In-situ X-ray transmission powder diffraction study of the kinetics of the light induced alteration of realgar (α-As$_4$S$_4$)

PAOLO BALLIRANO* and ADRIANA MARAS

Dipartimento di Scienze della Terra, Università di Roma "La Sapienza", P.le A. Moro 5, I-00185 Roma, Italy
*Corresponding author, e-mail: paolo.ballirano@uniroma1.it

Abstract: An *in-situ* X-ray transmission powder diffraction study of the kinetics of the light induced alteration of realgar (As$_4$S$_4$) has been carried out. Data indicate that the crystalline final products of the process are pararealgar (different As$_4$S$_4$ polymorph) and arsenolite (As$_2$O$_3$). Because of the chemical unbalance the evolution of SO$_x$ is hypothesized. In fact there are no evidences of the presence of amorphous As-S alloys or amorphous S. The alteration proceeds *via* the occurrence of an intermediate term along the β-As$_4$S$_4$-alacranite series joint with an estimated As$_4$S$_{4.2}$ composition. This phase reach a maximum wt. fraction of *ca.* 30 % in the early stages of the process and subsequently disappears. From the fraction X(t) of realgar and pararealgar transformed *vs.* time was determined the kinetic law of the digestion of realgar and formation of pararealgar according to the JMAK model. The refined *n* parameters indicate that the behavior of the two transformations is intermediate between that of a diffusion-controlled and a first-order model. The increased expansion of the realgar cell during the alteration could be possibly due to the requirement that structural coherency between at least two of the three sulfide phases is preserved. In particular the coherency between realgar and β-As$_4$S$_4$ is expected to exist along a_{realgar}*sin β and $c_{\text{β-As4S4}}$, respectively. According to our data we may hypothesize that the light induced alteration of realgar to pararealgar occurs *via* an intermediate As$_4$S$_{4+x}$ product because it is able to sustain the presence of As$_4$S$_5$-type cages. Following the model proposed by Kyono *et al.* (2005) the As$_4$S$_5$ cage release the extra S atom to form the As$_4$S$_4$ cage of pararealgar-type promoting the development of a new As$_4$S$_5$ cage in a cyclic process.

Key-words: sulfide phases, realgar, β-As$_4$S$_4$, pararealgar, arsenolite, alteration, X-ray powder diffraction, Rietveld method.

Introduction

Four different As$_4$S$_4$ polymorphs are known: α-As$_4$S$_4$ (realgar), β-As$_4$S$_4$, As$_4$S$_4$ (II), and pararealgar. The structure of realgar (Ito *et al.*, 1952; Mullen & Nowacki, 1972) and β-As$_4$S$_4$ (Porter & Sheldrick, 1972; Burns & Percival, 2001), are characterized by the presence of the same covalently bonded As$_4$S$_4$ cage-like molecule. This cage (Fig. 1) may be described as composed by an As$_4$ disphenoid bisected by a S$_4$ square. Each arsenic is linked to two sulphur and an arsenic. The cages possess an almost perfect $\overline{4}$2m symmetry and are arranged in a zigzag way resulting in a layer-like structure with corrugated layers that, in the case of realgar, are stacked along [010] (Fig. 2). In realgar (s.g. $P2_1/n$) alternating layers A and B are related by the *n* symmetry operator. The planes are linked *via* weak van der Waals forces giving rise to a fair (010) cleavage. The same type of planes are found in β-As$_4$S$_4$ (Fig. 2) but with a different stacking scheme, in fact layers repeat regularly following an ..AA… sequence along [110]. Similarly pararealgar (Bonazzi *et al.*, 1995) and As$_4$S$_4$ (II) (Kutoglu, 1976) are both characterized by the presence of a different type of As$_4$S$_4$ cage (Fig. 3). In this cage different As and S atoms do not show the same coordination. In particular one of the four independent As

atoms is linked to three S atoms, two to two S atoms and one As atom, whereas the remaining is linked to two As atoms and one S atom. Also in this case the two structures show a different molecules packing.

The light-induced alteration of realgar is a well recognised phenomenon that has been thoroughly investigated (Clark, 1970; Roberts *et al.*, 1980; Douglass *et al.*, 1992;
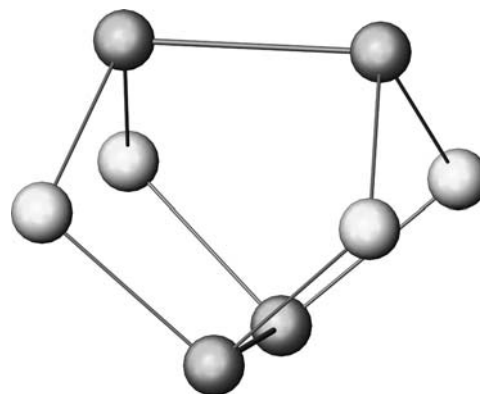

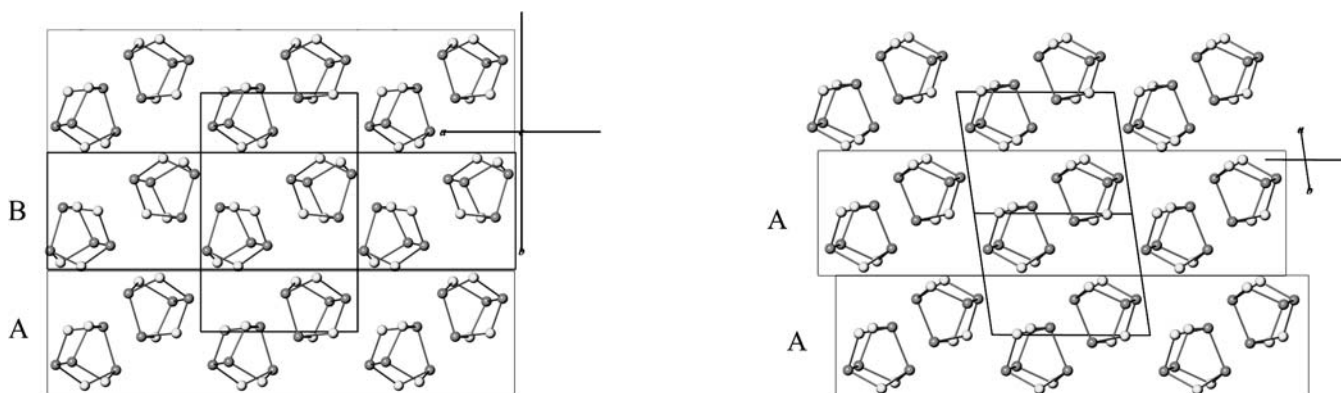Fig. 1. As$_4$S$_4$ cage as found in α-As$_4$S$_4$ (realgar) and β-As$_4$S$_4$. Dark gray As atoms, light gray S atoms.

Fig. 2. Crystal structure of realgar as seen along [001] (left) and crystal structure of β-As₄S₄ as seen along [110] (right). Below is reported the relationship existing between the A and B layers found in the structure of realgar. Dark gray As atoms, light gray S atoms.

Bonazzi *et al.*, 1996, Kyono *et al.*, 2005 among the others). Until the early 70's the alteration products of realgar were commonly considered to be orpiment As_2S_3 and arsenolite As_2O_3. However it becomes clear that the formation of As_2S_3 in ambient air is termodinamically not possible. Roberts *et al.* (1980) pointed out that pararealgar was the alteration product of realgar. This statement was subsequently confirmed by Douglass *et al.* (1992) and Bonazzi *et al.* (1996). In fact those authors found, as products, both pararealgar and the so-called χ-phase, a further As_4S_4 modification related to β-As_4S_4 but showing an expanded cell and possibly a different space-group (Bonazzi *et al.,* 1996). Bonazzi *et al.* (1994) in a preliminary study reported that the occurrence of the χ-phase is preceded by a strong anisotropic expansion of the cell of realgar. Moreover Bonazzi *et al.* (1996) were able to produce the same χ-phase by light-alteration of β-As_4S_4. More recently Bonazzi *et al.* (2003a) have found samples of As_8S_{9-x} composition showing different proportions of As_4S_4 and As_4S_5 molecules, the same molecules (Fig. 4) found in synthetic As_4S_5 (Whitfield, 1973) and its natural analogue uzonite (Bindi *et al.*, 2003). They also speculated that the increase of the unit-cell volume induced by light exposure might be due to an increase of the percentage of the As_4S_5 molecules in the structure. Recently Kyono *et al.* (2005) have shown that pararealgar is produced if oxygen is present. In that case the reaction $5As_4S_4 + 3O_2 \rightarrow 4As_4S_5 + 2As_2O_3$ proposed by Bindi *et al.* (2003) takes place. The extra sulfur atom of the As_4S_5 cage is released to form the As_4S_4 cage of pararealgar and is available to promote the formation of a new As_4S_5 cage in a cyclic process.

