

Carbon in ancient serpentinite-hosted hydrothermal systems: The northern Apennine ophiolites (Italy) and the Iberian Margin

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Exposure of ultramafic rocks on the ocean floor often leads to serpentinization and carbonate precipitation, which plays an important role in the global marine bio-geochemical cycles. The Lost City Hydrothermal Field (LCHF) is as yet the only known example of an active, low temperature system driven by serpentinization processes. Its serpentinite basement, cut by a network of calcite veins, is remarkably similar to ophiolites in ophiolite sequences. Here we present a carbon geochemical study comparing Lost City with ancient systems at the Iberian margin (ODP Leg 149) and in ophiolites from Liguria (northern Apennines, Italy). Petrographic studies and analyses of C and O isotopes, as well as C contents have been conducted on serpentinites and calcite veins to better understand physical and chemical conditions during serpentinization and to determine the origin of carbon and possible links to microbial activity in these systems.

Samples from Leg 149 show distinct changes with depth: total C contents (TC) are dominated by carbonate at the top of the serpentinite unit and strongly decrease with depth. This change corresponds to a shift from more positive $\delta^{13}\text{C}_{\text{TC}}$ to strongly negative values downhole. This trend, as well as $\delta^{13}\text{C}$ of total inorganic C (TIC) of -2 to +2‰ indicates a decrease in seawater penetration and marine carbonate precipitation with depth. However, $\delta^{18}\text{O}_{\text{TIC}}$ show no distinct trends and correspond to relatively constant T of <20°C. The Ligurian ophiolites show similar marine $\delta^{13}\text{C}_{\text{TIC}}$ but have $\delta^{18}\text{O}_{\text{TIC}}$ that vary with vein type and which record carbonate precipitation temperatures (up to 150°C), similar to the serpentinization temperatures at the Iberian margin. Total organic carbon (TOC), calculated from TC and TIC, are up to 4000 ppm in the Iberian Margin serpentinites and are considerably lower in the Ligurian ophiolites (up to 250 ppm). Values of $\delta^{13}\text{C}_{\text{TOC}}$ from both localities generally lie within a narrow range of -28 to -24‰, suggesting the presence of organic matter. The range in C compositions and a dominance of depleted C isotope compositions is similar to trends in serpentinites from Lost City and indicates that organic carbon is an important component of the carbon budget in marine serpentinites, regardless of the tectonic setting.

Simultaneous *in situ* analysis of U-Pb age and Hf isotopes of zircon by laser ablation sector-field (MC-) ICP-MS

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In situ analysis of U-Th-Pb-Hf isotope systematics is a powerful tool for tracking a variety of magmatic/metamorphic/sedimentary processes, and can give deep insight into the growth and recycling history of Earth's crust. Due to its refractory nature, zircon shows complex internal structure reflecting growth, recrystallization and/or alteration during multiple thermal events. These complexities are not always easily unravelled and misleading results can be obtained when ablated material used for U-Th-Pb age dating and Hf isotope composition analyses is not sampled from exactly the same volume. Because of the small sizes of individual growth domains and of single grains, this can be the case when Hf isotopes are analysed subsequently to U-Th-Pb during independent measurements at different laser spots.

In order to overcome the limitations of sequential sampling of U-Th-Pb and Lu-Hf isotopes from different spots, a fast scanning single collector and a multi-collector inductive coupled plasma-mass spectrometer have been coupled in parallel to a 213nm UV laser ablation system. A low-volume laser ablation sample chamber with fast response (< 1s) and rapid wash-out time was used to enable sequential sampling of heterogeneous grains during time-resolved data acquisition. The ablated material was transported in helium, split after the ablation cell via a Y-shaped connector and introduced simultaneously into the two mass spectrometers, the ThermoScientific Element 2 for U-Th-Pb analysis and ThermoScientific Neptune for high precision Lu-Hf isotope analysis.

The complete analytical protocol lasted for ~1 min with ~30s sample ablation and was tested with laser spot sizes of 30, 40, 60, and 80µm. Depth penetration was ~30µm and wash-out time <5 s allowed up to 30-50 analyses per hour. Accuracy and reproducibility of the applied method were evaluated by multiple analyses of reference zircons GJ-1, Temora, 91500, QGN, AS3, Mud Tank, and Plešovice.