A combined isotopic and XAS study of Cr incorporation into marine carbonates: Towards verifying Cr isotopes as a palaeoredox proxy

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Recent studies of Cr stable isotope fractionation in experimental and natural systems indicate that Cr isotopes can be used to track past changes in ocean oxygenation [1-3]. A record of dissolved oxygen concentration in seawater is crucial for understanding past climate changes, and for predicting future climate scenarios.

Marine carbonates are enriched in Cr by a factor of 10^4 relative to seawater and have shown potential as a suitable archive phase; they are thought to record the Cr isotopic composition of seawater, however, this assumption needs to be verified. It has been demostrated for other elemental systems e.g. Mg and B, that isotope fractionation can occur during elemental sequestration, thus we set out to determine the molecular mechanism of Cr incorporation into marine carbonates and to quantify any isotope fractionation that occurs during Cr uptake.

Synthetic calcite and aragonite were prepared in the presence of Cr, following the method of Bots *et al*.., 2011 [4]. Precipitates and initial solutions were analysed for Cr isotope composition by MC-ICP-MS. In tandem, selected subsets of the Cr-enriched precipitates were subject to synchrotron X-ray absorption spectroscopy, to determine the oxidation state and local coordination environment of Cr, and thus the molecular mechanism of Cr uptake in marine carbonates.

This work demostrates how a mechanistic understanding of trace element uptake can improve interpretation of empirically determined isotope fractionation factors and provide a theoretical underpinning for a novel and developing palaeo-redox proxy.

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Hydrochemical and isotopic study of CO_2 rich groundwater in the Gyeongsang sedimentary basin, South Korea

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As a natural analogue study of geologic carbon storage in deep aquifers hosted in clastic sedimentary formations, we investigated CO_2 rich groundwater in the Gyeongsang sedimentary basin, southeastern of South Korea. Data of hydrochemistry and multi isotopes ($\delta^{18}O$-δD of water, $\delta^{13}C$ of dissolved carbonate, $\delta^{34}S$ of dissolved sulfate), together with ^{14}C dates, were collected from 16 naturally seeping CO_2 rich groundwater. The CO_2 rich groundwaters are mainly of Ca-(Mg)-HCO_3 type (average pH = 6.1) and are very high in total dissolved solids (TDS) (up to 3393 mg/L) and alkalinity (up to 2512 mg/L). The concentrations of Ca^{2+}, Cl^- and SO_4^{2-} are also high with the positive correlations with TDS. Thus, it is suggested that CO_2 rich groundwater was evolved through strong water-rock interactions. The results of ^{14}C dating support a long residence time of inorganic carbon (35,720 to 44,780 BP). The $\delta^{18}O$ (-9.2 ± 0.6‰) and δD (-63.0 ± 4.4‰) data indicate that CO_2 rich waters were derived from local meteoric water. The $\delta^{13}C$ values of dissolved carbonates (-9.2 to -1.5‰) indicate the origin of dissolved carbon from mantle-derived CO_2. Careful examination of hydrochemical and isotopic data also indicates that mixing process occurred between uprising CO_2 and shallow groundwater during fluid ascending.

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