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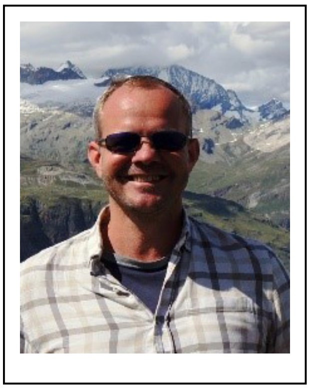

APPLICATION OF SECONDARY ION MASS SPECTROMETRY (SIMS) TO THE STUDY OF VOLATILES IN MELT INCLUSIONS

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1. *INTRODUCTION*

Melt inclusions are micrometre-sized pockets of melt trapped in crystals while they crystallise from magma. The crystal host acts as a robust container, shielding the melt inclusion from late stage volcanic processes such as eruption, crystallisation and degassing. Hence, melt inclusions may provide a wealth of information about pre-eruptive conditions of the magma, in particular the volatile species H_2O, CO_2, S, Cl and F, which are often lost from the magma during its evolution and eruption.

Several analytical techniques are capable of determining volatile concentrations in melt inclusions at the high spatial resolution needed (20 - 500 µm), but few are as versatile as secondary ion mass spectrometry (SIMS or ionprobe). This technique is capable not only of determining elemental concentrations of most volatiles down to ppm level, but also isotopic ratios of these species. In addition, many elements can be analysed simultaneously with volatiles, including fluid-mobile elements such as lithium and boron.

The SIMS technique works by sputtering small amounts of material of the sample surface using a high-energy focussed ion beam, typically composed of $^{16}O^-$ or $^{133}Cs^+$. This sputtered material is accelerated into a mass spectrometer and ion intensities are counted using an electron multiplier or Faraday cup. Multi-collector detection is also possible. The analysis pit is typically ca. 10 - 15 µm wide and several µm deep (Fig. 1). Sample requirements are modest, most importantly a flat surface and compatibility with high vacuum (10^{-9} mbar).

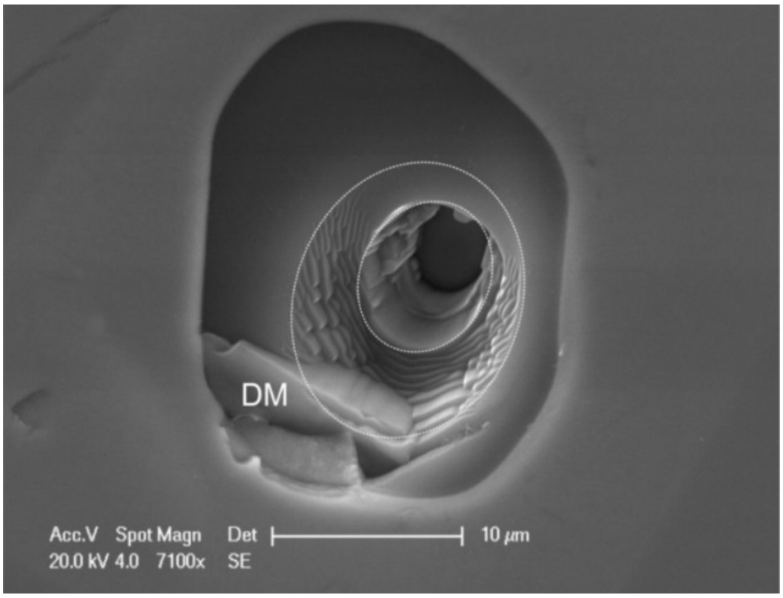

Figure 1. Secondary electron image showing the pits created by the two stages of SIMS analysis conducted on a zircon-hosted melt inclusion. The largest oval represents the pit generated by the boron isotope analysis, the smaller oval is the pit generated by the trace element analysis. Both analyses were about 20 min each. DM = daughter mineral (magnetite).

