Determination of halogens in some standard materials using the neutron irradiation noble gas mass spectrometric technique

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Halogens are among the most powerful tracers of volatile cycling in subduction zones, because of (i) the large contrast in concentrations between the surface and interior of the Earth [1], (ii) their high affinities to gas- and fluid-phases relative to mineral [2], (iii) distinct elemental and/or isotopic compositions in each reservoir in the Earth [3-7]. However, few analytical techniques can determine trace amounts of halogens, particularly bromine and iodine in mantle-derived samples. Consequently, there have been relatively few previous studies of halogens in mantle-derived samples.

The neutron irradiation noble gas mass spectrometric technique (NI-NGMS) is capable of measuring very low concentrations of halogens (<1 ppb) in very small samples (<1 mg). The NI-NGMS is an extension of the Ar-Ar and I-Xe dating methods [8-10]. Halogens (chlorine, bromine, and iodine) and other elements (potassium, calcium, barium, and uranium) are converted to corresponding isotopes of argon, krypton, and xenon by neutron irradiation in a nuclear reactor. The noble gas isotopes in neutron-irradiated samples are analyzed by noble gas mass spectrometry. Irradiation conditions such as neutron fluence are monitored using standard materials of the Ar-Ar and I-Xe dating methods. Relatively high cross-sections of halogens for neutron capture and high sensitivity of noble gas mass spectrometry enable determination of trace amounts of halogens using NI-NGMS.

We report new halogen concentrations determined for scapolite standards and geological reference materials distributed by Geological Survey of Japan and US Geological Survey using NI-NGMS. Consistent results with those regarded as reference values were obtained from scapolite standards, which indicate that the scapolite standards are reliable in halogen analysis. On the other hand, the halogen concentrations obtained from geological reference materials are systematically lower than the reference values for samples with low concentrations of halogens. The higher concentrations reported for the geological reference materials probably result from contamination on the sample surface during preparation of these reference materials. We also propose a fluorine determination method using NI-NGMS based on neon systematics, although reliable determination of fluorine has been thought to be impossible.

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