

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

### 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, komatiite 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.

キーワード: LA-ICP-MS, trace elements, matrix effect

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## 西南日本、新宮アルカリ玄武岩岩脈に含まれる超マフィック、マフィック岩における多様なマグマ活動の記録

### Multiple magmatic activities recorded in the mafic and ultramafic xenoliths in the Shingu alkali basaltic dike, SW Japan

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Miocene alkali basaltic dikes in the Shingu area, central Shikoku, brought up abundant crustal and mantle fragments that include information of the petrological structure beneath the region at a beginning of subduction of the Philippine Sea plate. Our detailed petrological examination of the xenoliths revealed that there is a larger geochemical and temporal diversity in magmatism at the east Eurasian continental margin than previously thought. Dunite, which had been probably formed as a cumulate from a basaltic magma, bears small gabbroic domains in the forms of discrete grains with a granoblastic texture (discrete-type) or fine-grained aggregates with an igneous texture (vein-type). From the gabbroic xenoliths, three groups, at least, can be distinguished: Hbl-bearing olivine gabbro (A type), oxide-bearing olivine gabbro (B type) and gabbro-norite (C type). The Hbl-bearing olivine gabbro group includes dunite, olivine clinopyroxenite and olivine gabbro and is characterized by smoky green Cpx partly replaced by reddish brown Hbl. The oxide-bearing olivine gabbro group is characterized by purplish brown Cpx and shows modal layering among olivine clinopyroxenite, clinopyroxenite and gabbro with concentrations of euhedral opaque minerals. The gabbro-norite group is characterized by an association of coarse-grained Opx and Cpx. There are two types of Cpx: Cpx1 with vermicular exsolution of Opx and Cpx2 with minor exsolution. Granular Opx and Cpx2 are followed by crystallization of interstitial Cpx2 and Pl. Mineral chemistry of Pl and Cpx in each gabbroic group shows distinct differentiation trend. This is most apparent in the K content of Pl: Or<sup>2</sup>~3.5 (A type), Or<sup>1</sup>~2 (B type), and Or<sup>3</sup>~9 (C type) in a range from An<sub>40</sub> to An<sub>60</sub>. Brown Cpx in B-type gabbro shows higher Mg# than green Cpx in A-type gabbro at a similar An content. The mineral chemistry of low K and Mg-rich A-type gabbro is in accord with that of phenocrysts in the host alkali basalt. Furthermore, Pl in vein-type gabbroic domains in dunite partly overlaps these trends and possibly represents the most undifferentiated one for three magmatic trends. Petrography and mineral chemistry of gabbros clearly show that they have different origins related to various magma processes in the crust-upper mantle. Correlation of geochemistry of mafic-ultramafic xenoliths will depict a complicate history of the crust-upper mantle evolution in the Shikoku fore-arc region.

## Dunite and wehrlite crystal aggregates in basalts from West Zealandia Seamount, Southern Mariana Volcanic Arc Dunite and wehrlite crystal aggregates in basalts from West Zealandia Seamount, Southern Mariana Volcanic Arc

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West Zealandia Seamount, at approximately 16° 53' N, lies behind the magmatic front of the Mariana Arc. It is part of the Sarigan-Zealandia volcanic complex, a group of mostly submarine volcanoes and parasitic cones, the highest of which are the island of Sarigan (538 m above sea level), and Zealandia Bank, which comes within a few meters of sea level. West Zealandia rises from about 2750 m below sea level to a summit depth of around 750 m and is separated from Zealandia Bank by a saddle that is as deep as 1050 m below sea level. Bathymetric surveys reveal that its summit has an unusual arcuate morphology, while radial ridges that extend for about 10 km from the summit, and may represent lava flows, mark its western and southern slopes. Sampling of the northwestern slopes from 1390-1135 m with the ROV Hyper-Dolphin during NT09-08 was undertaken in June 2009 and recovered primitive basalts, with whole rock MgO and SiO<sub>2</sub> contents of 10.7 wt.% and 47.9 wt.%, respectively. These primitive basalts contain dunite and wehrlite crystalline aggregates, which have been analyzed by electron microprobe (EPMA) for major elements. These analyses paid particular attention to the Ca and Ni contents of the olivine, which can be used to determine whether the aggregates are mantle xenoliths. The NiO contents of the olivine in the aggregates are too low and the CaO contents too high to be in equilibrium with mantle olivine, suggesting that the aggregates are crustal xenocrysts. With Fo<sub>85-91</sub>, the olivines in the crystal aggregates contain 0.15 to 0.24 wt.% NiO, whereas at these Fo contents mantle olivines contain at least 0.28 to 0.36 wt.% NiO, respectively (Takahashi, 1986, Bull. Volcanol. Soc. Japan, 30, S17-S40). Mantle olivines are also characterized by CaO less than 0.1 wt.% (Simkin & Smith, 1970, J. Geol., 78, 304-325); the olivines in the West Zealandia crystal aggregates contain more than 0.15 wt.%. Even so, the high Fo contents of the olivines in the crystal aggregates indicate that they crystallized from a primitive melt, and in addition they contain silicate melt inclusions that may provide access to this melt, and determine whether or not it is primary. As a result, initially the volatile, and then the major and trace element concentrations in the inclusions are being measured by micro-Fourier-transform infrared spectroscopy (FTIR), EPMA and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), respectively. The H<sub>2</sub>O contents of the inclusions range from 3.01 to 4.47 wt.%, with the exception of one inclusion that contains 1.87 wt.%. CO<sub>2</sub> contents range from below detection limits (60 ppm) to 809 ppm. Overall the H<sub>2</sub>O-CO<sub>2</sub> systematics are generally consistent with open system degassing, although a few inclusions require closed system degassing with the initial melt in equilibrium with 5% exsolved vapor. The highest volatile contents indicate entrapment pressures of up to 296 MPa, equivalent to about 11.7 km below sea level, which, beneath West Zealandia, is around the base of the middle crust, top of the lower crust (Takahashi et al., 2007, Geology, 35, 203-206). If so, the West Zealandia crystal aggregates may represent the first ever direct samples of Mariana crust from such depths.

キーワード: olivine, clinopyroxene, crystal aggregates, melt inclusions, major elements, volatiles

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