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ALACRANITE, As_4S_4: A NEW OCCURRENCE, NEW FORMULA, AND DETERMINATION OF THE CRYSTAL STRUCTURE*

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ABSTRACT

Between July 20 and August 3, 1998, cruise SO–133 aboard the *R/V Sonne* completed detailed mapping and sampling of the seafloor around Lihir Island in Papua New Guinea. Sampling of Conical Seamount resulted in the discovery of an unusual occurrence of alacranite and realgar associated with polymetallic vein mineralization consisting of pyrite, sphalerite, galena, minor chalcopyrite and sulfosalts, along with intense clay and silica (amorphous) alteration. Alacranite occurs as subhedral to euhedral tabular orange crystals that are transparent to translucent with a vitreous to resinous luster. Crystals occur both isolated and as groupings within vugs and on matrix, and have a maximum length of 0.1 mm. Single-crystal diffraction data were collected using Mo$K\alpha$ X-radiation and a CCD-based detector. The structure is monoclinic, space group $C2/c$, a 9.943(1), b 9.366(1), c 8.908(1) Å, β 102.007(2)°, and was refined to an agreement index ($R1$) of 6.6%. The structure determination indicates that the formula of alacranite is As_4S_4, $Z = 4$, rather than As_8S_9 as reported earlier from a Russian locality. Thus, alacranite is the third polymorph of this composition, after realgar and pararealgar. The structure contains covalently bonded As_4S_4 molecules that are linked by van der Waals forces to form the three-dimensional structure. The structure is identical to that of synthetic α–As_4S_4.

Keywords: alacranite, realgar, pararealgar, arsenic sulfide, structure determination, Conical Seamount, Lihir Island, Papua New Guinea.

SOMMAIRE

Entre le 20 juillet et le 3 août, 1998, la croisière SO–133 du navire *R/V Sonne* a porté sur la cartographie et l'échantillonnage des fonds marins autour de l'île de Lihir, en Papouasie Nouvelle Guinée. L'échantillonnage du guyot dit Conical a mené à la découverte d'un exemple inhabituel d'alacranite et de réalgar en association avec une minéralisation polymétallique en veines, comprenant pyrite, sphalérite, galène, avec la chalcopyrite et des sulfosels comme accessoires, et un développement intense d'argiles et de silice amorphe comme produits d'altération. L'alacranite se présente en cristaux tabulaires subidiomorphes à idiomorphes de couleur orange; ils sont transparents à translucides, avec un éclat vitreux à résineux. Les cristaux sont soit isolés ou en groupes dans des cavités et sur matrice, et atteignent une taille de 0.1 mm. Les données diffractométriques ont été prélevées sur cristal unique en utilisant un rayonnement Mo$K\alpha$ et un détecteur de type CCD. La structure est monoclinique, groupe spatial $C2/c$, a 9.943(1), b 9.366(1), c 8.908(1) Å, β 102.007(2)°; elle a été affinée jusqu'à un résidu $R1$ de 6.6%. D'après l'ébauche de la structure, la formule de l'alacranite serait As_4S_4, $Z = 4$, plutôt que As_8S_9, comme l'ont conclu les chercheurs antérieurs avec un matériau d'une localité russe. L'alacranite devient ainsi le troisième polymorphe de cette composition, après réalgar et pararéalgar. La structure contient des molécules As_4S_4 à liaisons covalentes, agencées dans une trame tri-dimensionnelle par liaisons de van der Waals. La structure est identique à celle du composé synthétique α–As_4S_4.

(Traduit par la Rédaction)

Mots-clés: alacranite, réalgar, pararéalgar, sulfure d'arsenic, détermination de la structure, guyot Conical, île de Lihir, Papouasie Nouvelle Guinée.

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INTRODUCTION

Alacranite was first observed associated with barite – quartz – calcite veins in the Alacrán silver mine, Pampa Larga mining district, Chile, by Clark (1970). He reported a realgar-like mineral with X-ray characteristics similar to the high-temperature α polymorph of As_4S_4 described by Hall (1966). Clark (1970) noted that realgar coats surfaces or cavity walls, whereas alacranite occurs in the interstices of barite plates. Popova *et al.* (1986) reported another occurrence of alacranite, in association with realgar and uzonite, as a cement in sandy gravels from the Uzon caldera, Kamchatka, Russia. They reported the composition as As_8S_9 on the basis of electron-microprobe analyses, and provided a detailed mineralogical description and its name.

As part of the Epithermal Deposits in the Southwestern Pacific Ocean (EDISON) project, one of us (JBP) participated in a recent cruise near Papua New Guinea and recovered specimens containing superb crystals of alacranite. This provided the opportunity for us to describe this unusual occurrence and to determine the structure and correct chemical formula of this mineral.

