



Molybdenum in carbonates as a potential new ocean redox proxy

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The redox dependant solubility and the low crustal abundance of Molybdenum make of it an important trace metal to investigate the paleo-redox conditions of Earth atmosphere and oceans. Also, it is known to be essential in biological systems, namely in the metabolism of nitrogen, sulfur and carbon compounds (Mendel, 2005). The main input of Mo into the ocean derives from weathering of the continental crust and river transport of dissolved Mo. With the tetrahedrally coordinated molybdate oxyanion MoO_4^{2-} as the most common form in the ocean, Mo is highly soluble under oxygenated conditions with a low reactivity. This results in a very long ocean residence time of 800 ky and makes of it the most abundant trace metal in the ocean, showing a homogeneous and heavy Mo isotopic composition (Siebert et al., 2003).

The isotopic composition of different Mo reservoirs have been investigated by Barling et al. (2001) and Siebert et al. (2003). While euxinic sediments have δ -values on or close to ocean water, oxic pelagic sediments and iron-manganese crusts show a remarkable and constant offset of around 3 permil. Enrichment of Molybdenum in seawater as well as significant Mo isotope fractionation require oxidizing conditions. Consequently, the Mo isotopic seawater signal is suggested as a proxy of paleo-redox conditions (Arnold et al., 2004; Siebert et al., 2005).

To date, Molybdenum isotope fractionation studies are generally based on black shales and Fe-Mn-crusts. Due to the sporadic nature of these deposits in the geological record the reconstruction of the Mo isotopic composition of seawater through time is limited. Molybdenum in marine carbonates is expected to give a more continuous indication of redox conditions and may serve as an archive of the Mo isotopic composition of coeval seawater. Furthermore, due to the important role of Mo in biological pathways, this

proxy may prove usefull in recognizing biological activity in paleo-environments. We present first results of Molybdenum measurements on limestones of different type and age. They show a large variation in concentration and isotopic composition, covering the whole range between recent seawater and oxic sediments. The obtained signals cannot be attributed to varying detrital input alone and thus fractionation in marine carbonate formation is indicated .