Gordaite [Zn$_4$Na(OH)$_6$(SO$_4$)Cl·6H$_2$O]: Second occurrence in the Juan de Fuca Ridge, and new data*

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ABSTRACT

A hydrous zinc- and sodium-rich hydroxy-chlorosulfate, discovered in a sulfide sample collected by the Deep Sea Recovery Vehicle (DSRV) Alvin in 1984, is identified as gordaite, Zn$_4$Na(OH)$_6$SO$_4$Cl·6H$_2$O, recently described as a new mineral species from Antofagasta, Chile. Results of re-examination of the original Alvin dive sample from the Juan de Fuca Ridge, northeastern Pacific Ocean, and additional data on gordaite, including vibrational and luminescence spectroscopy, X-ray diffractometry and thermal analysis, are presented.

INTRODUCTION

A sulfide chimney sample, collected by the Deep Sea Recovery Vehicle (DSRV) Alvin during a series of dives by U.S. Geological Survey geologists on the southern Juan de Fuca Ridge, was studied by Brett et al. (1987) who found, among other minerals, tiny white flakes of a hydrated Zn-rich hydroxy-chlorosulfate. Results of X-ray diffraction and energy-dispersive electron microprobe analyses led to the conclusion that this substance was a new mineral, identical to synthetic Zn$_{12}$(OH)$_{15}$(SO$_4$)$_3$Cl$_3$·5 H$_2$O (cf. MacEwan et al. 1966). However, neither the Alvin dive sample nor the synthetic material provided crystals large enough for single crystal structure determination.

Large, well shaped crystals (size up to about 0.7 mm) of a secondary phase, formed by weathering of Zn-rich slags from copper smelting, were found at a copper slag dump near Hettstedt, Mansfeld region, Germany (Witzke and Pöllmann 1996). Because the diffraction pattern of these crystals matches very well with the X-ray diffraction patterns of the two phases mentioned above, all three substances appear to be identical. One crystal from the Hettstedt material was subjected to detailed structure determination by Zhu et al. (1997). These authors found strong crystallographic evidence for the presence of Na in the structure, which was later analytically confirmed, and determined the chemical formula as Zn$_4$Na(OH)$_6$ SO$_4$Cl·6H$_2$O (two formula units per unit cell).

Schlüter et al. (1997) were the first to propose the hydrous zinc sodium hydroxy-chlorosulfate, found on a sample from Antofagasta, Sierra Gorda, Chile, as a new mineral species. These authors recently described the mineral as gordaite and pointed to its probable identity with the unnamed mineral discovered by Brett et al. (1987). In the present work, we re-examine the original material from the Juan de Fuca Ridge and present some additional data on gordaite.

SAMPLE ORIGIN AND DESCRIPTION

Gordaite was collected during Alvin dive 1457 on September 18, 1984. The sample ALV 1457-5R is from the Juan de Fuca Ridge, northeastern Pacific Ocean (130° 22′ 34″ West, 44° 38′ 53″ North), roughly 330 km west of the Oregon coast, at a depth of about 2200 m (cf. Normark et al. 1987). After re-examination, two pieces of the original sample (which contain about one half of the original sulfide chimney sample) were deposited in the mineralogical collection of Bergakademie Freiberg. The sample numbers are 77029 (U.S.G.S. sample number ALV 1457-5RA, base of chimney) and 77030 (ALV 1457-5RC, side to top of chimney).

