

## Geochemistry of the Arctic Loki's Castle hydrothermal vent products

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Loki's Castle is the northernmost hydrothermal vent field known to date in the Arctic Ocean [1]. It is located in the junction between the Monhs and Knipovich Ridge, an ultra-slow spreading center at a rate of 17mm/year [2]. ROV-collected samples of chimney fragments and their surrounding deposits revealed to be mostly composed of sphalerite, chalcopyrite, pyrite and anhydrite, their maximum metal contents for Fe 31wt%, for Zn 5.4wt% and for Cu >1wt%. The surrounding sediments contain a significant hydrothermal component, denounced by high metal contents that average 4.6 wt% Fe, 100 ppm Zn and 33 ppm Cu. Sediments from the same area collected at depth by gravity cores show equally high average metal contents; although the Cu and Zn enrichment may be more prominent in particular layers reaching 446 ppm Zn and 128 ppm Cu. The REE sediment patterns mimic those of the North American Shale Composite [3]. Major and trace element geochemistry of the less altered volcanic rock fragments collected near the vent field allows their classification as tholeiitic basalts.

[1] Pedersen, R.B., *et al.*, (2010) Discovery of a black smoker vent field and vent fauna at the Arctic Mid-Ocean Ridge. *Nat Commun.*, **1**(8): p. 126. [2] Peive, A.A. and N.P. Chamov, (2008) Basic tectonic features of the Knipovich Ridge (North Atlantic) and its neotectonic evolution *Geotectonics.*, **42** (Number 1): p. 7. [3] Gromet, L.P., *et al.*, (1984) The "North American shale composite": Its compilation, major and trace element characteristics. *Geochimica et Cosmochimica Acta*, **48**: p. 2469-2482.

## Metamorphic reaction rates from diffusion of Nb in rutile

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Determining the timescales over which metamorphic reactions occur has long been an important and difficult question to answer. Here we examine rutile replacement by titanite in a migmatized garnet amphibolite from Catalina Island, CA, and compare the data to results from an amphibolitized eclogite from Tromsø, Norway. We estimate the timescales and rates of the rutile-to-titanite reaction by fitting models of Nb back-diffusion during titanite replacement to measured Nb profiles in rutile.

Trace element concentrations in rutile and titanite were determined by LA-ICP-MS for grains from Catalina. Niobium profiles across two rutile grains show clear evidence for Nb back-diffusion into rutile during titanite growth at the grain boundary (from 2280 to 3050 ppm over 350  $\mu\text{m}$ ). The same feature was reported and modeled by Lucassen *et al.* [1] for Nb and Zr in a 7 mm rutile from Tromsø. Zr-in-titanite thermometry suggests 740-770°C for Catalina and 650-730°C for Tromsø. New experimentally-determined diffusion coefficients for Nb in rutile (R. Dohmen, pers. comm.) were used to model Nb diffusion in the Catalina rutile, and to revisit the Tromsø sample in light of the new diffusion data.

A simple 1-D moving interface diffusion model yields reaction front velocities, which were converted to rates using the distance the boundary had moved relative to the pre-reaction rutile surface. Reaction rates of  $0.2\text{--}2.0 \times 10^{-6} \text{ a}^{-1}$  were determined for Catalina, and  $0.03\text{--}4.99 \times 10^{-8} \text{ a}^{-1}$  for Tromsø. Reaction rates were then normalized to the surface area of the rate-limiting mineral per unit of rock (Rnet, g/cm<sup>2</sup>/a). Normalized reaction rates for Catalina are  $0.18\text{--}1.42 \times 10^{-5} \text{ g/cm}^2/\text{a}$  and for Tromsø are  $0.04\text{--}5.82 \times 10^{-7} \text{ g/cm}^2/\text{a}$ , which suggests 2-3 orders of magnitude difference in Rnet over  $\sim 120^\circ\text{C}$  change in temperature for the rutile-titanite reaction. Reaction rates for the Tromsø sample are consistent with those previously determined for regional metamorphism, whereas the Catalina reaction rates fall between those reported for regional and contact metamorphic settings [2]. This observation is consistent with the presence of free fluid or melt during subduction-related metamorphism.

[1] Lucassen *et al.* (2010) *Cont. Min. Pet.* **160**, 279-295. [2] Baxter (2003) *Geol. Soc. Lon. Spec. Pub.* **220**, 183-202.