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Mn zonation and fluid inclusions in genthelvite from the Taghouaji complex (Aïr Mountains, Niger)

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ABSTRACT

Be and Zn mineralization occurs in veins and breccia in a biotite granite and syenite in the Taghouaji alkaline ring Complex in the Aïr Mountains, Niger. Beryl, bertrandite, willemite, genthelvite, and berthierine are present, but beryl and genthelvite do not coexist. Analyses of genthelvite and berthierine indicate for the first time that intermediate solid solutions exist between genthelvite [$Zn_4(BeSiO_4)_3S$] and helvite [$Mn_4(BeSiO_4)_3S$] and between berthierine [$(Si_{2-x}Al_x)(Fe^{2+}_{3-x}Fe^{3+}_x)O_5(OH_4)$] and fraipontite [$(Si_{2-x}Al_x)(Zn_{3-x}Al_x)$-$O_5(OH_4)$]. Primary two-phase fluid inclusions in Mn-poor genthelvite contain a low-salinity aqueous solution and homogenize around 375 °C, close to the critical density. In the Mn-rich genthelvite and in the Mn-rich rim of zoned crystals, the homogenization temperatures are lower (up to 288 °C). It is concluded that genthelvite was precipitated from a low-salinity aqueous fluid at temperatures higher than 375 °C and pressures greater than 220 bars.

INTRODUCTION

The Zn end-member of the helvite group [$R_4(BeSiO_4)_3S$ where R = Mn, Fe or Zn], genthelvite, is rarely observed. It was first described by Glass et al. (1944) and subsequently found at various localities (Glass and Adams, 1953; Scott, 1957; Eskova, 1957; von Knorring and Dyson, 1959; Haapala and Ojanpera, 1972; Dunn, 1976). On the basis of 75 chemical analyses of minerals in the helvite group, Dunn (1976) has shown that there is a complete solid solution between helvite (Mn) and danalite (Fe), and between danalite (Fe) and genthelvite (Zn). Intermediate compositions between genthelvite (Zn) and helvite (Mn) are lacking. However, we document such intermediate compositions in the Taghouaji Complex (Aïr Mountains, Niger) (Fig. 1). An intermediate composition between berthierine [$(Si_{2-x}Al_x)(Fe^{2+}_{3-x}Fe^{3+}_x)O_5(OH)_4$] and fraipontite [$(Si_{2-x}Al_x)(Zn_{3-x}Al_x)O_5(OH)_4$] is also documented.

Chemical zoning has been observed in genthelvite crystals (Haapala and Ojanpera, 1972; Dunn, 1976; Clark and Fejer, 1976) but the physical and chemical conditions that created the zoning are not well understood. The presence of primary fluid inclusions in zoned Aïr Mountains genthelvite allows us to place constraints on the temperature, pressure, and mineralizing fluid composition.

ANALYTICAL CONDITIONS

The chemical compositions of genthelvite and bertrandite were determined with a MBX CAMEBAX electron microprobe with the following conditions: 15-keV accelerating voltage, 8-nA beam current and a 15-s counting time per element. Matrix corrections were made using the MBX Cor 2 program. The following standards were used: synthetic ZnO for Zn, synthetic Fe_2O_3 for Fe, rhodonite for Mn, quartz for Si, pyrite for S, and Al_2O_3 for Al. Microthermometric measurements on fluid inclusions were made on a heating and cooling stage described by Poty et al. (1976). The precision is ±0.2 °C for melting temperatures and ±5 °C for homogenization temperatures in the range 300–400 °C.

