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Osmium isotopic compositions and PGE abundances in volcanic emissions from Masaya Volcano, Nicaragua

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Platinum Group Elements (PGE: Os, Ir, Rh, Ru, Pt, Pd) and osmium isotopes measured in marine and terrestrial sediment, snow and ice records are important paleo-tracers of riverine, hydrothermal, extraterrestrial, volcanic and anthropogenic inputs into the global surficial environment. To assess the volcanic contribution to the global Re-Os-PGE cycle we have initiated a study to measure Os isotopic compositions and PGE abundances in volcanic emissions from volcanoes around the globe. Here we report preliminary data on PGE abundances and Os isotopes measured in gas and aerosol filter samples from inside the Santiago Crater of the Masaya volcano in Nicaragua. Samples were collected in November 2003 and analyzed by isotope dilution, using single collector ICPMS (Finnigan ELEMENT 2) at WHOI. The $^{187}Os/^{188}Os$ compositions of the filters are unradiogenic (0.1291±0.0012 to 0.174±0.009, 2σ). Osmium concentrations range from 28 to 97 pg/m^3 and are 3-4 orders of magnitude lower than those measured by Krähenbühl et al. [1] during the spring 1984 eruption of Mauna Loa just after the "lava fountaining" phase. Normalized PGE abundance patterns are fractionated relative to carbonaceous chondrites and two important features distinguish the pattern from other important PGE sources: 1) The Os/Ir of 4.3 is much higher than that of the continental crust, mantle and extraterrestrial matter; 2) The Pt/Pd of 0.18 is much lower than that of the continental crust, mantle, extraterrestrial matter and catalytic converters (1-2.5). If this PGE pattern from Masaya is typical of volcanic emissions and no further fractionation occurs during transport, the distinct PGE pattern of volcanic aerosols could be used to distinguish between major sources of PGE in the surficial environment.

References

[1] Kräehenbüehl, U., et al. (1992) *Earth Planet. Sci. Lett.* **10**, 95-98.

3.4.21

Toward calculation of the thermodynamic stabilities of proteins in the deep biosphere

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Experimental and theoretical investigations of the thermodynamics of reactions involving proteins from organisms that live near the Earth's surface yield considerable insight into the stability of proteins and their interactions with other biomacromolecules under ambient conditions. However, little is known about their counterparts in the deep biosphere because relatively few thermodynamic data are available for the proteins that are crucial to the metabolism of thermophilic organisms known to thrive there. To augment the relatively sparse set of thermodynamic data for thermophilic proteins at high temperatures, an approach combining group additivity algorithms, correlations, and equations of state was used to calculate the standard molal thermodynamic properties of solid and aqueous proteins in the deep biosphere. Contributions to thermodynamic properties and equations-of-state parameters by protein backbone and sidechain groups were derived from recent high- and low-temperature experimental thermodynamic data reported in the literature for nearly 100 amino acids, Gly-X-Gly tripeptides, and other polypeptides, including poly-amino acids, and proteins, in solid, gaseous and/or aqueous states. Parameters in the equations of state for model species were regressed from literature values of the standard molal isobaric heat capacities ($C_P°$) and volumes ($V°$) of both aqueous and solid species, and isothermal compressibilities ($\kappa_T°$) of aqueous species. The equations-of-state parameters thus determined, along with literature values of the standard molal enthalpies of formation ($\Delta H_f°$) and entropies ($S°$) of model species, formed the dataset for a global group additivity analysis of the contributions by protein backbone and sidechain groups. The group contributions can be used to calculate the standard molal thermodynamic properties of solid proteins, and aqueous proteins in various ionization states, and can be coupled with thermodynamic data over limited temperature and pH ranges from unfolding experiments to evaluate the stability of folded proteins at the conditions of temperature and pH obtaining in the deep biosphere. Preliminary calculations of this kind indicate that folded proteins from thermophilic organisms tend to be stable at high temperatures and low pH. In addition, estimates of the thermodynamic properties of thermophilic proteins at elevated temperatures can be used to quantify the oxidation-reduction conditions required for their stability in intra- and extracellular environments in the deep biosphere.