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Hiärneite, a new, Zr-Sb oxide mineral isostructural with calzirtite, from Långban, Sweden

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Abstract: Hiärneite is a new Sb-bearing mineral isostructural with calzirtite. It occurs in a skarn mineral assemblage, coexisting with phlogopite, calcite, arsenatian fluorapatite, svabite, jacobsite, magnetoplumbite, titanian bindheimite and pyrophanite, from the Långban deposit, Filipstad, Sweden. The crystals (<200 µm) are strongly coloured in red and include abundant mica grains. They are optically uniaxial (+) and weakly dichroic in shades of orange. Refractive indices calculated from reflectance data are $\omega = 2.12(2)$ and $\varepsilon' = 2.16(2)$ at 589 nm. The average composition, expressed as a calzirtite-type formula (9 cations, 16 oxygens, and Mn^{2+}/Mn^{3+} calculated to balance charge), is $Na_{0.17}Ca_{1.57}Mn^{2+}{}_{0.62}\,Zr_{4.19}\,Hf_{0.02}Sb^{5+}{}_{1.37}Ti_{0.59}Mn^{3+}{}_{0.36}Mg_{0.02}Fe_{0.09}O_{16}$; a general formula could be written as $(Ca, Na, Mn^{2+})_2(Zr, Mn^{3+})_5(Sb, Ti, Fe)_2O_{16}$.

Cell dimensions, obtained from single-crystal diffractometer data indexed on a tetragonal $I4_1/acd$ cell, are: $a = 15.264(1)$, $c = 10.089(2)$ Å and $V = 2350.5(5)$ Å^3 for $Z = 8$. The strongest powder diffraction lines are [d in Å$(hkl)(I/I_0)$]: 3.45 (411)(40), 2.92(332)(100), 2.539(600)(60), 1.792(604,660)(90) and 1.534(932)(80). $D_{calc} = 5.44(1)$ g · cm^{-1} for the empirical formula. The mineral is interpreted to have formed by metasomatic reactions of Sb-, Mn-rich fluids with a previously Si-depleted volcanite, followed by metamorphism under conditions of high f_{O_2}, silica undersaturation and relatively high T. The mineral name is for Urban Hiärne (1641–1724).

Key-words: hiärneite, calzirtite, new mineral species, metasomatism, Långban.

Introduction

Minerals bearing antimony or zirconium as major components are not rare. The lithophile Zr is confined in oxides and oxysalts, whereas Sb is mostly found in sulfides and sulfosalts, although many oxygen-containing compounds have also been described. About 360 species with either element as an essential constituent are presently known to science (Nickel & Nichols, 1991; Fleischer & Mandarino, 1995). Clearly, unusual geochemical conditions would be required to combine the two elements in a mineral. Such conditions have apparently been fulfilled for a Långban paragenesis, in which an oxide phase dominated by Ca, Zr and Sb recently was discovered. The new mineral, shown to be closely related to calzirtite, has been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association. It is named for Urban Hiärne (1641–1724), a universal scholar and a pioneer in Swedish geology (Frängsmyr, 1986). The name of the mineral, hiärneite, is approximately pronounced *year-ne-ite*. Holotype material is preserved in the mineral collection of the Swedish Museum of Natural History, under the catalogue number 920766.

Calzirtite, ideally $Ca_2Zr_5Ti_2O_{16}$, is known as a rare, accessory constituent of some carbonatites and affiliated alkaline massifs. Apart from carbonates the mineral is typically associated with perovskite, baddeleyite, pyrochlore, apatite and

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diopside in these rocks (*e.g.*, Bulakh *et al.*, 1967; Kogarko *et al.*, 1991). It belongs to the tetragonal system, space group $I4_1/acd$, and has an anion-deficient fluorite-type superstructure (Rossel, 1982).

Occurrence

The Långban iron-manganese deposit, situated in the Filipstad district, Värmland, central Sweden, is famous for its species diversity and well known to many mineralogists worldwide. It has been reasonably well documented overall (Magnusson, 1930; Moore, 1970), although many details remain to be investigated. The so-called *sköls* are of special interest for this paper. Appearing in proximity of the ore bodies, they are enclaves of a mica-rich rock believed to have been formed through leaching of Si, Na and K from felsic volcanite layers, to which primarily Mg and Ca have been added at the same time (Magnusson, 1930). Near the contacts between volcanite and ore, far-reaching exchange reactions, also involving mobilization of Mn, Fe, Pb, Ba, Sb and As have led to the formation of unusual metasomatic skarn products, including the new mineral described here.