Be-Zn MINERALIZATION: OCCURRENCE AND PARAGENESIS

The Taghouaji alkaline ring Complex is related to the Niger-Nigeria younger granites province, known for Sn and especially Zn mineralization in Nigeria (Bowden and Kinnaird, 1978). In Niger, it is the only complex where both alkaline granites containing pyroxene and amphibole and aluminous biotite granites are represented (Fabries and Rocci, 1965; Perez, 1985). The Sn, W, and Be-Zn (Pb) mineralization is either associated with biotite granites or occurs in the immediate vicinity of these gran-

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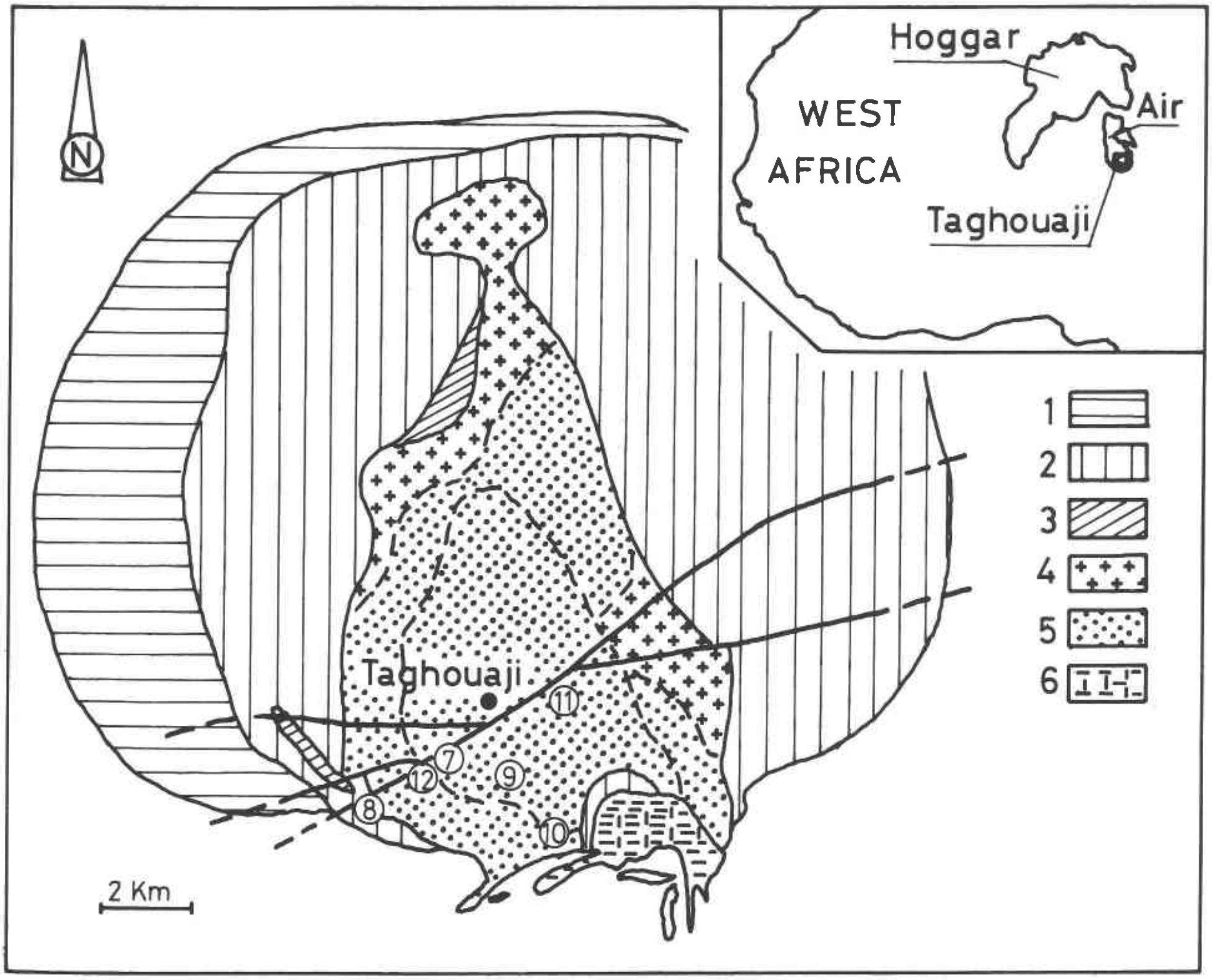

