Global fluxes of fluorine and sulfur efficiently released at mid-ocean ridges

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Fluorine and sulfur are major components of high temperature volcanic gases, and significantly affect surface environments due to high chemical activity. Therefore their fluxes between the mantle and surface environments are important to elucidate evolutionary histories of Earth's atmosphere and ocean. We estimated fluorine and sulfur fluxes at mid-ocean ridges (MOR) based on chemistry of submarine vent fluids and MORB vesicles which may reflect components efficiently released from magmas through upward propagation of film ruptures by bubble expansions during decompression[1]. Fluorine flux was constrained by two methods as follows:
1) Multiplication of fluorine concentrations in submarine hydrothermal fluids and the fluid flux at MOR may provide an estimate of fluorine flux at MOR. A worldwide vent chemistry research[2] suggested that vent fluids are depleted in fluorine (<0.74 ppm F) relative to seawater (1.29 ppm F). The global flux of vent fluids of $(8.0+/-2.1)\times10^{15}$ g/y was calculated using a numerical Bayesian inversion procedure to explain the relationship between compositions of hydrothermal fluids and altered sheeted dikes[3]. This value is not consistent with the flux of $(3.1+/-0.7)\times10^{16}$ g/y obtained based on the ^{3}He concentration of $(1.7+/-0.2)\times10^{-14}$ mol/g (1σ) in 10 high temperature (>200°C) hydrothermal fluids at EPR and MAR[4], and the MOR ^{3}He flux of (527+/-102) mol/y[5]. These two fluid fluxes, when multiplied by the maximum fluorine concentration of 3.88×10^{-8} mol/g, provides fluorine fluxes ranging from 3.1×10^{8} mol/y to 1.2×10^{9} mol/y with an average of $(7.6+/-4.5)\times10^{8}$ mol/y.
2) Multiplication of F/^{3}He ratios in MORB vesicles and ^{3}He flux will provide another fluorine flux. We analysed eight MORB vesicles (13°N,17°S on EPR; 15°N,30°N,37°N on MAR; 24°S-25°S on CIR) with a crushing technique extracting fluorine and helium simultaneously[6]. Fluorine was extracted into alkaline solution and measured by an ion chromatography (ICS-2100; Thermo Fisher Scientific Inc.), while helium was measured by a noble gas MS (VG5400; Waters Corp.), both housed at AORI. F/^{3}He ratios in vesicles range from 2.0×10^{5} to $<2.8\times10^{7}$ with an average of $(1.2+/-0.5)\times10^{6}$ (1σ), providing a global fluorine flux of $(6.4+/-3.1)\times10^{8}$ mol/y by multiplying the MOR ^{3}He flux.
One might calculate a weighted mean of two MOR fluorine fluxes to be $(6.8+/-2.5)\times10^{8}$ mol/y. However it should be noted that the actual MOR fluorine flux may be lower than this flux because the applied fluorine concentration in hydrothermal fluids is an upper limit, and seawater contamination was not deconvolved for MORB vesicles. We also note that this flux is much lower than flux (1.13×10^{12} mol/y) estimated using the F/CO_2 ratio in the MORB source and CO_2 flux from the mantle[7], implying that the most part of fluorine resides in the melt and is not released immediately after the oceanic crust production.
Sulfur flux, together with carbon, will be estimated based on chemistry of vent fluids and MORB vesicles, which is similar approach as for fluorine. In addition, comparing MOR and arc fluxes, the global cycles of fluorine, sulfur, and carbon will be discussed in the presentation.
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