

SHRIMP: Origins, impact and continuing evolution

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Abstract

The ion microprobe SHRIMP was engendered by the need for *in situ* micro isotopic analysis of minerals relevant to research in isotope geology at RSES. It was home-built and made large to avoid the loss of transmission that accompanies small ion probes of traditional design. The presence of high quality mechanical and electronic workshops at the RSES, the experience of S W J Clement in ion optical design, the advent of new mass-analyser designs by H Matsuda, and the funding regime then enjoyed at ANU that allowed long-term and high risk projects, were each an essential component in the decision to proceed. Some details are given of the history and construction of SHRIMP I, a description of an alternative model now under construction termed SHRIMP-RG, and an account of the initial applications to isotope geoscience that have been more widely developed since. Comparison is made between the performance of SHRIMP with other methods for *in situ* isotopic analysis now available or under development.

Introduction

This is an account of one particular analytical instrument, the Sensitive High Resolution Ion MicroProbe (SHRIMP), rather than of the development of ion microprobes in general. Such a restriction is appropriate to the present symposium because the first commercial SHRIMP was manufactured for the Perth Consortium, and John de Laeter was the driving force behind it. I wish to emphasize that the development of SHRIMP from its conception to realization has been very much a team effort. Finally, history has its own uncertainties, equivalent to experimental error in analytical sciences, the main one being the recollection of exactly what did happen rather than how it was rationalized later.

Development of SHRIMP I

The need for *in situ* micro-isotopic analysis

Since about 1960, use of the electron microprobe with its *in situ* capability for elemental analysis has transformed our understanding of the geochemical relationships between coexisting minerals. However, its performance for trace elements is limited by the high x-ray background continuum, and for the light elements by the very low energy of their characteristic x-radiation. In addition, the electron microprobe cannot measure the isotopic compositions of elements such as Pb, so that it cannot give direct *in situ* age determinations.

In the late 1960s, physical-chemist C Andersen of the Applied Research Laboratories (ARL) used a small ion microprobe designed by H Liebl to develop procedures for successful *in situ* determination of concentrations for many elements. Andersen & Hinthorne (1972) used the same instrument to measure the age of fine-grained U-

rich minerals in lunar rocks. At that time, their results were disparaged by some isotope geochemists, but the possible use of *in situ* instrumental analysis was a very appealing prospect for others struggling to develop clean laboratories and to miniaturise their chemical separation procedures for analysis of the very small amounts of returned lunar samples. No chemistry or mineral separation would be required, and the ion probe itself would pre-clean the area selected for analysis. The idea of obtaining an ion microprobe at the Australian National University for the purposes of geochemistry and within-grain age determinations thus arose directly from Andersen's demonstrations.

To buy or to build?

Mainly for its promise of sensitive and rapid elemental analysis, S R Taylor proposed in early 1971 that the ANU should purchase an ARL instrument. The Bureau of Mineral Resources in Canberra indicated its willingness to help with the purchase, but the proposal was abandoned shortly afterwards due to a prohibitive rise in the cost. This might be viewed in retrospect as a fortunate escape, as the extent of secondary molecular fragments that would interfere with the required elemental ions was not realized until later. Discussion began later that year between S W J Clement and myself on the possibility of building our own high resolution instrument.

The types and abundances of secondary molecular fragments produced by sputtering depend, among other factors, on the chemistry of the target. Andersen was able to identify the main such interferences for his lunar U-rich minerals, and to correct for them by subtracting a calculable fraction of the ion beams at other masses where the particular interference dominated (the 'peak-stripping' procedure). The procedure worked well with the old and U-rich lunar minerals for which the radiogenic Pb isotopes constituted a large fraction of each Pb mass. However, when the interferences dominate the latter, as for example for young and/or U-poor zircon, a

serious magnification of experimental errors must result. In addition, how could we know that all possible isobars from any given mineral had been identified? When these complications had been fully realised, our attention turned to the possibility of obtaining an ion microprobe that could operate routinely at *high mass-resolution*, at least 5000 in the case of zircon, enough to separate nearly all the unwanted isobars.

