

Facility Overview

The Northeast National Ion Microprobe Facility (NENIMF) was established at Woods Hole Oceanographic Institution by Nobumichi Shimizu in 1996. It is a multi-user facility specializing in Secondary Ionization Mass Spectrometry (SIMS), a powerful micro-analytical technique with broad applications to both earth and ocean sciences. The NENIMF specializes in *in situ* determinations of trace element abundances in minerals, glasses, biogenic carbonates and oxides, as well as industrial materials. We also carry out *in situ* determination of isotopic compositions of H, B, C, O, S, Cl, Pb in geological materials. The centerpiece of the facility is the Cameca IMS 1280, a new generation, high transmission-high mass resolution SIMS instrument, the latest version of a double focusing mass spectrometer with a large radius magnetic sector (585 mm), produced by Cameca Instruments. It is one of only five such instruments in the United States. The ion optics of the IMS 1280 are optimized to attain a mass resolving power ($MRP = M/\Delta M$, where M is the observed mass and ΔM is the difference between 2 masses that can be separated) of 6,000 without significant loss of secondary ion intensity. It is useful for chemical and isotopic analysis of wide varieties of materials. The instrument is flexible in that both the energy filtering and high-resolution approaches can be used, dependent on where analytical advantages lie. The NENIMF also operates a Cameca IMS 3f that has been used since 1978 for a wide spectrum of geochemical studies, and remains highly effective for *in situ* trace element analysis of rock-forming minerals and glasses (spatial resolution of 10 μm or less). Some technical aspects of the NENIMF operation are illustrated in this handout.

Management of the NENIMF is overseen by a steering committee, chaired by G. Gaetani, that is responsible for all financial and scheduling decisions, and is dedicated to outreach and to increasing the NENIMF user base. Nobu Shimizu, a pioneer in SIMS techniques, is the Chief Scientific Advisor of the NENIMF, consulting on all technical aspects of the facility. The steering committee works closely with an external advisory committee, chaired by J. Webster of the American Museum of Natural History.

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*NENIMF offers Secondary Ionization Mass Spectrometry (SIMS) for both earth and ocean sciences, specializing in *in situ* determinations of trace element abundances in minerals, glasses, biogenic carbonates and oxides, as well as industrial materials.*

NENIMF Fee Structure *(for government funded projects)*

IMS 1280
\$120/hr

IMS 3f
\$65/hr

Weekends & holidays discounted 15%.