Fig. 1. Geological map of the Taghouaji ring Complex with sample localities (9, 10, 11, and 12). (1) pyroxene granite, (2) amphibole granite, (3) amphibole microgranite, (4) coarse biotite granite, (5) biotite granite, (6) rhyolite, (7) beryl mineralization in granite pockets, (8) albitite containing bertrandite and hematite, (9) vein containing quartz, genthelvite, and hematite, (10) vein containing quartz, genthelvite, galena, sphalerite, and zincian berthierine, (11) syenite containing galena, willemite, and genthelvite, (12) breccia containing genthelvite, hematite, and bertrandite.

Fig. 2. Photomicrograph of the genthelvite + quartz + hematite (Ge-Qz-He) association. Note that genthelvite crystals show a perfect tetrahedral shape and that the euhedral hematite laths and xenomorphic quartz crystallized after genthelvite.

ites (Fig. 1). Beryl and sphalerite are present with other rarer minerals: bertrandite [$Be_4Si_2O_7(OH)_2$], willemite ($ZnSiO_4$), zincian-berthierine [$(Al,Fe,Zn)_{2\text{-}3}(Si,Al)_2O_5(OH)_4$], and genthelvite [$(Zn,Mn,Fe)_4(BeSiO_4)_3S$]. Beryl and genthelvite do not coexist, an observation consistent with the chemical-potential diagrams proposed by Burt (1980).

The crystal-chemical and fluid inclusion analyses focused on four occurrences, which are described below.

1. A vein containing quartz + genthelvite + hematite, approximately 10 cm in thickness and several meters in length, hosted by a biotite granite in which late muscovite has crystallized. Genthelvite, beige in color, shows a typical tetrahedral morphology (Fig. 2) and is optically zoned. Textural relationships indicate that quartz and hematite crystallized after genthelvite. Zircon crystals are also present in this vein (Perez, 1985).

