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BURTITE, CALCIUM HEXAHYDROXOSTANNATE, A NEW MINERAL FROM EL HAMMAN, CENTRAL MOROCCO

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ABSTRACT

Burtite, a calcium hexahydroxostannate, occurs as a late mineral in a tin-rich garnet skarn in the vicinity of the El Hamman fluorite deposit. The surface of the altered "octahedral" crystal (up to 2 mm) is composed of pale yellow varlamoffite; the core is colorless and shows an apparently cubic cleavage. This unaltered core material has hardness 3; its density is 3.28 g/cm^3 (meas.) and 3.22 g/cm^3 (calc.). The mineral is slowly soluble in cold, dilute HCl. It is transparent, colorless in thin section and optically uniaxial (+) with birefringence < 0.0003 and mean index $n = 1.633$ (meas.). Although X-ray-diffraction results (Strunz & Contag 1960, Cohen-Addad 1967 – on synthetic material) indicate cubic symmetry with space group $Pn3$ or $Pn3m$, a 8.128 Å and $Z = 4$, the optical orientation implies a rhombohedral departure from this symmetry. This leads to the most probable space group $R\bar{3}$ with a_{rh} 8.128 Å, $\alpha \simeq 90°$ and $Z = 4$. The strongest five lines in the X-ray Gandolfi powder pattern [d in Å (I)(hkl)] are 4.06(vs)(200), 1.814(s)(420), 1.657(s)(422), 0.9850(s)(820,644) and 0.9576(s)(822,660). Microprobe analysis gave CaO 20.6, SnO_2 56.3, MgO 0.3, total 77.2 wt. %. Adding 20.2 wt. % H_2O (calc.) to provide the correct stoichiometric number of hydroxyl groups gives the known chemical formula $CaSn(OH)_6$.

Keywords: burtite, new mineral, calcium hexahydroxostannate, El Hamman, Morocco.

SOMMAIRE

La burtite est un hexahydroxostannate de calcium apparaissant en phase tardive dans une grenatite stannifère de type skarn affleurant à proximité du gîte de fluorine d'El Hamman (Maroc). Les cristaux simulent des octaèdres dont la taille atteint 2 mm. Ils s'altèrent superficiellement en varlamoffite jaune pâle; au centre ils sont incolores, montrant un clivage d'apparence cubique. Ce matériau non altéré a une dureté 3 et une densité mesurée de 3.28 et calculée de 3.22. Il se dissout lentement à froid dans l'HCl dilué. Au microscope, le minéral est transparent, incolore, uniaxe (+) avec une biréfringence < 0.0003 et indice moyen $n = 1.633$ (mesuré). Les résultats obtenus en diffraction X indiquent une symétrie cubique, groupe spatial $Pn3$ ou $Pn3m$ avec a 8.128 Å et $Z = 4$. Cependant, l'orientation optique montre qu'il y a un écart par rapport à cette symétrie. Le minéral est très probablement rhomboédrique avec un groupe spatial vraisemblablement $R\bar{3}$, $a_{rh} = 8.128$ Å, $\alpha \simeq 90°$ et $Z = 4$. Les 5 raies principales du diagramme de poudre à la caméra de Gandolfi [d en Å (I)(hkl)] sont 4.06(vs)(200), 1.814(s)(420), 1.657(s)(422), 0.9850(s)(820,644) et 0.9576(s)(822,660). L'analyse à la microsonde donne CaO 20.6, SnO_2 56.3, MgO 0.3, total 77.2% poids. En ajoutant 20.2% poids H_2O (calculé) pour obtenir le nombre stoechiométrique de groupes OH, on retrouve la formule connue $CaSn(OH)_6$.

Mots-clés: burtite, espèce minérale nouvelle, hexahydroxostannate, El Hamman (Maroc).

GEOLOGICAL SETTING

During our investigations of the contact-metamorphic zone of Hercynian age enclosing the El Hamman fluorite deposit in central Morocco, 40 km southwest of Meknes, several skarns were discovered. These are developed as sporadic lenses in subvertical limestone–shale alternations (at about 10 cm intervals) owing to the influence of a buried batholith. Two types of mineralization occur: (1) clinopyroxene (ferrosalite) + scheelite; (2) stanniferous andradite (up to 5 wt. % SnO_2) ± malayaite ($CaSnSiO_5$) ± wollastonite, veined by hedenbergite + malayaite. A very widespread boron metasomatism affected the rocks of the metamorphic area and also the skarns. Datolite, ferroaxinite, manganaxinite (sometimes greenish blue with up to 1.7 wt. % SnO_2) and, to a lesser extent, tourmaline are the secondary minerals associated with this boron metasomatism in the Ca-rich rocks.

