



Determination of halogen abundances in terrestrial and extraterrestrial samples by the analysis of noble gases produced by neutron irradiation

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ABSTRACT

The lack of a reliable database for heavy halogens (bromine and iodine) in terrestrial and extraterrestrial samples is mainly due to the analytical challenges of determining their very low abundances (<1 ppm) in the materials of interest. The neutron irradiation noble gas mass spectrometric (NI-NGMS) technique initially developed in the 1960s is the only viable technique currently capable of determining concentrations below 1 ppb of iodine for small (<10 mg) sample sizes. We describe in detail the analytical protocols and provide a comprehensive and transparent overview of the data reduction procedures in order to fully explore the uncertainties of the technique. We demonstrate how the capabilities of modern mass spectrometers used for Ar-Ar dating, can be readily extended to incorporate halogen measurements. A new and critical assessment of the use of standards is presented based on results from multiple irradiations, including a meteorite (Shallowater aubrite), scapolite minerals introduced by Kendrick (2012) and a novel internal calibration method based on using barium.

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1. Introduction

Halogens are present as minor and trace elements in most geological samples. Studies of halogens have been applied to crustal and ore-forming fluids (e.g.; Böhlke and Irwin, 1992a,b; Turner and Bannon, 1992; Ballentine et al., 2002; Kendrick and Burnard, 2013) and more recently, the determination of heavy halogens (bromine and iodine) in mantle-derived samples has provided important constraints on the origin and the recycling of the major volatile elements in the Earth (Burgess et al., 2002, 2009; Sumino et al., 2010; Kendrick et al., 2011, 2012a,b, 2013a,b). However, low concentrations of halogens in the materials of interest, together with the lack of available techniques for their low level detection, means that reliable abundance data are relatively sparse compared to other volatile elements. Whilst the electron microprobe (EMP) can determine chlorine and fluorine abundances down to levels of 0.01 wt.%, bromine and iodine abundances are <1 ppm in most minerals and rocks. Chlorine and bromine can be determined by instrumental neutron activation analysis (INAA) but require >100 mg-size samples (e.g. Heinrich et al., 1993). Similarly, ion chromatography analysis requires crush-leaching of gram-sized samples to extract halogens

(e.g. Bottrell and Yardley, 1988). Recently, Heinrich et al. (2003) assessed the potential of Br and Cl quantification by LA-ICP-MS. However the halogens tend to have low ionisation efficiencies leading to relatively low sensitivity. Using LA-ICP-MS for scapolite minerals, Hammerli et al. (2013) determined detection limits of about 8 ppm Br and >500 ppm for Cl. Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) has been used with detection limits of 10 ppm for F and Cl (Joachim et al., 2015) and SIMS has attained limits of 0.6 ppm for Br and 0.035 ppm for I (Kusebauch et al., 2015).

An alternative technique for halogen determination is based upon extension of the ⁴⁰Ar-³⁹Ar technique (Merrihue, 1965; Turner, 1965; Turner et al., 1971; Turner and Bannon, 1992; Böhlke and Irwin, 1992a, b; Irwin and Roedder, 1995). Although fairly routinely used for Cl, this technique has only recently become more widely adopted for Br and I following a revival in the 2000s by the Manchester Isotope Geochemistry and Cosmoschemistry group (Johnson et al., 2000; Kendrick et al., 2001; Burgess et al., 2002). Kendrick (2012) summarises in detail the basic concepts of the neutron-irradiation noble gas technique. The author suggested the use of the mineral scapolite as a standard for halogen determinations to replace the existing meteorite standards (Shallowater or Bjurböle). Subsequently, Kendrick et al. (2013a) have revised the halogen values of the scapolite standards, reducing them by 22% and 27% for Br and I, respectively. This correction has been

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independently confirmed for Br by Hammerli et al. (2014) in scapolites, but no external standards or techniques have been used to verify I concentrations.

The introduction of scapolite standards has an impact on the way previous workers have reduced their data to estimate the halogen abundances in natural samples. We discuss the implications by describing different approaches to reduce the data. We compare results from five different irradiations using two different reactors. We introduce an alternative halogen standardisation method based on the barium content (when known independently) of irradiated samples, referred to from hereon as a barium calibration. Finally, the results obtained from the Shallowater meteorite and the barium correction are used to refine the I/Cl values of BB2/SP and BB1 scapolite standards of Kendrick et al. (2013a) and reduce their 2 -errors from 23% (BB2/SP) and 15% (BB1) to 14% and 10%, respectively.

