

THE EXPANDING WORLD OF THE SHRIMP: NEW DEVELOPMENTS AND FUTURE TRENDS

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The SHRIMP (Sensitive High Resolution Ion MicroProbe) was the first secondary ion mass spectrometer specifically designed for the analysis of geological materials. Since the development of the first SHRIMP at the Research School of Earth Sciences, the Australian National University, Canberra in the early 1980s, this innovative approach to isotope analysis has revolutionised many aspects of geochronology, isotope geochemistry and petrology. After some resistance and scepticism from many quarters, the SHRIMP technique of *in situ* analysis has been universally adopted and is now considered to be one of the “conventional” techniques, along with ID-TIMS (isotope dilution thermal ionization mass spectrometry).

It is in the field of geochronology, and specifically U-Pb dating of zircons, that the SHRIMP has had its biggest impact on the geosciences. There are several reasons for this, *viz.* it is a chemistry-free, virtually non-destructive (usual spot dimensions are ~20µm diameter by ~2µm depth) and a relatively rapid analytical technique, but the main reason has been in the recognition that zircons are complex minerals often requiring small-scale sampling. Age heterogeneity through inheritance is common in a significant number of rocks (*e.g.* in S-type granites) making single-grain and within-grain dating imperative in all but the simplest of populations. Further, recognition that internal complexities from multiple growth episodes are common and could be resolved (with the use of cathodoluminescence or backscattered electron imaging techniques) made the SHRIMP *in situ* option a powerful tool for geochronologists and petrologists - with a cascade effect through the Earth sciences. New technological breakthroughs have seen the SHRIMP technique applied to a growing range of applications.

The biggest recent advances in the hardware configuration of SHRIMP instruments have been the development of a multi-collector system and the flexibility to analyse samples in both positive and negative ion modes. Multiple collectors allow the measurement of several ion beams simultaneously, thereby (a) increasing precision of the isotope ratios by eliminating beam fluctuations, and (b) increasing the efficiency of the instrument by decreasing measurement times. Multiple collectors are commonly used on other mass spectrometers (*e.g.* thermal ionization instruments) but the requirements in a SHRIMP-type instrument are different and more problematical. The dynamic range of

ion beams measured can be very large – requiring ion multipliers for the small ion beams and the option of Faraday cups for the large ion beams. In order to accommodate this large range a configuration comprising a combination of five CDEMS (Continuous Dynode Electron Multipliers) and three Faraday cups has been designed and commissioned in the SHRIMP II at the Research School of Earth Sciences, ANU.

Some geological materials are best analysed in negative ion mode to enhance yields, and this has been achieved by the use of a Cs⁺ primary ion source on SHRIMP II instruments.

These new advances in SHRIMP capability are making it possible to more effectively analyse many more isotope species, and to apply new investigative techniques to the geosciences, still with the same unrivalled spatial resolution. Probably the most important recent advance has been in the field of light stable isotopes, especially oxygen and sulphur. Oxygen isotope ratios are important in many fields of the geosciences, and the future will undoubtedly see many new advances made in igneous and metamorphic petrology, the evolution of the Earth and the Solar System and environmental issues through this enhanced, virtually non-destructive analytical capability. The usefulness of oxygen isotope ratios to characterize igneous zircons and to trace crustal recycling in zircons has already been demonstrated in a number of recent studies (summarized in Valley *et al.*, 2005).

The importance and necessity for small-scale sampling to determine sulphur isotope compositions were demonstrated by a number of studies (*e.g.* Eldridge *et al.*, 1987) using the SHRIMP I instrument. For various reasons this has not been vigorously pursued on the more modern instruments, but the new developments detailed above have shown that sulphur isotopes can be measured with sub-permill precision using the new multi-collector and caesium primary ion beam configuration.

The development of stable isotope capability on the SHRIMP has been successful after overcoming a number of unforeseen problems. An overview of this process and results from a number of new applications of stable isotopes to the geosciences will be presented.

Although the impact of the SHRIMP has primarily been through U-Pb dating of zircons and other accessory minerals, it has always been an instrument of choice for a number of other studies that require its unique capabilities. Analyses of isotope anomalies in rare and

precious cosmogenic samples (e.g. Ireland, 1995) or the analysis of Pb isotope ratios in lunar minerals or sulphides are a few of the applications. The enhanced capabilities of the modern SHRIMPs, however, have allowed a number of important new applications to be attempted. The following are a few of the current research projects that have been developed on the SHRIMP:

(1) The ability to obtain multiple types of geochemical or isotopic data from small and/or rare samples is becoming increasingly important. Bennett et al. (2005) have demonstrated that full common Pb measurement of glass inclusions in volcanic rocks with very low Pb abundances of about 1 ppm are now possible on SHRIMP II.