In March 1973, in response to continued discussion, Anton Hales (first Director of the newly-established Research School of Earth Science) requested the advice of a formally-constituted RSES Ion Probe Committee comprising Taylor, S J B Reed and myself. One alternative was to buy one of the first commercially-available high resolution ion probes, which had been developed by Associated Electronic Industries by combining the highly-successful spark-source mass spectrograph, the MS7, with the primary probe-forming column developed by I W Drummond and J W P Long of Cambridge University. One of these instruments already had been ordered by the University of Chicago (J V Smith) and the University of Cambridge (J W P Long) for geological applications. The other alternative was to design and build our own ion probe in-house, including the employment of S W J Clement for the ion optical and engineering design as an essential ingredient.

Clement and I had become concerned that the sensitivity of the AEI and other small commercial machines then under development (Micromass, Cameca) would be too low at high resolution for effective use in U-Pb age determination. There was no doubt that the MS7 could achieve 5000 R, but we realized that like all other small mass-analyzers, it did so by the use of very narrow slits both at the source and the collector. The narrow source slit reduced the transmitted secondary ion beam and hence reduced the sensitivity for trace-element detection. The narrow collector slit removed the 'flat-top' from the mass spectral peaks that experience with thermal ionization mass spectrometry showed to be essential for accurate quantitative measurements. There was a fundamental trade-off here, sensitivity for high resolution.

The field of beam transport theory, which Clement had used in his PhD project, was obviously relevant for an optimal design. It was also clear that the use of a wide source slit for higher sensitivity at high mass-resolution would demand a much larger magnet than any available from mass spectrometer manufacturers. The latter (very sensibly) wished to make their ion probes as an assembly of mass-spectrometer components that had been developed already (and debugged) for other purposes, typified by the adaptation of the MS7 spark-source mass spectrograph. Manufacturers also aimed for small instruments to lower the price and reduce floor space. We felt that a custom-designed ion probe had to be superior.

Design, Personnel and Construction

Following support by Faculty Board, The RSES Director (A Hales) approved the proposal to build the ion probe in-house in late 1973. The decision was influenced by the favourable infrastructure for instrument construction that was the School's heritage from its former presence within the Research School of Physical Sciences.

RSES had well-equipped and expert machine and electronics shops, accustomed to the design and manufacture of new apparatus and much larger than found in contemporary geology departments elsewhere. The high-risk nature of the project was recognized from the outset. We hoped to progress with capital costs spread over a five-year period. The costs of establishment salaries were not included.

The initial working group comprised S Clement, F Burden (mechanical), N Schram (electronics), D Millar (technical officer) and myself, with Professor G Newstead from the Department of Engineering Physics joining in early 1974 for magnet design and D Kerr of the BMR for computer-control in 1975. This group met each month from 1975 to ensure a full exchange of information, with reports to Faculty Board.

The Matsuda mass-analyser. Clement arrived in early 1974 to make the detailed design. The key part of the instrument was the mass-analyzer, which needed to give simultaneous high resolution and high sensitivity. Clement had completed an original analysis for a double-focussing mass analyzer by mid-1974, but then H Matsuda of Osaka University published his most relevant paper on sector mass-analyzer design (Matsuda 1974). We needed a design that minimized the complex image-aberrations inescapably present in ion optical systems, as well as one that seemed to lie within our practical capabilities such as employing a cylindrical rather than toroidal electrostatic analyzer (ESA). Matsuda (1974) addressed exactly those conditions. He considered the ion optics of sector mass analyzers as an integrated whole, as distinct from aberration-free individual components. Just as the energy-dispersion of the ESA, which as energy-spread represents a first-order aberration of the image, is adjusted to be equal but opposite to that in the magnet to obtain a double-focussing system, Matsuda arranged the various ion optical components so that their second-order aberration coefficients also cancelled each other. An essential part of this was the introduction of an electrostatic quadrupole lens (the 'Matsuda' lens) between the ESA and magnet. There was also curvature in the z-direction of the entrance edges to the ESA plates. For the particular Matsuda design that we favoured, the theoretical image-aberrations would sum to ≤ 6 microns for the magnet turning radius of 1 metre (which we considered to be the largest that we could manage) and for angular divergences and energy-window of ± 0.005 . Clement confirmed Matsuda's calculations using an independent computer program (from C Stevens of the Argonne Laboratory at the University of Chicago) based on phase-space transformations. We concluded that there could be no better design for our purpose, and adopted it henceforth.