BACKGROUND AND GEOLOGICAL SETTING

The EDISON project is a component of a multidisciplinary program to study regional tectonics, submarine volcanism and seafloor hydrothermal activity in the New Ireland fore-arc basin of Papua New Guinea (Fig. 1). This largely uncharted area surrounding the Tabar-to-Feni island chain was initially mapped aboard the German research vessel *R/V Sonne* between March 11 and April 5, 1994 (cruise SO–94). This cruise led to the first documentation of seafloor hydrothermal activity associated with alkaline volcanism and represented a new type of setting on the seafloor for shallow marine

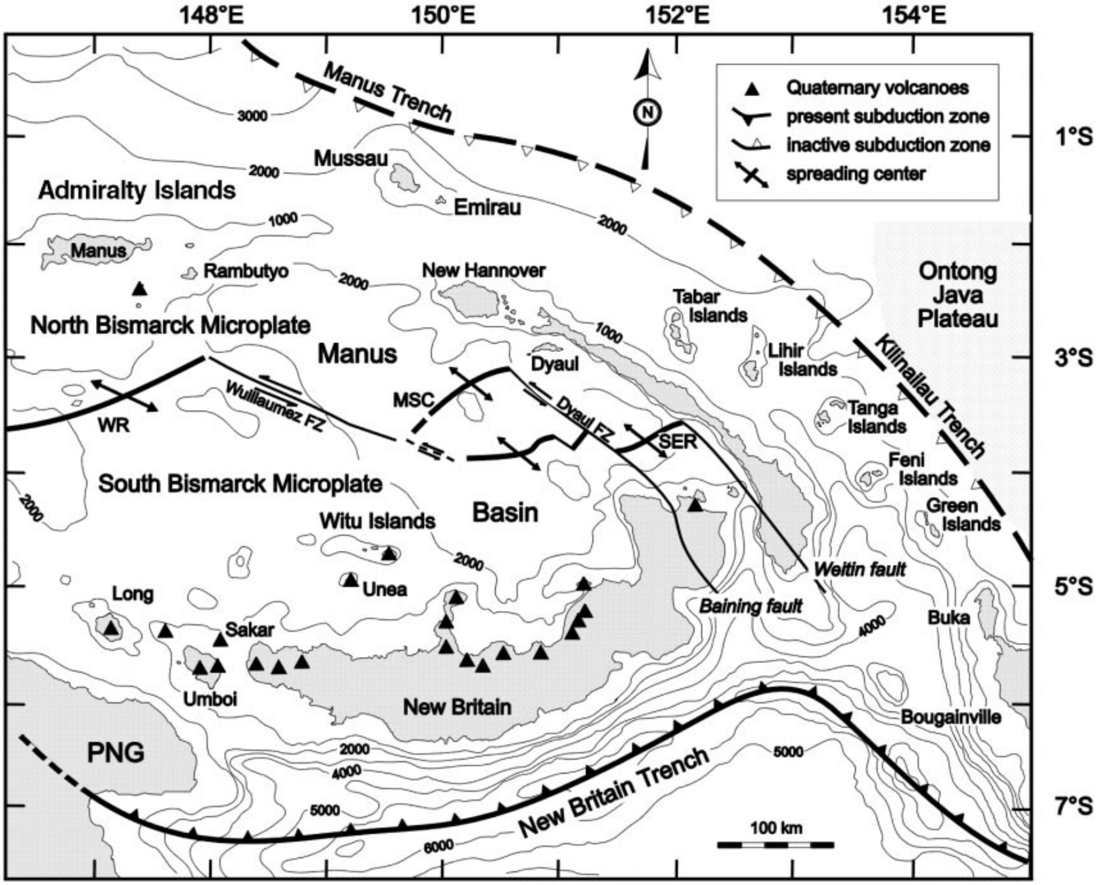

FIG. 1. Regional map showing the location of the Tabar–Feni Island chain and structural and volcanic elements of the New Ireland fore-arc and Manus Basin (after Herzig *et al.* 1994b).

epithermal systems (Herzig & Hannington 1994, Herzig *et al.* 1994a, b). The presence of alunite associated with disseminated sulfides and Mg-rich smectite, as well as the occurrence of kaolinite and halloysite, are consistent with an acid–sulfate alteration assemblage, which is more typical of subaerial epithermal systems than of submarine volcanic cones (Arribas 1995, Herzig *et al.* 1998a, Percival *et al.* 1999).

