

Arsenic sulphides: nucleation and growth from aqueous solution.

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Introduction.

Arsenic, one of the most toxic of all naturally-occurring trace metals, is a major water pollutant in water resources world-wide⁽¹⁾. The arsenic cycle is controlled mainly by the precipitation of sparingly soluble As^{III} and As^V compounds such as sulphides and oxides, together with As^V species adsorbed onto Fe- and Mg- substrates^(2,3). Little is known about the geochemistry of most arsenic sulphides, despite their well documented occurrence in a large variety of environments (i.e, anoxic sediments, contaminated soils- and waste-waters and ancient and modern ore forming systems⁽⁴⁻⁸⁾). Arsenic sulphides also play a major role in scavenging gold and other metals (e.g., Hg, Tl) from geothermal solutions⁽⁹⁾ and may also have been involved in primordial metabolic cycles through the bacterial reduction of arsenate (As^V) promoting the precipitation of amorphous to poorly crystalline As^{III}-sulphides^(7,9,10). The two main As-S phases forming from hydrothermal solutions at temperatures below 300°C are orpiment, As₂S₃, and realgar, AsS^(6,11,12). Together with a variety of other As-S phases coexisting on the tie line between As and S (e.g., uzonite, alacranite, dimorphite), they form exclusively under very specific chemical conditions and are, therefore, very accurate geochemical indicators. However, despite their ubiquitous presence and importance, their formation mechanisms are poorly understood due to the lack of thermodynamic and kinetic data constraining the physico-chemical conditions favouring their formation. At low temperatures, mixing an As^{III} and a H₂S solution promotes the formation of an orange-yellow amorphous As^{III} sulphide colloid. The transformation of this colloid into orpiment or realgar requires a change in sulphur oxidation state that may also provide the necessary electrons for the reduction of As^{III} in As₂S₃ to As^{II} in AsS⁽¹¹⁾, however, the controls on these reactions are poorly constrained. Recently, new methods have been designed and tested that permit the *in situ* observation of nucleation and growth processes in aqueous solutions and under fully anaerobic conditions (batch or synchrotron-based energy-dispersive X-ray diffraction, ED-XRD)⁽¹⁴⁻¹⁶⁾. In such experiments the time and composition dependent changes in X-ray patterns are used to derive accurate information about the nucleation and growth processes for metal sulphides in equilibrium with reduced, aqueous solution. Presented here are data from a study that utilizes batch reactors and ED-XRD to determine the transformation of freshly precipitated amorphous As₂S₃ into crystalline arsenic sulphide phases under various conditions of temperature, pH and reduced sulphur concentrations.

Experimental methods.

The batch experiments were carried out in an anaerobic chamber, in heated and stirred 500 mL glass reactors following the methods described elsewhere⁽¹⁵⁾. The precipitation of an orange-yellow amorphous colloid is induced by saturating a As(III) solution with H₂S gas. In some experiments, this colloid was washed, dried and subsequently re-equilibrated with a saturated H₂S solution. Temperature, pH and redox conditions were varied and the chemical shifts in the fluid (As speciation, ΣH₂S) and solids (crystallinity, paragenesis) were monitored with time. The synchrotron-based experiments were performed at the energy dispersive X-ray powder diffraction station 16.4 at the Daresbury Laboratory (UK). The various starting materials were transferred under anaerobic conditions into quartz tubes, that were evacuated prior to heat-sealing. The experiments were conducted using a heater equipped with slits for the passage of the incident and diffracted X-ray beam (Fig. 1), and X-ray patterns were collected via three detectors every 30 to 240 seconds.

