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TRACE-ELEMENT CONTENTS OF HELVITE-GROUP MINERALS FROM METASOMATIC ALBITITES AND HYDROTHERMAL VEINS AT SUCURI, BRAZIL AND DAJISHAN, CHINA

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ABSTRACT

Trace-element data are presented for helvite-group minerals representing various parageneses and compositions, found in albitites from Sucuri (Goias, Brazil), and in W-bearing quartz veins from Dajishan (Jiangxi, China). Even though Ag, Au, Ta, W, and Ga are more likely to occur in small inclusions of sulfide, oxide, or mica, the rare-earth elements (*REE*), Sc, Co, Na, and Cd substitute isomorphously in helvite for the major cations Fe, Mn, and Zn. The sum of *REE* in helvite-group minerals ranges from 25 to 675 ppm, and shows a positive correlation with the abundance of *REE* in the associated granites. However, helvite-group minerals have a strong affinity for heavy *REE* (*HREE*), leading to highly fractionated patterns. An estimation of the equilibrium constant for the exchange of La and Yb between helvite and fluid yielded values in the range 0.004–0.011. The variability of Sc and Cd contents is high (7 to 120 ppm and less than 100 to 200 ppm, respectively), and may in part be related to the substitution among Zn, Mn and Fe, on the basis of examination of ionic radii.

Keywords: helvite, danalite, albitite, hydrothermal vein, trace elements, rare-earth elements, Goias, Brazil, Jiangxi, China.

SOMMAIRE

L'analyse des éléments traces contenus dans des fractions séparées de minéraux du groupe de l'helvine dans deux contextes géologiques différents (albitites de Sucuri, Goias, Brésil et veines à quartz–wolframite de Dajishan, Jiangxi, Chine) a permis de distinguer les éléments présents dans le réseau en remplacement des cations majeurs Fe, Zn et Mn (terres rares, Sc, Co, Na et Cd), des éléments présents dans des microinclusions de sulfures (Ag et Au), d'oxydes (W, Ta) et de micas (Ga). La concentration des terres rares dans les minéraux du groupe de l'helvine varie de 25 à 675 ppm, en liaison avec l'abondance des terres rares dans les massifs granitiques associés aux gisements. Cependant, les minéraux du groupe de l'helvine présentent une affinité marquée pour les terres rares lourdes, avec des spectres très fractionnés. La constante d'équilibre pour l'échange de La et Yb entre helvine et fluide a été estimée à 0,004–0,011. Les variations en teneurs de Sc et Cd sont fortes (respectivement 7 à 120 et <100 à 200 ppm), et sont probablement en partie expliquées par les substitutions impliquant Fe, Mn et Zn.

Mots-clés: helvine, danalite, albitite, veine hydrothermale, élément-trace, terres rares, Goias, Brésil, Jiangxi, Chine.

INTRODUCTION

Chemical variations within the helvite group are expressed by the general formula $(Fe,Zn,Mn)_8Be_6(SiO_4)_6S_2$ (Dunn 1976), and result in solid solution between the three end-members helvite *sensu stricto* (Mn), danalite (Fe) and genthelvite (Zn). The extent of ternary solid-solution is complete, and intermediate compositions are known within the whole helvite (*sensu lato*) series (Dunn 1976). The cubic cell is similar to that of sodalite $Na_8Al_6(SiO_4)_6Cl_2$ (Hassan & Grundy 1984, 1985). The Be, (Fe,Mn,Zn), and S sites of the helvite structure are equivalent to Al, Na, Cl sites of the sodalite structure, respectively. Unlike the other main Be-bearing mineral, beryl, their occurrence is favored by low activities of alumina, and high activities of sulfur, and iron, zinc, or manganese in the mineralizing solution. The acidity in the solution also influences the sulfur fugacity and, therefore, the stability fields of helvite and beryl (Bilal & Fonteilles 1988).

Owing to the structural differences between beryl and helvite, it may be expected that trace-element patterns in helvite-group minerals differ from those observed in beryl, the latter being characterized by a strong affinity for Li, Na, and Cs (Aurisicchio *et al.* 1988). This paper presents data on trace elements in helvite-group minerals of different compositions, from albitites in the Sucuri granite massif (Goias State, Brazil), and from wolframite-bearing quartz veins in the Dajishan tungsten deposit (Jiangxi Province, China).

DESCRIPTION OF THE OCCURRENCES OF HELVITE-GROUP MINERALS

Albitite veins in the Sucuri granite massif, Brazil

The Sucuri granite massif, *ca.* 8 km^2 in area, is located in Goias State, northeast of Cavalcante, and 300 km north of Brasilia. A radiometric age of 1.77 Ga is given by Pimentel *et al.* (1991) for this granite emplaced in Archean gneisses.