The hiärneite specimen is from recently collected, mine-dump material. It consists chiefly of fine-grained phlogopite. Irregular, colourless grains of an arsenatian fluorapatite, *ca.* $Ca_5(P_{0.8}$-$As_{0.2}O_4)_3F$, with a bluish fluorescence colour under short-wave UV radiation, are quite common in the assemblage. Grains of yellowish svabite are less abundant. Calcite occurs as veinlets and interstitial grains. Magnetoplumbite, jacobsite, bindheimite and pyrophanite appear in the rock as scattered crystals, 0.1–2 mm in size; jacobsite is sometimes found surrounding a core of magnetoplumbite. Chemical data for the latter two oxides in the sample are given by Holtstam (1994). Pyrophanite is close to the ideal $MnTiO_3$ composition, whereas bindheimite is represented by a titanian variety.

Hiärneite appears as single grains and in aggregates up to 0.5 mm wide. Individual crystals are subhedral, with a short-prismatic habitus, and do not exceed 200 μm in their greatest dimension. They all have a poikiloblastic texture with abundant mica inclusions (Fig. 1). The modal abundance of hiärneite is low, with only 3–6 aggregates or single grains noted in each standard petrographic section.

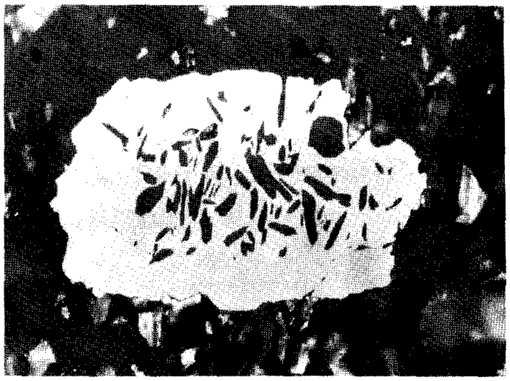

Fig. 1. Microphotograph (reflected light) of a hiärneite grain that measures 90 × 165 μm.

Mineral data

Chemical composition

Preliminary, qualitative microanalyses (energy-dispersive scans) of the mineral revealed no other elements with atomic number >10 than noted below. Quantitative analyses were obtained using a Cameca SX50 microprobe, for which operating parameters included counting times up to 40 s, a 20-kV accelerating voltage and a 12-nA beam current. Standards used were albite (Na), periclase (Mg), wollastonite (Ca), pyrophanite (Mn, Ti), zirconium metal, stibnite (Sb) and hematite (Fe). Data were processed in the Cameca version of the PAP (Pouchou & Pichoir, 1984) program.

Representative analyses obtained from points on two different grains are given in Table 1. The data are given with two decimal figures to avoid future rounding-off errors. Uranium was specifically sought but not detected, whereas aluminium was at or below the detection level ($\leq$ 0.05 wt.% Al_2O_3). Traces of hafnium were indicated, but no suitable standard was available to quantify the amount. From the Hf$L\alpha$ peak in the energy-dispersive spectrum the HfO_2 content was determined to be approximately 0.5 wt.% using a standardless calculation procedure (employing pure element intensity factors). This concentration value has been added to the analytical data throughout Table 1. The atomic proportions were calculated on the basis of nine cations per formula unit, and the Mn^{2+}/Mn^{3+} ratios were subsequently adjusted to balance 16 oxygen atoms. A general, simplified formula for the mineral could be given

Table 1. Selected chemical analyses of hiärneite (wt.%).

