

**Paradimorphite,  $\beta$ -As<sub>4</sub>S<sub>3</sub>, a vintage new mineral from Solfatara di Pozzuoli and Vesuvius,  
Napoli, Italy**

Italo Campostrini<sup>1</sup>, Carlo Castellano<sup>1</sup>, Francesco Demartin<sup>1\*</sup>, Ivano Rocchetti<sup>2</sup>, Massimo Russo<sup>3</sup> and Pietro Vignola<sup>4</sup>.

<sup>1</sup>Università degli Studi di Milano, Dipartimento di Chimica, via Golgi 19, I-20133 Milano, Italy.

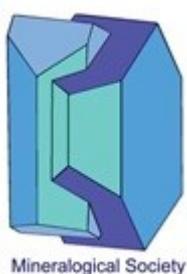
<sup>2</sup>MUSE, Museo delle Scienze di Trento, Corso del Lavoro e della Scienza 3, I-38122 Trento, Italy.

<sup>3</sup>Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Napoli | Osservatorio Vesuviano, Via Diocleziano, 328, I-80124 Napoli, Italy, <https://orcid.org/0000-0001-5161-5951>.

<sup>4</sup>CNR-Istituto di Geologia Ambientale e Geoingegneria, Via Mario Bianco 9 - 20131 Milano, Italy,  
<https://orcid.org/0000-0001-5396-9358>.

\* Corresponding author: Francesco Demartin

Università degli Studi di Milano, Dipartimento di Chimica, via Golgi 19, I-20133 Milano, Italy.  
<https://orcid.org/0000-0003-2942-3990>, E-mail: francesco.demartin@unimi.it



Mineralogical Society

This is a 'preproof' accepted article for Mineralogical Magazine. This version may be subject to change during the production process.

DOI: 10.1180/mgm.2022.47

## Abstract

The new mineral paradimorphite corresponds to the high temperature polymorph of As<sub>4</sub>S<sub>3</sub>, whose existence was supposed by Arcangelo Scacchi since 1850 in the fumaroles at the Solfatara di Pozzuoli, Campi Flegrei, near Napoli, Italy.

Crystals of paradimorphite are orange yellow, transparent or semitransparent, with adamantine lustre. Habit is prismatic and observed forms are {110}, {101}, {111}, {100}, {010}, {001}. Tenacity is brittle, no distinct cleavage is observed, fracture is conchoidal. The mineral does not fluoresce in long- or short-wave ultraviolet light. No twinning is apparent. The streak is saffron yellow. Hardness (Mohs) = 1-2. The observed density is 3.510(3) g/cm<sup>3</sup>, that calculated is 3.500 g/cm<sup>3</sup>. The mineral is orthorhombic, space group *Pnma*, with *a* = 9.1577(7), *b* = 8.0332(6), *c* = 10.2005(8) Å, *V* = 750.41(10) Å<sup>3</sup> and *Z* = 4. The eight strongest X-ray powder diffraction lines are [*d*<sub>obs</sub> Å(*I*(*hkl*))]: 6.299(48)(011), 5.186(100)(111), 4.174(31)(201), 3.133(34)(022), 3.116(58)(212), 2.980(41)(122), 1.846 (27)(413) and 1.808(23)(134). The structure was refined to *R* = 0.0229 for 979 reflections with *I* > 2σ(*I*). Crystals of paradimorphite contain As<sub>4</sub>S<sub>3</sub> molecules, of idealized C<sub>3v</sub> symmetry, with the four arsenic atoms in a triangular pyramidal arrangement, with sulfur atom bridges on the three adjacent apical edges. Molecular dimensions and conformation are identical within standard uncertainties with those of the low-temperature polymorph dimorphite. No substantial differences neither in the molecular packing nor in the molecular orientation could be observed, minor differences being related to intermolecular distances only.

**Keywords:** paradimorphite, new mineral, arsenic sulfide, dimorphite, fumaroles, Solfatara di Pozzuoli, Vesuvius volcano.

## Introduction

In his “*Memorie geologiche sulla Campania*”, a detailed report of the mineralogical phases occurring in the fumaroles of the Campi Flegrei, near Napoli, Italy, Arcangelo Scacchi (1850) observed the presence of an arsenic sulfide, with probable composition  $\text{As}_4\text{S}_3$ , displaying two distinct crystalline forms. From accurate goniometric measurements, he found two distinct morphologies and axial ratios, corresponding to two possibly distinct phases, a more abundant form I with  $a: b: c$  1: 1.287: 1.153 and a form II with  $a: b: c$  1: 1.658: 1.508. (Figure 1). Nevertheless, Scacchi considered his own analyses indecisive for establishing a definitive chemical formula and the real existence of two different mineral species, because of the small quantity of material used in the analysis and because the method used involved quantitative analysis only for sulfur. For these reasons the name “*dimorfina*” or later dimorphite (from the Greek), with reference to the two forms in which it was thought to exist, was used with no distinction for the two minerals.

