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GEOSTANDARDS and GEOANALYTICAL RESEARCH

Ion Implants as Matrix-Appropriate Calibrators for Geochemical Ion Probe Analyses

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Ion microprobe elemental and isotopic determinations can be precise but difficult to quantify. Error is introduced when the reference material and the sample to be analysed have different compositions. Mitigation of such 'matrix effects' is possible using ion implants. If a compositionally homogeneous reference material is available which is 'matrix-appropriate' (i.e., close in major element composition to the sample to be analysed, but having an unknown concentration of the element, *E*, to be determined) then ion implantation can be used to introduce a known amount of an *E* isotope, calibrating the *E* concentration and producing a matrix-appropriate calibrator. Nominal implant fluences (ions cm^{-2}) are inaccurate by amounts up to approximately 30%. However, ion implantation gives uniform fluences over large areas; thus, it is possible to 'co-implant' an additional reference material of *any* bulk composition having known amounts of *E*, independently calibrating the implant fluence. Isotope ratio measurement standards can be produced by implanting two different isotopes, but permil level precision requires postimplant calibration of the implant isotopic ratio. Examples discussed include (a) standardising Li in melilite; (b) calibrating a ^{25}Mg implant fluence using NIST SRM 617 glass and (c) using Si co-implanted with ^{25}Mg alongside NIST SRM 617 to produce a calibrated measurement of Mg in Si.

Keywords: secondary ion mass spectrometry, ion probe, SIMS matrix effects, ion implants, geochemistry.

Les déterminations élémentaires et isotopiques à la microsonde ionique peuvent être précises mais difficile à quantifier. L'erreur est introduite lorsque le matériau de référence et l'échantillon à analyser ont des compositions différentes. L'atténuation de ces "effets de matrice" est possible en utilisant des implants d'ions. Si un matériau de référence de composition homogène est disponible et est de type "matrice appropriée," c'est-à-dire avec une composition en éléments majeurs proche de celle de l'échantillon à analyser mais ayant une concentration inconnue, à déterminer, pour l'élément E, l'implantation ionique peut être utilisé pour introduire une quantité connue d'un isotope E, l'étalonnage de la concentration en E et la production d'un étalon de matrice appropriée. Les fluences nominales des implants (ions cm^{-2}) sont inexactes pour des quantités allant jusqu'à environ 30%. Cependant, l'implantation ionique donne des fluences uniforme sur de grandes surfaces, il est donc possible de "co-implanter" un matériau de référence supplémentaire de n'importe qu'elle composition ayant des quantités connues de E, étalonnant de façon indépendante la fluence de l'implant. Les mesures des rapports isotopiques des standards peuvent être produites par l'implantation de deux isotopes différents, mais un niveau de précision au niveau du pour mille nécessite l'étalonnage post-implant du rapport isotopique de l'implant. Les exemples étudiés sont les suivants: (1) la standardisation du Li dans la mélilite; (2) l'étalonnage de la fluence de l'implant Mg^{25} en utilisant le verre NIST SRM 617; et (3) l'utilisation du Si co-implanté avec le Mg^{25} dans le NIST SRM 617 pour produire une mesure calibrée du Mg dans Si.

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Mots-clés : spectrométrie de masse d'ion secondaire, sonde ionique, effets de matrice SIMS, implants d'ions, géochimie.

In this paper, we set forth the advantages and disadvantages of using ion implants to produce both *reference measurement* and *working measurement standards* (Table 1) for geochemical secondary ion mass spectrometry (SIMS; ion probe) analyses. The primary advantage is that ion implantation can provide a measurement standard in the same host phases as used for an analysis, and in some cases may be the only way to produce a matrix-appropriate calibrator (i.e., a reference material close in composition to the unknown sample to be analysed). The only significant disadvantage is that, for accurate analyses, independent calibration of the implant is required, but we demonstrate that this is feasible and straightforward.

In analysing captured solar wind from the NASA Genesis Discovery mission (Burnett 2013), we have acquired considerable experience in the use of ion implant calibrators. This paper applies our experience to geochemical applications and to Si, an important Genesis collector material.

Despite the high statistical precision, the accuracy of SIMS analyses can be problematic. For elemental determinations, the conversion of secondary ion counting rates into concentrations is possible only by comparison with a measurement standard of known concentration. For homogeneous samples, counting rates of the element to be determined are normalised to those from a matrix-element isotope and related to concentration by the use of some form of sensitivity factor, *F*, commonly defined from Equation (1) (e.g., Zinner and Crozaz 1986):

$$[E]/[M] = F(E/M), \quad (1)$$

where *E* is the element of interest and *M* is a matrix element of known concentration. Brackets ([]) refer to concentrations, usually in mass fraction. (*E*/*M*) is the ratio of the counting rate or current of isotopes of *E* and *M*, respectively. *F* is defined to give total element concentrations despite the measurement of single isotopes; this assumes that reference material (RM) and unknown have the same isotopic compositions (uncertainties resulting from this assumption are usually negligible). For the RM, the left hand side of Equation (1) is known and *F* can be calculated. The derived value of *F* can be used to calculate the concentration of *E* in an unknown sample measured under the same analytical conditions. The relations between the terms 'samples', 'reference materials' and 'standards' discussed here is confusing, so Table 1 contains definitions based on VIM-3 (2012).

