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LETTER

Crystal chemistry of ZnS minerals formed as high-temperature volcanic sublimates: matraite identical with sphalerite

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The crystal chemistry of ZnS minerals formed as high-temperature volcanic sublimates from Iwodake volcano, Satsuma-Iwojima, Japan, has been studied by means of single-crystal X-ray diffraction (XRD), electron microprobe (EMP), micro-XRD, and micro-Raman scattering analyses. These minerals were identified as sphalerite and matraite by using a four-circle automated X-ray diffractometer. However, these two minerals were virtually the same in XRD pattern, chemical composition and micro Raman-scattering spectrum. A close examination of the observed reflections for the matraite sample revealed that all of them can be identified as reflections diffracted from (001)-twinned matraite. Moreover, all the reflections from (001)-twinned matraite were completely identical with those from (111)-twinned sphalerite. Consequently, it is evident that matraite is not a distinct mineral species but can be treated as (111)-twinned sphalerite. Occurrences of this twinned sphalerite may be characteristic of high-temperature volcanic sublimates.

Keywords: Sphalerite, Matraite, Twinned minerals, Reciprocal lattice, High-temperature volcanic sublimate, Iwodake volcano, Satsuma-Iwojima

INTRODUCTION

The most common polytypes of ZnS minerals occurring in nature are sphalerite, which has a cubic close-packed (3C-ZnS) structure, and wurtzite, which has a hexagonal close-packed (2H-ZnS) structure (Pósfai et al., 1988). In addition, matraite (3R-ZnS) was reported to be trimorphous with sphalerite and wurtzite (Koch, 1958).

3R-ZnS was first prepared by Buck and Strock (1955) based on the powder X-ray diffraction (XRD) pattern of thermally treated synthetic sphalerite. Koch (1958) described this phase as "matraite" based on a study of the polymetallic ores of Gyöngyösoroszi, Hungary. From an oscillation photograph of matraite, Sasvári (1958) assumed the matraite to be a twinned crystal with an oppositely directed *c* axis. Subsequently, Minčeva-Stefanova (1993) suggested that the matraite and sphalerite from the lead-zinc deposits in Zvezdel, Bulgaria, were distinguished by their morphologies and S content and concluded that matraite is distinct from the other ZnS minerals. Koch (1958) and Minčeva-Stefanova (1993) emphasized that matraite is optically anisotropic, while sphalerite is not. However, previous studies suggested that sphalerite anisotropy arises due to either small chalcopyrite inclusions or the presence of small domains with hexagonal symmetry (Haapara and Laajoki, 1969; Seal et al., 1985). On the other hand, Pósfai et al. (1988) and Weiszburg et al. (2000) suggested that ZnS minerals from Gyöngyösoroszi can be treated as either twinned sphalerite or the more randomly faulted structure that is more similar to wurtzite than to the sphalerite polytype based on electron diffraction patterns. Thus, the Commission on New Minerals and Mineral Names (CNMMN) of the International Mineralogical Association (IMA) discredited matraite (Burke, 2006; Nickel and Nichols, 2007).

Sphalerite and wurtzite occur as high-temperature

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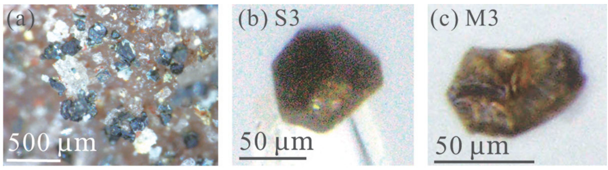


Figure 1. Stereomicrophotographs of high-temperature volcanic sublimates from Iwodake. (a) The sphalerite zone. The black crystals are ZnS minerals denoted by (b) S3 and (c) M3. These crystals were chosen from sample No. 022403-2 reported by Hamasaki (2002).

Table 1. Summarized crystal data and details of refinement parameters*

Sample	S2**	M1**
Scan type	ω-2θ	
Direct method ***	SIR92	
Refinement system ****	SHELXL-97	
Space group	$F\bar{4}3m$	$R3m$
Crystal size (mm)	0.1×0.1×0.1	
a (Å)	5.4159(8)	3.8283(12)
c (Å)	5.4159(8)	9.382(4)
V (Å^3)	158.86(4)	119.07(7)
D_{calc} (g/cm^3)	4.073	4.077
Z	4	3
μ (mm^{-1})	15.89	15.93
Collected reflections	30	269
Unique refrections	22	54
Rejected reflections	0	182
R_{int}	0.0519	0.0291
$R1$	0.0168	0.1136
$wR2$	0.0499	0.2558
GooF (=S)	1.199	1.339
No. of parameters	5	8

* Unit cell parameters and XRD data were measured at 293 K for all samples.