After Scacchi’s discovery, there has been considerable discussion about whether dimorphite is indeed a distinct mineral or instead a morphologically unusual orpiment,  $\text{As}_2\text{S}_3$ , which was not recognized by Scacchi (Kenngott, 1870; Dana, 1885; Palache *et al.*, 1944).  $\text{As}_4\text{S}_3$  could be synthesized by direct combination of the elements mixed in stoichiometric proportion (Schuller, 1894; Krenner, 1907), and their works allowed to demonstrate the existence of the synthetic counterparts of one of the two dimorphites. Krenner (1907) showed in fact that the forms and angles of the second type of dimorphite discovered by Scacchi (form II) agree closely with those of synthetic  $\text{As}_4\text{S}_3$  prepared by Schuller (1894) and that Scacchi’s second type of dimorphite should have to be considered a valid mineral species. In the CNMNC list of mineral species updated January 2022, dimorphite is indeed considered a valid mineral and corresponds to Scacchi’s form II, the polymorph, stable at room temperature, with  $a = 11.21(2)$ ,  $b = 9.90(2)$ ,  $c = 6.58(1)$  Å, space group *Pnma*, whose structure was determined by Whitfield (1973) on the synthetic phase. Whitfield called this phase  $\beta$ -form, despite of being this polymorph stable at room temperature. The structure of the other polymorph with  $a = 9.12(2)$ ,  $b = 7.99(2)$ ,  $c = 10.10(2)$  Å, space group *Pnma*, had been reported earlier

(Withfield, 1970) by the same author, who called this phase  $\alpha$ -form. The existence of the two distinct natural polymorphs was confirmed, either by X-ray powder diffraction and single-crystal precession data by Frankel and Zoltai (1973), working on samples of dimorphite from Vesuvius, obtained by the Swedish Natural History Museum. They also observed that in some crystals, having the morphology of the form I, both polymorphs were present, and they concluded that the existence of dimorphite II crystals pseudomorph after dimorphite I suggests that dimorphite I is unstable under conditions to which it was exposed after crystallization, and transforms to dimorphite II. The contemporary presence of both polymorphs was also observed by us in some specimens. An accurate structure refinement on both phases of natural origin was later carried out by some of us (Gavezzotti *et al.*, 2013) together with a theoretical evaluation of the stability of both polymorphs at room temperature. In a crystallographic review of arsenic sulfides by Bonazzi and Bindi (2008) the two forms are labelled according to their field of stability, *i.e.*  $\alpha$ -dimorphite the phase stable at room temperature and  $\beta$ -dimorphite the phase stable above 130 °C.

As we can see, much confusion exists in the literature for the use of  $\alpha$ - and  $\beta$ -descriptors of the  $\text{As}_4\text{S}_3$  polymorphs (see Table 1). Following the rules in the nomenclature of temperature-depending phase transitions, the low-temperature and the high-temperature forms should be labelled as  $\alpha$ - and  $\beta$ -form, respectively, as reported by Bonazzi and Bindi (2008).

As a part of our studies on fumarolic minerals (Russo *et al.* 2017; Camposstrini and Demartin, 2021; Camposstrini *et al.*, 2019a,b; Demartin *et al.*, 2014), we have investigated some “dimorphite” crystals from Solfatara di Pozzuoli and from Vesuvius crater and the results of a crystallographic study on both natural polymorphs of  $\text{As}_4\text{S}_3$  have already been reported in Gavezzotti *et al.* (2013). A recent complete characterization of the high temperature phase, not yet recognized as a valid mineral species, prompted us to submit a proposal to the IMA Commission on New Minerals, Nomenclature and Classification (CNMNC), to include this phase in the list of the mineral species (IMA. 2020-101). On April 2021 we received a communication from the chairman of the Commission reporting that the

proposed new mineral had major YES votes but, as the CNMNC was going to consider revision of the guidelines for the nomenclature of polymorphs and polysomes, the voting result for the approval was suspended. According to the new rules established by IMA CNMNC only recently, the mineral name was finally approved as paradimorphite, by analogy with the low temperature polymorph dimorphite. This decision overcomes the confusion arisen using the  $\alpha$ - and  $\beta$ -descriptors. The approved mineral name abbreviation is *pdim* (Warr, 2021).

The holotype (from Solfatara di Pozzuoli) and cotype (from Vesuvius) specimens of paradimorphite are deposited in the Reference Collection of the Dipartimento di Chimica, Università degli Studi di Milano, catalogue numbers 2020-03/6121 and 2020-04/4226, respectively.

In the classification of Strunz paradimorphite is classified as 2.FA.10 (Dimorphite group) 2: SULFIDES and SULFOSALTS (sulfides, selenides, tellurides; arsenides, antimonides, bismuthides; sulfarsenites, sulfantimonites, sulfbismuthites, etc.) F: Sulfides of arsenic, alkalies; sulfides with halide, oxide, hydroxide, H<sub>2</sub>O, A: With As, (Sb), S. In the Dana's classification belongs to the 2.6.1.1 class, 2: SULFIDES 6: A<sub>m</sub>B<sub>n</sub>X<sub>p</sub>, with (m+n):p = 4:3.

## Occurrence

The Solfatara di Pozzuoli is an explosion volcano formed 4285 years ago, located in the central part of the Campi Flegrei caldera. The deposits of the Solfatara consist of pyroclastic products dispersed over an area of about one square kilometer. Inside the crater the deposits are strongly altered by the intense fumarolic activity. The morphological characteristics of the volcano represent a unicum for the Campi Flegrei area as it is a maar-diatreme. The holotype specimen of paradimorphite was collected here at the Bocca Grande fumarole. Associated minerals are realgar, salammoniac, mascagnite, alacránite, adranosite and russoite (Russo *et al.*, 2017).

The Somma-Vesuvius is a strato-volcano, whose oldest part is represented by Monte Somma in whose interior the “Gran Cono” of Vesuvius was formed. The volcano's explosive activity took place in

some "Plinian" eruptions (*e.g.* Pomice di Avellino eruption, about 4000 years ago and Pompei eruption, 79 A.D.); subsequently the formation of the Vesuvius cone began. After the great eruption of 1631, Vesuvius entered a state of "*open conduit*" activity with frequent eruptions, on average one every 7 years. The most important eruptions of the last century were those of 1906 and the last one in March 1944. Currently, Vesuvius is in state of quiescence with some seismic and fumarolic evidence. The cotype specimen of paradimorphite was collected from an active fumarole after the 1906 eruption and was found among old specimens belonging to the collection of the Istituto Geomineralogico Italiano (Camposolini and Russo, 2012). Associated minerals in the cotype specimen are anhydrite and sassolite. Realgar, lafossaite, anhydrite, bonazziite and an unknown arsenic thallium chloride, probably related to lucabindiite are associated to paradimorphite in other specimens. In both localities the mineral is a fumarolic sublimate.