The present work investigates *in-situ* by transmission X-ray powder diffraction the light-induced variations occurring in realgar and products of the process the aim being to obtain quantitative data on the kinetics of the process.

Experimental methods

X-ray powder diffraction data were collected on a parallel beam Siemens D5005, equipped with a capillary sample holder and two sets of Soller slits (divergence of 2.3°) on both incident and reflected beams. Data were collected in 2θ scan mode. Analyses were regularly reiterated, in order to follow the evolution of the phenomenon. The data set comprises a total of 270 diffraction patterns. Experimental details are reported in Table 1. An optically pure ruby-red realgar single-crystal from Monte Sughereto, Latium, Italy, collected by one of the authors (P.B.) *ca*. 20 years ago, was crushed into an agate mortar. The resulting powder was loosely charged into a 0.3 mm diameter borosilicate-glass capillary in order to allow a more uniform light incidence on the grains. The diffractometer cabinet was continuously lighted inside by a white-light 15 W neon lamp. A low-power irradiation source was chosen in order to slow-down the
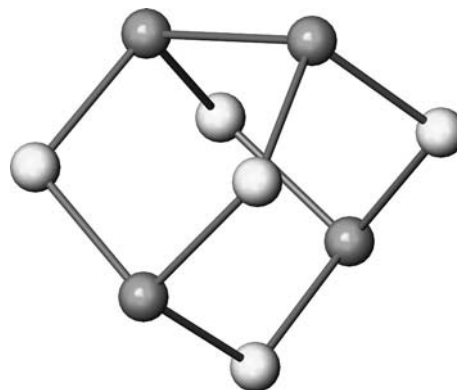

Fig. 3. As₄S₄ cage as found in pararealgar and As₄S₄ (II). Dark gray As atoms, light gray S atoms.

Fig. 4. As₄S₅ cage as found in uzonite. Dark gray As atoms, light gray S atoms.
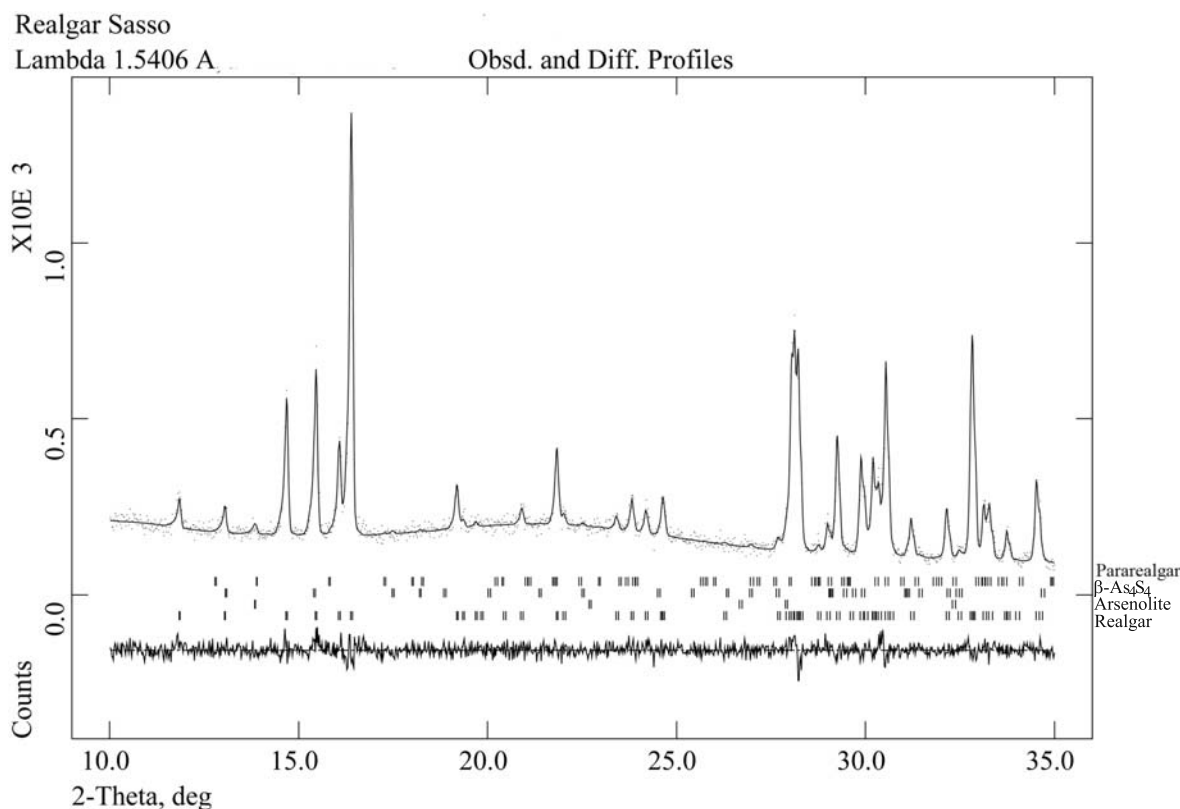
Fig. 5. Magnified view of the experimental, calculated, and difference plot of the refinement of the second spectrum collected after an irradiation of 3 days. Vertical markers indicate the position of the Bragg reflection of (from above to below) pararealgar, β-As$_4$S$_4$, arsenolite, and realgar, respectively.

transformation process differently from the experiments carried out by Bonazzi *et al.* (1996) using optical fibers. Data were collected in the 10–100° 2θ angular range with a step size of 0.02° 2θ and a counting time of 20 s. Total collection time for a single scan was therefore of 25 h. On the contrary, the first spectrum was collected, with the same step size, in the 10–150° 2θ angular range and a counting time of 40 s. Because of the slowness of the reaction (see below) the time collection for each spectrum may be considered as negligibly small.

Data evaluation

The powder diffraction pattern of the starting material is that of realgar. No extra-phases were detected. The second spectrum (Fig. 5) clearly indicates the presence, besides realgar, of traces of pararealgar, an intermediate term along the β-As$_4$S$_4$-alacranite series, and arsenolite (As$_2$O$_3$). In fact the two weak extra peaks at d = 6.50 Å and d = 3.20 Å attributed by Bonazzi *et al.* (1996) to the so-called χ-phase are in effect the strongest 111 (I/I$_0$ = 44; PDF 36-1490) and 222 (I/I$_0$ = 100) reflections of arsenolite. Therefore there is a possible confirmation of the occurrence of the reaction 5As$_4$S$_4$ + 3O$_2$ → 4As$_4$S$_5$ + 2As$_2$O$_3$ as indicated by Bindi *et al.* (2003). At the beginning of the refinements we decide to approximate the structure of the intermediate term along the β-As$_4$S$_4$-alacranite series with the structural data of β-As$_4$S$_4$. Subsequently, on the basis of the refined cell parameters of this

Table 1. Experimental details of the X-ray powder diffraction data collection.

