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Estimation of S, F, Cl and Br fluxes at Mid Ocean Ridges

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Introduction

Superficial volatile elements of the Earth have been accumulated mainly by degassing from the solid Earth. Noble gases have been used as tracers for constraining the degassing history. Argon isotopic systematics suggested that the significant degassing occurred in the early Earth, ˜4 billion years ago [1, 2]. Carbon and nitrogen fluxes from the Earth mantle have so far been well documented by calibrating against the helium-3 (^{3}He) flux, which constrains the models of atmospheric evolution [3, 4].

However, evolutions of other volatiles, such as sulfur (S) and halogens (fluorine, chlorine and bromine) forming various chemical species on the Earth's surface due to their high reactivity, have been poorly constrained. Additionally, halogen fluxes at Mid Ocean Ridges have been estimated by comparison with concentration and flux of CO_2 [5], while CO_2 flux itself was estimated by calibrating against the ^{3}He flux. Thus, direct comparison of the volatile elements with ^{3}He is more straightforward. In this study, we analyzed concentrations of S and halogens with ^{3}He trapped in vesicles in Mid Ocean Ridge basalts (MORBs) and back-arc basin basalts (BABBs) to estimate their fluxes from the mantle by comparison with ^{3}He directly.

Analysis

Approximately 1 g of fresh glassy aliquots were picked up from basalts and were put in a stainless-steel crusher with 1-2 cm^3 of diluted aqueous sodium hydroxide (1-4 mol/L) and a stainless-steel ball. The alkaline solution was frozen at the temperature of liquid nitrogen (77K). When the crusher was shaken up and down, the glassy aliquots were crushed together with the frozen solution by the stainless-steel ball. Highly reactive elements including S, F, Cl and Br were extracted from vesicles of glasses by mechanical fracturing and immediately dissolved into a small portion of melted alkaline solution. While helium (He), not dissolved into the solution, was introduced into a vacuum line and purified. Helium-4 (^{4}He) intensity and ^{3}He/^{4}He ratio were measured by a VG5400 mass spectrometer. S, F, Br and Cl concentrations in the alkaline solution were measured by ion chromatography (Dionex-320).

Results and Discussion

Concentrations trapped in vesicles were (4-31) x 10^{-15}mol/g for ^{3}He, (20-430) x 10^{-9}mol/g for S, (60-5000) x 10^{-9}mol/g for F, (160-450) x 10^{-9}mol/g for Cl and (5-1300) x 10^{-9}mol/g for Br. Under an assumption that the samples analyzed in this study represent typical MORBs, global fluxes of S, F, Cl and Br were estimated using mole ratios X/^{3}He of the samples and the ^{3}He flux of (527+-102) mol/yr from the mantle [6]. They are (1-26) x 10^{10}mol/yr for S, (2-120) x 10^{11}mol/yr for F, (2-120) x 10^{10}mol/yr for Cl and (4-230) x 10^{10}mol/yr for Br when bulk MORBs and BABBs emit their volatiles entirely. We compared S, F and Cl fluxes at Mid Ocean Ridges with those at volcanic arcs, recycling rates at subduction zones, and accretion rates to continental crust. Thus, the respective lower limits of calculated accumulation times that is required to form the present atmosphere, are 92 Myr for S, 11 kyr for F and 1.0 Gyr for Cl. These values are significantly shorter than the age of the Earth, 4.55 Gyr. This may reflect the highly reactive natures of S, F and Cl contrasting to argon or nitrogen, which causes different accumulation histories.

Reference

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