

## Geochemical evidence for environmental changes at Frasnian-Famennian boundary leading to the mass extinction

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Sedimentologic and geochemical evidence from Iran and south China indicate that environmental changes were concentrated in the F/F boundary interval. Typical feldspathic arkose with kaolinite and illite rich matrix suggest the intense humid weathering of feldspathic terrains. The ferruginous ooids with alternating micro lamina of hematite and dominance of kaolinite over illite (4:1 ratio) in clay matrix support intense chemical weathering under humid conditions. Significant positive excursion in <sup>87</sup>Sr/<sup>86</sup>Sr ratio at the F/F boundary interval suggests an increased <sup>87</sup>Sr contribution from deep continental weathering. On the other hand, high Sr concentration of carbonates due probably to precipitation of aragonite indicates high alkalinity of sea water under the atmosphere of high CO<sub>2</sub> level. Collectively this evidence suggest the F/F boundary interval was a more intense warm and humid greenhouse condition superimposed in the general greenhouse condition in the Late Devonian. The synchronicity of the δ<sup>13</sup>C anomaly with the high concentration of redox sensitive elements such as U, As, and Th suggest a close causal relation between these two anomalies and the F/F boundary mass extinction.

Although the evidence for such variation is indirect at the Late Devonian, dissociation of gas hydrate in marine sediments is thought to be an important control of the global environmental changes across the F/F boundary. Widespread tectonic and geochemical evidence indicate that northern Iran was part of Turan Plate and the East European Platform, which experienced one of the largest volcanic episodes in the Phanerozoic. The Late Frasnian greenhouse was initially fed by volcanic CO<sub>2</sub>. Increased climatic warming resulted in the dissociation of gas hydrate as suggested by the negative spike of δ<sup>13</sup>C at the base of F/F boundary interval. The methane released from the gas hydrate intensified greenhouse condition resulting in hyper greenhouse condition and poorly oxygenated seawater. The extremely warm and humid climate resulted in intense weathering on land. The subsequent dissociation of gas hydrate is supported by the sharp negative δ<sup>13</sup>C spike right at the F/F boundary resulted in global oceanic anoxia evidenced by widespread distribution black shale and anomalously high concentration of redox sensitive elements. Finally, subsequent anoxia resulted in the mass extinction of marine organisms.

## Spectroscopic investigation of di- and trivalent ion interaction with sulfate in aqueous solutions

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Aluminum and iron are the most common metals in acid mine drainage (AMD) waters, and the most abundant counter ion in these waters is sulfate. Upon physical (e.g., temperature) or chemical (e.g., pH) changes, these waters may precipitate a variety of X-ray amorphous or crystalline solids. The goal of our study is to characterize the interaction of Al(III), Fe(II), and Fe(III) with sulfate in acidic aqueous solutions, before the solid precipitation takes place. Chromium (III) and nickel (II) were also included in the study for comparative purposes.

The solutions were prepared by dissolving appropriate amount of metal chlorides, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, and Na<sub>2</sub>SO<sub>4</sub>. The molality of SO<sub>4</sub> was always 15 mM, molality of the metals (Fe, Al, Cr, Ni) was 10, 20, and 50 mM. The solutions were acidified to the desired pH (1, 2, 3) by small amount of concentrated HCl. Using attenuated total reflectance Fourier transform infrared spectroscopy and Raman spectroscopy, we monitored changes in the spectral region of 1300-900 cm<sup>-1</sup>, where the ν<sub>3</sub> and ν<sub>1</sub> bands of sulfate or bisulfate occur. X-ray spectroscopy at sulfur K-edge (~2480 eV) complemented the vibrational spectroscopy.

Among the metals probed, only Fe(III) shows stronger interaction with sulfate, as indicated by splitting, shift, or intensity variation of IR and Raman bands. The other metals, at all pH values, show only sulfate (1102 cm<sup>-1</sup>) and bisulfate (1200 and 1050 cm<sup>-1</sup>) bands in varying proportions, and occasionally a very weak ν<sub>1</sub> band at ~980 cm<sup>-1</sup>.

In the Fe(III)-SO<sub>4</sub> solutions, we anticipate the presence of sulfate and bisulfate ions, inner-sphere iron-sulfate complex, and iron oligomers interacting with sulfate via hydrogen bonds. Interaction of Fe(III) with Cl<sup>-</sup> or NO<sub>3</sub><sup>-</sup> seems to have no effect on Fe(III)-SO<sub>4</sub> relations, as shown by no difference between IR spectra of Fe(III)-SO<sub>4</sub>-Cl and Fe(III)-SO<sub>4</sub>-NO<sub>3</sub> solutions. Hydrogen bonding between sulfate and iron oligomers is suggested by the shift of the bisulfate bands to ~1190 and ~1040 cm<sup>-1</sup>. Approximately 10% proportion of the inner-sphere Fe(III)-SO<sub>4</sub> complex was determined by a linear combination of XANES spectra of copiapite, Na<sub>2</sub>SO<sub>4</sub> and Fe(III)-SO<sub>4</sub> solutions.

We are planning to perform similar experiments on natural or more complex synthetic samples to address the questions of speciation of metals and sulfate in AMD waters.