



Mo and Ca isotope systems: Carboniferous cements and the quest for paleo seawater composition

K. von Allmen (1), **A. R. Voegelin (2)**, Th. F. Nägler (2), E. Samankassou (1), A. Immenhauser (3), J. R. Bahamonde (4) and I. M. Villa (2)

(1) Department of Geoscience, University of Fribourg, Switzerland, (2) Institute of Geology, University of Bern, Switzerland, (3) Institute for Geology, Mineralogy and Geophysics, Ruhr-Universität Bochum, Germany, (4) Department of Geology, University of Oviedo, Spain, (katja.vonallmen@unifr.ch, voegelin@geo.unibe.ch)

The identification and characterization of marine archives that record the isotopic paleo-seawater composition is important for the interpretation of past changes in ocean chemistry. Our study uses the non-traditional isotope systems of molybdenum and calcium to investigate the interrelation between seawater and inorganic carbonate precipitates.

Mo is a redox-sensitive trace element whose isotopic signature can be used for the investigation of paleo-redox conditions of Earth's atmosphere and oceans. Carbonates may provide a continuous record of ocean oxygenation. Results from modern ooids (Voegelin et al., 2007, GCA) suggest, that non-skeletal precipitates have the potential to store the isotopic signature of coeval seawater. Ca is becoming an increasingly versatile isotope system, which is used for investigations such as paleoceanographic changes, paleoclimatic evolutions, stratigraphic correlations or biological fractionation. So far, several Ca isotopic seawater composition proxies are used (e.g. brachiopods, belemnites, foraminifers, phosphates). Information on isotopic composition of calcite cements however is scarce and may provide a complementary record.

We present isotope data obtained from Mid- to Late Carboniferous, chemically precipitated marine cements. The sampled material comprises early marine radiaxial fibrous calcite, botryoidal cements (primarily aragonitic), a late diagenetic burial cement and

microbial mats. These samples are especially suited for this study because they were precipitated in close contact with seawater. Our Mo data indicate that cements may record seawater composition: Neither differences in original mineralogy (aragonite vs. calcite) nor post-depositional alteration seem to considerably affect the isotopic composition. However, encasing, isotopically light skeletal material seems to locally (e.g. in semi-closed pores) influence the composition of fluids from which cements are precipitated. We believe this effect to be responsible for the light signature detected in some of the Carboniferous cements, which are in contact with skeletal rich sediment. The same effect was previously observed in ooids with nuclei of skeletal debris. Ca isotopes behave differently from Mo isotopes in these samples. The isotopic compositions of botryoidal cements differ from those of calcitic cements. The values of botryoidal cements approach modern mean seawater values, while the calcitic cements are isotopically lighter. This contrasts with experimental inorganic carbonate fractionation where aragonite was found to incorporate preferentially light Ca isotopes compared to calcite. This indicates that recrystallization of aragonite cements significantly alters the Ca isotopic composition. In contrast, calcitic cements appear to be a reliable seawater reference.