SIMS Applications to Biogeochemistry

Analysis of Microcrystalline Fe Sulfides

Inter and intra-grain sulfur isotopic analysis by SIMS

Iron sulfide minerals, particularly pyrite (FeS_2), represent a substantial geologic reservoir of sulfur. Sedimentary pyrites have proven to be invaluable archives for reconstructing local environmental conditions as well as global-scale changes in biogeochemistry. Typically, Secondary Ion Mass Spectrometry (SIMS) studies of pyrites rely on spot analyses within grains (≥10 µm-diameter). While spot analysis methods may be sufficient in many cases, they preclude the investigation of small pyrite grains (diameters <10 µm) or the characterization of intra-grain variability. In this study, a method based on SIMS scanning ion imaging is presented that provides the spatial resolution (≤1 µm) necessary to measure inter-and intra-grain $\delta^{34}S$ variability in microcrystalline pyrites.

SIMS scanning ion imaging results

The validity of the SIMS imaging method was first tested on micron-scale fragments of cm-scale isotopically homogeneous hydrothermal pyrite and marcasite crystals. Data obtained on these S-isotopic standards showed little inter- or intra-fragment variability in the $\delta^{34}S$ value (figure 1). The method is suitable for the detection of the potentially large variations in $\delta^{34}S$ values that may exist within or between sedimentary iron sulfide grains.

The same method was applied to study the Cenomanian-Turonian Boundary Ocean Anoxic Event (OAE-2), which was an interval of geographically extensive enhanced organic matter burial. Total reduced inorganic S isotope ratios ($\delta^{34}S_{CRS}$) shift toward more negative values across much of the southern North Atlantic just before the onset of the OAE-2.

Dynamic SIMS was used to investigate the negative shift in $\delta^{34}S_{CRS}$ values and their divergence from organic S (figure 2). Using the SIMS imaging approach, grain-specific S isotopic analyses were performed on a diverse array of Fe sulfide minerals and textures from samples before and during OAE-2 at Demerara Rise.

Conclusion

The scanning ion imaging SIMS method developed for the analysis of microcrystalline Fe sulfides makes it possible to investigate both inter- and intra-grain variability with optimized spatial resolution.

Spatially resolved S isotope analyses of iron sulfides by SIMS produce results that significantly enrich existing bulk isotope data. By applying this method in a comparative study of Fe sulfides from pre- and syn-OAE-2 sediments at Demerara Rise, one could establish the various contributions to, and mechanisms responsible for, the observed secular decrease in $\delta^{34}S_{CRS}$ values. This provides important information about changes to the regional biogeochemical cycles of C, S, and Fe leading up to and during OAE-2.

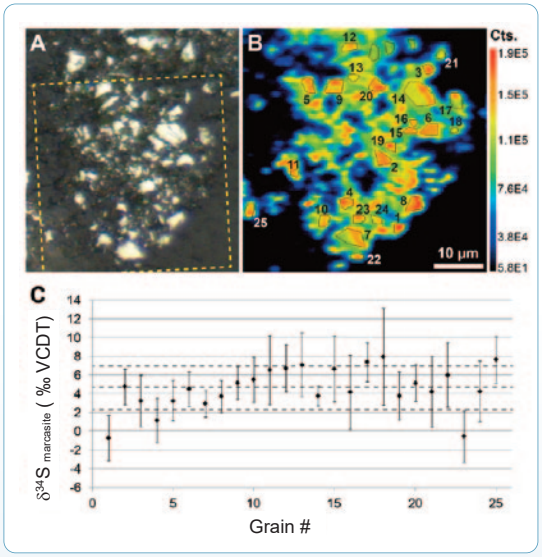


Figure 1
A: Optical microscope image of marcasite fragments embedded in epoxy
B: $^{32}S^-$ SIMS ion image of 50 × 50 µm² region from A, accumulated over 375 cycles
C: Corrected S isotopic composition of ≥1-µm-diameter fragments shown in B
Data from: R.N. Bryant et al, Rapid Commun. Mass Spectrom. (2019)

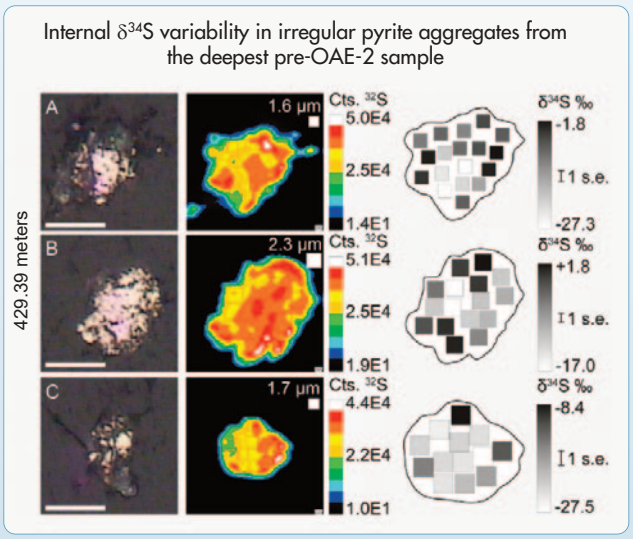
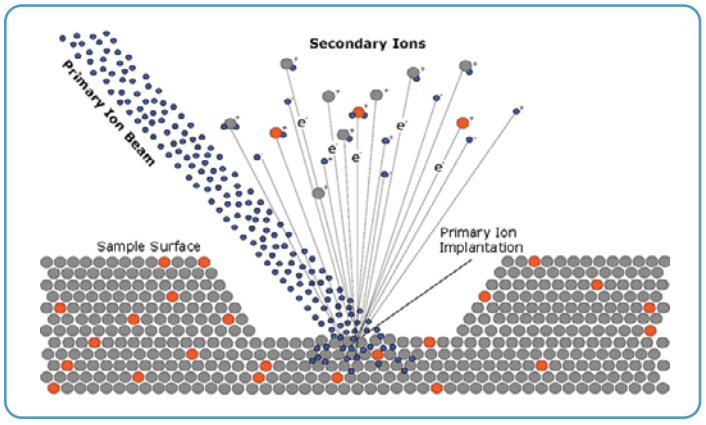