Instrument	Siemens D5005
X-ray tube	Cu operating at 40 kV and 40 mA
Incident beam optics	Multilayer X-ray mirror
Sample mount	Rotating capillary (30 r.min^{-1})
Soller slits	2 (2.3° divergence)
Divergence and antidivergence slits	1 mm
Detector slit	0.1 mm (0.05°)
Detector	Scintillator
2θ range	10–100°
Step size	0.02° (4501 points)
Counting time	20 s

phase (unit cell volume ranging from *ca*. 820 to 827 Å^3) and taking into account the relationship between the unit cell volume and S atoms reported by Bonazzi *et al.* (2003b), a composition of As$_4$S$_{4+x}$ (0.18 < x < 0.25) was estimated. Therefore we selected the structural data of the sample ALA15, characterized by the presence of *ca*. 20 % of As$_4$S$_5$, reported by Bonazzi *et al.* (2003a). According to this fact a composition of As$_4$S$_{4.2}$ will be considered throughout the discussion. Data were evaluated by the Rietveld method using the GSAS crystallographic package (Larson & von Dreele, 1985). Starting positional and displacement parameters of realgar, pararealgar, and arsenolite were those, respectively, of Mullen & Nowacki (1972), Bonazzi *et al.*

(1995), and Ballirano & Maras (2002). An absorption correction was carried out as a part of the Rietveld refinements. Peak shape was modelled by means of a pseudo-Voigt function modified to incorporate asymmetry (Finger *et al.*, 1994). The peak cut-off was set to 0.3 % of the peak maximum. The background was fitted with a 22-terms shifted Chebyshev polynomial of the first kind to take into account the amorphous capillary contribution. No correction for preferred orientation was carried out. The profile parameters of realgar, $As_4S_{4.2}$, and pararealgar were constrained to be equal while those of arsenolite were allowed to vary independently. This is because a preliminary scrutiny of the patterns clearly indicated that peaks of arsenolite were significantly sharper than those of the remaining phases. Apart from the first spectrum, refined parameters were GW (angle-independent Gaussian term), LY (tan θ-dependent Lorentzian parameter), and S/L, and H/L (asymmetry parameters, constrained to be equal in magnitude) for the three sulfide phases and GU ($\tan^2$ θ-dependent Gaussian parameter), GV (tan θ-dependent Gaussian parameter), GW, LX ($\frac{1}{\cos\theta}$ -

Table 2. Comparison of relevant bond distances (Å) and angles (°) of unirradiated realgar between reference data and the present work.

			Present work	Mullen and Nowacki (1972)	Kyono *et al.* (2005)
As1	-S1		2.238(6)	2.242(2)	2.240(4)
	-S2		2.237(6)	2.232(2)	2.230(5)
As2	-S1		2.247(6)	2.243(2)	2.248(4)
	-S3		2.241(6)	2.238(2)	2.247(4)
As3	-S2		2.251(6)	2.247(2)	2.249(4)
	-S4		2.246(6)	2.238(2)	2.240(4)
As4	-S3		2.235(6)	2.231(2)	2.232(4)
	-S4		2.226(6)	2.228(2)	2.235(5)
	average		2.240(7)	2.237(6)	2.340(7)
As1	-As4		2.575(2)	2.571(1)	2.570(2)
As2	-As3		2.566(2)	2.566(1)	2.571(1)
	average		2.570(4)	2.568(2)	2.570(1)
S1	-As1-	S2	95.0(1)	95.03(7)	94.9(1)
	-As2-	S3	94.3(2)	94.51(8)	94.3(1)
S2	-As3-	S4	94.8(2)	95.11(7)	95.1(1)
S3	-As4-	S4	95.1(2)	94.92(8)	94.9(1)
	average		94.9(2)	94.9(2)	94.8(3)
As1	-As4-	S3	99.8(1)	99.85(6)	99.9(1)
		S4	99.9(2)	99.99(7)	99.9(1)
As2	-As3-	S2	99.2(1)	99.24(6)	99.0(1)
		S4	99.3(1)	99.32(6)	99.4(1)
As3	-As2-	S1	99.6(1)	99.55(6)	99.5(1)
		S3	99.3(1)	99.17(6)	99.1(1)
As4	-As1-	S1	99.2(2)	98.67(6)	98.7(1)
		S2	99.0(1)	99.07(6)	99.2(1)
	average		99.4(2)	99.4(4)	99.3(4)
As1	-S1-	As2	101.4(1)	101.26(8)	101.3(1)
	-S2-	As3	101.3(1)	101.23(8)	101.3(1)
As2	-S3-	As4	100.9(1)	100.87(8)	100.9(1)
As3	-S4-	As4	100.9(1)	100.76(8)	100.8(1)
	average		100.9(1)	101.0(2)	101.1(2)

dependent Lorentzian parameter), LY, and S/L and H/L (constrained to vary as in the three preceding phases) for arsenolite. A preliminary cycle of refinements however indicated that:

a) the GW parameter for the three sulfide phases consistently refined to very similar values (*ca.* 6);
b) S/L (and therefore H/L) refined to an average value of 0.023;
c) the peak shape of arsenolite was equal to that reported by Ballirano & Maras (2002) and does not appreciably change throughout the process. Therefore the values of GU = 3.9, GV = –8, GW = 17.6, LX = 1.0, LY = 4.3 were used and kept fixed.
d) the only parameter significantly variable was therefore LY for the three sulfide phases.

Because of these facts we decided to refine exclusively two independent LY parameters, one for realgar and one for pararealgar, and $As_4S_{4.2}$. During the refinement, besides a sample-shift correction, cell parameters of realgar, pararealgar, and $As_4S_{4.2}$ were refined whereas the *a* parameter of arsenolite was kept fixed to the value of 11.07344(5)Å reported by Ballirano & Maras (2002). Moreover the positional parameters of realgar and pararealgar were refined. Because of the relatively large number of refined parameters (97 variables), restraints with a unit weight were applied upon the geometry of the As_4S_4 cage in both realgar and pararealgar. The restraints on realgar structure were As-S 2.240(5) Å, S-As-S, As-S-As, and As-As-S bond angles of 94.9(2), 101.0(2) and 99.4(4)°, respectively. The geometry of pararealgar was restrained allowing a ±0.01 Å and a ±0.02 Å variation with respect to reference data on bonding As-S and As-As and non-bonding As-As, As-S, and S-S intermolecular distances. The use of restraints is justified by the fact that the geometry of the As_4S_4 cages in realgar is unchanged by light irradiation, as observed by Kyono *et al.* (2005). The contribution of the restraints to χ^2 never exceeded 0.5 %. In the case of a low weight fraction of the sulfide phases, the cell parameters refined to very scattered values due to peak broadening. Therefore they were fixed to values obtained from regression of the remaining data (see Fig. 6–8). Final refined weight fractions differ less than 1σ from those previously obtained.

Discussion

Characterization of the starting material

The refined structure of realgar from Mt. Sughereto is in good agreement with that reported by Mullen & Nowacki (1972) for a sample from Binnatal (Switzerland) and that of Kyono *et al.* (2005) for a sample from Getchell mine, Nevada, U.S.A. A comparison of bond distances and angles is reported in Table 3. Average difference in bond distances and angles are of 0.8 σ and 0.7 σ, respectively, in the case of data of Mullen & Nowacki (1972) and of 1.1 σ and 1.0 σ, respectively, in the case of data of Kyono *et al.* (2005). The refinement has been used to refine the absorption $\lambda A_B = \mu R$ of the sample that was of 1.70(11). This value was kept fixed during the refinement of the remaining patterns of the data set.

a)

b)

c)