The sample is a cone-shaped segment of a sulfide chimney, 32 cm in height and 12 cm (base) to 5 cm (top) in diameter, having a weight of 2.5 kg. The segment predominantly consists of porous sulfides (98%; mainly FeS$_2$ and sphalerite-wurtzite with very minor chalcopyrite) and sulfates (2%). The sample shows a concentric layering, which is defined by concentrations of pyrite (particularly in the core region) and variations in pore space. Narrow tunnelways and cavities oriented parallel to the longitudinal axis of the chimney occur preferentially in the core region. Fibrous layers with a thickness of less than 1 mm and consisting of amorphous silica, which is probably biogenic in nature, are observed in outer regions subparallel to the chimney walls. The outside walls are coated
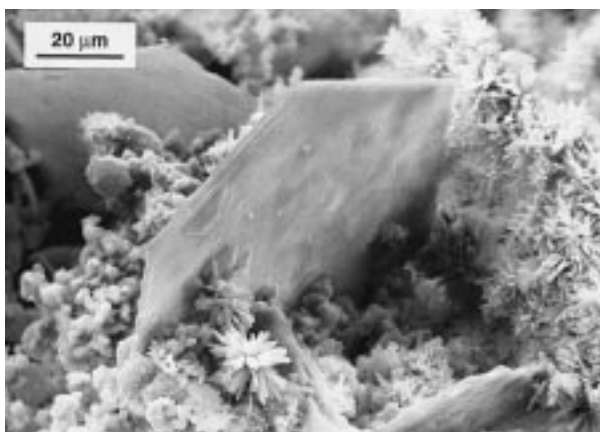

FIGURE 1. SEM photograph of a thin, tabular gordaite crystal of hexagonal habit, associated with tiny barite aggregates from the Juan de Fuca Ridge, northeastern Pacific Ocean.

with a thin, orange-red oxidic layer. The chimney, residual of an ocean floor "smoker", grew when hot hydrothermal fluids rich in S, Fe, Zn, and Cu, were discharged into cold sea water.

Sulfate minerals are mainly concentrated in concentric layers in the outer ZnS-rich areas and particularly on the oxidized exterior of the chimney. Gordaite was found on sample ALV 1457-5RC, forming colorless to white crystals, blades, or flakes of thin tabular habit, up to 100 μm in size. Euhedral crystals showing a pseudo-hexagonal shape (Fig. 1) are rarely observed. Gordaite is associated with sphalerite and barite, with minor pyrite, pyrrhotite, sulfur, and Fe-hydroxides (Fig. 2). Because gordaite is mostly accompanied by tabular barite, identification under the binocular microscope is difficult. The discovery that different sulfur species (sulfides, sulfates, and native sulfur) occur virtually together confirms the extreme degree of disequilibrium on a scale of a few micrometers in this type of submersible smoker (cf. Brett et al. 1987). In this environment, which is highly inhomogeneous in terms of thermal regime and composition, gordaite was formed by reaction of discharging hydrothermal fluids with sea water. The interpretation that gordaite must be primary in nature (and not a weathering product, for example formed under surface conditions after sampling) is supported by the observation that barite crystals overgrow gordaite.