2. A vein containing quartz + sphalerite + galena +

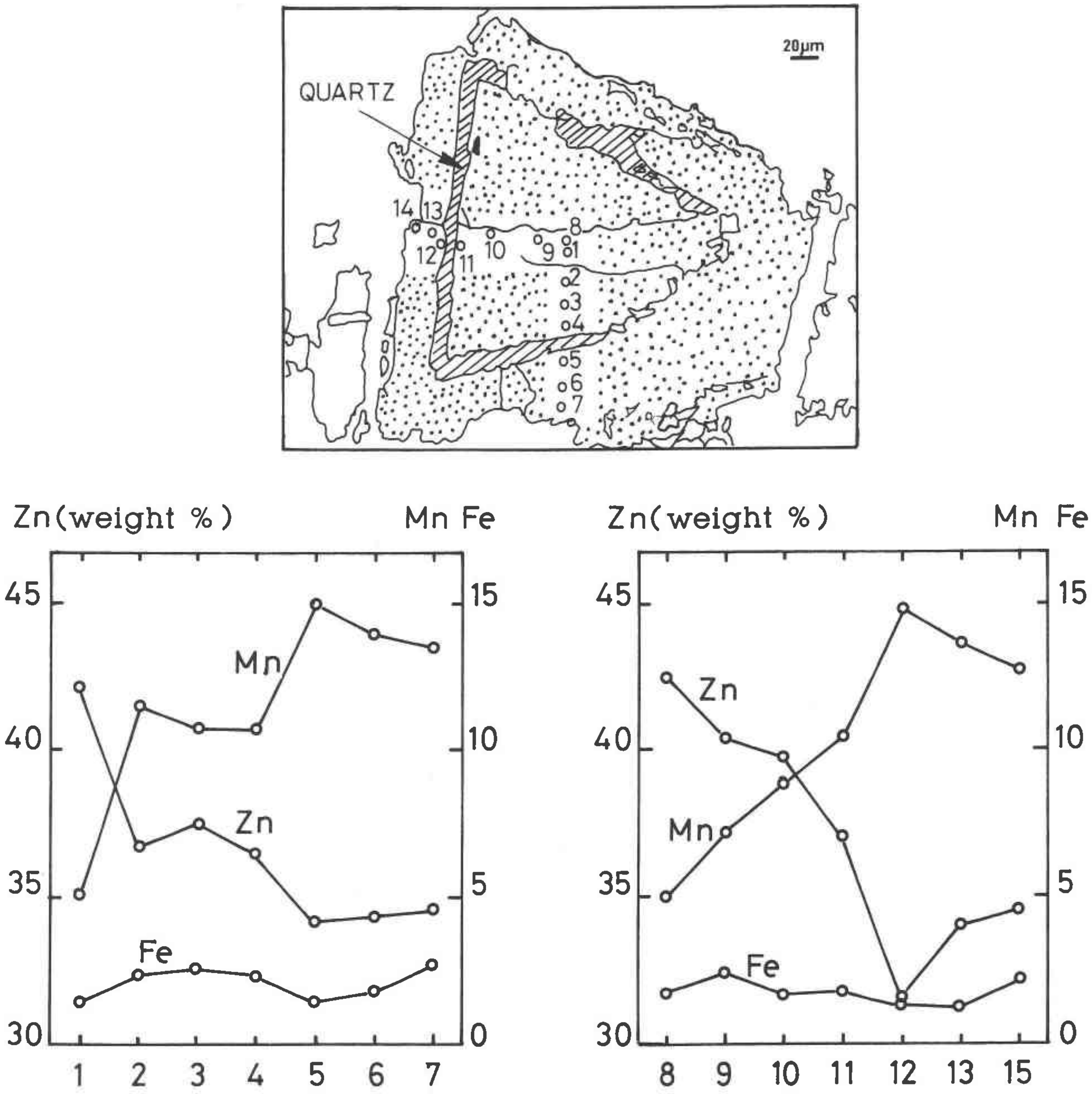

Fig. 3. Chemical zonation of a genthelvite crystal: **Above:** Sketch of a zoned genthelvite crystal from the quartz-hematite vein with a discontinuous quartz zone. Two perpendicular series of electron microprobe analyses are noted by numbers. **Below:** Variation of Mn, Fe, and Zn across the genthelvite crystal.

genthelvite, approximately 1 m in thickness, located in a biotite granite (Fig. 1). Genthelvite occurs as beige tetrahedral crystals and is associated with automorphic quartz crystals. A second phase of mineralization is responsible for quartz crystallization on the genthelvite and euhedral quartz crystals. The second quartz generation is associated with galena, sphalerite, and chalcopyrite, the latter often altered to chalcocite and covellite. Hematite is the last mineral to crystallize. The last stage of mineralization occurs in small cavities (0.5 to 1.5 mm) in the form of radiating aggregates of small green zincian-berthierine crystals (10–100 μm in size) which form a rim on the preceding paragenesis.

3. An association of willemite + galena and genthelvite located in a syenite. The syenite contains striped and patchy perthites and acmite with up to 5 wt% MnO. Late mineralization consists of willemite, galena, genthelvite, quartz, and accessory minerals, including titanite and oxides of Fe and Mn. Genthelvite occurs as xenomorphic crystals coating willemite and galena, the latter partly replaced by anglesite.