As with all mass spectrometers, ion probes fractionate isotopes, introducing a mass-dependent 'instrumental mass fractionation' (IMF). The IMF is normally calibrated by the use of reference materials of known isotopic composition measured under the same instrumental conditions. The IMF can

Table 1.
Glossary of terms used in this paper

Term	Definition used herein
Measurement standard	Generic definition of the term 'standard'. VIM (2012, 5.1, 6.1): realisation of the definition of a given quantity, with stated quantity value and associated uncertainty
Working measurement standard	Measurement standard that is used routinely to calibrate or verify measuring instruments or measuring systems (VIM 2012, section 5.7, 6.7)
Reference measurement standard	Measurement standard designated for the calibration of other measurement standards for quantities of a given kind in a given organisation or at a given location (VIM 2012, section 5.6, 6.6)
Unknown	Sample to be analysed
Reference material (RM)	Material sufficiently homogeneous and stable with reference to specified properties, which has been established to be fit for its intended use in measurement or in examination of nominal properties (VIM 2012, 5.13, 6.13)
Matrix effect	Differences in SIMS sensitivity factors due to differences in composition
Matrix-appropriate calibrator	RM with composition close to that of unknown
Implant calibrator	Measurement standard used to calibrate the fluence of an implant
Transient effect	Non-linear sputtering of secondary ions observed prior to achieving steady-state sputtering, which will vary with the element and analysis conditions
Internal standardisation	For an implant calibrator, the implanted element and element intrinsic to the measurement standard are determined simultaneously
External calibration	Calibration based on separate depth profiles of working measurement standard and reference material
Nominal (implant) fluence	Fluence of implant from vendor by integrating ion beam current

be expressed approximately as a ‰/amu deviation from the isotope ratios accepted for the RM. In SIMS, the major portion of the IMF is generated by the sputtering process, which normally favours the production of low atomic number isotopes relative to higher ones by a few ‰/amu.

Matrix effects in SIMS analysis

Both *F* and IMF vary with chemical composition, usually referred to as a 'matrix effect'. If the reference material and unknown differ in composition, then the matrix effect may introduce significant systematic errors into the final concentrations or isotope ratios. Ideally, the RM and sample should have exactly the same composition; in practice, this is difficult to achieve.

A matrix effect can be quantified as the fractional difference in *F* (or IMF) between the working standard and a perfect measurement standard of identical composition to the sample being analysed. As minor elements may affect sensitivity factors, 'identical' is hard to document, so the more nuanced terms, 'matrix-appropriate' or 'matrix matched', are in current use in the literature. These terms imply that compositional differences between sample and reference material should produce negligible errors.

There is a relatively large literature on matrix effects in SIMS analyses. Here, we note only a few examples of both relatively large matrix effects and, for contrast, cases where matrix effects appear to be absent.

Bell *et al.* (2009) compared SIMS and inductively coupled plasma-mass spectrometry (ICP-MS) analyses of $^{7}Li/^{6}Li$ in olivine, finding a systematically increasing SIMS Li IMF ranging from 0 to 20‰ for samples with mg# ranging from 0.95 through 0.74 (mg# = molar Mg/(Mg+Fe) of the olivine). Thus, an olivine having mg# = 0.95 would have an uncertainty in the corrected $^{7}Li/^{6}Li$ ratio of 20‰ if measured relative to a matrix-inappropriate olivine RM with mg# = 0.74.

In contrast, using the same approach as Bell *et al.* (2009), Williams *et al.* (2011) found nearly identical Li IMF for six of eight clinopyroxene samples for mg# ranging from 0.6 to 0.95. For two clinopyroxenes, the deviations in Li IMF were less than 5‰, but still significant within the precision of the measurements. The deviant samples (mg# 82 and 90) were not extremes in mg#, so there appear to be small clinopyroxene matrix effects for Li not determined solely by mg#.

Chaussidon *et al.* (1997) found no measurable matrix effects for the analysis of B concentrations or isotopic compositions in ten synthetic glass samples ranging over a factor of 10^5 in B/SiO_2. Similarly, Hervig (2002) found no significant matrix effects for Be/Si for a wide variety of silicate glasses and minerals with Be/Si concentrations ranging over a factor of 10^5.

In contrast, large matrix effects are present in the measurement of [Mn] and [Cr] in iron-rich meteoritic olivine, important for obtaining ages with the $^{53}Mn/^{53}Cr$ radioisotope chronometer. Doyle *et al.* (2013) found 20% variations in sensitivity factors among synthetic olivine with mg# = 70 to mg# = 0, although the differences are not clearly correlated with mg#. The sensitivity factors for the synthetic olivine are approximately 1.5 times that for San Carlos olivine (mg# = 90). Even larger matrix effects in olivine, up to 60%, were found for Mn/Cr by McKibbin *et al.* (2013).

In summary, although cases exist where matrix effects are small, there is no *a priori* way of knowing this unless a specific study has been made. Furthermore, even when a study indicates a lack of matrix effects, in the absence of theoretical understanding, one can never be sure whether a sample being studied might be an exception. The above examples show that matrix-appropriate calibrators are necessary for analyses when high accuracy is required. Nevertheless, even when the RM being used appears to be matrix-appropriate, it is difficult to estimate the uncertainty associated with the assumption that matrix effects are negligible.

Ion implantation allows introduction of measurable amounts of any element into a reference material with (ideally) the same composition as the unknown. In some cases, it may be possible to implant the unknown itself. The use of ion implants for creating measurement standards for SIMS is routine in materials science (e.g., Wilson *et al.* 1989), but rare for geochemical analyses, although previously proposed by Zinner and Walker (1975) and Leta and Morrison (1980). Examples of geochemical applications include quantification of H concentrations in silicate glasses (Hervig *et al.* 2003), measurement of surface deposits of low atomic number elements in lunar soils (Zinner *et al.* 1976), and of Au concentrations in ore samples (e.g., Chryssoulis *et al.* 1989).