** Structural formulae of ZnS minerals were calculated by normalizing Σcations and ΣS to 1 apfu, respectively.

** S2: $(Zn_{0.968}Fe_{0.023}Cu_{0.005}In_{0.002}Cd_{0.002})_{\Sigma 1.000}S_{1.000}$.

** M1: $(Zn_{0.965}Fe_{0.025}Cu_{0.005}In_{0.003}Cd_{0.002})_{\Sigma 1.000}S_{1.000}$.

*** Altomare et al. (1992).

**** Sheldrick (1997).

volcanic sublimates that are either precipitated directly from the gas phase by vapor deposition processes or formed after gas mixing (Symonds, 1993; Magazina et al., 1996; Cheynet et al., 2000; Africano et al., 2002; Nitta et al., 2006; Yudvskaya et al., 2006; Chaplygin et al., 2007); however, thus far, matraite has not been reported to occur in the same manner. Further, detailed investigations of the crystal-chemical characteristics of these ZnS minerals, precipitated as high-temperature volcanic sublimates, are technically difficult because of the small crystal sizes (less than 100 μm).

The objectives of this study are (1) to describe the crystal-chemical characteristics of ZnS minerals formed as high-temperature volcanic sublimates and (2) to clarify the crystallographic relation between matraite and other ZnS minerals.

SAMPLES AND ANALYTICAL METHODS

The ZnS mineral samples used in this study were collected from Iwodake volcano, Satsuma-Iwojima, Kyushu, SW Japan. The continuous emission of high-temperature (up to 900 ºC) volcanic gases (Shinohara et al., 2002) leads to the precipitation of volcanic sublimates (Africano et al., 2002). The geology and mineralogy of Iwodake volcano have been studied by Hamasaki (2002), Africano et al. (2002), and Nitta et al. (2006). The ZnS minerals were in the form of small (50-100 μm) black euhedral crystals and were coexistent with transparent crystals of halite (NaCl) and sylvite (KCl) (Fig. 1). Six crystals, labeled S1, S2, S3, M1, M2, and M3, were selected from the ZnS minerals from Iwodake.

Single-crystal XRD datasets for the ZnS minerals were collected using a four-circle automated diffractometer (Rigaku AFC7R) with graphite-monochromated Mo-$K\alpha$ radiation and a rotating anode generator at the Center for Tsukuba Advanced Research Alliance, University of Tsukuba. The details of the single-crystal XRD analysis are tabulated in Table 1. Furthermore, the ZnS minerals were identified using a micro-Raman scattering spectrometer and an X-ray micro-diffractometer equipped with the Gandolfi crystal movement system (Kimata et al., 1990); the analytical procedures have been described in detail by Nitta et al. (2006). The chemical compositions of the ZnS minerals were determined using an electron microprobe analyzer (JEOL JXA-8621) equipped with three wavelength-dispersive spectrometers at the Chemical Analysis Division, University of Tsukuba.

RESULTS AND DISCUSSION

The crystal data, atomic positional parameters, and anisotropic displacement factors are listed in Tables 1 and 2. The detailed crystal data, atomic coordinates, and anisotropic displacement parameters of S1, S2, S3, M1, M2, and M3 can be obtained from E. Nitta. The ZnS minerals were identified as sphalerite and matraite by the single-crystal XRD method (Table 1). The refinement of their crystal structures indicated that some of the sphalerite was identical with (111)-twinned sphalerite. The refined structures of matraite posed two serious problems: (1) the absence of convergent R-factors and (2) the presence of many unused reflections that systematically violated the

