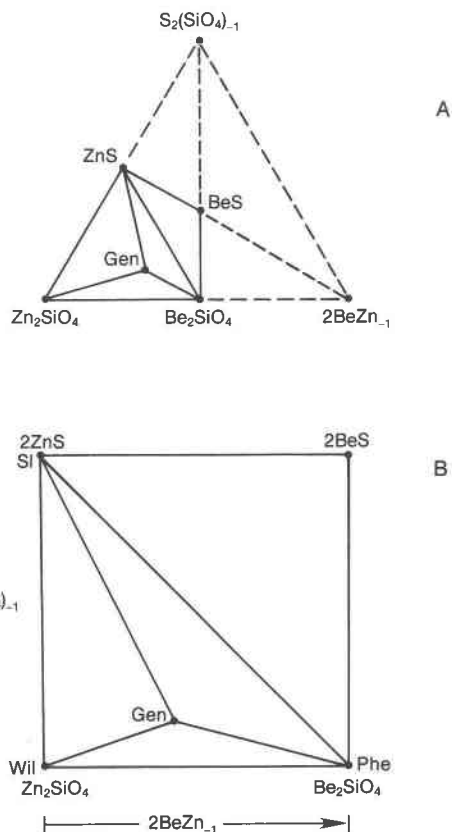hange operator notation of Burt (1974). (That is, 2Be can be exchanged for each 2Zn and 2S for each SiO_4.) Figure 1A is a composition triangle using exchange operators as points; Figure 1B a reciprocal square based on the exchange operators as orthogonal vectors (cf. Thompson, 1982; Černý and Burt, 1984). Points outside of the reciprocal quadrilateral Zn_2SiO_4-Be_2SiO_4-BeS-ZnS in Figure 1A are physically unattainable, although their compositions can be represented algebraically. The two representations of the quadrilateral are seen to be equivalent. (Note that in Fig. 1A, genthelvite is straightforwardly plotted from the relation 2 Gen = $7Zn_2SiO_4$ + $3Be_2Zn_{-2}$ + $S_2(SiO_4)_{-1}$; in Fig. 1B from the ratios Be:Zn = 3:4; S_2:(SiO$_4$) = 1:6, that is, genthelvite plots 3/7 of the way across and 1/7 of the way up the square.)

This system is a subsystem of the four-component system $ZnO-BeO-SiO_2-SO_{-1}$, where SO_{-1}, another exchange operator, can be thought of as the "oxide of (reduced) sulfur" or the "acid anhydride" of H_2S. The operator SO_{-1} is useful for defining the relative chalcophile-lithophile tendencies of the elements (Burt, 1974, 1979a).

Table 2 lists nine compounds in this system. As mentioned, Be and Zn have analogous (and isostructural) sul-
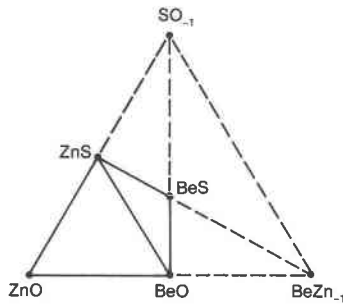
Fig. 2. Presumed low-pressure mineral compatibilities in the reciprocal system /Zn,Be//O,S/, showing that Zn is more chalcophile than Be.

Fig. 3. Presumed low-pressure mineral compatibilities in the reciprocal system /Zn,Be//O,SiO$_4$/, which could also be described as the system $ZnO-BeO-SiO_2$. The figure shows that Zn has a greater affinity for silica than Be does.

fides (although BeS, not a mineral, is isostructural with wurtzite, not sphalerite), oxides, and silicates. (The nonmineral SiS_2 is included only for completeness; it is not isostructural with quartz.) These analogies are further emphasized in the presumed low-pressure mineral compatibilities shown on Figures 2 and 3. Figure 2 is for the system /Zn,Be//S,O/, and Figure 3, for the system /Zn,Be/ /O,SiO$_4$/. Only triangular representations are shown. Note that Figure 3 could also be described as the system ZnO-BeO-SiO_2 (studied experimentally by Chatterjee and Ganguli, 1975), inasmuch as the operator $(SiO_4)O_{-2}$ can also be written as SiO_2 (silica or quartz; i.e., this component has a physical counterpart). Figure 2 shows that Zn, relative to Be, prefers S to oxygen (i.e., is more chalcophile); Figure 3 shows that Zn, relative to Be, prefers SiO_4 to oxygen (i.e., has a greater affinity for silica). Somewhat surprisingly, according to the data in Pankratz et al. (1984), Be has even less of an affinity for S than does Si (that is, the assemblage $BeO-SiS_2$ is more stable than $BeS-SiO_2$).

For all three figures, the most basic phase is generally placed at the lower left, and the exchange operators are generally acidic (in the electronic or Lewis sense: Lewis, 1938; Burt, 1974, 1979a). $BeZn_{-1}$ is clearly acidic, owing to the much smaller size of Be (its greater attraction for electrons), as is $(SiO_4)O_{-2}$ (it is silica, after all). SO_{-1} is likewise acidic (it is the "acid anhydride" of H_2S, S^{2-} is a weaker base than O^{2-}, and sulfides are more polarizable and covalent than oxides). The exception is $S_2(SiO_4)_{-1}$ in Figure 1, which can be written as $2SO_{-1}$ minus $(SiO_4)O_{-2}$; that is, as the difference between two acidic operators; its acidity is therefore difficult to predict. It may be considered as generally basic because reactions such as the following go to the right: $2CaS + Zn_2SiO_4 = 2ZnS + Ca_2SiO_4$, and $2MnS + Zn_2SiO_4 = 2ZnS + Mn_2SiO_4$; the exchange operators $ZnCa_{-1}$ and $ZnMn_{-1}$, on the basis of ionic radii, should be acidic.