Here, we present our techniques for using ion implantation to make calibrated, matrix-appropriate, measurement standards. In this paper, we give examples for elemental determinations; however, as discussed further below, implantation of more than one isotope can produce isotope ratio measurement standards.

Experimental procedure

Implant fabrication

Commercial ion implanters have the capability of implanting ions covering most of the periodic table at fluences (atoms cm^{-2}) in the range 10^{12}–10^{16} cm^{-2} at energies of ~ 10–200 keV. Implantation energies giving peak depths in the 50–200 nm range are optimal. Theoretical depth profiles can be calculated with the SRIM (stopping and ranges of ions in matter) free software (Ziegler *et al.* 2008). Our implants were done at 7° off normal incidence to minimise channelling effects of incident ions along crystallographic axes. Implant ion beams are mass-analysed with a mass resolution sufficient to clearly resolve masses 1 mass unit removed from the desired implant mass. The integrated beam current is carefully measured, typically with Faraday cups at each corner of the rastered ion beam, to ensure laterally uniform implantation over dimensions larger than the size of the samples. Implant fluences are thus approximately known even prior to independent calibration. Comparisons between independently measured and nominal fluences are discussed below.

Ion implants used here are from Kroko, Inc. (Tustin CA), from R.G. Wilson (Hughes Research Lab) or on loan from Evans Analytical Group (Sunnyvale, CA, USA). Multiple samples were simultaneously implanted ('co-implanted') with the same fluence (Figure 1); this is of considerable importance, as discussed below. Samples were mounted with carbon tape or carbon paint. For insulating samples, a thin conductive coating (C or Al in our case) was evaporated onto the surface, and the coating was electrically grounded to the mounting plate with carbon paint. For a 75 mm × 75 mm mounting plate (Figure 1), the ^{25}Mg ion beam from the Kroko facility was rastered over 100 mm × 100 mm producing a uniform implant over the typically 75 mm × 75 mm area of the sample array. Implant beam currents in the 1–10 μA range were used. For handling convenience, samples greater than millimetre sizes are desirable. However, polished mounts of smaller samples can also be implanted, allowing 50–100 μm mineral grains to be used as RMs.

Fluence uniformity

Tests on Kroko implants showed uniform fluences (< 3% for elemental analysis; < 3 permil for the ratio of two isotope implants). The best-constrained test of homogeneity was from a 5 × 10^{15} cm^{-2} ^{56}Fe implant into Si, for which high-accuracy Rutherford backscattering spectroscopy (RBS) analysis was possible. Specifically, in pieces from the centre and near the edge (~ 70 mm span), measured ^{56}Fe fluences agreed to within about 1%.

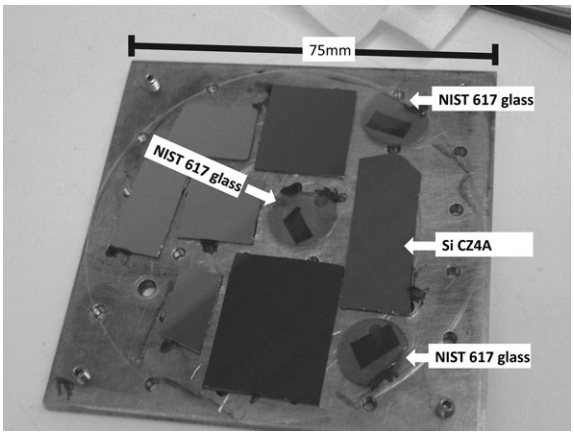

Figure 1. Ion implanter beams can be uniformly rastered over large areas (up to 10 cm × 10 cm) compared with sample sizes used for geochemical SIMS analyses. Samples such as CZ4A Si are 'co-implanted' with the same fluence as the NIST SRM 617 glass samples used to calibrate the fluence. With co-implantation, a matrix-appropriate SIMS measurement standard (here Mg in Si) with a calibrated fluence can be produced as long as some other sample of *any bulk* composition but with a known concentration of the implanted element (here Mg determined by ICP-MS) is available to calibrate the implant, here the NIST SRM 617 glass. The dark sample in the figure is diamond-like carbon. The remaining samples are Si.

Calculating concentrations from an implant

Following Wilson *et al.* (1989), a relative sensitivity factor, RSF, is defined:

$$n(x) = RSF\, E_i(x)/M, \quad (2)$$

where n is atomic concentration (atoms cm^{-3}) which in the case of an implant is a function of depth, x. RSF has units of atoms cm^{-3}. $E_i(x)$ refers to the depth profile of the counting rate or current of the *implanted E* ions, that is any background *E* (from either instrument or sample) has been subtracted. *M* is the counting rate or current of the matrix isotope used for normalisation, which is assumed not to be a function of depth. RSF in Equation (2) for an implant is equivalent to *F* in Equation (1), which applies to elemental determinations in homogeneous samples. Small drifts in primary ion current or in secondary ion transmission, for example from minor charging in insulating samples, are approximately cancelled by use of the *E*/*M* ratio.

The implant fluence, Ψ, in atoms cm^{-2} is related to concentration and RSF:

$$\Psi = \int n(x)\,dx = RSF \int E_i(x)/M\,dx. \quad (3)$$

Other symbols are as defined for Equation (2). The limits of the integral go from the surface to a depth where the implant concentration is negligible.