Anal. no.	1	5	8	10	11	13	14	15
Na_2O	0.59	0.46	0.72	0.62	0.50	0.42	0.45	0.59
MgO	0.09	0.10	0.13	0.11	0.07	0.03	0.08	0.10
CaO	9.15	9.08	8.87	8.83	9.36	9.41	9.02	9.14
MnO	4.01	5.24	3.74	4.78	4.07	3.83	5.81	4.58
Mn_2O_3	3.71	0.98	3.90	2.98	3.13	4.39	1.65	3.03
TiO_2	4.66	5.26	4.30	4.25	5.28	6.09	4.57	4.60
ZrO_2	53.94	54.63	52.90	52.28	54.11	53.40	53.23	53.31
Sb_2O_5	22.87	21.97	23.45	24.31	21.93	21.01	24.07	23.91
Fe_2O_3	0.81	1.12	0.71	0.67	0.88	0.52	0.57	0.70
HfO_2*	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Total	100.33	99.34	99.22	99.33	99.83	99.60	99.95	100.46
9 cations								
Na^+	0.18	0.15	0.23	0.19	0.16	0.13	0.14	0.18
Mg^{2+}	0.02	0.02	0.03	0.03	0.02	0.01	0.02	0.02
Ca^{2+}	1.57	1.57	1.54	1.54	1.60	1.61	1.56	1.57
Mn^{2+}	0.54	0.72	0.51	0.66	0.55	0.52	0.80	0.62
Mn^{3+}	0.45	0.12	0.48	0.37	0.38	0.53	0.20	0.37
Ti^{4+}	0.56	0.64	0.52	0.52	0.64	0.73	0.56	0.55
Zr^{4+}	4.20	4.30	4.17	4.13	4.22	4.15	4.19	4.16
Sb^{5+}	1.36	1.32	1.41	1.46	1.30	1.24	1.44	1.42
Fe^{3+}	0.10	0.14	0.09	0.08	0.11	0.06	0.07	0.09
Hf^{4+}	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Total	9.00	9.00	9.00	9.00	9.00	9.00	9.00	9.00

* Hafnium concentration determined with energy-dispersive X-ray spectrometry.

as $(Ca, Na, Mn^{2+})_2(Zr, Mn^{3+})_5(Sb, Ti, Fe)_2O_{16}$. On backscattered-electron images a slight heterogeneity in composition of the grains was indicated. The pattern could be traced as a decrease in Sb towards the darker rims, with a concomitant increase in Ti.

X-ray crystallography

Preliminary single-crystal work indicated a tetragonal phase with a = 15.2 Å and c = 10.1 Å. The systematically absent reflections are consistent with the space-group symmetry $I4_1/acd$. X-ray powder photographs were obtained on a polycrystalline sample with a 57.3-mm-diameter Gandolfi camera and produced patterns similar to that for calzirtite (PDF card 15–121). Measured and calculated interplanar spacings are given in Table 2 together with visually estimated intensities. The dimensions of the tetragonal unit cell were refinced from the powder data by the least-squares method to a = 15.265(6) Å, c = 10.102(6) Å and V = 2354(2) Å^3. To obtain more precise data, a set of reflections was collected from a single crystal using a four-circle diffractometer with graphite-monochromatized Mo$K\alpha$ radiation. Refinement of these reflections produced the unit-cell dimensions a = 15.264(1) Å, c = 10.089(2) Å and V = 2350.5(5) Å^3 . They are close to parameters obtained on synthetic calzirtite: a = 15.220 Å, c = 10.124 Å, V = 2345 Å^3 (Rossel, 1982).

Physical properties

The colour of hiärneite, a translucent mineral, is bright red; in thin section it is weakly dichroic in orange and yellow-orange. The optical character is uniaxial positive, as for calzirtite. In reflected

Table 2. Powder X-ray diffraction data for hiärneite.

I/I_0	$d_{\text{meas.}}$ (Å)	$d_{\text{calc.}}$ (Å)	*h*	*k*	*l*
40	3.45	3.48	4	1	1
30	3.38	3.41	4	2	0
100	2.92	2.93	3	3	2
60	2.539	2.544	6	0	0
20	2.433	2.436	6	1	1
30	2.168	2.169	5	2	3
10	2.053	2.053	7	2	1
20	1.945	1.946	5	4	3
20	1.861	1.861	7	4	1
90	1.792	1.799	6	6	0
		1.792	6	0	4
20	1.688	1.690	6	5	3
10	1.649	1.650	7	4	3
80	1.534	1.533	9	3	2
30	1.520	1.525	3	3	6
20	1.464	1.465	6	6	4
10	1.385	1.385	10	1	3
20	1.354	1.353	10	5	1
30	1.2726	1.2721	12	0	0
30	1.1636	1.1633	9	3	6
20	1.1358	1.1361	12	0	4
10	1.1190	1.1187	10	2	6
20	1.0345	1.0367	12	6	4
		1.0335	6	6	8

Ni-filtered Cu$K\alpha$ radiation.

light the mineral is colourless to gray with weak anisotropy and frequent yellow internal reflections. At a wavelength of 589 nm the calculated refractive indices (*cf.* below) are $\omega = 2.12(2)$ and $\varepsilon' = 2.16(2)$.