When the above configuration is chosen, a diagonal relation between mineral stabilities is usually seen, as in Figures 2 and 3, or in cases involving pure oxides (cf. Korzhinskii, 1959b; Burt, 1979a). The most basic phases
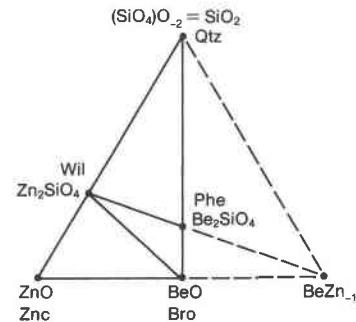
will be at the lower left, the most acidic at the top (for composition triangles) or upper right (for recpirocal systems), and they will tend to react with each other to yield diagonal tie lines (from upper left to lower right) between the stable assemblages.

Figures 1, 2, and 3 merely represent three planar sections through the system ZnO-BeO-SiO_2-SO_{-1} (or /Zn,Be,Si//O,S/), which is depicted as a triangular prism on Figure 4. In order to understand the phase compatibilities, one could draw tie lines for the entire system, or else draw some planar views of it that are projected through the compositions of pure phases. The latter procedure is much easier, particularly inasmuch as there is little interest in and almost nothing is known about the parts of the prism outside the tetrahedron ZnO-BeO-SiO_2-ZnS (to the right of the ruled plane BeO-SiO_2-ZnS in Fig. 4). In particular, from natural occurrences, nothing can be known about sulfides in the triangular face ZnS-BeS-SiS_2 on the back of the diagram.

Figures 5 and 6 show two such views, respectively projected through quartz and bromellite (and onto the planes of Figs. 2 and 3). All seven of the presumably stable mineral assemblages of interest can thus be depicted; they are the numbered triangles on Figures 5 and 6. Assemblage 7, for example, can be seen from Figure 5 to be quartz + phenakite + sphalerite + genthelvite.

CHEMICAL POTENTIAL DIAGRAMS

The stability of genthelvite can also be represented on schematic diagrams involving the chemical potential (μ) of SO_{-1} and SiO_2, that is, as a function of the reduced S and silica activities of the magma or postmagmatic fluid. Silica activity or chemical potential is of interest inasmuch as genthelvite occurs in syenites and other silica-undersaturated rocks. The diagram (Fig. 7) must remain schematic, given the lack of thermochemical data on genthelvite, although it is drawn roughly consistent with available data on the sulfides, oxides, and silicates of Be and Zn (Robie et al., 1979; Barton, 1986). The method of drawing such diagrams is given in Korzhinskii (1959a).

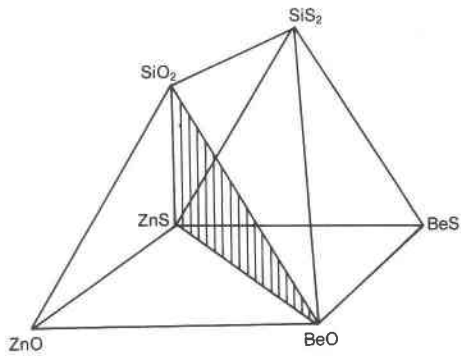The main topological (and arbitrary) assumption made

Fig. 4. System $ZnO-BeO-SiO_2-SO_{-1}$ (or $/Zn,Be,Si//O,S/$, written to show it is a reciprocal system) depicted as a triangular prism. The subsystem of interest, $ZnO-BeO-SiO_2-ZnS$, is that to the left of the ruled plane.
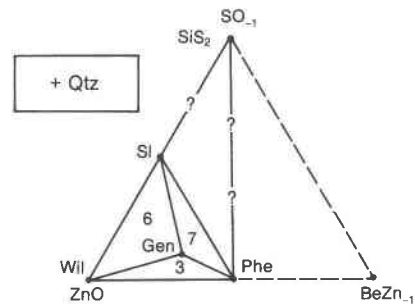

Fig. 5. Presumed low-pressure mineral compatibilities in the system $ZnO-BeO-SiO_2-SO_{-1}$, projected through SiO_2 onto the plane of Fig. 2. Numbers identify stable four-phase assemblages that plot as invariant points in Fig. 7 and are reactions (SO_{-1} indicators) in Table 2. For abbreviations, see Table 1.

in drawing Figure 7 is that genthelvite is not stable with zincite, that is, that the genthelvite stability field is relatively restricted. This is equivalent to assuming that the following reaction goes to the right:

$$Zn_4(BeSiO_4)_3S + 3ZnO$$

Genthelvite   Zincite

$$= ZnS + 3BeO + 3Zn_2SiO_4. \quad (2)$$

Sphalerite   Bromellite   Willemite

Either assemblage would only occur in extremely S- and silica-depleted rocks; relevant natural occurrences appear to be lacking at Franklin and Sterling Hill, New Jersey (Pete Dunn, pers. comm., 1987) or elsewhere (although genthelvite inclusions in the Zn end-member clinopyroxene petedunnite have recently been reported by Essene and Peacor, 1987). The dashed line shows the appearance of the diagram for the case of genthelvite stable with zincite; only the invariant point numbered 4 is affected. For more silica-rich rocks, those containing phenakite or quartz, the qualitative phase relations are unaffected.