2. Method of investigation

2.1. General principle

The ^{40}Ar – ^{39}Ar technique is widely used for geological dating and can be adapted for a range of elements forming noble gas isotopes during (n, p), (n,  ), (n,  ), (n,  ,  ) or neutron-induced fission reactions (Table 1; Turner, 1965). During neutron irradiation $^{39}\text{K}(n, p)^{39}\text{Ar}$ and $^{40}\text{Ca}(n,  )^{37}\text{Ar}$ reactions are activated only by fast neutrons i.e. having energy >1 MeV. In contrast, halogen-derived noble gas isotopes are produced by low energy thermal neutrons (10^{-11} – 2.5×10^{-8} MeV) and epithermal neutrons (2.5×10^{-8} –1 MeV). Halogen determinations are accessible through (n,  ,  ) reactions forming noble gas isotopes (Fig. 1; Table 1) in amounts readily detected by noble gas mass spectrometers.

Integrated neutron fluences are typically in the range 10^{18} – 10^{19} n cm² with most halogen absorption reactions involving thermal and epithermal neutrons (Fig. 2) leading to conversion factors between 10^{-6} and 10^{-4} of the parent halogen atoms.

Using the approach of Chilian et al. (2006) for INAA, upon irradiating a sample containing an amount m (grams) of an element, then the quantity of a given nuclide ^iX (moles) produced by a (n,  ,  ) reaction is given by:

$$^i\text{X} = \frac{m}{M_{\text{at}}} \cdot \theta \cdot \sigma_{\text{th}} \cdot Y \cdot \varphi_{\text{th}} \cdot \frac{Q_0}{f} \quad (1)$$

where M_{at} is the atomic mass, θ is the isotopic abundance; Y is the fractional yield for branched isotope decay; σ_{th} is the thermal neutron absorption cross section (2200 ms^{-1}); $Q_0 = \sigma_{\text{epi}}/\sigma_{\text{th}}$ is the ratio of resonance integral to thermal neutron cross-section, $f = \varphi_{\text{th}} / \varphi_{\text{epi}}$ with φ_{th} and φ_{epi} being the thermal and epithermal neutron fluences, respectively (Table 2). The parameter f is usually not known *a priori* and will vary with reactor and irradiation position; however it can be determined experimentally from standards. The proportion of

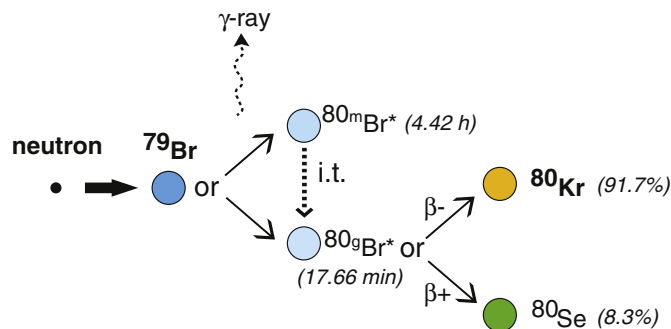


Fig. 1. Schematic example of neutron irradiation for ^{79}Br . ^{79}Br can be either activated to radioactive $^{80\text{m}}\text{Br}^*$ or $^{80\text{g}}\text{Br}^*$ (m = metastable state and g = ground state). $^{80\text{m}}\text{Br}$ decays to $^{80\text{g}}\text{Br}$ during an isomeric transition (i.t.), which then decays to ^{80}Se (8.3%) or ^{80}Kr (91.7%).

epithermal neutron-induced isotope production can be estimated as $Q_0 / (Q_0 + f)$, or expressed by the F-factor as:

$$F = \frac{Q_0 + f}{f} \quad (2)$$

As an example, our irradiation MN2014b carried-out in the GRICIT Facility at the TRIGA reactor Oregon gave $f = 11.3 \pm 2.3$ (Table 2), with $^{80}\text{Kr}Q_0 = 11.9 \pm 0.3$ and $^{128}\text{Xe}Q_0 = 24.9 \pm 0.7$ (Table 2), this indicates that 51% of the $^{80}\text{Kr}_{\text{Br}}$ and 69% $^{128}\text{Xe}_{\text{I}}$ is formed by epithermal neutron absorption.