The depth profiles are measured as a function of time, *t*. The depth and time scales are related via a sputtering rate, *S* (nm s^{-1}):

$$dx = S\,dt. \quad (4)$$

Because crater depths are measured postanalysis, the sputtering rate is usually regarded as constant, and the adopted *S* is an average, measured from the depth of the final sputtered crater, *X*, and the total profile time, t_{max}:

$$S = X/t_{max}. \quad (5)$$

Crater depths for this study were measured with a stylus profilometer at Arizona State University and with a similar profilometer at NIST. Intercomparison of measurements of the same pits on both instruments yielded good agreement (better than 2% in all cases), as did measurements of NIST-traceable step height standards with the ASU profilometer.

If there is evidence of beam current drift during the course of the analysis, variable sputtering rate models can be used. However, variations in the matrix counting rate alone cannot be assumed to reflect changes in sputtering rate; these variations can also be due to changes in secondary ion production or transmission.

Table 2.
SIMS analytical conditions

Instrument (Cameca)	Figure 2 Caltech 7f Geo	Figure 3 Caltech 7f Geo
Implant ion[a]	^{6}Li	^{25}Mg
Implant energy (keV)	50	75
Implant fluence (ions cm^{-2})	1×10^{13}	3×10^{13}
SIMS primary ion	O^-	O^-
Impact energy (keV)	22	22
Primary ion current (nA)	21	21
M/ΔM[b]	800	800
Matrix ion[c]	^{40}Ca	^{28}Si
Raster size (μm)	100	75
Field aperture (μm)	400	400
Diameter analysed (μm)	35–40	35–40
Electronic gating	Yes	No
Oxygen flood	No	Yes

Both samples Au coated for analysis.
[a] Measured with electron multiplier detector.
[b] ΔM defined at 1/10 peak height.
[c] Measured with Faraday cup detector.

SIMS analyses for this work were done with the Cameca 7f Geo at the California Institute of Technology (Caltech) and the Cameca 6f instruments at Arizona State University or the Carnegie Institute of Washington. Specific analytical conditions are given in Table 2.

Results

Example 1– Calibration of a mineral for use as a concentration measurement standard

This example illustrates how an implant can be used to calibrate an elemental concentration in a reference material to produce a matrix-appropriate calibrator. It assumes that the implant fluence is known. For precise work, the fluence must be calibrated, but this is a separate issue considered further below.

Figure 2 shows ^{6}Li and ^{7}Li depth profiles for a ^{6}Li implant into a polished single crystal of melilite, in this case the åkermanite ($Ca_2MgSi_2O_7$) end member. Implant and SIMS analytical conditions are summarised in Table 2. There was no evidence for implanted ^{7}Li, so the steady state ^{7}Li counting rate deeper than 60 nm is due to intrinsic Li in the åkermanite. Except for a negligible amount of surface contamination, the ^{6}Li counting rate reflects the implant until about 1400 nm where the background ^{6}Li level from the åkermanite is reached. The background ^{6}Li count rate is compatible with the ^{7}Li counting rate and the natural terrestrial $^{7}Li/^{6}Li$ isotope abundance (≈ 12.2). Subtracting a constant background ^{6}Li gives the implant ^{6}Li profile. Normalising this to the ^{40}Ca matrix ion intensity (not shown on Figure 2) and integrating gives the RSF as defined in Equation (3). Then, Equation (2) can be used to calculate the åkermanite ^{7}Li concentration based on the åkermanite ^{7}Li counting rate. Additional details and uncertainties are discussed in Appendix S1 (online supporting material).

Example 2 – Calibration of implant fluence with a sample of known, uniform concentration (^{25}Mg implant into NIST SRM 617 glass)

Nominal implanter fluences are sufficient for most materials science applications. However, for some geochemical applications, where greater accuracy is required, it is necessary to calibrate the reported fluence. Accurate fluence calibration is possible by analysing a separate sample of independently known concentration and, using

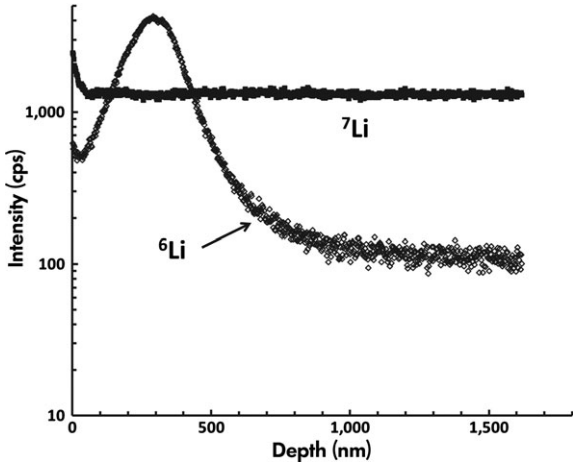

Figure 2. Depth profiles for implanted ^{6}Li and matrix ^{7}Li in a sample of crystalline synthetic melilite (åkermanite end member). The known implant fluence can be used to determine the bulk Li concentration in this sample, which is then used as a working measurement standard in determination of Li in meteoritic melilite.