The three lines sloping gently ($+\frac{1}{2}$) to the upper right are lines of equal $\mu_{S_2(SiO_4)_{-1}}$ (sulfidation, desilication). The

lowest marks the formation of genthelvite from willemite + phenakite; the intermediate one, the alteration of willemite to sphalerite; and the third, the breakdown of genthelvite to sphalerite + phenakite (or at low temperatures in nature, bertrandite). Each of these intersects the vertical line of silica saturation in an invariant point involving quartz; the points are respectively numbered 3, 6, and 7.

These and the other invariant points are numbered in approximate order of increasing $\mu_{SO_{-1}}$. They can also be considered as reactions involving only SO_{-1}, as in Table 2. The reactions of major interest—those occurring with increasing reduced S content in quartz-bearing alkaline granites—are again 3, 6, and 7, with 3 being the first appearance of genthelvite with quartz, 6 being the disappearance of willemite and first appearance of sphalerite, and 7 being the disappearance of genthelvite. Natural occurrences of these phases are reviewed below.

EXTENDED SYSTEM (ADDED Al AND F)

Natural occurrences of these minerals mainly involve Na, Al, and F in addition to the components used above.

TABLE 2. Mineral assemblages in the system $ZnO-BeO-SiO_2-SO_{-1}$ that indicate $\mu_{SO_{-1}}$

1. $BeO + Be_2SiO_4 + 2Zn_2SiO_4 + SO_{-1} = Zn_4(BeSiO_4)_3S$
   Bro   Phe   Wil   Gen
2. $ZnO + SO_{-1} = ZnS$
   Znc   Sl
3. $3Be_2SiO_4 + 4Zn_2SiO_4 + 2SO_{-1} = 2Zn_4(BeSiO_4)_3S + SiO_2$
   Phe   Wil   Gen   Qtz
4. $3BeO + 3Zn_2SiO_4 + 3SO_{-1} = Zn_4(BeSiO_4)_3S + 2ZnS$
   Bro   Wil   Gen   Sl
5. $3BeO + Zn_4(BeSiO_4)_3S + 3SO_{-1} = 3Be_2SiO_4 + 4ZnS$
   Bro   Gen   Phe   Sl
6. $Zn_2SiO_4 + 2SO_{-1} = 2ZnS + SiO_2$
   Wil   Sl   Qtz
7. $2Zn_4(BeSiO_4)_3S + 6SO_{-1} = 3 Be_2SiO_4 + 8ZnS + 3SiO_2$
   Gen   Phe   Sl   Qtz

Note: The assemblages are listed as reactions in approximate order of increasing $\mu_{SO_{-1}}$, that is, in order of their appearance as the numbered points in Fig. 7.
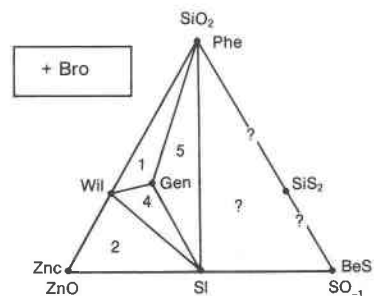

Fig. 6. Presumed low-pressure mineral compatibilities in the system $ZnO-BeO-SiO_2-SO_{-1}$, projected through BeO (bromellite) onto the plane of Fig. 3. Numbers identify stable four-phase assemblages that plot as invariant points in Fig. 7 and as reactions (SO_{-1} indicators) in Table 2. For abbreviations, see Table 1.
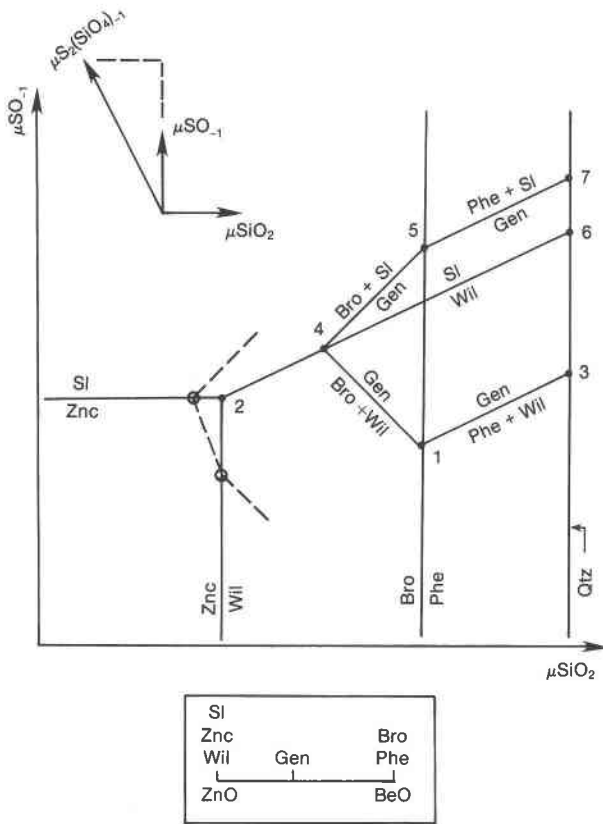
Fig. 7. Schematic isobaric, isothermal $\mu_{SO_{-1}}$-μ_{SiO_2} diagram for the system ZnO-BeO-SiO_2-SO_{-1}, drawn at moderate temperatures and pressures, showing the stability of genthelvite in silica-saturated (vertical line to right) and undersaturated environments. For abbreviations, see Table 1.