d)
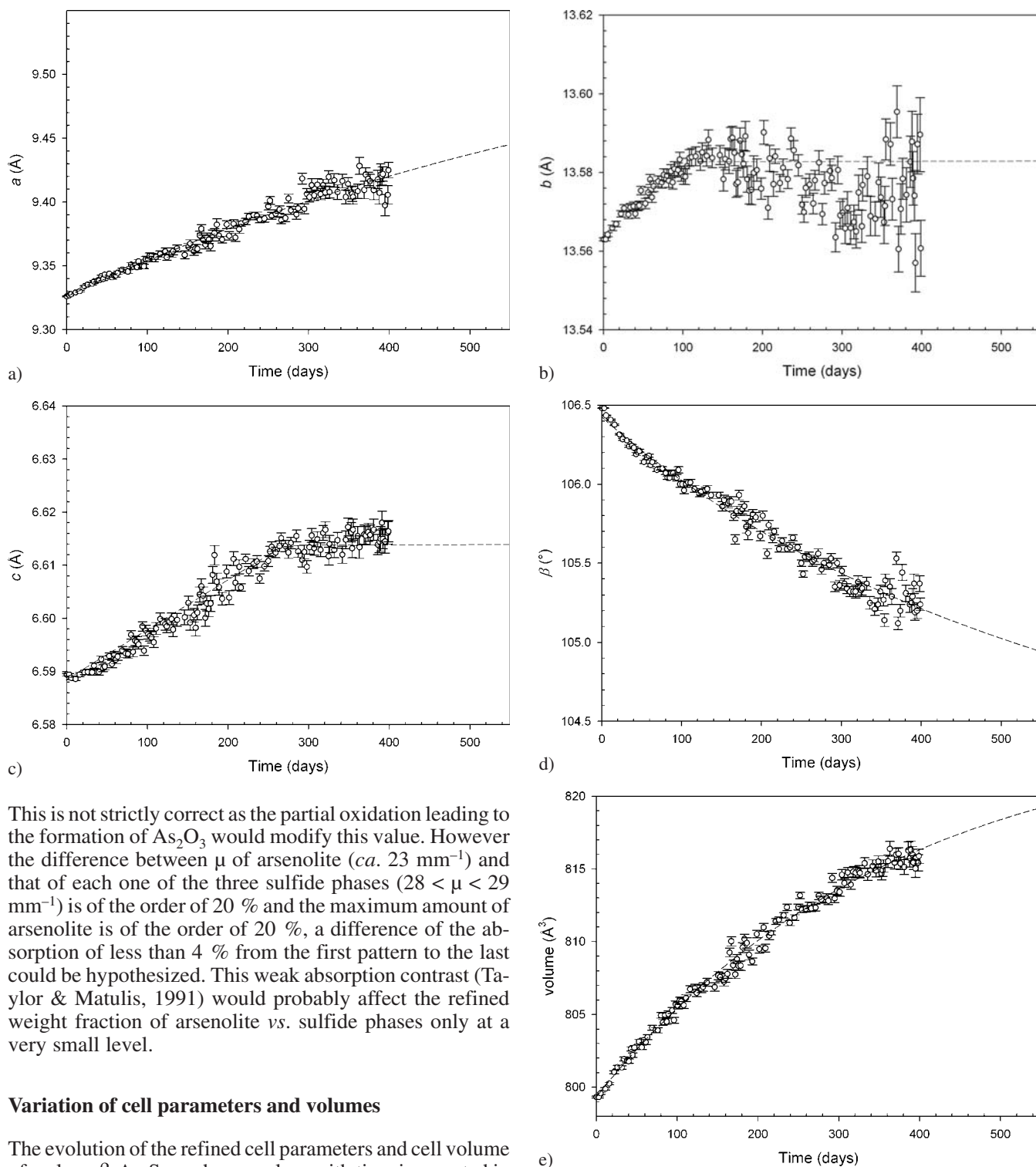
This is not strictly correct as the partial oxidation leading to the formation of As$_2$O$_3$ would modify this value. However the difference between μ of arsenolite (*ca.* 23 mm^{-1}) and that of each one of the three sulfide phases (28 < μ < 29 mm^{-1}) is of the order of 20 % and the maximum amount of arsenolite is of the order of 20 %, a difference of the absorption of less than 4 % from the first pattern to the last could be hypothesized. This weak absorption contrast (Taylor & Matulis, 1991) would probably affect the refined weight fraction of arsenolite *vs.* sulfide phases only at a very small level.

Variation of cell parameters and volumes

The evolution of the refined cell parameters and cell volume of realgar, β-As$_4$S$_4$, and pararealgar with time is reported in Fig. 6–8. Data are markedly scattered due to the strong peak broadening of the three sulfide phases. Such broadening is prevalently due to strain broadening as indicated by the LY parameter (Fig. 9a,b). The refined LY value of realgar reaches a maximum and subsequently becomes constant after about 100–150 days whereas LY of the remaining two As$_4$S$_4$ polymorphs decreases. These results are indicative of an increase of strain of realgar and, at the same time, a release of the strain for β-As$_4$S$_4$, and pararealgar.

e)

Fig. 6. Evolution of the cell parameters and cell volume of realgar; a) *a* cell parameter; b) *b* cell parameter; c) *c* cell parameter; d) β angle; e) volume.

The *a* parameter of realgar increases regularly up to *ca.* 9.45 Å, following a sigmoidal behavior (Fig. 6a), the β angle decreases to *ca.* 105.0° (Fig. 6d), whereas both *b* (Fig. 6b) and *c* (Fig. 6c) tend to a maximum value (13.58 and 6.615 Å respectively) and subsequently become con-
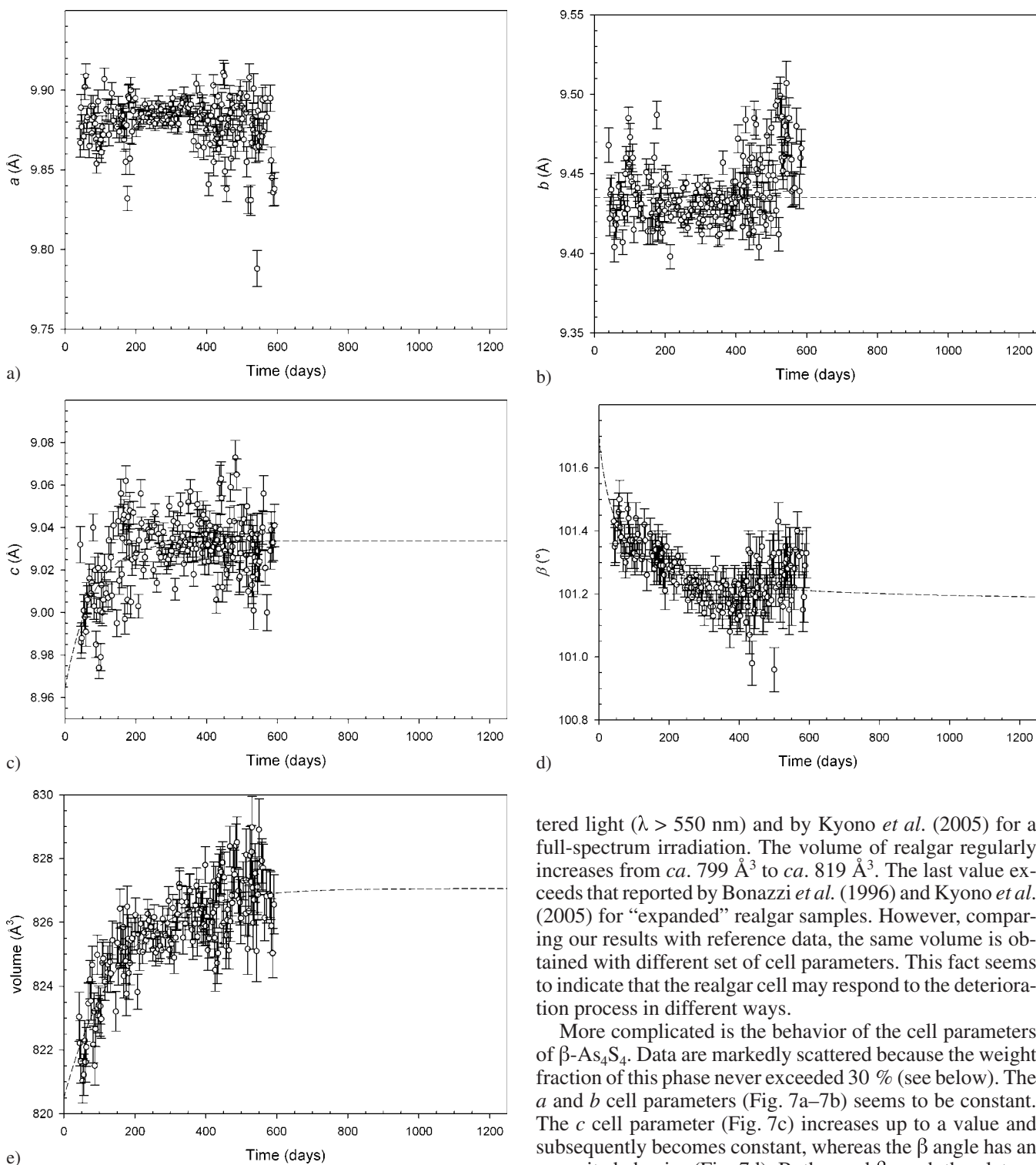
Fig. 7. Evolution of the cell parameters and cell volume of β-As$_4$S$_4$; a) a cell parameter; b) b cell parameter; c) c cell parameter; d) β angle; e) volume.

stant. These plateaux are both reached at *ca.* 150–250 days roughly in correspondence of the achievement of the maximum strain of realgar (see above). The evolution of cell parameters is, therefore, quite similar to that reported by Bonazzi *et al.* (1996) for realgar single crystals exposed to fil-

tered light (λ > 550 nm) and by Kyono *et al.* (2005) for a full-spectrum irradiation. The volume of realgar regularly increases from *ca.* 799 Å^3 to *ca.* 819 Å^3. The last value exceeds that reported by Bonazzi *et al.* (1996) and Kyono *et al.* (2005) for "expanded" realgar samples. However, comparing our results with reference data, the same volume is obtained with different set of cell parameters. This fact seems to indicate that the realgar cell may respond to the deterioration process in different ways.