No fluorescence effects are discernible under ultra-violet light generated by a mercury lamp attached to the microscope. Neither cleavage planes nor fractures have been observed. The mineral is insoluble in cold mineral acids. A single hardness measurement using a microhardness tester gave $VHN_{50} = 1254$, which is approximately equal to a Mohs hardness of 7. The calculated density, based on the unit-cell contents (formula averaged from data in Table 1), is 5.44(1) g · cm^{-1}, with Z = 8 (as for calzirtite).

Spectroscopic data

Unpolarized micro-Raman spectra were obtained on a clear portion of a grain for three spectral regions, 100–700, 800–1300 and 3300–3700 cm^{-1}, using a Microdil-28 multichannel spectrometer.

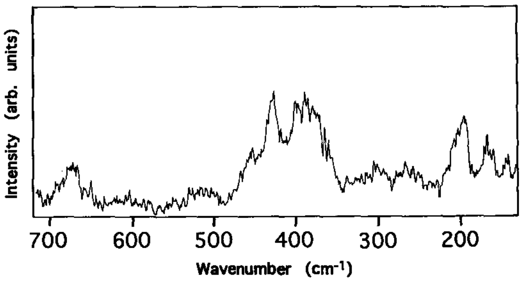

Fig. 2. Laser Raman spectrum for hiärneite.

The material was excited with the 514.5 nm line of an Ar$^+$ ion laser operated at 200 mW. No significant bands were detected in the high-frequency spectrum, which corresponds to the O-H stretching region. This supports the assumption that the phase is essentially anhydrous. Prominent Raman bands, most likely due to metal-oxygen linkages, were only observed in the 100–700 cm^{-1} region (Fig. 2).

An unpolarized optical absorption spectrum (Fig. 3) was obtained using a Zeiss MPM800 microscope-photometer equipped with a PMT-detector, a Neofluar 20×/0.50 objective, and a grating monochromator which provided a spectral resolution of 5 nm. The light source was a 75W Xenon arc lamp and the condenser an Ultrafluar 10×/0.20 objective. Data were recorded in the 350–800 nm (~28500–12500 cm^{-1}) region directly from a grain in a petrographic thin section, where the measured spot was restricted to 10 μm in diameter. The spectrum can be resolved into two (or more) relatively broad Gaussian bands (full width at half maximum ≤4000 cm^{-1}), from which it can be concluded that spin-allowed *d*–*d* transitions of a metal ion are the most likely absorption mechanism. Of the transition metal cations be-

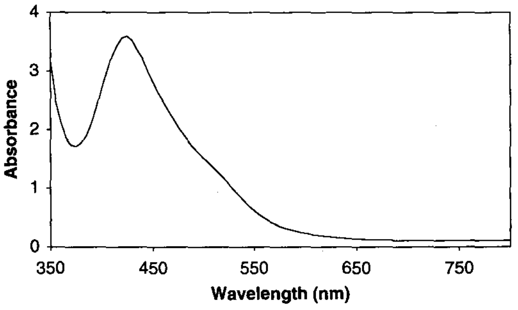

Fig. 3. Unpolarized optical absorption spectrum for hiärneite. Sample thickness is approximately 30 μm.

Table 3. Reflectance data (%) for hiärneite.

λ (nm)	$R_{E'}$	R_O	λ (nm)	$R_{E'}$	R_O
400	14.5	13.4	560	13.5	12.8
420	14.2	13.3	580	13.5	12.8
440	14.1	13.2	600	13.5	12.8
460	14.0	13.1	620	13.5	12.8
480	13.8	13.0	640	13.4	12.8
500	13.7	12.9	660	13.4	12.8
520	13.6	12.8	680	13.4	12.8
540	13.5	12.8	700	13.3	12.7

lieved to be present, only Mn^{3+} is an intense absorber; it is known to produce colours from red to green in minerals (Burns, 1993).

Using the spectrophotometer equipment described above (100 W tungsten lamp), configured for reflected-light measurements, reflectance data for hiärneite were collected from 400 to 700 nm in 20-nm steps. Basal-section SiC (Zeiss no. 846) was used as a reflectance standard. The measured spot was restricted to 20 μm in diameter, taking care to avoid areas with visible internal reflections. R values for two vibration directions (O and E') are given in Table 3. From the absorption spectrum it is justified to assume that k (the absorption coefficient) is close to zero at 589 nm. Accordingly, the refractive indices of the substance given above have been calculated using the familiar Fresnel equation, $n = (1 + \sqrt{R})/(1-\sqrt{R})$ (*e.g.*, Cervelle & Moëlo, 1990).