A garnetite, situated in a tin skarn located 33°31′26" Long., 5°49′50" Lat., in the cliffs of the west bank of the river Beht, was found to contain an unusual late hydrothermal paragenesis. It includes wickmanite $MnSn(OH)_6$, stokesite $CaSnSi_3O_9{\cdot}2H_2O$, datolite $CaBSiO_4(OH)$, pectolite $NaCa_2Si_3O_8(OH)$, a member of the apophyllite group $KCa_4Si_8O_{20}(F,OH)\cdot 8H_2O$, varlamoffite $(Sn,Fe)(O,OH)_2$ and the new mineral, burtite $CaSn(OH)_6$. The rock is a dark green, medium grained garnetite (3 mm ϕ andradite averaging 3.5 wt. % SnO_2) enclosing coarse grained datolite lenses (a few cm thick) that parallel the bedding. Under the microscope, this datolite replaces wollastonite, as shown by remnants of a fibrous cleavage sometimes preserved in the datolite. The garnetite, where massive, contains malayaite, clinopyroxene and löllingite as primary minerals that are locally corroded by a small quantity of coarse datolite. In places, the minerals are partly replaced by chalcedony and late pearly fibrous datolite or are totally dissolved, with the creation of vugs a few mm across in which the late hydrothermal minerals occur. The most abundant late mineral, wickmanite, occurs as yellow-orange octahedra (up to 4 mm) or as vug fillings. It is present in various hues, ranging from nearly colorless to orange-brown. Microprobe analyses show this wickmanite to be poor in MgO (less than 3.5 wt. %) and FeO (1.5 wt. %) but, in places, richer in CaO (1.3 wt. %) compared with previously analyzed material (Nefedov *et al.* 1977). Wickmanite locally encloses needles of löllingite, malayaite and pearly datolite and forms the support for tiny spherules of stokesite. In contrast to the wickmanite, which is unaltered, there is another mineral present in octahedra up to 2 mm across; it resembles wickmanite but has an earthy, yellowish surface. This appearance results from extensive replacement by powdery pale yellow varlamoffite. The altered octahedra are accompanied as a rule by late fibrous pectolite. Stokesite also occurs as spherules or crusts of minute colorless grains on the octahedra. The cores of some octahedra were sometimes found to be unaltered, and fragments were selected for examination. X-ray powder diffraction proved the mineral to be similar to the synthetic $CaSn(OH)_6$ described by Strunz & Contag (1960) and Cohen-Addad (1967, 1968). Microprobe examination also showed some vug fillings in a wickmanite-rich thin section to be $CaSn(OH)_6$.

Burtite is named for Donald M. Burt, Professor of Mineralogy and Ore Deposits at Arizona State University, for his work on mineral equilibria in skarn and greisen deposits. The specimens are preserved in the mineralogy collection of the Université catholique de Louvain, Louvain-la-Neuve, Belgium. The mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names, I.M.A.

THE HEXAHYDROXOSTANNATE GROUP

Strunz & Contag (1960) demonstrated the existence of an isomorphous series of synthetic cubic hydroxostannates with the general formula $M^{2+}Sn(OH)_6$. Mg, Mn, Fe, Ca, Co, Ni, Zn and Cd equivalents were successfully synthesized at room temperature or hydrothermally (Morgenstern–Badarau *et al.* 1965, Christensen & Hazell 1969). The unit-cell content Z is 4, and the space group is believed to be $Pn3$ according to the structure determination by Cohen-Addad (1968), who performed a comprehensive I.R., N.M.R. and neutron-diffraction study on synthetic $CaSn(OH)_6$ and $ZnSn(OH)_6$. The structure can be described as a framework of octahedra linked by their apices with approximately linear hydrogen bonding along the O–O lines joining two octahedra. An excess of water trapped in the crystalline structure has been detected by DTA, TGA and measurement of the cell dimension after heating (Morgenstern-Badarau *et al.* 1969, Faust & Schaller 1971).