More complicated is the behavior of the cell parameters of β-As$_4$S$_4$. Data are markedly scattered because the weight fraction of this phase never exceeded 30 % (see below). The a and b cell parameters (Fig. 7a–7b) seems to be constant. The c cell parameter (Fig. 7c) increases up to a value and subsequently becomes constant, whereas the β angle has an opposite behavior (Fig. 7d). Both c and β reach the plateau value after *ca.* 200 days similarly to what happens for the b and c cell parameters of realgar. The volume of β-As$_4$S$_4$ expands from *ca.* 820 Å^3 to *ca.* 827 Å^3. This value is comparable to *ca.* 829 Å^3 (recalculated) reported by Bonazzi *et al.* (1996) for the χ-phases obtained by light exposure of both realgar and β-As$_4$S$_4$ *s.s.* Because of the regular volume increase we could hypothesize a small variation of the composition of this phase up to the final As$_4$S$_{4.2}$. However, the final a, b, c, and β values are different as indicated in Table 3.
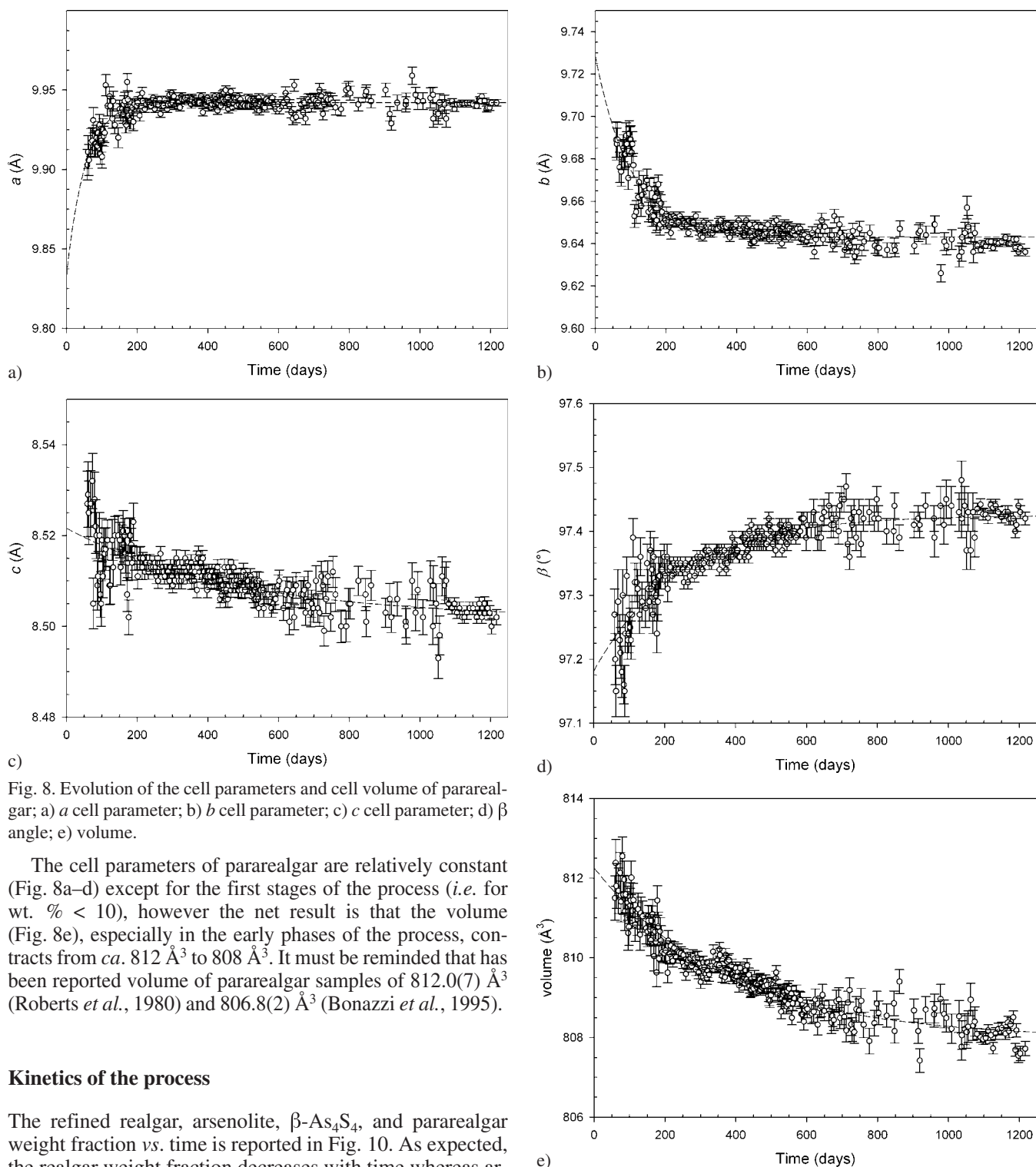
Fig. 8. Evolution of the cell parameters and cell volume of pararealgar; a) *a* cell parameter; b) *b* cell parameter; c) *c* cell parameter; d) β angle; e) volume.

The cell parameters of pararealgar are relatively constant (Fig. 8a–d) except for the first stages of the process (*i.e.* for wt. % < 10), however the net result is that the volume (Fig. 8e), especially in the early phases of the process, contracts from *ca*. 812 Å^3 to 808 Å^3. It must be reminded that has been reported volume of pararealgar samples of 812.0(7) Å^3 (Roberts *et al.*, 1980) and 806.8(2) Å^3 (Bonazzi *et al.*, 1995).

Kinetics of the process

The refined realgar, arsenolite, β-As$_4$S$_4$, and pararealgar weight fraction *vs.* time is reported in Fig. 10. As expected, the realgar weight fraction decreases with time whereas arsenolite and pararealgar weight fraction increases. In the case of arsenolite the increase is almost linear up to 700 days. After this period the linearity is still maintained but with a different slope. This difference may be ascribed to the reduced oxygen availability within the hermetically sealed capillary. More complex is the behavior of β-As$_4$S$_4$ that reaches a maximum weight fraction of *ca*. 30 % in the early stages of the process and subsequently tends to decrease toward zero. However a check of the chemical balance of the

alteration products clearly indicates that there is some sulfur missing. In fact, because the process tend to have pararealgar and arsenolite as final products, and the volume of pararealgar is only marginally higher than that reported by Bonazzi *et al*. (1995), it is not possible to assume that expansion is related to the occurrence of As$_4$S$_5$ cages. The presence of *ca*. 5 wt. % of As$_4$S$_{4.2}$ cannot be sufficient to balance the presence of *ca*. 20 wt. % of As$_2$O$_3$. According to this we

Table 3. Comparison of the cell parameters of $As_4S_{4.2}$ at the end of the process (estimated from regression) and those reported by Douglass *et al.* (1992) for the χ-phase obtained from irradiation of a realgar sample and those reported by Bonazzi *et al.* (1996) *for* χ-phases obtained by irradiation of 1) realgar and 2) alacranite, respectively. Cell parameters of sample ALA15 of Bonazzi *et al.* (2003a) are also reported.

	a (Å)	*b* (Å)	*c* (Å)	β (°)	vol(Å³)
Present work	9.888	9.435	9.035	101.20	826.9
Douglass *et al.* (1992)*	9.722(5)	9.473(6)	9.065(6)	100.90(4)	819.8(5)
Bonazzi *et al.* (1996) 1*	9.783(10)	9.517(6)	9.069(6)	100.84(6)	829.2(7)
" 2*	9.770(9)	9.513(7)	9.086(5)	100.93(5)	829.1(5)
Bonazzi *et al.* (2003a)	9.940(2)	9.398(2)	9.033(2)	102.12(2)	825.0(3)

* Recalculated by the authors using LSUCRIPC (Garvey, 1986).

may hypothesize the formation and evolution of SO_x and/or the formation of amorphous As-S alloys (as found by Žaček & Ondruš, 1997 and Bonazzi *et al.*, 2003a, in association with alacranite) or amorphous S. A careful inspection of the various spectra does not show any modification of the background from the first to the last measurement to be ascribed to the occurrence of any amorphous component. Therefore we may favor the hypothesis of the evolution of SO_x. Attempts to detect *in-situ* the presence of such gases by micro-IR and microRaman were however unsuccessfully because of the expected low concentration of the gas.

