

## **The influence of thermal maturity on the concentrations and isotope ratios of transition metals in organic-rich sedimentary rocks**

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The concentrations and isotope ratios of metals in organic-rich mudrocks are frequently used as tracers for Earth's chemical history. However, the influence of thermal maturation on these proxies, including the loss of organic compounds during catagenesis and migration, is not well understood.

Closed-vessel pyrolysis experiments of two thermally immature mudrocks demonstrate that the bulk isotopic compositions of molybdenum, cadmium and zinc do not appreciably change across a large maturity gradient. However, the bulk rock concentrations of these elements increase by tens of percent towards higher maturities. These increases in concentration are explained by the progressive breakdown of kerogen to bitumen (fluid), which can migrate away from the rock, lowering its mass. The concentrations of metals in these fluids are much lower than in the immature bulk rock, thus driving concentrations in the remaining rock residue to higher values.

These results imply that Mo, Zn and Cd in ancient thermally mature mudrocks accurately retain their original isotopic compositions and can thus be used for paleoenvironmental reconstructions. However, Mo, Zn and Cd concentrations of thermally mature rocks from which hydrocarbon fluids have been expelled may be significantly elevated above their syn-depositional values. These observations imply that metal concentrations in thermally mature shales may overestimate the metal concentrations of paleo-seawater which needs to be taken into account when using metal/TOC ratios for paleohydrographic reconstructions.