The Lihir island area (Fig. 2) was revisited between July 20 and August 3, 1998 (cruise SO–133) to conduct more detailed mapping and sampling. Among the objectives of this cruise, we sought to determine the ex-

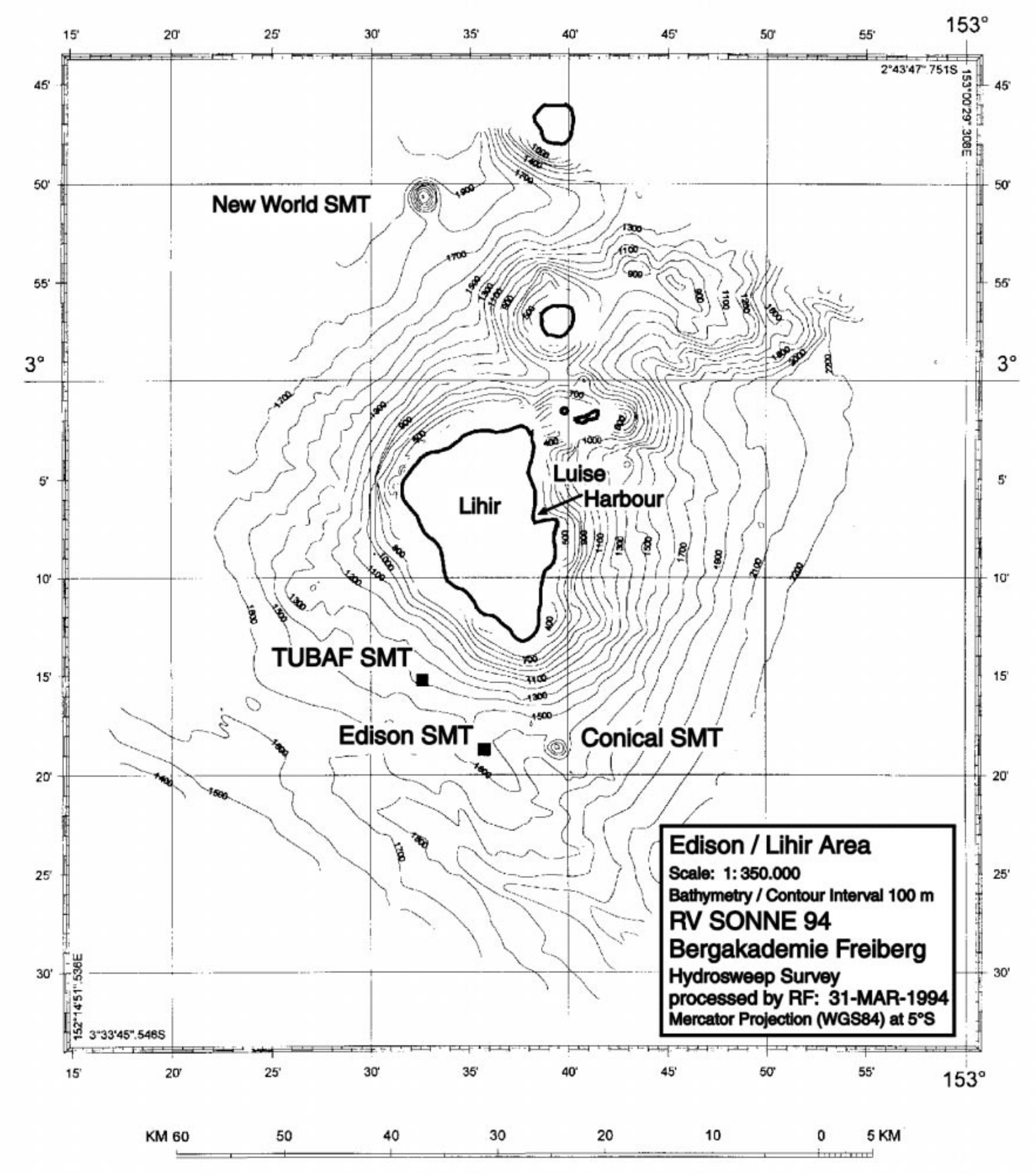

FIG. 2. Detailed multibeam bathymetric map at Lihir Island group and location of newly discovered seamounts (after Herzig *et al.* 1994b).

tent and character of alteration and epithermal gold mineralization at Conical Seamount. During this cruise, the occurrence of epithermal-style gold mineralization was confirmed.

Conical Seamount, discovered in 1994, was the site of detailed surveys during the 1998 cruise. It is located southeast of Lihir, has a 2000 m base and rises over 600 m above the seafloor to a minimum water depth of 1050 m (Fig. 2). The cone is built of massive basaltic flows, pillow lavas and talus breccias composed of scoria and fragments of vesicular basalt. The sides of the cone are covered by foraminiferal ooze. In 1994, recovered rocks included fresh alkaline olivine basalts and clinopyroxene-rich basalts (ankaramites) containing phenocrysts of clinopyroxene, plagioclase, olivine and magnetite (McInnes *et al.* 1994). Samples collected in 1998 showed distinctive polymetallic (Zn + Cu + Pb + As + Sb + Ag) epithermal-style vein mineralization and pyritic stockwork with locally intense clay–silica alteration (Herzig *et al.* 1999a, b, Petersen *et al.* 1999). Mineralization consists of clay minerals, pyrite, polymetallic sulfides including sphalerite, galena, chalcopyrite, sulfosalts, and As-bearing sulfides (*e.g.*, realgar and alacranite). The top of the deposit in the central clay–silica zone is intensely altered, and basalt is replaced by illite + smectite + chlorite ± kaolinite + K-feldspar + silica. This zone of intense alteration grades outward into weakly altered basalt breccias that are veined by pyrite. Massive sulfides were not observed; thus only a small amount of the hydrothermal fluid was vented onto the seafloor. Realgar, alacranite and possibly orpiment appear to be intimately associated with amorphous silica at the outer margin of the mineralized zone. They occur as fine fracture fillings in the silicified breccias and as vesicle linings in the basalt (Petersen *et al.* 1999, Herzig *et al.* 1998b). The features discovered at Conical Seamount are similar to those seen at the Ladolam epithermal gold deposit on Lihir Island.