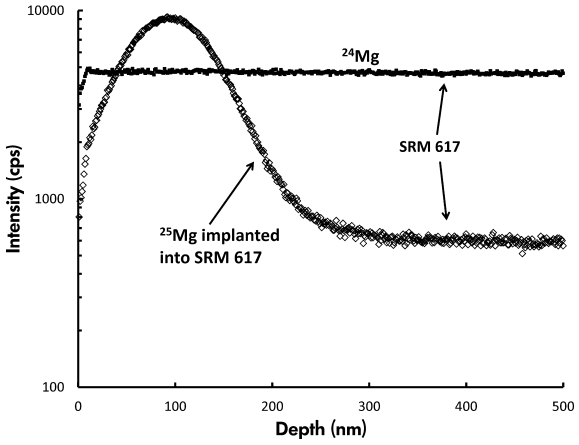

Figure 3. Depth profiles for implanted ^{25}Mg and bulk ^{24}Mg in a sample of NIST SRM 617 glass. In this case, the Mg concentration of this glass RM was known and the fluence of the implant could be calibrated.

Equations (2) and (3), inverting the calculations made in Example 1. Here, the known concentration in a sample is used to calibrate the fluence; whereas in Example 1, the implant fluence was used to calibrate a concentration. In Example 2, the known Mg concentration in a soda lime glass reference material was used to calibrate a ^{25}Mg implant fluence.

NIST SRM 617 soda lime glass was purchased as a set of six ~ 1 cm diameter by 1-mm-thick glass discs. Magnesium is not certified in this glass, so to avoid confusion, we hereafter just refer to '617 glass'. Magnesium was not deliberately added to NIST SRM 617 glass during manufacture and, as a contaminant, might not be uniform in all batches. Consequently, one of the NIST SRM 617 glass discs in our batch was independently measured by ICP-MS at Florida State University using isotope dilution with a ^{26}Mg spike, giving a Mg concentration of 26.5 ± 0.4 μg g^{-1} for our batch. As shown in Figure 1, three other discs were simultaneously implanted permitting our assumption of uniform Mg concentration within our set of discs to be tested.

Figure 3 shows an example of the ^{25}Mg implant and intrinsic ^{24}Mg profiles for the 617 glass. Analytical conditions were similar to Example 1 (Appendix S1) and are given in Table 2.

The derived ^{25}Mg implant fluence based on our measured Mg concentration of 617 glass is quite accurate because the ^{25}Mg and ^{24}Mg are measured simultaneously; thus, the ^{24}Mg serves as an *internal standard* for the calibration of the implant ^{25}Mg. When a RM and unknown are not measured simultaneously but instead in separate analyses (i.e., in an *external* mode), variations in sensitivity can result from differences in sample mounting, edge effects, instrumental drifts in secondary ion intensity, etc. (e.g., Deng and Williams 1989). The use of matrix ion normalisation partially mitigates these differences, but not completely. In this example, the sample (implanted ^{25}Mg in this case) and RM (intrinsic ^{24}Mg) are analysed essentially simultaneously, eliminating many of the above sources of uncertainties. RSF is much more sensitive to variations in analytical conditions than IMF due to the similar ionisation properties of isotopes as opposed to different elements (e.g., Schuhmacher *et al.* 1994).

Transient effects can produce RSF variations at shallow depths prior to achieving steady-state sputtering (below 100 nm in Si, see below). In conventional SIMS bulk analyses of homogeneous materials, the transient effects are mitigated by so-called presputtering before quantitative analysis; but, for implants, presputtering is not possible because (ideally) the analysis must start from the surface. With implants, uncertainties from transient effects can be minimised by adjusting analytical procedures (see below) or, as illustrated in Figure 2, by choosing a sufficiently high implant energy so that a negligible fraction of the implanted ions are in the transient region. Some additional discussion is given in Appendix S1.

For the 617 glass, to minimise transient effects, analyses were made in the presence of about 10^{-5} torr of O_2 in the

sample chamber. Transient effects on the Mg profiles are less important than for Si. In Figure 3, the ^{24}Mg counting rate becomes constant at around 9 nm, and a break in slope of the ^{25}Mg counting rate can be seen in the ^{25}Mg profile near this depth. The small, but significant, transient effects for ^{28}Si are best illustrated by the $^{24}Mg/^{28}Si$ counting rate profile (Figure 4) where the $^{24}Mg/^{28}Si$ ratio does not reach a constant value until about 100 nm. Although the Si transients are fairly small in this case, (less than about 10%), they must always be considered. Additional details of the implant fluence calculation, along with estimates of uncertainties, are given in Appendix S2 (online supporting material).

Fluences from the three discs agree well, within a standard deviation of 1.5% (Appendix S2). This agreement supports our assumption of uniform Mg concentration within our set of 617 glass discs. The average measured fluence is 87% of the nominal fluence value by the ion implanter, so that a significant error would have resulted without the calibration. Our adopted fluence was 2.63×10^{13} cm^{-2} with a total uncertainty of around 4%, one standard deviation.