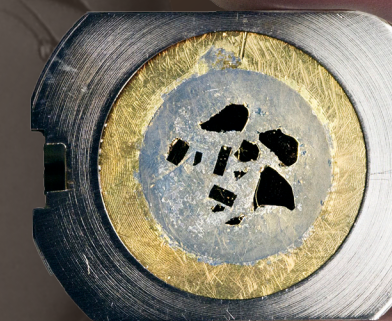
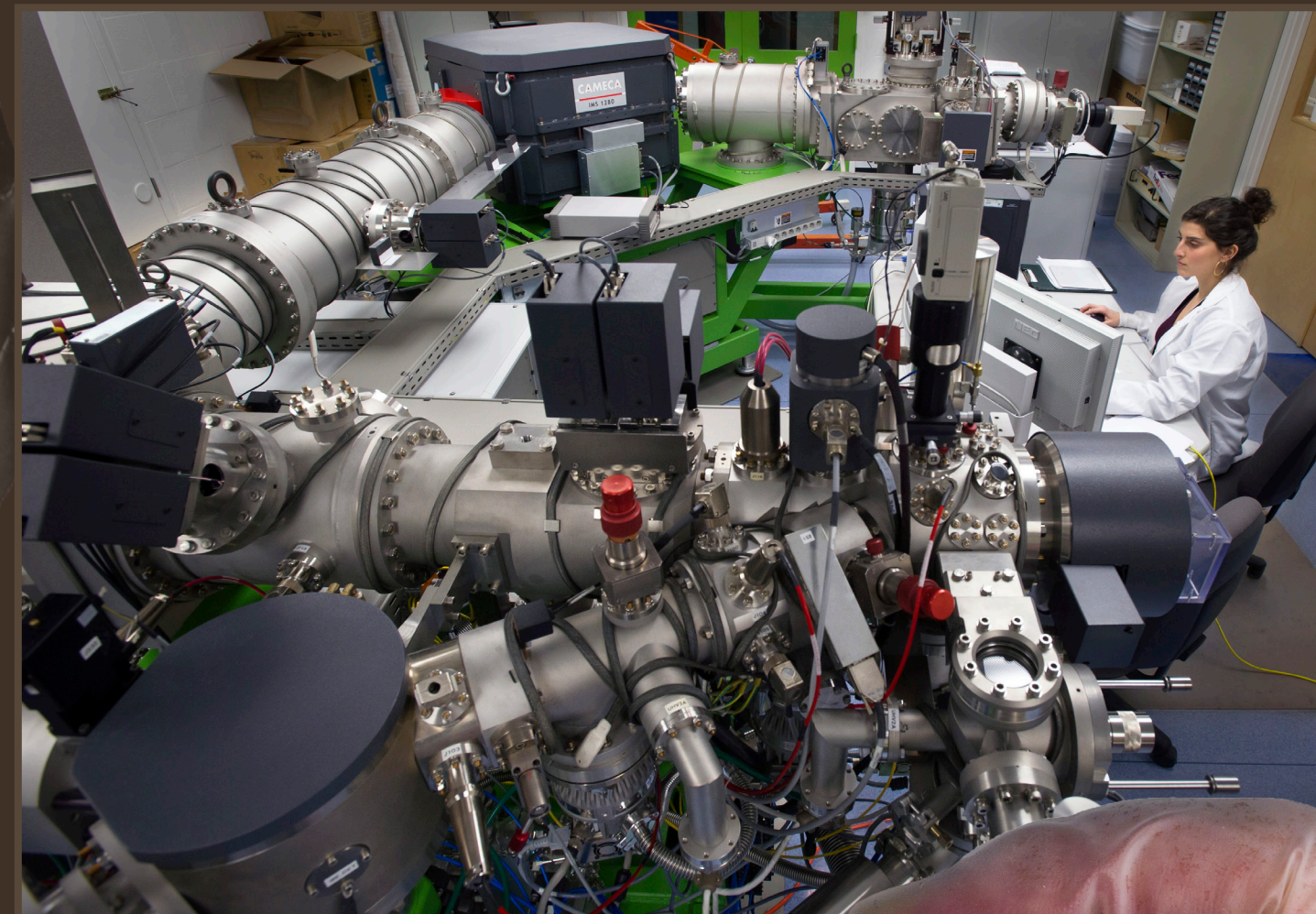
Non-federally funded projects, including foreign funding, are subject to a 15% administrative fee.

Industrial users are charged double the NSF rates. The facility also offers analytical services (i.e., fixed per-sample measurements) with a limited scope and a different fee structure.



NENIMF

Northeast National Ion Microprobe Facility



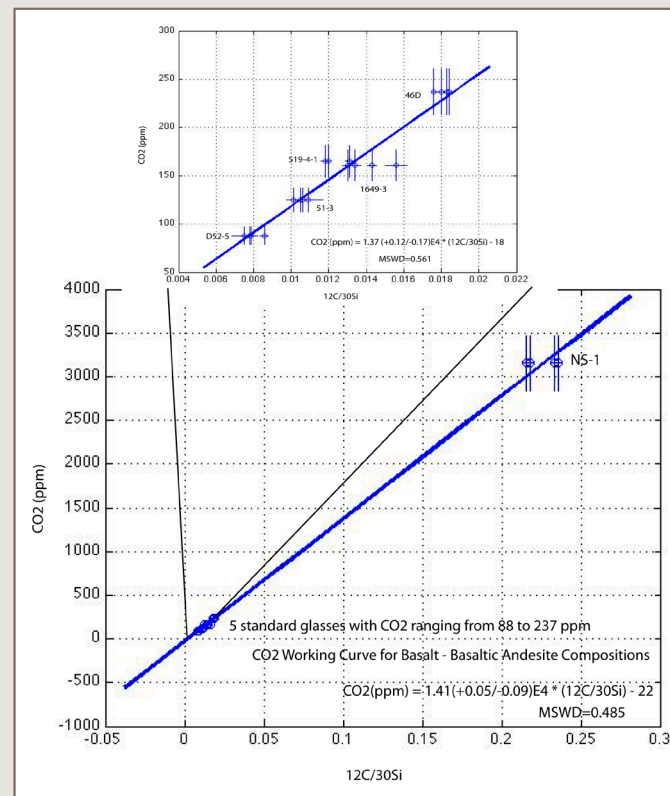
www.whoi.edu/nenimf

The analytical capabilities and expertise of the NENIMF are focused in 2 areas: determination of magmatic volatiles in silicate glasses and analysis of biogenic carbonates as recorders of climate change and its impacts on marine organisms. Analytical protocols and the requisite standard materials are available for determination of H₂O, CO₂, F, S, and Cl in silicate glasses and of B, Mg, Sr, Ba, and U in carbonates. There are many additional analytical protocols and applications available. The emphasis on these areas makes NENIMF a unique interdisciplinary resource to the geosciences community, with minimal overlap to other ion microprobe facilities.