4. A breccia containing genthelvite + hematite + ber-

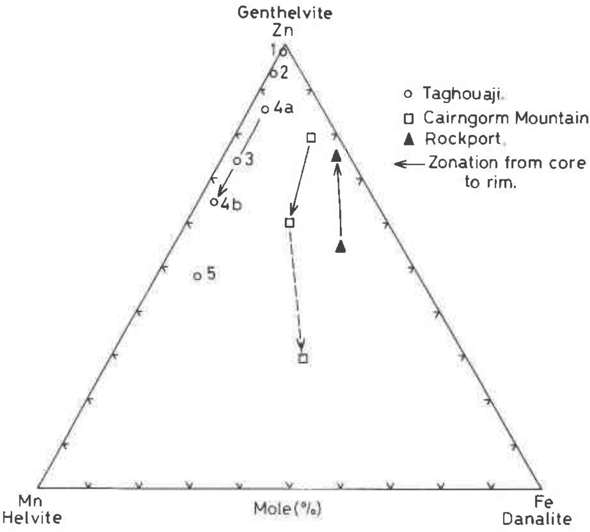

Fig. 4. Composition of genthelvite on a Zn-Fe-Mn ternary plot (numbers refer to analyses given in Table 1). For the Taghouaji Complex, the arrow indicates the chemical evolution, from 4a to 4b, in the same crystal. Chemical zonation in a genthelvite crystal from Cairngorm Mountains, Scotland (Clark and Fejer, 1976), and Rockport, Massachusetts (Dunn, 1976) are given for comparison.

trandite located on a major fault zone, N70°E south of the Taghouaji Complex (Fig. 1). Genthelvite, bertrandite, clays, quartz, hematite, and rare cassiterite crystals constitute the cement of hematite-rich elements. White banded zones contain mainly transparent to translucent tetrahedra of genthelvite, with marked growth zones containing quartz inclusions (Fig. 3). The X-ray lattice parameter obtained on genthelvite is 8.165 (3) Å, an intermediate value between that of the Zn end-member, 8.11 Å and the Mn end-member, 8.27 Å (Oftedal and Saebo, 1963).

MINERAL CHEMISTRY

Electron microprobe analyses were obtained, mainly for genthelvite but also for berthierine. The chemical composition of genthelvite from the Taghouaji Complex (Table 1 and Fig. 4) is variable and depends on the mode of occurrence; all analyses are poor in Fe. In the vein containing quartz + genthelvite + sphalerite + galena, the composition is close to pure genthelvite. In the syenite, genthelvite is poor in Mn (4.5 wt% MnO). In the vein containing quartz + genthelvite + hematite and in the breccia, genthelvite is zoned and rich in Mn; the MnO content reaches 20 wt% in the microcrystals. A detailed study of the chemical zoning (Fig. 3) shows that the MnO content is about 5 wt% in the crystal cores, increases to 15 wt% toward the discontinuous quartz rim, and then slightly decreases in the outer zone.

