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In situ quantification of Br and Cl in minerals and fluid inclusions by LA-ICP-MS: A powerful tool to identify fluid sources

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ABSTRACT

Bromine and chlorine are important halogens for fluid source identification in the Earth's crust, but until recently we lacked routine analytical techniques to determine the concentration of these elements in situ on a micrometer scale in minerals and fluid inclusions. In this study, we evaluate the potential of in situ Cl and Br measurements by LA-ICP-MS through analysis of a range of scapolite grains with known Cl and Br concentrations. We assess the effects of varying spot sizes, variable plasma energy and resolve the contribution of polyatomic interferences on Br measurements. Using well-characterised natural scapolite standards, we show that LA-ICP-MS analysis allows measurement of Br and Cl concentrations in scapolite, and fluid inclusions as small as 16 μm in diameter and potentially in sodalite and a variety of other minerals, such as apatite, biotite, and amphibole. As a demonstration of the accuracy and potential of Cl and Br analyses by LA-ICP-MS, we analysed natural fluid inclusions hosted in sphalerite and compared them to crush and leach ion chromatography Cl/Br analyses. Limit of detection for Br is ~8 $\mu g\ g^{-1}$, whereas relatively high Cl concentrations ($>500\ \mu g\ g^{-1}$) are required for quantification by LA-ICP-MS. In general, our LA-ICP-MS fluid inclusion results agree well with ion chromatography (IC) data. Additionally, combined cathodoluminescence and LA-ICP-MS analyses on natural scapolites within a well-studied regional metamorphic suite in South Australia demonstrate that Cl and Br can be quantified with a ~25 μm resolution in natural minerals. This technique can be applied to resolve a range of hydrothermal geology problems, including determining the origins of ore forming brines and ore deposition processes, mapping metamorphic and hydrothermal fluid provinces and pathways, and constraining the effects of fluid–rock reactions and fluid mixing.

1. Introduction

Chlorine and bromine are common constituents of fluids derived from various sources and because they have relatively low abundances in the majority of silicate minerals, they can be used to trace the origin of fluids in sedimentary and hydrothermal/magmatic systems. Halogens are important ligands for metal transport in hydrothermal solutions, hence Br and Cl behaviours in hydrothermal environments may be crucial for ore forming processes. Numerous studies have investigated Cl and Br contents in hydrothermal fluids in various geological environments (e.g. Banks and Yardley, 1992; Böhlke and Irwin, 1992; Yardley et al., 1993; Banks et al., 2000a,b; Kendrick et al., 2001, 2002, 2008; Nahnybida et al., 2009). However halogen studies can be challenging especially if crucial samples lack fluid inclusions or contain multiple fluid inclusion generations, which limits effective use of routine bulk techniques. Bromine in particular is not easily measured by routine analytical tools such as electron probe microanalysis (EPMA) and quantification of iodine is limited by its low ppb abundance in most materials. Bromine and Cl concentrations in minerals and fluid inclusions have respectively been determined by instrumental neutron activation analyses (INAA) (e.g. Heinrich et al., 1993; Lieftink et al., 1993) and leachate ion chromatography analyses (e.g. Bottrell et al., 1988; Banks and Yardley, 1992; Yardley et al., 1993; Svensen et al., 1999; Nahnybida et al., 2009). Both, INAA and ion chromatography represent bulk analyses of fluid inclusions or minerals. The properties of different generations of fluid inclusions within a single mineral or chemical zoning in minerals cannot be resolved by these techniques. Other methods such as laser microprobe noble gas mass spectrometry (Böhlke and Irwin, 1992; Irwin and Reynolds, 1995; Irwin and Roedder, 1995; Kendrick et al., 2008; Kendrick, 2012), proton-induced X-ray emission (PIXE) (e.g. Heinrich et al., 1992; Ryan et al., 1993; Vanko et al., 2001), synchrotron X-ray fluorescence (SXRF) (e.g. Vanko et al., 2001; Foriel et al., 2004) or secondary ion mass spectrometry (SIMS) (e.g. Hauri, 2002) have been used to obtain halogen concentrations and ratios in minerals and fluid inclusions. However, these methods have not been applied extensively. Compared to the above techniques, LA-ICP-MS is now a widespread