According to our data the occurrence of the χ-phase (β-As_4S_4) is contemporary (and not preceded as reported by Bonazzi *et al.*, 1996) to the anisotropic expansion of realgar and the expansion of χ-phase (β-As_4S_4) is still accompanied by a further expansion of realgar. Careful scrutiny of Fig. 10 reveals that, by interpolation, realgar is possibly present within the mixture up to 600–650 days. However because of peak broadening the weight fraction becomes unrefinable after 550 days and therefore realgar is excluded from the refinement hereinafter. This accounts for the small discontinuity of the weight fraction of β-As_4S_4 that seems to be slightly overestimated in the 550–650 days irradiation period.

The fraction X(t) of realgar and pararealgar transformed *vs.* time was subsequently calculated in order to determine the kinetic law of the digestion of realgar and formation of pararealgar. In fact the time evolution of a phase with time may be often represented by a phenomenogical model describing the kinetics of isothermal phase transition proceeding through nucleation and growth. This model, known as JMAK, may be described via a simple equation known as the Avrami equation $X(t)=1-exp[-(kt)^n]$ (Avrami, 1939; 1940; 1941) where X(t) represents the transformed fraction, t the elapsed time, *k* a kinetic constant of the process and *n* a constant related to the dimensionality of the process. By non linear-fitting an *n* parameter of 0.736(3) and a *k* parameter of $1.164(9) \cdot 10^{-7}$ s^{-1} was obtained for realgar with an R² value of 0.995 (Fig. 11a), whereas for pararealgar an *n* parameter of 0.935(6) and a *k* parameter of $6.8(3) \cdot 10^{-8}$ s^{-1}, were obtained with an R² value of 0.995 (Fig. 11b). The refined *n* parameters indicate that the behavior of the two transformations is intermediate between that of a diffusion-controlled and a first-order model.
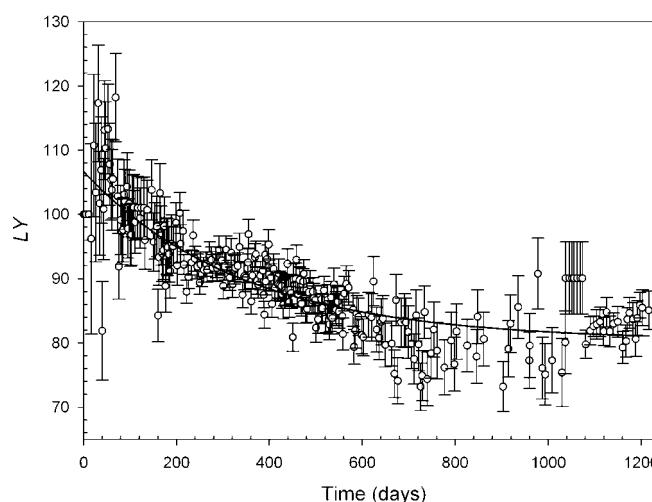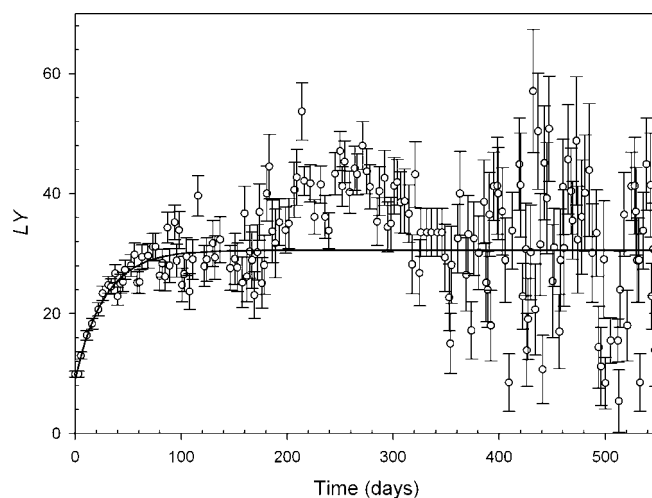

Fig. 9. The dependence of the refined LY parameter describing the peak-shape of: a) realgar; b) β-As_4S_4 and pararealgar.
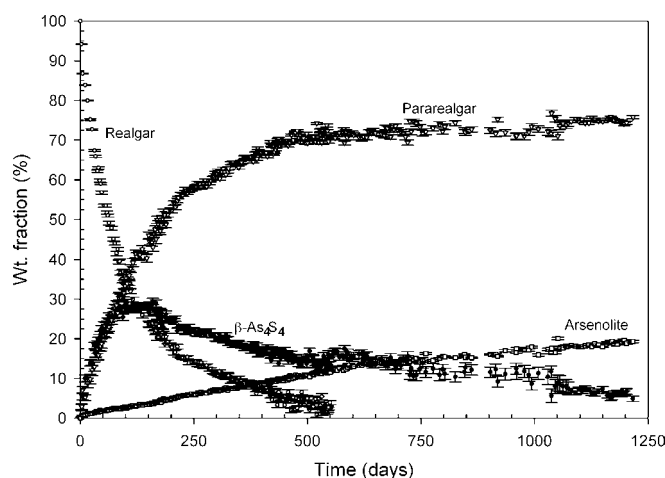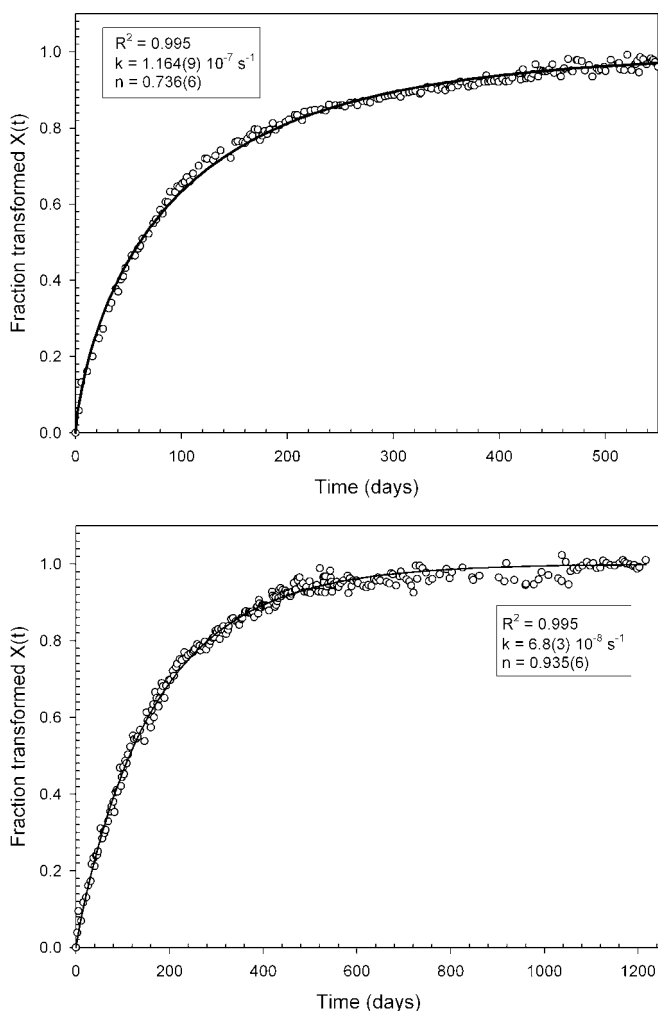

Fig. 10. Refined weight fraction *vs.* time of realgar, arsenolite, β-As_4S_4, and pararealgar.