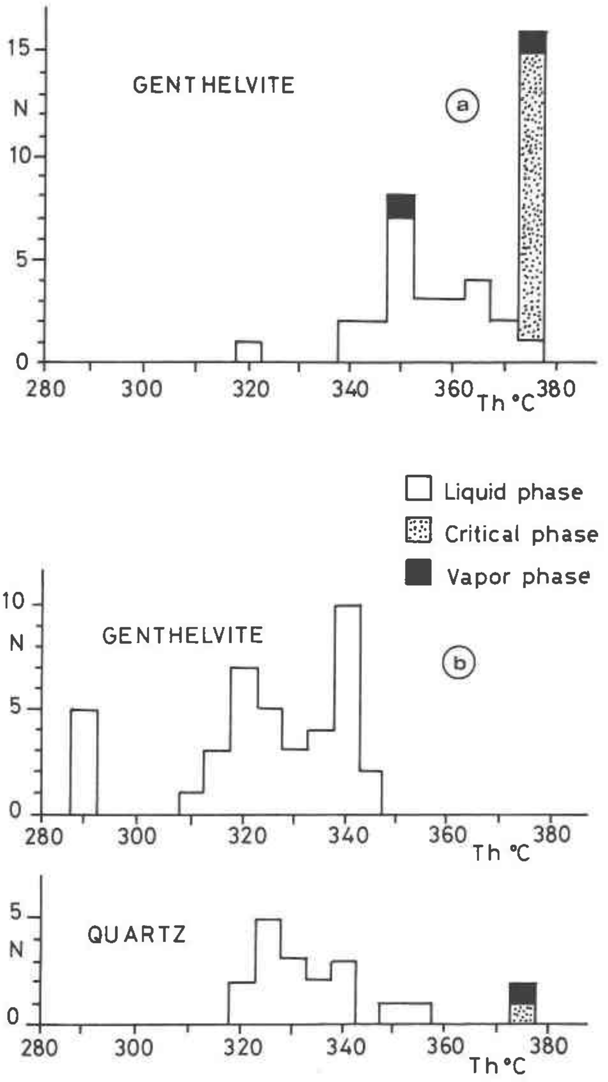

Fig. 5. Distribution of homogenization temperatures for fluid inclusions in genthelvite and quartz: **(a)** quartz-genthelvite-sulphide association, **(b)** quartz-genthelvite-hematite association.

The chemical composition of berthierine from the assemblage quartz + genthelvite + sphalerite + galena is intermediate between berthierine (Fe) and fraipontite (Zn). From the structural formula $(Si_{1.49}Al_{0.51})(Al_{0.78}Fe^{2+}_{1.14}Zn_{0.83}Mg_{0.10}Ca_{0.02})O_5(OH_4)$, this mineral could be called zincian berthierine.

FLUID INCLUSIONS IN GENTHELVITE

The presence of two-phase aqueous inclusions in genthelvite crystals is noted here for the first time. The inclusions are scarce and range up to 40 μm in size with an average of 15 μm. They are often isolated or grouped but never occur along trails. The inclusions are sometimes located unambiguously along growth planes. They are primary fluid inclusions, i.e., inclusions that formed during crystal growth. Their form is the negative shape of a tetrahedral crystal. The homogenization temperatures vary between 288 and 377 °C in all samples studied

TABLE 1. Chemical composition of genthelvite and Zn-berthierine from the Taghouaji Complex (Camebax electron microprobe)

	Genthelvite						Berthierine
	Quartz + sphalerite + galena + berthierine vein	Syenite containing willemite + galena	Quartz + hematite vein	Breccia			Quartz + sphalerite + galena + genthelvite vein
				Zoned crystal*		Microcrystals	
				Core	Rim		
Reference	1	2	3	4a	4b	5	
Number of analyses	5	7	4	1	1	3	7
ZnO	52.09	49.23	39.61	42.49	34.19	25.85	19.56
FeO(total)	0.20	0.31	1.31	1.67	1.47	4.02	23.61
MnO	0.64	2.76	10.52	5.00	15.04	20.55	0.04
SiO_2	32.10	32.54	32.60	33.65	33.04	32.54	25.73
S	5.38	5.50	5.37	5.12	5.23	5.48	—
BeO**	12.22	12.15	12.25	11.53	12.23	12.43	—
Al_2O_3	n.d.	—	n.d.	0.10	0.15	n.d.	19.00
Total	102.63	102.49	101.66	99.56	101.35	100.87	89.26†
O = S	2.69	2.75	2.68	2.56	2.61	2.74	—
Total	99.94	99.74	98.98	97.00	98.74	98.13	99.62‡

* The extreme values for MnO are considered.

** BeO is calculated following Dunn (1976), (Zn + Mn + Fe):Be = 4:3.

† Including MgO = 1.06; CaO + Na_2O + K_2O = 0.26.

‡ Including calculated H_2O = 10.36.

