

The evolution of a serpentinizing environment inferred from andradite vein networks

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Serpentinization of the oceanic lithosphere produces a unique geochemical environment. Vein networks from the Feragen Ultramafic Body (Norway) provide new insight into the evolution of a serpentinizing system and the critical role of ortho- and clinopyroxene. The veins are composed of polyhedral serpentine spheres, botryoidal andradite spheres, ferroan brucite, and awaruite. By combining X-ray fluorescence mapping and reactive transport modeling we illustrate how Ca from the dissolving clinopyroxene serves as a proxy for the determination of the system's geochemical evolution. Crystal morphology analysis allows us to infer that stagnant fluid domains were present during vein formation. Microtomography reveals that isolated andradite spheres float in a serpentine matrix within the vein. Calculated particle settling velocity in the vein indicates that rapid crystallization or a gel-type framework prevented the andradite spheres from descending to the vein walls. We infer that the required geochemical conditions, in terms of silica activity and redox conditions were short-lived and vein minerals precipitated rapidly once critical supersaturation was reached. Our observations have implication for the lifetime of the distinct geochemical conditions within a serpentinizing environment.

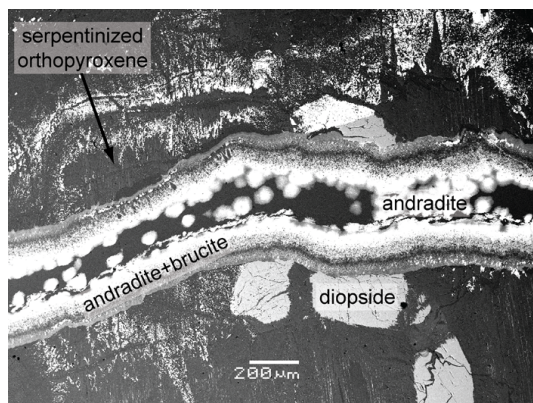


Figure 1: Andradite vein within a meta-harzburgite inter-layering meta-dunite.

Se isotope evidence for atmospheric oxidation at ~0.6 Ga

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It is generally thought that atmospheric O₂ levels rose irreversibly twice during Earth history, with the 2nd rise at ~0.8-0.6 Ga [1]. However, the magnitude of the O₂ increase is unclear (estimates range between ~10–100% of the present level), and the specific causes and consequences are uncertain. Knowledge of redox change is fundamental for our understanding of biological evolution and climate systems, because redox constrains the development of a modern biogeochemical cycle. Here we explore the 2nd O₂ rise, using the novel tracer of selenium (Se) isotopes.

Se is a micronutrient. It is strongly redox-dependent and chemically similar to sulphur (S). However, its redox reactions occur at different Eh-pH from S, and therefore Se can provide additional constraints on global redox transitions [2]. Se isotopes are significantly fractionated by microbial reduction, and the degree of fractionation likely depends on atmospheric O₂ in a way similar to S isotopes. This is because when little O₂ is present, microbes will utilise all isotopes, whereas as O₂ increases, more fractionation will occur.

We have analysed Se isotopes in black shales spanning the time of the 2nd O₂ rise, from the Yangtze Platform and the Mackenzie Mountains. Se concentrations in the shales range from the lowest levels so far recorded in shales [3], and show an increase of ~2 orders of magnitude (from 0.02-0.1 to ~10 μg/g), with the highest concentrations in the most recent shales. An overall increase in oceanic Se is consistent with greater supply via oxidative weathering and less hydrothermal scavenging into seafloor selenides once the deep ocean becomes fully oxic. Se isotope ratios in the same samples (δ^{82/76}Se) show a negative excursion of >6‰ across the same period, with a correlated trend of Se and δ⁸²Se. These characteristics suggest that the O₂ content of the atmosphere rapidly increased, providing more selenate and nutrients to the oceans via chemical weathering, allowing microbial reduction to fractionate Se isotopes to a greater degree.

[1] Catling & Claire (2005) *EPSL*, **237**, 1–20. [2] Johnson & Bullen (2004) *Reviews Min. Geochem.* **55**, 289–317. [3] Wen & Carignan (2011) *GCA* **75**, 1411–1427.