



Matrix effects on the relative sensitivity factors for manganese and chromium during ion microprobe analysis of carbonate: Implications for early Solar System chronology

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Abstract

The short-lived radionuclide ^{53}Mn decays to ^{53}Cr providing a relative chronometer for dating the formation of Mn-rich minerals in meteorites. Secondary ion mass spectrometry (SIMS) has been extensively used for *in situ* dating of meteoritic olivine and carbonate by the ^{53}Mn – ^{53}Cr system, however a significant analytical challenge has been realising accurate measurements of the Mn/Cr ratio in individual minerals of differing chemical compositions. During SIMS analysis, elements are ionised with differing efficiencies and standard materials are required to calibrate measured ion intensities in terms of relative elemental concentrations. The carbonate system presents a particular analytical difficulty since such standards are not naturally available due to low and variable Cr contents. Here, we utilise ion implantation of Cr into carbonate and other phases to accurately determine the relative sensitivity factors of Mn/Cr during SIMS analysis. We find significant variations in Mn/Cr RSF values among different carbonate minerals that depend systematically on chemical composition and we propose an empirical correction scheme that quantitatively yields an accurate RSF for carbonates of diverse chemical compositions. Correction of SIMS carbonate data for this strong matrix effect may help to reconcile some outstanding problems regarding the timescales of aqueous alteration processes in carbonaceous chondrites. Mn–Cr ages, revised based on our new understanding of the matrix effect, are, in general, earlier than previously thought and the duration of carbonate formation is shorter.

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1. INTRODUCTION

Secondary ion mass spectrometry (SIMS, or ion microprobe analysis) is a widely used analytical technique for *in situ* determination of isotopic ratios and trace element abundances. SIMS analysis is commonly applied to natural and synthetic samples at length-scales typically ranging

from tens of micrometers to sub-micrometer. Compared to most other mass spectrometry methods, SIMS offers significant advantages where high spatial resolution and/or low blanks are a major priority (see Ireland, 1995, for a review). However, due to the nature of the sputtering process, ion yields in SIMS vary dramatically from one element to another. Measured ion ratios must therefore be corrected by a relative sensitivity factor (RSF) in order to compute accurate inter-element ratios in the sputtered volume of a given sample. In practical terms, this is addressed by analysing a standard material under instrumental conditions as similar to those used for the analysis of the unknown as is possible to achieve. The standard, whether natural

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or synthetic, must have a known concentration of the element of interest and it should be homogeneous at a scale larger than the scale of analysis. Ideally, it should also have the same bulk chemical composition and crystallographic structure as the analyte sample.

For many applications, well characterised minerals are readily available for use as standards, however, in other cases it can be nearly impossible to find (or difficult to produce) materials which are a close match to the analyte. In such cases, accuracy of analyses can be potentially compromised by uncalibrated differences in the RSF (for a given element or isotope ratio) between that determined on a standard and that appropriate for the unknown analyte. Such differences arise because sputtering and ionisation yields in SIMS depend on complex interactions of the primary ion beam with the matrix of the solid sample being analysed and hence are generically referred to as ‘matrix effects’.

In this contribution, we focus on a solution to a particularly troublesome matrix effect that has vexed an important SIMS application: the use of the short-lived radionuclide ^{53}Mn (half-life of 3.7 Ma, [Honda and Imamura, 1971](#)) as a chronometer for dating the formation of carbonate minerals in the early Solar System ([Endress et al., 1994, 1996; Hutcheon et al., 1998; Hoppe et al., 2007; de Leuw et al., 2009; Petit et al., 2011; Fujiya et al., 2012, 2013; Jilly et al., 2013](#)). In general, the analytical requirement for determining the former abundance of any short-lived (now-extinct) radionuclide in an early Solar System object is the demonstration of a spatial correlation of excesses of the daughter isotope with the parent to daughter elemental ratio (see [McKeegan and Davis, 2003](#) for a discussion). Because ^{53}Mn decays to ^{53}Cr , the inference of the initial ^{53}Mn abundance in a carbonate mineral is based on the slope of the correlation between the $^{53}\text{Cr}/^{52}\text{Cr}$ isotope ratio and the $^{55}\text{Mn}/^{52}\text{Cr}$ elemental ratio. Here we show that SIMS measurements of this elemental ratio may be inaccurate by up to a factor of two over the range of carbonate compositions found in meteorites. This large matrix effect has not been previously documented because of the lack of availability of carbonate minerals with known, homogeneously distributed Cr impurities that can serve as standards. We quantify Mn/Cr RSFs for a range of carbonate mineral compositions by the method of ion implantation ([Leta and Morrison, 1980; Burnett et al., 2015](#)) and suggest implications for early Solar System chronology.

