

Appendix A2. Methods

The major element compositions of most olivines analyzed in this study were determined on polished samples using a JEOL JXA-8900R electron probe microanalyzer at the Department of Geology, University of Maryland, with 15 kV accelerating potential, a 20 nA focused electron beam current, and a 10 μm spot size. Major elements have been determined with an accuracy of $\leq 3\%$ and an external precision of $\leq 3\%$ (2-sigma), whereas minor elements (< 1 wt.%) have been determined with an accuracy of $\leq 5\%$ and an external precision of $\leq 4\%$ (2-sigma). Some olivine grains from Western Australia were analyzed using a Cameca SX-100 electron microprobe in the Geochemical Analysis Unit (GAU), GEMOC/CCFS at Macquarie University with 15 kV acceleration voltage, a 20 nA sample current and a spot size of 5 μm . Major elements have been determined with an accuracy of $\leq 3\%$ and an external precision of $\leq 3\%$ (2-sigma); minor elements (< 1 wt. %) have been determined with an accuracy of $\leq 4\%$ and an external precision of $\leq 4\%$ (2-sigma).

The first row transition element, Ga and Ge contents of the olivine grains were determined using a Photon Machines Analyte G2 ArF Excimer laser ablation system, which produces > 15 J/cm² of 193 nm radiation in < 5 ns pulses at up to 300 Hz and offers spot sizes ranging from 2 up to 150 microns, coupled to a Nu Instruments AttoM high resolution ICP-MS in the Planetary Environments Laboratory at NASA Goddard Space Flight Center. The ArF excimer laser system with 193 nm wavelength was selected to avoid potential problems associated with laser-sample coupling during the ablation of variably opaque materials (i.e., semi-opaque basaltic glass and semi-transparent olivine grains). Deeper UV wavelengths couple better with optically transparent minerals and amorphous geological phases, thus increasing the

rate of ablation (mass removal), producing finer particle size distributions, and attenuating laser-induced elemental fractionation (Guillong et al., 2003).

Elemental abundances were determined using the USGS glass reference material BHVO-2G as a bracketing standard. The USGS glass reference material BIR-1g was analyzed as an unknown to assess the accuracy and precision of the analyses. The ICP-MS analyses were conducted in medium resolution mode ($M/\Delta M = 2500$, measured at 5% peak intensity) using the tunable slits offered by the Nu AttoM. Multiple isotopes for each element (when available) were monitored in order to identify potential isobaric interferences, namely: ^{45}Sc , $^{47,49}\text{Ti}$, ^{51}V , $^{52,53}\text{Cr}$, ^{55}Mn , $^{56,57}\text{Fe}$, ^{59}Co , $^{60,62}\text{Ni}$, $^{63,65}\text{Cu}$, $^{66,67,68}\text{Zn}$, $^{69,71}\text{Ga}$, $^{72,73,74}\text{Ge}$. In order to maximize counting times, two spots per grain were analyzed using different mass ranges. Firstly, Sc through Fe were analyzed using Fe values determined by electron microprobe as the internal standard. Secondly, Co through Ge were analyzed using electron microprobe Ni values as the internal standard. The analyses used 75-150 μm beam sizes, a pulse rate of 10 Hz and a fluence of 4.47 J/cm^2 . The data reduction followed the methodology described by Arevalo et al. (2011).

Repeated BIR1g analysis during this study show that the accuracy for most elements and/or masses is $\leq 5\%$ when compared to the preferred published values (1), with an external precision of $\leq 4\%$ (2SD; Extended Data Table 1). Vanadium displays a notably higher deviation between the measured concentration (321 ppm V) and the preferred published value (282 ppm V; deviation of 14%). However, the V concentration measured during this study is within uncertainty of the recommended GeoReM value (326 ppm V; (Jochum et al., 2005), suggesting V inhomogeneity rather than an analytical problem (also observed/reported by Arevalo et al., 2011). A V inhomogeneity in the distributed BIR1g glasses is also supported by the wide range of composition reported in the GeoReM database (i.e. 281-370 ppm V). The Ge measurements

also yielded a lower accuracy of 13% with an external 2-sigma precision of 19%, which reflects the low concentration of Ge in BIR2g (1.43 ppm; (Jochum et al., 2005).

Table A2-1. Multiple analyses of the BIR1g basaltic glass standard and comparison with reference values.

BIR1g-1 BIR1g-2 BIR1g-3 BIR1g-4 BIR1g-5 BIR1g-6 BIR1g-7										Average	2 σ precision	Reference value (Arevalo et al., 2011) ^a	Deviation from Arevalo et al. (2011) ^a	GeoReM value ^b	Deviation from GeoReM value ^b
Sc	40.3	41.1	38.7	38.6	39.1	38.8	39.9	39.5	2%	40.6	-3%	43	-8%		
Ti	5744	5867	6077	5761	5805	6033	6082	5910	2%	5680	4%	5400	9%		
V	330	332	311	320	318	319	316	321	2%	282	14%	326	-2%		
Cr	425	424	409	412	418	417	408	416	1%	428	-3%	392	6%		
Mn	1400	1397	1420	1409	1385	1386	1388	1398	1%	1330	5%	1471	-5%		
Fe lsc	78800	78800	78800	78800	78800	78800	78800	78800	0%	78800	IS	80840	-3%		

BIR1g-1 BIR1g-2 BIR1g-3 BIR1g-4 BIR1g-5 BIR1g-6 BIR1g-7										Average	2 σ precision	Reference value (Arevalo et al., 2011) ^a	Deviation from Arevalo et al. (2011) ^a	GeoReM value ^b	Deviation from GeoReM value ^b
Co	51.2	52.5	50.6	50.6	51.4	51.5	51.6	51.4	1%	52.8	-3%	52	-1%		
Ni lsc	169	169	169	169	169	169	169	169	0%	169	0%	178	-5%		
Cu	115	112	112	113	111	118	111	113	2%	115	-2%	119	-5%		
Zn	65.6	62.1	63.1	65.7	67.9	71.4	62.1	65.4	4%	60.8	8%	78	-16%		
Ga	15.8	16.5	15.4	15.5	15.1	16.8	16.3	15.9	3%	15.7	1%	15	6%		
Ge	1.16	1.26	1.02	1.18	2.55 ^d	1.82	1.06	1.25	19%	1.43	-13%	1.2	4%		

^aArevalo et al. (2011) Geostandards and Geoanalytical Research

^bJochum et al. (2005) Geostandards and Geoanalytical Research

^cIS=Internal standard (i.e., 57Fe or 60Ni)

^dStatistical outlier (outside of 3 x interquartile range) not included in mean/standard deviation analysis

REFERENCES CITED

- Arevalo Jr, R., McDonough, W.F., and Piccoli, P.M. (2011) In Situ Determination of First-Row Transition Metal, Ga and Ge Abundances in Geological Materials via Medium-Resolution LA-ICP-MS. *Geostandards and Geoanalytical Research*, 35, 253-273.
- Guillong, M., Horn, I., and Günther, D. (2003) A comparison of 266 nm, 213 nm and 193 nm produced from a single solid state Nd:YAG laser for laser ablation ICP-MS. *Journal of Analytical Atomic Spectrometry*, 18, 1224-1230.
- Jochum, K.P., Nohl, U., Herwig, K., Lammel, E., Stoll, B., and Hofmann, A.W. (2005) GeoReM: A New Geochemical Database for Reference Materials and Isotopic Standards. *Geostandards and Geoanalytical Research*, 29, 333-338.