The massif consists of several facies, ranging from biotite-bearing, medium- to fine-grained granites, to granite porphyry in the eastern edge of the massif. The granites are foliated, and secondary muscovite is developed throughout the massif. Aplitic dykes cross-cut the main medium-grained facies. At Vaca Velha (Fig. 1), metasomatic Sn–W–Be-bearing siderophyllite-rich veins are developed in the main granite at the upper contact of the fine-grained granite, indicating that the emplacement of the latter melt occurred after the crystallization of the former. This suggests a multistage emplacement of successive melts. Moreover, petrographic, mineralogical (*e.g.*, monazite composition) and geochemical (*e.g.*, Zr/Hf ratios) arguments rule out a cogenetic relationship between the two former facies and the granite porphyries (Bilal 1991). This massif appears as a composite intrusion. Contents of Nb, Y, Rb and Ga in the Sucuri granites are high, and similar to those of the alkali granites in the Oslo Province (Neumann *et al.* 1977).

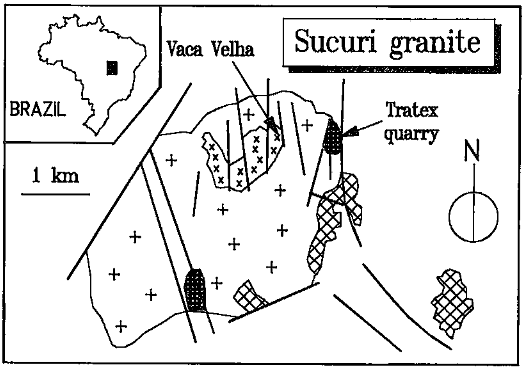

FIG. 1. Geological map of the Sucuri granite massif (Goias, Brazil). large +: medium-grained biotite-bearing granite; small ×: fine-grained granite; square pattern: granite porphyry; dark grid: zones with albitite occurrences.

TABLE 1. SUMMARY OF MINERAL TRANSFORMATIONS IN ZONES IN THE SUCURI ALBITITES

Biotite-bearing granite	Albitite			
	Zone 1	Zone 2	Zone 3	Zone 4
Biotite (I) Fe/Mg = 22.4	Biotite (II) Fe/Mg = 12	<—— Biotite (II) ——> <—— Fe/Mg = 10 ——>		
Muscovite	Muscovite –>	<—— Albite ——>		
Plagioclase An20-16	<—— Albite ——> <—— An0.5 ——>			
K-Feldspar	K-Feldspar ——>		<—— Albite ——>	
Quartz	Quartz ——>			Albite
	<—— Helvite ——> $Ge_{24}Da_{51}He_{25}$	$Ge_{30}Da_{49}He_{21}$	$Ge_{64}Da_{10}He_{26}$	
	Pyrrhotite, Chalcopyrite, Sphalerite, Pyrite, Galena and Cubanite			

The composition of the helvite-group minerals was determined by electron microprobe [see Bilal (1991) for complete results, and Table 2 for representative compositions].

Albitite developpment was found at several places in the massif. The main occurrence of albitite, located in the northeastern part of the massif, in the Tratex quarry (Fig. 1), has been prospected for tin. Meter-wide bodies of albitized rocks are developed within the biotite granite, the foliation of which disappears in these vein-like bodies. Albitization thus postdated the episode of deformation responsible for the foliation. The initial association of minerals is altered in several successive metasomatic zones, within which usual minerals occurring in granite are replaced by albite (Table 1). Contacts between the zones correspond to sharp replacement-fronts, involving the successive disappearance of oligoclase (zone 1), secondary muscovite (zone 2), K-feldspar (zone 3), and quartz (zone 4).

Helvite-group minerals are present in all zones (Bilal & Fonteilles 1988). In the first zone, characterized by the replacement of magmatic oligoclase by albite, the composition of danalite varies within a narrow range around $Ge_{24}Da_{51}He_{25}$ (Table 2). Danalite is associated with biotite, sulfides and, locally, fluorite. In the second zone, characterized by the breakdown of the secondary muscovite, the composition of danalite has a slightly lower helvite component $Ge_{30}Da_{49}He_{21}$. The more internal zones correspond to the replacement of first K-feldspar and then quartz by albite. Helvite (*sensu lato*) crystals are zoned, with a core of genthelvite $Ge_{64}Da_{10}He_{26}$ surrounded by a rim of danalite $Ge_{25}Da_{52}He_{23}$. This latter composition is quite similar to that of the danalite in the external zones. The main change in helvite composition in the albitite vein thus occurs between "internal" fourth and third zones, and "external" second and first zones. Starting with a high component of genthelvite, the composition evolves toward danalite (Table 2, Fig. 2).

