

High sensitivity laser ablation MC-ICP-MS

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The Thermo Scientific NEPTUNE *Plus* MC-ICP-MS with Jet Interface option has previously been demonstrated to offer the highest ICP-MS analyte sensitivities for desolvated solutions [1] and for laser ablation [2]. A combination of nitrogen addition, special cones and a high capacity interface pump improved laser ablation Hf sensitivity by a factor of more than seven. The resulting sensitivity enabled highly precise and accurate ¹⁷⁶Hf/¹⁷⁷Hf isotope ratios to be measured from zircon 91500 using 25 µm diameter laser ablation spots, whereas typically 100 ppm 2σ external precision is only achieved using 50 µm diameter spots (with four times the ablated volume). It was noted that with increased sensitivity the Yb and Hf fractionation factors diverge further, highlighting the importance of independent measurement of the Yb fractionation factor used for the ¹⁷⁶Yb correction.

For these experiments a Photon Machines Analyte.G2 193 nm laser ablation system was operated with moderate fluence and repetition rate (6.22 J/cm² at 7 Hz). The short pulse width and short wavelength of this excimer laser ablation system is ideal for ablation of zircon mineral grains. The Analyte.G2 is equipped with a two-volume HELEX 2 cell for the fastest washout time. The combination of improved ICP-MS sensitivity and fast response laser ablation cell is critical for the emerging field of 'geochron, imaging' by LA-ICP-MS.

In this study we investigate the factors that influence external precision of ¹⁷⁶Hf/¹⁷⁷Hf isotope ratios from zircons, including the effects of nitrogen addition on analyte sensitivity and mass bias stability. We also describe a new multi-ion counting collector configuration that has been designed for the Thermo Scientific NEPTUNE *Plus*. This allows for increased flexibility of analysis, using combinations of ion counters and Faraday cups to accommodate the range of U-Pb isotope beam intensities expected from both young and old zircons.

[1] Bouman et al (2009) *Geochim. Cosmochim. Acta* **73**(13, Supplement 1), A147. [2] Lloyd et al. (2011) *Min. Mag.* **75**(3), 1351.

Setting and Styles of Hydrothermal Mudstones near the Lemarchant volcanogenic massive sulfide deposit, Newfoundland Appalachians.

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In some volcanogenic massive sulfide (VMS) deposits there is a close association of black shales and hydrothermal mudstones and massive sulfide mineralization, yet our understanding of the relationship of these muds to VMS deposit genesis and exploration is incomplete. The Lemarchant VMS deposit, Central Mobile Belt, Newfoundland Appalachians, Canada, is an excellent location to study the relationship of black shales/hydrothermal muds to VMS mineralization because there is an intimate relationship between precious-metal bearing Zn-Pb-Cu sulfides and hydrothermal sedimentary rocks. The Lemarchant VMS deposit is hosted by the late Cambrian Tally Pond volcanic belt and represents a bimodal felsic VMS deposit with a typical stratigraphic sequence consisting of rhyolite domes and/or breccias with a stockwork stringer zone, overlain by the massive sulfides, one or more barite bed(s), and capped by hydrothermal sediments/mudstones. Mafic volcanic flows, predominantly pillowed basalts, are deposited on top of this sequence and represent a new cycle of volcanic activity. Metalliferous mudstones represent a hiatus in this volcanic activity, where the deposition of hydrothermal matter dominates over the abiogenic pelagic background sedimentation. These hydrothermal sediments comprise brown to black graphite-rich mudstones and fine laminated shales, which can be intercalated by siliclastic and/or kidney-shaped chert layers as well as by fine layers of organic matter. The main sulfide phases are pyrite and pyrrhotite plus minor amounts of chalcopyrite, sphalerite, arsenopyrite and galena. Pyrite mostly occurs as diagenetic euhedral grains or as framboids, whereas pyrrhotite forms fine granulates or irregular shaped grains to massive grains that infill veins.

Preliminary lithogeochemical results illustrate that relative to upper crust normal shales, the hydrothermal sedimentary rocks have anomalous base and precious metals, volatile metals (e.g., Tl, Sb), high Fe/Al ratios, variable Ce/Ce*, Y/Ho ~27, and have Eu/Eu* ≥ 1, indicative of deposition from reduced, hot hydrothermal fluids with only a minor detrital input. Ongoing research includes detailed mineralogical-petrographical studies of the sulfides, additional whole-rock lithogeochemical analyses, and sulfur isotope geochemistry. The research is aimed at understanding both the role that basin redox conditions has on the genesis of the Lemarchant deposit, discriminating the relative contributions of hydrothermal, detrital or hydrogenous (seawater-derived) materials in the genesis of the shales, distinguishing between hydrothermal, diagenetic and biological sulfur sources in the sediments, and utilizing the latter to create potential exploration vectors at Lemarchant and for other shale-associated VMS systems.