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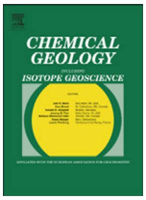

High-precision analysis of multiple sulfur isotopes using NanoSIMS

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A B S T R A C T

We report here data of multiple sulfur isotopes (^{32}S, ^{33}S, and ^{34}S) measured by NanoSIMS 50L ion microprobe in Fe–Ni–Cu standards, and pyrite grains recovered from the Neoarchean Abitibi Supracrustal Terrain, Canada. Careful attention to instrument tuning, sample preparation and sample stage positioning results in highly precise and accurate data for ^{32}S–^{33}S–^{34}S similar to that of larger radius SIMS instruments. Our results using a multi-Faraday collection system demonstrate that the NanoSIMS 50L instrument is capable of high-precision measurements of multiple isotopes of sulfur capable of resolving mass-independent variations in ^{33}S (Δ^{33}S) on the order of 0.4‰ (2σ) with improvements possible with higher S count rates. Pyrite grains from the Abitibi Supracrustal terrane have a large range of δ^{34}S values between −9.6 and +6.3‰, and corresponding Δ^{33}S values between −0.8 and +1.5‰, consistent with other datasets from Neoarchean sedimentary rocks. The new data indicate the incorporation of atmospheric sulfur affected by mass-independent fractionation (MIF) of ^{33}S into the Neoarchean marine sulfur cycle and point to subsequent sulfate reducing microorganisms at that time.

1. Introduction

Natural geochemical processes often result in the variability of the stable isotopes of elements, and these compositional variations have long been exploited to gain insight into the processes at work in the Earth's crust, mantle and atmosphere (Thiemens and Heidenreich, 1983; Valley et al., 1986; Farquhar et al., 2000; Valley and Cole, 2001; Ono et al., 2003) as well as processes operating in other planetary objects (Greenwood et al., 2000; Mittlefehldt et al., 2008; Thiemens, 1999) and indeed throughout the solar system and beyond (Clayton, 2003; Messenger et al., 2003; Mittlefehldt et al., 2008). Terrestrial variations in stable isotope compositions of certain elements can be small, requiring high-precision measurements using significant amounts of analyte (e.g. Ono et al., 2006). However when the available amount of sample is limited, or the physical domains of geochemical interest are small, microbeam methods are required to obtain the data of interest. This choice yields a trade-off between the high spatial resolution obtainable by microbeam analytical methods, and the precision achievable at that spatial resolution.

Multiple isotopes of sulfur have proven very useful in studies of the Earth's sulfur cycle and its variability through time, in particular in examining the interaction of the crust and atmosphere during the first half of Earth's evolution. In particular, in situ analyses of the mass-independent variability of ^{32}S, ^{33}S and ^{34}S that results from photolytic reactions, compared to the mass-dependent fractionation of these isotopes that results from kinetic and equilibrium reactions, has been used as a powerful tracer for the recycling of atmospheric sulfur into the Earth's crust and deep mantle (Farquhar et al., 2002; Mojzsis et al., 2003; Papineau and Mojzsis, 2006; Papineau et al., 2005; Whitehouse et al., 2005; Kamber and Whitehouse, 2007; Cates and Mojzsis, 2006; Papineau et al., 2007; Phillippot et al., 2007; Xiao et al., 2010; Kozdon et al., 2010; Williford et al., 2011; Reuschel et al., 2012; Evans et al., 2014). SIMS analyses of Neoarchean sulfides have recently been combined with SQUID magnetic microscopy to distinguish sulfur fractionated by sulfate reducing microorganisms from diagenetic and metamorphic sulfur (Fischer et al., 2014). Analyses by SIMS (7f Geo, IMS 1270, or 1280 ion probes) typically require a primary beam current between 0.3 and 5 nA, which yield a spot size of about 10 to 30 μm and a crater depth of several microns.

The Cameca NanoSIMS 50L, a multicollector SIMS instrument designed for high spatial resolution, has also been used for sulfur isotope analyses applied to a range of geological problems, including tracing the activity of Paleoarchean sulfate reducing microorganisms in basalts from the Hoogenoeg Formation in the Barberton Greenstone Belt (McLoughlin et al., 2012) and in sandstones from the Strelley Pool Formation in the Pilbara Craton (Wacey et al., 2010, 2011). Sulfur isotope analyses by NanoSIMS have also recently been used to trace thermochemical sulfate reduction in Carboniferous bitumen (King et al., 2014). So far however, no reliable high-precision ^{33}S data has

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been reported using the NanoSIMS. In this paper, we describe the results of efforts to measure the isotopic composition of multiple sulfur isotopes using the NanoSIMS 50L ion microprobe at the Carnegie Institution of Washington. We show for the first time that this instrument is capable of high-precision measurements of sulfur isotopes in terrestrial sulfide samples with precision and accuracy comparable to that of large radius SIMS instruments. We also demonstrate its utility by examining a small suite of sulfide minerals from metasedimentary rocks from the ~2.7 Ga Deloro and Michipicoten Groups of the Abitibi Supracrustal Terrain in Ontario, Canada.