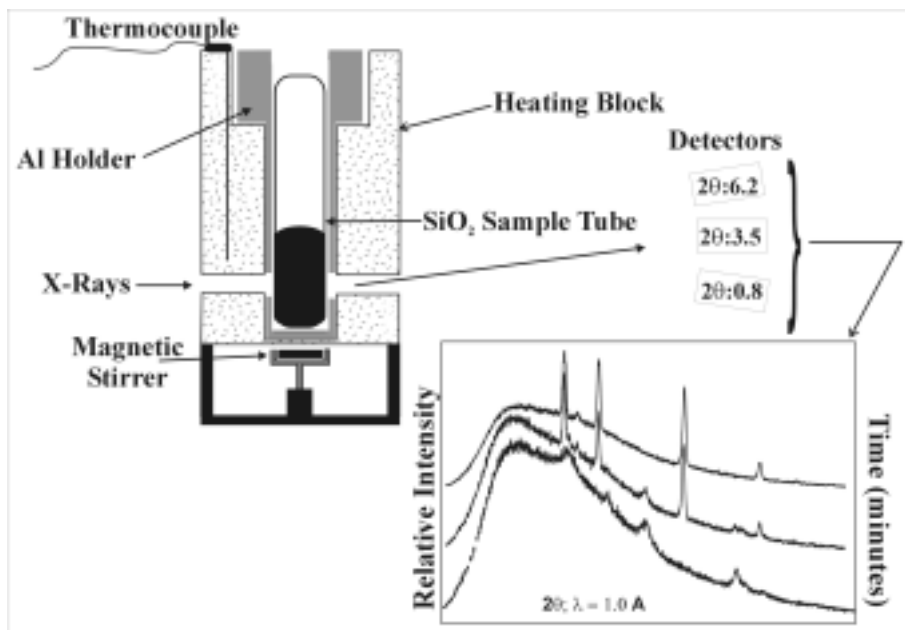


Fig. 1 Schematic diagram of the set-up for the energy-dispersive X-ray diffraction experiments.

Results

The synchrotron data show that amorphous As_2S_3 can be crystallized to a mixture of amorphous As_2S_3 and realgar (2b, 3b), or a mixture of orpiment and realgar (3a), or to orpiment (2a, 4a+b). The obvious change in colour from the starting orange yellow amorphous As_2S_3 to a canary-yellow orpiment and to a red-orange realgar is shown in Fig. 2. However, the XRD and EDS analyses show that the end-product is not always monomineralic i.e., that the transformation reactions have not always reached the end-point. The data show that complete transformation is dependent on (a) the starting material - fresh, dried, etc (b) the temperature (c) the redox conditions and (d) the ionic strength of the solution in equilibrium with the amorphous colloid. For example, a fresh colloid precipitated from a NaCl doped solution will react to form a realgar containing mixture (3b, 3c) with the end point being a function of temperature and ionic strength only. On the other Hand, a freshly precipitated amorphous As_2S_3 colloid, that is washed, dried and just prior to heating, re-suspended in a 0.1 m H_2S solution will transform to orpiment as shown in Fig. 2a, 4a+b.

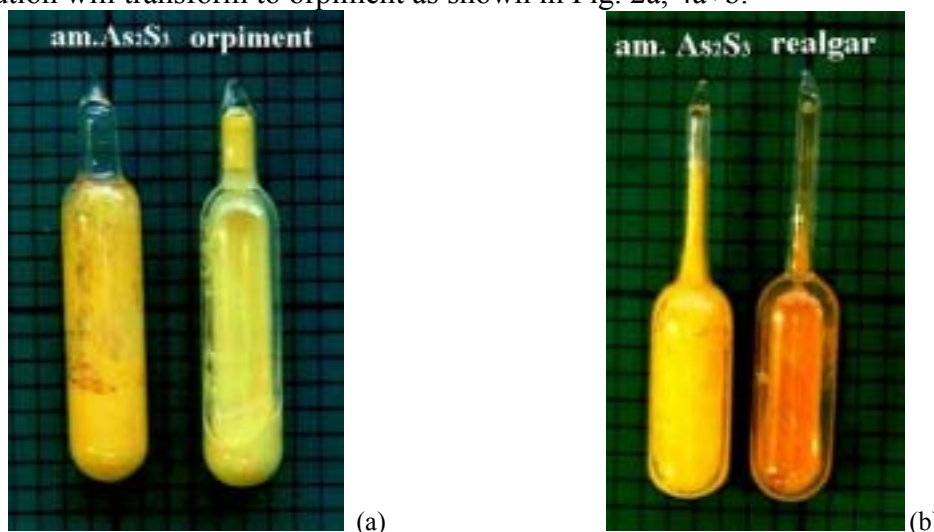


Figure 2. Quartz tubes used in the *in situ* ED-XRD experiments. (a) left = starting material = amorphous As_2S_3 (orange-yellow); right = reaction product = orpiment (canary yellow); (b) left = starting material = amorphous As_2S_3 (orange-yellow) right, reaction product = realgar (red-orange);