Some sulfides (pyrrhotite, chalcopyrite, pyrite, sphalerite, and galena) are associated with helvite. Iron contents of the sphalerite differ from the first zone (14

TABLE 2. REPRESENTATIVE CHEMICAL COMPOSITIONS[*] OF HELVITE

Massif	Sucuri				Dajishan	
	Internal zone		External zone		qz-wolfr. vein	
SiO_2 wt%	32.9	33.0	32.9	33.2	32.7	33.2
Al_2O_3	–	–	–	0.07	0.07	0.07
FeO	4.95	15.4	24.2	25.2	15.1	13.9
MnO	12.1	10.05	9.66	12.9	30.1	31.9
ZnO	35.5	26.8	18.5	13.6	5.81	5.08
S	5.51	5.55	5.54	5.53	5.64	5.66
Total	90.96	90.80	90.80	90.50	89.42	89.81
S≡O	2.75	2.77	2.76	2.76	2.81	2.82
Total#	88.21	88.03	88.04	87.74	86.61	86.99
Atoms per formula unit on the basis of 18 oxygen atoms						
Si	6.16	6.14	6.07	6.09	6.04	6.08
Al	–	–	–	0.02	0.02	0.02
Fe	0.78	2.39	3.74	3.86	2.33	2.13
Mn	1.92	1.58	1.51	2.00	4.71	4.95
Zn	4.91	3.68	2.52	1.84	0.79	0.69
S	1.93	1.93	1.92	1.90	1.95	1.94
End-member composition						
Ge	64.6	48.1	32.5	23.8	10.1	8.9
Da	10.2	31.2	48.1	50.2	29.8	27.4
He	25.2	20.7	19.4	26.0	60.1	63.7

[*] Composition determined by electron-microprobe analysis. Analytical conditions: accelerating voltage 20 kV, current 20 nA; olivine (Si), oxides (Al, Fe, Mn, Zn) and pyrite (S) used as standards. Data were corrected following the ZAF procedure. Absolute uncertainties at the 95% level of confidence (±2σ): SiO_2, 0.2%; FeO, 0.09 to 0.2%; MnO, 0.14 to 0.3%; ZnO, 0.11 to 0.3%; S, 0.09%. Detection limit for Al_2O_3, 0.04%. All Fe is assumed to be FeO (Dunn 1976). [#] Low total is due to lack of data on concentration of BeO by electron microprobe. ICP-AES analyses of four separates yielded a mean value of 13.1% BeO.

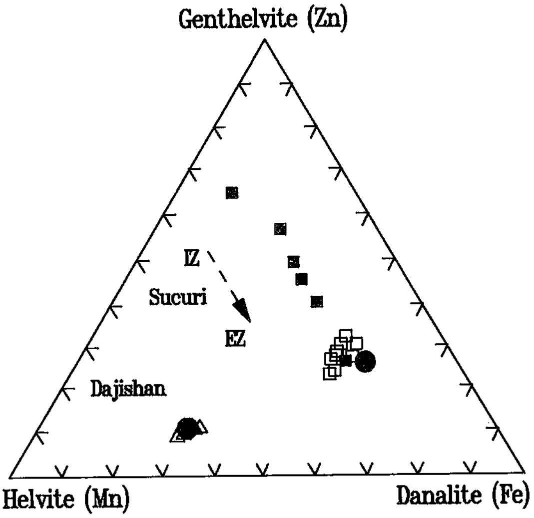

FIG. 2. Helvite (*sensu lato*) compositions in terms of helvite *sensu stricto* (Mn end-member) – genthelvite (Zn) – danalite (Fe) diagram (molar basis). Small symbols refer to results of electron-microprobe data. Open triangles: helvite from Dajishan quartz–wolframite veins; open squares: danalite from external zones (EZ) in Sucuri albitites; filled squares: genthelvite–danalite from internal zones (IZ) in Sucuri albitites; large filled circles: composition of bulk fractions determined by ITNAA.

mole % FeS) to the third and fourth zones (19–20 mole % FeS). These values are consistent with a formation in the pyrite field, near the pyrite–pyrrhotite equilibrium (Barton & Skinner 1967). These variations, together with the presence of early pyrrhotite, suggest that the evolution of the system is driven by an increase in sulfur fugacity at a constant temperature. Taking into account the presence of Cu (up to 0.57 wt%) in sphalerite from Sucuri, identical temperatures of about 525°C are obtained for the two groups of sphalerite compositions (Wiggins & Craig 1980).