Natural equivalents have been discovered for the Mn, Mg and Fe hydroxostannates. These are, respectively, wickmanite (Moore & Smith 1967), schoenfliesite (Faust & Schaller 1971) and the mineral $FeSn(OH)_6$, which is still unnamed (White & Nelen 1973, Marshukova *et al.* 1978, Grubb & Hannaford 1966, Pinch & Wilson 1977). Besides the cubic hydroxostannates, a family of isomorphous tetragonal minerals has been indicated by White & Nelen (1973); these are stottite $FeGe(OH)_6$ (Strunz *et al.* 1958), tetrawickmanite and tetragonal $FeSn(OH)_6$ (White & Nelen 1973).

CHEMISTRY

Analysis was carried out with a four-spectrometer CAMEBAX microprobe on five fragments selected from three crystals. Analytical conditions were 15 kV, 15 nA on brass and ZAF data reduction, with oxygen assumed by difference during computation. Standards used were andradite for Ca, malayaite for Sn and olivine for Mg (all of known composition).

Surface pitting was observed on the sample after a few tenths of a second, even with a sweeping electronic beam. As a result, the total of wt. % oxides increased with counting time. Although cation stoichiometry remained unchanged in both cases, low-irradiation analysis showed a deficit, whereas high-irradiation analysis showed an excess after adding H_2O to provide the stoichiometric quantity of hydroxyl groups. These facts suggest a strong loss of

TABLE 1. CHEMICAL ANALYSIS AND DERIVATION OF THE FORMULA OF BURTITE

Average of 14 analyses		Variability		Structural formula		
Oxide	wt. %	Oxide	wt. %	based on 6 oxygens		
SnO_2	56.3	SnO_2	55.7 - 57.2	Sn	0.999	
CaO	20.6	CaO	20.3 - 20.9	Ca	0.982	1.002
MgO	0.3	MgO	0.3 - 0.5	Mg	0.020	
Σ ox.	77.2	Σ ox.	76.3 78.4			
H_2O^*	20.2			OH^*	6.000	
H_2O^{**}	2.6			H_2O^{**}	0.39	
Total	100.0					

$^*H_2O$ necessary to provide the stoichiometric quantity of hydroxyl groups.

**By difference, excess of water possibly trapped in the structure.

Si, Mn and Fe possible but somewhat below minimum detectable concentration (about 0.1 %) for 10" second counting time. Aℓ, Ti, Na, K, F, Cℓ, Ge not detected with microprobe. Actual formula : $(Ca_{0.982}Mg_{0.020})_{1.002}Sn_{0.999}(OH)_6$. Idealized formula: $CaSn(OH)_6$.

TABLE 2. COMPATIBILITY BETWEEN PHYSICAL CONSTANTS AND CHEMICAL COMPOSITION

$D_{(meas)}$: 3.28 ± 0.01

$D_{(calc)}$: 3.22 (excess water non essential)
3.31 (excess water essential)

$n_{(meas)}$: 1.633 ± 0.001

$n_{(calc)}$: $K_c \cdot D_{(meas)} + 1 = 1.630$

$$\left.\begin{array}{l} K_p = \dfrac{n_{(meas)} - 1}{D_{(meas)}} = 0.192 \\ K_c = \dfrac{\Sigma ki \cdot pi}{100} = 0.192 \end{array}\right\} 1 - \frac{k_p}{k_c} = 0.000$$

volatiles during analysis and, possibly, an excess of water in the structure. Since step-scanning analysis showed the grains to be of constant composition, analyses were performed by continuous movement of the sample (5 *μm per* second) in order to minimize water loss during the 10-second counting time. This proved to cause less damage to the sample surface. Lack of material prevented direct quantitative measurement of H_2O. Furthermore, a pure concentrate of burtite could not be separated from the bulk rock owing to the presence of colorless wickmanite as an impurity.

The chemical data and the derivation of the formula are given in Table 1. In view of the basic similarity of the X-ray pattern of natural material and synthetic $CaSn(OH)_6$, the presence of OH is postulated and the mineral formula is calculated on the basis of 6 oxygens. The excess water that remains once the proper amount of H_2O is added to the oxides may tentatively be considered as trapped in the structure. However, it is more likely due to analytical errors, and it was thus not included in the formula derived for burtite.