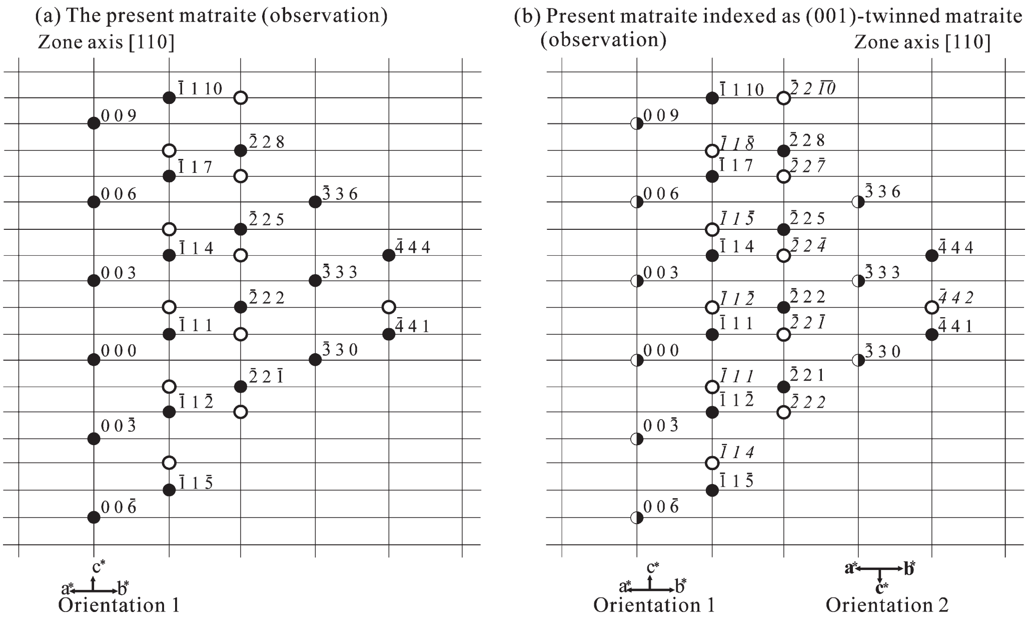
Table 2. Atomic coordinates and anisotropic displacement parameters

Sphalerite (S2)										
Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	Ueq
M[*]	0	0	0	0.0112(10)	0.0112(10)	0.0112(10)	0	0	0	0.0112(10)
S	0.25	0.25	0.25	0.0083(10)	0.0083(10)	0.0083(10)	0	0	0	0.0083(10)

Matraite (M1)										
Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	Ueq
M[**]	0	0	0.0317(15)	0.006(2)	0.006(2)	0.008(2)	0	0	0.003(12)	0.007(2)
S	0	0	0.7848(15)	0.005(4)	0.005(4)	0.006(5)	0	0	0.002(19)	0.005(3)

[*] Site occupancies: Zn, 0.968(10); Fe, 0.023(7); Cu, 0.005(2); In, 0.002(1); Cd, 0.002(1).

[**] Site occupancies: Zn, 0.965(1); Fe, 0.025(1); Cu, 0.005(2); In, 0.003(1); Cd, 0.002(1).

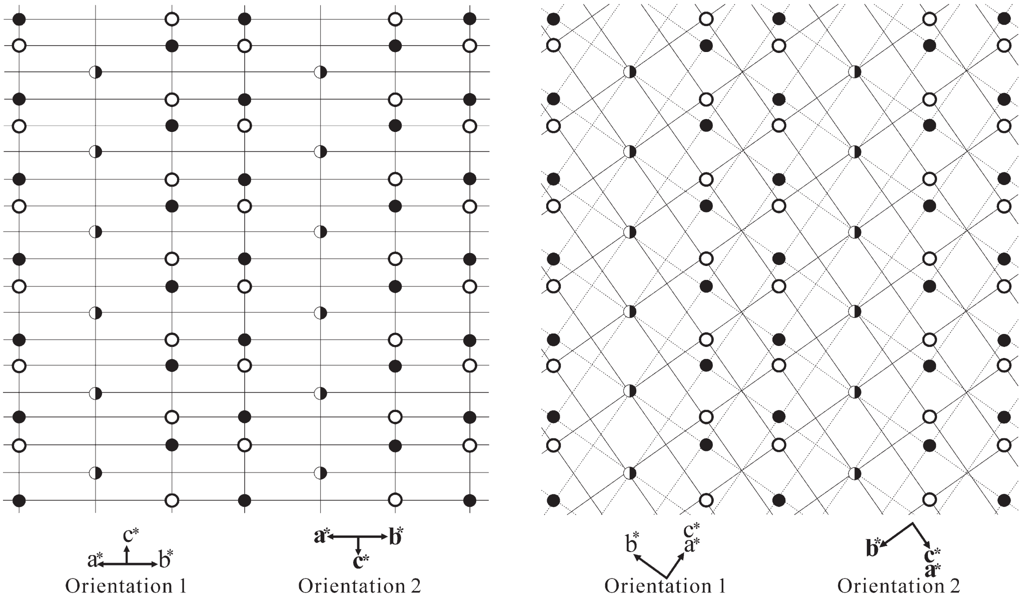

(a) The present matraite (observation) Zone axis [110]

