Do δ^{98}Mo values in marine euxinic sediments reflect seawater?

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The Molybdenum (Mo) stable isotope composition of seawater provides a characteristic measure of the global redox state of the ocean. A method to infer seawater δ^{98}Mo values from the sedimentological record would offer a measure of ocean oxygenation through time, Arnold *et al.* [1]. Mo is readily scavenged in sulfidic settings and the δ^{98}Mo values in modern marine euxinic sediments fall close to the seawater value. Hence, euxinic sediments are good candidates to record seawater δ^{98}Mo values.

We studied the Mo removal pathway and its isotopic consequences from sulfidic waters to the sediments in Lake Cadagno, Switzerland, by examining both water column and sedimentary samples. These allow us to assess conditions at which euxinic sediments reflect δ^{98}Mo in overlying waters.

Our results show that Mo scavenging occurs through particle adsorption in the sulfidic water column, and support a model where molybdate (MoO_4^{2-}) reacts with H_2S to form particle reactive oxy-thiomolybdates ($MoO_{4-x}S_x^{2-}$) as proposed by Erickson and Helz [2]. $MoO_{4-x}S_x^{2-}$ species then adsorb onto sinking particles and eventually accumulate in the sediment. These particles were fractionated -0.6‰ from dissolved Mo and resembled the sedimentary δ^{98}Mo value.

The observed isotope fractionation in Lake Cadagno is not expressed in sediments of the deep Black Sea, Neubert *et al.* [3], even though the lake contains twice as high $[H_2S]_{aq}$, ca. 200 μM, supporting faster reaction kinetics. We present models based on theoretically predicted isotope fractionation between the $MoO_{4-x}S_x^{2-}$ species, Tossell [4], to show that the offset between sediments and water column depends both on H_2S, time available for reaction, particle affinity for $MoO_{4-x}S_x^{2-}$ species, and style of particle adsorption.

Our conclusion is that marine sulfidic systems with high H_2S concentration (>>11μM) and hydrodynamical conditions allowing a long time (>years) for sulfidation reactions are best suited to transfer seawater δ^{98}Mo value to the sediments.

[1] Arnold *et al.* (2004) *Science* **304,** 87-90. [2] Erickson & Helz (2000) *GCA* **64**, 1149-1158. [3] Neubert *et al.* (2008) *Geology* **36**, 775-778. [4] Tossell (2005) *GCA* **9**, 2981-2993.

Gas-source correlation of marine source rocks in the Sichuan Basin

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Except the Lower Permian marine-terrestrial transitional Longtan coal measures, all the formations from Middle Triassic to Cambrian in the Sichuan Basin belonged to marine deposition. The source rocks consist of Lower Cambrian, Silurian, Lower and Upper Permian. Gases from them were accumulated in the Sinian Dengying, Carboniferous Huanglong, Permian Maokou and Changxing, Triassic Feixianguan, Jialingjiang and Leikoupo carbonates[1]. The gas-source correlation is complicated due to various marine source rocks and carbonate reservoirs. Here stable carbon isotopes were used to correlate the gas sources of different reservoirs [2] and it was concluded as following.

Gases from the Lower Cambrian were migrated downward and accumulated in the Dengying Formation with $\delta^{13}C_1<\delta^{13}C_2$. $\delta^{13}C_1$ and $\delta^{13}C_2$ are -32.3~-32.7‰ and -31.0~-31.9‰, respectively. Gases from Huanglong and Maokou formations have $\delta^{13}C_1>\delta^{13}C_2$ or $\delta^{13}C_1>\delta^{13}C_2<\delta^{13}C_3$. The $\delta^{13}C_1$, $\delta^{13}C_2$ and $\delta^{13}C_3$ are -31.4~-37.5‰, -32.9~-40.7‰, -29.2~-38.1‰ for Huanglong and -29.8‰~-34.7‰, -31.0~-37.2‰, -29.9~-31.9‰ for Maokou formations, respectively. Hence these gases sourced from the Silurian source rocks. $\delta^{13}C$ in the Changxing, Feixianguan and Jialingjiang formations are characterized by two types: 1. $\delta^{13}C_1>\delta^{13}C_2$ or $\delta^{13}C_1>\delta^{13}C_2< \delta^{13}C_3$. The $\delta^{13}C_1$, $\delta^{13}C_2$ and $\delta^{13}C_3$ are -31.6~-34.5‰, -31.7~-38.9‰, -28.9~-33.4‰ for Changxing, -29.8‰~-33.3‰, -31.2~-41.4‰, -27.7~-40.7‰ for Feixianguan and -29.4‰~-33.1‰, -32.4~-37.6‰, -21.1~-35.1‰ for Jialingjiang, respectively. 2. $\delta^{13}C_1<\delta^{13}C_2$. The $\delta^{13}C_1$ and $\delta^{13}C_2$ are -27.5~-32.8‰, -21.7~-27.7‰ for Changxing and -28.5~-31.0‰, -22.8~-27.0‰ for Feixianguan, respectively. Gases of these two formations originated from the coal-related gases in the Longtan Formation. Another kind of gas from the Jialingjiang and Leikoupo formations is characterized as $\delta^{13}C_1<\delta^{13}C_2<\delta^{13}C_3$. The $\delta^{13}C_1$, $\delta^{13}C_2$ and $\delta^{13}C_3$ are -32.2~-35.5‰, -28.7~-34.5‰, -23.5~-30.9‰ for Jialingjiang and -23.2~-35.7‰, -27.1~-30.5‰, -26.3~-30.1‰ for Leikoupo, respectively. These gases should have the same sources. Studies demonstrated that such gases in the Jialingjiang Formation should come from some of the rocks in the Changxing Formation.

[1] Dai *et al*. (1992) *Natural Gas Geology in China.* Petroleum Industry Press. [2] Dai (1992) *Sci China Ser* B, 185-193.