General Appearance and Physical Properties

The mineral is colorless with a good cubic cleavage. It is very brittle and the hardness is about 3. The lustre is vitreous, and there is no fluorescence under short- or long-wave UV light. It is slowly soluble in cold, dilute HCl. In thin section, burtite is colorless, with the cubic cleavage traces visible. It is apparently isotropic; however, a very weak birefringence (<0.0003) can be observed on thick grains (0.5 mm). The interference figure is clearly seen on these grains and is uniaxial positive. The index of refraction was measured with sodium light and calculated according to the Gladstone–Dale rule (Table 2). The specific refractivity values were taken from Mandarino (1976) except for SnO_2, which took the value proposed by Faust & Schaller (1971) in their study of schoenfliesite. The density was measured by flotation in a mixture of diiodomethane and monochloronaphtalene checked by measuring the index of refraction. Two densities were calculated, depending on the essential or nonessential role ascribed to the excess water in the structure.

The compatibility of n_{meas}, D_{meas} and the chemical composition (without excess water) was tested by comparing the physical specific refractivity K_P with the chemical specific refractivity K_C (Mandarino 1979). The zero value for $1 - K_P/K_C$ is deemed "superior" in the compatibility scale presented by this author (Table 2).

Crystallography

The X-ray powder-diffraction data for burtite agree fairly well with the data given on PDF card 9–30 for synthetic cubic $CaSn(OH)_6$ (Table 3). X-ray single-crystal study apparently shows no deviation from the cubic symmetry. Rotation (about *a*), Weissenberg (*hk*0 *and hk*1) and precession (0*kl*, 1*kl* and *h*0*l*) films reveal a *m*3*m* Laue symmetry. The appearance of the 0*kl*: *k* + *l* even reflections is consistent with the *Pn*3 or *Pn*3*m* space group (*Pn*3 is most probable: see above).

These data, however, conflict with the optical anisotropy of the mineral. Figure 1 shows the relations between cubic cleavage, twinning and optical orientation, as observed commonly on thick fragments under the microscope with

TABLE 3. X-RAY POWDER DIFFRACTION DATA

BURTITE This study*			SYNTHETIC $CaSn(OH)_6$ JCPDS card 9-30		
$d_{(obs)}$	$d_{(calc)}$	$I_{(obs)}$	d	I/I_1	hkl
4.68	4.69	ms	4.69	50	111
4.06	4.06	vs	4.06	100	200
2.87	2.87	ms	2.87	40	220
2.57	2.57	vw	2.57	10	310
2.45	2.45	w	2.45	10	311
2.33	2.35	m	2.34	15	222
2.17	2.17	vw	2.17	5	321
2.03	2.03	w	2.03	10	400
1.864	1.865	vw	1.863	5	331
1.814	1.817	s	1.814	20	420
1.657	1.659	s	1.658	15	422
1.562	1.564	w	1.563	5	511,333
1.435	1.437	m	1.435	5	440
	non observed		1.393	5	530,433
1.373	1.374	vw	1.374	5	531
1.353	1.355	m	1.353	5	600,442
1.283	1.285	w	1.285	5	620
1.238	1.240	vw	1.237	1	533
1.224	1.225	m	1.225	5	622
1.172	1.173	vw	1.174	5	444
1.137	1.138	vw	1.138	1	711,551
1.126	1.127	m	1.127	5	640
1.085	1.086	ms	1.086	5	642
1.058	1.058	w	1.058	5	731,553
1.015	1.016	vw	1.015	1	800
0.9850	0.9857	s	0.9852	5	820,644
0.9576	0.9579	s	0.9575	5	822,660
0.9385	0.9385	w	0.9385	1	751,555
0.9322	0.9323	ms	0.9320	5	662
0.9085	0.9087	m	0.9090	5	840
	not measured		0.8926	5	911,753
	not measured		0.8867	5	842
	not measured		0.8668	5	664
	not measured		0.8522	5	931
	not measured		0.8299	5	944
	not measured		0.8180	1	933,771,755
	not measured		0.8133	1	10.0.0,860