Tribulations of fabrication. The 6 tonne magnet was powered without pole-pieces in late 1976. Each pole-piece was intended to be an assembly of five insulated segments of silicon steel but this material was abandoned after very slow delivery followed by external handling mistakes. They were made instead of soft-iron segments machined and annealed in-house with great care. In 1979, segments laminated from transformer shim were tried to permit faster field switching. This indeed was the case but the refocussed image at the collector appeared to be variable in quality, which may or may not

have been due to the laminations (see below), and we returned to the solid segments.

Practice can never be quite as good as theory. Matsuda (1974) envisioned perfectly uniform magnetic and electric fields and perfect geometry, but it is hard to achieve perfection with real materials and real engineering. A further example concerned with the magnet will illustrate this. No magnetic field terminates exactly at the edges of the pole-pieces; rather, it falls off sharply over a finite distance beyond them so that it is necessary to determine the position of an *effective* field boundary. In practice, the magnet for small sector instruments is traversed on rails at right angles to the line joining the source and collector slits until the narrowest image is found empirically. The shape and weight of our ion probe magnet did not allow it to be moved, so instead the collector had to be traversed along the beam-line to find the exact image point. However, the image quality was found to depend strongly on the particular mass collected, and also on the preceding values for the magnetic field.

These observations produced the lowest points of morale in the project. What was wrong with the magnet? No such effects were previously described, although we had noticed with thermal ionization instruments that Sr and Pb ions needed slightly different positions of the magnet for the best refocussing. The discovery that the image point moved in reproducibly with decreasing field when the magnetic field was kept in a fixed cycle of steps saved the situation. The collector could then be driven under computer control to a preset optimum position for each required mass. This remains our solution to the problem. We learned later that at least one manufacturer corrected the effect when making wide-range scans at high mass-resolution by an in-built computer-driven einzel lens. This was not publicised as if the need for such a correction was an admission of deficiency. We have since found that the size of the effect (several mm per 50 daltons) can vary with different SHRIMP magnet designs and may even be reversed. The effect might be due to very slight change in the pole-gap width as the field is changed, or to slight changes in field distribution due to changes in flux-density in the yoke, or both.

The fabrication of the ESA vacuum housing and 1.3 m radius electrodes was subcontracted to the Bendigo Ordnance Factory in late 1975, and delivered in early 1977. J Coles was appointed to assist in final assembly and testing of the ion probe in late 1977, and to develop its application to light element stable isotope ratios. The first detailed report on the testing of the ion probe mass-analyser using a thermal ionization source appeared in the Annual Report of the Research School of Earth Sciences (Clement *et al.* 1978). The first secondary ions generated by sputtering were produced a year later (Clement *et al.* 1979).

First geological applications

S and Pb isotopes in sulfides. Using an Ar⁺ primary beam, the first geological tests of the instrument were for Pb⁺ isotopic ratios from Broken Hill galena by ion-counting (Coles *et al.* 1980). The beam was very stable and the results precise. Tests were extended to the isotopically variable Mississippi Valley sulfides and to the use of

large PbS⁻ and PbS₂⁻ beams measured via the Faraday cup, with peak-stripping of the sulfur isotopes. Significant variations both in Pb and S isotopic ratios were found, but the work was never submitted to any refereed scientific journals. S isotopic ratios in galena, measured both as S⁺ by ion-counting and as S⁻ by the Faraday cup, were also demonstrated.