To keep things relatively simple Na is omitted from phases such as nepheline, albite, villiaumite, cryolite, chiolite, chkalovite, and possibly its zinc analogue (cf. Burt, 1979b; Burt and London, 1982), and genthelvite is simply noted as being stable approximately in the field of phenakite (i.e., conditions that are alkaline or F-rich or both so that Al is tied up in feldspar or topaz: Burt, 1981) on acidity-salinity or other diagrams involving Na (or K) and F. H_2O is also omitted in low-temperature phases such as bertrandite, euclase, eudidymite, epipidymite, and many others. This approach leaves Al and F as variables.

Some additional phases introduced with the addition of Al_2O_3 and F_2O_{-1} (again, the "oxide" of F or the "acid
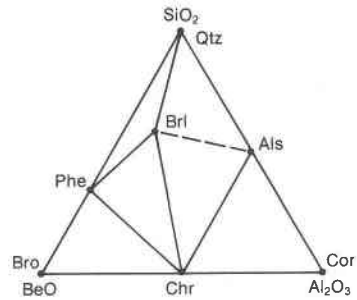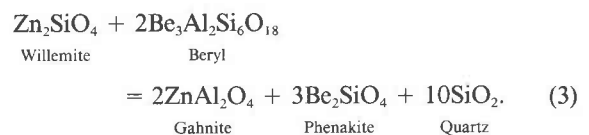

Fig. 8. Assumed mineral compatibilities in the system BeO-Al_2O_3-SiO_2 at moderate temperatures and pressures. For abbreviations, see Tables 1 and 3.

anhydride" of HF) are listed on Table 3. Of these, AlF_3 is not a mineral, although ralstonite in nature is not too far away from it in composition. Note that although $ZnAl_2O_4$ and $BeAl_2O_4$ have analogous formulas, the former is a normal spinel with Zn in four-coordination and the latter has the olivine (Mg_2SiO_4) structure with Al in the Mg sites and Be in the Si site (cf. Ross, 1964).

Mineral compatibilities in the system BeO-Al_2O_3-SiO_2 (Fig. 8) were studied on the basis of natural assemblages by Burt (1978) and experimentally by Barton (1986). The main area of disagreement involved chrysoberyl, which very rarely occurs in quartz-bearing pegmatites (commonly those that also contain sillimanite), and, according to the experimental work, is stable with quartz only above 600 °C. This time (unlike in 1978) I have therefore shown beryl + andalusite as stable (with a dashed line), although in nature the Al is usually present in feldspars, topaz, or mica rather than andalusite.

The system ZnO-Al_2O_3-SiO_2 (Fig. 9) is much simpler; the common occurrence of gahnite in quartz-bearing pegmatites rules out any ambiguity (cf. Bunting, 1932), omitting, of course, Zn pyroxenes (Morimoto et al., 1975; Olesch et al., 1982) or other phases that might appear at high pressure.

Projecting through quartz, these data can be combined as shown in Figure 10 for the system ZnO-BeO-Al_2O_3-SiO_2. Chrysoberyl would appear on this figure only at high temperatures (Barton, 1986). Gahnite plus quartz is assumed stable with all of the Be minerals; the assemblage gahnite + beryl is commonly seen in pegmatites (Němec, 1973; Černý and Hawthorne, 1982), whereas the assemblage gahnite + phenakite is based on the assumption that the following reaction goes to the right:

$$Zn_2SiO_4 + 2Be_3Al_2Si_6O_{18}$$

Willemite   Beryl

$$= 2ZnAl_2O_4 + 3Be_2SiO_4 + 10SiO_2. \quad (3)$$

Gahnite   Phenakite   Quartz

This assumption seems reasonable based on the rareness of willemite, commonness of gahnite, and the discussion that accompanies Figure 11.
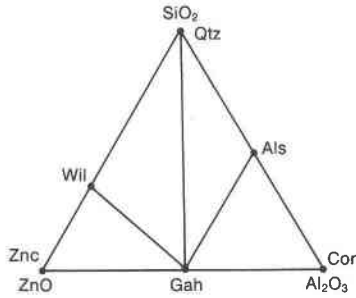
TABLE 3. Phases added with Al_2O_3 and F_2O_{-1}

Mineral	Symbol	Formula
Aluminum fluoride		AlF_3
Corundum	Cor	Al_2O_3
Gahnite	Gah	$ZnAl_2O_4$
Chrysoberyl	Chr	$BeAl_2O_4$
Beryl	Brl	$Be_3Al_2Si_6O_{18}$
Andalusite, etc.	Als	Al_2SiO_5
Topaz	Tpz	$Al_2SiO_4F_2$

Fig. 9. Assumed mineral compatibilities in the system ZnO-Al_2O_3-SiO_2 at moderate temperatures and pressures. For abbreviations, see Tables 1 and 3.
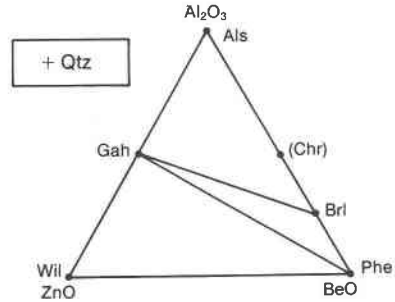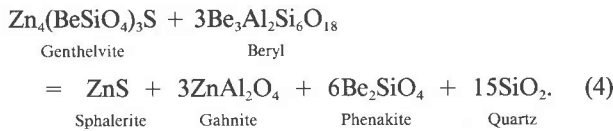

Fig. 10. Assumed mineral compatibilities in the system ZnO-BeO-Al_2O_3-SiO_2, projected through quartz, at moderate temperatures and pressures. For abbreviations, see Tables 1 and 3.