Evolution of the structure of realgar and pararealgar

The structure refinements gave reasonable results up to a wt. fraction of *ca.* 10 %, roughly corresponding to one year of

Table 4. Comparison of fractional coordinates of the realgar starting material and after *ca.* 360 day of irradiation.

| | starting material | | | after *ca.* 360 days | | |
	x	y	z	x	y	z
As1	0.1212(4)	0.0216(2)	–0.2369(7)	0.137(6)	0.031(3)	–0.226(7)
As2	0.4230(4)	–0.1386(3)	–0.1460(7)	0.428(5)	–0.135(4)	–0.128(8)
As3	0.3220(5)	–0.1258(3)	0.1769(5)	0.317(5)	–0.120(4)	0.186(4)
As4	0.0386(4)	–0.1601(3)	–0.2844(7)	0.048(5)	–0.148(4)	–0.281(7)
S1	0.3431(7)	0.0066(4)	–0.3014(9)	0.362(7)	0.011(4)	–0.281(9)
S2	0.2152(7)	0.0242(4)	0.1154(10)	0.220(6)	0.032(4)	0.123(7)
S3	0.2368(9)	–0.2255(4)	–0.3616(8)	0.244(8)	–0.218(4)	–0.349(7)
S4	0.1067(7)	–0.2089(4)	0.0519(11)	0.104(6)	–0.198(4)	0.054(8)

Fig. 11. Plot of the fraction X(t) of realgar (a) and pararealgar (b) transformed *vs.* time and corresponding non-linear fitting using the Avrami equation.

Table 5. Relevant intermolecular bond distances (Å) of realgar for the starting material and after *ca.* 360 day of irradiation. For comparison purpose, data of Kyono *et al.* (2005) after 24h of irradiation are reported.

| | | *Present work* | | Kyono *et al.* (2005) |
		starting material	after *ca.* 360 days	after 24h irradiation
As1	-As1	3.610	3.97	3.67
	-As4	3.610	3.63	3.63
	-S2	3.507	3.70	3.54
	-S3	3.668	3.58	3.65
	-S4	3.732	3.60	3.86
As2	-As4	3.583	3.72	3.61
	-S1	3.607	3.40	3.62
	-S2	3.667	3.59	3.68
	-S3	3.517	3.65	3.59
	-S4	3.621	3.76	3.65
As3	-As4	3.505	3.80	3.50
	-S1	3.404	3.33	3.42
	-S1	3.834	3.83	3.92
	-S3	3.616	3.58	3.65
	-S4	3.803	3.97	3.78
As4	-S2	3.426	3.37	3.41

after an irradiation time of 360 days are reported in Table 4. Both rearrangement and volume expansion reflect on the contact distances among neighboring cages (Table 5).

The structure refinements of parareagar start to give reasonable results only in correspondence of a wt. fraction of *ca.* 30 %, roughly corresponding to 100 days of irradiation. A comparison of fractional coordinates of pararealgar obtained after *ca.* 100 and 1250 days of irradiation of realgar is reported in Table 6, relevant bond distances (Å) and angle (°) are listed in Table 7, and intermolecular bond distances in Table 8. Similarly to the realgar-type cage, also the geometry of the pararealgar-type cage remains unchanged during irradiation. The compression of the cell affects only the intermolecular contacts. Variations are, as expected, smaller than those observed in realgar coherently with a smaller cell volume contraction of pararealgar with respect to the expansion of realgar.

Final remarks about the process

First of all why there is the need of an intermediate term along the β-As$_4$S$_4$-alacranite As$_8$S$_9$ joint for the development of the light induced alteration of realgar? Kyono *et al.*

irradiation, before the statistics became insufficient. The strong volume expansion of realgar lead to some arrangement of the molecules inside the structure. In spite of using a very small statistic weight for the bond-length and bond-angle restraints, the geometry of the cage has been proved to be substantially unchanged during irradiation confirming the results of Kyono *et al.* (2005). A comparison between the fractional coordinates of the starting material and those

Table 6. Comparison of fractional coordinates of pararealgar obtained after *ca. 100 and 1250 days of irradiation of realgar.*

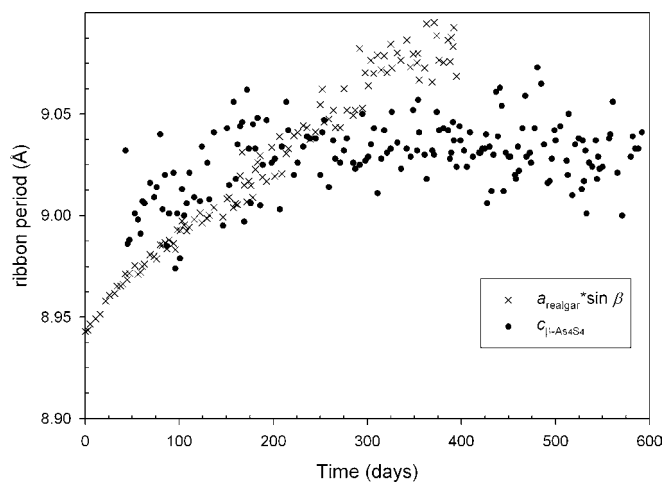|	*after ca.* 100 days			*after ca.* 1250 days		
	x	y	z	x	y	z
As1	0.317(3)	0.635(3)	0.047(4)	0.3194(10)	0.6347(9)	0.0462(10)
As2	0.082(3)	0.540(4)	0.336(4)	0.0811(9)	0.5436(9)	0.3247(12)
As3	0.372(3)	0.355(3)	0.340(5)	0.3706(9)	0.3624(9)	0.3462(14)
As4	0.144(3)	0.344(3)	0.168(4)	0.1459(10)	0.3408(9)	0.1682(12)
S1	0.170(4)	0.717(2)	0.205(5)	0.1669(14)	0.7195(10)	0.1951(18)
S2	0.262(5)	0.469(5)	0.514(3)	0.2518(15)	0.4795(17)	0.5110(12)
S3	0.471(2)	0.524(4)	0.217(6)	0.4729(10)	0.5257(14)	0.2191(19)
S4	0.191(4)	0.450(4)	–0.045(3)	0.2002(16)	0.4452(12)	–0.0440(13)

Table 7. Comparison of relevant bond distances (Å) and angle (°) of pararealgar obtained after *ca.* 100 and 1250 days of irradiation of realgar. For comparison purpose, data of Bonazzi *et al.* (1995) are reported.

			Present work		Bonazzi *et al.* (1995)
			after *ca.* 100 days	after *ca.* 1250 days	
As1	-S1		2.255(10)	2.251(7)	2.254(9)
	-S3		2.240(9)	2.239(7)	2.238(8)
	-S4		2.262(10)	2.256(7)	2.261(8)
As2	-S1		2.248(10)	2.250(7)	2.251(9)
	-S2		2.252(10)	2.253(7)	2.252(9)
	-As4		2.484(10)	2.496(7)	2.484(4)
As3	-S2		2.242(10)	2.250(7)	2.244(10)
	-S3		2.227(9)	2.229(7)	2.228(10)
	-As4		2.535(10)	2.539(7)	2.534(4)
As4	-S4		2.187(10)	2.194(7)	2.190(9)
S1	-As1-	S3	102.9(8)	104.6(5)	103.6(3)
		S4	96.5(7)	97.1(4)	96.2(3)
	-As2-	S2	105.9(9)	104.6(6)	105.5(3)
		As4	100.2(5)	100.9(4)	100.0(3)
S2	-As2-	As4	86.8(5)	86.4(3)	87.0(3)
	-As3-	S3	103.2(9)	104.9(6)	103.2(4)
		As4	85.8(5)	85.4(3)	86.0(3)
S3	-As1-	S4	98.5(7)	97.3(4)	98.3(3)
	-As3-	As4	100.1(5)	101.0(3)	100.0(3)
S4	-As4-	As2	101.7(7)	100.8(4)	101.7(2)
		As3	100.9(7)	99.3(4)	101.0(3)
As2	-As4-	As3	83.3(4)	83.5(3)	83.4(1)
As1	-S1-	As2	109.1(6)	109.1(4)	109.2(4)
	-S3-	As3	110.6(5)	109.5(4)	110.5(3)
	-S4-	As4	104.5(5)	105.4(4)	104.4(4)
As2	-S2-	As3	95.9(5)	96.2(3)	95.9(4)

Table 8. Relevant intermolecular bond distances (Å) of of pararealgar obtained after *ca.* 100 and 1250 days of irradiation of realgar. For comparison purpose, data of Bonazzi *et al.* (1995) are reported..