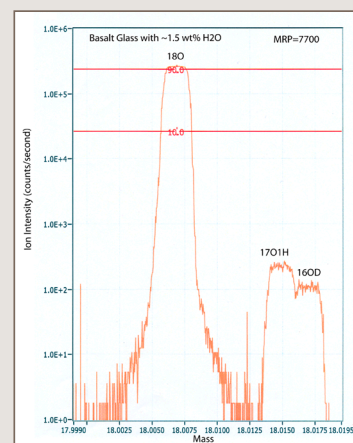
Determination of Magmatic Volatiles in Silicate Glasses

Magmatic volatiles play a key role in driving volcanism at plate margins and in facilitating mass transfer between the mantle and its exospheric reservoirs, and thus are of fundamental importance to earth and ocean sciences. SIMS techniques have a number of advantages over Fourier Transform Infrared spectroscopy (FTIR) and electron microprobe techniques for measuring volatiles. First, the spot size required for ion microprobe analyses is significantly smaller than for FTIR measurements. Second, ion microprobes have a higher sensitivity, as compared to electron microprobes, for measuring F and Cl at low concentrations. Finally, unlike other techniques, SIMS allows acquisition of all volatile measurements (H₂O, CO₂, F, S and Cl) during a single analysis. The NENIMF is the only open, multi-user facility in the eastern United States that presently offers this analytical capability

The analytical protocol developed for the IMS 1280 use the Cs⁺ primary ion beam. The concentration of H₂O is determined by measuring ¹⁶O¹H, rather than ¹H. The ¹H ion trajectory in the secondary ion optics of the large-radius IMS 1280 is very different from higher-mass ions, so that measuring the OH⁻ ion is more convenient. An MRP of 5,500 is routinely used for separation of ¹⁷O from ¹⁶O¹H (MRP required = 4711). At such an MRP, all commonly occurring molecular ion interferences are completely separated: ²⁹Si¹H from ³⁰Si, ¹⁶O₂ and ³¹P¹H



A working curve for CO₂ in glasses of basaltic to basaltic andesite composition. Note that the working curve obtained for natural glasses with CO₂ ranging from 88 to 237 ppm (inset) is identical within error to the one including a synthetic high-CO₂ glass (NS-1). Analyses were carried out using a Cs⁺ ion beam with a current ~1.5 nA, rastered over an area 30 x 30 μm. A mechanical aperture (Field Aperture) was used so that only the central 15 x 15 μm area was analyzed.



A high-mass-resolution mass spectrum collected at mass 18 using the IMS 1280, showing separation of ¹⁸O, ¹⁷O¹H, and ¹⁶OD at MRP = 7700 with flat topped peaks. Spectrum was collected on a basalt glass containing ~1.3 wt% H₂O. This result suggests that D/H ratios could be measured with an internal precision of ~6‰ for glasses containing ~0.5 wt% H₂O, and could be useful for studies of diffusion and degassing processes.

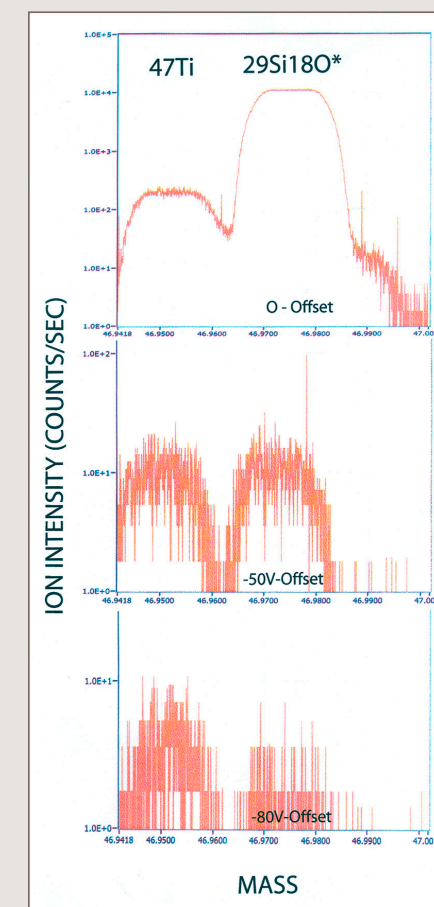
from ³²S, ¹⁸O¹H from ¹⁹F, ³⁴S¹H and ¹⁹F¹⁶O from ³⁵Cl. Natural and synthetic reference glasses with known concentrations of volatile components are used to determine reproducible working curves.

