

The volatile content of subduction zone melts and fluids

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Harzburgite xenoliths from the andesitic Avacha volcano (Kamchatka, Russia) contain two types of spinel-hosted melt inclusions: (a) high-T inclusions (homogenized at 1200°C) containing $\text{opx} \pm \text{cpx} + \text{glass}$ and (b) low-T inclusions (homogenized at 900°C) containing $\text{amph} \pm \text{sulf} + \text{glass}$. Homogeneous glass in the high-T inclusions is similar in major element composition to basaltic andesite experimentally produced by high-degree, hydrous melting of peridotite [1]. Homogeneous glass in the low-T inclusions is silica oversaturated, Al- and Ca-rich, enriched in LREE_N and LILE_N relative to MREE_N - HREE_N ; it displays a strong slab-related chemical overprint. The xenoliths also contain melt pockets originating from local, fluid-assisted melting, produced shortly before the entrapment of the xenoliths.

We analyzed the volatile content of melt inclusions and pockets by Secondary-Ion Mass Spectrometry (SIMS) with Cameca IMS 1280. Most inclusions contain much more CO_2 and H_2O than predicted by saturation curves for these species in silicate melt at 600 bar, implying that the melt entrapment occurred at mantle depth. High-T inclusions have 0.20 ± 0.02 wt.% CO_2 , 2.05 ± 0.01 wt.% H_2O and 130 ± 1 ppm S. Low-T inclusions display a wide range of CO_2 (0.01 - 0.57 ± 0.01 wt.%) and H_2O (0.86 - 7.45 ± 0.02 wt.%). The abundances of CO_2 and H_2O are positively correlated. The low-T inclusions define also an F-enrichment trend (from 50 to 672 ± 5 ppm) with less variable Cl (540 - 759 ± 14 ppm) and are strongly enriched in S (up to 0.59 wt.%). Glass in the melt pockets has the lowest CO_2 and H_2O contents (respectively $\leq 0.03 \pm 0.01$ and $\leq 1.58 \pm 0.02$ wt.%). The $\delta^{34}\text{S}$ range of $+7.0$ to $+11.0\text{‰}$ ($\pm 0.6\text{‰}$, 2σ) in the melt inclusions indicates the presence of heavy oxidized sulfur, likely with surface provenance [2].

The results suggest and/or confirm that (1) the high-T inclusions trapped a mantle-derived primary melt, (2) the low-T inclusions are produced by polybaric entrapment of fluid-rich, hydrous melts in the lithospheric mantle; and provide the first “in situ” evidence for volatile recycling in the lithospheric mantle above a subducting slab.

[1] Grove *et al.* (2003) *CMP* **145**, 515-533. [2] Shimizu, N. *et al.* (2010) *GCA* **74** (S1), A953.

Laser-induced photo-luminescence spectroscopies: Probes for sulfide crystal-chemistry

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We combine Two-Photon Fluorescence (TPF), Confocal Laser Scanning Microscopy (CLSM) and Confocal Laser-Induced Luminescence (LIL) to acquire 2-D and 3-D-resolved luminescence emission spectra from transition metal- and (Ca, REE)-bearing mantle-derived and meteoritic (enstatite chondrite) sulfides. The latter include primary condensates and high-degree metamorphic crystals. A wide range of excitation λ (442-800 nm) is tested; Raman microspectrometry adds qualitative constraints on sulfide crystallinity. Despite the small amount of luminescence emitted by the sulfides, TPF and CLSM are sensitive enough to perform 3-D imaging with a resolution of ~ 0.5 μm laterally and ~ 5 μm axially, in particular using Near Infra-Red (NIR) femtosecond excitation (TPF). Versatile confocal microscopes allow to scan collected luminescence with a 20 nm spectral window to record spectra of roughly 10×10 μm regions of interest.

All sulfides emit a characteristic band at 710 nm under TPF NIR radiation that can be related to the sulfur $3s\sigma$ state [1]; its increased sharpness may be due to higher crystallinity degree. Pyrrhotite has a continuous emission along a broad λ range (400-710 nm) that allows to distinguish it both from lower temperature, NiAs-type monosulfide polymorphs with two individualized Gaussian-shaped bands (centered at 460 and 650 nm) and troilite (one major band at 710 nm). We seek to identify *4d*- and *5d*-metal monosulfide heterogeneities (PtS and PdS clusters) with the super-resolution of the TPF.

Under a 633 nm LIL excitation, CaS emits the 710 nm band characteristic of sulfur while below 442 nm, the *4f* and *5d*-derived levels of $^{14}\text{Ce}^{3+}$ are excited with the appearance of the $\Gamma_8(^2T_{2g}) \rightarrow ^2F(\Gamma_7, \Gamma_8(^2F_{5/2}); \Gamma_6, \Gamma_7, \Gamma_8(^2F_{7/2}))$ transitions. With the use of point charge crystal-field modelling at constant Ce valency, we infer a direct correlation of the *5d* orbitals (t_{2g} - e_g set) splitting parameter Δ_0 to the CaS lattice spacing, controlling in turn Ce partitioning. We investigate REE fluorescence mapping with the TPF super-resolution.

[1] Raybaud *et al.* (1998) *JPCM* **9**, 11085-11106.