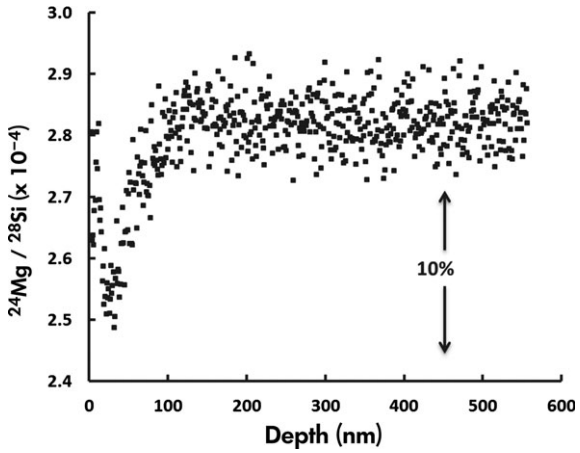

Figure 4. The $^{24}Mg/^{28}Si$ counting rate ratio profile for the same analysis as Figure 3. Unlike the Mg isotopes in Figure 3, the counting rate for ^{28}Si took a relatively long time to reach an equilibrium value, actually exceeding the asymptotic value until around 80–90 nm, which causes the dip in $^{24}Mg/^{28}Si$ in this figure. These Si transient effects are relatively small and are observed in all profiles of NIST SRM 617 glass. A constant asymptotic $^{24}Mg/^{28}Si$ ratio was observed beyond 90 nm in all six NIST SRM 617 glass profiles (Appendix S2) even when decreases of 2–11% in the separate counting rates were observed. The depth at which $^{24}Mg/^{28}Si$ becomes constant varied from 35 to 90 nm among six profiles.

Example 3 – Mg in Si: Producing a matrix-appropriate calibrator with a calibrated implant fluence by co-implantation

This example is a simple, but important, extension of the concepts involved in Examples 1 and 2, showing that a fluence-calibrated, matrix-appropriate, measurement standard can be produced in a single implant. As illustrated in Figure 1, a large number of samples can be 'co-implanted' with the same fluence. This is possible because ion implanters can uniformly raster the implantation beam over areas that are large compared to the size of samples used for geochemical SIMS analyses.

Figure 1 shows a typical sample mounting arrangement for our implants, in this case including the NIST SRM 617 glass samples used to calibrate the ^{25}Mg implant, as discussed in Example 2. The glasses spatially bracketed Si sample CZ4A during the implant (Figure 1). Therefore, the CZ4A Si implant has the same ^{25}Mg fluence as the glasses and is a calibrated reference measurement standard (VIM 2012) for the determination of Mg in Si.

In most cases, co-implanted samples will have different compositions, and a fluence correction (usually small) for differential backscattering during the implant is required. A significant number of ions from the implantation beam will backscatter off a target of higher atomic number, for example gold, but will be implanted more efficiently into an adjacent material of low atomic number. The backscattering correction can be done with sufficient accuracy by using SRIM (Ziegler *et al.* 2008) as shown in Heber *et al.* (2009, 2011). In the case of ^{25}Mg co-implanted into both Si and the 617 soda lime glasses, the correction was small (less than 1%) because the mean atomic numbers are similar.

Discussion

We have shown how implants can be used as ion probe working measurement standards and how co-implanted samples can be used to produce fluence-calibrated, matrix-appropriate implant calibrators for high-accuracy SIMS elemental determination. In this technique, a matrix-appropriate reference material is co-implanted alongside a sample of known concentration that is used to calibrate the implant fluence. It is important to note that *any* material of known and (ideally) uniform composition can be used for the fluence calibration. This implant calibrator need not have the same composition as the reference material.

How to select implant parameters

As illustrated in Figures 2 and 3, it is desirable to select an implant energy so that the peak of the implant profile is at least 100 nm deep to minimise errors from surface contamination and transient effects. SRIM (Ziegler *et al.* 2008) can be used to select the appropriate energy of the implanted ion beam for any material.

The SRIM output gives the number of implanted atoms at a given depth that is proportional to the atoms cm^{-3} concentration at that depth. For a chosen fluence, Equation (3) allows calculation of a depth profile in units of atoms cm^{-3}, which can then be compared with the intrinsic level of a particular isotope in the sample. To choose a fluence, at least an order of magnitude estimate of the concentration of the element to be analysed is required, but in many cases, 'over implanting' with a high fluence is possible to allow for the uncertainty in the estimate. The intrinsic levels of the determined element can always be measured after sputtering through the implant (e.g., Figure 2).

Either for a reference material to be calibrated (Example 1) or for an implant fluence calibration (Example 2) the intrinsic concentration of the element in question cannot be so high relative to the concentration of the implant that significant uncertainties result from the required background correction to the implant depth profile. In most cases, the background is constant, so that subtraction is accurate, and a peak concentration as low as a factor of 2–3 above background is acceptable, although a higher ratio is desirable.

The examples given involve elements with more than one isotope. The use of a minor isotope (e.g., ^{25}Mg) extends the range of concentrations that can be used both for reference materials and for implant calibrators (Williams *et al.* 1983, Franzreb *et al.* 2004). An un-implanted major isotope, for example ^{24}Mg in Example 2, can also be used to monitor and correct for drifts in secondary ion intensity (Appendix S2). The techniques described here are applicable to mono-isotopic elements, without significant increases in uncertainties. In most cases, use of matrix normalisation (Figure 4, Appendix S2) adequately compensates for drifts. Surface contamination is potentially more important for mono-isotopic elements, but normal surface cleaning procedures for SIMS analyses are usually adequate and checks can be made prior to implanting. If there is lingering concern about surface contamination, relatively high fluences, in the 10^{14} cm^{-2} range, can be used.

Although rarely significant issues, a maximum fluence limit in the 10^{15} cm^{-2} range is set by radiation damage and by the possibility of the implant itself causing a matrix effect by changing the RSF (Appendix S3, online supporting material).

When are implants required?