BURTITE (pseudo-cubic cell) a(Å)	SYNTHETIC $CaSn(OH)_6$ a(Å)
8.128 ± 0.001	8.134 Felten (1957) JCPDS card 8.135 Strunz & Contag (1960) 8.128 ± 0.002 Morgenstern-Badarau *et al.* (1965) 8.15 ± 0.01 Cohen-Addad (1967) 8.150 ± 0.002 Christensen & Hazell (1969)

*Fe-filtered Co-radiation, Kα = 1.79021 Å
Powder pattern on a monocrystal with a 114.6 mm Gandolfi camera.
Corrected for film shrinkage.

the grain resting on the cubic cleavage. In this instance, the grain is twinned. Each individual, when parted, shows diagonal extinction on whichever plane it rests. This indicates that the optic axis lies along the diagonal of the cube, which is the threefold axis. The optical orientation and the twin law thus strongly suggest a rhombohedral departure from cubic symmetry. The space group $R\bar{3}$ is the most probable, since it can be derived from $Pn3$ by simple distortion ($\alpha \neq 90°$). The space groups $R3$, $R32$, $R3m$ and $R\bar{3}m$ are, nevertheless, not completely excluded. The frequency of twinning in the burtite fragments offers a likely explanation for the discrepancy between optical and X-ray results. The cubic symmetry observed in the "single-crystal" study may be due to the presence of twinning that could not be detected.

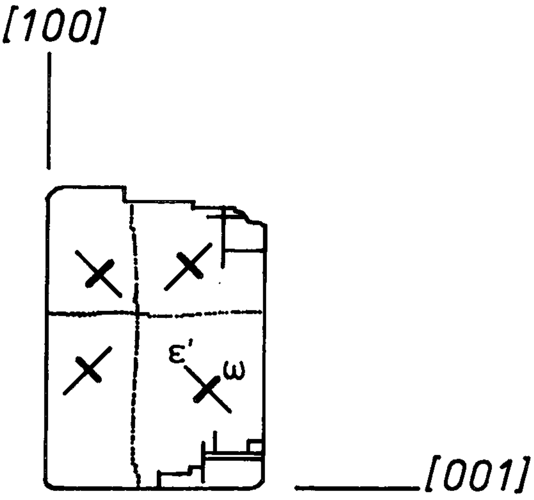

FIG. 1. Relation between cleavage, twinning and optical orientation for a thick grain of burtite resting on a cleavage plane. Indices refer to the individual in the lower right-hand corner. The plane of the drawing is (010) for that individual.

The reflections observed on burtite (Table 3) can be indexed by analogy with the PDF card for synthetic $CaSn(OH)_6$. This indexation permits the derivation of the parameter of a pseudocubic cell. The value $a = 8.128$ Å was obtained by extrapolation against $\cos^2\theta$. This pseudocubic cell dimension is in close agreement with the values published for synthetic $CaSn(OH)_6$ and gives d_{calc} values very close to d_{obs}. However, strictly speaking, the mineral must be considered rhombohedral. Based on the pseudocubic cell edge, the parameters are thus a_{rh} 8.128 Å and $\alpha = 90°$ in rhombohedral setting, and a 11.49 Å and c 14.08 Å in hexagonal setting.

STABILITY FIELD

$CaSn(OH)_6$ is readily synthesized at room temperature by the reaction of $Na_2Sn(OH)_6$ or $K_2Sn(OH)_6$ with calcium chloride or nitrate in aqueous solution (Strunz & Contag 1960, Christensen & Hazell 1969). It was found to be stable at 150°C at 7 bar and 298°C at 82 bar in the presence of H_2O; at a higher temperature it converts to anhydrous calcium stannate (Christensen & Hazell 1969). The dehydration temperature at atmospheric pressure is 355°C, according to the DTA data obtained by these authors.

Phase-equilibrium analysis of natural mineral associations led Burt (1978) to predict the stability field of a hypothetical natural $CaSn(OH)_6$. The appearance of this phase in the system $CaO–SnO_2–SiO_2–H_2O–B_2O_3–CO_2–F_2O_{-1}$ is presumably restricted to very low $X(CO_2)$ and low-temperature conditions. The first natural occurrence corroborates his predictions: burtite occurs indeed with low T and low $X(CO_2)$ hydroxylated minerals (datolite, stokesite, pectolite, apophyllite) and without calcite.

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