In contrast, nucleogenic production of ^{38}Ar from ^{37}Cl has a relatively low Q_0 value ($=0.7 \pm 0.1$) and therefore is used to monitor the thermal neutron fluence. Eq. (1) can be useful for irradiation planning if the epithermal/thermal fluence ratio of a reactor irradiation position has been previously characterised and remains relatively constant over time. However, Eq. (1) does not include the effects of neutron self-shielding on isotope production. Analytical formulae for correcting self-shielding effects in cylindrical samples (appropriate for samples irradiated in silica glass tubes) are given by Chilian et al. (2006, 2008, 2010). The effects of self-shielding are likely to be negligible for most samples used in ^{40}Ar – ^{39}Ar irradiations, because of their relatively low mass (usually <0.01 g) and the low concentrations of target elements (for halogens typically at ppb–ppm levels). Self-shielding effects should be considered when irradiating samples with high concentrations of halogens (e.g. halogen salts), in which self-shielding by epithermal neutrons at resonance peaks could be severe (Chilian et al., 2006). For example, using the method of Chilian et al. (2006), it is estimated that epithermal self-shielding of a 1g cylindrical (radius = 1 cm; height = 2 cm) sample of iodide salt (NaI or KI) could lead to an erroneous underestimate of I abundance from $^{128}\text{Xe}_{\text{I}}$ of up to 38%.

The halogen abundances in samples can be evaluated either from the derived neutron fluence, or from standards of known parent element

Table 1
Summary of the neutron-induced reactions forming noble gas isotopes used in this study. Thermal neutron cross-sections are given for neutrons with energy of 0.0253 eV. Barn = 10^{-24} cm².

Parent	Isotopic abundance	Noble gas product	Reactions	Neutron involved	Thermal cross section (barns)	Resonance integral (barns)	Yield
^{37}Cl	0.2424	$^{38}\text{Ar}_{\text{Cl}}$	$^{37}\text{Cl}(n, \gamma)^{38}\text{Cl}(\beta)^{38}\text{Ar}$	Thermal	$0.433 \pm 0.006^{\text{a}}$	$0.30 \pm -0.04^{\text{a}}$	1
^{39}K	0.9326	$^{39}\text{Ar}_{\text{K}}$	$^{39}\text{K}(n, p)^{39}\text{Ar}$	Fast	$2.1 \pm 0.1^{\text{a}}$	$1.1 \pm 0.1^{\text{a}}$	1
^{40}Ca	0.9694	$^{37}\text{Ar}_{\text{Ca}}$	$^{37}\text{Ca}(n, \alpha)^{37}\text{Ar}$	Fast	$0.43 \pm 0.02^{\text{a}}$	$0.22 \pm 0.02^{\text{a}}$	1
^{79}Br	0.5069	$^{80}\text{Kr}_{\text{Br}}$	$^{79}\text{Br}(n, \gamma)^{80}\text{Br}(\beta)^{80}\text{Kr}$	Thermal + epithermal	$10.89 \pm 0.05^{\text{b}}$	$129.6 \pm 3.0^{\text{b}}$	0.917
^{81}Br	0.4931	$^{82}\text{Kr}_{\text{Br}}$	$^{81}\text{Br}(n, \gamma)^{82}\text{Br}(\beta)^{82}\text{Kr}$	Thermal + epithermal	$2.36 \pm 0.03^{\text{b}}$	$46.3 \pm 1.7^{\text{b}}$	1
^{127}I	1.0000	$^{128}\text{Xe}_{\text{I}}$	$^{127}\text{I}(n, \gamma)^{128}\text{I}(\beta)^{128}\text{Xe}$	Thermal + epithermal	$6.16 \pm 0.04^{\text{b}}$	$153.4 \pm 3.9^{\text{b}}$	0.94
^{130}Ba	0.00106	$^{131}\text{Xe}_{\text{Ba}}$	$^{130}\text{Ba}(n, \gamma)^{131}\text{Ba}(\beta)^{131}\text{Xe}$	Thermal + epithermal	$7.75 \pm 0.34^{\text{c}}$	$197.3 \pm 10^{\text{c}}$	1

^a Data source: Pritychenko and Mughabghab (2012).

^b See Supplementary data-Tables C1–C3–3–.

^c Dauenhauer and Krane (2012) and see section 4.3.

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