Quartz–wolframite veins from the Dajishan tungsten deposit, China

Dajishan is an important deposit of wolframite in Jiangxi. Wolframite occurs in a series of parallel or nearly parallel vertical veins over a height of 300 m. Surrounding rocks consist of a thick series of Cambrian sandstones interbedded with minor slates, and cross-cut by a diorite dyke considered to be of Caledonian age. Various granitic rocks of early Yenshanian (Jurassic) age occur in the area. They include a large body of porphyritic biotite granite with a total areal extent of 92 km^2, outcropping 3 km to the north of the Dajishan mine. The lowest level of the mine at Dajishan cuts across a tongue-like flat body of fine-grained garnet-bearing albite granite (Fig. 3). This intrusive body is 500 m in diameter. It is connected at depth to a biotite granite geochemically related to the main massif.

Based on *REE* geochemistry of fluorite, apatite, and scheelite, the hydrothermal activity in Dajishan wolframite-bearing veins can be divided into two stages. The first one is the main mineralizing event, and is

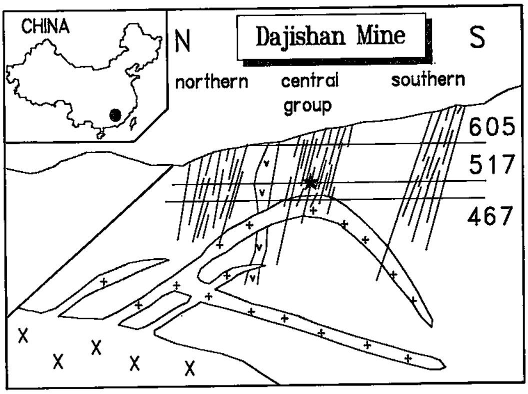

FIG. 3. Cross-section through the Dajishan tungsten deposit (Jiangxi, China). Large X: biotite granite; small +: garnet-bearing albite granite; v: diorite dyke; white: Cambrian strata; straight lines: quartz–wolframite veins, divided into three groups; 467, 517, and 605: mine levels. The location of the samples of helvite analyzed is indicated by the star.

characterized by large veins of quartz–wolframite with abundant radially disposed books of muscovite at the border. Fine-grained molybdenite is found as disseminated crystals in muscovite. Fluorite is intimately associated with wolframite and muscovite; K-feldspar is present in the lower part of the system, near the granitic cupola, to which this stage is related, as evidenced by the similarity of *REE* patterns in apatite and granite. The second stage is developed in the same veins as channels, and is characterized by the alteration of wolframite and the crystallization of euhedral, honey-colored scheelite in the central part of the veins. Garnet is present in both stages as a reaction product with wall-rock hornfelses. From the concentrations of the *REE*, it can be concluded that the mineralizing fluids of the two stages have a quite different origin (Raimbault *et al.* 1986).

Beryllium minerals are present at both stages. Beryl occurs as an early phase that crystallized from the beginning of the process, together with feldspar, up to later assemblages with muscovite and molybdenite. From field and petrological evidence, beryl can be related to the first stage. Helvite has been found only in large polycrystalline aggregates occurring in the central part of the veins, locally in close relationship with scheelite of stage II. Moreover, its field appearance strongly suggests a close relation with the second stage. The dominant cation is Mn, corresponding to helvite *sensu stricto* (Table 2, Fig. 2).

The occurrence of Be minerals seems to be intimately correlated with the nature of the fluid. Beryl is related to a F-rich, felsic-magma-related fluid, whereas helvite is linked with the alteration of the association of earlier minerals. This evolution is the product of a Ca-rich fluid, as shown by the composition of garnet, the Ca content of which increases from 2.4 wt% CaO in the first stage to 16.8% CaO in the second.

RESULTS

Analytical methods

Trace-element analyses have been performed on helvite separates from the Sucuri and Dajishan occurrences. The use of instrumental thermal neutron-activation analysis (ITNAA) allows a low level of detection for a wide range of elements on the same sample preparation. Moreover, sample weight needed for the analysis is low enough (around 15 mg or less) to allow a very efficient separation of mineral grains by careful hand-picking of fragments having a grain size of 125–315 μm or 315–800 μm under the binocular microscope after partial grinding. Examination of Figure 2 shows negligible difference between microprobe determinations and bulk-mineral analyses. Unfortunately, the zoned character as well as the small size of the genthelvite from the internal zones of the albitite veins at Sucuri precluded separation of pure crystals of genthelvite from there.

