The marine sulfate-oxygen isotope record of the early Toarcian anoxic event

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Here we present two records of marine SO₄-O isotopes derived from carbonate associated sulfate (CAS) across the Toarcian anoxic event, one from a Tethyan open ocean margin (Tibet) and the other from within the European Epicontinental Sea (EES, Yorkshire, UK). Limestones from Tibet record average SO₄- δ^{18} O of +13.1±1.3% across the interval with no systematic change. Belemnites from Yorkshire however record considerably heavier values which change in a systematic way. These start at ~+15% in the uppermost Pliensbachian and rapidly climb to +19% across from the *paltum* to *clevelandicum* ammonite subzones in the lowermost Toarcian. A SO₄- δ^{18} O value of +19% is then maintained until the top of the *exaratum* subzone (which also marks the end of the Toarcian OAE in the EES), whereupon a slow but variable decline begins back to ~+15% in the *levesqui* subzone.

These differences are paralleled by changes in the SO₄- δ^{34} S isotope composition in the two sections with Tibet showing little change (mean +19.1±1.8‰) and Yorkshire exhibiting a large positive excursion (+17 to +23‰). This excursion does not begin unil the basal *exaratum* subzone, 4 subzones after that in SO₄-O. The differences in S isotope composition between the two sections provide evidence of the isolation of the EES from the global ocean.

The isotopic composition of SO₄-O in marine waters reflects the cycling of S between reduced and oxidised states, rather than the simpler balance of inputs and outputs that control the sulfate-sulfur isotope signal. This shortens the residence time of sulfate in marine waters by at least an order of magnitude - a feature apparent in the lag between these excursions. The change to heavier values in predominantly oxic sediments is more problematic to explain. Two potential mechanisms are suggested; the first involves the development of a gradient in dissolved oxygen isotopes, and the second an increase in intermediate S species driven by increased sulfate reduction and reoxidation. Both of these would have to be driven by increased productivity and oxidation of organic matter. If this interpretation is correct the EES SO₄-O data must therefore record the change in conditions (nutrient availability?) that ultimately lead to the Toarcian anoxic event in the EES.

Thermodynamics of SiO₂-H₂O at the second critical end point

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At >8 kbar, quartz solubility in the vapor phase increases sharply along the H₂O-saturated melting curve, and projected compositions of liquid and vapor become coincident at a proposed critical end point near 10 kbar and 1080 °C [1]. To constrain thermodynamic properties and speciation near the possible end point, we measured quartz solubility in H₂O at 10 kbar and 700-1130 °C, extending results of earlier work [2]. Results confirm that the compositional dependence on temperature possesses a vertical tangent near 1080 °C, as required at a critical point. The critical fluid is a nearly equimolar mixture of SiO₂ and H₂O. The SiO₂ activity (a_{SiO2}) in near-critical quartz-saturated SiO2-H2O fluids, determined from depression of the melting point of quartz, is nearly constant at 0.65 at SiO₂ mole fraction (X_{SiO2}) of 0.2 to 0.6. Corresponding H₂O activities are surprisingly high $(a_{\rm H2O} \approx 0.93)$ in the same composition range. The thermodynamics of quartz dissolution is defined by the reaction $SiO_2(q) + n H_2O = Si(OH)_4 \bullet H_2O_{(n-2)}$, where n is the hydration number of the monomeric reference solute and n-2is the number of hydrogen-bonded H₂O molecules. Newton and Manning [3] measured quartz solubility in NaCl-H₂O and CO₂-H₂O fluids at high P and T. New data was collected in the latter system as part of the present study. A Walther-Orville [4] plot of log a_{SiO2} activity (determined from polymerization theory [5]), versus $\log a_{\rm H2O}$ (from measurements in the two fluid subsystems [6, 7]) at 800 °C and 10 kbar shows that n=2for NaCl-H₂O; that is, that hydrogen bonded H₂O is negligible in the ionic salt system. In quartz-saturated CO₂-H₂O fluids, however, n varies from 4 at high $a_{\rm H2O}$ to 2 at low $a_{\rm H2O}$. We infer from these finding that hydrogen bonding to polymeric silica clusters explains both the high H₂O activity of nearcritical SiO₂-H₂O fluids and the monotonous melting point of quartz, independent of melt composition, as a result of high H₂O activity in the melts.

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