Gordaite (or, more exactly, a geologically-modified anthropogenic analogue) was discovered on weathered slags from copper smelting, found on a dump near the city of Hettstedt, Mansfeld region, Germany. The colorless to
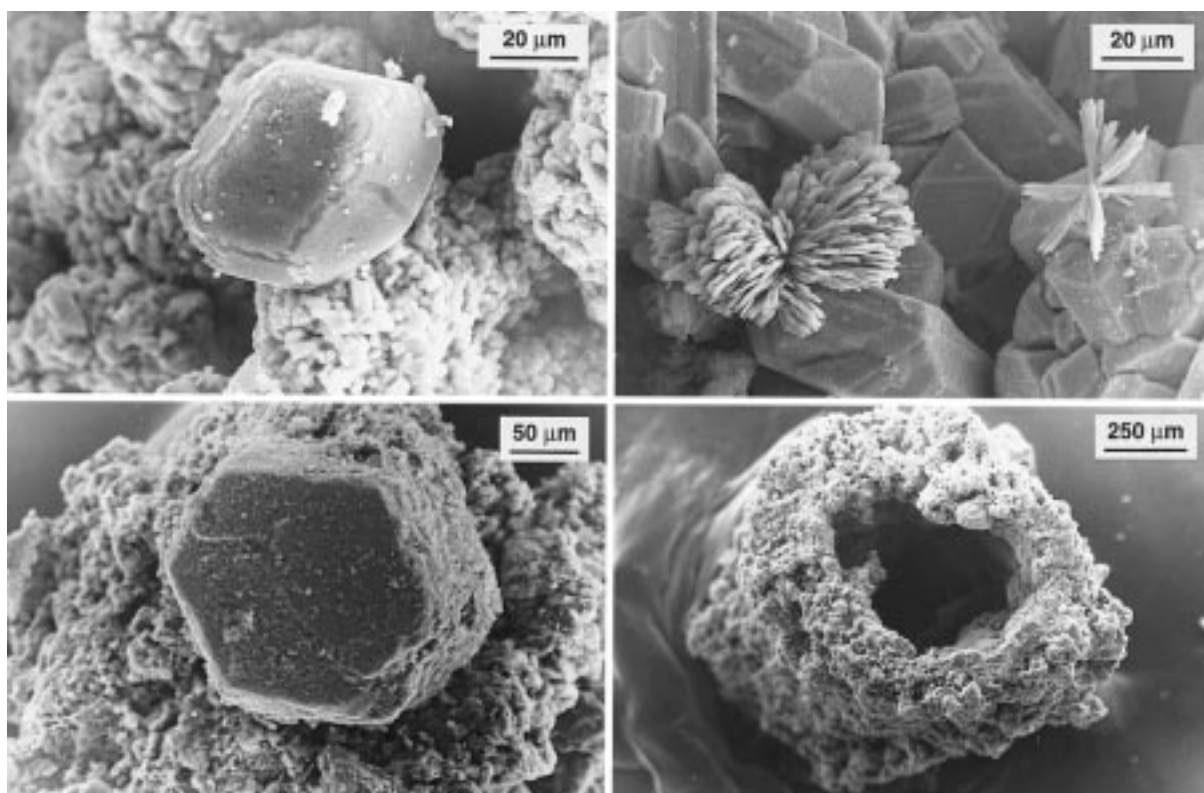

FIGURE 2. SEM photographs of minerals occurring with gordaite, from sample ALV 1457-5RC. Upper row, left: Rounded sulfur crystal on barite. Right: Two barite aggregates of rosette-like habit on sphalerite. Lower row, left: Pseudo-hexagonal, prismatic pyrrhotite crystal. Right: Tube-like FeS_2 aggregate, overgrown by Fe-oxides and -hydroxides, tiny pyrite cubes, and chalcopyrite crystals.

TABLE 1. X-ray diffraction data for various gordaites

	Hettstedt, Germany				Juan de Fuca*		Antofagasta[†]	
	measured		calculated					
hkl	d_{meas}	I_{meas}	d_{calc}	I_{calc}	d_{meas}	I_{meas}	d_{meas}	I_{meas}
001	13.08	100	13.05	100	13.19	100	12.950	100
002	6.523	11	6.523	8	6.60	5	6.501	23
101	6.311	<1	6.333	2				
102	4.836	<1	4.847	2			4.838	2
003	4.349	5	4.349	4			4.339	15
110			4.182	4	4.173	10	4.175	2
103	3.726	1	3.728	4	3.737	24	3.722	4
112	3.521	1	3.521	6	3.524	20	3.515	4
004	3.261	4	3.261	3			3.258	14
202			3.166	2			3.162	2
113			3.014	2			3.012	3
104	2.971	2	2.974	5	2.967	30	2.967	10
203			2.783	1			2.780	1
120	2.740	1	2.738	7	2.737	24	2.734	4
121	2.675	1	2.679	8	2.675	34	2.676	5
114	2.572	<1	2.572	2	2.574	16	2.569	3
122	2.524	1	2.524	10	2.523	30	2.523	6
105	2.455	<1	2.455	2			2.453	4
204			2.424	2	2.425	14	2.421	3
300	2.417	<1	2.414	1				
123	2.313	<1	2.317	4	2.319	10	2.315	3
006			2.174	<1			2.173	2
205			2.117	1				
124			2.097	3	2.098	24	2.095	2
220			2.091	<1				
106	2.084	<1	2.082	<1			2.082	2
132			1.920	<1				
125	1.889	1	1.889	5	1.8909	20	1.888	4
223			1.884	<1			1.884	4
206			1.864	<1			1.863	5
007	1.863	1	1.864	<1				
133			1.824	<1				
402			1.745	<1				
134			1.710	1	1.7062	16		
126	1.704	<1	1.703	5			1.700	5
008			1.631	<1			1.630	2
232			1.610	1				
135			1.592	1				
108			1.591	<1			1.590	2
404			1.583	<1				
140	1.581	<1	1.581	4	1.5789	20	1.580	3
141			1.569	3	1.5665	20	1.569	2
127			1.541	3			1.540	4