Ti isotopic composition of terrestrial minerals. With the discovery of small nucleogenic ⁵⁰Ti isotopic anomalies in Ca-Al-rich chondrites using thermal ionization mass-spectrometry, one of the first ion probe applications to be examined was the accurate and precise measurement of Ti isotopes in several terrestrial minerals (Compston *et al.* 1981). The crucial need for accurately-known and constant values for the dead-time of the detector and counting system was encountered first-hand, and also the presence of systematic differences in mass-discrimination in the sputtering of different mineral species.

U-Pb dating. The potential of within-grain analysis for determining the crystallization history of zircons had been appreciated since the early 1970s, following discoveries using conventional dating techniques that old grains had preserved their ages through Alpine-age granulite-facies metamorphism, and that xenocrysts in some granites had survived fusion temperatures. I S Williams, who had analysed zircons and other U-rich minerals by the conventional method, was appointed at RSES in 1981 to participate in the hoped-for use of SHRIMP for this purpose. We sought to find an analytical method that would allow us to generate realistic values for the radiogenic ²⁰⁷Pb/²³⁵U and ²⁰⁶Pb/²³⁸U per analysed spot, that could be plotted on the Concordia diagram.

The particular problem for zircon was the need to determine ²⁰⁶Pb/²³⁸U reliably, as it was quickly established that its ²⁰⁷Pb/²⁰⁶Pb as measured using sputtered secondary ions agreed to within ion counting statistics with that measured by thermal ionization. In great contrast, the observed Pb⁺/U⁺ from sputtering and mass-analysis was about three times larger than the ²⁰⁶Pb/²³⁸U in the target for zircons of known age, with repeat analyses from grains having the same age varying over a 10% range. The previous work by Andersen & Hinthorne (1973) on transforming their measured ion probe data into chemical concentrations, combined with our practice from thermal ionization of normalizing to a fixed ratio to correct for variable discrimination, led us to an empirical but successful procedure. Reasonable linear correlations were found between the observed Pb⁺/U⁺ and the observed UO⁺/U⁺ in zircons that have the identical age (Williams *et al.* 1981). This allowed us to correct Pb⁺/U⁺ as measured for variable discrimination by normalizing to a fixed value for UO⁺/U⁺, then to use the corrected Pb⁺/U⁺ of a concurrently measured zircon of known age as a comparison-standard. With continued development, the procedure now allows us to measure the ²⁰⁶Pb/²³⁸U ages of very young zircons with sufficient accuracy and precision both to compete with the conventional method and to detect inherited zircons as whole grains and inclusions that are not otherwise detected (Compston & Williams 1992).

Impact of Shrimp in Isotope Geoscience

There is no doubt that zircon U-Th-Pb measurement has been the dominant use of SHRIMP so far. Of a minimum

of ca. 150 articles that have appeared in refereed research journals to the end of 1995, only ca. 15 % deal with isotope ratios of the 'light' elements (S, Ti, Mg). The remainder have used zircon geochronology for geological reconnaissance or to test various geological hypotheses. However, the 15 % light element applications demonstrate that SHRIMP can be used over the whole nuclidic range, and the dominance of zircon studies simply reflects our current perceptions of what has been the most rewarding scientifically. This balance may change in the future.

We regard the following projects as originating a number of important types of applications of SHRIMP to the earth sciences that have been used widely and developed further.

Accurate age measurements on terrestrial zircons. Antarctic zircons, previously dated using the original (small) ARL ion probe and its peak-stripping methods for isobaric interferences, were reanalysed by SHRIMP. The ages found were wholly consistent with geological constraints, and previously contentious results were shown to be an artefact of uncorrected isobaric interferences in the ARL data (Williams *et al.* 1982; Williams *et al.* 1983).

Ages of zircon overgrowths in polymetamorphic episodes. The main reason for the development of SHRIMP was *in situ* microanalysis, with the prospect of detecting age-differences between different growth-zones within a single mineral. This capability was first illustrated for zircons from the Archaean Napier Complex in Antarctica and in zircon xenocrysts from Palaeozoic granites in Eastern Australia (Williams *et al.* 1981, 1982). Unsupported radiogenic Pb within a single zircon was observed in high-grade gneiss at Mt Sones (Williams *et al.* 1983, 1984), and the growth at high metamorphic grade of characteristically low-Th/U zircon rims around Proterozoic grains was documented first in the Scandinavian Caledonides (Williams & Claesson, 1987).