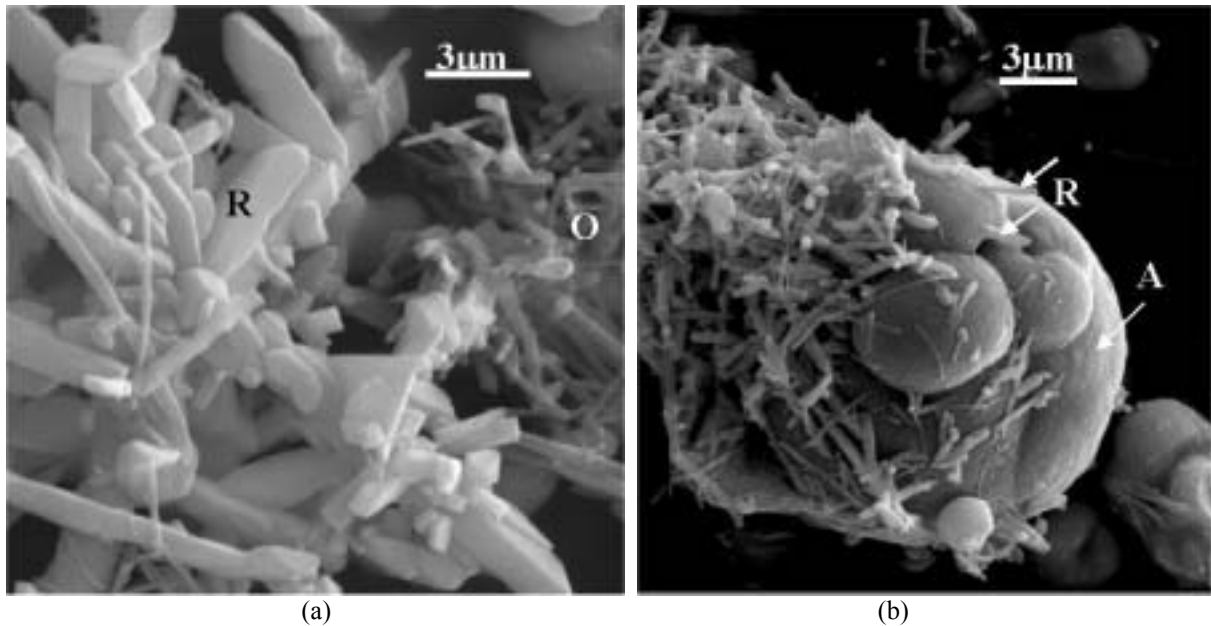


Figure 3. SEM photographs of the reaction products of the various experiments: (a) mixture of realgar (R) and orpiment (O); (b) mixture of amorphous As_2S_3 (A), and realgar (R); Note that in (b) the white arrows next to the 'R' indicate where new realgar prisms grow out of the amorphous starting material. The composition of each phase was corroborated by XRD and EDS analyses (As:S ratios of 2:3 for amorphous As_2S_3 and orpiment and a 1:1 ratio for realgar)