Note: The calculation for Hettstedt was done using the atomic parameters of Zhu et al. 1997. Calculated Bragg reflections with $I_{rel} < 0.5$ are listed only if there is an equivalent in the measured data. Note that the samples from Hettstedt, Germany and Antofagasta, Chile were analyzed using powder diffractometers whereas the sample from the Juan de Fuca Ridge was analyzed using a Debye-Scherrer camera. Therefore, intensities cannot be directly compared.
* Brett et al. (1987).
† Schlüter et al. (1997).

white crystals have a tabular to platy habit with pseudo-hexagonal shape. They occur in association with sphalerite, boleite, and gypsum (Witzke and Pöllmann 1996). Because these crystals are comparatively large, this material was used as an analogue for performing analyses that require larger sample amounts than could readily be obtained from the Juan de Fuca material (single crystal study by Zhu et al. 1997; powder diffractometry and thermal analysis, this work).

CHARACTERIZATION OF GORDAITE

X-ray powder diffractometry and thermal analysis

X-ray powder diffraction data of gordaite were obtained by means of a Siemens D5000 diffractometer with secondary monochromator, using Cu$K\alpha$-radiation. A diffractogram recorded from the Juan de Fuca Ridge material confirmed the data of Brett et al. (1987) but, due to the small amount of sample, its quality was insufficient for precise calculation of unit-cell parameters. The sample from Hettstedt has a trigonal unit cell with $a_0 = 8.364(3)$Å and $c_0 = 13.046(4)$Å. Table 1 compares powder data measured on the Hettstedt material with the theoretical X-ray powder diffractogram, calculated using the atomic parameters of Zhu et al. (1997), and the gordaite powder data measured by Brett et al. (1987) with $a_0 = 8.353(2)$Å and $c_0 = 13.087(8)$Å and Schlüter et al. (1997) with $a_0 = 8.363(4)$Å and $c_0 = 13.018(6)$Å. Detailed descriptions of the layered structure of gordaite, which con-

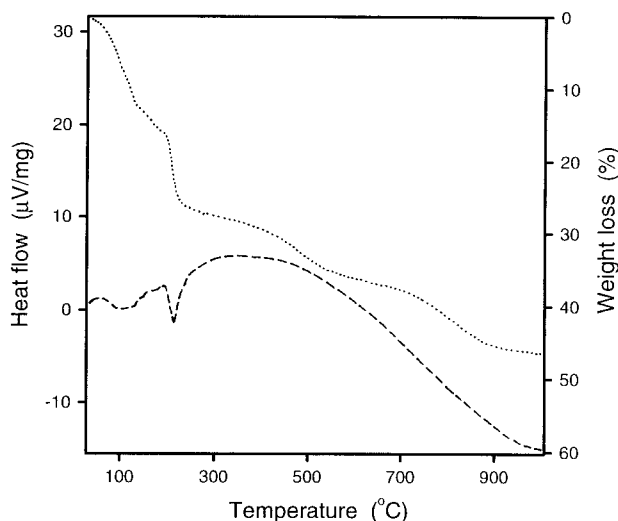**FIGURE 3.** Thermogravimetric (dotted line) and heat flow (dashed line) curves measured on 1.68 mg of powdered gordaite from Hettstedt.

Figure 4. Comparison of the infrared transmission spectrum and the Raman spectrum of gordaite from the Juan de Fuca Ridge.

sists of complex $[Zn_4(OH)_6(SO_4)Cl]^-$ layers alternating with $[Na(H_2O)_6]^+$ interlayers, are given by Zhu et al. (1997) and Adiwidjaja et al. (1997).

