Abstract

This dissertation contributes to applications of laser ablation plasma source mass spectrometry (LA ICP-MS) in Earth sciences. The primary goal of the thesis is to address some of the fundamental processes related to laser ablation of solid samples that result in decoupling of elements during laser ablation ICP-MS analysis. Better understanding of mechanisms that cause the elemental fractionation and matrix effects is necessary before the accuracy and precision of laser ablation ICP-MS analyses can be improved.

The chemical and phase compositions of particles produced by laser ablation (266 nm Nd:YAG) of silicate NIST glasses and zircon were studied by SIMS and HR-TEM techniques with a particular focus on Pb/U fractionation. This is of great importance in geology as the Pb/U elemental fractionation hampered the precision and accuracy of the measured accessory mineral ages. The data suggest that chemical composition and mineralogy of particles produced at the ablation site during laser ablation differs from the original sample and varies with their size. This can result in elemental fractionation (non-stochiometric sampling) in material delivered to the ICP-MS for quantitative analysis. Evidence of the element fractionation is preserved in chemically zoned ejecta deposited around the ablation pit. Evidence of the phase changes of zircon to baddeleyite and SiO_2 is preserved in the wall of the ablation pit, and may be responsible for the commonly observed increase in Pb/U ratio during laser ablation ICP-MS analysis. It implies that a matrix-matched external calibration is essential for achieving highly precise and accurate laser (266 nm wavelength) ablation ICP-MS analysis of Pb and U in silicate samples because mechanisms of Pb/U elemental fractionation are dependent on the phase and chemical composition of the ablated material.

Laser ablation ICP-MS and SIMS were used to determine differences in sample composition before and after laser interaction with the silicate reference glasses (NIST-610, BCR-2G, alkali element-doped andesite glasses), and crystalline mineral albite ($NaAlSi_3O_8$) with a particular focus on alkali elements fractionation. It has importance in the study of geological materials including geochronology (Rb–Sr, K–Ar) and thermobarometry. The fractionation trends of the alkali elements are different from those of other lithophile elements, and the rate of fractionation varies for different sample matrices and for different alkali elements in the same matrix. Data from SIMS analyses of the ejecta blanket suggest a matrix dependent fractionation of alkali elements in different particle size fractions at ablation site. The extent of fractionation varies for different alkali elements and is independent of their ionic radii. SIMS depth profiling into the bottom of laser craters showed laser ablation-

induced chemical changes in the sample that involved alkali elements and major matrix elements including Si and Ca. This suggests that a combination of thermally-driven diffusion and size-dependent particle fractionation is responsible for the observed fractionation of alkali elements during laser ablation of silicate samples.

Laser ablation MC ICP-MS and SIMS were used to determine the boron isotopic compositions of several natural tourmaline group minerals with variable chemical composition. This study evaluates the effects of laser ablation ICP-MS instrument parameters and sample matrix composition on data precision and accuracy. Isotopic composition of boron is a powerful tracer of various types of geochemical transfer and mixing processes. It was demonstrated that the tourmaline matrix affects significantly the obtained $\delta^{11}B$ values and impacts on data accuracy if a non matrix-matched reference material is used to calibrate ICP-MS analyses. Also the ICP-MS instrument parameters influence the measured $^{11}B/^{10}B$ ratios if the signal intensity varies between sample and reference material and by interference of $^{40}Ar^{4+}$ peak tail on ^{10}B mass. The relation of offset between the measured and expected $\delta^{11}B$ values to the composition of the reference material matrix remains same for all studied samples, suggesting a systematic matrix effect related to composition differences between the unknown tourmaline sample and reference tourmaline material. In case of matrix-matched calibration, the accuracy of LA MC ICP-MS boron isotopic data is comparable to the previously published values obtained by the TIMS technique. SIMS accuracy in this specific study is biased compare to TIMS values. The measurement precision associated with the average $\delta^{11}B$ values achieved by LA MC ICP-MS are about double compare to TIMS and are estimated between 0.2 and 0.5‰ (1s). SIMS precision in this specific study is estimated at 1.3‰ (1s).