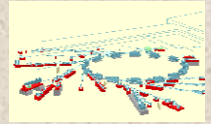
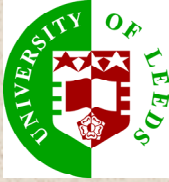


Arsenic sulphides: *in situ* nucleation and growth kinetics.

Liane G. Benning

School of Earth Sciences, University of Leeds, United Kingdom (liane@earth.leeds.ac.uk)



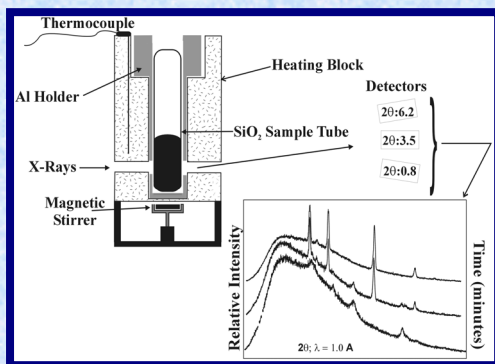
Introduction:

The precipitation of sparingly soluble As^{III} sulphides occurs in a large variety of environments and their formation controls a large part of the global arsenic cycle^(1,3). However, the formation mechanisms of the main arsenic sulphide phases are poorly understood due to the lack of thermodynamic and kinetic data favouring their nucleation and growth. The main crystalline As-S phases in aqueous solutions below 300°C are orpiment, As_2S_3 , and realgar, AsS and these phases form under very specific chemical conditions and are therefore, very accurate geochemical indicators^(4,5).

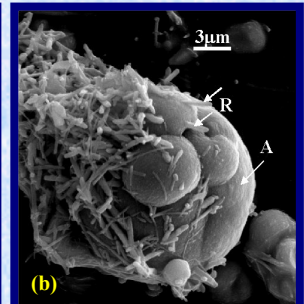
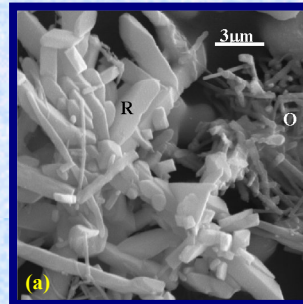
Goals and means:

- kinetics of nucleation + growth of **crystalline As-S phases from amorphous As_2S_3**
- in situ*, in aqueous solution and under fully anaerobic conditions.
- synchrotron-based energy-dispersive X-ray diffraction (ED-XRD)

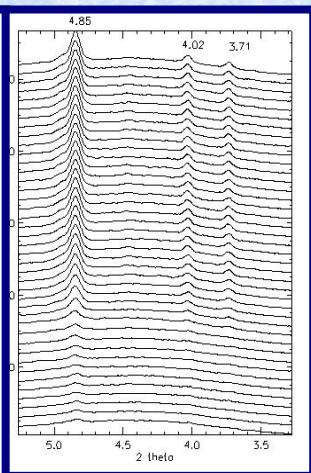
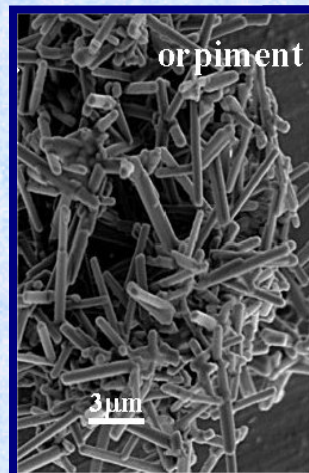
Experimental methods.



Where : ED-XRD station 16.4 at the Daresbury Laboratory (UK).
 Sample: amorphous As_2S_3 and various solutions in evacuated quartz tubes at 75 to 265°C
 How: realtime X-ray patterns collected via three detectors
 Time frame: spectra every 30 to 240 seconds for up to 6 hours.

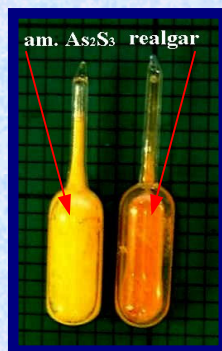
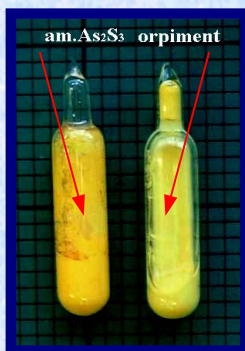


SEM photographs of reaction products: (a) mixture of realgar (R) and orpiment (O); (b) mixture of amorphous As_2S_3 (A), and realgar (R). Note that in (b) the white arrows next to the 'R' indicate where new realgar prisms grow out of the amorphous starting material. The composition of each phase was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



SEM photograph and time resolved plot of orpiment produced from amorphous colloidal As_2S_3 . The marked peaks ($2\theta = 4.85, 4.02$ and 3.71) represent the three main orpiment peaks. The change in area under the peaks is used to define the extent of reaction and to derive the rate constant (k) and the growth mechanism (n)⁽⁶⁾

Results



Depending on (a) the starting material [fresh, dried]
 (b) the temperature
 (c) the redox conditions and
 (d) the ionic strength of the solution
 amorphous $As_2S_3 \Rightarrow$ a mixture of (i) amorphous As_2S_3 and realgar or
 (ii) orpiment and realgar, or
 (iii) to monomineralic orpiment.

Discussion and Conclusions

Colloidal amorphous $As_2S_3 \Rightarrow$ crystalline As-S phases only possible under very specific physico-chemical conditions.

- most important parameters: (a) drying
 (b) ionic strength,
 (c) temperature,

The drying effect also explains why, for example in the active geothermal system at Champagne Pool (Waiotapu, New Zealand) most of the arsenic is precipitated as amorphous As_2S_3 and why this phase remains stable as long as it is equilibrated with the hot (75°C) H_2S rich pool solution⁽⁷⁾. However, crystalline realgar and orpiment have been found but only in the silica sinter terraces that have undergone several drying cycles⁽⁸⁾.

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References: ¹Nriagu JO (1995) (ed.) Arsenic in the environment, Wiley Series: Adv. Environ. Sci. Technol. 26; ²Weissberg BG, Dickson FW and Tunell G. (1966) Geochim. Cosmochim. Acta 30:815-827; ³Hedenquist JW (1991) Geochim. Cosmochim. Acta 55:2753-2765; ⁴Benning LG and Mountain BW (1996) In: Geochemistry of Crustal Fluids, Seefeld, p. 32; ⁵Migdisov AA and Bychkov AY (1998) J. Volcanol. Geotherm. Res. 84:153-171; ⁶Benning et al 2002 Chem Geol submitted; Jones B, Renaou RW and Rosen MR (2001) J. Geol. Soc. London 158:895-911; ⁷Benning unpublished results