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放射化学的中性子放射化分析法を用いた、地球化学的固体試料中の微量ハロゲンの分析

Determination of Trace Amounts of Halogens (Cl, Br and I) in Geochemical Reference Materials by Radiochemical Neutron Activation Analysis

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INTRODUCTION: Accurate and reliable data of halogen abundance have been rarely reported for terrestrial samples, such as crustal rocks and mantle materials. Since halogens differ in volatility from element to element, their content and relative abundance are highly informative when discussing the petrogenesis of such samples. Among the halogens, iodine is important element in discussion of the geochemical circulation in the earth's surface, oceanic crust, continental crust, and mantle [1]. Simply, the scarcity of reliable data for terrestrial rock samples prevents the geochemical discussion of halogens.

There is a shortage of accurate and reliable data of halogens even for geological reference rocks, as can be witnessed in the data libraries, where only preferable, not certified, values and, for some rocks, no values are listed. This deficit must be largely due to the difficulty in determining trace amounts of halogens within these samples. Recently, we have improved the radiochemical neutron activation analysis (RNAA) procedure for trace amounts of halogens (Cl, Br and I), and demonstrated that our RNAA data for Br and I are more reliable and accurate than the data obtained by inductively coupled plasma mass spectrometry (ICP-MS) coupled with pyrohydrolysis preconcentration [2].

In this study, our RNAA procedure was applied to 17 U.S. Geological Survey (USGS) geochemical reference materials (listed in Table 1), where certified values of halogens have never been reported. We will present reliable data for three halogens in 17 USGS reference materials.

Table 1: USGS geochemical reference materials analyzed in this study.

Sample	Type	Sample	Type
BHVO-2	Basalt	COQ-1	Carbonatite
BCR-2		GSP-2	Granodiorite
BIR-1a		SDC-1	Mica Schist
W-2a	Diabase	Nod-P-1	Manganese nodule
AGV-2	Andesite	Nod-A-1	
DNC-1a	Dolerite	DTS-2b	Dunite
CLB-1	Coal	QLO-1a	Quartz Latite
SBC-1	Shale rock	DGPM-1	Disseminated gold ore
SGR-1b			

EXPERIMENTS: The USGS materials, together with a set of three reference halogen samples for quantification, were irradiated for 10 min with a thermal neutron flux of 3.3 x 10^{12} cm^{-2} s^{-1} at Kyoto University Research Reactor Institute. After irradiation, the USGS materials were held for a few minutes to enable the decay of ^{28}Al, and were then subjected to radiochemical separation of neutron-activated halogen radionuclides (^{38}Cl, ^{82}Br, and ^{128}I). The radiochemical separation scheme used in this study was essentially the same as that described in Ref[2].

RESULTS & DISCUSSION: The RNAA data of the three halogens were compared with corresponding literature data and some inconsistencies were found. Those inconsistencies can be explained by the following three findings;

1. The loss of iodine in pretreatment of the solution that is subjected to inductively coupled plasma mass spectrometry (ICP-MS) for BHVO-2, BCR-2, BIR-1a, and AGV-2.
2. Incomplete quantitative collection of chlorine in pyrohydrolysis preconcentration for ICP-MS for BHVO-2, BCR-2, BIR-1a, and AGV-2.
3. Overestimation due to the interference in the ICP- double focusing sector field MS (ICP-SFMS) instrument for Nod-P-1 and Nod-A-1.

Using the relative standard deviation (RSD) that accompanies the mean value and uncertainties that accompany the individual analytical values in each USGS material, heterogeneity of halogens in the USGS materials has been discussed. Materials CLB-1, Nod-P-1 and DNC-1a may be inhomogeneous, suggesting that extreme care should be taken when using those three as reference materials.

REFERENCES:

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