It remains to sulfidize and fluorinate the system of Figure 10 to create assemblages containing genthelvite, sphalerite, and topaz. This is done on the $\mu_{SO_{-1}} - \mu_{F_2O_{-1}}$ diagram (Fig. 11). It was assumed in drawing the figure that the following reaction goes to the right:

$$Zn_4(BeSiO_4)_3S + 3Be_3Al_2Si_6O_{18}$$
$$\text{Genthelvite} \qquad \text{Beryl}$$

$$= ZnS + 3ZnAl_2O_4 + 6Be_2SiO_4 + 15SiO_2. \quad (4)$$
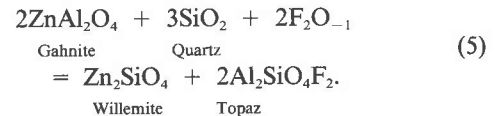$$\text{Sphalerite} \quad \text{Gahnite} \qquad \text{Phenakite} \qquad \text{Quartz}$$

This assumption is consistent with keeping the genthelvite field relatively restricted, and it leads to a simpler configuration of the diagram. An "association" (not necessarily assemblage) between impure genthelvite and beryl is reported only by Vasil'ev (1961) and implied by Chistyakova and Moleva (1966; cf. Chistyakova, 1968) and Haapala (1977, p. 68; in a 1988 personal communication he reports never finding the two phases touching); no other associations are reported. However, assemblages between the much more widespread helvite-danalite series minerals and beryl are reported fairly commonly (e.g., DeMark, 1981; Gallegher and Hawkes, 1966; Orlov et al., 1961; Kalenov, 1959), and so my assumption may be wrong.

If so, the alternative configuration of the multisystem (see Korzhinskii, 1959a, for a definition of multisystems) would be stable, as shown in configuration B to the lower left of Figure 12. The multisystem, as represented by Reaction 4 above, is made up of the phases Gen, Brl; Sl, Gah, Phe, Qtz. By the stable-to-metabstable topological relation of Burt (1971, 1978), the invariant points that are stable are labeled by the phase assemblage that is metastable in each of the two alternative configurations of the multisystem. Inasmuch as Figure 11 assumes that the assemblage Gen + Brl is metastable, these two "absent" (or nonparticipating) phases can be chosen to label the two stable invariant points 3 and 4. This is done to the upper right (A) of Figure 12, with the invariant-point labels placed in brackets, [Gen] (above) and [Brl] (below). In the alternative configuration (B) to the lower left, the assemblage Sl + Gah + Phe + Qtz is metastable, and

the points bearing those labels become stable. I am projecting through Qtz, and therefore its point cannot be seen, but the other three points are seen: [Sl] at the bottom, [Phe] nearly at the top, and [Gah] at the top. The two points [Brl] and [Gen] that were stable in configuration A are now metastable, and they have switched places, as shown by their labels and the dashed, now metastable, reaction lines. The assemblage genthelvite + beryl is now stable over a limited area of the diagram (in the half-open rectangle closed to the right by the invariant point labeled [Gah] above and [Sl] below).

The SO_{-1} indicators to the left of invariant points 1, 2, and 3 of Figure 11 correspond to 3, 6, and 7 on Table 2, respectively. Two new SO_{-1} indicators appear, to the left of points 4 and 5. The higher is gahnite + quartz going to sphalerite + andalusite, the lower is gahnite + phenakite going to sphalerite + beryl. The two F_2O_{-1} indicators that are the vertical lines beneath points 5 and 4 have been reported elsewhere (Burt, 1977, 1981), the first is the conversion of andalusite to topaz, the second the breakdown of beryl to topaz, phenakite, and quartz. A still higher F_2O_{-1} indicator occurs to the right, beneath point 2 and passing through 1; it is

$$2ZnAl_2O_4 + 3SiO_2 + 2F_2O_{-1}$$
$$\text{Gahnite} \qquad \text{Quartz} \qquad\qquad (5)$$
$$= Zn_2SiO_4 + 2Al_2SiO_4F_2.$$
$$\text{Willemite} \qquad \text{Topaz}$$

No natural examples of the right-hand assemblage are reported, although the association willemite-topaz is implied for alkaline metasomatites and greisens in Table 23 of Zubkov et al. (1976, p. 92–93). One reason might be that willemite-bearing rocks are commonly peralkaline (see below), in which case F occurs mainly as sodium fluorides, rather than in topaz (Burt and London, 1982). Thus Zubkov et al. (1976, Table 23, p. 92–93) imply a strong aluminofluoride-willemite association in mica-quartz-feldspar metasomatites and greisens.

