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

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Vanadium isotope compositions ($\delta^{51}V$) in marine carbonates are a potential proxy to trace global redox states of ancient oceans. Although high-precision $\delta^{51}V$ analyses are available for lots of geological materials, carbonate-hosted $\delta^{51}V$ 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 $\delta^{51}V$ 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 $\delta^{51}V$ standard, USTC-V. The mean $\delta^{51}V$ 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 $\delta^{51}V$ 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 $\delta^{51}V$ 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 $\delta^{51}V$ analyses is better than ±0.14‰ (2SD). Our method can be applied to measure $\delta^{51}V$ in ancient carbonates to trace the evolution in global marine redox states throughout the Earth history.