SAMPLE COLLECTION AND OCCURRENCE

During the cruise, 75 sites were sampled using TV grabs, dredges, box and piston (gravity) cores. Samples of interest (*e.g.,* fine-grained sulfides, surface coatings, crusts, muds) were routinely analyzed by X-ray powder diffractometer for identification. Samples collected from Conical Seamount, station 26 (GTVA–TV grabs) contained megascopically unidentified small orange and red

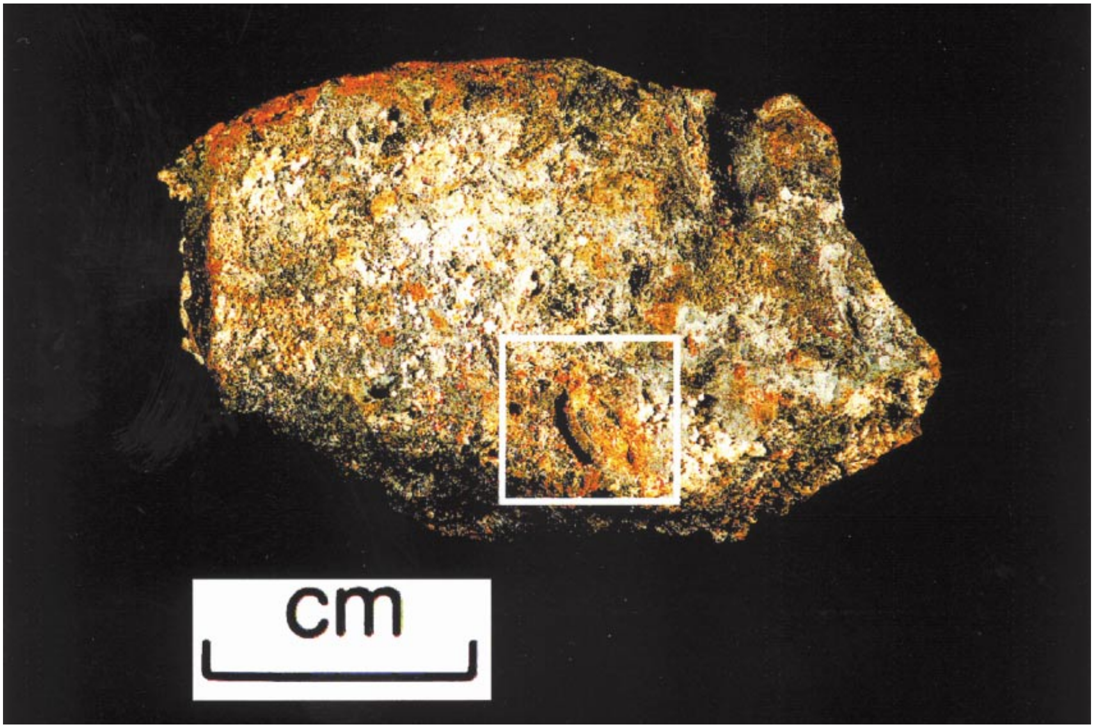

FIG. 3. Original sample from station 26GTVA examined using X-ray powder-diffraction methods. Red crystals are realgar, orange crystals are alacranite, and white masses are amorphous silica. Alacranite crystals used for detailed analysis of the structure were taken along the cavity outlined by box.

crystals. At the time of collection, an X-ray powder diffractogram of a few crushed grains was collected, but the sample remained unidentified. X-ray diffraction using film methods for red, orange and white individual crystals from a sample collected from station 26GTVA (Fig. 3) were later obtained at the GSC using a Debye–Scherrer camera. This sample was also examined using a Hitachi S3200N environmental scanning electron microscope. The X-ray powder-diffraction data permitted unambiguous identification of realgar and alacranite. The red crystals were identified as realgar (Fig. 4), the orange crystals as alacranite (Fig. 5), and the white material, as amorphous silica. Alacranite and realgar appear to coexist in the specimen. The subhedral to euhedral orange tabular alacranite crystals are transparent to translucent with a vitreous to resinous luster. They occur both as isolated crystals and as groupings of crystals within vugs and on the matrix, and have a maximum length of 0.1 mm.

We attempted to obtain quantitative chemical analyses of the alacranite using an electron microprobe, but found the crystals to be highly unstable under the electron beam at the conditions of analysis.