A second reason for the lack of topaz + willemite assemblages might be that they are unstable with respect to end-member AlF_3 (instead of just Na-Al fluorides). This
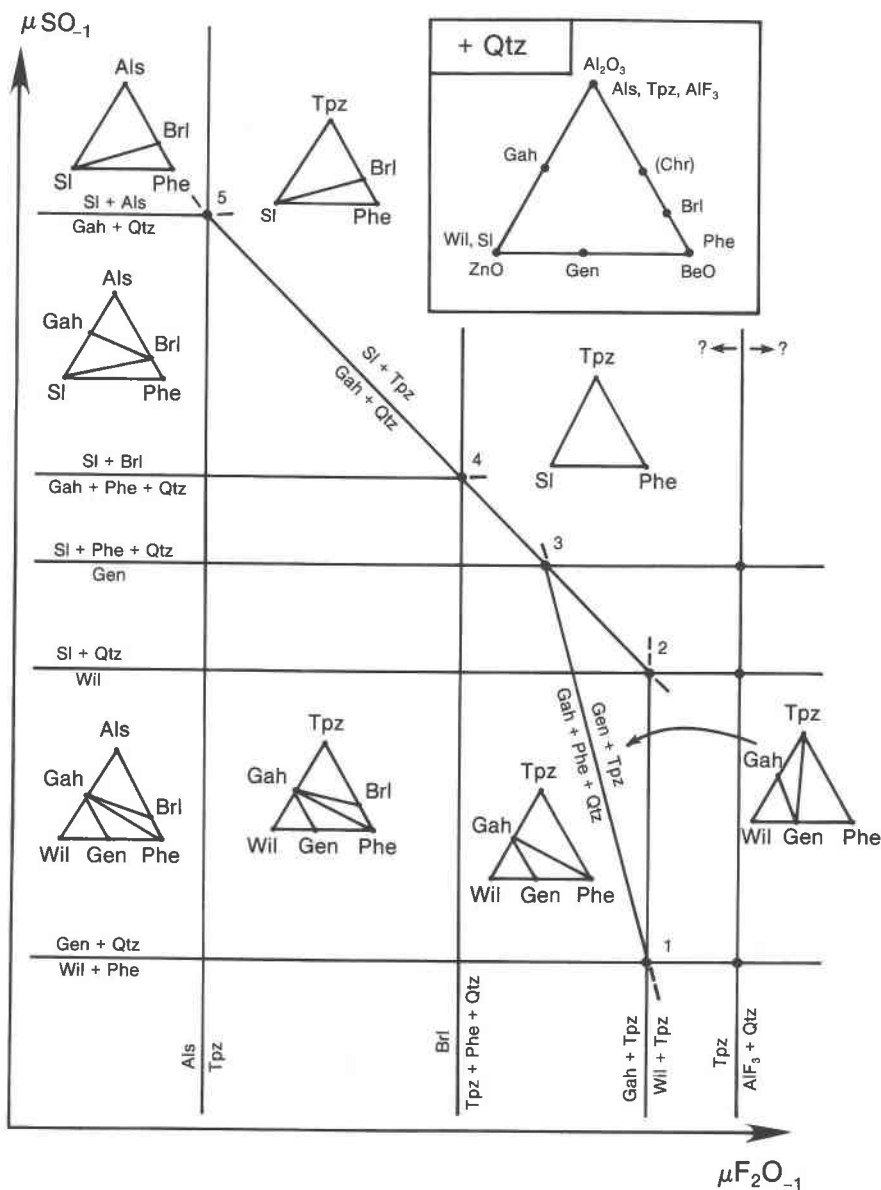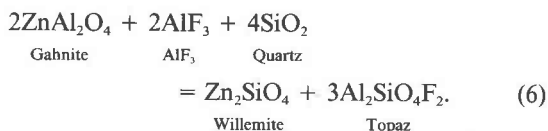
Fig. 11. Schematic isobaric, isothermal $\mu_{SO_{-1}}$-$\mu_{F_2O_{-1}}$ diagram for the system ZnO-BeO-Al_2O_3-SiO_2-SO_{-1}-F_2O_{-1}, in the presence of quartz, at moderate temperatures and pressures. Genthelvite is assumed to be unstable with beryl. The five invariant points are numbered in order of increasing $\mu_{SO_{-1}}$ and decreasing $\mu_{F_2S_{-1}}$, or log a_{HF}^2/a_{H_2S}. Inset shows chemography of phases (see Tables 1 and 3 for abbreviations).
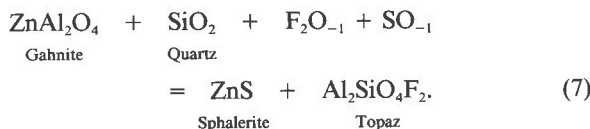
phase is shown as forming from topaz along the vertical line to the far right of Figure 11. If the AlF_3-forming reaction is moved sufficiently far to the left, Reaction 5 above becomes metastable, owing to the multisystem relation

$$2ZnAl_2O_4 + 2AlF_3 + 4SiO_2$$
$$\text{Gahnite} \qquad \text{AlF}_3 \qquad \text{Quartz}$$

$$= Zn_2SiO_4 + 3Al_2SiO_4F_2. \qquad (6)$$
$$\text{Willemite} \qquad \text{Topaz}$$

Inasmuch as neither the left- nor right-hand side of this relation is definitely known (AlF_3 is not reported as a mineral), perhaps this would be a good point to stop drawing more phase diagrams. However, the wide gap between the breakdown of albite to cryolite + topaz + quartz and the breakdown of topaz to AlF_3 + quartz, as a function of increasing $\mu_{F_2O_{-1}}$ (Anovitz et al., 1987, Fig. 5, p. 3098), especially with falling temperature, suggests that this reaction goes to the right, as assumed in drawing Figure 11. The albite breakdown to cryolite, topaz, and quartz (Burt, 1979b) would then be a vertical line (not

shown) between the breakdown of beryl (passing through point 4) and that of gahnite plus quartz (passing through points 1 and 2).

