

SECONDARY ION MASS SPECTROMETRY IN THE EARTH SCIENCES*

The Mineralogical Association of Canada Short Course Series Volume 41, *Secondary Ion Mass Spectrometry in the Earth Sciences – Gleaning the Big Picture from a Small Spot*, is a collection of review papers edited by Mostafa Fayek. The papers were presented in a short course held prior to the Joint Assembly of AGU, GAC, MAC, CGU, and IAH, in Toronto, Ontario, May 22–23, 2009.

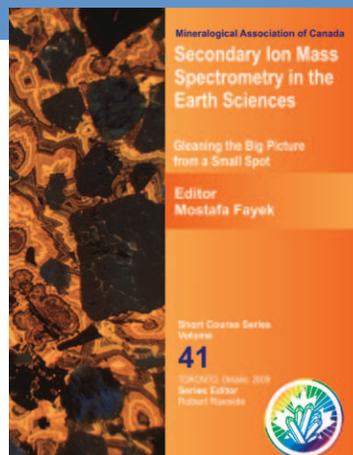
A variety of applications of secondary ion mass spectrometry (SIMS) to geological investigations are presented, in a mix of introductory and advanced discussions. While SIMS instruments have been employed since the 1950s in the semiconductor industry, the application to mapping chemical compositions of solid surfaces was pioneered by Raimond Castaing and George Slodzian (Paris, France) in the 1960s. Applications to Earth sciences have developed since the 1970s, and this volume presents a few of the methods most recently developed using modern instruments.

The introductory chapter by Richard Stern (University of Alberta) includes a glossary of terms for SIMS instrumentation and methods. This is a helpful tool for those interested in learning SIMS applications and understanding the literature. Stern emphasizes the point that useful analyses of geological materials depend on having standards with compositions similar to those of the unknowns being analyzed. The best analyses are obtained when a standard is mounted together with the unknown. High-quality analyses rely on chemically similar standards because the physical-chemical process of extracting ions from a solid surface is not theoretically constrained. For now, the key to reliable in situ analyses of minerals is to use appropriate standards measured under identical instrumental conditions.

Each of the next three chapters gives an introduction to the analytical setup options specific to different instruments and a presentation of geological applications. John Valley and Noriko Kita (University of Wisconsin) review oxygen isotope applications and provide a valuable discussion of the statistical analysis of SIMS results, ultimately based on useful ion yields (ions detected per atom sputtered). The volume of atoms available in the area of interest thus limits the analytical precision of SIMS data. Efficient detection of ions from a mineral surface depends on the chemical composition of the surface, ease of ionization of the element of interest, transmission of the mass spectrometer, sensitivity of the electrometers, and detection efficiency of the electron multipliers.

The third chapter, by Mostafa Fayek (University of Manitoba), focuses on H, C, N, and S analyses used for studying the interactions between minerals and organic compounds. The matrix effects of samples with mixed mineralogy or organic compositions remain the most difficult challenge to interpreting these analyses, which can routinely reach per mil-level precision. Because of the rapid development of SIMS in Earth science, many new studies show the versatile uses of different primary ion beams for sputtering and detection of secondary ions. It is now common to use an O^- primary ion beam to study electronegative secondary ions (e.g. C, F, S, and Cl). A Cs^+ primary beam is best for measuring very low concentrations of H and C and for determining D/H ratios, but careful adjustment of the electron gun (for charge compensation) is required on the small-radius SIMS instruments due to the proximity of the secondary magnet to the charge-compensating electrons. Small shifts in the electron cloud during shifts of the magnet significantly affect the measured ion ratios. Discoveries of such instrumental effects and analytical solutions lead advances in this field.

Other light-element isotopic systems (i.e. B, Li, and Cl) are now increasingly used to investigate geologic problems. These isotopic systems vary by 10–100‰ in natural rocks and associated waters, potentially revealing more significant variations in source, temperature, and chemical conditions of formation than the major elements. The chapter by Graham Layne (Memorial University of Newfoundland) discusses many of the advantages and disadvantages of the analyses of B, Li, and Cl.



Contamination is a critical problem when studying trace elements; therefore presputtering the sample is essential for removing surface contaminants. Chemical pretreatments may also be used to remove contaminants from drilling, sawing, and polishing fluids that may contaminate samples. Sputtering of mineral surfaces to clean off contaminants is not always adequate, especially when analyzing nanominerals with high relative surface areas (e.g. clays). The discussion of mass resolving power and energy filtering as options to remove interfering species is well explained and demonstrates the versatility of SIMS for exploring many new isotopic systems. Layne discusses the effect of the instrument on production and detection of ions. Using standards, one can measure the instrumental mass fractionation. Emphasis is placed on the magnitude of the instrumental fraction for each isotope, which differs depending on the ionization potential and detection, but is inconsequential as long as the standards constrain the fractionation for each analytical session. A good analysis depends on limited instrumental drift during the analysis of unknowns.

Axel Schmitt (University of California, Los Angeles) gives a thorough review of uranium-series dating of minerals by SIMS and of applications of SIMS to Quaternary geology. The focus is on eliminating interferences from a variety of molecular ions. Such analyses require very high mass resolving powers, readily achieved by larger SIMS instruments. The advantage of such instruments in the future development of dating techniques lies in their high spatial resolution and low sample consumption.

Jerry Hunter (Virginia Tech), in the final chapter, addresses depth profiling, which is the primary technique for which SIMS is known in the semiconductor industry. Depth resolution is very good and ideal for evaluating chemical gradients due to diffusion of elements in minerals. This chapter provides an excellent discussion of the variables that affect ion yields and detection, the effects of surface roughening during analysis, methods to enhance ion yield (e.g. oxygen flooding), and the interpretation of data. A good summary is given of improvements to standard semiconductor depth profiling most applicable to geological samples.

Awareness of the SIMS analytical capabilities in the geological sciences is the goal of this volume, and it is a much-appreciated beginning. Mostafa Fayek notes in the preface that there are some omissions, particularly in the areas of geochronology, trace element analysis, cosmochemistry, ion imaging, and nanoSIMS. There are many applications of SIMS yet to be established as primary techniques for the geological sciences. The future requires collaboration between the scientists who study the physical chemistry of the ionization process and those who apply the analytical capability to geological problems. This volume is a good representation of the melding of these disciplines and bodes well for the future of SIMS as an important tool in the geological sciences.

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