High mass resolution plasma mass spectrometry of Cr isotopes

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Natural mass dependent isotope fractionation of Cr is linked to changes in its oxidation state, and is a promising tracer for secular variations in the reductive capacity of the oceans. The expected isotope variations of a few permil in nature require high precision measurements. We developed a double spike technique, with high mass resolution that renders molecular interferences (e. g., from ArN) negligible at relatively small ion beams of 4–5x10^{-11} A for ^{52}Cr. The double spike approach for correcting instrumental mass bias was compared with the standard-bracketing technique by using aliquots of a double spiked Cr standard. Reproducibility of the double spike-corrected ^{53}Cr/^{52}Cr ratios was 20 ppm (2σ), similar to internal isotope normalization of unspiked samples for TIMS. The most precise data were obtained by combining double spike and standard bracketing of data obtained in a measurement sequence. The instrumental mass bias was corrected using the double spike, and the δ-values were constructed as deviations from the mean value of the standards measured in the sequence. This approach yielded 10 ppm precision (2σ) for δ^{53}Cr, which is twice as good as the double spiked ^{53}Cr/^{52}Cr ratios by themselves, or for δ-values constructed with an assumed constant value of the normalizing ^{53}Cr/^{52}Cr ratio. Eliminating the instrumental mass bias through standard bracketing yielded an overall uncertainty of ~100 ppm, reflecting drift in the instrumental mass bias during the duty cycle (not optimized for this experiment). The double spike measurements are unaffected by changes in mass bias drift, which in practice is dominated by subtle differences in the levels of matrix ions between samples and standards.

Fe isotope composition in Neoproterozoic dolomite rocks and banded iron formations

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The Neoproterozoic geological record provides evidence of some of the most extreme environmental changes in Earth history; however, the cause(s) behind these changes remain controversial. Here we present a novel Fe-isotope dataset from Neoproterozoic dolomicrites and banded iron formations (BIFs) from the Otavi Group, southern Congo Craton, NW Namibia. Samples bracket two distinct glacial intervals, the lower Chuos Fm. and the upper Ghaub Fm. [1]. Fe-isotope compositions were measured relative to IRMM-014 and determined by high-resolution, multiple collector, ICP-MS with an external precision (1 σ) on δ^{56}Fe of ± 0.05 ‰. The initial 65 m of cap dolomite deposited after the lower Chuos glacial is characterised by negative ^{56}Fe composition of – 0.45 ‰. The overlying deposits show an increase in δ^{56}Fe values of -0.1 to 0.1 ‰, consistent with pre-glacial compositions. BIFs deposited throughout the Chuos glacial interval have an average δ^{56}Fe composition of - 0.03 ‰. The pre- and postglacial successions around the upper Ghaub glacial interval show consistent δ^{56}Fe values of c. – 0.27 ‰. Notably, the postglacial cap dolomite exhibits a negative δ^{13}C excursion up to – 4.5 ‰ [2]. Significant Fe-isotope excursions have been predicted to occur in oceans during major glacial events because of changes in sources of Fe fluxes entering the oceans [3]. The lack of significant changes in Fe-isotope composition in the upper Ghaub cap dolomite, where a negative δ^{13}C excursion occurs, implies that either a major change in Fe-source fluxes did not occur or that the signal has not been preserved, thus necessitating a better understanding of fluid-mineral fractionations in the Fe-dolomite system.

References

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