As every analytical technique, SIMS has its limitations, the most critical one being the need of well-characterised and matrix-matched calibration standards. The following sections will briefly discuss the analytical details of different volatile and fluid-mobile elements as currently employed by the Edinburgh Ion Microprobe Facility (*EIMF*). This NERC-supported facility hosts two ion microprobes each with their own strengths, a small geometry Cameca IMS 4f and a large geometry, high-resolution Cameca IMS 1270. The Cameca IMS 4f will be replaced by a Cameca IMS 7f later this year (autumn 2018).

2. *H_2O*

Water is typically the most abundant volatile in melt inclusions and provides key information about pre-eruptive volatile contents, magma storage depths, volcanic gas emissions and water content of the magma source (e.g., [1]). It can be measured in silicate glasses as ^{1}H or $^{16}O^{1}H$. Of all volatiles, good vacuum conditions are most critical for water analyses ($<10^{-9}$ mbar). Therefore, where possible samples are mounted in indium, which has superior outgassing properties compared to more commonly used epoxy resins.

At *EIMF*, H_2O is generally measured using the Cameca IMS 4f using a $^{16}O^{-}$ primary beam and collecting H^{+} ions. This allows it to be measured at the same time as light volatile elements and trace elements up to $z = 50 - 70$. The Cameca IMS 4f is preferred due to its fast peak switching capability and excellent vacuum control, including an eight-sample air lock and a cryogenic pump.

During analysis of silicate glasses, ion intensities are commonly counted relative to that of ^{30}Si and corrected for the amount of SiO_2 in the sample (determined independently by, e.g., electron probe microanalysis, EPMA). Working curves are calculated by measuring several standard reference materials and plotting known H_2O/SiO_2 vs measured $^{1}H/^{30}Si$. Doing that, a strong matrix-induced bias is observed between basalts (SiO_2 ca. 50 wt%) and rhyolites (SiO_2 ca. 70 wt%). This effect, rather fortuitously, scales with the amount of SiO_2 in the sample. Omitting the SiO_2 correction for H_2O analyses results in working curves that are very similar for basalts and rhyolites (Fig. 2), and can therefore be used for intermediate melt inclusion compositions (SiO_2 = 55-65 wt.%).

Our analytical protocol and extensive collection of glasses with known H_2O contents allows water concentrations in nearly all natural silicate glasses with H_2O contents from 0.01 - 4 wt% H_2O to be determined with an accuracy of ca. 10 %.

3. *CO_2*

CO_2 is for volcanologist a volatile species as important as H_2O and usually measured in conjunction. At *EIMF* C is generally measured in positive ion mode like other trace elements and

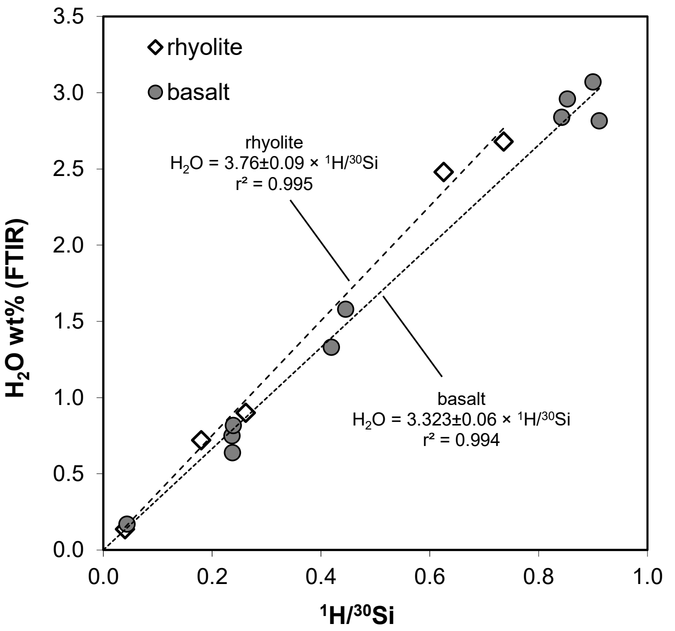

Figure 2. Typical working curves for water in basalt and rhyolite glasses as measured in positive ion mode using the Cameca IMS 4f. Note on the x-axis is plotted ${}^1H/{}^{30}Si$ to correct for matrix-induced fractionation; without this correction the equation would have been ${}^1H/{}^{30}Si \times SiO_2$ (wt.%).