TABLE 3. ANALYTICAL CONDITIONS FOR NEUTRON-ACTIVATION ANALYSES

Element	Radio isotope	Gamma-transition energy (keV)	Irradiation time	Cooling time	Typical analytical uncertainty
Na	^{24}Na	1368.5	30 s	24 h	7 - 18 %
Sc	^{46}Sc	889.3	3 h	30 d	0.4 - 6 %
Cr	^{51}Cr	320.1	3 h	30 d	#
Mn	^{56}Mn	846.6	30 s	24 h	1 %
Fe	^{59}Fe	1099.3	3 h	30 d	0.7 - 1.1 %
Co	^{60}Co	1332.5	3 h	30 d	2 - 3 %
Zn	^{65}Zn	1115.5	3 h	30 d	1 %
Ga	^{72}Ga	834.0	30 s	24 h	40 %@
Se	^{75}Se	264.5*	3 h	30 d	20 %
Ag	^{110m}Ag	657.7	3 h	30 d	20 - 40 %@
Cd	^{115}Cd	527.9	3 h	8 d	18 %
Sb	^{124}Sb	1691.0	3 h	30 d	21 - 26 %
La	^{140}La	1596.2	3 h	8 d	17 - 20 %
Ce	^{141}Ce	145.4	3 h	30 d	19 - 25 %
Sm	^{153}Sm	103.2	3 h	8 d	2 - 6 %
Eu	^{152}Eu	1407.9	3 h	30 d	5 - 15 %
Gd	^{153}Gd	103.2	3 h	30 d	13 %
Tb	^{160}Tb	879.3	3 h	30 d	10 - 15 %
Yb	^{175}Yb	396.1	3 h	8 d	2 %
Lu	^{177}Lu	208.3	3 h	8 d	1.5 %
Ta	^{182}Ta	1221.3	3 h	30 d	11 - 15 %
W	^{187}W	685.7	3 h	8 d	12 %
Au	^{198}Au	411.8	3 h	8 d	20 - 40%@
Th	^{233}Pa	311.9	3 h	30 d	3 - 15%

* Peak intensity corrected for ^{182}Ta interference. # Detection limits only have been found. @ Order of magnitude only is valid; detection limits have mostly been found.

A 3-hour irradiation of aluminum-packaged samples and international geochemical standards (granite ACE, basalt BEN, and jasperoid GXR–1, Govindaraju 1984) was performed in the Orphée reactor at the C.E.N. Saclay, in a neutron flux of *ca.* $2.45 \cdot 10^{13}$ n·cm^{-2}·s^{-1}. Irradiation was followed by a one-week decay, a first count 1 to 3 hours long of "short"-lived radioisotopes, and after one month, a second count of long-lived radioisotopes (Table 3). For some fractions, Na, Mn, Ga and W contents were determined using short irradiation, cooling, and counting times. The method of calculation of concentrations in unknown samples was done by a direct comparison of sample activities with those of well-known standards. An exception was made in the case of some early determinations of Cd in Dajishan samples, for which no Cd standard was included in the irradiated package. Cadmium concentrations were calculated using an estimate of neutron flux and an absolute method. Although less precise, because of the uncertainties of many parameters such as neutron-capture cross-section, this method gives results in agreement with those of the comparative one.

Results and preliminary discussion

Analytical results are presented in Table 4. Three samples from Sucuri and two samples from Dajishan were analyzed. For the latter, one sample of helvite was separated into two fractions, based on fragment size, and the three separates were analyzed in duplicate in independent runs. This allowed an estimate of analytical reliability, and a discussion of the mode of occurence of the elements, either in the mineral or in inclusions. Indeed, helvite from Dajishan occurs as large crystals, and microscope observations showed neither systematic inclusions of minerals nor optical zonation. However,