STRUCTURE DETERMINATION AND DESCRIPTION

Experimental

A crystal of alacranite with approximate dimensions 0.14 × 0.10 × 0.06 mm was mounted on a Bruker PLATFORM 3-circle goniometer equipped with a 1K SMART CCD (charge-coupled device) detector with a crystal-to-detector distance of 5 cm (Burns 1998).

Data were collected using monochromatic Mo$K\alpha$ X-radiation and frame widths of 0.3° in ω, with 50 s used to acquire each frame. Data were analyzed to locate peaks for the determination and refinement of the unit-cell dimensions (Table 1). Data were collected for 2θ up to 56.7° in approximately 20 h; intensities of equivalent reflections collected at different times during the data collection showed no decay. The three-dimensional data were integrated and corrected for Lorentz, polarization, and background effects using the Bruker program SAINT. An empirical absorption-correction was applied using SADABS (G. Sheldrick, unpublished program) and lowered the R_{INT} from 6.8 to 2.5%. A total of 4055 intensities were collected. Systematic absences indicated that the lattice is C-centered; of the collected

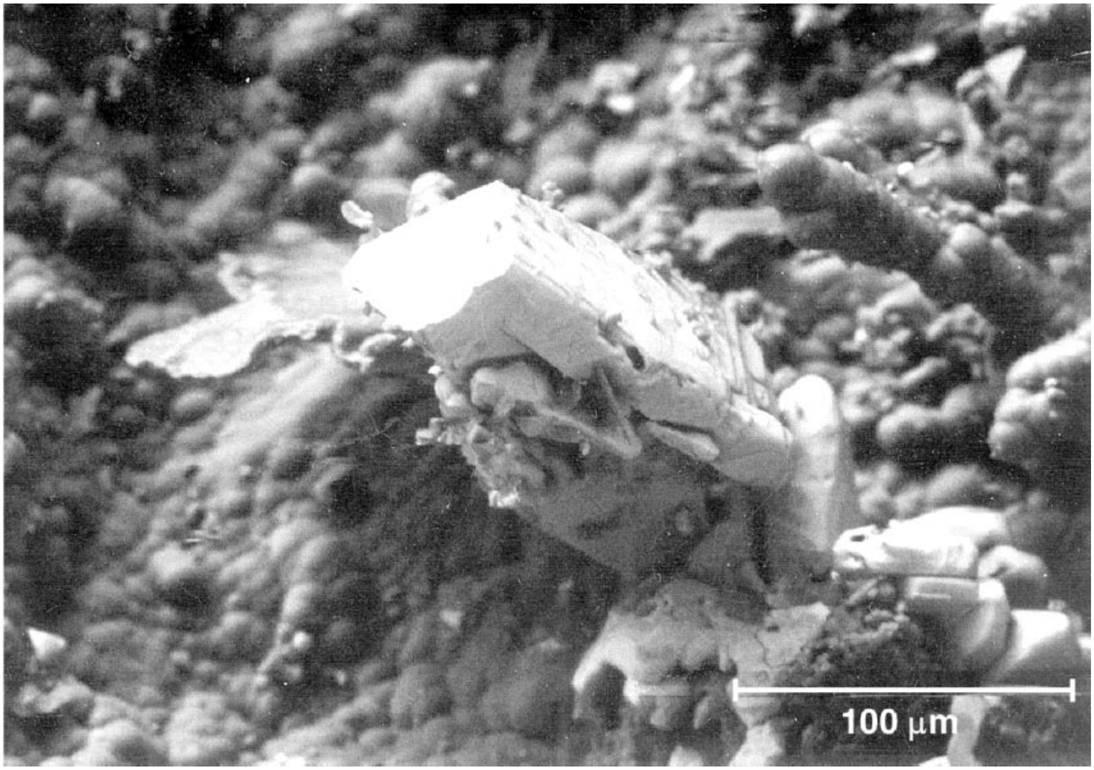

FIG. 4. SEM photomicrograph, back-scattered image, of realgar from alacranite-rich zone shown in Figure 3 (magnification 350x).

