Advantages and limitations of quantifying melt inclusion chemistry by LA-ICPMS, EMP and SIMS

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Laser-ablation inductively-coupled-plasma mass-spectrometry (LA-ICPMS) has unique advantages for the chemical analysis of melt inclusions (MI), because it allows bulk compositional reconstitution of heterogeneous (crystallized) MI trapped in chemically complex minerals, without prior thermal homogenisation. Our LA-ICPMS consists of a 193 nm ArF Excimer laser with energy-homogenizing beam optics coupled to an ELAN6100 quadrupole ICPMS. We analysed glassy and crystallized MI from coeval populations by EMP, SIMS and LA-ICPMS to evaluate (i) analytical precision and accuracy, (ii) the quantification procedure for LA-ICPMS data obtained from unexposed MI (Halter et al., 2002, Chem. Geol. 183, 63-86), both for homogeneous (glassy) as well as heterogeneous (crystallised) inclusions.

Analysis of exposed, glassy MI in plagioclase (An82) from a MORB reveals excellent agreement (± 3% RSD on average) between the methods, demonstrating analytical accuracy. This is also true for unexposed MI, hence the numerical re-integration of inclusion compositions is also accurate.

Analysis of crystallized MI trapped in clinopyroxene (cpx) from the 79AD pumice horizon of Somma Vesuvius reveals: (i) agreement of data obtained on homogenized MI by the different analytical methods; (ii) consistency of LA-ICPMS data of crystallized MI with EMP and SIMS data of homogenized MI from the same sample; (iii) clear recognition of outliers from readily obtained large data sets, caused by accidental trapping of a solid phase; (iv) statistically significant chemical variation of MI populations in different cpx phenocrysts, which had not been apparent in the smaller SIMS/EMP data set.

Advantages of LA-ICPMS include the concurrent analysis of up to 40 major to trace elements in MI and the host mineral without prior thermal homogenisation, the large sample throughput (up to 50 MI per working day) and the fact that matrix-matched standards with similar concentrations levels are not required – in contrast especially to SIMS. Advantages of SIMS and EMP include the higher spatial resolution at similar detection capabilities of SIMS, the external standardization of SIMS and EMP without independent knowledge of an internal standard – in contrast to LA-ICPMS, and the possibility of measuring H_2O, F, S and Cl by SIMS and/or EMP. Furthermore, it will be demonstrated that internal standardization allows for the mathematical correction of post-entrapment sidewall crystallization of MI (both glassy and crystallized) measured by either method.

Os, Ir, Pt, Pd and Re in Hole 504B

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Alteration of oceanic crust is one of the most poorly constrained processes affecting the geochemical cycles of Re and PGE. We have analyzed a representative suite of 43 rocks from DSDP/ODP Hole 504B to investigate the distribution and mobility of Re and PGE in oceanic crust. The weighted average $^{187}Os/^{188}Os$, $^{187}Re/^{188}Os$ and initial $^{187}Os/^{188}Os$ of this 6.7 Ma crust are 0.213, 354, and 0.173, respectively, indicative of net addition of radiogenic Os during hydrothermal alteration. Weighted average concentrations for the entire core are Os=21 ppt, Ir=9 ppt, Pt=304 ppt, Pd=265 ppt, and Re=1.5 ppb. Osmium and Ir concentrations tend to decrease down core from 30 ppt to 18 ppt and 12 ppt to 6 ppt, respectively. The Transition Zone, located between the Volcanic Zone and the Sheeted Dike Complex, has the highest $^{187}Os/^{188}Os$=0.329 and $^{187}Re/^{188}Os$=885 of the three zones. It is also characterized by the highest Pt, Pd, and Re concentrations, as well as the most radiogenic initial $^{187}Os/^{188}Os$=0.23.

Weighted average values for the three major lithologic units (pillow lavas, flows/dikes, breccias) show that breccias, affected most strongly by hydrothermal alteration, have unusually high $^{187}Os/^{188}Os$=0.829, $^{187}Re/^{188}Os$=4209, and initial $^{187}Os/^{188}Os$=0.355. We contend that the low PGE (e.g., 8 ppt Os) and high Re (4.9 ppb) concentrations in breccias reflect net loss of PGE and gain of Re during alteration. Massive flows/dikes have the least radiogenic $^{187}Os/^{188}Os$=0.183, initial $^{187}Os/^{188}Os$=0.157, low $^{187}Re/^{188}Os$=230, as well as highest Os (23 ppt) and lowest Re (1.0 ppb) Re concentrations. Flows/dikes thus appear least affected by alteration.

Our results provide clear evidence for addition of Re and radiogenic Os to, and loss of unradiogenic Os from altered crust. Other PGE, particularly Pt and Pd, also appear to be mobile. Unfortunately, the lack of similar data for the lower oceanic crust and the question whether Hole 504B is representative of altered crust in general limit our ability to calculate fluxes to and from oceanic crust. Global mass balances for Re and Os place limits on the average gain of Re and gain/loss of Os during alteration of oceanic crust. If hydrogenous Re were quantitatively added to oceanic crust, the crustal Re inventory would increase by less than 1%. Up to 5 ppt of hydrogenous Os could be added to oceanic crust if alteration of oceanic crust were the only sink of hydrogenousOs. Conversely, oceanic crust could lose up to 1.5 ppt unradiogenic Os if hydrothermal alteration of oceanic crust were the only source of unradiogenic Os to seawater. Additional studies of deep sections through oceanic crust are needed to test whether the trends observed in Hole 504B are representative.