TABLE 4. RESULTS OF ITNA ANALYSES OF HELVITE-GROUP MINERALS

Locality	Sucuri			Dajishan					
Sample	$Su3^{B2}$	$Su3^{C1}$	$Su3^{C3}$	517-36		517-39			
Fraction*				A	B	A1	B1	A2	B2
%									
MnO	7.63	9.14	na	na	24.8	na	28.4	na	27.7
FeO	25.7	28.2	25.9	14.00	15.01	13.87	14.76	14.37	14.43
ZnO	14.7	15.6	13.9	4.82	4.97	4.41	4.75	4.47	4.43
ppm									
Na	123	262	na	na	<17	na	14	na	15
Sc	106.4	119.8	118.3	6.84	7.36	8.58	9.63	8.17	8.51
Cr	<8	<6	<8	na[b]	<2	na	<3	na	<2
Co	12.3	14.2	9.8	2.45	2.73	2.18	2.40	2.13	2.44
Ga	<21	<13	na	na	9	na	<14	na	17
Se	8	5	<2	2.9	2.3	1.9	1.9	1.3	2.7
Ag	18	5	8	1.2	2.5	0.2	0.7	0.6	1.0
Cd	<100[d]	<110[d]	<110[d]	226[c]	175[d]	203[c]	174[d]	145[c]	171[d]
Sb	<1.2	2.3	<1.4	3.1	4.8	0.51	0.82	0.26	0.52
Ta	<1.6	1.4	4.5	0.58	7.5	0.42	0.35	0.49	0.52
W	<30	<18	na	2880	1344	na	33	na	<30
Au (ppb)	<23	<24	<25	24	9	na	<9	na	<7
Th	3.4	2.4	26.8	<0.2	0.20	<0.2	<0.3	<0.2	0.13
La	2.4	0.9	10.4	1.21	1.01	0.60	0.81	0.63	0.63
Ce	5.0	4.2	53.0	2.3	2.0	1.4	2.6	1.3	1.9
Sm	3.32	3.93	34.6	0.28	0.31	0.37	0.46	0.37	0.54
Eu	0.14	0.13	1.27	0.30	0.21	0.27	0.36	0.32	0.32
Gd	nd[b]	nd	63.5	nd	nd	na	nd	na	nd
Tb	1.8	1.9	12.4	0.43	nd	0.67	0.63	0.50	0.40
Yb	57.4	63.2	146	7.35	8.14	8.16	9.35	7.41	7.88
Lu	19.7	22.6	42.0	1.81	1.86	1.65	1.94	1.55	1.66

ITNA: Instrumental Thermal Neutron Activation analysis. Analytical conditions are given in Table 3. Significal digits only are indicated. * A, B: results of independent analyses of the same mineral separate; 1: crystal size 315–800 μm; 2: crystal size 125–315 μm. [b] na: not analyzed, nd: not detected. [c] Analysis for Cd using neutron flux monitoring. [d] Analysis for Cd by comparison with a synthetic standard.

the presence of small isolated inclusions cannot be excluded. Since such inclusions do not present a systematic character, the elements included in impurities will be characterized by rather scattered results. On the contrary, a narrow range of variation can be expected for elements occurring in the helvite structure, for each sample analyzed in duplicate (sample 517–36) or in quadruplicate (sample 517–39).

From Table 4, we conclude that Ga, W, Ta, Ag, and Au are likely to be located outside the helvite structure, whereas Na, Sc, Co, Cd and the *REE* seem to be incorporated in helvite, in substitution for the major elements Fe, Zn, Mn. The cases of Se and Sb are somewhat intermediate, because Se can replace the major helvite-forming anion S, and Sb, the major cations, but a rather high variance in the results, together with the chalcophile nature of Ag and Au, which suggests the presence of small inclusions of sulfide, may indicate that Se and Sb are, at least in part, present in these inclusions. The sodium content is high in the albite-rich environment of the Sucuri albitites, whereas it is low in the veins at Dajishan, the mineralizing fluids for which appear to have been Ca-rich rather than Na-rich. Sodium contents in helvite thus seem to be strongly related to the composition of the fluid.

As a preliminary conclusion, Sc, Co, and probably other 3d transition elements (3dTE) can be assumed to enter the helvite structure in isomorphous replacement after Fe, Mn or Zn. Cadmium is usually associated with Zn in S-bearing minerals such as sulfides (chiefly sphalerite), and thus probably substitutes for Zn in helvite. It is noteworthy that Cr contents remain undetectable, despite the presence of large contents of Sc and, to a lesser extent, Co. This behavior is in complete opposition to the ability of beryl structure to accomodate Cr (Aurisicchio *et al.* 1988). Finally, of the *REE*, the structure distinctly favors the heavy rare-earths (Fig. 4), which also enter helvite in isomorphous replacement of major cations.

DISCUSSION

REE in helvite-group minerals

Helvite from both occurrences display a strong *HREE* enrichment (Fig. 4). The $(La/Yb)_n$ chondrite-normalized ratios range from 0.009 to 0.05 and from 0.05 to 0.11 in Sucuri and Dajishan samples, respectively, indicative of a distinctly *HREE* enrichment. The contents of ligands and the *REE* pattern of the fluid, as well as crystallographic effects, can lead to the observed partitioning. As shown before, fluids responsible for helvite precipitation had a chiefly alkaline rather than acid character. Under such conditions, carbonate or phosphate anions can be efficient ligands for the *REE* (Mineyev 1963). Both resulting complexes have higher stability constants for the *HREE* than for the *LREE* (Sillen & Martell 1964, Dumonceau *et al.* 1979). This could explain the differential behavior of individual *REE*. On the other hand, $Ln(OH)_3$ complexes (where *Ln* stands for any lanthanide cation) also have high stability-constants in alkaline fluids (Sillen & Martell 1964), but *LREE* and *HREE* stability constants are not different. Moreover, carbonates and phosphates are not observed in association with helvite at Dajishan, although early apatite and late calcite are known in the deposit. A minor effect of ligands on *REE* distribution in helvite cannot be excluded, but it seems unlikely that the distinctive *HREE* enrichment is due to this phenomenon only.

