

XANES evidence of Cr species in carbonates: Implication for the use of Cr isotope as a proxy for atmospheric oxygenation

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Chromium (Cr) isotopes in marine carbonates have been used to trace atmospheric oxygenation through geologic history [1]. Laboratory experiment studies suggest that marine carbonates can directly incorporate Cr(VI) in the ocean and could effectively record the Cr isotope composition of the seawater [2]. However, the precipitation of natural carbonate could be affected by complex processes so that the Cr behavior might be different from the carbonate coprecipitation experiment. Here we studied the valence state of chromium in carbonates deposited at different geological times (1.44Ga~0.25Ga) using X-ray absorption near edge structure (XANES) based on the distinct pre-edge features of XANES spectra between Cr(VI) and Cr(III). Some of the samples have positive $\delta^{53}\text{Cr}$ values, which are expected to record seawater Cr(VI) according to the existing Cr cycling model.

Our results showed that the pre-edge peak of all the five carbonate samples are not obvious, indicating a very small, if any, contribution of Cr(VI) to the total Cr in these samples. The pre-edge features of three samples (formed at ~0.63Ga, ~0.61Ga, ~0.35Ga) are very similar to that of Cr(III) standard, suggesting that almost all Cr in these samples exists as Cr(III). A small pre-edge peak appears at ~5993eV in the spectra of two samples formed at ~1.44Ga and ~0.25Ga. The calculation results show that the Cr(VI)/Cr_{carbonate} is 28.2% and 74.1%, respectively. However, these peaks are not resolvable from the background due to the poor signal to noise ratio of the two spectra. We suggest that Cr(VI) in the past seawater might have been reduced prior to coprecipitation with carbonates by microbial or during early diagenesis in the porewater, or Cr(III) is the major state of Cr cycling.

[1] Frei et al. (2011). *EPSL*, **312**(1), 114-125.

[2] Rodler et al. (2015). *GCA*, **164**, 221-235.