***In situ* age measurements on lunar zircons and initial Pb in lunar feldspars.** Ion probe geochronology started and continued for 10 years on lunar zircons that have been discovered by diligent search of many lunar thin-sections by Lunar Sample Curator Charles Meyer (Compston *et al.* 1983). Serial lunar magmatism since 4.35 Ga has been established. Meteoritic zircons have been dated also (Ireland & Wlotzka 1992). More recently, the high sensitivity and within-grain targeting capability of SHRIMP showed that the extremely radiogenic composition of Ba-rich feldspars in lunar felsites is an original magmatic characteristic rather than a product of the 'terminal lunar cataclysm' (Compston *et al.* 1988; Compston *et al.* 1991).

Oldest-known terrestrial zircons. This discovery arose from our use of the age-spectra of detrital zircons in Archaean sediments to explore the ages and nature of their source rocks (Froude *et al.* 1983). It generated studies of detrital zircon ages in other Archaean metasediments, and of trace-elements, especially REE, in inclusions within the old zircons (Maas *et al.* 1992) that bear on the nature of the primary zircon sources.

The dating of young zircons. Palaeozoic zircons were at first considered to be too young for ion probe dating

because the amount of ^{207}Pb is usually too low to obtain useful $^{207}\text{Pb}/^{206}\text{Pb}$ ages. Consequently, the dating of young grains by ion probe must rest mainly on their $^{206}\text{Pb}/^{238}\text{U}$ ages, which in turn are limited by the ability to control the variable discrimination of ^{206}Pb relative to ^{238}U during sputtering and secondary ion extraction. Mainly for this reason, we obtained and analysed zircons from the collection made by R Ross and others from bentonites in the British Ordovician stratotypes (Compston *et al.* 1982). The project has developed into continuing applications of SHRIMP to the definition of the geological time-scale (Compston & Williams 1992; Compston *et al.* 1992), with the realization that some of the zircon samples used for conventional time-scale dating were probably composite in age due to inheritance, a point hotly disputed and now in the process of resolution. The capability of SHRIMP to determine extremely young zircon ages was first illustrated by analyses of 2 Ma-old zircons from the western Himalaya (Zeitler *et al.* 1989).

Terrane mapping in Archaean gneisses. The high blocking-temperature of zircon means that intense deformation and repeated metamorphism does not erase earlier zircon ages in gneisses that contain multiple age components, which in many instances allows their detailed history to be unravelled in a single sample. This was evident for the Napier Complex (Williams *et al.* 1982), and was used to decipher the history of the Narryer Gneiss terrane (Kinny *et al.* 1990; Nutman *et al.* 1991) during the search for intact 4.2 Ga rocks. Our study of the Narryer region has shown clearly that correlations between isolated exposures of gneiss cannot be made reliably without zircon geochronology. Currently, the oldest terrestrial rock known is the 4.0 Ga Acasta gneiss in Canada, first indicated as very old by thermal ionization mass-spectrometry then determined accurately as 4.0 Ga by SHRIMP (Bowring *et al.* 1989).

SHRIMP dating of other U-bearing minerals. The first lunar paper (Compston *et al.* 1984) also included the essential analytical and data-reduction procedures for zircon ion-probe work that, with various refinements, we continue to use today. The same correction method for variable discrimination in zircon analysis has been applied successfully to a number of other U-bearing minerals; perovskite (Compston *et al.* 1985), and baddeleyite, monazite, titanite and rutile (Camacho *et al.* 1993).

***In situ* Hf isotopic analysis.** The potential for hafnium as a radiogenic isotope fingerprint is well-known from thermal ionization mass-spectrometry, but Hf is a difficult element to separate chemically and to mass-analyze with the necessary precision. Because of the high Hf contents of zircons, an early reconnaissance study of the potential of SHRIMP for Hf isotopic analysis was made, with encouraging results (Compston *et al.* 1982; Kinny *et al.* 1991). Mathematical procedures for peak-stripping were developed to correct for hydride, oxide, Lu and Yb isobars, which cannot be mass-resolved by SHRIMP II without losing sensitivity. Further analyses of Hf have been deferred pending the development of the SHRIMP-RG and/or the availability of the multicollector for SHRIMP II.

