

Germanium incorporation into authigenic marine silicate minerals: an experimental approach

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As group IVA elements in the periodic table, Ge and Si are geochemically similar and behave in systematic ways relative to one another in many surficial environments. For this reason, much focus has been directed at developing Ge as a tracer for Si cycling. However, unequivocal application of the Ge proxy has been hampered by unknowns in the global Ge cycle, in particular the suggestion of additional, but unrecognised, marine Ge sinks.

Ge uptake from suboxic/anoxic marine sediment pore waters points strongly toward an early diagenetic Ge removal process [1-4]. The depositional and chemical conditions characterising these locations show a striking resemblance to those marked by diagenetic silicate formation (or reverse weathering), as previously suggested [5,6]. Here, we employ an experimental approach to test the hypothesis that reverse weathering and silicate diagenesis might remove Ge (disproportionately from Si) following opal dissolution in Fe-rich reducing marine sediments.

Our experiments are focused on Fe-rich layer silicate neof ormation from synthetic seawater as a function of pH, [SiO₂(aq)], [Fe] and [Ge]. Here, pH was buffered using the non-metal complexing MOPS buffer, and varied from 7.0-8.0. Experiments were prepared and executed in a glovebox maintained at O₂(g) < 1ppm, triply-wrapped in Al-foil and periodically sampled. Solids were filtered and air dried in the glovebox, and analysed by XRD (under glycerol), FT-IR (in the glovebox), and by TGA/DTA, and HR-TEM.

Results indicate that layer silicate nucleation is relatively rapid (on the order of weeks-months) and often involves the significant sequestration of Ge from solution. This suggests that reverse weathering-type reactions may represent an important Ge uptake mechanism, helping to reconcile Ge pore water studies and possibly bringing the Ge cycle a step closer towards mass balance.

[1] Murnane *et al* (1989) *GCA* **53**, 2873-2882 [2] Hammond *et al* (2000) *GCA* **64** (14), 2453-2465 [3] McManus *et al* (2003) *GCA* **67** (23), 4545-4557 [4] King *et al* (2000) *GCA* **64** (8), 1375-1390 [5] Froelich and King (1997) *EOS* **78**, F383 (abstr.). [6] Kurtz *et al* (2001) *Goldschmidt Conference*, Abstr. #3644