Determination of Vanadium Isotope Compositions in Carbonates Using a Fe Co-precipitation Method and MC-ICP-MS

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Vanadium isotope compositions (δ51V) in marine carbonates are a potential proxy to trace global redox states of ancient oceans. Although high-precision δ51V analyses are available for lots of geological materials, carbonate-hosted δ51V have not been reported yet due to extremely high matrix elements and low V contents (generally below 10 μg g⁻¹). In this study, we developed a Fe co-precipitation method combined with a Fe column to preconcentrate V from major matrix elements, and following four-step chromatographic procedures to further purify V in carbonates. The δ51V were measured using a sample-standard bracketing method by MC-ICP-MS. The robustness of this method was assessed by analyzing element-doping and matrix-spiking synthetic carbonate solutions containing an in-house δ51V standard, USTC-V. The mean δ51V of the synthetic solutions (0.06±0.08‰; 2SD, n=33) is in good agreement with the recommended value of the USTC-V (0.07±0.08‰; 2SD, n=347). The robustness was further validated by the consistent δ51V of the igneous carbonatite standard, COQ-1, which were processed with the whole purification (-0.48±0.04‰; 2SD, n=3) and only four-step chromatographic procedures (-0.43±0.08‰; 2SD, n=3). For the first time, we obtained δ51V of four carbonate reference materials: JDo-1, -0.56±0.09‰ (2SD, n=27); JLs-1, -0.61±0.14‰ (2SD, n=33); GBW07217a, -0.79±0.09‰ (2SD, n=6); and GBW07214a, -0.51±0.13‰ (2SD, n=48). The long-term external precision of carbonate-hosted δ51V analyses is better than ±0.14‰ (2SD). Our method can be applied to measure δ51V in ancient carbonates to trace the evolution in global marine redox states throughout the Earth history.