A ‘framboid gap’ at the Permo-Triassic boundary

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The role of the sulfur cycle in the Permo-Triassic boundary extinction has been receiving increased attention in recent years. Here we document pyrite morphhology changes from a Chinese P-T boundary section at Chaotian, which records a curious dissappearance of framboids directly above the extinction horizon for an interval of 1.7 m. Framboids return at about the level of the P-T boundary and remain present to the top of the section. Pyrite remains abundant within this interval, forming 0.4 to 4 wt% of the sediment. Framboid size distributions mostly record dysoxic conditions with only two characteristic of a euxinic setting.

The cessation of framboid formation coincides with low, but not unique, S-isotope compositions of carbonate associated sulfate (CAS) and pyrite, minima in both CAS-$\delta^{18}O$ and carbonate concentration, and a jump to higher CAS concentrations. The CAS-S isotopes of the section in general range very widely (-11.9 to +25.8‰), as do CAS concentrations (228-1889 ppm SO_4) and are similar to those elsewhere in China [1]. The restarting of framboid formation does not coincide with any obvious features in any of the datasets, but precedes a general rise CAS-$\delta^{34}S$ and CAS-$\delta^{18}O$ as seen by Newton *et al* [2] in the early Triassic.

Framboids are ubiquitous in pyrite containing marine sediments deposited in a very wide range of redox environments [3, 4] so their absence in sediments with plentiful pyrite is extraordinary. Framboidal pyrite is thought to form via a gregite intermediary and to do this needs an oxidant to form. One specualtive explanation for the absence of framboids would be the complete removal of oxidants from the water column. This would only be possible if there was no chemocline within the water column and this inteval may therefore represent a period characterised by H_2S saturation in surface waters, and even the active degassing of H_2S to the atmosphere. Further work is necessary to determine how widespread this interval is and whether other measures of redox support this hypothesis.

[1] Riccardi *et al.* (2006) *GCA.* **70**, 5740-5752. [2] Newton *et al.* (2004) *Earth Plan. Sci. Let.* **218**, 331-345. [3] Wilkin *et al.* (1996) *GCA.* **60**, 3897-3912. [4] Wignall & Newton. (1998) *Am. Jour. Sci.* **298**, 537-552.

Equation of state for quartz solubility in H_2O-CO_2 at high *P-T*

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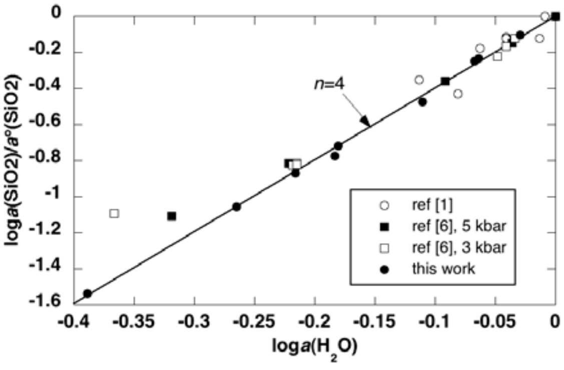
A plot introduced by Walther and Orville [1] makes possible a depiction of the thermodynamics of quartz solubility in binary aqueous fluids at high *P* and *T* when the non-aqueous component does not complex with silica. The reaction is $SiO_2(qz)+nH_2O=Si(OH)_4\bullet(n-2)H_2O$(monomeric silica), where n is the total hydration number of the standard state solute complex and there are n-2 hydrogen-bonded H_2O per silica. Thus, the SiO_2 activity, a_{SiO2}, is determined directly by a_{H2O} and a plot of $\log a_{SiO2}$ vs. $\log a_{H2O}$ at constant *P* and *T* has slope n. In addition to the effect of decreasing a_{H2O}, there is a further decrease by dimer formation, $SiO(OH)_6\bullet mH_2O$ [2]. In a quasi-ideal solution model [3], a_{SiO2} is taken to be the molar concentration of the monomer. Solubility data on quartz-undersaturated SiO_2-buffering assemblages define a_{SiO2} over considerable *P-T* ranges, except near the second critical end point [4]. The figure shows measured solubilities in H_2O-CO_2. Minor dissolved SiO_2 is assumed not to significantly affect a_{H2O} [5]. SiO_2 activities are normalized to those in pure H_2O at the same *P* and *T*. All measurements together describe a constant slope of n=4, in accord with the previously unsubstantiated model of two hydrogen-bonded H_2O per silica of the monomeric complex. Some data depart from the straight line at $X_{CO2}>0.5$ [6], probably due to difficulty in accurately characterizing CO_2-H_2O fluids from oxalic acid mixtures. The plot suggests that quartz solubility in H_2O-CO_2 is easily computed from a_{H2O} over a wide range of *P-T*.



[1] Walther & Orville (1983) *Amer. Mineral.* **68**, 731-744. [2] Newton & Manning (2002) *Geochim. Cosmochim. Acta* **66**, 4165-4176. [3] Newton & Manning (2003) *Contrib. Mineral. Petrol.* **146**, 135-143. [4] Newton & Manning (2008) *Earth Planet. Sci. Lett.* **274**, 241-249. [5] Aranovich & Newton (1999) *Amer. Mineral.* **84**, 1319-1332. [6] Novgorodov (1975) *Geokhimiya* **10**, 1484-1489.