H_2O, using either the Cameca IMS 4f or the 1270. Due to potential interference of ${}^{24}Mg^{2+}$ on the ${}^{12}C^+$ signal this species needs to be measured at high mass resolution of ca. 1,200 to allow interference-free measurement. This is particularly important for basaltic and intermediate melt compositions (Fig. 3) . Only in rhyolitic and granitic systems where MgO < 0.5 wt% can the measurements be done using low mass resolution, but still requires peak stripping of ${}^{24}Mg^{2+}$ signals based on measured ${}^{25}Mg^{2+}$ signals.

In contrast to H_2O, most carbon contamination does not come from the vacuum but from the sample surface. Therefore, a stringent pre-cleaning routine by rastering the ionbeam for several minutes prior to data collection is vital. Adopting this approach we routinely achieve ~1 cps ${}^{12}C$ backgrounds even on Mg-rich materials, equivalent to ca. 15 ppm CO_2. Several well-characterised sets of calibration standards obtained by *EIMF* over the last few years have shown that little matrix effect exist between basaltic and rhyolitic glasses (Fig. 4), allowing measurement of nearly all natural silicate glasses with 20 ppm - 1 wt% CO_2 with an accuracy of ca. 10 %.

4. *HALOGENS (F, Cl)*

Halogens are preferably measured in negative ion mode but can be measured in positive ion mode, which allows simultaneous analysis with H_2O and light fluid-mobile elements (Li, B ± CO_2). Detection limits are at the low ppm level.

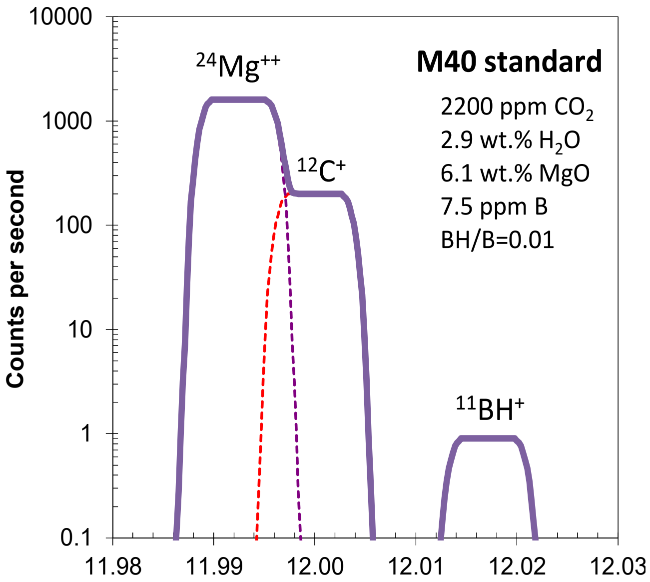

Figure 3. Typical mass spectrum for basaltic glass in the ^{12}C mass region. Note that even though $^{24}Mg^{2+}$ and ^{12}C are not fully resolved at M/ΔM = 1200, the Mg signal is negligible at the centre of the ^{12}C peak at mass 12.00. Using a higher resolution would lead to unnecessary loss of C sensitivity. The ^{11}BH peak is fully resolved.