The fluid's *REE* distribution during the second stage of mineralization at Dajishan can be estimated using scheelite, whose distribution is inherited from a fluid with only minor distortion (Cottrant 1981, Raimbault 1985). Using values given by Raimbault (1988) for La–Yb exchange between fluid and scheelite, the $(La/Yb)_n$ ratio in fluid can be estimated to range from roughly 22 (sample 517–36) to 4.8 (sample 517–39). Similarly, this ratio can be calculated for a hydrothermal fluid in equilibrium with the Sucuri granitic melt, using the experimentally determined partition coefficients of Flynn & Burnham (1978). A value of *ca.* 26 (Bilal 1991) is derived for the fluid. Although metasomatic transformation occurred in an already solidified mass of granite, this approach remains valid, provided that all granite facies have quite similar *REE* patterns. If this requirement is not satisfied, an approximate indication of the tendency of *REE* fractionation can at least be obtained in the area. Again, the observed distribution of the *REE* in helvite cannot be related to an unusually high concentration of the *HREE* in hydrothermal fluids.

From these considerations, we may conclude that the main control on *REE* contents in helvite is a crystal-

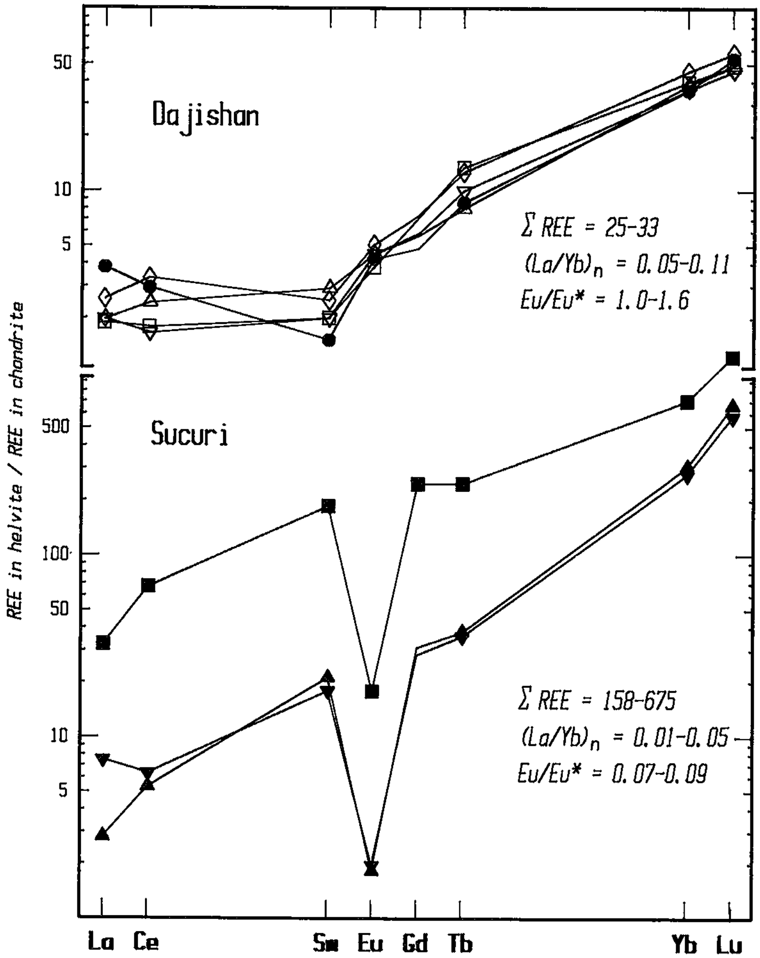

FIG. 4. Chondrite-normalized *REE* patterns in helvite-group minerals. Upper part: helvite ($He_{56-61}Da_{30-34}Ge_{8-10}$) from Dajishan quartz–wolframite veins; lower part: danalite ($Da_{55-6}Ge_{26-28}He_{16-18}$) in the albitites from Sucuri.

