A SHRIMP II Ion Microprobe at the Geological Survey of Canada

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SUMMARY

Early in 1996, the Geological Survey of Canada acquired a Sensitive High-Resolution Ion Microprobe (SHRIMP). Now operating, this instrument permits precise *in situ* measurement of isotopes in mineral grains. SHRIMP complements the widely used isotopic dating method of isotope dilution thermal ionization mass spectrometry. Although SHRIMP is less precise than isotope dilution methods, the material sampled is much smaller, offering better spatial resolution and faster analysis. SHRIMP's most important application is the determination of U-Pb isotopic ages of zircon. Studies particulary suited to SHRIMP include analysis of minerals *in situ* where context is vital (*e.g.*, complex metamorphic rocks), detrital zircon chronology in sedimentary basin analysis, and reconnaissance zircon chronology with application to geological mapping and mineral exploration projects. SHRIMP will be accessible to academia/industry researchers in Canada in late 1996, following development of requisite analytical/scientific expertise.

RÉSUMÉ

Au début de l'année 1996, la Commission géologique de Canada a acquis une microsonde ionique à haute résolution ultrasensible appelée SHRIMP. Cet instrument qui est fonctionnel maintenant, permet de faire des mesures isotopiques précises *in situ* sur le grain minéral même. La microsonde SHRIMP constitue un complément à la méthode de datation isotopique très répandue qu'est la spectrographie de masse thermoionique par diluton isotopique. Bien que la microsonde SHRIMP ne permette pas des déterminations aussi précises que celles obtenues par les méthodes par dilution isotopique, l'échantillon requis est beaucoup plus petit, ce qui permet une bien meilleure résolution spatiale et une analyse plus rapide. La détermination des âges U-Pb sur le zircon constitue la plus importante application de la microsonde SHRIMP. L'utilisation de cette microsonde est particulièrement indiquée dans les études où la connaisance du contexte est primordial et qui requièrent des mesures *in situ*, comme l'étude de roches métamorphiques complexes, la chronologie des zircons détritiques dans les analyses des bassins sédimentaires, et l'établissement des principaux repères chronologiques lors de campagnes de reconnaissance géologique ou de projets d'exploration minérale. La microsonde SHRIMP pourra être utilisé par les chercheurs des milieux académiques et industriels canadiens vers la fin de 1996, dès que le savoir-faire analytique et scientifique approprié aura été acquis.

In late 1995, as Ottawa shovelled out from a blustery November snow storm, the Geological Survey of Canada (GSC) took delivery of a Sensitive High Resolution Ion Microprobe (SHRIMP II). Thirty wood crates weighing approximately 10 metric tonnes were lifted by crane onto a temporary platform outside the ground floor laboratory and then shuttled into the room, ending a journey that had begun in Fyshwick, Australia (Fig. 1). Two weeks later, the first Pb^+ ion beam was detected at the collector, marking the beginning of a new era in isotopic research in Canada.

A unique instrument in Canada and only the fourth of its kind operational in the world, the SHRIMP II (Clement and Compston, 1989) is a modified version of the highly successful SHRIMP I prototype, which was designed and built at the Research School of Earth Sciences, Australian National University (RSES-ANU; Clement *et al.*, 1977). The GSC SHRIMP II was manufactured by Australian Scientific Instruments, a division of Anutech Pty., which is the commercial arm of ANU. The designers of SHRIMP I had one simple, but ambitious, goal in mind: to build an instrument that would permit precise *in situ* measurement of isotopes in mineral grains.

Over the past 15 years, both SHRIMP I and later SHRIMP II have proven highly successful performers throughout a

Figure 1 *Overview of the Geological Survey of Canada's new SHRIMP II ion microprobe in the ground floor laboratory at 601 Booth Street, Ottawa.*

Geological Survey of Canada Contribution No. 1996242

range of analytical tasks, including the measurement of isotopes of U, Pb, Th, Hf, Ca, Ti, rare earth elements (REEs), and S in targets of several different minerals. By far the most important application, however, has been the determination of U-Pb isotopic ages of zircon (Compston *et al.*, 1982, 1984). The zircon dating capabilities of the SHRIMP became more widely recognized following the discovery of the oldest terrestrial zircons (Froude *et al.*, 1983). During the last decade, the SHRIMP has become Australia's geochronological workhorse, having been used to determine literally thousands of zircon U-Pb ages in a remarkable variety of rocks. Compston's research group at RSES-ANU has developed a wider reputation, however, in using the SHRIMP to solve the most difficult geochronological problems, such as the dating of the oldest rocks on Earth (Bowring *et al.*, 1989).