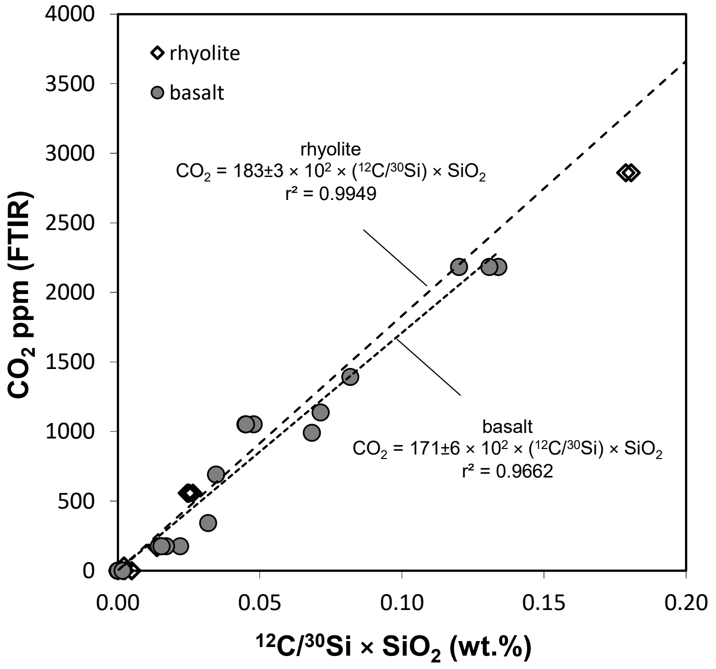

Figure 4. Working curves for CO_2 in basalt and rhyolite glasses. Matrix-induced bias is negligible. Note that the highest concentration rhyolite CO_2 standard (1.03 wt.%) is not shown but has been included in the calibration.

The main issue is the availability of reliable standards, particularly for F, as for many glass standards values in the literature vary by up to a factor two. A considerable matrix effect is apparent between basaltic and rhyolitic glasses but quantification of this awaits better characterised standards. These matrix effects are also apparent when measured in negative ion mode, despite the much higher ionisation yields. In positive ion mode, the estimated difference in relative ion yield for F and Cl (relative to Si) between basalts and rhyolites is about a factor 2, which limits the accuracy to no better than about 25 %. Therefore, for Cl the preferable analytical technique is EPMA as long concentrations are more than ca. 200 ppm.

The two remaining halogens Br and I are in a region of the mass spectrum which has many complex molecular interferences. Therefore, these can only be measured with the Cameca 1270 using very high mass resolutions of ca. 20,000. Lack of suitable standards, which need to be very closely matrix matched, has so far hampered development of a robust analytical setup.

5. SULPHUR

Sulphur is an important volatile as it produces sulfate aerosols in the stratosphere following large volcanic eruptions, which induces significant, but short-lived, climatic effects [2]. In melt inclusions it is often present in high enough concentrations that it can be measured by EPMA and therefore demand at *EIMF* has not been high. Due to interference of O_2 molecular species it can only be measured at high mass resolution, preferably in negative ion mode using a $^{133}Cs^+$ primary beam on the Cameca IMS 1270. It is therefore not routinely measured with the other volatiles, which are predominantly measured in positive ion mode using the Cameca IMS 4f. However, it can be measured simultaneously with C and halogens in negative ion mode.

6. NITROGEN

A very recent development is the ability to measure nitrogen concentrations in silicate glasses and minerals down to ppm level. Despite N being a key nutrient for life, due to the difficulty of measuring N contents its geochemical cycle is less well understood than many other elements [3]. SIMS analysis is challenging in silicates as nitrogen ionizes very poorly in both negative and positive mode. This contrast the situation for diamonds, where N is readily measured as a CN^- molecular ion. In addition, experimentally prepared calibration standards have only recently become available [4].

At EIMF nitrogen is measured in an analytical setup which is very similar to that to measure CO_2, and can indeed be done at the same time. Nitrogen is measured as $^{14}N^+$, as measuring as SiN^+ or NO^+ molecular ion does not appear to beneficial with the instrumental setup used. As is the case for ^{12}C, ^{14}N suffers from several potential interferences (Fig. 5), but these are fully resolved at the mass resolution used. As the main interference is ^{28}Si, N measurements in silicates will always have to be done in high-resolution mode, as opposed to carbon, which can be measured at low resolution in rhyolites (see Section 3). The ion yield is about half that of ^{12}C measured using the same conditions. Note that the method is still under development and not yet routinely available at EIMF, mainly due to limited availability of calibration standard materials.