### Physical and optical properties

Crystals of paradimorphite are orange yellow, transparent or semitransparent, with adamantine lustre. Habit is prismatic and observed forms are {110}, {101}, {111}, {100}, {010}, {001} (Figures 2-5). Tenacity is brittle, no distinct cleavage is observed, fracture is conchoidal. The mineral does not fluoresce in long- or short-wave ultraviolet light. No twinning is apparent. The streak is saffron yellow. Hardness (Mohs) = 1-2. Hardness (Micro-indentation):  $VHN_{25} = 70$  (range 59-80  $\text{kg}/\text{mm}^2$ ) Vickers hardness obtained using a Shimadzu type-M microhardness tester; average of five indentation measurements. The density, measured by flotation in a thallium malonate/formate solution (Clerici solution) for the Solfatara sample (holotype), is  $3.510(3)$   $\text{g}/\text{cm}^3$ . The calculated density is  $3.500$   $\text{g}/\text{cm}^3$  (Solfatara),  $3.520$   $\text{g}/\text{cm}^3$  (Vesuvius), using the empirical formula and single-crystal cell data. Refractive indices were not measured conventionally, because it was found to be them higher than available reference liquids ( $>1.9$ ). The mineral is biaxial (+), dispersion is weak to very weak.  $r > v$ . Pleochroism is barely noticeable.

The Raman spectrum was obtained with an ANDOR 303 spectrometer equipped with a CCD camera iDus DV420A-OE and using the 532 nm line of a OXXIUS solid state laser for excitation. Figure 6 shows a comparison of the Raman spectrum of paradimorphite with that of a dimorphite recently collected at Vesuvius. Due to the similarity in the packing of the molecules in the two polymorphs (see below), frequencies related to lattice modes should essentially occur at very similar values. A broad band at about  $52\text{ cm}^{-1}$ , in indeed observed in paradimorphite whereas the corresponding band of dimorphite appears at  $47\text{ cm}^{-1}$  with a shoulder at  $56\text{ cm}^{-1}$ . All the other bands fall in the range of vibrational frequencies ( $125 - 386\text{ cm}^{-1}$ ) calculated by Gavezzotti *et al.* (2013) for the  $\text{As}_4\text{S}_3$  molecule in the gas phase. It should be pointed out the lack of a shoulder at  $337\text{ cm}^{-1}$  in paradimorphite with respect to dimorphite and the presence of a band at  $224\text{ cm}^{-1}$ .

### Chemical Analysis

Quantitative chemical analyses (6) were carried out in WDS mode using a JEOL JXA-8200 WDS electron microprobe (15 kV excitation voltage, 5 nA beam current, 5  $\mu\text{m}$  beam diameter). The following mineral and pure elements served as standards: realgar (As and S), pure elements (99.99% for Se, Sb and Te). X-ray intensities were converted to wt% by ZAF quantitative analysis software. Chemical data for the Solfatara and Vesuvius samples are reported in Table 2. The empirical formula, calculated on the basis of 7 atoms per formula unit, for the Solfatara sample is:  $\text{As}_{3.986}\text{S}_{3.011}\text{Se}_{0.003}$ , that of the Vesuvius crater sample is:  $(\text{As}_{3.975}\text{Sb}_{0.007})(\text{S}_{2.982}\text{Se}_{0.032}\text{Te}_{0.004})$ . The simplified formula is:  $\text{As}_4\text{S}_3$ . The ideal formula is  $\text{As}_4\text{S}_3$  which requires: As 75.70, S 24.30 wt%. Total 100 wt%.

### X-ray crystallography and crystal structure determination

X-ray powder diffraction data were collected for the Solfatara specimen with a Rigaku DMAX II powder diffractometer with graphite monochromatized  $\text{CuK}\alpha$  radiation. Data (in  $\text{\AA}$  for  $\text{CuK}\alpha$ ) are listed in Table 3. Unit cell parameters refined from the powder data using UNITCELL (Holland and

Redfern, 1997) are  $a = 9.1596(9)$ ,  $b = 8.0365(9)$ ,  $c = 10.1195(10)$  Å,  $V = 744.92(9)$  Å<sup>3</sup>. None of the intense reflections corresponding to dimorphite were observed in the powder pattern of this sample. Single crystal data for paradimorphite were obtained from a crystal fragment of the Solfatara sample. Details about the data collection and refinement are summarized in Table 4, whereas the final atom coordinates and anisotropic displacement parameters and selected interatomic distances have already been reported by Gavezzotti *et al.* (2013). Single-crystal data of the Vesuvius sample gave the following unit-cell parameters:  $a = 9.155(3)$ ,  $b = 8.026(2)$ ,  $c = 10.201(6)$  Å,  $V = 749.55(20)$  Å<sup>3</sup>. The  $a:b:c$  ratio calculated from the unit-cell parameters is 1.1400 : 1 : 1.2698 (single-crystal data, Solfatara sample), 1.1407 : 1 : 1.2710 (single-crystal data, Vesuvius sample).

