Cryogenic Applications of NanoSIMS-HR

Isotopic Composition of Fluid Inclusions in Quartz

Introduction

Fluid inclusions are small liquid bubbles trapped inside minerals, often in the µm-mm size range. These inclusions are found in a variety of minerals and can differ in nature. While the most common inclusions are aqueous, some also contain organic materials. They have been observed in many terrestrial rocks such as quartz and halites, but also in extraterrestrial samples, meteorites or asteroidal samples brought to Earth by sample return missions. In samples from asteroid Ryugu (Hayabusa2 mission), fluid inclusions have been found in pyrrhotite grains.

Primary fluid inclusions are valuable as they capture the fluid present during crystal formation, providing insights into the mineral's formation environment and the rock or parent body history. Secondary inclusions form later, after the host mineral fractures and crystallizes, capturing fluid from subsequent geological events.

Secondary Ion Mass Spectrometry (SIMS) is a powerful technique to reveal the history of rock materials by measuring elemental and isotopic composition with high precision and sensitivity. In the case of small micrometric objects, NanoSIMS-HR, with its high lateral resolution (down to 30 nm) is the most appropriate instrument. However, by their fluid nature, fluid inclusions are impossible to analyze at room temperature. It is necessary to freeze the samples down to a temperature where they do not evaporate in the vacuum, making it possible to analyze them as any solid sample.

Protocol

Prior to NanoSIMS-HR analysis, fluid inclusions in quartz grains were located by transmitted light with an optical microscope or marked with FIB (Fig. 1). On NanoSIMS-HR, the sample's surface was then sputtered with high current at the location of each inclusion. Ion images of the inclusion were subsequently obtained at lower current and high resolution (Fig. 2) and isotopic ratios extracted from the acquired image.

NanoSIMS-HR analyses were conducted using a cryogenic stage, cooled down to -140°C via a liquid nitrogen cold trap. The 2 L cold trap was refilled every >15 hours to keep the stage cool during the entire session. Measurements were performed using Cs+ primary ion bombardment at 16 keV impact energy. $^{16}O^-$, $^{16}O^1H$, ^{18}O, ^{28}Si, and ^{35}Cl species were measured in multicollection mode at a Mass Resolving Power (MRP) ≃ 7000. In a different session, ^1H and D were measured at lower MRP. Samples were embedded in epoxy and coated with Pt, and the e-gun was used for charge compensation.

Results

At -140°C, fluid inclusions remain solid and can be easily analyzed as any solid material. Once thermal equilibrium is reached, the cold temperature does not affect the instrument performance and even improves the vacuum. No degassing was observed when sputtering through inclusions at cold temperature.

δD and $\delta^{18}O$ were obtained with a precision better than 16 ‰ and 5 ‰ (1 S.D.) respectively. At higher lateral resolution, ion images reveal the heterogeneity of the internal structure of the fluid inclusions (Fig. 3).

Conclusion

The NanoSIMS-HR with a cryogenic stage enables previously impossible analyses of the isotopic and elemental composition of fluids. Tracking single fluid inclusions now makes it possible to challenge complex geological models involving multiple fluid generations.

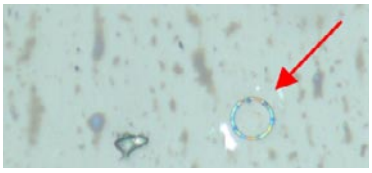


Figure 1: Optical image of a fluid inclusion marked with a 10 µm Ø FIB.

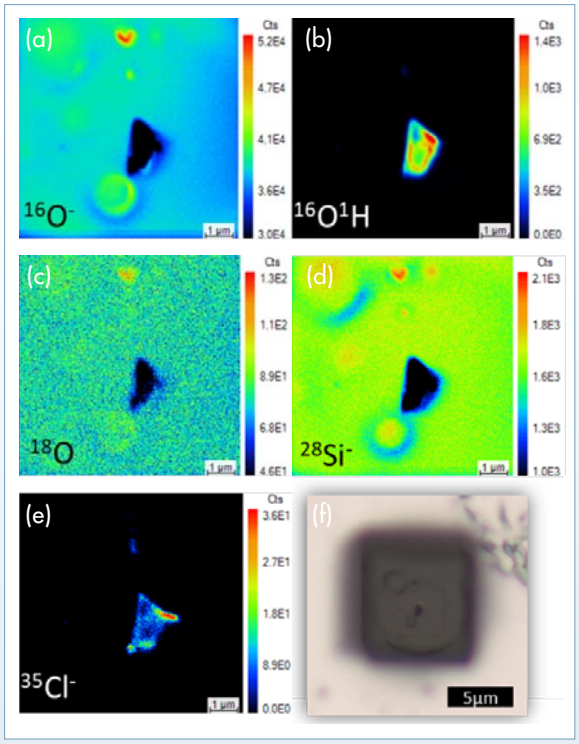


Figure 2:
a, b, c, d, e: Ion images of a fluid inclusion inside a quartz grain obtained on a NanoSIMS-HR, using a cryogenic stage at -140°C.
f: Optical microscope image of the crater after NanoSIMS-HR analysis.