Figure 2
From left-right: optical microscope images, where scale bars are all 10 µm; $^{32}S^-$ SIMS ion images, with inset showing the size of sub-sampled regions; and $\delta^{34}S$ values of the sub-sampled regions.
Data from: R.N. Bryant et al, Chemical Geology (2020)

The technology behind



Dynamic SIMS

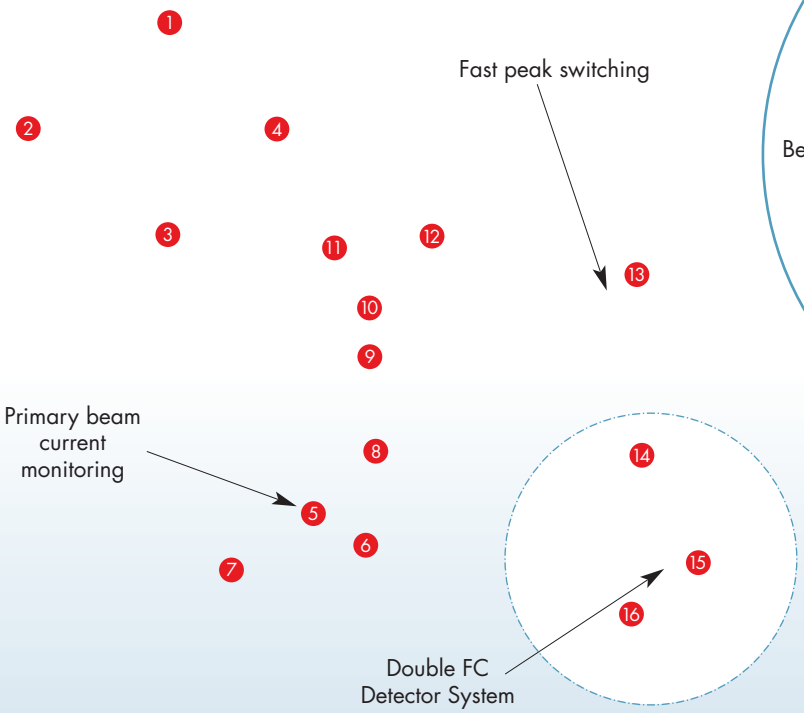
When a solid sample is sputtered by primary ions of few keV energy, a fraction of the particles emitted from the target is ionized. Secondary Ion Mass Spectrometry consists of analyzing these secondary ions with a mass spectrometer.

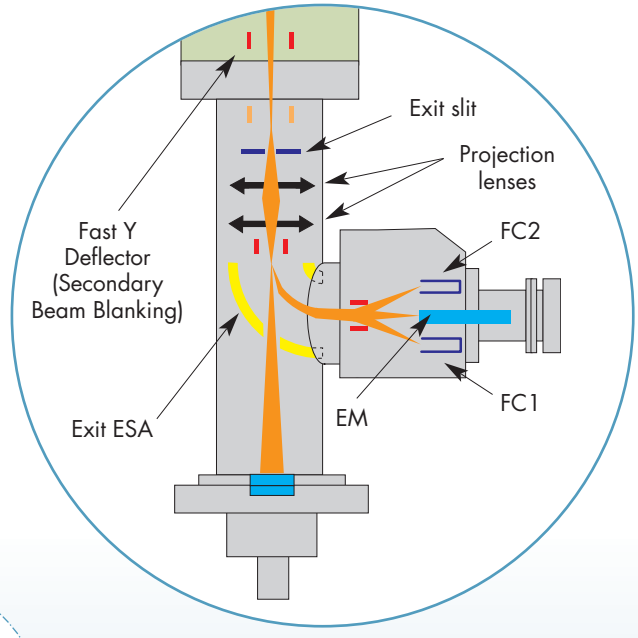
The SIMS technique is "destructive" by its nature (sputtering of material). It can be applied to any type of flat, solid material that can be kept under vacuum.

In dynamic SIMS, bulk composition and in-depth distribution of trace elements are investigated with a depth resolution ranging from sub-nm to tens of nm. SIMS is recognized as the most sensitive elemental and isotopic surface analysis technique.

CAMECA IMS 7f-GEO

The IMS 7f-GEO is a mono-collection SIMS model that combines the well-proven features of the IMS 7f with a specific detection system including two Faraday cups and one Electron Multiplier.





1 Microbeam Cesium ion source
2 Duoplasmatron ion source
3 Primary Beam Mass Filter (PBMF)
4 Cesium source isolation option
5 Primary Faraday cup
Motor driven primary column aperture
6 Sample (-10kV to +10kV) (Z axis in option)
7 UHV airlock system (Sample storage chamber in option)
8 Normal incidence Electron Gun (NEG)
9 Motor driven contrast aperture and entrance slit
10 Motor driven field aperture
11 Electrostatic Analyzer (ESA)
12 Motor driven energy slit
13 Fast laminated magnet
14 Motor driven exit slit
15 Electron Multiplier and double FC detectors
16 Ion image detector

For more information please visit www.cameca.com/products/sims/ims7f-geo

Ref. AP 7f-geo-biogeo-sulfure upd 2023