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technique where Cl and Br are measured simultaneously, potentially with large range of other elements. Furthermore, LA-ICP-MS requires minimal sample preparation and is a very cost- and time effective method. Heinrich et al. (2003) assessed the potential of Cl and Br quantification by LA-ICP-MS and very recently Seo et al. (2011) successfully demonstrated the feasibility of in situ LA-ICP-MS Br and Cl quantification. Leisen et al. (2012) also quantified Br by LA-ICP-MS, but were unable to determine Cl using their method. In many cases, minerals contain fluid inclusions belonging to several generations, each of which may represent very different stages of fluid evolution and/or fluid composition. A major advantage of fluid inclusion analyses by LA-ICP-MS is that single fluid inclusions in specific fluid inclusion assemblages can be easily targeted. Single fluid inclusion analyses have the unique benefit that fluid-mixing trends within one fluid generation can be recognized, whereas such information is lost by bulk crush and leach ion chromatography analyses.

Laser ablation inductively coupled plasma mass-spectrometry (LA-ICP-MS) can yield precise compositions of individual fluid inclusions (e.g., Audétat et al., 1998; Günther et al., 1998; Heinrich et al., 1999; Rusk et al., 2004; Klemm et al., 2007) and trace element compositions of minerals (e.g., Pearce et al., 1992; Heinrich et al., 2003; Spandler et al., 2011; Rusk et al., 2011). However, analysis of halogens by LA-ICP-MS is not standard practice, as halogens tend to have relatively low ionisation efficiencies that lead to lower analyte sensitivity, and thus increased detection limits. The energy required to positively ionise fluorine (17.42 eV) makes it impossible for quantification via an Ar (ionisation energy: 15.76 eV) plasma typically used in LA-ICP-MS systems. Bromine, Cl and I are not yet routinely measured by LA-ICP-MS, not only because of their high ionisation energies (Cl: 12.97 eV, Br: 11.81 eV, and I: 10.45 eV), but also because of the lack of suitable standard materials for these elements. Nevertheless, Seo et al. (2011) have demonstrated the feasibility of Cl and Br analyses by LA-ICP-MS. These authors present Cl and Br concentrations in fluid inclusions using scapolite as an external standard, but there are a range of potential analytical problems that remain to be tested, such as the extent of interferences between element signals, elemental fractionation during ablation and potential problems of matrix matching between sample materials and standards.

In this study, we assess the potential of determining in situ Br and Cl concentrations by LA-ICP-MS through analysis of several scapolite grains that have previously been studied for halogen contents (Lieftink et al., 1993; Kendrick, 2012). We compare our LA-ICP-MS analyses of Br and Cl concentrations with existing and new microprobe data and with existing INAA and Noble Gas Method values (Lieftink et al., 1993; Kendrick, 2012). By using a homogenous scapolite that was previously characterised for Br and Cl by the Noble Gas Method (Kendrick, 2012), as our Br and Cl standards, we determine the accuracy and precision of the quantification of Cl, Br, and Cl/Br over a range of Cl and Br concentrations in scapolite, amphibole and sodalite. We evaluate the effects of interferences, down-hole fractionation, and plasma energies at different laser aperture sizes. As a demonstration of the method, we determine Cl/Br of a series of scapolite standards (Lieftink et al., 1993; Kendrick, 2012) and individual fluid inclusions from the Lucky Dog, Coy, and East Tennessee Mississippi Valley type (MVT) Pb–Zn deposits (Roedder, 1971; Viets et al., 1996; Wilkinson et al., 2009). Our results compare well with those obtained by ion chromatography and the Noble Gas Method on the same samples. We also apply the method to metamorphic scapolite from the Adelaide Fold Belt, South Australia, to show changes in fluid composition during scapolite formation.