(b) Present matraite indexed as (001)-twinned matraite (observation) Zone axis [110]

Figure 2. Observed reciprocal lattice points. (a) The present matraite. Filled circles, observed reflections following the extinction rules; open circles, observed reflections violating the extinction rules; indexed points, observed reflections following the extinction rules; and solid lines, reciprocal cell. (b) Present matraite indexed as (001)-twinned matraite. Filled circles, reflections of twin orientation 1 (observation); open circles, reflections of twin orientation 2 (observation); half-filled circles, reflections common to twin orientations 1 and 2 (observation); indexed points of normal letters, observed reflections of twin orientations 1; indexed points of italicized letters, observed reflections of twin orientations 2; and solid lines, reciprocal cell.

extinction rule (Table 1). On closer examination, it was noted that all the rejected reflections follow the extinction rules for the transformed, oppositely directed (001) plane of the matraite sample (Figs. 2a and 2b). Moreover, all the reflections of (001)-twinned matraite are completely identical with those of (111)-twinned sphalerite (Figs. 3a and 3b). Consequently, this identity is consistent with the simple interpretation of Pósfai et al. (1988) and Weiszburg et al. (2000). In addition, the reciprocal lattice points projected from the [110] zone axis, calculated from the single-crystal data for refined matraite, are perfectly consistent with those projected from the $[\bar{1}01]$ zone axis for refined sphalerite (Figs. 3c and 3d). Furthermore, with respect to the arrangement of ZnS_4 tetrahedra, the crystal structure of matraite is exactly the same as that of sphalerite in both the orientation and the stacking mode of the tetrahedral layer, and hence selection of both the more reduced cell and the higher crystal system determines the space group ($F\bar{4}3m$) which is the most appropriate for the crystal structure. The trigonal unit cell ($R3m$) of matraite is transformed into the cubic unit cell ($F\bar{4}3m$) of sphalerite by the following axial transformation: $a_H^* = (1/2)(-a_1^* + a_2^*)$, $b_H^* = (1/2)(-a_2^* + a_3^*)$, $c_H^* = a_1^* + a_2^* + a_3^*$ (matraite lattice axes: a_H, b_H, c_H, sphalerite lattice axes: a_1, a_2, a_3; Sásvari, 1958). Thus, matraite is not a distinct mineral species; it is completely identical with sphalerite (Figs. 3c and 3d).

The micro-XRD patterns in Figure 4 show that the


(a) (001)-twinned matraite (calculation) Zone axis [110]

(b) (111)-twinned sphalerite (calculation) Zone axis [$\bar{1}$01]

(c) Single crystal of matraite (calculation) Zone axis [110]

(d) Single crystal of sphalerite (calculation) Zone axis [$\bar{1}$01]