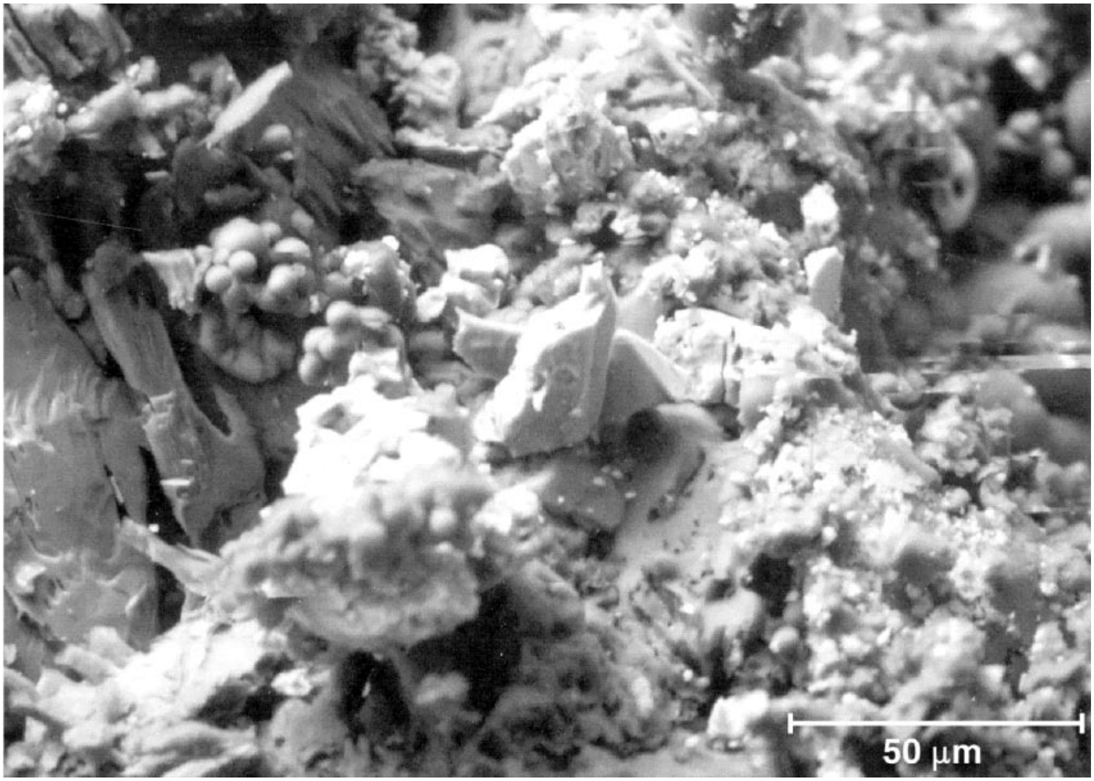

FIG. 5. SEM photomicrograph, back-scattered image, of alacranite from alacranite-rich zone shown in Figure 3 (magnification 600x).

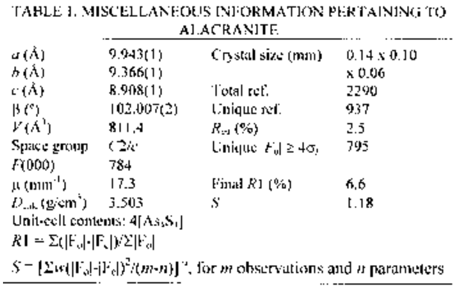

TABLE 1. MISCELLANEOUS INFORMATION PERTAINING TO ALACRANITE

a (Å)	9.943(1)	Crystal size (mm)	0.14 x 0.10
b (Å)	9.366(1)		x 0.06
c (Å)	8.908(1)	Total ref.	2290
β (°)	102.007(2)	Unique ref.	937
V (Å^3)	811.4	R_{int} (%)	2.5
Space group	$C2/c$	Unique $\vert F_o\vert \geq 4\sigma_F$	795
$F(000)$	784		
μ (mm^{-1})	17.3	Final $R1$ (%)	6.6
D_{calc} (g/cm^3)	3.503	S	1.18

Unit-cell contents: 4[As_4S_4]

$R1 = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$

$S = [\Sigma w(|F_o|-|F_c|)^2/(m-n)]^{1/2}$, for m observations and n parameters

intensities, 2290 are consistent with the *C*-centered lattice. Merging of equivalent reflections gave 937 unique reflections (R_{INT} = 2.5%) with 795 classed as observed ($F_o \geq 4\sigma_F$).

Structure solution and refinement

Scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from *International Tables for X-Ray Crystallography*, Vol. IV (Ibers & Hamilton 1974). The Bruker SHELXTL Version 5 system of programs was used for the determination and refinement of the crystal structure.

Systematic absences and reflection statistics indicated space group *C*2/*c*, with verification provided by the successful solution and refinement of the structure. The positions of all atoms were obtained from a direct-methods solution. The structure was refined on the basis of F^2 using all unique data. Following refinement of the atomic positional parameters with allowance for anisotropic displacement, together with a weighting scheme of the structure factors, the agreement index ($R1$) was 6.6%, calculated for the 795 unique observed reflections ($|F_o| \geq 4\sigma_F$), and the goodness-of-fit (S) was 1.18. In the final cycle of refinement, the average parameter shift/esd was 0.000, and the maximum peaks in the final difference-Fourier maps were 3.21 and –0.84 e/Å^3. The larger peaks were located within 1 Å of the As positions, and may be attributed to limited positional disorder of the atoms. The final atomic-positional parameters and anisotropic-displacement parameters are given in Table 2, and selected interatomic distances and angles are given in Table 3. Observed and calculated structure-factors are available from the Depository of