2. Description and tuning of the NanoSIMS 50L

The measurements reported in this paper were obtained with a NanoSIMS 50L ion microprobe at the Carnegie Institution of Washington's Department of Terrestrial Magnetism (DTM) in 2008. The NanoSIMS 50L is a new-generation ion microprobe developed by Cameca Instruments SA (Fig. 1). Compared with the original NanoSIMS 50 instrument, the 50L consists of a larger-radius magnet (increased from 550 mm to 650 mm), seven collectors, and the addition of Faraday Cups and associated amplification. The instrument consists of a primary optical column, where ion beams generated by cesium or oxygen sources are accelerated, collimated and focused at normal incidence onto a flat sample residing in a computer-controlled sample stage with ±2 μm position reproducibility. The final stages of primary ion beam focusing, and initial focusing of sputtered ions, are achieved by a common co-axial lens stack (EOW, EOP, EOS, Fig. 1). The location of this lens stack close to the sample surface (~400 μm between sample surface and EOW lens) is an important design feature that permits the instrument to achieve very small probe diameters (minimum 30 nm

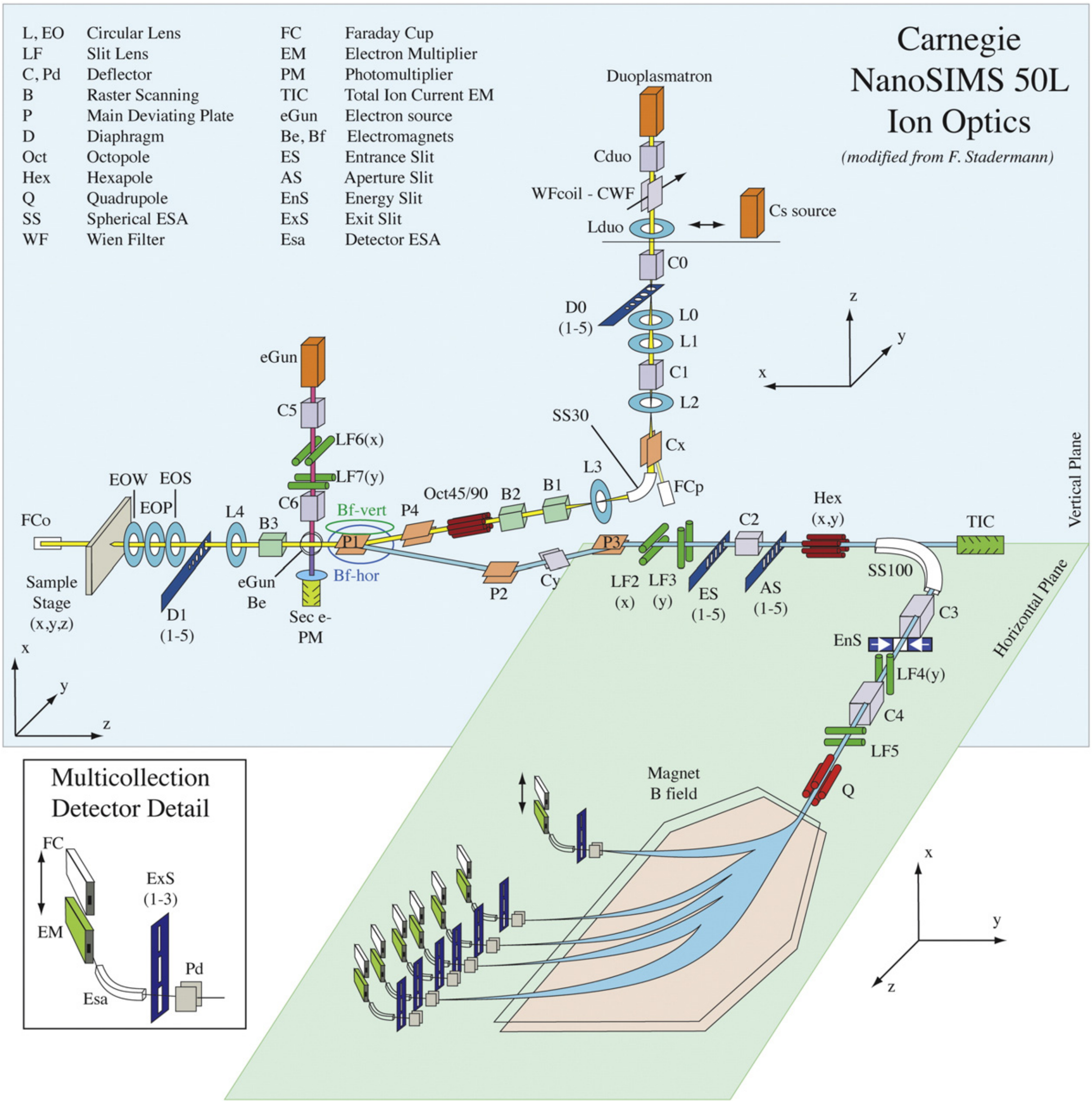

Fig. 1. Schematic diagram of the ion optical elements of the DTM Cameca NanoSIMS 50L, modified from the NanoSIMS 50 drawing by Frank Stadermann. The primary ion column is oriented in the vertical plane, while the mass spectrometer is oriented in the horizontal plane. Light-blue elements are circular lenses, red elements are multi-pole lenses, dark-green elements are slit lenses, gray elements are deflectors, light-green elements are used for synchronized rastering of the primary and secondary ions (dynamic transfer). Dark blue elements are user-positioned circular apertures for the primary beam (D0, D1) and slits for the mass spectrometer (ES, AS, EnS, ExS). The co-axial lens stack near the sample (EOW, EOP, EOS, L4) acts on both the primary and secondary ion beams, and requires the primary and secondary ions be of opposite polarity and equal energy.