

## Determining rare earth elements “without” fractionation effect in geochemical samples by laser ablation-inductively coupled mass spectrometry

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The major challenges to the use of laser ablation (LA) sample introduction, combined with inductively coupled plasma mass spectrometry (ICP-MS), are the problems of matrix effect and fractionation effect. Using fused lithium borate glasses of powdered solid geochemical samples, as a strategy to homogeneously distribute could reduce matrix effect between standards and samples effectively. In this work, the method to reduce fractionation effect for determining rare earth elements (Rees) in fused glasses by LA-ICP-MS has been investigated. In general, the element fractionation factor (*EFF*) formula was used to describe the fractionation effect in LA-ICP-MS determination. But a limitation for this formula was that it could not characterize the fluctuation of laser signals. A new method was proposed to describe the fractionation effect. Firstly, a linear fitting was done through the stable fractionation region, and then, calculated the residuals from the experimental data to the relative points on the fitted line in the whole stable region, the absolute values of the residuals were used to calculate the relative residuals. Thus, the mean relative residual (MRR) and the relative standard deviation (RSD) of the relative residuals could be used as the parameters for evaluating the fluctuation of signals, and the slope of the fitted line as the parameter for fractionation effect. Using the proposed evaluation method, the influence of laser conditions, including laser energy, frequency, spot diameter and acquirement mode (single point or line scan) on the fractionation effect for Rees were investigated. At the optimum laser condition, i.e. 660v laser power (610v relative to 10% energy and 760v relative to 100% energy), 10Hz laser frequency, 150 $\mu$ m spot diameter and 30 $\mu$ m/s scan speed,  $EFF(^{89}Y) = 1.01$ ,  $EFF(^{139}La) = 1.02$ ,  $EFF(^{157}Gd) = 1.02$  and  $EFF(^{175}Lu) = 1.02$ . Using fused glasses for the determination of Rees in geochemical samples by LA-ICP-MS, the fractionation effect could be ignored.