### Description of the crystal structure and discussion

A comparison of the structures of the two polymorphs paradimorphite and dimorphite is shown in Figure 7. Crystals of both phases contain cage-like As<sub>4</sub>S<sub>3</sub> molecules of  $C_{3v}$  idealized symmetry located about a crystallographic mirror, packed together by weak van der Waals interactions. Other cage-like covalently bonded As<sub>4</sub>S<sub>n</sub> ( $n = 4$  and 5) molecules are also the building blocks of some arsenic sulfides (see Bonazzi and Bindi, 2008 for a general review), such as the As<sub>4</sub>S<sub>4</sub> molecules in realgar (Mullen and Nowacki, 1972) pararealgar (Bonazzi *et al.*, 1995) and bonazziite (Bindi *et al.*, 2015), the As<sub>4</sub>S<sub>5</sub> molecules in uzonite (Bindi *et al.*, 2003) and those in alacránite, As<sub>8</sub>S<sub>9</sub> (Bonazzi *et al.*, 2003), that contains both As<sub>4</sub>S<sub>4</sub> and As<sub>4</sub>S<sub>5</sub> molecules. In the As<sub>4</sub>S<sub>3</sub> molecules of paradimorphite and dimorphite, the four arsenic atoms are arranged with a triangular pyramidal geometry, and the sulfur atoms bridge the three apical edges of the pyramid. Molecular dimensions and conformation are within standard uncertainties the same for the molecules in the two polymorphs. These are also very similar to those observed in the tetrakis(tris( $\mu_2$ -sulfido)-tetra-arsenic)-tetraphenylphosphonium chloride complex (Siewert and Müller, 1992) where the As-As bonds are in the range 2.464(3) - 2.494(3) Å and the As-S bonds in the range 2.229(6) - 2.243(6) Å. For paradimorphite, the As-As bonds of the triangular base are in the range 2.4673(4) - 2.4855(6) Å and are on the average significantly shorter than those

observed for the  $\text{As}_4\text{S}_4$  molecules in realgar (2.566(1) - 2.571(1) Å), bonazziite (2.579(1) Å), pararealgar (2.484(4) - 2.534(4) Å) and alacránite (2.579(5) Å) and those in the  $\text{As}_4\text{S}_5$  molecules in uzonite (2.527(1) Å) and alacránite (2.566(6) Å). The As-S bonds fall in the range 2.2155(7) - 2.2360(10) Å and are again on the average shorter than those observed in realgar (2.228(2) - 2.247(2) Å), pararealgar (2.228(10) - 2.261(8) Å), uzonite (2.237(1) - 2.261(1) Å), but closer to those found in alacránite (2.205(9) - 2.238(7) Å) and bonazziite (2.222(1) - 2.234(1) Å). These geometrical differences can be ascribed to the different bonding pattern in the  $\text{As}_4\text{S}_n$  molecules. For  $n = 4, 5$ , instead of being arranged in a pyramidal fashion as in  $\text{As}_4\text{S}_3$ , the As atoms are located at the vertices of a more or less regular disphenoid where there are  $(6 - n)$  disphenoidic edges corresponding to As-As bonds and the sulfur atoms bridge  $n$  among the six disphenoidic edges. Thus, the number of As-S bonds formed by each As atom, combined with the steric hindrance of the additional S atom, determines the geometry of the  $\text{As}_4$  framework.

From a comparison of the projections of the structure of both polymorphs reported in figure 7 it seems that there are no substantial differences in the molecular packing and orientation of the  $\text{As}_4\text{S}_3$  molecules. A detailed study of the intermolecular interactions, carried out by Gavezzotti *et al.* (2013), showed that slight but significant differences in the packing of the  $\text{As}_4\text{S}_3$  molecules could be inferred from radial distribution curves of the centers of mass of the molecules, that are essentially rigid cages. In dimorphite the  $\text{As}_4\text{S}_3$  molecules are oriented with their pseudo threefold axis along [102] and [10-2] whereas in paradimorphite the threefold axes are along [101] and [10-1] but these directions form similar angles with the crystallographic axes. These features can account for that the space group is maintained during the transition from one polymorph to the other, due to slight deformation of the lattice. The larger unit-cell volume of paradimorphite with respect of that of the low-temperature form dimorphite (see Table 4) is in line with its stability at higher temperatures.

The lack of a distinct cleavage and the conchoidal fracture in paradimorphite are in keeping with the absence of molecular layers that are instead present in other molecular arsenic sulfides like realgar.

**Competing interests:** The authors declare none

### Acknowledgements

Valuable suggestions and constructing comments for improving this paper have been given by the Principal Editor Dr. Stuart Mills, Prof. Peter Leverett, Dr. Sergey M. Aksenov and by an anonymous referee.

### References

- Bindi L., Popova V.I. and Bonazzi P. (2003) Uzonite, As<sub>4</sub>S<sub>5</sub>, from the type-locality: X-ray single crystal study and lighting experiments. *Canadian Mineralogist*, **41**, 1463-1468.
- Bindi L., Pratesi G., Muniz-Miranda M., Zoppi M., Chelazzi L., Lepore G.O. and Menchetti S. (2015) From ancient pigments to modern optoelectronic applications of arsenic sulfides: bonazziite, the natural analogue of β-As<sub>4</sub>S<sub>4</sub> from Khaidarkan deposit, Kyrgyzstan. *Mineralogical Magazine*, **79**, 121-131.
- Bonazzi P. and Bindi L. (2008) A crystallographic review of arsenic sulfides: effects of chemical variations and changes induced by exposure to light. *Zeitschrift für Kristallographie*, **223**, 132-147.
- Bonazzi P., Bindi L., Popova V.I., Pratesi G. and Menchetti S. (2003) Alacranite As<sub>8</sub>S<sub>9</sub>: structural study of the holotype and re-assignment of the original chemical formula. *American Mineralogist*, **88**, 1796 - 1800.
- Bonazzi P., Menchetti S. and Pratesi G. (1995) The crystal structure of pararealgar As<sub>4</sub>S<sub>4</sub>. *American Mineralogist*, **80**, 400-403.
- Campostrini I. and Demartin F. (2021) Kaliochalcite e bonazziite delle fumarole del Vesuvio. *Micro, periodico dell'Associazione Micromineralogica Italiana*, **19**, 61-64.