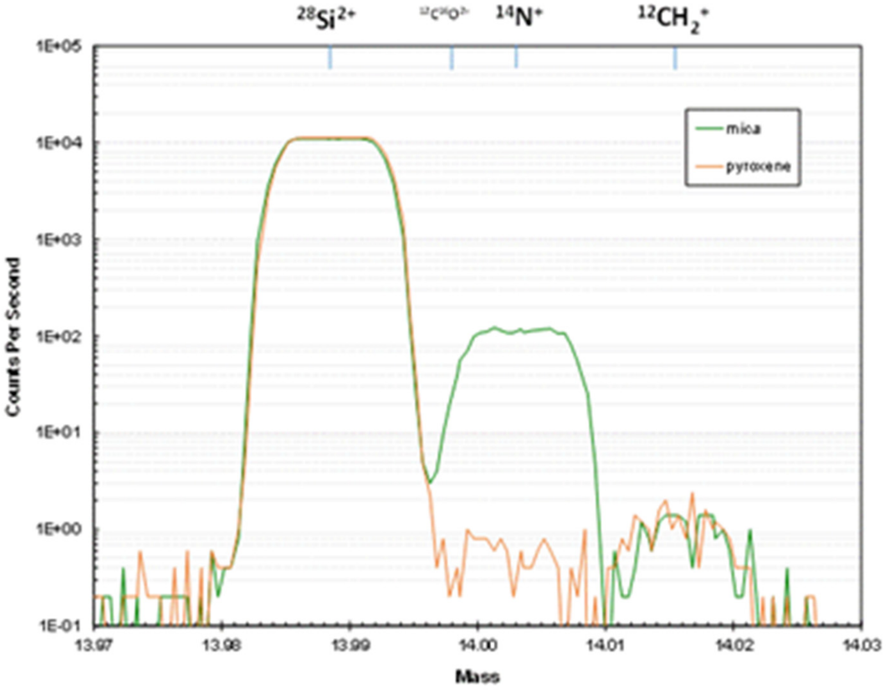

Figure 5. Mass spectrum of mass station 14 (measured at 0 V offset) shows a large $^{28}Si^{2+}$ peak, a clear $^{14}N^{+}$ peak in Phengite 80-3 (90 ppm N) but not in pyroxene, and a small $^{12}CH_2^{+}$ peak. The small N signal in pyroxene (< 1 ppm) may be due to nitrogen background but could also be N in the mineral itself. Mass resolution (M/ΔM at 5 % peak width) ca. 1,200.

7. STABLE ISOTOPES

SIMS is particularly well-suited for measuring isotope ratios due to its production of very stable ion beams over long time periods. The rewards of developing the stable isotope systems for H, C, Cl and S will be high, as these may provide detailed information about volatile sources and degassing processes that are difficult to obtain otherwise (e.g., [5]).

However, progress for the measurement of these stable isotope system has been hampered by difficulties in obtaining calibration standards with a large enough compositional range to cover that of natural samples. Therefore, matrix-induced isotope fractionation effects have not been fully assessed. Synthesising standards, as has been successfully done for volatile concentrations, has been less successful as it has proven difficult to obtain isotopically homogenous glasses in large enough quantities to allow analysis by independent techniques. Natural glasses may be better suited, but sourcing samples with sufficiently high volatile concentrations has so far been largely unsuccessful. Preliminary results in the literature suggested limited matrix-induced fractionation for sulphur isotopes [6], but this awaits further verification by other labs.

Analysis of H, C, Cl and S isotopes can be done at EIMF on a case-by-case basis, and is largely dependent on whether the sample material matches the composition of the small set of standards available.

7.1. Boron isotopes

One of the more successful stable isotope systems is that of boron. Boron occurs in nature as two isotopes, ^{10}B and ^{11}B in a ratio of about 1:4. Although technically not a volatile, boron isotopes are strongly fractionated at the Earth's surface and therefore provide an excellent tracer of recycling of crustal material in subduction zones and the Earth's mantle, as well as hydrothermal processes [6]. In addition, due to its mobility in fluids boron is an excellent tracer of fluid sources.

