## Extreme Hf isotope signals from basement weathering and its influence on the seawater Hf-Nd isotope array

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Differential weathering of Lu and Hf host minerals in rocks leads to Hf isotope composition of river water with a more radiogenic composition than the bulk rock that they drain [1]. In contrast, the Nd isotope composition of river water is very similar to that of bulk rock due to congruent weathering of Sm and Nd from their shared mineral hosts. We measured Hf and Nd isotope ratios in seawater and from the Hudson River in NY. The Hf isotopic composition of the upper Hudson draining Grenville-aged metamorphic rocks is extreme, with  $\varepsilon_{Hf}$  values of +24 to +128. Associated marble and amphibolite bedrock have normal crustal  $\varepsilon_{Hf}$  values (0 to -11), whereas apatite and garnet from these rocks have  $\varepsilon_{\rm Hf}$ values as high as +2250 and +103 [2,3]. In contrast, Nd compositions of the upper Hudson are similar to bulk rocks  $(\varepsilon_{Nd} = -8)$ . After the Mohawk River, which drains Ordovician-Devonian limestone and shale, joins the main stem of the Hudson, river water  $\epsilon_{Hf}$  and  $\epsilon_{Nd}$  decrease to +6 and -10. On the New Jersey Bight,  $\varepsilon_{Hf}$  and  $\varepsilon_{Nd}$  are +3 and -8.

The Hf and Nd isotope composition of filtered seawater in the Atlantic overlap data for ferromanganese nodule crusts. Vertical profiles exhibit almost negligible  $\varepsilon_{Hf}$  gradients suggesting rapid vertical, but little lateral, transport. Surface water  $\varepsilon_{Hf}$  is less radiogenic close to the Saharan dust plume suggesting an eolian source of Hf with a signal that is not fractionated through weathering processes.

We suggest that the radiogenic Hf character of the seawater Hf-Nd array is due to the preferential weathering of high Lu/Hf phases in basement rocks such as apatite. When this source rock is old evolved crust, dissolution of these high Lu/Hf phases contributes a very radiogenic Hf isotope composition, as evidenced by the upper Hudson river water samples. This differential chemical weathering will be prominent at times when there are no glaciers, and particularly prominent when glacial action has exposed fresh surfaces containing less resistant minerals to weathering [4].

## References

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## The source and fate of silica in mineralized porphyries revealed by SEM-CL textures of quartz

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Economic mineralization in porphyry systems (e.g., Cu-Mo-Au) is traditionally attributed to precipitation from metal-enriched hydrothermal fluids that derive at the closure of crystallization of andesite-dacite magmas. Different forms of silica (mainly quartz) are dominant in such systems, and thus controversial in terms of silica solubility in aqueous solutions, amounts of magmatic  $H_2O$ , and rates of the fluid flow. The compositions of mineralizing fluids, as argued by the fluid inclusion research, are dominantly chloridic and often halite-saturated, and thus the absence of chloride minerals precipitated with ores remains enigmatic.

We studied shapes and textures (by optical, cathodoluminescence-CL and backscattered electron-BSE microscopy) of quartz grains, and distribution of quartz-hosted fluid inclusions in different porphyries (Batu Hijao, Indonesia; Climax, USA; Panguna, PNG; Dinkidi, Philippines; Rio Blanco, Chile). Silica (analyzed as SiO<sub>2</sub>) is present throughout the groundmass as interconnected network of shapeless blebs and individual quartz grains (0.2-2 mm). Most quartz grains are round or even spherical in shape (so-called "quartz eyes"), and have distinct zoning or layering in CL. The number of layers/ bands varies from a few to several tens, and have shapes from nebulous to ellipsoidal to perfect crystallographic. Egg-like and crystallographic shapes of layers are found interspersed within a single grain. The bands are randomly intersected by healed fractures (usually dark in CL), which are always decorated by aqueous  $\pm$  salts fluid inclusions. The fractures often cause rupture, displacement and inflection of some bands towards the core of grains. Where large fractures intersect the grain surface the outmost bands are spit and curved towards the fracture. The splits are conical in shape and filled with the groundmass. Although such splits look like typical embayments, the curved banding around them is inconsistent with quartz dissolution. The fractures in split grains often border several domains with individual solidification history. In many cases crystallization from internal fracture or from the outermost boundary of the quartz grain can be implied from the observed banding.

The textures of quartz grains are inconsistent with their origin as phenocrysts. We envisage in-situ segregation of residual  $SiO_2$ - and  $H_2O$  rich liquid (e.g. silica-gel) into blebs and globules after magma emplacement. The solidification of globules was unlike crystallization, as they were developing coeval banding and fractures (possibly as a result of compaction). They possibly remained in a plastic state even at low temperatures, when healing of fractures and trapping of fluid inclusions occurred.