(2) Results of experimental studies applied to ancient detrital zircons have demonstrated that the concentration of Ti in zircon is directly correlated with temperature of crystallisation (Watson and Harrison, 2005). This has, for example, significant implications for the Hadean history of the Earth. The analytical protocols for Ti analyses have been developed on the SHRIMP II and some very significant results on the usefulness and robustness of this potential geothermometer are discussed.

(3) The analysis of a large number of detrital zircons for provenance and other studies has become an important area of research. Clearly there is a balance between quality of analysis and cost to be considered. A new protocol for the very rapid automated analysis of a large number of zircons has been developed at the Research School of Earth Sciences, ANU, and will be demonstrated.

(4) The use of the Lu-Hf geochronometer (in combination with U-Pb age data) in zircons is important for provenance and crustal/mantle evolution studies. Given the internal complexity of many zircons, it is essential that the U-Pb and Hf isotope data be obtained on the same growth zone within the analysed zircon. Any mixed analysis is meaningless. The combination of an initial SHRIMP U-Pb measurement followed by a LA-ICP-MS Hf isotope measurement on the same spot is the optimum procedure. If required, oxygen isotopes can also be measured before the destructive LA-ICP-MS analysis, altogether yielding a wealth of important information (e.g. Kemp et al., 2006) on a precisely dated zircon grain.

(5) The SHRIMP remains the only instrument capable of measuring U-Pb ages on very small (<20µm) grains or overgrowths. Dating of authigenic xenotime (McNaughton et al., 1999) or monazite provides unique age constraints on sedimentation and/or low-grade metamorphism. Dating of very rare, and very small baddeleyite grains in thin section has recently been shown to be possible (Müller et al., 2005) using SHRIMP. This provides a new way to date mafic

magmatic rocks that contain baddeleyite too small to retrieve by crushing and normal heavy mineral concentration procedures.

Apart from the significant advances made in the hardware development of the SHRIMP II, software developments on all SHRIMP instruments have led to enhanced flexibility in the operation of these instruments. Most after-hours analytical sessions at the Research School of Earth Sciences are now run in a fully automatic mode, with the capability of remote monitoring and intervention. This development negates the requirement of a full-time operator and apart from the obvious cost benefits, this also eliminates any operator bias that could affect some results.

The development of the SHRIMP was motivated by the recognition that geological materials are complex and heterogeneous on all scales. This requires *in situ* analysis of areas within grains at a scale that allows resolution of the internal complexity. It is also a virtually non-destructive technique. These factors are as important today as they have ever been, with the result that the SHRIMP technique is being adopted throughout the world, with new applications and instrumental advances pushing the technique into new and exciting areas.

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RESUMEN

Desde a construção da primeira SHRIMP (Sensitive High Resolution Ion MicroProbe) na Research School of Earth Sciences da Australian National University, em Canberra, no início da década 1980, esse novo enfoque de análise isotópica tem revolucionado muitos aspectos da geocronologia, geoquímica isotópica e petrologia. Ela é hoje, com razão, considerada uma das técnicas analíticas “convencionais” em geoquímica isotópica, porém com várias vantagens sobre outras. Entre elas, o fato de não envolver procedimentos químicos, ser virtualmente não destrutiva, relativamente rápida e com alta resolução espacial, necessária para decifrar a maioria das complexas estruturas e idades.

Numerosos novos avanços e saltos tecnológicos têm permitido que a técnica SHRIMP seja empregada em um número crescente de aplicações. O maior avanço na configuração instrumental foi a instalação de um sistema de multi-coleção de isótopos e a facilidade em analisar amostras nos modos íons positivos e negativos. Melhorias nos programas informáticos permitiram que o SHRIMP seja, hoje, completamente automatizado. Esses novos avanços em capacidade tornaram possível a análise de muitas outras espécies isotópicas (incluindo isótopos leves de oxigênio e enxofre) e a aplicação de novas técnicas de investigação nas geociências com a mesma incomparável resolução especial. Esta palestra enfatiza os novos avanços e avalia futuros desafios na análise isotópica *in situ*.