1.1. SIMS Relative sensitivity factors for Mn/Cr ratios

The RSF is defined here as the scaling factor that multiplies measured ion ratios to derive relative concentrations:

$$\text{RSF} = \frac{C_a/C_b}{I_a/I_b} \quad (1)$$

where the subscripts a and b denote elements a and b , respectively, and C_x represents the true concentration of the element and I_x the measured signal intensity during SIMS analysis. This factor must be measured under the same conditions as the measurement of the unknowns,

but once determined to sufficient precision it does not need to be repeated as long as the conditions of analysis are stable. There were early efforts to theoretically determine the sensitivities for analyses, however, due to the complexity of the sputtering process, these were found to be less accurate than empirical determination based on calibrated standards ([Smith and Christie, 1978](#)).

1.2. Previous studies of Mn/Cr RSF for Mn–Cr dating

In order to maximise the isotopic shift due to decay of the radiogenic parent isotope, materials with very high parent to daughter ratios are chosen for analysis. Thus, for Mn/Cr dating minerals are chosen which preferentially incorporate Mn, possibly as a major lattice forming element, and exclude Cr from the crystal structure.

Numerous studies have examined the Mn/Cr chronologies of meteoritic olivine ([Glavin et al., 2004; Sugiura et al., 2005; Ito and Ganguly, 2006; Matzel et al., 2009; McKibbin et al., 2013a,b](#)) and carbonate ([Endress et al., 1994, 1996; Hutcheon et al., 1998; Hoppe et al., 2007; de Leuw et al., 2009; Petit et al., 2011; Fujiya et al., 2012, 2013; Jilly et al., 2013](#)). These studies provide a good illustration of the problems associated with RSF calibration and the different approaches employed to obtain relative Mn/Cr chronologies.

Although use of the Mn/Cr chronometer in meteoritic olivine has a long history (e.g., [Hutcheon et al., 1998](#)) a systematic investigation of the Mn/Cr RSF in olivine has been undertaken only recently ([Matzel et al., 2009; McKibbin et al., 2013b](#)). [McKibbin et al. \(2013b\)](#) investigated the variation in Mn/Cr RSF in olivine using the SHRIMP-RG ([Ireland et al., 2008](#)) by analysing Mn/Cr ratios in different olivines ranging from forsteritic to more fayalitic compositions. Interestingly, [McKibbin et al. \(2013b\)](#) and [Doyle et al. \(2016\)](#) found significant variation in the Mn/Cr RSF, up to ~50%, between different compositions of olivine. This underlines the importance of systematically investigating the variation in the Mn/Cr RSF in meteoritic carbonates, which generally exhibit more compositional complexity than does the Fe–Mg solid solution series in olivine. Unfortunately, for the reasons discussed below, appropriate natural standards do not exist and synthesis of carbonates with uniform Cr contents is difficult so the approach of [McKibbin et al.](#) is not generally viable for carbonates.

1.3. Mn/Cr RSF in carbonates

Some carbonates preferentially incorporate Mn as a matrix element at percent levels, while excluding Cr to only trace amounts, resulting in Mn/Cr ratios that can reach the 10^6 range. This magnitude of parent/daughter ratios yields large anomalies in the Cr isotope composition meaning that the age, or ($^{53}\text{Mn}/^{55}\text{Mn}_0$) ratio, can generally be determined very precisely by SIMS.

[Hoppe et al. \(2007\)](#) attempted to determine the Mn/Cr RSF by direct measurement of carbonates, and while the Cr concentration could be precisely determined by bulk methods, individual carbonate grains were found to be highly heterogeneous on the scale of a few microns when

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