The SHRIMP is a Nier-Johnson type double-focussing secondary ion mass spectrometer (SIMS) that analyses secondary ions generated at the target mineral by a beam of primary oxygen ions. The primary oxygen ions generated in a duoplasmatron are accelerated across a 10 kV potential, and probe 10-30 microns-wide, 1-5 microns-deep regions of a mineral, hence the name ion microprobe. The secondary ions of interest created during the mechanical sputtering of the target mineral (*e.g.*, Pb$^+$, U$^+$, Th$^+$) are accelerated through a 10 kV potential into an electrostatic sector for filtering according to energy, and then into a magnetic sector for mass dispersion. Ion collection is accomplished with a single secondary electron multiplier fitted with an ion counter. The SHRIMP is designed to operate routinely at high mass resolutions with the flat-topped peaks required for precise isotopic analysis. For U-Pb age determinations of zircon, a mass resolution of approximately 5000 (1% peak height) is required to separate the isotopes of interest from interfering isotopes of nominally identical integral mass number. In order that the widest possible beam of secondary ions extracted from the target can be analyzed, large radius electrostatic (r=1.3 m) and magnetic (r=1.0 m) sectors are required (Matsuda, 1974), giving the instrument its somewhat ironic acronym (the footprint of the instrument is approximately 3.5×6.0 m: anything but a "shrimp"!). The SHRIMP is, therefore, highly sensitive to the presence of U and Pb (and other elements) in the mineral sample. Our measurements show that approximately three in every one thousand Pb atoms in a particular target are detected at the collector, a figure that compares well with thermal ionization analysis of Pb. The SHRIMP is also highly sensitive spatially compared to other dating techniques, as the typical mass of target mineral sputtered during an age determination is only 1-10 ng, virtually nondestructive.

The most common type of sample suitable for SHRIMP analysis is a 2.5 cm diameter epoxy disk on which are exposed the polished mid-sections of the target mineral grains. Hundreds of grains can be mounted on a single epoxy disk. Prior to SHRIMP analysis, the grains are examined optically and with cathodoluminescence and backscattering electron imaging at GSC's electron microbeam facility. The electron imaging often reveals internal growth features, such as cores, that may not be observable optically (*e.g.*, Hanchar and Miller, 1993). Minerals exposed on the surface of a standard polished thin section or rock slab can also be analyzed, for cases where the context of the mineral in the rock is important.

In the early part of 1996, the GSC SHRIMP underwent a testing and break in period, during which the analytical performance of the instrument was scrutinized and optimized. Zircon material dated by isotope dilution methods at the GSC was examined with the SHRIMP for the purpose of testing the agreement of the two methods (Fig. 2). Also initiated during this period was the search for a suitable zircon standard material. Zircon grains with known and uniform Pb/U ratios are required to be analyzed in the same analytical session as the unknown zircon because Pb and U secondary ions are not generated with equal efficiency during the sputtering process. The measured 206Pb$^+$/238U$^+$ ratio in a given spot is typically 2-3 times that actually in the sample, but this fractionation can be corrected for by comparison with a standard. SHRIMP determination of the 206Pb/238U ages within fragments of 994 Ma megacrystic zircon from the Kipawa Syenite Complex (Currie and van Breemen, 1996) have a one standard deviation of 1.5-2.5% per spot, depending on the particular analytical session. The dispersion in 206Pb/238U ages in the

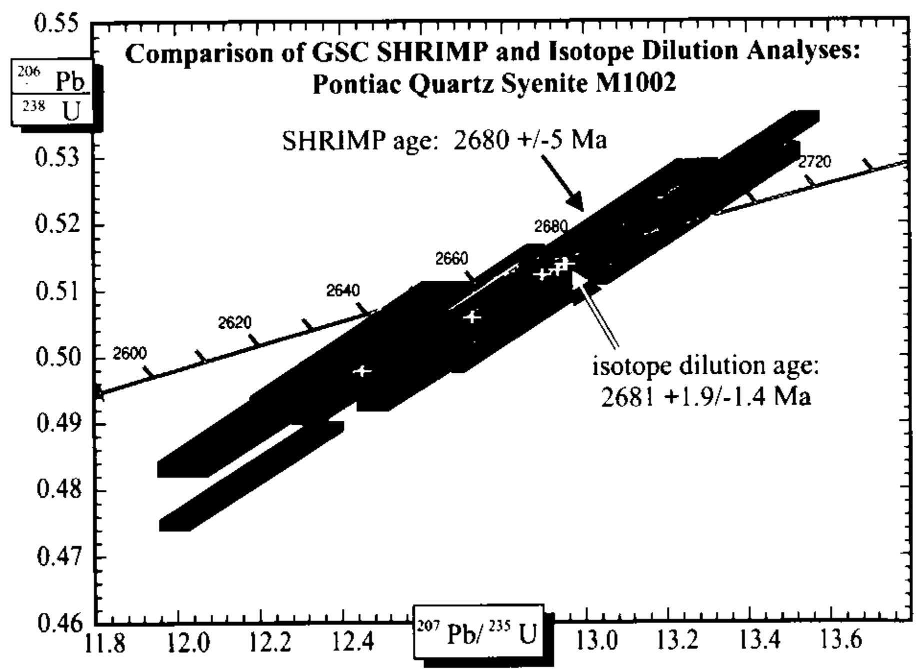

Figure 2 *Comparison of isotope dilution and GSC SHRIMP II age determinations of zircons from an Archean quartz syenite (Mortensen and Card, 1993). The SHRIMP II 68% confidence limits are shown as black polygons, whereas the much more precise isotope dilution analyses are shown as crosses for clarity. The SHRIMP age of 2680 ± 5 Ma (95% confidence limit) is derived from the pooled 207Pb-206Pb data on 18 concordant spots, and is identical within error to the upper intercept age of 2681 Ma determined by linear regression of the isotope dilution data.*

Table 1 Comparison of relative performance of GSC SHRIMP II and ID-TIMS in U-Pb zircon dating.