lographic one. *REE* cations replace the major cations Fe, Mn and Zn. It is well known that the garnet structure, which involves a Fe–Mn solid solution as in helvite, accomodates *HREE* much more easily than *LREE*. This is true in magmatic conditions (*e.g.*, Irving & Frey 1978), but also in hydrothermal environments (Raimbault, unpubl. data). We propose that *REE* incorporation into the helvite structure obeys the same principles, which are mainly due to variations of ionic radii. In octahedral coordination, Fe^{2+}, Mn^{2+}, and Zn^{2+} ionic radii are 0.86, 0.91, and 0.83 Å respectively, whereas trivalent *REE* ionic radii range from 1.13 for La to 0.94 Å for Lu (Whittaker & Muntus 1970). From the above estimations of La–Yb fractionation in Dajishan fluids, we infer values ranging from 0.004 to 0.011 for the La–Yb exchange constant between helvite and fluid, defined as the ratio $(La/Yb)_{helvite}/(La/Yb)_{fluid}$. In other words, Yb is roughly 100 to 200 times more concentrated than La in helvite relative to the fluid from which it precipitates. It should, however, be emphasized that the present data do not allow inferences about the influence of the extent of Fe–Mn–Zn substitution on incorporation of the *REE*. Finally, these data point out the ability of helvite to concentrate *REE*, since helvite crystals from Dajishan veins are as Yb-rich as the coexisting scheelite, which is known to trap *REE*.

Incorporation of Sc, Co, and Cd into the structure of helvite

As previously discussed, it can be expected that Sc, Co and Cd are present within the helvite structure. It is therefore useful to compare their abundances and their ratios to major elements in samples analyzed from the two occurrences.

Scandium and cobalt are 3dTE, like the major cations Mn, Fe, and Zn. Ionic radii of both Co^{2+} and Sc^{3+} are equal to 0.83 Å (Whittaker & Muntus 1970), a value very close to those of Fe^{2+} (0.86 Å) and Zn^{2+} (0.83 Å), but somewhat different from that of Mn^{2+} (0.91 Å). In our samples, the Sc content of helvite varies within narrow values in each occurrence, but displays a large scatter between the two deposits (108 to 118 ppm at Sucuri *versus* 7 to 9 at Dajishan). The same also is true for Co, although values remain low (10 to 13 ppm at Sucuri *versus* 2.0 to 2.5 at Dajishan). Such low values may be due to the low abundance of cobalt in these granitic environments. The relative enrichment in Sc in helvite at Sucuri could be due to differences in the mineralizing fluid, but that seems unlikely because both environments are linked to a Sc-poor granitic environment. Moreover, helvite at Dajishan is linked with a late fluid phase not associated with the granitic rocks, which has experienced a large degree of exchange with wallrocks, from which it could extract Sc. Helvite at Sucuri has a (danalite + genthelvite)-rich composition (sum of the two end-member components in the range 82–84 mol %), whereas helvite at Dajishan has a distinctly helvite-rich composition (*sensu stricto*) (Da+Ge in the range 39–44 at.%), and Sc can more easily replace Fe or Zn than Mn in the helvite structure. For all of these reasons, we prefer to relate variations in Sc (and, to a lesser extent, in Co) to crystallochemical controls of the composition of helvite, although the present data do not allow a presentation of quantitative relationships between helvite composition and the degree of incorporation of Sc.

The geochemistry of cadmium is strongly related to that of Zn, owing to the chalcophile character of both elements and their chemical similarity (Vlasov 1966). The ionic radius of Cd^{2+} in octahedral coordination (1.03 Å) is, however, somewhat higher than that of Zn^{2+}, but approaches that of Mn^{2+}. In our samples, the highest concentrations of Cd are found in helvite from Dajishan (172 ppm), which are Mn-rich (56–61% of the Mn end-member), whereas Cd contents in Sucuri samples (16–18% of the Mn end-member) remain below 100 ppm. The behavior of Cd is thus just the opposite of that of Zn in our samples. This can be interpreted as reflecting the influence of crystallochemical factors, besides other factors such as Zn/Cd ratios in fluids or nature of the ligands (high Cl concentrations are known to enhance Cd solubility relatively to Zn: Mookherjee 1962). On the basis of the present data, definitive conclusions cannot be made about the respective roles of both phenomena, crystallographic control *versus* fluid composition. The analysis of associated Zn- and Cd-bearing phases such as sphalerite, as well as the study of other types of helvite occurrences, may contribute to the solution of this problem.

CONCLUSIONS

From the analysis of helvite crystals from various parageneses and compositions, it can be concluded that *REE*, Sc, Co, Na, and Cd occur in helvite in isomorphous replacement of the major cations, whereas Ag, Au, Ta, W, and Ga in the samples examined are more likely to occur in small inclusions of sulfide, oxide, or mica. The picture is more complicated for Se and Sb, and needs further refinement. Helvite-group minerals have a strong affinity for *HREE*, leading to highly fractionated patterns, resembling those of hydrothermal garnet. No fractionation among the *REE* can presently be attributed to bulk composition in terms of Zn–Mn–Fe substitutions, whereas such effects can be suspected for Sc and Cd contents.

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