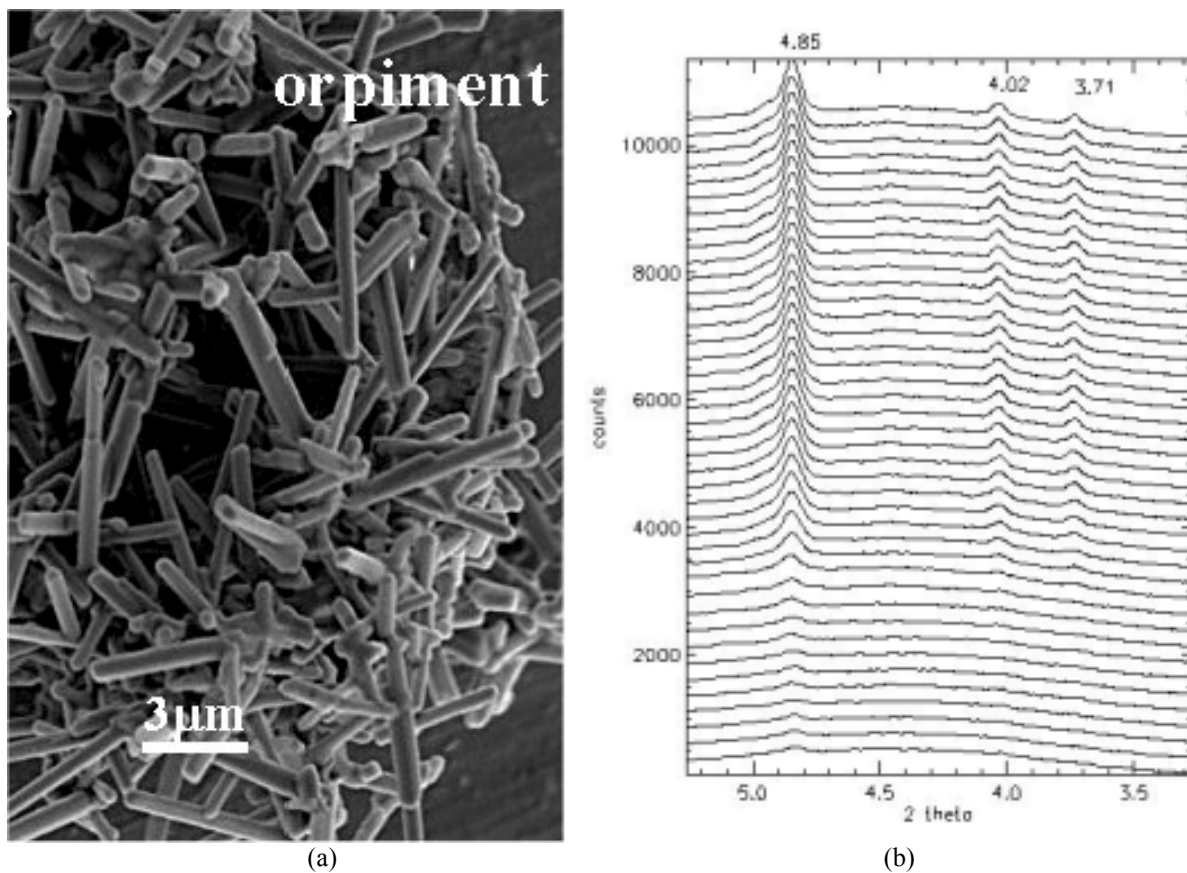


Figure 4. (a) SEM photograph of orpiment. (b) Time resolved formation of orpiment from amorphous As_2S_3 . The data correspond to the reactions that occurred in the right quartz tubes shown in Fig. 2a, with the reaction product - orpiment - shown in Fig. 4a. The marked peaks (2 theta values = 4.85, 4.02 and 3.71) represent the three main orpiment peaks.

Discussion and Conclusions

Theoretical studies indicate that As-S compounds form via the aggregation of monomeric and oligomeric As-S clusters^(17,18). Amorphous As₂S₃ is slightly S-deficient and is ordered only in the first shell around arsenic⁽¹⁷⁾. Crystalline As₂S₃ has a layered sheet-like structure composed of two dimensionally polymerised As₂S₃ pyramids, while realgar consists of large, ordered, oligomeric As₄S₄ species⁽¹⁹⁾. The experimental evidence above shows that the kinetics of transformation of the amorphous colloid to the various crystalline As-S phases is only possible under very specific chemical conditions and that drying, temperature, redox and ionic strength play an important role in these processes. These results can help understand some of the observations in active geothermal systems, where amorphous As₂S₃ is often found together with orpiment and realgar (i.e., Kamchatka, New Zealand). Field studies in the active geothermal system in the Uzon Caldera (Kamchatka)^(7,8) have indicated that the transition from amorphous As₃S₃ to the crystalline As₂S₃ and/or AsS is largely dependent on redox and temperature. However, the experimental evidence provided above shows, that ionic strength and drying of the amorphous colloidal phase will have a strong effect on the transformation reactions. The drying out effect could explain why in the active geothermal system at Champagne Pool (Waiotapu, New Zealand) most of the arsenic is precipitated as amorphous As₂S₃ and this phase remains stable as long as it is equilibrated with the hot (75°C) H₂S rich pool solution^(20,21). However, realgar and orpiment are also found but only in the silica sinter terraces that have undergone several drying cycles^(22,23). This is in agreement with the experimental evidence shown above which demonstrates that drying of the precursor material leads to the crystallization of the amorphous As₂S₃.

Acknowledgements: The financial support provided by the UK Natural Environment Research Council (grant # GR9/04623) and by NERC Direct Access to Synchrotron Radiation Source grant (#37060) are greatly acknowledged.

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