Use of an implant calibrator may be the only viable solution when very small amounts of a reference material with an appropriate matrix composition are available. If sufficient material is available, and other techniques for calibration could be used, there remain advantages to using an implant calibrator. If a large number of different working measurement standards are required, for example members of a mineral solid solution series, they can all be co-implanted with the same fluence instead of making a separate bulk analysis for each composition. Also, implants have the advantage that all steps are done with SIMS analysis and access to external facilities is not required. Finally, there are cases where pure commercial reference materials are available (e.g., Si, diamond, Al_2O_3) but do not contain the element of interest in easily analysed concentrations. Here, instead of using the implant to calibrate the reference material, as in Example 1, the implant in the pure material is analysed directly to provide the required sensitivity factors.

An important issue is the homogeneity of the element to be standardised in a matrix-appropriate reference material. Minor and trace elements are often very heterogeneous, especially in natural minerals. The problem of heterogeneity can be solved by implant calibration. The implant gives a 'local area calibration' of the standard in addition to a sensitivity factor that can be used to analyse unknowns. If available, and not too heterogeneous, an un-implanted piece of the reference material can be intercalibrated relative to the local area on the implant. An intercalibrated un-implanted piece has another advantage in that there is no need to measure a complete implant depth profile, although a typical analysis time for a depth profile is only 0.5–1 hr. If a multi-isotope element is being analysed, a *local* calibration of a different isotope from that implanted can be used. In example 1, ^{7}Li in a local area of the ^{6}Li-implanted sample serves as a working measurement standard for Li concentrations in melilite without measuring the ^{6}Li depth profile every time.

As an implant calibrator, a homogeneous sample is desirable. In the special case where concentrations of an element with ($8 < Z < 32$) are around 100 $\mu g\ g^{-1}$, analysis can be made with an electron microprobe, allowing local area calibration. Thus, assuming homogeneity on the scale of the SIMS beam spot, the implant can be calibrated by

SIMS analysis on the exact spot analysed with the electron microprobe. Recall that, with co-implantation, the implant calibrator will differ in composition from the reference material to be calibrated by the implant.

In some cases, the extra work to make implant calibrators is not justified. With the exception of elemental analyses made in conjunction with geochronology studies, many geochemical elemental analyses do not require high accuracy in the measured *absolute* concentration. Concentrations of a trace element in the same phase in different grains within a given sample or among closely related samples may vary by orders of magnitude with only the relative concentrations scientifically significant and absolute concentrations un-interpretable, or of secondary interest. If the *largest* matrix effects in SIMS elemental determinations in silicates are a factor of 1.6, as in the Mn/Cr case discussed in the Introduction, and if systematic errors up to 60% are acceptable, then there may be nothing wrong with simply calibrating using a NIST SRM glass, as is commonly done. However, the 1.6 factor is illustrative, and we cannot rule out that larger factors may exist in specific cases, even among silicate minerals.

Accuracy of implant measurement standards: Is calibration necessary?

Ion implants can eliminate uncertainties due to matrix effects, but is it really necessary to calibrate the implants, as discussed here? Even without any constraints on the composition of the implant calibrator, it can be difficult to find a material of known and uniform concentration of a given element, and which has concentration in the right range for a convenient fluence, although NIST SRM 610 would be suitable for many elements.

Once an implant calibrator is obtained, as with CZ4A Si for ^{25}Mg (Example 3), then other implants of the same element in the same matrix can be intercalibrated. This is a situation that would be rare in most geochemistry laboratories, but the study of Genesis solar wind samples has produced several such examples. Combined, they allow some insight into the accuracy of nominal ion implant fluences.

Part A of Table 3 lists two sets of implants (^{25}MgSRIV and ^{56}Fe KB Si) with accurate fluences that serve as *reference measurement standards* (VIM 2012, part 5.6) from which other implants can be intercalibrated. Table 3B summarises the intercalibration of nine Mg or Fe implants. These are all independent implants produced over a multi-year time span from at least two different implanters. The reference measurement standards were independently calibrated, for example by RBS, or represent samples like CZ4A, which are co-implanted with a fluence calibration sample. The intercalibrated samples were 'externally' calibrated; that is, the measured fluence is based on the comparison of separate profiles from the reference measurement standards and the implant sample to be intercalibrated. To maintain accuracy, analytical conditions in the SIMS analyses (position in mount, location of sample edge, etc.) were carefully controlled.

Table 3.
Comparison of nominal and intercalibrated implant fluences

A. Fluences of Genesis reference measurement standards

Implant designation	RM used for calibration	Nominal fluence (cm^{-2})	Measured fluence (cm^{-2})	Variance (%)
^{25}Mg SR IV	NIST SRM 617 glass Mg	3×10^{13}	$2.61 \pm 0.04 \times 10^{13}$	13
^{56}Fe KB Si	^{56}Fe KB Si[a]	5×10^{15}	$5.00 \pm 0.05 \times 10^{15}$	0

B. Fluences of Genesis intercalibrated measurement standards (externally calibrated)

Implant designation	Intercalibrated from	Nominal fluence (cm^{-2})	Measured fluence (cm^{-2})	Variance (%)
^{25}Mg K7A	CZ4A Si[b]	1×10^{12}	$9.0 \pm 0.3 \times 10^{11}$	10
^{25}Mg K7B	^{25}Mg K7A	5×10^{13}	$5.0 \pm 0.3 \times 10^{13}$	0
^{25}Mg K7C	^{25}Mg K7A	3×10^{15}	$2.5 \pm 0.1 \times 10^{15}$	17
^{25}Mg KA-1	^{25}Mg K7A	1.9×10^{13}	$1.44 \pm 0.07 \times 10^{13}$	24
^{56}Fe EAG 3683 Si	^{56}Fe KB Si	3.4×10^{14}	$3.19 \pm 0.06 \times 10^{14}$	6
^{56}Fe KA	^{56}Fe KB Si	4×10^{14}	$3.4 \pm 0.2 \times 10^{13}$	15
^{54}Fe CZCFA2 Si	^{56}Fe KB Si	1×10^{12}	$5.5 \pm 0.3 \times 10^{11}$	45

[a] Rutherford backscattering measurement on implant.
[b] From ^{25}Mg SR IV (i.e., co-implanted with NIST SRM 617 glass).