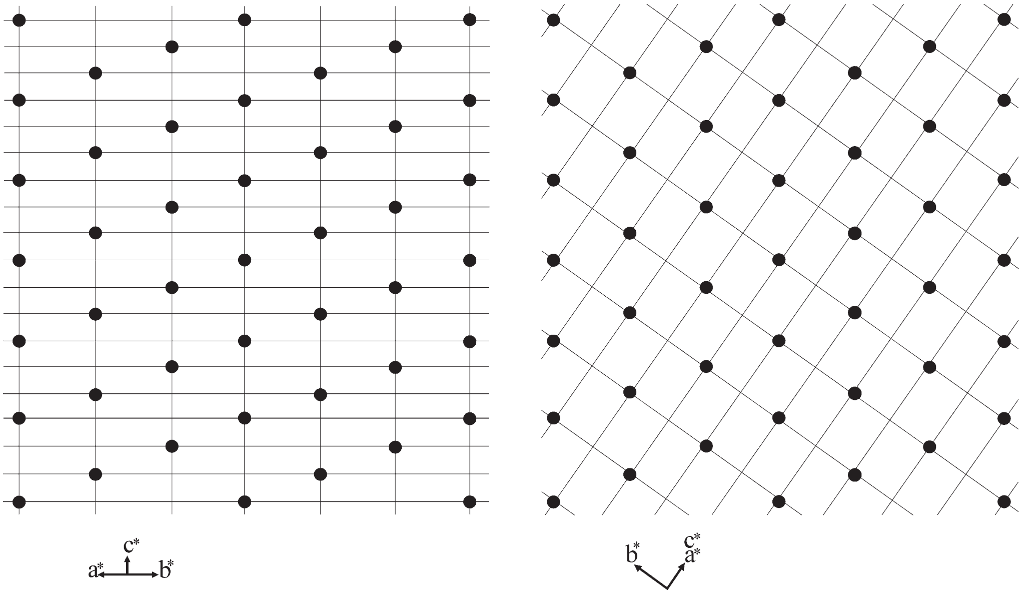


Figure 3. Calculated reciprocal lattices points. (a) (001)-twinned matraite, (b) (111)-twinned sphalerite, (c) single crystal of matraite, and (d) single crystal of sphalerite. Filled circles, reflections of twin orientation 1; open circles, reflections of twin orientation 2; half-filled circles, reflections common to twin orientations 1 and 2; and solid and dotted lines, reciprocal cell.

sample matraite and sphalerite are indistinguishable from each other, which is consistent with the suggestion of Pósfai et al. (1988). The splitting of the (111) reflection, which Buck and Strock (1955) observed in a powder XRD pattern of a matraite sample, could not be confirmed by the present study. Additionally, the powder XRD patterns of these two minerals, calculated from the present single-crystal structural refinements (Tables 1 and 2), are exactly identical (Fig. 4). Moreover, these two minerals displayed similar characteristics in the micro-Raman scattering spectrum (Fig. 5). The equivalence between these minerals in the micro-XRD patterns and the micro-Raman scattering spectra is consistent with the interpretation that the present matraites are densely twinned sphalerites.

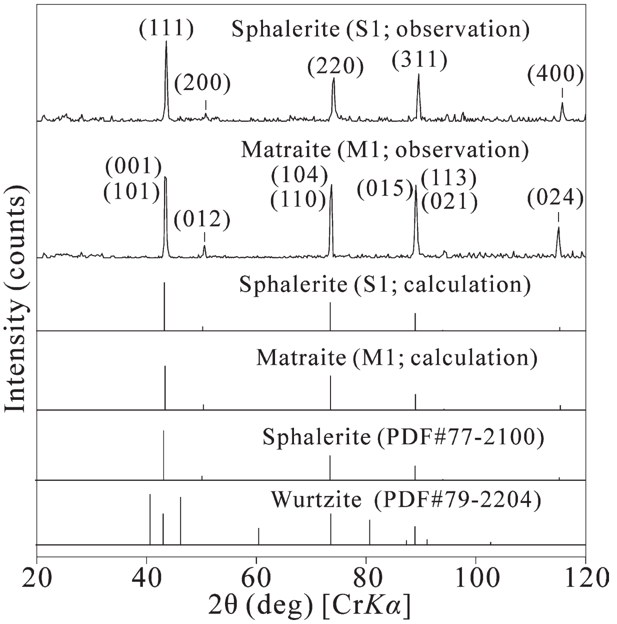


Figure 4. X-ray micro-diffraction patterns of ZnS minerals. ZnS minerals from Iwodake volcano were selected from the sphalerite zone shown in Figure 1a.

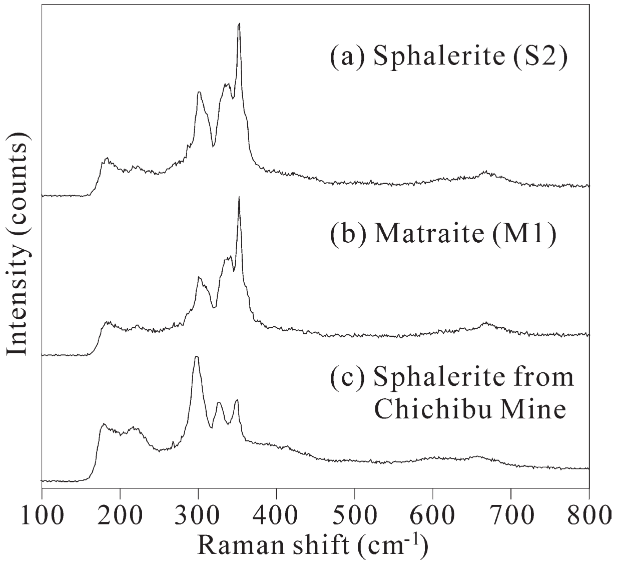


Figure 5. Micro-Raman spectra of ZnS minerals: (a) sphalerite from Iwodake, (b) matraite from Iwodake, and (c) sphalerite from the Chichibu mine.