Thermal analysis of powdered gordaite from Hettstedt was performed using a Seiko Instruments TG/DTA 320 U thermal analyzer, in the temperature range 25 to 1000° C, with a heating rate of 20°/min (Fig. 3). X-ray diffraction showed that, after heating up to 1000° C, the residual sample consists of zincite (ZnO) only. SEM analysis (energy-dispersive X-ray detection) of this residual indicated the presence of Zn and O only. Provided that no other X-ray-amorphous phase exists, a theoretical weight loss of 47.0% is calculated, what corresponds well to the measured value (Fig. 3). The heat flow curve shows a distinct endothermic peak (onset temperature about 190° C). This reaction is connected with a weight loss of more than 10%, assigned to hydroxyl escaping the zinc hydroxide layers: After heating up to 225° C, the X-ray diffractogram revealed the presence of some zincite, indicating the breakdown of the main layer. An SEM analysis showed that S and Cl are still present at this stage. Water loss from the very weakly bonded $[Na(H_2O)_6]^+$ groups is believed to have commenced well below 190° C. After heating to 650° C, S is still detected whereas Cl is not, probably having volatilized between 225 and 650° C. The measured loss of 9.1 wt% between 650 and 1000° C (Fig. 3) corresponds reasonably with the theoretical overall SO_2 loss of 10.23 wt%.

Luminescence and vibrational spectroscopy

Gordaite from the Juan de Fuca Ridge shows very low intensity, whitish to pale yellowish fluorescence under ultraviolet light. Luminescence spectra were obtained using a high-sensitivity luminescence spectrometer with a charge-coupled device (CCD) detector (for description
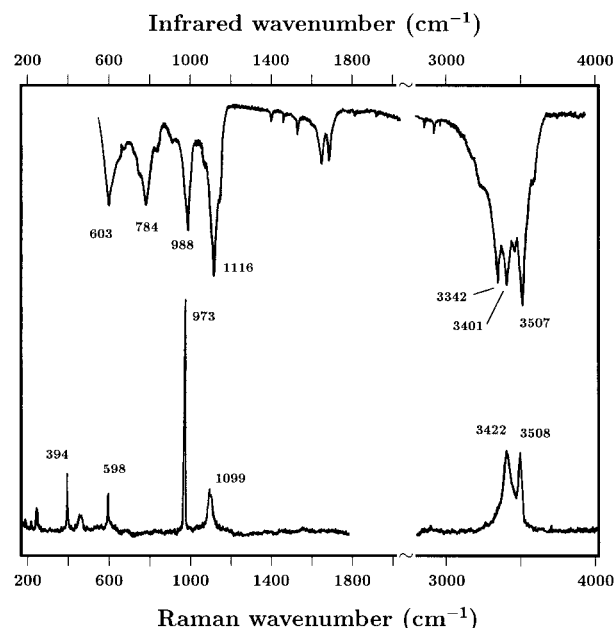
see Rieser et al. 1994). The spectra were stimulated using a long wave, broad band UV lamp with Schott UG11 and BG39 glass filters for 330 to 400 nm broad range excitation and Carl Zeiss Jena IF365 interference filter and Schott BG39 glass filter for 365 nm narrow range excitation. Background-corrected spectra were integrated for 100 s in the subtractive mode. The detection range was 450 to 700 nm. Independent of broad range or narrow range stimulation, a broad, low intensity luminescence band with a maximum at 530 to 560 nm is observed.

Infrared and Raman spectra were recorded from thin-tabular chips of gordaite (thickness less than 10 μm). Infrared analysis was performed using a Bruker IFS66 spectrometer with Bruker IR microscope, and a BioRad FTS 40A spectrometer with UMA 500 microscope. In both cases spectra were obtained in transmission mode in the range 500 to 4000 cm^{-1}. The spectral resolution was 4 cm^{-1}, and 200 scans were made. Raman analysis was done using a Dilor XY spectrometer (focal length 600 mm) with a confocal entrance optics system and a Jobin Yvon T 64000 spectrometer (focal length 640 mm). Both systems are equipped with an Olympus microscope and CCD detector. An Olympus 50× long distance objective (free working distance 8 mm, numerical aperture 0.55) was used. Raman spectra were excited using the Ar+ 5145 Å line (1 mW), and the spectral resolution was about 3 cm^{-1}. Spectra were recorded in the subtractive mode in the range 100 to 4000 cm^{-1}. Ten signal/dark accumulations per 60 s were done.