Discussion

Some interesting points are raised by the discovery of this new mineral. First, the appearance of a calzirtite-type mineral in a non-magmatic environment is somewhat unexpected. A find of calzirtite in chlorite schist in the Italian Alps (Boscardin & Mattioli, 1982) is probably the only known counterpart. Furthermore, it is the first discrete zirconium phase reported from a Långban skarn assemblage. The Zr content of these rocks is probably generally low; a recent analysis of oxide-bearing *sköl* skarn (Holtstam, 1994) showed only 100 ppm Zr, which is below the average concentration in crustal rocks (Wedepohl, 1995). Moreover, to the best of the author's knowledge it is the only mineral recorded that contains both Zr and Sb in significant amounts. All these points are related to the unusual conditions of formation for the phase.

Clearly, high values of f_{O_2} have been required to stabilize Mn^{3+} and Sb^{5+}, the more lithophile forms of the elements, in the present paragenesis. The calculated average Mn^{3+}/Mn^{2+} ratio of hiärneite equals 0.58 and should be compared to values obtained for jacobsite (0.32) and magnetoplumbite (0.58) in this assemblage. As in the case of carbonatitic calzirtite, which never has been found to coexist with quartz or feldspar, silica undersaturation can also be inferred. Relatively high crystallization temperatures and conditions of high P_{CO_2} are two other common features, but it is unclear what bearing they have on the formation of calzirtite-type phases. The Filipstad area underwent deformation and metamorphism during the Svecofennian orogeny, locally reaching amphibolite facies at the peak around 1.8 Ga (Björk, 1986). A recent estimation (Grew *et al.*, 1994) of the conditions for formation of Mn skarn at Långban included $P \leq 2$ kbar and $T \geq 500$°C.

Hiärneite is itself an indicator of the metasomatic processes, which have been inferred for the *sköl* association. Zr and Ti were probably derived largely from volcanite precursors (*e.g.*, zircon, rutile) that were destabilized during hydrothermal alteration. However, the relative immobility of these elements has prevented extensive leaching. Fluids derived from adjacent protore layers and enriched in *i.a.* Sb and Mn have infiltrated the silica-depleted volcanite. Later, at metamorphic conditions, recrystallization processes, similar to those responsible for the formation of vast amounts of reaction skarns accompanying the Mn and Fe ore layers at Långban, produced the present, peculiar mica-oxide assemblage.

The present X-ray crystallographic data indicate that the new mineral is isostructural with calzirtite. In the calzirtite structure, Ca, Ti and 80% of the Zr atoms have 8-, 6- and 7-fold coordination by oxygen, respectively, whereas the remaining Zr resides in a 4- to 8-coordinated site with a purported statistically disordered central atom (Rossel, 1982; Sinclair *et al.*, 1986). The chemical analyses (Table 1) show that Sb > Ti in hiärneite. A preliminary crystal-structure refinement has demonstrated that this Sb is located at the octahedrally coordinated M2 site in hiärneite. The antipathetic relationship between Sb and Ti supports the diadochy of these elements in the phase. This should be analogous to the incorporation of niobium in calzirtite from Jacupiranga, Brazil (Sinclair *et al.*, 1986). Considering the similarity in ionic charge and radius (0.60 and 0.64 Å, respectively, Shannon, 1976) between Sb^{5+} and Nb^{5+}, it is only natural that they play the same crystallochemical role in this structure type. Fe^{3+} (with a radius of 0.645 Å) is crystallochemically akin to these cations and is believed to reside at the same site. The deficit in calcium relative to an ideal calzirtite-type formula (2 Ca atoms per formula unit) is best explained by substitution with some Na and Mn^{2+}; no significant indications of vacancies could be obtained from the refined single-crystal data.

Hiärneite is furthermore distinguished from calzirtite in that Zr is no longer the dominant cation in the M1 polyhedron (defining a 4- to 8-coordinated site), but is replaced, probably mainly by Mn^{3+}. By virtue of its ionic size and electron configuration, Mn^{3+} predominantly occupies octahedral positions in crystal structures; however, a d^4 ion is normally susceptible to large Jahn-Teller distortions and can be stabilized in a different kind of site, provided that a significant degree of distortion exists. The maximum number of electronic transitions, and hence absorption bands, for Mn^{3+} in low-symmetry environments is four, but the present optical data are not enough evidence to assign unequivocally the Mn^{3+} ions to a particular crystallographic site.

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