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Determination of Cr isotopic composition in low-level carbonates by MC-ICP-MS: a sensitive proxy for redox changes?

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Geochemical data suggest that atmospheric oxygen increased during two major steps: the Great oxidation event ($\sim$2.4 Ga) and the Neoproterozoic ($\sim$1Ga-545Ma). The O_2 concentration in the atmosphere is strongly linked to the redox condition of the oceans. Therefore the study of redox sensitive elements in marine sediments can be used to evaluate the evolution of O_2 concentrations in the atmosphere. Chromium is a redox sensitive element which significantly fractionates its isotopes during the reduction of Cr(VI) to Cr(III) (Ellis et al., 2002). Thus, Cr isotopes can be used to assess redox changes in the past oceans. Chromium isotopic compositions in sedimentary rocks (BIFs) have been used to determine the evolution of the O_2 concentration in the atmosphere during the Proterozoic (Frei et al., 2009). We have developed a chemical procedure for the purification of Cr in carbonates by using a single cation column to separate the Cr from the matrix, Fe, Ti and V. Cr isotopic compositions are determined used a ^{50}Cr-^{54}Cr double spike method and analysed on a ThermoFisher Neptune MC-ICP-MS using HR and MR in order to be able to discriminate Ar interferences. Standards and samples are analysed as 50ppb Cr solutions and yield an external reproducibility 50 and 70ppm. This new method allowed us to analyse samples with a Cr concentrations as low as 1ppm.
We have analysed a suite of Neoproterozoic carbonates from Australia, but also modern ooids and oolithic limestones through the Phanerozoic. The Cr isotopic data for carbonates record a range of δ^{53}Cr between -0.1 and +1.7. This range indicates that some of these carbonates clearly reflect oxidising conditions in the ocean. By comparison, the Neoproterozoic samples have Cr isotopic compositions close to the continental crust value (-0.1 to 0.1), indicating the Neoproterozoic samples reflect deposition under more reducing conditions
These data suggests that the redox condition during the deposition of shallow-water carbonates reflects the oxygen concentration in the atmosphere and therefore Cr isotopes are potentially a sensitive proxy for understanding the evolution of the atmosphere.

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Frei, R., Gaucher, C., Poulton, S.W., and Canfield, D.E., 2009, Fluctuations in Precambrian atmospheric oxygenation recorded by chromium isotopes: Nature, v. 461, p. 250-U125.