

## Stability of garnets to chemical weathering: An experimental study

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### Introduction

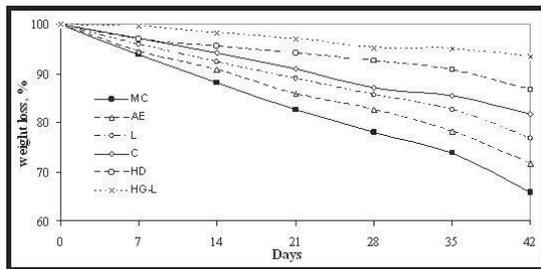
Garnets from kimberlites, mainly pyropes, are unstable to lateritic weathering and dissolve to produce distinct surface patterns [1]. Low-Cr orange garnets are less stable than Cr-rich violet varieties, this being a control for trends in placer pyrope assemblages changing away from the primary deposit. The naturally occurring patterns were reproduced in earlier HF etching experiments on pyropes with monitored weight loss. However, those experiments did not include analysis of composition changes in etched pyropes.

### Methods and samples

The chemical stability of garnets from kimberlite has been studied in new experiments in which etching in HF was a good model of natural lateritic weathering. We used 226 pyrope grains of main kimberlite-hosted pyrope varieties. The work included weight loss monitoring and analysis of chemistry and parageneses of the output grains.

### Results and Conclusion

The etching experiments demonstrated different degrees of chemical stability in garnets of different parageneses, as a function of Cr contents (Fig. 1).



**Fig. 1.** Stability (weight loss) of garnets to etching in HF. The curves are coded according to assemblages of garnets: MC – megacrysts, AE – wehrilite, L – high-temperature depleted lherzolite, C – normal depleted lherzolite, HD – harzburgite-dunite, HG-L – TiO<sub>2</sub>-rich harzburgite-dunite.

The experimental results are well consistent with data from natural pyrope assemblages, specifically, from unweathered pyropes of the Mir kimberlite compared to the weathered ones in the Vodorazdelny Galechniki (Watershed pebble) placer derived from the same pipe.

### References

[1] Afanasiev V.P., Zinchuk N.N., Pokhilenko N.P. (2010) *Mineralogy for Diamond Exploration*. GEO Publishers, Novosibirsk (in Russian), 650 p.

## Clumped isotopes role in a multi-proxy paleoclimate reconstruction

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Carbonate clumped isotopes ( $\Delta_{47}$ ) is a temperature proxy that is based on the temperature-dependent preference of <sup>13</sup>C and <sup>18</sup>O to bond with each other.  $\Delta_{47}$  of biogenic calcite and aragonite in aquatic organisms (with the exception of fast growing, shallow-water corals) is consistent with a calibration based on laboratory precipitation. Being a thermodynamically controlled proxy that does not depend, at equilibrium, on the composition of the solution in which the carbonate forms,  $\Delta_{47}$ -based temperatures are better constrained than those from inorganic proxies such as  $\delta^{18}\text{O}$  and Mg/Ca. It is also better understood than organic proxies such as TEX<sub>86</sub> that rely on uncertain biological assumptions and unclear calibration. The main disadvantage is the large sample size required, preventing in most cases high-resolution  $\Delta_{47}$  records. In a multi-proxy approach, clumped isotopes could play a role in high-resolution records, by providing absolute temperatures (and hence water compositions) that are required to constrain the assumptions in other proxies.

We applied clumped isotopes in bivalve shells in concert with the organic temperature proxy TEX<sub>86</sub> during the Eocene in the Gulf of Mexico and in Seymour Island (Antarctica). Clumped isotope temperatures are consistent with TEX<sub>86</sub> estimates, although the TEX<sub>86</sub> calibration that provides the best fit with clumped isotope results varies between high and low latitude environments.

Being independent of the composition of water,  $\Delta_{47}$  based temperatures can be used to reconstruct water  $\delta^{18}\text{O}$ , often using laboratory precipitation experiments for calibration [1]. However, such laboratory measurements involve relatively fast mineral growth, leading to potential disequilibrium. Calcite growing at an extremely slow rate in Devils Hole (Nevada) is likely to reflect formation under isotopic equilibrium, thus providing a test for the laboratory-based calibrations.  $\Delta_{47}$  results from Devils Hole calcite yield a constant paleo-water temperature, during both glacial and interglacial periods over the last 180 Ky; it agrees with the modern-day groundwater temperature and confirms that the calcite precipitated at isotopic equilibrium. However,  $\delta^{18}\text{O}$  is significantly enriched in Holocene calcite as compared to laboratory precipitation calibration [2]. We attribute this difference to the preferential incorporation of light oxygen isotopes during fast mineral growth in laboratory experiments (but not in slow growing Devils Hole calcite), without affecting the <sup>13</sup>C-<sup>18</sup>O distribution that is reflected in  $\Delta_{47}$ .

[1] Kim and O'Neil (1997) *Geochim. Cosmochim. Acta* **61**, 3461.

[2] Coplen (2007) *Geochim. Cosmochim. Acta* **71**, 3948.