CO_2/N_2 in MORB vesicles using Raman spectroscopy: Implications for global volatile fluxes

D. CHAVRIT*, Y. MORIZET, A. BÉZOS AND E. HUMLER

Laboratoire de planétologie et géodynamique (UMR 6112, CNRS), université de Nantes, 44300 Nantes, France (*correspondence: deborah.chavrit@univ-nantes.fr, yann.morizet@univ-nantes.fr, antoine.bezos@univ-nantes.fr, eric.humler@univ-nantes.fr)

The estimations of volatile fluxes released by volcanic activity at mid-ocean ridge are based on sample volatile contents. Vesicle gas contents are usually analysed by crushing and extraction experiments. However, the residue shows that a high proportion of the smallest vesicles is not crushed, and so non-analysed. This may have an influence on the mean volatile ratios of the samples and consequently on global volatile fluxes.

In order to evaluate quantitatively this process, we selected 80 mid-ocean ridge basalts (Pacific, Atlantic and Indian), characterised by 7.96 ± 0.59 wt% MgO and $2.1 \le Na_{8.0} \le 4.13$. 85% are N-MORBs ($0.32 \le (La/Sm)_N \le 1.24$). Dissolved volatile contents are between 1106-5378 ppm H_2O and 88-377 ppm CO_2. The H_2O/Ce ratio is 240 ± 73 (1σ), in agreement with typical MORB values. The samples underwent important CO_2 degassing ($CO_2/Nb=147\pm108$ - 1σ).

Vesicle size distribution (VSD) studied on more than 20 samples shows that vesicularities range from ~0 to 16.8%. We measured at micrometric scale gas contents by Raman spectroscopy in vesicles. We found a mean CO_2/N_2 molar ratio of 6.9 ± 6.9 (1σ), for a mean vesicle diameter of 53 ± 32 (1σ) μm. These ratios are much lower than those reported in Cartigny *et al.* [1] (i.e 316-3900). These latter were obtained by crushing on vesicles mainly >1 mm diameter (~55% of the crushing residue is in the >1 mm fraction, implying that the smaller vesicles are uncrushed). VSD data show that a maximum of 10% vesicle volume is in the range >1 mm diameter, which represents the main fraction analysed by crushing. Therefore CO_2/N_2 ratio of the smallest vesicles can highly affect the mean CO_2/N_2 ratio of the sample. Consequently, a first order calculation shows that crushing may overestimate the CO_2/N_2 ratio by 10 to 90%, according to the sample VSD. For a given CO_2 flux, it leads to decrease the global N_2 flux at oceanic ridges by a maximum factor of ~2.

[1] Cartigny *et al.* (2001) *EPSL* **194,** 241-257.

An EXAFS and FTIR study on the sulfate and arsenate configurations of schwertmannite

C.-J. CHEN AND W.-T. JIANG*

Dept. Earth Sciences., National Cheng Kung Univ., Tainan, Taiwan (*correspondence: atwtj@mail.ncku.edu.tw)

Sorption experiments showed that a saturation state was reached invariably with 85-90% of the original sulfate concentration replaced by arsenate anions in synthetic schwertmannites of different initial sulfate compositions. The saturated products have arsenate compositions similar to the maximal arsenate concentration contained in As-bearing schwertmannite synthesized by a co-precipitation method.

Arsenic K-edge EXAFS analyses of the schwertmannites suggested a tetrahedral coordination with a single As-O bonding distance of 0.168 nm and an As-Fe distance of 0.322-0.326 nm. The FTIR result showed a decrease in the extent of the splitting of the ν_3(S-O) band at 1000~1200 cm^{-1} with no apparent splitting of the As-O stretching band at ~830 cm^{-1} as the substitution of arsenate for sulfate increases. The data imply that the surface-adsorbed sulfate tetrahedra consist of 85-90% of the contained sulfate content and are asymmetrically distorted while the distortion of the tunnel sulfate tetrahedra are symmetrical or minimal. In contrast, the arsenate tetrahedron is symmetrically or not distorted and largely adsorbed on the structural surface.

A configuration model involving a bidentate binuclear [2]C corner-sharing coordination between arsenate tetrahedra and edge-sharing $Fe(O,OH)_6$ octahedra at the structural surface (instead of the structure tunnel) and additional bonding with hydrogen ions on the unshared tetrahedral oxygens is required to conform to the measured bond lengths and facilitates the formation of relatively undistorted or symmetrically distorted $AsO_2(OH)_2$ tetrahedra. On the other hand, bonding through hydrogen ions with the $Fe(O,OH)_6$ octahedra may be needed for the $SO_2(OH)_2$ tetrahedron to accommodate its asymmetrical distortion and the large discrepancy between its edge length and the distance between octahedral apical oxygens. The preferential uptake of arsenate anions at the surface adsorption sites can be attributed to its larger radius, less polyhedral distortion, and corner-sharing with the structural polyhedra. The exclusion of arsenate anions from the structure tunnel and their dominance on adsorption collectively imply that a high concentration of arsenate anions may inhibit the precipitation of schwertmannite although an arsenate-adsorbed schwertmannite structure is relatively stable.