- Campostrini I., Demartin F. and Russo M. (2019a) Sbacchiite, a new fumarolic mineral from the Vesuvius volcano, Napoli Italy. *European Journal of Mineralogy*, **31**, 153-158.
- Campostrini I., Demartin F. and Scavini M. (2019b) Russoite,  $\text{NH}_4\text{ClAs}^{3+}_2\text{O}_3(\text{H}_2\text{O})_{0.5}$ , a new phylloarsenite mineral from Solfatara di Pozzuoli, Napoli, Italy. *Mineralogical Magazine*, **83**, 89-94.
- Campostrini I. and Russo M. (2012) Lafossaite e dimorphina: due nuove specie per il Vesuvio. *Micro, periodico dell'Associazione Micromineralogica Italiana*, **3**, 136-141.
- Dana E.S. (1885) *The System of Mineralogy of James Dwight Dana. Descriptive Mineralogy*, sixth edition. John Wiley and Sons, New York.
- Demartin F., Campostrini I., Castellano C. and Russo M. (2014) Parascandolaite,  $\text{KMgF}_3$ , a new perovskite-type fluoride from Vesuvius. *Physics and Chemistry of Minerals*, **41** 403-407.
- Frankel L.S. and Zoltai T. (1973) Crystallography of dimorphites. *Zeitschrift für Kristallographie*, **38**, 161-166.
- Gavezzotti A., Demartin F., Castellano C. and Campostrini I. (2013) Polymorphism of  $\text{As}_4\text{S}_3$ , (tris-( $\mu_2$ -sulfido)-tetra-arsenic). Accurate structure refinement on natural  $\alpha$ - and  $\beta$ - dimorphites and inferred room-temperature thermodynamic properties. *Physics and Chemistry of Minerals*, **40**, 175-182.
- Goldschmidt V. (1913) Atlas der Krystallformen. Carl Winters Universitätsbuchhandlung, Heidelberg.
- Holland T.J.B. and Redfern S.A.T. (1997) Unit cell refinement from powder diffraction data: the use of regression diagnostics. *Mineralogical Magazine*, **61**, 65-77.
- Kenngott A. (1870) Über die Kristallgestalten des dimorphin. *Neues Jahrbuch für Mineralogie, Geologie und Paleontologie, Monatshefte*, **B**, 537-541.
- Krenner J. (1907) Die Kristallform und optischen Eigenschaften des Schullerschen Arsensulfides. Über den Dimorphin der Solfatara in den phlegräischen Feldern. *Zeitschrift für Kristallographie und Mineralogie*, **43**, 476-484.

- Mullen D.J.E. and Nowacki W. (1972) Refinement of the crystal structures of realgar, AsS and orpiment, As<sub>2</sub>S<sub>3</sub>. *Zeitschrift für Kristallographie*, **136**, 48-65.
- Palache C., Berman H. and Frondel C. (1944) *The System of Mineralogy of James Dwight Dana and Edward Salisbury Dana*, seventh edition. John Wiley and Sons, New York, pp. 197-198.
- Russo M., Campostrini I. and Demartin F. (2017) I minerali di origine fumarolica dei Campi Flegrei: Solfatara di Pozzuoli (Napoli) e dintorni. *Micro, periodico dell'Associazione Micromineralogica Italiana*, **3**, 122-192.
- Scacchi A. (1850) Memorie geologiche sulla Campania. *Rendiconti Accademia Napolitana delle Scienze*, 99-104.
- Schuller A. (1894) Adalék az arzén kénvegyületeinek ismeretéhez. *Matematikai és Természettudományi Értesítő*, **12**, 255-261 (In Hungarian. Contributions to the knowledge of the arsenic sulfides).
- Siewert B. and Müller U. (1992) Formation of PPh<sub>4</sub>[WOCl<sub>4</sub>·THF] and PPh<sub>4</sub>Cl·4As<sub>4</sub>S<sub>3</sub> from W(CO)<sub>6</sub> and PPh<sub>4</sub>[As<sub>2</sub>SCl<sub>5</sub>] and their crystal structures. *Zeitschrift für anorganische und allgemeine Chemie*, **609**, 77-81.
- Warr L.N. (2021) IMA–CNMNC approved mineral symbols. *Mineralogical Magazine*, **85**, 291-320.
- Whitfield H.J. (1970) The crystal structure of tetra-arsenic trisulphide. *Journal of the Chemical Society A*, 1800-1803.
- Whitfield H.J. (1973) Crystal structure of the β-form of tetra-arsenic trisulphide. *Journal of the Chemical Society, Dalton Transactions*, 1737-1738.