Raman and IR spectra of gordaite from the Juan de Fuca Ridge in (Fig. 4) does not significantly differ from Hettedt samples (not shown). The IR spectrum shows an

intense group of bands in the O-H stretching region, with four distinct peaks at 3342, 3401, 3442, and 3507 cm^{-1} and shoulders at 3250 and 3600 cm^{-1}. These strong bands are probably stretching vibrations of the six (OH)$^-$ groups in the zinc hydroxide layer, but could be also due to structurally bound water. Interlayer H_2O molecules could produce a broad underlying band. The finding of four main bands and additional shoulders supports the conclusion from the single-crystal X-ray data that slightly different (OH)$^-$ and H_2O positions exist in the structure . Accompanying bands of HOH bending vibrations may occur at 1639 and 1672 cm^{-1}. However, the widths are narrow for this assignment and the 1672 cm^{-1} position (very strong hydrogen bonding) is inconsistent with those of the stretching bands. Possibly, the 1672 cm^{-1} band is due to organic material, for example, the intense C = O stretching mode in that hydrocarbon contamination is inferred from occurrence of low intensity peaks at about 1400 to 1500 cm^{-1} and around 2900 cm^{-1}. The IR bands in the range 600 to 1200 cm^{-1} are caused by vibrations of the Zn-bearing layers, particularly by internal vibrations of the distorted SO_4 tetrahedra. The most intense bands are at 603 [$v_4(SO_4)$], 784 (probably Zn-OH stretching), 988 [$v_1(SO_4)$], and 1116 cm^{-1} [$v_3(SO_4)$; cf. Fig. 4].

The Raman spectrum of gordaite is dominated by the symmetric stretching vibration of the tetrahedral sulfate group (v_1 mode; sharp peak at 973 cm^{-1}). The broad band at 1099 cm^{-1} consists of at least two overlapping Raman peaks that are probably assigned to $v_3(SO_4)$ vibrations. Raman bands in the range 100 to 700 cm^{-1} might be caused by further internal SO_4 vibrations [because $v_4(SO_4)$ vibrations are expected at about 600 cm^{-1}, the peak at 598 cm^{-1} could be interpreted as an internal sulfate band], Zn-Cl stretching librations, and other low-frequency vibrations of the zinc hydroxide layers. In the OH stretching region, two peaks at 3422 and 3508 cm^{-1} are observed. However, these Raman peaks are comparatively lower in intensity than their counterparts in the IR absorption spectrum, consistent with the higher sensitivity of IR spectroscopy for detecting hydrous species, compared with Raman spectroscopy. H_2O-bending vibrations in the Raman spectrum of gordaite are observed only as broad bands of very low intensity, consistent with interlayer water.

Electron microprobe analysis

Accurate analysis of the chemical composition of gordaite by means of an electron microprobe appears to be extremely problematic. Energy-dispersive X-ray detection was performed by means of a Philips XL 30 SEM equipped with Edax DX4 system. The accelerating voltage was 25 kV, the beam current was in the 10^{-11} A range, and the focal spot area of the electron beam had a diameter of about 3μm. Under these conditions, gordaite remained stable under the electron beam. However, it was impossible to analyze Na with reasonable accuracy because the Na-K lines (Na-Kα 1.039 keV) are obscured by the intense Zn-L lines (Zn-Lα lines 1.012 keV, Zn-Lβ_1 1.031 keV).

