Japan Geoscience Union Meeting 2011
(May 22-27 2011 at Makuhari, Chiba, Japan)

SMP006-P01 Room:Convention Hall Time:May 25 10:30-13:00

Matrix effect and calibration strategy in trace element analysis of geological glasses using 193 nm excimer LA-ICP-MS

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Quantifying trace elements of solid samples by LA-ICP-MS is usually based on external calibration using a reference material (typically, NIST synthetic glasses SRM 612 and 610) and a predetermined major element composition for correction of ablated mass of the sample and calibration standard. However, chemical and physical properties difference between sample and standard may result in considerable bias, thereby compromise analytical accuracy. Short wavelength and short pulse width of the laser beam (i.e. recently developing trend towards DUV and femto-second laser systems) are supposed to be superior in reducing such matrix biases. Using a 193 nm argon fluoride (ArF) excimer laser ablation system coupled to quadrupole type-ICP-MS, we investigated the elemental responses of various standard glasses ranging from synthetic (SRM 612) to naturally-sourced chemical compositions (GSD-1G, BHVO-2G, and BCR-2G basalt glasses). Our results showed a clear matrix effect affecting on the accuracy of measured trace elements including REEs and HFSEs. Calibration against SRM 612 introduced analytical bias of about 20% from preferred values for the basalt glasses and natural minerals. Accuracies were improved when chemically matched standards were used for calibration. This was also demonstrated by analyzing a set of MPI-DING naturally-sourced glasses. The MPI-DING basalt, andesite and komatiite glasses were accurately determined by using BHVG-2G and BCR-2G basalt standards. Neither SRM 612 glass nor basalt glass standards were appropriate for the MPI-DING rhyolite, although the former gave better results perhaps due to similarly high silica contents. Difference in plasma mass loading of major element from different sample matrices would explain the above observations. It appears that the more silica fraction was introduced into the plasma, the higher the sensitivity enhancement of easily ionized elements occurred. This plasma loading effect greatly affects relative elemental responses, and it is hard to be corrected. Laser fluence apparently influences less on the relative elemental responses. Our results suggest that use of matrix-matched standard is one of the most practical means to achieve accurate analysis of trace elements in geological samples by 193 nm excimer LA-ICP-MS. Glass standards with natural composition (MPI-DING and USGS glass standards) cover a wide compositional range for geological applications (basalt, andesite, rhyolite, komatiiate etc.). However, concentrations of some elements are too low for precise calibration. Use of trace element-doped natural rock-based standards potentially improves calibration precision. A caveat in using such the standard is its non-natural elemental abundances, which may additionally introduce unusual interferences on some elements.

Keywords: LA-ICP-MS, trace elements, matrix effect