**Table 1.** History of the different naming of the two As<sub>4</sub>S<sub>3</sub> polymorphs.

Paradimorphite				
Name	a (Å)	b (Å)	c (Å)	reference
dimorphite type A				Dana (1885)
dimorfina form I				Scacchi (1850)
α-form (synthetic As <sub>4</sub> S <sub>3</sub> )	9.12(2)	7.99(2)	10.10(2)	Whitfield (1970)
dimorphite I	9.07	8.01	10.30	Frankel and Zoltai (1973)
α-dimorphite	9.1577(7)	8.0332(6)	10.2005(8)	Gavezzotti <i>et al.</i> (2013)
β-dimorphite	9.159(1)	8.033(1)	10.199(2)	Bonazzi and Bindi (2008)
Dimorphite				
dimorphite type B				Dana (1885)
dimorfina form II				Scacchi (1850)
β-form (synthetic As <sub>4</sub> S <sub>3</sub> )	11.21(2)	9.90 (2)	6.58(2)	Whitfield (1973)
dimorphite II	11.24(2)	9.90(3)	6.56(2)	Frankel and Zoltai (1973)
β-dimorphite	11.2175(15)	9.9224(13)	6.6075(9)	Gavezzotti <i>et al.</i> (2013)
α-dimorphite				Bonazzi and Bindi (2008)

**Table 2.** Analytical data (in wt%) for paradigmorphite (average of 6 analyses).

## Paradimorphite, Solfatara di Pozzuoli

Constituent	Mean	Range	Stand. Dev. ( $\sigma$ )	Reference Material
As	75.38	74.65-76.15	0.54	Realgar
S	24.36	24.30-24.79	0.18	Realgar
Se	0.06	0.04-0.07	0.01	Se 99.99%
<b>Total</b>	<b>99.80</b>			

The empirical formula calculated on the basis of 7 atoms per formula unit is: As<sub>3.986</sub>(S<sub>3.011</sub>Se<sub>0.003</sub>)

## Paradimorphite (cotype), Vesuvius crater

Constituent	Mean	Range	Stand. Dev. ( $\sigma$ )	Reference Material
As	75.45	74.85-76.35	0.60	Realgar
S	24.22	23.40-24.53	0.42	Realgar
Se	0.64	0.57-0.83	0.09	Se 99.99%
Sb	0.21	0.11-0.32	0.04	Sb 99.99%
Te	0.12	0.04-0.24	0.03	Te 99.99%
<b>Total</b>	<b>100.64</b>			

The empirical formula calculated on the basis of 7 atoms per formula unit is:



**Table 3.** X-ray powder-diffraction data for paradimorphite.

$I/I_0$ (meas.)	$I/I_0^*$ (calc.)	$d$ (meas.)	$d^{**}$ (calc.)	$hkl$
16	17	6.788	6.791	1 0 1
48	50	6.299	6.293	0 1 1
100	100	5.186	5.187	1 1 1
1	2	4.571	4.580	2 0 0
4	3	4.444	4.429	1 0 2
31	37	4.174	4.172	2 0 1
7	6	4.005	4.018	0 2 0
21	25	3.889	3.879	1 1 2
16	17	3.457	3.458	1 2 1
3	5	3.401	3.395	2 0 2
19	10	3.152	3.165	1 0 3
34	30	3.133	3.147	0 2 2
58	65	3.116	3.127	2 1 2
11	8	3.015	3.020	2 2 0
41	46	2.980	2.978	1 2 2
15	27	2.921	2.923	3 0 1
14	23	2.733	2.717	2 0 3
18	12	2.568	2.573	2 1 3
5	9	2.453	2.439	1 0 4
3	10	2.362	2.364	3 2 1
1	5	2.320	2.333	1 1 4
3	13	2.308	2.312	2 3 0
6	8	2.287	2.290	4 0 0
4	12	2.270	2.264	3 0 3
6	14	2.256	2.250	2 2 3, 2 3 1
1	4	2.226	2.233	4 0 1
3	6	2.102	2.103	2 3 2
2	4	2.088	2.086	4 0 2, 1 2 4
2	5	2.050	2.045	1 3 3
4	12	1.867	1.867	0 4 2
27	16	1.846	1.844	4 1 3
23	20	1.808	1.803	1 3 4
7	6	1.758	1.759	5 1 1
8	18	1.718	1.715	4 3 1
1	8	1.690	1.687	3 0 5
3	8	1.655	1.656	3 4 1
1	5	1.617	1.624	1 1 6
1	4	1.577	1.576	3 3 4

\* Calculated from the refined structure.

\*\*Calculated from the unit cell  $a = 9.1596(9)$ ,  $b = 8.0365(9)$ ,  $c = 10.1195(10)$  Å,  $V = 744.92(9)$  Å<sup>3</sup>

obtained from least-squares refinement of the above data using the program UNITCELL (Holland and Redfern, 1997).

**Table 4.** Crystal data of the two As<sub>4</sub>S<sub>3</sub> polymorphs, data collection and structure refinement details for paradimorphite.

	paradimorphite <sup>\$</sup> (Solfatara di Pozzuoli)	dimorphite <sup>\$</sup> (Vesuvius)
<b>Crystal data</b>		
Crystal system, space group	Orthorhombic, <i>Pnma</i> (n. 62)	
<i>a</i> (Å)	9.1577(7)	11.218(2)
<i>b</i> (Å)	8.0332(6)	9.922(1)
<i>c</i> (Å)	10.2005(8)	6.609(1)
<i>V</i> (Å <sup>3</sup> )	750.41(10)	735.44(17)
<i>Z</i>	4	
<b>Data Collection</b>		
Radiation type	MoKα	
$\mu$ (mm <sup>-1</sup> )	18.377	
2θ <sub>max</sub> (°)	63.16	
Reflection range	-13 ≤ <i>h</i> ≤ 13 -11 ≤ <i>k</i> ≤ 11 -14 ≤ <i>l</i> ≤ 14	
<i>d</i> <sub>x</sub> (g/cm <sup>3</sup> )*	3.500	
Measured reflections	7553	
Independent reflections, <i>R</i> <sub>int</sub>	1284, 0.0399	
<b>Refinement</b>		
Observed reflections [ <i>I</i> > 2σ( <i>I</i> )]	979	
Parameters refined	37	
Final <i>R</i> [ <i>I</i> > 2σ( <i>I</i> )] and <i>wR</i> 2 (all data)	0.0229, 0.0474	
Weighting scheme q = [max(0, <i>F</i> <sub>o</sub> <sup>2</sup> ) + 2 <i>F</i> <sub>c</sub> <sup>2</sup> ] / 3; 1/[σ <sup>2</sup> ( <i>F</i> <sub>o</sub> <sup>2</sup> ) + (0.0218q) <sup>2</sup> ]	0.995	
<i>Goof</i>	-0.71, 0.63	
Δρ <sub>min</sub> , Δρ <sub>max</sub> (e/Å <sup>3</sup> )		

<sup>\$</sup> Data from Gavezzotti *et al.* (2013); \* calculated using the empirical formula and single-crystal cell data.