The above problem is not expected when analyzing a sodium-bearing zinc mineral using wavelength-dispersive X-ray detection. Therefore, tests were made to analyze gordaite from the Juan de Fuca Ridge by means of a Cameca SX 50 electron microprobe. However, even when the energy of the electron beam was considerably decreased compared with normally used experimental conditions, the mineral bubbles and degases within a few seconds of switching on the beam (wavelength-dispersive X-ray detection requires excitation with considerably higher beam currents, compared with energy-dispersive X-ray detection). Gordaite is immediately altered when the polished sample surface is hit by an electron beam of 3 kV and 1 nA, independent of the size of the irradiated area (the beam diameter was varied from about 2.5 to 90 μm). The alteration is connected with considerable changes of the sample's surface topography, resulting in great instability at the experimental conditions.

Consequently, quantitative analysis of Na requires a different method, as was done by Schlüter et al. (1997). We proved the presence of Na in the gordaite samples from the Juan de Fuca Ridge and Hettstedt qualitatively by SHRIMP ion probe analysis (quantitative Na analysis would have required extensive methodical tests and the availability of a well-investigated standard material). Several SHRIMP mass scans revealed that the Na content in both samples is about the same, because the measured ^{23}Na/^{32}S, ^{23}Na/^{35}Cl, and ^{23}Na/^{66}Zn isotopic ratios showed variations of less than 15%.

A Cu-rich variety of gordaite and even its copper-analogue (light blue flakes up to 0.3 mm in size forming rosette-like aggregates, accompanied by connellite, anglesite, and chlorian bromargyrite) were recently discovered on a sample from a Kupferschiefer dump near the city of Helbra, Mansfeld region, Germany. The distribution of the divalent metal positions was in the range $Zn_{2.1}Cu_{1.9}$ to $Zn_{1.7}Cu_{2.3}$. A solid solution probably exists between the zinc- and copper-dominant species.

Gordaite occurs in an arid, sub-tropical environment (Schlüter et al. 1997), a temperate environment with moderate rainfall from a Kupferschiefer dump (above), and from a decidedly wet, sea-floor environment at about 2° C (Brett et al. 1987; this paper). This wide range of environments suggests that this easily overlooked mineral may be much more common than has previously been thought.

References cited

Adiwidjaja, G., Friese, K., Klaska, K.-H., and Schlüter, J. (1997) The crystal structure of gordaite NaZn$_4$(SO$_4$)(OH)$_6$Cl·6H$_2$O. Zeitschrift für Kristallographie, 212, 704–707.

Brett, R., Evans, H.T., Gibson, E.K., Hedenquist, J.W., Wandless, M.-V., and Sommer, M.A. (1987) Mineralogical studies of sulfide samples and volatile concentrations of basalt glasses from the Southern Juan de Fuca Ridge. Journal of Geophysical Research, 92, B11, 11,373–11,379.

MacEwan, D.M.C., Cumplido, M.I.C., and Ruiz, J.C. (1966) Hidroxisales. II. Sobre estructura del hidroxiclorosulfato de Zn partir de diagramas de polvo. Anales de Fisica y Quimica, LXII-B, 25–36.

Normark, W.R., Morton, J.L., and Ross, S.L. (1987) Submersible observations along the Southern Juan de Fuca Ridge: 1984 Alvin program. Journal of Geophysical Research, 92, B11, 11,283–11,290.

Rieser, U., Krbetschek, M.R., and Stolz, W. (1994) CCD-camera based high sensitivity TL/OSL-spectrometer. Radiation Measurements, 23, 523–528.

Schlüter, J., Klaska, K.-H., Friese, K., Adiwidjaja, G., and Gebhardt, G. (1997) Gordaite, NaZn$_4$(SO$_4$)(OH)$_6$Cl·6H$_2$O, a new mineral from the San Francisco Mine, Antofagasta, Chile. Neues Jahrbuch für Mineralogie, Monatshefte, 1997, 155–162.

Witzke, T and Pöllmann, H. (1996) Mineralneubildungen in den Schlacken der Kupferschieferverhüttung des Mansfelder Reviers, Sachsen-Anhalt. Hallesches Jahrbuch für Geowissenschaften, B18, 109–118.

Zhu, L., Seff, K., Witzke, T., and Nasdala, L. (1997) Crystal structure of Zn$_4$Na(OH)$_6$SO$_4$Cl·6H$_2$O. Journal of Chemical Crystallography, 27, 325–329.