Nanoscale environment of metal coordination states in humic subtances: A molecular dynamics study

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Sequestration of metal cations within natural organic colloids influences biogeochemical processes, contaminant transport, and soil aggregation. We performed molecular dynamics simulations [1] of a deprotonated model humic substance (HS) saturated with Ca or Mg to examine the binding environment of the cation. The metal-O coordination radial distribution functions revealed smaller distances for the adducts of both HS carbonyl and carboxylate O atoms with Mg^{2+} as compared to Ca^{2+} indicating that Mg formed stronger complexes with the HS O atoms than did Ca, corroborating experimental observations [2] that the extent of compression of metal-HS complexes is correlated to the ionic potential of the cation. For Ca, up to two waters in its solvation shell were replaced by HS O atoms. However, the localization of Mg affected its coordination state: the cation was typically chelated by more than two HS O atoms within the interior of the HS molecule whereas, on the periphery, it was either highly hydrated or coordinated to two or less HS O atoms. The conformations of the metal-HS complexes support the proposal [4] that sequestered cations could be excluded from the bulk aqueous phase by non-polar pockets that impede the entry of solvating waters and cation hydrates whereas the coordination environment of the cations located on the HS outer part may facilitate exchange with the bulk phase.

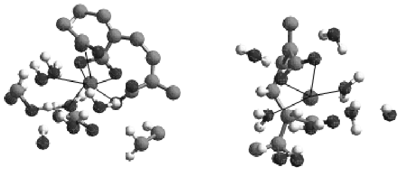

Figure 1. Coordinated H_2O and HS O atoms with Mg^{2+} located within (left) and on the periphery (right) of the HS molecule. *Color code*: Gray: C, red: O, white: H, pink: Mg^{2+}.

[1] Sutton *et al.* (2005) *Environ. Tox. Chem.* **24**, 1902-1911. [2] Wall & Choppin (2003) *Appl. Geochem.* **18**, 1573-1582. [4] King *et al.* (2001) *Phys. Chem. Phys.* **3**, 2080-2085.

Sm-Nd geochronology of the Zermatt-Saas ophiolite, northern Italy

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The Zermatt-Saas Ophiolite (ZSO) is a remnant of the Piedmont-Ligurian ocean basin that underwent eclogite facies metamorphism during subduction under the Adriatic margin. The duration of burial and subsequent exhumation of the ZSO has been a focus of recent work [eg. 1,2] because it provides a unique opportunity to study the rates of subduction processes as well the internal geometry of the subduction channel. We present new Sm-Nd age data of a garnet-bearing blueschist that co-exists with eclogite from the St. Marcel region, northern Italy. The high-pressure mineralogy of the samples include glaucophane + clinozoisite + white mica + garnet + rutile; retrograde alteration is minor.

A 5-point Sm-Nd isochron age of 44.1±3.4Ma (2σ; MSWD=0.41) was measured from white-mica, clinozoisite, whole rock, and garnet. Two garnet aliquots were used in the isochron but were processed differently. Both garnet aliquots were aggressively acid leached before digestion following [3] to ensure that only a pure garnet fraction was analysed. After acid leaching, the garnet fraction was split into two aliquots – one digested in Paar-bombs and the other digested using a tabletop technique similar to [4], yielding $^{147}Sm/^{144}Nd = 0.75$ and 1.00, respectively. The higher Sm/Nd ratio of the tabletop digestion method relative to the bomb method reflects increased dissolution of LREE-rich phases by the latter.

In order to correctly interpret the Sm-Nd age with respect to the garnet growth interval [2], we have measured the core-to-rim zoning of Sm and Nd in garnet by LA-ICPMS and calculated an age weighting factor with respect to the garnet growth interval. Our preliminary results indicate that the Sm-Nd age is weighted toward the garnet rim and likely represents near-peak metamorphic conditions. Our age is similar to but older than a 40.6 ± 2.6 Ma Sm-Nd age determined from UHP eclogites at Lago di Cignana [1], suggesting a diachronous burial of components within the ZSO.

[1] Amato *et al.* (1999) *Ear. Planet. Sci. Lett* **171**, 425-438. [2] Lapen *et al.* (2003) *Ear. Planet. Sci. Lett* **215**, 57-72. [3] Baxter *et al.* (2002) *Jour. Geol. Soc. London* **159**, 71-82. [4] Lagos *et al.* (2007) *Chem. Geol.* **243**, 16-35.