Systematics of water partitioning in damp mantle melting models

PAUL D. ASIMOW

Div. Geological & Planetary Sciences, California Institute of Technology, Pasadena, CA (asimow@caltech.edu)

In regions of the mantle where water is a trace species in the nominally anhydrous minerals (rather than a free vapor phase or a hydrous mineral), melting is controlled by water partitioning into melt and the resulting freezing-point depression. Modeling undersaturated melting therefore requires a well-constrained formalism for the bulk partition coefficient (D_{H2O}) and its variations, as well as an accurate model for hydrous melt-mineral equilibria. Hirth and Kohlstedt [1] developed a water partitioning model that leads to a solely pressure-dependent D_{H2O}. Their model expresses the *solubility* of H_2O in minerals and melts as a function of the *standard state fugacity* f°_{H2O} (linear for minerals, square root for melts). In the absence of data on undersaturated systems, they assume Henry's law, such that D_{H2O} is the ratio of solubilities, at any water content. Thermodynamically, however, one expects a square root dependence of H_2O content in the melt on the *actual water fugacity* ($f^{\circ}_{H2O} = a_{H2O} f^{\circ}_{H2O}$). This implies that D_{H2O} decreases with decreasing water content as $a^{1/2}_{H2O}$, approaching zero as the system dries out. The coupling of this partitioning model to pMELTS is the basis of one approach to damp mantle melting [2]. The prediction of a concentration-dependent D_{H2O} has some important but difficult-to-observe consequences (e.g., the removal of H_2O from the residue would be an accelerating process, leading to a more abrupt viscosity transition) but also makes the direct prediction that water should behave more compatibly in more-water rich systems. There has been considerable argument as to which is the most appropriate analogue trace element for water partitioning. Estimates have ranged from (as incompatible as) La in depleted MORB to (as compatible as) Nd in BABB [3], though Ce is presently a popular choice [4]. This variation can be a natural and systematic consequence of partitioning rather than a complex combination of source and process effects, and is due to the non-Henrian behavior of water in the melt rather than a pressure dependence. Direct mineral-melt water partitioning data from undersaturated experiments are needed to test this prediction.

References

[1] G. Hirth, D.L. Kohlstedt (1996) Earth and Planetary Science Letters 144, 93-108

[2] P.D. Asimow, C.H. Langmuir (2003) Nature 421, 815-820

[3] L.V. Danyushevsky, S.M. Eggins, T.J. Falloon, D.M. Christie (2000) Journal of Petrology 41 1329-1364

[4] P. Michael (1994) Earth and Planetary Science Letters 131, 301-320.

Isotopic ($\delta^{13}C$, $\delta^{15}N$) fractionation of organic matter during sorption to minerals

A. K. AUFDENKAMPE[1,2] J. I. HEDGES[2], P. D. QUAY[2] AND J. E. RICHEY[2]

[1] Stroud Water Research Center, 970 Spencer Rd., PA 19311, USA (aufdenkampe@stroudcenter.org)

[2] University of Washington, School of Oceanography, Seattle, WA 98195-5351

Introduction

The importance of organo-mineral associations in stabilizing organic carbon and nitrogen in soils, sediments and the marine water column have become increasingly appreciated over the last decade. However, relatively little attention is given to how sorption processes might affect or alter commonly used biochemical and isotopic compositional signatures relative to organic matter sources.

In an earlier study (Aufdenkampe et al. 2001), we show that sorption processes are responsible for the characteristic carbon-to-nitrogent (C/N) ratios (6-12), high amino acid contents (5-40% of OC and 10-70% N) and amino acid compositions (elevated basic and hydrophobic functional groups) of mineral-associated organic matter (OM) found in both sediments and soils. To follow up on these results, we conducted a set of experiments to examine whether other compositional signatures, such as $\delta^{13}C$ and $\delta^{15}N$, are affected by sorption under both sterile and microbially active conditions. To adequately characterize kinetic and equilibrium processes, more than 150 incubations were performed over a variety of dissolved OM concentrations and a range of time scales.

Results and Discussion

All experimentally sorbed OM exhbited isotopic signatures that were 1.5‰ to 2.4‰ enriched in ^{13}C and 2‰ to 4‰ enriched in ^{15}N relative to the initial dissolved OM. As previously, experimentally sorbed OM exhibited molar C/N ratios of 6 to 14 relative to a C/N of 24 for the parent dissolved OM. These patterns likely result from preferential sorption of proteins, which in general are isotopically enriched relative to the bulk OM and biomass of sources.

These findings are of substantial consequence to a wide range of biogeochemical applications. For example, a very common observation in pristine soils is a 2-3 ‰ increase in $\delta^{13}C$ with soil depth, yet possible explanations continue to be hotly debated in the literature. Given that these trends covary with increasing proportions with depth of mineral-associated OM versus low density detrital material, our results could help resolve the mechanisms for observed $\delta^{13}C$ profiles, which is critical to modeling carbon turnover rates in soils.

References

Aufdenkampe A.K., Hedges J.I., Richey J.E., Krusche A.V. and Llerena C.A., (2001). *Limnol. Ocean.* **46**, 1921-1935.