Notes:  $R = \Sigma \|F_o - F_c\| / \Sigma |F_o|$ ;  $wR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$ ;

$Goof = \{\sum [w(F_o^2 - F_c^2)] / (n-p)\}^{1/2}$  where n is the number of reflections and p is the number of refined parameters.

**Dimorphin**

Fig. 1.

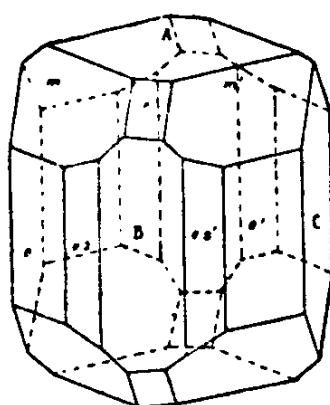
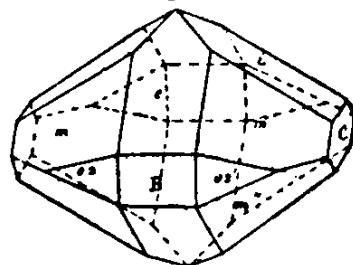
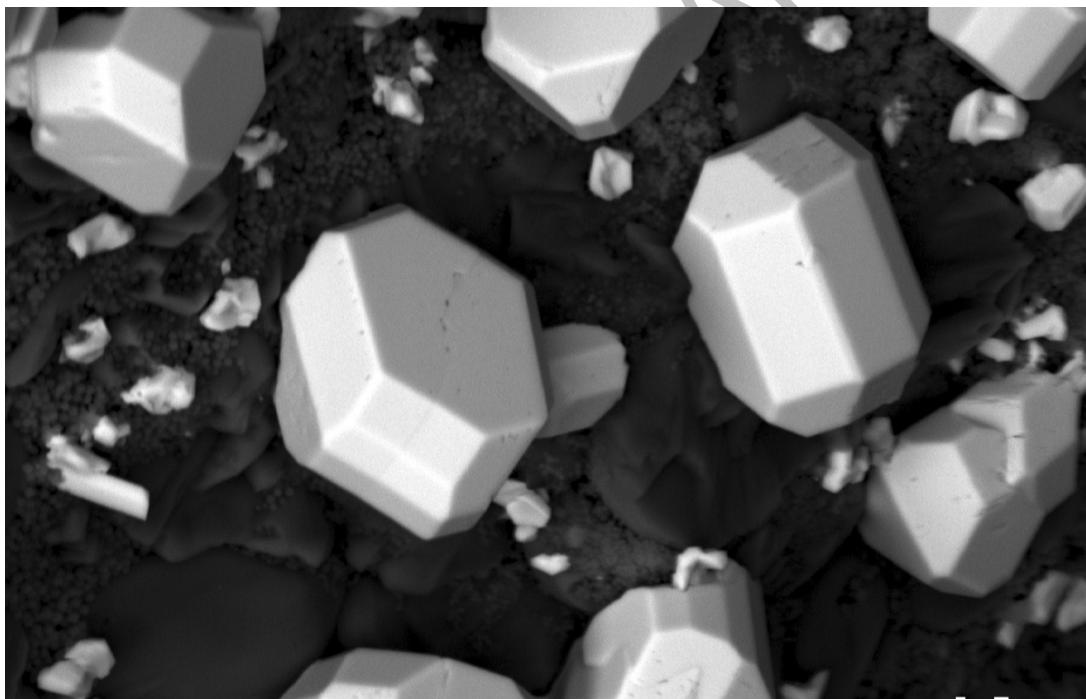


Fig. 2.



**Fig 1.** Morphology of the two  $\text{As}_4\text{S}_3$  forms observed by Scacchi (1850) and redrawn in the “Atlas der Kristallformen” by Goldschmidt (1913). Form I (paradimorphite) left, form II (dimorphite) right.



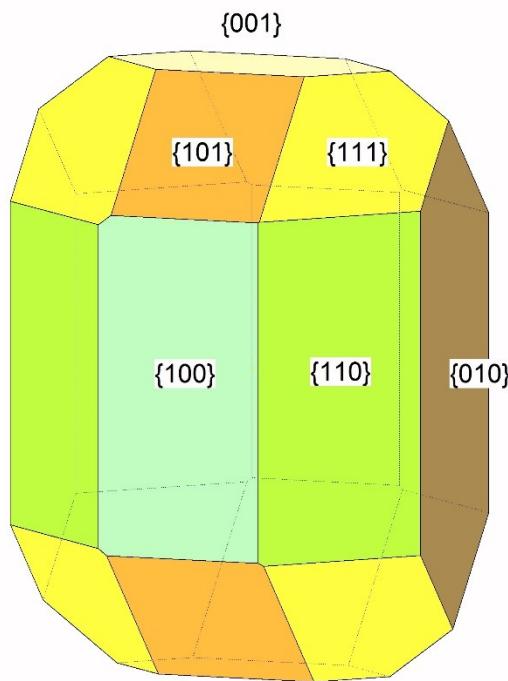
**Fig. 2.** BSE-SEM image of paradimorphite from Solfatara di Pozzuoli (Field of view 120  $\mu\text{m}$ ).