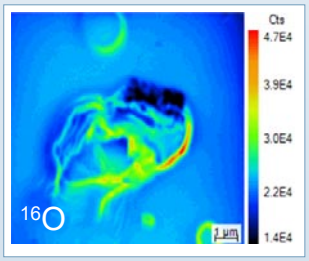


Figure 3: Details of the structure inside a fluid inclusion revealed by NanoSIMS-HR.

Samples provided and prepared by Pr. Motoo Ito, JAMSTEC, Japan. NanoSIMS-HR analyses conducted at CAMECA Application Laboratory, France.

The Technique Behind

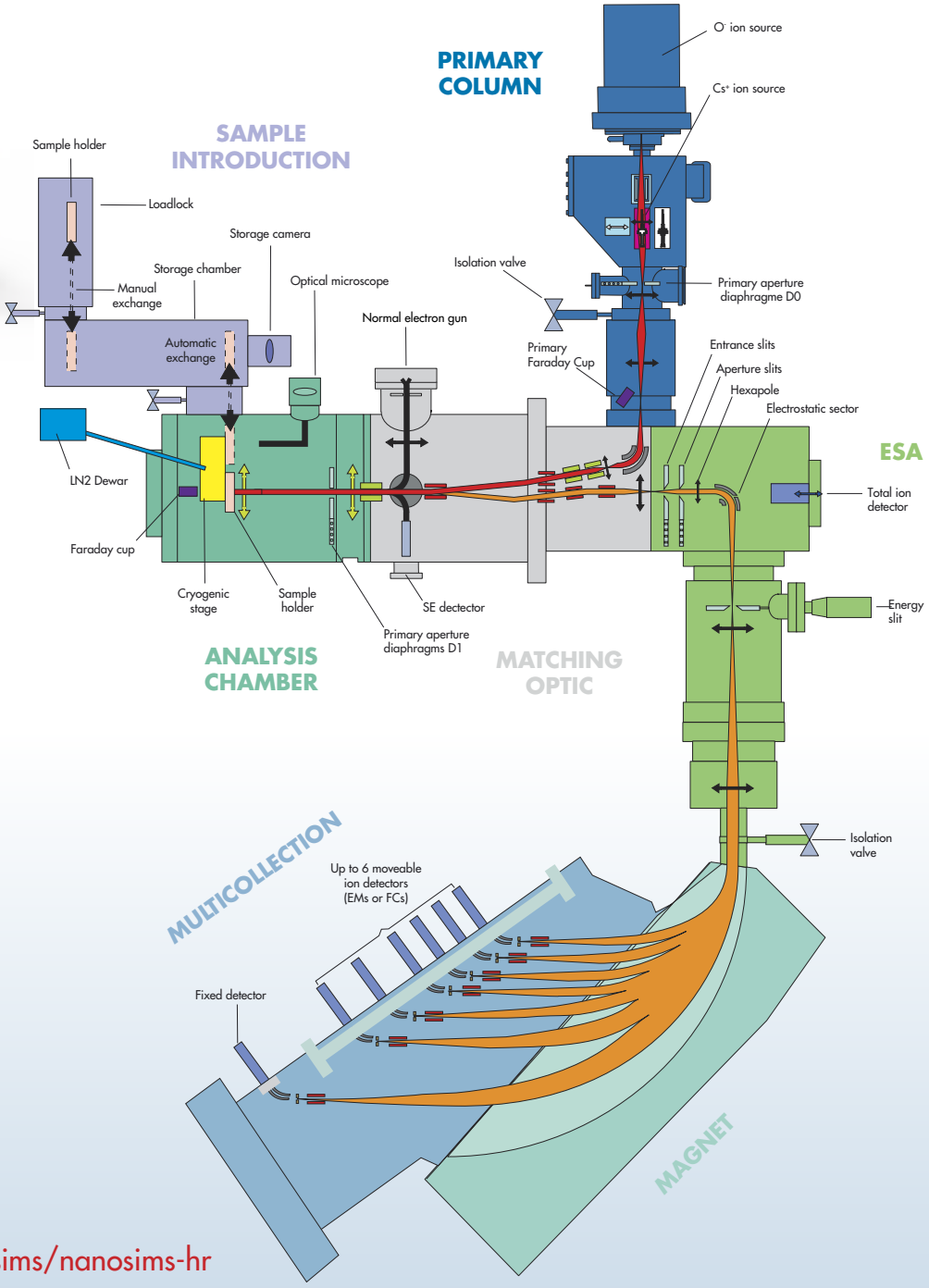
CAMECA NanoSIMS-HR

The **NanoSIMS-HR** is the next generation of the world-acclaimed NanoSIMS 50/50L Secondary Ion Mass Spectrometer series which have contributed to major advances in the most diverse fields of fundamental research and industrial innovation: material sciences and semiconductor, geo- and cosmochemistry, plant and soil sciences, environmental microbiology, cell biology and medical research.



With the **NanoSIMS-HR**, CAMECA delivers breakthrough instrumental innovations that boost the versatility of this unique ion microprobe, improve data quality, and enable scientists and engineers to accelerate discovery under ever increasing workloads and tighter deadlines.

- Unprecedented lateral resolution (≤30 nm)
- Superior depth profiling using low impact energy
- High throughput: x2.5 faster image acquisition
- Cryogenic stage for fluid inclusion analysis



For more information:
www.cameca.com/products/sims/nanosims-hr

Ref. AP NS02_Fluid inclusions