An experimental study of reductive cleaning procedures for investigating metal isotopes in ancient carbonates

K.D. MÜSING[1*], Z. HE[2,1*], M.O. CLARKSON[1], D. VANCE[1]

[1] Institute of Geochemisty and Petrology, Department of Earth Sciences, ETH Zurich, Switzerland.
(*kim.muesing@erdw.ethz.ch)
[2]School of Earth and Space Sciences, University of Science and Technology of China, Hefei, Anhui, 230026, China.
(*zhiwei.he@erdw.ethz.ch)

Recent studies have begun to exploit the potential of transition metal isotopes in ancient marine carbonates as geochemical proxies to reconstruct palaeoceanographic conditions (e.g. [1]). However, Fe-Mn-oxides which are commonly present in these carbonates, could cause significant bias on isotope ratio measurements, as they readily adsorb trace metals to their surface as well as incorporate them into their structure [2], and they are often isotopically fractionated relative to seawater (e.g. [3]). Here, we conducted a series of experiments to explore the effects of reductive cleaning techniques on the removal of Fe-Mn oxides while concurrently limiting dissolution of the carbonate phase.

A reductive solution containing ammonium citrate and hydroxylamine hydrochloride (HH) at neutral pH was applied in the procedure as described in [4]. The carbonate samples were subjected to different temperatures (25, 60 and 90°C) for varying durations (1, 3, 6, 12, 24h). The results show that extraction yields for Mn, Ca and transition metals (e.g. Ni, Cu, Zn) generally increase with increasing temperature and duration. Extraction yields for Mn increase at nearly identical rates as Ca, indicating a similar response of Mn-oxides and carbonate to citrate and HH. The Fe-oxide phase was not very susceptible to this reductive solution, as a maximum of 15% of the Fe-fraction was leached. These findings imply that the Fe-Mn oxides are not preferentially removed by a citrate and HH solution, but it does induce carbonate dissolution. In further experiments, the focus will be laid on the use of hydrazine as reductive reagent. We will discuss the elemental results in the context of the isotopic compositions of key metals in the different leached fractions.

[1] Kunzmann et al. (2013) *Geology.* 41, 27-30. [2] Atkins et al. (2014) *Geochim. Cosmocim. Acta.* 144, 109-125. [3] Little et al. (2014) *Geochim. Cosmochim. Acta.* 125, 673-693 [4] Whitney, P.R. (1981) *J. of Geochem. Explor.* 14, 95-117.