Biogenic Carbonate Records of Climate Change and Related Impacts on Marine Organisms

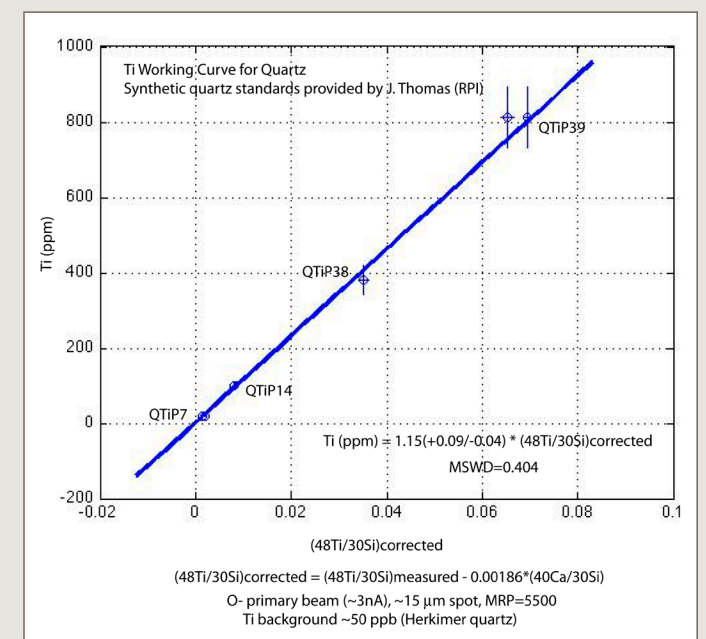
The second key focus area for NENIMF analytical capabilities and expertise is the analysis of biogenic carbonates as records of climate change and related impacts on marine organisms. Much of what we know about past climate variability and the role of the oceans in climate change on decadal through orbital timescales, comes from proxy data contained within the carbonate skeletons of marine organisms. Nevertheless, there are fundamental questions concerning the detailed interpretation of geochemical proxies, the role of diagenesis in distorting the climate signals and the impacts of climate change on marine organisms. Many of these questions can only be addressed with the unparalleled spatial resolution and precision afforded by SIMS. Since its first application to the fine-scale analysis of biogenic carbonates, SIMS techniques have played a key role in shaping our understanding of the relationships between skeletal composition and

environmental variables and the factors that distort them (so-called “vital effects”).

Trace element analysis in marine carbonates began at NENIMF more than 15 years ago, using the IMS 3f with the energy filtering approach. Mg/Ca, Sr/Ca, and Ba/Ca ratios are analyzed with a negatively charged oxygen ion (O⁻) with a current of ~15 nA focused to a spot ~20 μm in diameter. With an energy offset of -60V, molecular ion interferences are sufficiently suppressed so that the measured ⁸⁶Sr/⁸⁸Sr ratio is identical to the natural abundance ratio (0.1194) within counting statistic uncertainties. The energy filtering-based approach has since been transferred to the IMS 1280, which has a greater sensitivity relative to the 3f. Working curves for these ratios are determined based on three carbonate standard samples (OKA carbonatite, 0785 “Blue” calcite, and AG-1 aragonite).



A mass spectrometry demonstration of how energy filtering works. Mass spectra collected on mass 47, using the IMS 1280, with energy offsets of 0, -50 and -80V, showing the effectiveness of energy filtering for suppressing molecular ion (SiO) intensities relative to single-atom ions (Ti). Mass spectrum was collected on a glass with ~30 ppm Ti. ²⁹Si¹⁸O* denotes two SiO molecular ions, ²⁹Si¹⁸O and ³⁰Si¹⁷O, not separated with an MRP~2000.



A working curve for Ti in quartz. Synthetic quartz crystals with Ti ranging from 20 to 813 ppm were provided by Dr. J. Thomas (RPI). Analyses were carried out on the IMS 1280 with an O⁻ primary ion beam with a current ~3 nA, focused to a spot ~15 μm in diameter. An MRP = 5500 was used. The Herkimer quartz with 3 ppb Ti was analyzed to determine the instrumental background for Ti to be ~50 ppb. Applications of this working curve include geothermometry of metamorphic rocks and determination of temperature of deformation process.