A third and more probable reason is that HF-rich natural environments such as greisens are normally also enriched in H_2S, so that the typical reaction terminal to gahnite is the diagonal one (with a -1 slope) that joins points 2 and 5, namely

$$ZnAl_2O_4 + SiO_2 + F_2O_{-1} + SO_{-1}$$

Gahnite   Quartz

$$= ZnS + Al_2SiO_4F_2. \quad (7)$$

Sphalerite   Topaz

The left-hand assemblage is typical of pegmatites; the right-hand one of greisens. The rare greisen assemblage genthelvite + topaz (Haapala and Ojanpera, 1972; Haapala, 1977) is stable to the right of the line joining point 1 to point 3, again, very F rich, low S conditions.

Subtracting SO_{-1} from F_2O_{-1} yields F_2S_{-1}. The chemical potential of this component (or the log a_{HF}^2/aH_2S, for an activity ratio in the presence of H_2O) increases to the lower right of Figures 11 and 12, as indicated by the vectors to the upper left of Figure 12. If specific mineralogic indicators of this tendency (toward F-rich, S-poor) are desired, the five numbered invariant points of Figure 11 could serve as guides.

NATURAL ASSOCIATIONS

As mentioned above, genthelvite is the rarest mineral of the helvite group, and genthelvite occurrences are mainly restricted to alkaline granites, pegmatites, syenites, and related metasomatic rocks (Gurvich et al., 1965; Galetskii et al., 1970; Haapala and Ojanpera, 1972; Dunn, 1976). Common associates are quartz, feldspars, micas, other Zn-bearing phases such as sphalerite (Haapala, 1977; Bowden and Kinnaird, 1978), willemite (Gurvich, 1965; Galetskii, 1966, 1971), and gahnite (Gurvich, 1965; Haapala, 1977), as well as other Be-bearing phases, mainly phenakite (Gurvich, 1965; Gurov and Marchenko, 1970), but also bertrandite (Chistyakova and Moleva, 1966).

The common occurrence of willemite in these associations, particularly those from peralkaline rocks, is one that was not known until relatively recently (e.g., Pough, 1941, did not mention them). More recently, Metcalf-Johnson (1977) reported willemite from the Ilimaussaq complex with chkalovite as the only accompanying Be mineral; genthelvite occurs elsewhere in the complex (Bollinberg and Petersen, 1967). Similarly, Bank (1975) reported willemite from Mont St. Hilaire in Canada; Dunn (1976) reported genthelvite. In such peralakaline willemite-bearing associations it would be unlikely to find topaz; rather sodium fluorides are typical. For example Kudrin (1978) reported peralkaline metasomatic rocks from the USSR with willemite, phenakite, and genthelvite; fluorine occurs in sodium fluorides such as pachnolite,
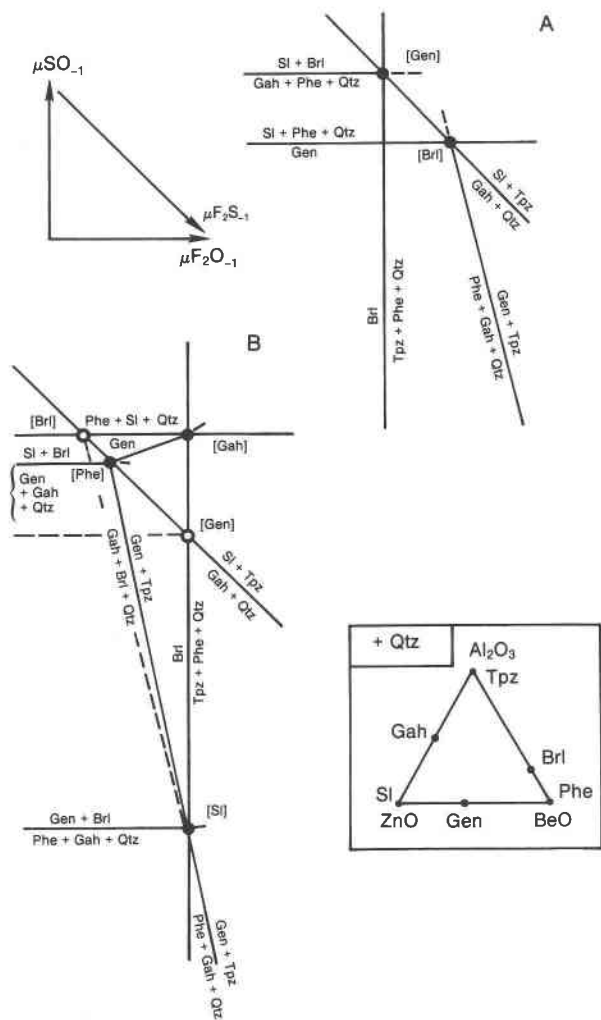

Fig. 12. Two alternative configurations for the multisystem derived from Reaction 4. Configuration A, to the upper right, is that of Fig. 11, in which the assemblage Gen + Brl is unstable. Configuration B, to the lower left, assumes that the assemblage Sl + Gah + Phe + Qtz is unstable. See text for discussion; for abbreviations, see Tables 1 and 3.