At *EIMF* are measured preferably using the Cameca IMS 1270 in positive ion mode. Due to the Cameca IMS 1270's large geometry, even at its lowest resolution all potentially interfering species (such as ^{10}B^{1}H and ^{9}Be^{1}H) are fully resolved. Boron isotope ratios can be measured on materials with as little as 1 ppm B to a precision of ca. 1 permil (1σ) in 30 minutes using mono-collection mode and an electron multiplier detector. For concentrations of 10 ppm or higher we can achieve < 0.5 ‰ precision in 15 minutes.

As isotope ratios measured by SIMS typically show significant instrumental mass fractionation, particularly for light elements, measured isotope ratios are corrected using measurements of reference glasses with known isotopic composition (Fig. 6). Many stable isotope systems show significant matrix-dependent isotope fractionation but for boron isotopes it is negligible, as a diverse range of glass standards with SiO_2 ranging from 45 - 74 wt% fall within 1.5 permil of the certified values. The largest source of uncertainty is the apparent heterogeneity of some of the reference materials.

7.2. Lithium isotopes

Lithium occurs in nature as two isotopes, ^{6}Li and ^{7}Li in a ratio of about 1:12. Geochemically, it provides much the same information as boron, but is more prone to kinetic fractionation [8]. Analytical conditions are virtually identical to those of boron isotopes described above. However, SIMS analysis of lithium isotopes suffers from significant matrix-dependent isotope fractionation even within single mineral species [9]. This is in part mitigated by the availability of a diverse suite of glass standards with SiO_2 ranging from 45 - 74 wt%. Lithium ionises more efficiently than B, so precision is about two times better at equal concentration, but accuracy is somewhat less due to uncertainty associated with matrix-induced fractionation.

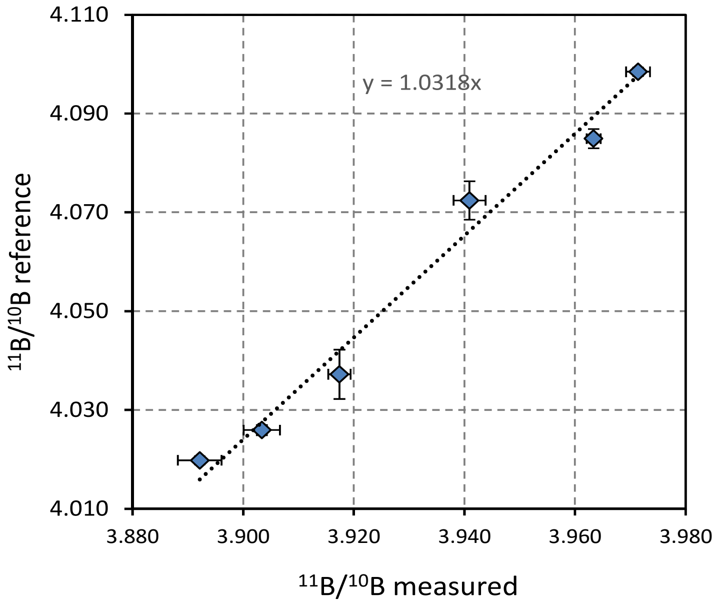

Figure 6. Typical working curve for boron isotopes in silicate glasses with B contents ranging from 4 - 190 ppm and with SiO_2 contents between 45 - 74 wt%. Error bars represent 2s uncertainties. Instrumental mass fractionation in this example is 31.8 ‰.

8. *CONCLUSIONS*

The analysis at *EIMF* of H_2O and CO_2 concentrations in melt inclusions is now routine with good sets of calibration standards and well-tested analytical protocols. The same can be said about boron and lithium isotope ratios. Halogen concentrations are still somewhat challenging, but recently more standard material has become available and these are now being tested as well as cross-calibrated with other materials. Stable isotope analysis of H, C and S still awaits reliable standard material, which is actively being worked on. Work in other labs suggest that matrix-induced fractionation is limited for S isotopes, so this is probably the most promising application in the short term.

9. *ACKNOWLEDGEMENTS*

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