

Buried ikaite precipitates in Antarctic sediments: Are they fossil indicators of microbial sulfate reduction or AOM?

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Ikaite is a calcium carbonate hexahydrate ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) formed at low temperature and high concentration of dissolved inorganic carbon (DIC) in organic-rich sediments [1]. Two microbial processes, bacterial sulfate reduction of organic matter and anaerobic methane oxidation (AOM) by archaeal/bacterial consortia can trigger ikaite precipitation by increasing DIC concentration. To determine which of these processes may contribute to ikaite formation, we studied a 500-cm sediment core from the northern Antarctic Peninsula that contained 4 large ikaite crystals ($\sim 50 \text{ cm}^3$ each) at depths > 300 cm. Apolar (fossil) lipids were extracted from six sediment horizons: at the surface, within the modern sulfate-methane transition zone (85 cm), and the four horizons where ikaite was found (304, 454, 480 and 505 cm). Stable carbon isotopic compositions of bacterial fatty acids (FA), and archaeal biphytanes (BP), archaeol (AR), and hydroxy-archaeol (OH-AR) were analyzed. $\delta^{13}\text{C}$ values of FA and BP ranged from -30‰ to -20‰ (ave = -23 ± 2.3 ‰) from the six sample horizons. AR and OH-AR was extracted from the same horizons, but isotope values were only measurable at the 454 and 500-cm horizons due to low concentrations. In these two horizons, AR was depleted in ^{13}C (ave = -49‰) as well as OH-AR (ave = -87‰). The ^{13}C -enriched values of C_{15-18} FA (bacterial markers for AOM) and of BP (archaeal marker for AOM) suggest they are not derived from AOM because lipids derived from AOM are significantly depleted (-110‰ to -60‰) [2,3]. Although the ^{13}C -depleted AR and OH-AR can from AOM related Archea, they could be also from methanogenic Archaea [4]. $\delta^{13}\text{C}$ in ikaite, DIC and methane will provide a scope on ancient carbon flow and help to reveal ancient microbial activities contributed ikaite formation.

[1] Suess (1982) *Science* **216**, 1128-1131. [2] Elvert (2003) *Geomicrobiology Journal* **20**, 403-419. [3] Hinrichs (1999) *Nature* **398**, 802-805. [4] Londry (2008) *Organic Geochemistry* **39**, 608-621.

Boron and sulfur isotopic variations during subduction of hydrated lithosphere: The Erro Tobbio case

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Exhumed high-pressure serpentinites provide unique opportunities for advancing our understanding of geochemical changes in hydrated lithosphere during subduction and deep recycling of elements. The Erro Tobbio serpentinitized peridotites represent Jurassic oceanic lithosphere which underwent low-T hydration ($T < 300^\circ\text{C}$) followed by high-T serpentinitization and recrystallization at $\sim 550^\circ\text{C}$, 2 – 2.5 GPa during Alpine subduction. Covariations observed for whole-rock δD , $\delta^{18}\text{O}$, Sr, and H_2O indicate that hydration continued at high temperatures, placing the Erro Tobbio massif in the mantle wedge. During hydration whole-rock boron concentrations varied from 10 to 32 ppm with $\delta^{11}\text{B}$ from +3.8 to +23‰ for low-T serpentinites, and from 12 to 36 ppm with $\delta^{11}\text{B}$ from +17 to +24‰ for high-T rocks. In-situ analysis of sulfur isotopic composition of individual sulfide grains (pentlandite with minor heazlewoodite) has revealed that $\delta^{34}\text{S}$ varies from -2.5 to +4‰ for low-T rocks, consistent with whole-rock data (Alt *et al.*, 2012), while high-T rocks display a much larger range in $\delta^{34}\text{S}$ from -2 to +18‰ with significant increases in modal sulphide. B isotopes, S isotopes, and other geochemical variations observed for the Erro Tobbio peridotites suggest that hydration and mass transfer from slab to wedge occurred at relatively shallow level, resulting in the formation of hydrated mantle wedge with high $\delta^{11}\text{B}$, high $\delta^{34}\text{S}$, enrichment in B, Sr, and other fluid-mobile elements, suitable for the sources for arc magmas and heterogeneous sources for MORB and OIB.