TABLE 2. FINAL ATOMIC PARAMETERS FOR ALACRANITE

	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
As(1)	0.0001(1)	0.2058(1)	0.0562(1)	0.0452(4)	0.0479(8)	0.0500(8)	0.0365(7)	-0.0097(6)	0.0062(5)	-0.0095(5)
As(2)	-0.1596(1)	0.4024(1)	0.1278(2)	0.0453(4)	0.0353(7)	0.0476(8)	0.0476(8)	0.0001(5)	-0.0040(5)	0.0107(6)
S(1)	0	0.0560(5)	¼	0.049(1)	0.054(3)	0.034(2)	0.053(3)	0	0.006(2)	0
S(2)	0.2023(3)	0.3044(4)	0.1606(4)	0.0510(9)	0.035(1)	0.066(2)	0.054(2)	-0.007(1)	0.014(1)	-0.010(2)
S(3)	0	0.5527(5)	¼	0.057(1)	0.051(3)	0.034(2)	0.077(3)	0	-0.006(2)	0

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN THE STRUCTURE OF ALACRANITE

As(1)-S(1)	2.225(3)	S(1)-As(1)-S(2)	94.8(1)
As(1)-S(2)	2.232(3)	S(1)-As(1)-As(2)	99.09(9)
As(1)-As(2)	2.596(2)	S(2)-As(1)-As(2)	98.5(1)
As(2)-S(2)a	2.216(4)	S(2)a-As(2)-S(3)	95.1(1)
As(2)-S(3)	2.228(3)	S(2)a-As(2)-As(1)	98.6(1)
As(2)-As(1)	2.596(2)	S(2)a-As(2)-As(1)	99.1(1)

a = -x, y, ½-z

TABLE 4. CRYSTALLOGRAPHIC PARAMETERS OF MINERAL POLYMORPHS OF As_4S_4

	Space Group	a (Å)	b (Å)	c (Å)	β (°)	Ref.
Alacranite	$C2/c$	9.943(1)	9.366(1)	8.908(1)	102.007(2)	1
Realgar	$P2_1/n$	9.325(3)	13.571(5)	6.587(3)	106.4(1)	2
Pararealgar	$P2_1/c$	9.909(2)	9.655(1)	8.502(1)	97.29(1)	3

References: (1) this work. (2) Mullen & Nowacki (1972). (3) Bonazzi *et al.* (1995)

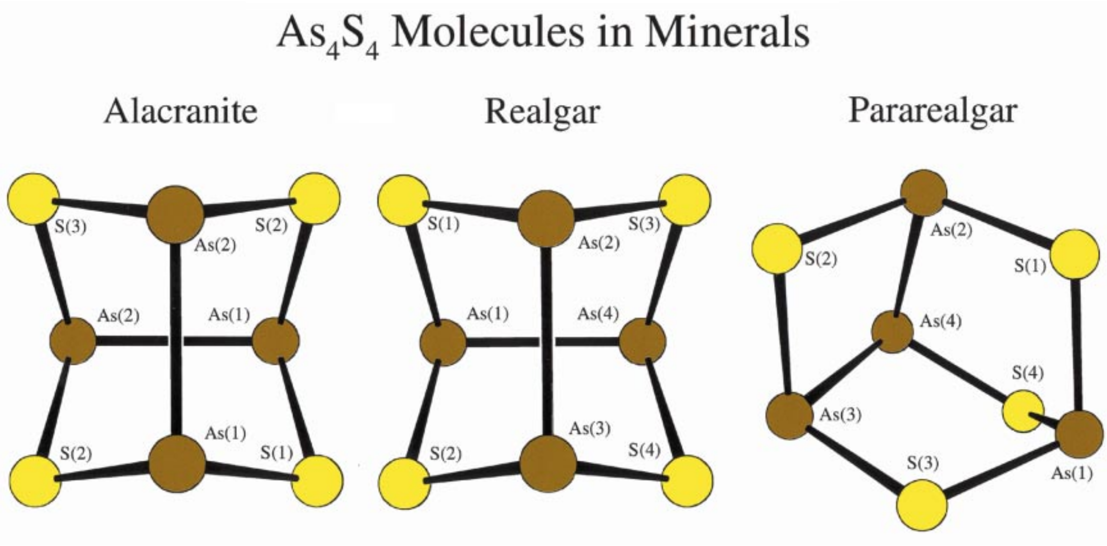

FIG. 6. Discrete covalently bonded As_4S_4 molecules in the structures of alacranite, realgar and pararealgar.

Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

Results of the structure determination

The structure determination reported herein demonstrates that alacranite is isostructural with the compound α–As_4S_4 (Porter & Sheldrick 1972, Pertlik 1994), and that the formula is As_4S_4, not As_8S_9 as reported on the basis of chemical analysis by Popova *et al.* (1986). Thus, alacranite is the third mineral polymorph of this composition, the others being realgar and pararealgar. Crystallographic parameters of each structure are presented in Table 4.