(Fig. 5) and occur in the liquid phase or the critical phase, with very few homogenizing in the gas phase. The melting temperatures of ice are between −0.1 and −0.7 °C. In quartz, similar homogenization temperatures are observed (Fig. 5), and the melting temperatures are in the same range. This gives us confidence about the reliability of fluid inclusions in genthelvite for geothermometry. In genthelvite from the quartz + sulphide association, a large majority of inclusions homogenize at the critical density around 375 °C, and others homogenize to a liquid, the lowest temperature being 318 °C. In the quartz + hematite association, fluid inclusions have smaller sizes, (around 10 μm) and their homogenization temperatures in the liquid phase are between 288 and 344 °C. There is no apparent correlation between homogenization temperatures and melting temperatures.

DISCUSSION

Crystal zoning in the helvite group

Crystal zoning has been observed in the helvite group, (Dunn, 1976), especially in danalite, but few descriptions are available. Clark and Fejer (1976) report that genthelvite crystals from the Cairngorm Mountains, Scotland, show zoning comparable to that of Taghouaji (Fig. 3) but contain equimolar proportions of Mn and Fe. On the other hand, Haapala and Ojanpera (1972) observe inverse oscillatory zoning in a crystal from Eurajoki, Finland. Dunn (1976) also describes the existence of an inverse zoning in the Zn-Fe compositions in a crystal from Rockport, Massachusetts. Zubkov and Metalidi (1972), studying various generations of genthelvite crystals in a granitic massif, show that the Zn substitution by Mn increases when the temperature decreases. Because temperatures were obtained directly from fluid-inclusion analyses for the different generations of genthelvite from the Taghouaji Complex, this interpretation can be tested.

Genthelvite crystallization temperatures

In the case of an aqueous solution where no boiling is evident, the homogenization temperatures are minimum trapping temperatures, and a pressure correction must be made (see Roedder and Bodnar, 1980, for example). The slope of the isochore depends on the salinity of the solution (Potter, 1977). Melting temperatures of ice in the range −0.1 to −0.7 °C indicate very low-salinity aqueous solutions, 0.2 to 1.2 equivalent wt% NaCl. Homogenization temperatures at the critical density around 375 °C are consistent with the critical point of pure water at 374 °C and 221 bars. All the microthermometric data are consistent with almost pure water with a critical density around 0.32 g/cm^3. The absence of boiling implies that the pressure was higher than 220 bars during genthelvite crystallization. However, anorogenic complexes, such as the Taghouaji Complex, are emplaced at shallow levels in the crust. If 500 bars is considered as the maximum trapping pressure, the corresponding temperature is 480 °C. If there was no intense erosion and in the absence of later high-temperature thermal events, the variation of pressure is not a parameter that can adequately explain the variation of homogenization temperatures between Mn-poor and Mn-rich genthelvite. This indicates that the trapping temperatures of fluid inclusions in Mn-rich genthelvite are lower and that, because the inclusions are primary, the temperature of formation of Mn-rich genthelvite is lower than that for Mn-poor genthelvite. A difference in f_{O_2} could explain the Mn content of genthelvite. We observe that sulfides are predominant with Mn-poor genthelvite and hematite with the Mn-rich genthelvite. A high f_{O_2}, as indicated by hematite, could explain the observed lack of solid solution towards danalite. However, the sulfides and hematite are not texturally contemporaneous with the genthelvite crystallization.

CONCLUSIONS

1. Intermediate solid solutions between genthelvite and helvite have been found for the first time in veins and breccia in a biotite granite and syenite in the Taghouaji alkaline ring Complex in the Aïr Mountains.
2. A zincian-berthierine, also evidenced for the first time, has been identified in an assemblage of quartz + genthelvite + sphalerite and galena.
3. The Mn-poor genthelvite has precipitated from a low-salinity aqueous fluid at temperatures higher than 375 °C and pressures greater than 220 bars.
4. The temperature of formation of Mn-rich genthelvite is lower than that for Mn-poor genthelvite. A difference in oxygen fugacity could explain the Mn content of genthelvite.

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