

Determination of Eu/Eu^* and rare earth element contents in olivine by laser ablation-sector field-inductively coupled plasma-mass spectrometry

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Europium anomaly (Eu/Eu^*) and rare earth elements (REEs) contents are important geochemical tracers in multiple fields of geochemistry. Because REEs are extremely incompatible in olivine, precise determination of the ultra-trace Sm, Eu, Gd (ranging from ng g^{-1} to sub ng g^{-1}) in olivine is challenging, which strongly restricts the application of olivine Eu/Eu^* . In this study, we develop a method for precise determination of olivine Eu/Eu^* and REEs contents using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). Due to the extremely low contents of REEs (down to sub ng g^{-1}) in olivine, measurement using higher-sensitivity instruments, such as sector field (SF) ICP-MS, has advantages over more commonly used quadrupole (Q) ICP-MS instruments. Using a Thermo Element XR SF-ICP-MS, we demonstrated that the Jet + H cone combination with the guard electrode in Ar- N_2 plasma (a small amount of N_2 added into carrier gas flow) conditions provides the optimal condition for measuring ^{147}Sm , ^{153}Eu , and ^{158}Gd . Although the Jet + X cone combination could achieve the highest sensitivity, the usage of the X skimmer cone led to an extremely high oxide formation ($\text{ThO}^+/\text{Th}^+ > 30\%$ and severe inter-element fractionation, and thus it may not be suitable for the determination of low-Eu samples in particular for the samples with high Ba/Eu ratios. Under optimized laser parameters (spot size: 160 μm , ablation frequency: 15 Hz, energy density: 8 J cm^{-2}) and ICP-MS conditions, the detection limits of Sm, Eu, and Gd are 0.033 ng g^{-1} , 0.011 ng g^{-1} , and 0.026 ng g^{-1} , respectively. The accuracy and precision were evaluated using GOR132-G reference glasses and three olivine reference materials (MongOL Sh11-2, 06JY31OL, and 06JY06OL). The analytical accuracy of Eu/Eu^* for GOR132-G is within 5% and the precision of Eu/Eu^* for olivines are within 10% (2RSD, Fig.1). Finally, we report the REEs concentration data for five samples (olivine: MongOL Sh11-2, 06JY31OL, and 06JY06OL, orthopyroxene: 06JY34OPX, and powder pellet: DTS-2b-NP), these data are useful for the further characterization of these reference materials.