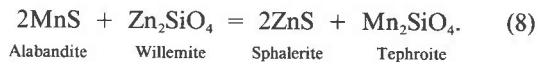thompsenolite, ralstonite, weberite, neighborite, and gagarinite.

Nigerite (Jacobson and Webb, 1947) is another accessory Zn mineral of granites and pegmatites, but no occurrences with genthelvite are reported; common associates are sillimanite, chrysoberyl, and gahnite (cf. Kloosterman, 1974; Burke et al., 1977; Cech et al., 1978). These data suggest that nigerite is restricted to peraluminous, high-temperature environments. As mentioned and discussed above, occurrences of genthelvite with aluminous minerals such as beryl and topaz seem to be quite restricted.
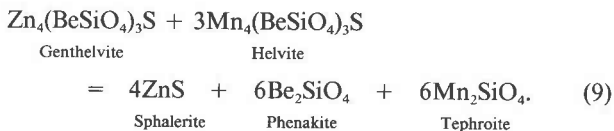
SOLID SOLUTION RELATIONS

Despite their somewhat similar crystal chemistry, Zn is very much more chalcophile than Be. In fact, Be is not

chalcophile at all (probably less so than Si), but Zn is more chalcophile than Fe, and much more so than Mn (e.g., Marakushev and Bezmen, 1974; Maurel, 1969). This fact presumably explains (Burt, 1977) the otherwise inexplicable lack of Zn-Mn solid solutions in the Zn-Fe-Mn helvite-group minerals noted by Dunn (1976). That is, under environments rich enough in SO_{-1} [i.e., under sufficiently high H_2S fugacities; actually, the operator involved is $S_2(SiO_4)_{-1}$] that the FeS or especially MnS component of helvite would be stable, the Zn_2SiO_4 component would have been sulfidized to ZnS. Conversely, under the low SO_{-1} conditions needed to stabilize genthelvite, the FeS and particularly MnS components of danalite and helvite would not yet be stable, and Fe and particularly Mn, if present, would occur in coexisting silicates or oxides.

In terms of specific reactions, data given by Robie et al. (1979) as well as common natural assemblages confirm that the following reaction goes to the right among the end members:

$$2MnS + Zn_2SiO_4 = 2ZnS + Mn_2SiO_4. \quad (8)$$
$$\text{Alabandite} \quad \text{Willemite} \quad \text{Sphalerite} \quad \text{Tephroite}$$

Presumably also the following end-member reaction would go to the right:

$$Zn_4(BeSiO_4)_3S + 3Mn_4(BeSiO_4)_3S$$
$$\text{Genthelvite} \qquad\qquad \text{Helvite}$$

$$= 4ZnS + 6Be_2SiO_4 + 6Mn_2SiO_4. \quad (9)$$
$$\quad \text{Sphalerite} \quad \text{Phenakite} \quad \text{Tephroite}$$

or, if not tephroite, some other manganese silicate.

SUMMARY

The extremely high chalcophilicity of Zn explains, in part, why genthelvite is such a rare mineral. It is only somewhat more stable than willemite and is therefore restricted to the extremely low-S environments provided by alkaline granites and syenites (where it typically occurs with other Zn minerals such as willemite and gahnite). These alkali-rich environments also tie up all available Al as feldspars or feldspathoids; this tendency destabilizes beryl and allows the occurrence of phenakite and of members of the helvite group (Burt, 1981). It is unclear (Reaction 4 above) whether beryl is stable with genthelvite at all, although beryl is reported with other minerals of the helvite group. Under strongly peralakaline (agpaitic) conditions, genthelvite or phenakite are replaced by sodium-beryllium silicates such as chkalovite and possibly a zinc analogue (synthesized by Litvin et al., 1974) or by hydrous phases such as eudidymite and epididymite.

Figure 7 shows that genthelvite becomes stable at a lowered SO_{-1} potential under conditions of silica activity less than one; conversely, a raised SO_{-1} potential destroys genthelvite more readily under these conditions. That is, genthelvite will be the most resistant to sulfidation ("burning off") in a silica-saturated environment; with rising H_2S it will break down to a mixture of sphalerite, phenakite, and quartz (an assemblage that could coexist with a danalite-enriched member of the helvite group).

Assemblages of sphalerite with aluminum silicates (or pyrophyllite) indicate the instability of gahnite under relatively high H_2S, low HF conditions (as in metamorphosed sulfide deposits). Assemblages of topaz with ZnO-rich minerals such as gahnite, genthelvite, and willemite (the latter not reported with topaz, to my knowledge) indicate an environment unusually rich in HF and poor in H_2S, as indicated by the operator F_2S_{-1} or log a_{HF}^2/aH_2S. Details are given in Figure 11. The more normal assemblage is topaz with sphalerite, especially in greisens; this assemblage indicates an environment enriched in both HF and H_2S. The topaz + sphalerite assemblage is compositionally equivalent (Reaction 7 above) to the pegmatite assemblage gahnite + quartz, which indicates an environment depleted in both HF and H_2S.

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