		Present work		Bonazzi *et al.* (1995)
		after *ca.* 100 days	after *ca.* 1250 days	
As1	-S1	3.41	3.47	3.473
	-S2	3.89	3.78	3.789
	-S3	3.61	3.60	3.607
	-As3	3.61	3.80	3.799
As2	-S2	3.85	3.76	3.775
	-S4	3.48	3.44	3.388
	-As2	3.56	3.67	3.657
	-As4	3.74	3.65	3.687
As3	-S3	3.63	3.67	3.653
	-S4	3.66	3.60	3.618
As4	-S1	3.63	3.65	3.652
	-S2	3.56	3.58	3.592
	-S4	3.90	3.68	3.720
S1	-S2	3.62	3.45	3.478
S2	-S3	3.28	3.34	3.345
S3	-S4	3.84	3.76	3.777

Fig. 12. Comparison of $a_{realgar}$*sin β and $c_{\beta-As4S4}$ *vs*. time.

(2005) have shown that pararealgar is produced if oxygen is present. In that case the reaction $5As_4S_4 + 3O_2 \rightarrow 4As_4S_5 + 2As_2O_3$ takes place. The extra sulfur atom of the As_4S_5 cage is released to form the As_4S_4 cage of pararealgar and is available to promote the formation of a new As_4S_5 cage in a cyclic process. The presence of such extra S accounts, following those authors, for the anisotropic expansion for the *a* and *c* axis of realgar. However the process is dynamic as no evidences of additional S positions resulted from their structural data. On the contrary, according to our data the As_4S_5 cage is firmly located within As_4S_{4+x}. The second point is related to the fact that the three sulfide phases are character-

ized by approximately the same cell volume (*ca.* 800 Å³) and that in the case of realgar and β-As_4S_4 the building unit is the same. Third observation is that the strain broadening, as derived from the Rietveld refinement, has a peculiar behavior within the phases. In the case of realgar it increases, whereas in the case of β-As_4S_4 and pararealgar decreases.

According to all these facts it is possible to hypothesize that the volume increase of realgar is only due to the fact that the alteration proceeds in such a way that structural coherency between at least two of the three phases is preserved. In particular from evaluation of Fig. 2 it is possible to see that each ribbon has a period of two cages corresponding to $a_{realgar}$*sin β and $c_{\beta-As4S4}$, respectively. Comparison of the values of $a_{realgar}$*sin β and $c_{\beta-As4S4}$, at least in the period $50 <$ days < 300, until cell parameters become markedly scattered due to the reduced weight fractions of the two sulfides, indicates a marked similitude. Therefore we may hypothesize that the light induced alteration, promoted by the presence of oxygen, of realgar to pararealgar develops *via* an intermediate As$_4$S$_{4+x}$ phase because it represents the only sulfide phase that is able to sustain the presence of As$_4$S$_5$-type cages. Following the model proposed by Kyono *et al.* (2005) this cages release the extra S atom to form the As$_4$S$_4$ cage of rarealgar-type promoting the development of a new As$_4$S$_5$ cage in a cyclic process.

References

Avrami, M. (1939) Kinetics of phase change. I. General theory. *J. Chem. Phys.*, **7**, 1103–1112.

– (1940) Kinetics of phase change. II. Transformation-time relations for random distribution of nuclei. *J. Chem. Phys.*, **8**, 212–224.

– (1941) Kinetics of phase change. III. Granulation, phase change, and microstructure. *J. Chem. Phys.*, **9**, 177–184.

Ballirano, P. & Maras, A. (2002) Arsenolite As$_2$O$_3$ from X-ray powder diffraction data. *Z. Krist.* New Crystal Structures, **217**, 177–178.

Bindi, L., Popova, V., Bonazzi, P. (2003) Uzonite, As$_4$S$_5$, from the type locality: single-crystal X-ray study and effects of exposure to light. *Can. Mineral.*, **41**, 1463–1468.

Bonazzi, P., Menchetti, S., Pratesi, G. (1994) Light-induced structural variations in realgar. XV European Crystallographic meeting, Dresden, Germany (abs. book, p. 142).

–, –, – (1995) The crystal structure of pararealgar, As$_4$S$_4$. *Am. Mineral.,* **80**, 400–403.

Bonazzi, P., Menchetti, S., Pratesi, G., Muniz-Miranda, M., Sbrana, G. (1996) Light-induced variations in realgar and β-As$_4$S$_4$: X-ray diffraction and Raman studies. *Am. Mineral.*, **81**, 874–880.

Bonazzi, P., Bindi, L., Olmi, F., Menchetti, S. (2003a) How many alacranites do exists? A structural study of non-stoichiometric As$_8$S$_{9-x}$ crystals. *Eur. J. Mineral.*, **15**, 283–288.

Bonazzi, P., Bindi, L., Popova, V., Pratesi, G., Menchetti, S. (2003b) Alacranite, As$_8$S$_9$: structural study of the holotype and re-assignment of the original chemical formula. *Am. Mineral.*, **88**, 1796–1800.

Burns, P.C. & Percival, J.B. (2001) Alacranite, As$_4$S$_4$: a new occurrence, new formula, and determination of the crystal structure. *Can. Mineral.*, **39**, 809–818.

Clark, A.H. (1970) Alpha-arsenic sulphide, from Mina Alacran, Pampa Larga, Chile. *Am. Mineral.*, **55**, 1338–1344.

Douglass, D.L., Shing, C., Wang, G. (1992) The light-induced alteration of realgar to pararealgar. *Am. Mineral.*, **77**, 1266–1274.

Finger, L.W., Cox, D.E., Jephcoat, A.P. (1994) A correction for powder diffraction peak asymmetry due to axial divergence. *J. Appl. Cryst.,* **27**, 892–900.

Garvey, R.G. (1986) LSUCRIPC, Least squares unit-cell refinement with indexing on the personal computer. *Powder Diffraction*, **1**, 89.

Ito, T., Morimoto, N, Sadanaga, R. (1952) The crystal structure of realgar. *Acta Cryst.*, **5**, 775–782.

Kutoglu, A. (1976) Darstellung und Kristallstruktur einer neuen isomeren Form von As$_4$S$_4$. *Z. anorganische und allgemeine Chem.*, **419**, 176–184.

Kyono, A., Kimata, M., Hatta, T. (2005) Light-induced degradation dynamics in realgar: in situ structural investigation using single-crystal X-ray diffraction study and X-ray photoelectron spectroscopy. *Am. Mineral.*, **90**, 1563–1570.

Larson, A.C. & von Dreele, R.B. (1985). *GSAS: General Structure Analysis System.* LAUR 86-748, Los Alamos National Laboratory, Copyright, 1985–1994, The Regent of the University of California.

Mullen, D.J.E. & Nowacki, W. (1972) Refinement of the crystal structures of realgar, AsS and orpiment, As$_2$S$_3$. *Z. Krist.,* **136**, 48–65.

Porter, E.J. & Sheldrick, G.M. (1972) Crystal structure of a new crystalline modification of tetra-arsenic tetrasulphide (2,4,6,8-tetrathia-1,3,5,7-tetra-arsatricyclo[3,3,0,0^{3,7}]-octane. *J. Chem. Soc.*, Dalton Transactions, **13**, 1347–1349.

Roberts, A.C., Ansell, H.G., Bonardi, M. (1980) Pararealgar, a new polymorph of AsS from British Columbia. *Can. Mineral.,* **18**, 525–527.

Taylor, J.C. & Matulis, C.E. (1991) Absorption contrast effects in the quantitative XRD analysis of powder by full multiphase profile refinement. *J. Appl. Cryst.*, **24**, 14–17.

Whitfield, H.J. (1973) Crystal and molecular structure of tetraarsenic pentasulphide. *J. Chem. Soc.,* Dalton Transactions, 1973, 1740–1742.

Žáček, V. & Ondruš, P. (1997) mineralogy of recently formed sublimates from Kateřina colliery in Radvanice, Eastern Bohemia. Czech Republic. *Bull. Czech Geol. Surv.,* **72**(3), 289–302.