2. Methods

To determine Cl and Br concentrations and ratios in situ in minerals and individual fluid inclusions, a homogenous standard with known concentrations of Cl and Br is needed. To test the accuracy of our data across a wide range of Cl and Br concentrations, we analysed 4 different scapolites for trace element concentrations using electron probe microanalysis (EPMA) and LA-ICP-MS. These scapolites were previously characterised for chemical homogeneity by SEM imaging, for major elements by EPMA and for halogen concentrations (Br, Cl and I) using the Noble Gas Method and INAA by Kendrick (2012) (SY, BB1 and BB2) and INAA by Lieftink et al. (1993) (DL137). Thirty-four electron probe analyses and over 230 LA-ICP-MS analyses at different spot sizes were carried out on polished grain mounts. To verify the chemical homogeneity of all of the scapolites analysed in this study, wavelength dispersive spectrometry (WDS) element maps of Ca, Na, Cl, and Si were acquired and SEM-CL images were used to identify subtle compositional variations that are not evident from transmitted light petrography. Scapolites SY, BB1, BB2 and DL137, several other Cl-bearing minerals (sodalite and hastingsite amphibole from Bancroft, Ontario, Canada and Little Chief Mine, Washington, USA, respectively) and scapolites from Tanzania, Canada, Switzerland and East Africa were also analysed with EPMA and LA-ICP-MS to compare results of these two methods across a wide compositional range.

2.1. Background

The two stable isotopes of bromine, ^{79}Br and ^{81}Br, are present in roughly equal proportions of 50.69% and 49.31% respectively. Chlorine has two stable isotopes, ^{35}Cl (75.78%) and ^{37}Cl (24.22%). The masses of the Cl and Br isotopes are therefore very close to stable isotopes of Ar (^{36}Ar, ^{38}Ar, and ^{40}Ar), and the biatomic $2(^{40}\mathrm{Ar})^+$ molecule of mass 80. Because Ar is so abundant in the plasma of the ICP-MS, peak tailing of ^{36}Ar and ^{38}Ar has the potential to cause interference on ^{35}Cl and ^{37}Cl, and the combination of two ^{40}Ar ions causes a large peak at mass 80 whose peak tail could interfere with either stable isotope of Br. In addition, there are several potential interferences on ^{79}Br or ^{81}Br; the most significant being $(^{40}\mathrm{Ar}^{39}\mathrm{K})^+$ interference with ^{79}Br and $(^{65}\mathrm{Cu}^{16}\mathrm{O})^+$ and $(^{41}\mathrm{K}^{40}\mathrm{Ar})^+$ interference with ^{81}Br signals. We have conducted a series of analytical tests to quantify the relative contributions from these interferences. No polyatomic species are likely to interfere significantly with ^{35}Cl as $^{70}\mathrm{Zn}^{++}$ did not produce measurable ^{35}Cl when ablating sphalerite. The polyatomic species $(^{36}\mathrm{Ar}^{1}\mathrm{H})^+$ and $(^{23}\mathrm{Na}^{14}\mathrm{N})^+$ possibly interfere with ^{37}Cl. However due to the high backgrounds for ^{37}Cl we did not investigate these possible interferences any further in this study.

2.2. Characterisation of scapolite standards

2.2.1. EPMA analysis

Quantitative major element analysis of scapolite, sodalite and amphibole was carried out using a JEOL JXA 8200 superprobe, at the Advance Analytical Centre, James Cook University. Acceleration voltage and beam current were set to 15 kV, and 20 nA respectively. A defocused 5 μm beam was used to avoid potential diffusion of Na and Cl upon interaction with the electron beam. Counting times were 20 s on peak and 10 s on background for each element. The data were processed using φρz corrections and standardised against a set of well-characterised, in-house oxide (hematite) and silicate (albite, almandine, orthoclase, wollastonite, olivine), sulphate (barite) and tugtupite (chlorine) standards. The detection limit for Cl was ~120 μg g^{-1}.

2.2.2. CL analysis

Cathodoluminescence (CL) imaging was conducted at James Cook University on carbon-coated polished thin sections and grain mounts using a JEOL JSM5410LV SEM and a Robinson CL detector and photomultiplier. The photomultiplier covers the spectral range of 310 to 650 nm, thus is more sensitive in gathering light in the blue to ultraviolet range than in the red to infrared range. Instrument