

Significant vanadium isotope fractionation revealed in V minerals by femtosecond LA-ICP-MS

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Vanadium (V) is a very redox-sensitive trace metal that occurs in nature as V^{III}, V^{IV}, and V^V, e.g. in a variety of ore-forming minerals like vanadates (hosting V^V), sulfides (e.g., patrónite: V^{IV}S₄), silicates (e.g., roscoelite, hosting V^{III}), and hematite [1]. Similar to other redox-sensitive metals (e.g., Fe, Cu, U), the V isotope compositions of V minerals may provide valuable information for source fingerprinting and redox-controlled processes during ore formation. This, however, has not yet been constrained.

Here, we present the first *in situ* V isotope analyses of several natural V minerals (vanadinite, descloizite, cavansite, patrónite, sincosite) conducted with femtosecond-laser ablation-high mass resolution-MC-ICP-MS. Measurements of V isotopes are challenging because of a very high ratio of ⁵¹V (99.75%) to ⁵⁰V (0.25%), and isobaric interferences of ⁵⁰Cr and ⁵⁰Ti, and ³⁶Ar¹⁴N⁺ on the low-abundant ⁵⁰V during MC-ICP-MS analyses. Thus, our approach is limited to minerals with high V and low Ti and Cr contents. For mass bias control, a Fe standard was added to the sample aerosol before and during analyses (see [2] for comparison). The $\delta^{51}\text{V}$ values were determined via standard-sample bracketing, where a pure V metal foil (Alfa-Aesar) served as the standard.

First results indicate a significant variation of $\delta^{51}\text{V}$ values between the analyzed minerals, ranging from -0.1 to -1.1‰ (2s.d.: 0.2‰). This spread is significantly larger than reported for peridotites and MORBs [3], and also exceeds the difference for $\delta^{51}\text{V}$ between the bulk silicate Earth and the meteorite average [4]. The extended range of $\delta^{51}\text{V}$ values suggests dissolution and/or reprecipitation processes due to redox variations, and demonstrates that V isotopes provide a new means for research in low-temperature environments.

[1] Nriagu J.O. (1998) *Vanadium in the environment*. J. Wiley & Sons. [2] Oeser M., et al. (2014) *Geostandards Geoanalytical. Res.* **38**, 311-328. [3] Prytulak J., et al. (2013) *Earth Planet Sci. Lett.* **365**, 177-189. [4] Nielsen S., et al. (2014) *Earth Planet Sci. Lett.* **389**, 167-175.