1.1.14

Water in the interlayer region of birnessite: An infrared spectroscopic study

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Birnessite, $(Na,Ca,Mn^{2+})Mn_7O_{14}\cdot 2.8H_2O$, is an important scavenger of trace metals in soils and aqueous environments. The hydrous species in the birnessite structure may play an important role in cation retention and exchange processes. The basic birnessite structure has been solved by X-ray diffraction techniques, and consists of sheets of Mn octahedra separated by 7 Å interlayer regions filled with cations and water. This study uses infrared spectroscopy to investigate the bonding environments of water in the interlayer region of birnessite-type minerals containing Na^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}, Zn^{2+}, and Pb^{2+}.

Birnessites with K^+, Cs^+, Ca^{2+}, or Pb^{2+} in the interlayer region were created by cation exchange of synthetic Na birnessite with a 0.5-1 M solution of the nitrate or chloride salt of the appropriate cation at room temperature. Previously synthesized Mg birnessite and a natural sample of chalcophanite $(ZnMn_3O_7\cdot 3H_2O)$ were also investigated. Mid-infrared spectra (6000-600 cm^{-1}) were obtained on KBr pellets and on thin films of birnessite deposited onto a BaF_2 window. Spectra were also collected *in situ* from -180°C to 350°C using a heating and cooling stage in conjunction with an infrared microscope.

Chalcophanite has one type of ordered interlayer water site, consistent with the well-ordered structure of defects in the Mn layers and Zn^{2+} in the interlayer region. Synthetic Mg birnessite, similar in structure to chalcophanite, contains a distorted structural water and possibly a hydroxyl site. In contrast, the Na, K, Cs, and Pb synthetic birnessites each contain two to three structurally different water sites, as evidenced by multiple H_2O bending and stretching modes in the infrared spectra. The complexity of the water bands in these spectra is due to disordering of cations on the interlayer sites. The small difference in the width of the water stretching modes between room temperature and -180°C also indicates that the water molecules are structurally, rather than dynamically, disordered. Birnessites containing cations with relatively large ionic radii (Na, K, Ca) undergo significant changes in structural water environments upon heating to 70-90°C. Those containing smaller cations (chalcophanite, Mg birnessite) retain the structure of interlayer water to 150-200°C. This pattern of water loss is consistent with changes in the X-ray diffraction data of birnessites obtained at elevated temperatures.

1.1.21

Partitioning of H_2O between mantle minerals and silicate melts

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We present initial data from the first systematic study of the partitioning of water between common upper mantle minerals (olivine, pyroxenes, garnet, amphibole, mica) and hydrous silicate melt. This study takes advantage of new SIMS techniques for measuring the abundance of water in nominally anhydrous minerals [1]. To date we have made 361 measurements in 23 experiments [2-4] from 1-4 GPa , 1000-1380 C and melt water contents of 1-22wt% total H_2O. Detection limit for H_2O was 1-4 ppmw.

Partition coefficients were calculated as wt% H_2O in the mineral divided by total wt% H_2O in the glass. Partitioning of water between all minerals and silicate melt appears to be independent of pressure, temperature, and total water content over the range of conditions studied. Mineral/glass partition coefficients for olivine (0.00125), orthopyroxene (0.0145), clinopyroxene (0.0139), garnet (0.00316), amphibole (0.160) and mica (0.496) are reproducible between different experiments to within 30-40%. Experiments multiply-saturated with an upper mantle mineral assemblage (ol + opx + cpx ± spinel ± garnet) reproduce opx/olivine (11.6), cpx/olivine (11.1) and garnet/olivine (2.5) partitioning to within 20%.

Water is thus confirmed as a highly incompatible element during upper mantle melting, but amphibole and mica will increase the bulk D for H_2O significantly. A fertile upper mantle peridotite mineralogy (56% ol, 28% opx, 14% cpx, 2% sp) will have a bulk solid/melt $D(H_2O)$ of ~0.007, and this value will change more slowly with %F than D(Ce) as clinopyroxene is consumed during melting. Bulk $D(H_2O)$ is lower for fertile garnet lherzolite, in much the same way as for Ce. The lack of variation of $D(H_2O)$ with melt water content is not predicted by H speciation observed in glasses, but is consistent with T-dependence of water speciation [5]. This observation indicates that water speciation in basaltic melts is likely dominated by OH^- radicals under the conditions of our experiments.

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