As can be seen in Table 3, the measured implant fluences are less than nominal fluences with differences ranging from 0 to 45%. A similar range of deviations from the nominal fluence was observed for several C, N and O implants (Heber *et al.* 2014). The 45% case in Table 3 represents a difficult, low fluence ^{54}Fe implant. If nominal fluences greater than 10^{13} cm^{-2} are considered, the range is 0–30%. The 30% figure is significantly larger than expected based on the uncertainties assessed by the implant vendors. Our results show that if systematic errors of up to 30% in geochemical SIMS elemental determinations are not acceptable, calibration of an implant measurement standard is necessary. But calibration is feasible with the techniques described here.

The fact that the calibrated fluences are always lower than the nominal fluences based on integrating current onto the targets suggests that some other species at the same mass/charge may be present as impurities in the ion implanter beam. The ion implants are mass-analysed, but the mass resolution is typically low ($M/\Delta M \approx 0.5$). SIMS analyses to check for the interfering species is usually possible; we have not done this systematically, relying instead on calibration of the implanted fluence of the desired species.

Alternative methods of implant calibration

For a SIMS laboratory, the approach to calibrating implants described in Examples 2 and 3 above will be the most convenient. However, non-SIMS approaches can also be used to calibrate implant fluences. For example, we have used RBS to calibrate a nominal 5×10^{15} cm^{-2} ^{56}Fe implant into Si, giving $5.00 \pm 0.05 \times 10^{15}$ cm^{-2}. However, RBS can only be used for the highest fluences ($> 10^{15}$ cm^{-2}) and for heavy elements implanted into low atomic number element substrates. Also, Heber *et al.* (2009) used laser ablation extraction of known areas to calibrate noble gas implants.

Isotopic implant calibrators

Ion implanter beams are mass-analysed; thus, an isotopic ratio measurement standard requires at least two implants. For example, we have produced isotopic measurement standards for Mg in Si by implanting ^{25}Mg and, separately, ^{26}Mg. An alternative is to implant a heteronuclear diatomic molecular ion which provides an isotope ratio of exactly unity for the two isotopes, for example implant of HD into silicon allowed the mass fractionation of the two isotopes during sputtering to be determined (Williams *et al.* 1983). For a permil level isotope ratio measurement standard, great care is required in a diatomic molecule implant to avoid small contributions from tails of neighbouring mass molecular peaks and interfering molecules with one of the isotopes at the same mass.

A compensating factor for needing two implants is that the implant isotopic ratio can be adjusted, for example, to be different from the natural isotopic ratio, thus enabling surface contamination effects to be readily recognised. Because higher isotopic ratio precision is required for geochemical analyses, a postimplantation calibration of the isotopic ratio is required, for example by multi-collector ICP-MS, but with co-implantation, *any* easily analysed material can be used for the postimplantation isotopic ratio calibration.

Cost

The cost of ion implantation varies with the element, the fluence and the company. During the course of Genesis sample analyses, we have made roughly forty implants at costs ranging typically from US$200 to US$600 per implant. Since SIMS laboratories are built around multi-million dollar instruments, these costs are not unreasonable. Moreover, because large areas can be uniformly irradiated, many working measurement standards of different matrix compositions can be produced in one implant. Since the matrix-appropriate reference material to be calibrated and the implant calibrator are co-implanted, additional costs are not incurred to produce calibrated implants. With the mounting arrangement shown in Figure 1, 20–30-cm-sized samples can be implanted, although costs may increase with implant area.

Conclusions

Ion implantation is essential for cases where there are no existing natural or synthetic materials that can be utilised as working measurement standards (e.g., Genesis solar wind analyses). Ion implantation is also useful when only small (few mm or less) samples are available of a reference material of appropriate bulk composition, but for which the concentration of the element, *E*, to be determined is unknown. The known implant fluence of an isotope of *E* can be used to measure the concentration of *E* in the reference material, as illustrated in Example 1 and Figure 2. This calibration process is simple. Many details are discussed above and in the Appendices, but these are primarily differences in analytical procedures compared to SIMS analyses of homogeneous materials. Significant uncertainties are relatively easily avoided. The only major source of systematic error is the accuracy of the nominal implant fluence, which can be in error by as much as 30%. However,

because multiple samples can be co-implanted (Figure 1), an implant calibrator, of *any* material, which has a known concentration of *E*, can be implanted in the same implant as the reference material and used to calibrate the implant fluence (Examples 2 and 3; Figure 3). Accuracy in the per cent range is readily achieved, even for low concentrations of either bulk or implanted elements. With attention to detail, the uncertainties associated with using an implant as a measurement standard are no greater than those for measurements using a conventional homogeneous reference material, and the range of geochemically relevant materials available as SIMS measurement standards is greatly expanded.

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Supporting information

Supporting information may be found in the online version of this article:

Appendix S1. Akermanite Li concentration: Details of calculations and errors.

Appendix S2. Calibration of ^{25}Mg implant into NIST SRM 617 glass.

Appendix S3. Limits to implant fluences.

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