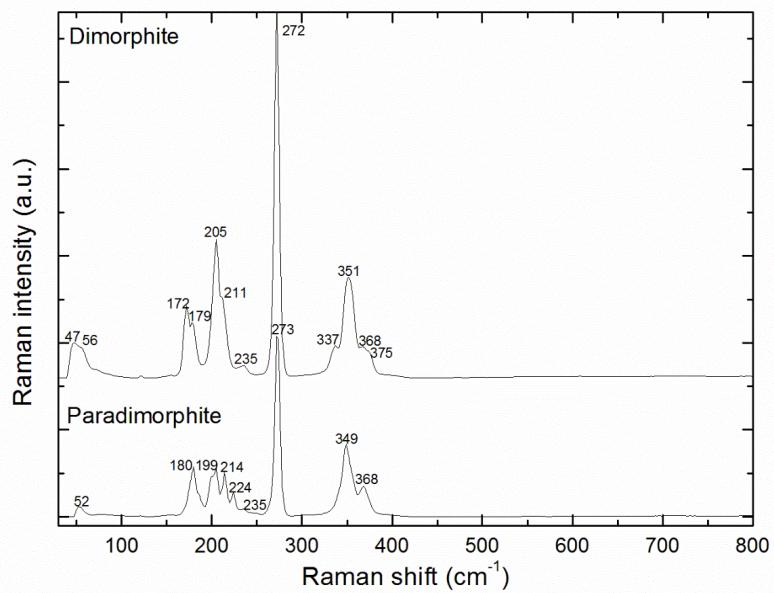
**Fig. 3.** Paradimorphite crystals on mazzagnite with realgar from Solfatara di Pozzuoli (Field of view 3 mm).



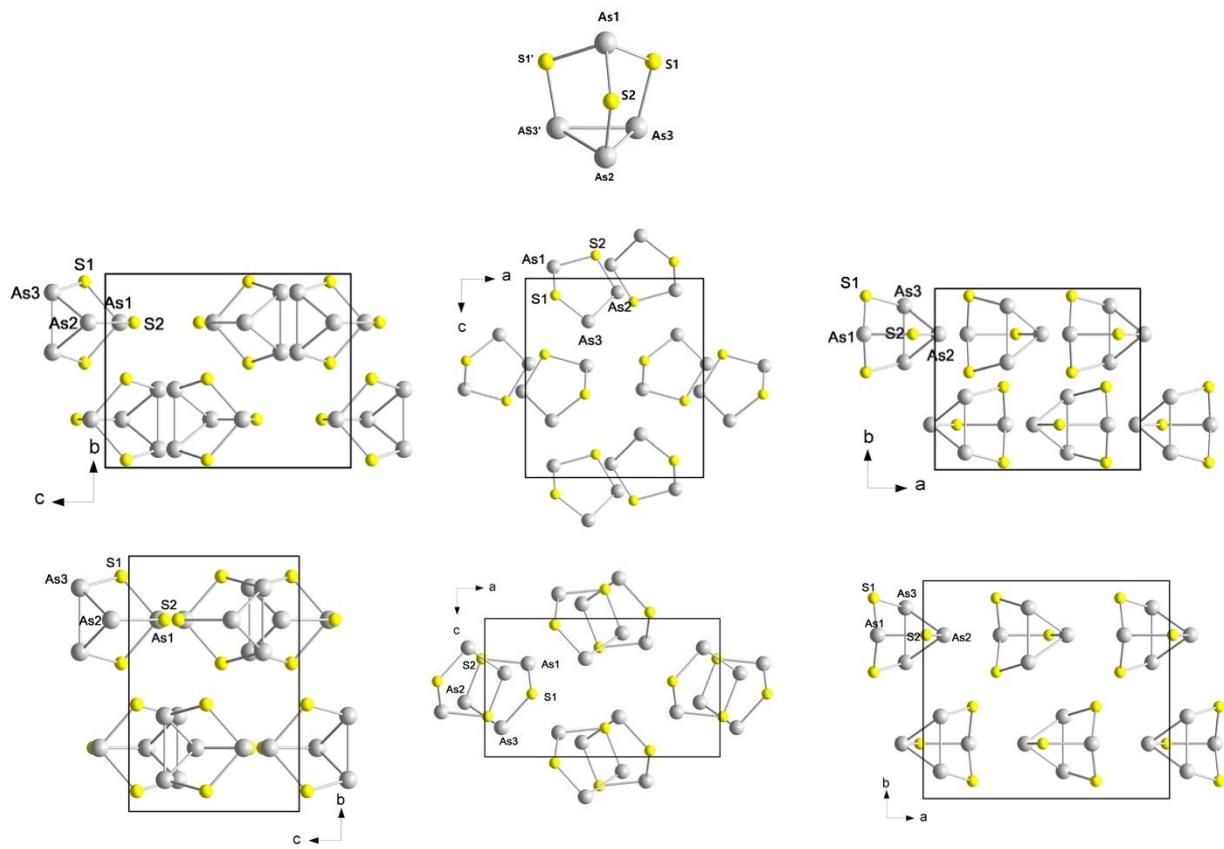
**Fig. 4.** Paradimorphite crystals with anhydrite, cotype sample, from Vesuvius crater (Field of view 3 mm).



**Fig. 5.** Kristall 2000 idealised drawing of a paradimorphite crystal similar to that on the right of Figure 2.



**Fig. 6.** Raman spectra of paradimorphite from Solfatara di Pozzuoli and dimorphite from Vesuvius.



**Fig. 7.** The  $\text{As}_4\text{S}_3$  molecule and comparison of the structures of paradigmorphite (up) and dimorphite (down); (Diamond drawings).