

## Metal micronutrients for anaerobic oxidation of methane

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Methane is produced and consumed by microbes via metabolic pathways that involve metalloenzymes [1]. Our focus is trace metal requirements for anaerobic oxidation of methane (AOM) performed by microbial consortia of sulfate-reducing bacteria (SRB) and anaerobic methanotrophic euryarcheota (ANME) in marine methane seep sediments, where porewaters are highly sulfidic (up to 25 mM HS<sup>-</sup>) and scavenging by sulfide mineral precipitation may reduce the availability of bioessential metals.

Using both metagenomic and metaproteomic data, we are characterizing the “metallome” of ANME/SRB consortia enriched from methane seep sediments. Iron-sulfur and heme-containing proteins are involved in reverse methanogenesis, sulfate reduction and the Wood-Ljungdahl carbon fixation pathway. Iron is likely transported by ferrous iron transporters in both symbiotic partners. Cobalt as vitamin B<sub>12</sub> is present in enzymes involved in reverse methanogenesis, carbon fixation and methionine synthesis. Genes for high-affinity cobalt uptake and vitamin B<sub>12</sub> biosynthesis are present in both symbiotic partners. Nickel as the tetrapyrrole cofactor F<sub>430</sub> and as Ni-Fe-S clusters is involved in reverse methanogenesis and carbon fixation, respectively. Molybdenum-iron nitrogenases [2] and molybdate (MoO<sub>4</sub><sup>2-</sup>) transporters are found in both partners, and a Mo or tungsten-containing enzyme is also involved in reverse methanogenesis.

Measurements of dissolved metal concentrations in methane seep sediment porewaters revealed that Co, Ni and Fe levels were below those required for optimal growth of cultured methanogens [1]. In contrast, dissolved Mo concentrations were generally high (~1 μM), suggesting that thiomolybdates (MoS<sub>4</sub><sup>2-</sup>) are soluble in these porewaters. The similarity in size and charge between MoS<sub>4</sub><sup>2-</sup> and MoO<sub>4</sub><sup>2-</sup> may allow anaerobes to transport both species through the same transporters. Results from incubation experiments using sediment with a well-characterized ANME/SRB population and low dissolved metals, designed to test if Fe, Co and Ni additions stimulate AOM activity and/or ANME/SRB growth, will also be presented.

[1] Glass and Orphan (2012) *Front. Microbiol.* **3**:61,1-20. [2] McGlynn *et al.* (2013) *Front. Microbiol.* **3**:419,1-8.

## A role for liquid immiscibility in granites and granodiorites

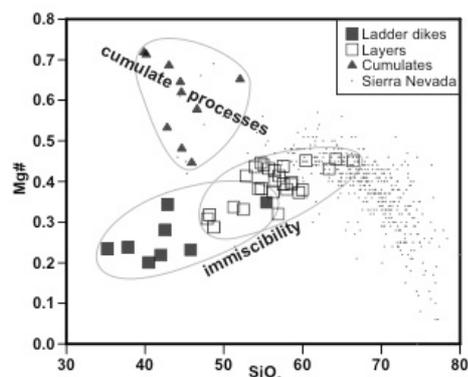
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Mafic segregations in granodioritic and granitic bodies, such as layered granodiorites (LGs) and ladder dikes (LDs), are typically interpreted to have formed by separation of mafic minerals from a more silicic magma body via processes such as gravitational settling and shear flow. In the Sierra Nevada of California and other examples, the whole-rock geochemistry and mineral chemistry of the mafic layers rule out such an interpretation and instead suggest that these layers are the heavily recrystallized products of liquid immiscibility.

LGs and LDs consist of high concentrations of biotite, hornblende, magnetite, titanite, apatite, and zircon, leading to extreme enrichments in REE, Fe, Zr, P, and Ti; Fe<sub>2</sub>O<sub>3</sub><sup>t</sup> in some LD mafic layers approaches 35 wt%, and La 1000x chondrite. LGs and LDs also have low Al and low Mg numbers (Fig. 1). These features require that the minerals in the layers were not derived from the surrounding pluton by crystal-liquid separation. Instead, they are consistent with crystallization from an Fe-rich immiscible liquid exsolved from high-silica liquid during the latter stages of crystallization. Although immiscibility is obscured in plutonic rocks owing to crystallization of the immiscible liquids, it has been proposed for several layered mafic complexes, and we suggest that it is a minor but widespread process in the late-stage evolution of granitic systems.



**Figure 1:** Mg number vs. SiO<sub>2</sub> for the Sierra Nevada batholith and occurrences of cumulate rocks, LDs, and LGs therein. LDs and LGs have much lower Mg numbers than cumulate rocks, consistent with immiscibility.