Lithium and boron isotopic ratio analyses using laser ablation-multiple Faraday collector-ICPMS

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We report the origin of isotope fractionation induced by laser parameters, and instruments optimization for accurate *in situ* measurement of lithium (d7Li) and boron (d11B) isotope ratios in glasses and minerals using laser ablation multiple Faraday collector ICP-MS. Laser ablation parameters were examined using 266 nm femtosecond (266 fsLA) and 193 nm nanosecond excimer (193 exLA) laser ablation systems for crater diameters of 30–200 mm. We found that higher laser repetition rates and larger crater diameters have led to enhanced fractionation of lighter isotopes, as much as -8 permil for both d7Li and d11B. Fractionation was primarily affected by the ICP aerosol loading and secondly by the thermal fractionation at the LA site. The former was accounted for by mass loading effects, which lowered the plasma temperature and led to insufficient aerosol vaporisation. The latter was related to the molten layer on the crater walls, which resulted in coarser and heavier d7Li and d11B aerosols that did not reach the ICP. Both processes can result in Rayleigh fractionation during aerosol formation and vaporisation. Controlled ablation using a constant crater size, repetition rate, and high laser fluence of 193ExLA enabled reproducible ablation for the standard NIST SRM 61x glasses and unknown basalt glasses. Based on the principles of isotopic fractionation deduced from our experiments, we propose a novel ablation volume correction (AVC) protocol for accurate isotopic analyses of various samples with different matrices. Both the repeatability and the laboratory bias of the d7Li and d11B measurements using the new AVC protocol were better than 1 permil for samples containing a few tens to a few tens of thousands ppm Li and B. We also report significant local heterogeneity of up to several permil found in some basalt glasses, but not in NIST SRM 612 and 610.

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