Electron microprobe analyses (EMPA) demonstrated that not only Fe and Cd but also In and Cu were present in the matraite and sphalerite samples (Table 3). Sphalerite formed as high-temperature volcanic sublimate is rich in In, Cu, and Cd (Kovalenker et al., 1993; Nitta et al., 2006; Chaplygin et al., 2007). The sample ZnS minerals are characterized by low EMPA totals (Table 3), and this weight loss is probably due to the microporosity of high-temperature volcanic sublimates. A similar loss has been observed in sphalerites occurring as high-temperature volcanic sublimates from Kudriavy volcano (Chaplygin et al., 2007). Minčeva-Stefanova (1993) stated that the Fe and Cd content in matraite is higher than that in sphalerites and that the S content of the former is slightly lower than 50 at% whereas that of the latter is slightly higher than 50 at%. However, the EMPA revealed that matraite

Table 3. Electron microprobe analyses of ZnS minerals from Iwodake

Sample	S1		S2		S3*		M1		M2		M3*	
N**	5		5		7		5		5		6	
wt%	mean	s.d.***	mean	s.d.	mean	s.d.	mean	s.d.	mean	s.d.	mean	s.d.
Zn	62.05	0.12	62.19	0.52	59.28	1.39	61.34	0.35	61.71	0.91	58.67	1.42
Fe	1.41	0.06	1.26	0.40	2.14	0.09	1.33	0.05	1.24	0.26	2.29	0.34
Cu	0.19	0.05	0.30	0.13	0.87	0.49	0.28	0.10	0.36	0.18	0.62	0.41
In	0.29	0.05	0.24	0.08	1.02	0.34	0.36	0.09	0.49	0.26	0.41	0.09
Cd	0.26	0.03	0.27	0.05	0.42	0.04	0.25	0.08	0.23	0.03	0.47	0.02
S	33.22	0.59	33.55	1.19	33.63	1.54	33.11	0.26	32.73	0.32	35.87	2.03
Total	97.42	0.60	97.81	1.05	97.36	1.88	96.67	0.48	96.76	0.55	98.33	1.81
apfu.												
Zn	0.941	0.009	0.937	0.007	0.898	0.018	0.936	0.004	0.944	0.009	0.866	0.037
Fe	0.025	0.001	0.022	0.007	0.038	0.002	0.024	0.001	0.022	0.005	0.040	0.006
Cu	0.003	0.001	0.005	0.002	0.014	0.008	0.004	0.002	0.006	0.003	0.009	0.006
In	0.002	0.000	0.002	0.001	0.009	0.003	0.003	0.001	0.004	0.002	0.003	0.001
Cd	0.002	0.000	0.003	0.000	0.004	0.000	0.002	0.001	0.002	0.000	0.004	0.000
S	1.027	0.009	1.031	0.029	1.037	0.021	1.031	0.004	1.022	0.005	1.078	0.032
Total	2.000		2.000		2.000		2.000		2.000		2.000	

* Nitta et al. (2006).

** Number of analytical points.

*** Standard deviation of the samples.

is not clearly distinct from sphalerite in chemical composition (Table 3); this is consistent with the interpretation that matraite is not a distinct mineral species. According to Johan (1988) and Šrot et al. (2003), Fe, Mn, Cu, and In tend to preferentially concentrate in the (111) growth plane of the sphalerite crystals. Their observations suggest that these minor elements have the preferential concentration to form the (111)-twinned sphalerite. Therefore, the enrichment of minor elements such as Fe, Cu, In, and Cd may result in the formation of twinned sphalerites that occur as high-temperature volcanic sublimates.

3R-ZnS crystals which may be (111)-twinned spalerite were formed at high temperatures (600-1200 ºC) and with a rapid crystal-growth rate (Buck and Strock, 1955; Minčeva-Stefanova, 1993). Such conditions are similar to those of the sphalerite formed as high-temperature volcanic sublimates. Moreover, Chaplygin et al. (2007) reported that Cd-bearing sphalerite from the Kudriavy volcano exhibits "spinel-twinning." Thus, the dense (111)-twinning mentioned above may be characteristic of the sphalerites formed as high-temperature volcanic sublimates.

CONCLUDING REMARKS

We performed the first single-crystal XRD analysis of matraite; based on the results of the study, we state that all the matraite from Iwodake consisted of (001)-twinned crystals. We demonstrated that the chemical composition and crystal structure of (001)-twinned matraite are identical with those of (111)-twinned sphalerite. Thus, matraite is not a distinct mineral species. The twinned crystals in ZnS minerals formed as high-temperature volcanic sublimates are caused by a high enrichment of trace elements (e.g., Cu, In, and Cd) in these minerals.

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