As in the structures of realgar (Mullen & Nowacki 1972) and pararealgar (Bonazzi *et al.* 1995), alacranite contains discrete covalently bonded As_4S_4 molecules (Fig. 6). These molecules are chemically identical to those in realgar, in that each As atom is bonded to one As and two S atoms, with S atoms bonded only to two As atoms. The molecule in pararealgar is distinct in its arrangement, with one As atom bonded to two As and one S, two As atoms bonded to one As and two S each, and one As atom bonded only to three S. In pararealgar,

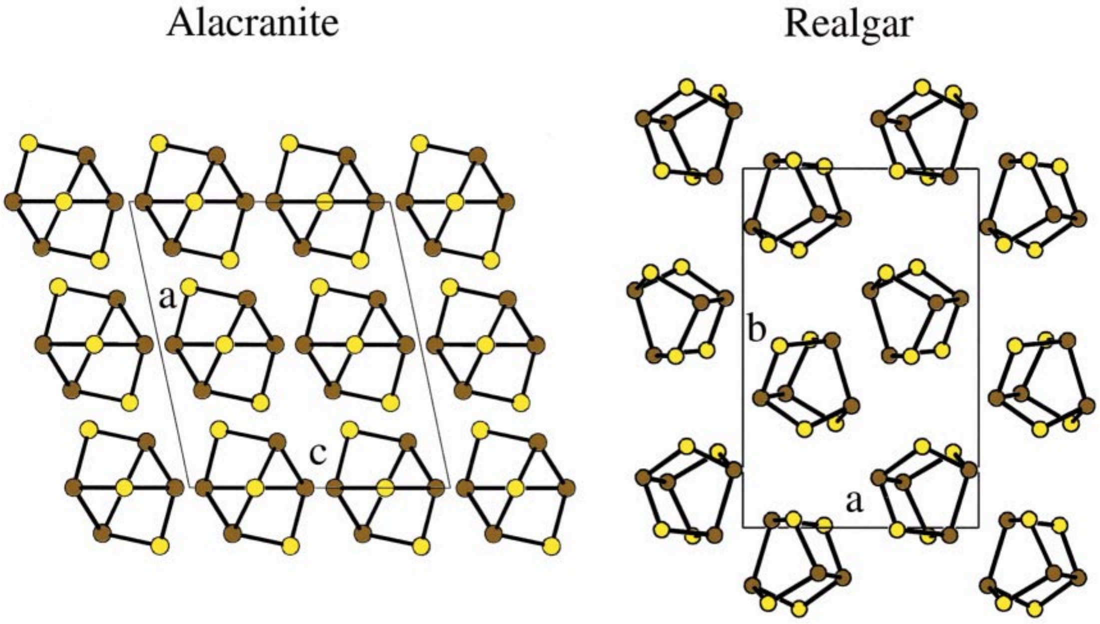

FIG. 7. The structures of alacranite and realgar. S atoms are shown in yellow, As atoms, in brown.

the S atoms all bond to two As atoms (Bonazzi *et al.* 1995).

The distinction between the structures of alacranite and realgar lies in the arrangement of the As_4S_4 molecules, which are only weakly held together by van der Waals forces to form the three-dimensional structure (Fig. 7). The *C*-centered unit cell of alacranite is smaller than the primitive cell of realgar, and inspection of Figure 7 shows that alacranite possesses a more orderly and closely packed structure than realgar.

DISCUSSION

Clark (1970) suggested that alacranite formed at a higher temperature than realgar, during an early phase of hydrothermal deposition. The high-temperature polymorph was reported to be stable (in the system As–S) between its melting point at 307 ± 5°C (Hall 1966) and 252 ± 2°C (Roland 1972) in the presence of vapor.

Recent experiments using microwave technology to recover gold from arsenopyrite and pyrite concentrates have produced alacranite and dimorphite (As_4S_3) as some of the by-products (Thompson 1999). The alacranite and dimorphite begin to appear when the bulk temperature reaches about 500°C, with a definite increase in rate of production between 520 and 540°C. Individual particles seem spherical, suggesting condensation from a gas (L.M. Thompson, pers. commun., 1999).

Migdisov & Bychkov (1998) have shown that alacranite forms in association with realgar, orpiment and uzonite in the condensation zone, between 50 and 75°C, due to sharp gradients in temperature and redox conditions. According to Migdisov & Bychkov (1998), the distribution of minerals observed in the Uzon hydrothermal system is probably similar to that in other shallow ore-deposition environments.

Modern geothermal systems are analogues of epithermal gold deposits (White 1981). In both of these systems, trace amounts of As commonly occur (Ballantyne & Moore 1988). According to Heinrich & Eadington (1986), As–S minerals, such as realgar and orpiment, tend to form at low temperatures, between late-hydrothermal-stage activity (*e.g.*, as in hot springs) and the onset of weathering, and are stable under more oxidizing conditions than native As. The alacranite found on the Conical Seamount samples appears to be of late-stage origin and probably formed under low-temperature hydrothermal conditions (I.R. Jonasson, pers. commun., 1999). This inference supports the findings of Migdisov & Bychkov (1998), that alacranite forms at relatively low temperatures.

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