	SHRIMP	ISOTOPE DILUTION*
Mass of zircon analyzed	1-10 ng	>1000 ng
Typical mass of Pb analyzed	~0.1 pg	>100 pg
Reproducibility of $^{206}Pb/^{238}U$ age at 68% confidence level	~2.0% per spot	0.2% per fraction
Reproducibility of $^{207}Pb/^{206}Pb$ age at 68% confidence level	0.5-10.0% per spot (depends on age)	0.05-0.08% per fraction
Overall instrumental Pb sensitivity (collected Pb/total Pb)	0.3%	0.6%
Number of data points in one year (GSC potential)	4000 (20 spots·d^{-1} × 200 days)	1200
Ability of determine precise (<0.1% at 95% confidence level) ages of geological events	Possible for Archean rocks, but resource intensive	Routine in many cases, but difficult if zircon is complex
Ability to tackle complex dating problems (inheritance, Pb-loss, overgrowths, *etc.*)	Very strong, if sufficient age contrasts exist	Possible in some cases; resource intensive; may be uncertainties in age interpretation
Ability to tackle detrital studies	Excellent for rapid surveys of protolith ages; weaker at precise determination of youngest zircon	Highly resource intensive; excellent for precise determination of youngest zircon
Ability to carry out *in situ* (contextual) studies	Excellent: thin sections and rock slabs	Not possible
Fate of analyzed material	Essentially non-destructive	Sample destroyed

*isotope dilution statistics from W.J. Davis and M.E. Villeneuve, GSC (pers. comm.)

Kipawa zircon is partly due to sporadic zones of Pb-loss in the mineral and is the main source of error in the Pb/U ages assigned to the unknowns. This zircon is relatively rich in Th, and is also suitable for calibration of the 208Pb/-232Th ages. The Kipawa zircon has been adopted as the GSC's SHRIMP standard.

The SHRIMP has particular strengths and weaknesses (Table 1) that complement, but do not replace, isotope dilution thermal ionization mass spectrometry (ID-TIMS) dating methods currently in use at the GSC and elsewhere throughout the country. The most important differences between a SHRIMP datum (a single spot) *versus* an ID-TIMS datum (a zircon "fraction") are: 1) the mass of zircon sampled by a SHRIMP spot is at least one thousand times smaller than a typical fraction, resulting in less favourable counting statistics, but much better spatial resolution; and 2) the method of determining the Pb/U ages (*i.e.*, comparison with a standard, as described above) is intrinsically less precise, but much faster than isotope dilution analysis. Consequently, the isotopic ages of a single SHRIMP spot can be determined within approximately 20 minutes, but only at about ten times greater uncertainty than an ID-TIMS analysis. More precise SHRIMP ages may be calculated by statistical pooling of data from several spots, or specific grains can be plucked out of the mount following a SHRIMP session and analyzed by ID-TIMS.

The focus of SHRIMP research at the GSC during the next few years will be on applications of zircon geochronology, where lies the greatest demand for the instrument. There will also be an emphasis on zircon studies that use the particular strengths of the instrument, *e.g.*:

- detrital zircon chronology, with full characterization (50 grains) of age populations, essential for basin analysis and provenance related to geological and continental reconstruction;
- isotopic analysis of minerals *in situ* in the rock, where context is vital or material difficult to recover (*e.g.*, complex metamorphic rocks, mantle and crustal xenoliths);
- dating of igneous and metamorphic rocks with zircon inheritance and complex zircon growth and Pb-loss;
- "reconnaissance" zircon chronology (*i.e.*, a large number of relatively low precision ages) to aid ongoing geological mapping projects and mineral exploration in remote areas.

The initial period concentrating on zircon geochronology is to be followed by U-Pb-Th dating of other minerals, such as monazite, titanite and baddeleyite. Any new isotopic system or mineral requires the development of specific analytical protocols and a suitable standard material. Stable isotope analysis will commence with sulphur, but to become effective in this avenue of research a Cs gun will have to be acquired eventually.

The SHRIMP is a national facility for the GSC, and will also be accessible to researchers in academia and industry throughout Canada in late 1996, following the period of development at the GSC of the requisite analytical and scientific expertise. We are currently establishing an organizational structure that will be able to respond to the research needs of the GSC as well as scientists in other agencies. Researchers interested in the SHRIMP program are encouraged to contact the author for more information.

ACKNOWLEDGEMENTS

I wish to thank O. van Breemen for a review of this article. M. Gerasimoff, O. van Breemen, and other staff members of the Geochronology Subdivision continue to provide tireless support and encouragement.

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Accepted, as revised, 31 July 1996.