Isotopic mapping of trace-element distribution within minerals. With the advent of the computer-controlled sample-stage in SHRIMP II, it has been possible to construct

detailed maps of the spatial distribution of any nuclidic or molecular secondary ion at high mass-resolution (Clement *et al.* 1992). This facility has been combined with imaging by back-scattered electrons and cathodoluminescence using the electron microscope to obtain very powerful targetting and interpretive information (Williams *et al.* 1995).

Depth-profiling using SHRIMP. The lens configuration of the primary-beam focusing column was designed originally for two-stage demagnification of the duoplasmatron extraction-aperture to produce the ca. 20 μm probe itself. However, the probe was plagued by a low-intensity but wide halo that caused a slow release of surface-related common Pb during analysis. Initially, as an experiment, it was modified to implement 'Köhler illumination' (Compston *et al.* 1983). This was successful; the probe now had a sharply-defined edge plus a highly-uniform ion-density within the sputtered area. It was then realized that 'Köhler illumination' had an advantage over spot-rastering for depth-profiling; it gave 'parallel' information over the full width of the spot rather than 'serial' as in rastering, which means a much higher sensitivity per second. In addition, it removed the need for the very small probe diameter required for depth-profiling by rastering.

Depth-profiling in this way was first employed in experiments on the diffusion of radiogenic Pb from the (high-U) SL3 zircon standard (Williams *et al.* 1988). Diffusion was induced, holding the samples at constant high temperature under hydrothermal conditions, and profiles for the escape of Pb, U and Th were determined. Results for diffusion coefficients were not then reported because it was realized that the process was not pure volume-diffusion. It was found that annealing of the samples prior to the experiments failed to remove zones of structural breakdown due to radiation damage. The work has been repeated recently using the low-U zircon SL13 and with improved control and documentation (Lee *et al.* 1995).

Ti and Mg isotopic anomalies in meteoritic minerals. Small isotopic anomalies in ^{50}Ti observed using thermal ionization in bulk refractory inclusions in carbonaceous chondrites were transformed into huge anomalies, from 2.0 % to -4.0 %, when the carrier mineral hibonite was selectively probed (Ireland *et al.* 1985). Mg isotopic analysis of the same hibonites revealed the presence of excess ^{26}Mg , attributable to *in situ* decay of ^{26}Al in some grains, ranging up to more than 1000 % in one instance (Ireland & Compston, 1987).

***In situ* S isotope analysis as an isotopic fingerprint.** Detailed SHRIMP analyses of different S-bearing mineral species confirmed that isotopic discrimination during sputtering is controlled mainly by the crystal bond-strengths, and that accurate differences in S isotopic composition can be measured relative to standards of the same mineral-type (Eldridge *et al.* 1985; Eldridge *et al.* 1987). The established techniques were first tested by applications to fine-grained sulfide ores from Mt Isa (Australia) and the classical ore deposits at Rammelsberg (W Germany), demonstrating that different generations of sulfides of the same species may be precipitated and co-exist without any isotopic equilibration between younger and older despite superposed metamorphism.

Future Developments

The continued development of SHRIMP is subject to the possibility that it might be made redundant overnight by the arrival of some new instrumental technique that is both better and much cheaper. I am aware of two micro-techniques that have been predicted as substitutes for SHRIMP. These are accelerator mass spectrometry (AMS) and laser-sampling, inductively-coupled plasma ionization mass-spectrometry (ICPMS).

Accelerator mass spectrometry

AMS for trace-element and isotope ratios is currently being developed in Australia at CSIRO, North Ryde, under the project name AUSTRALIS (Sie & Suter 1994). It involves the use of sputtering to take a continuous micro-sample just as SHRIMP does, but it uses a quite different method of dealing with isobaric interferences. Negative secondary ions of the one nominal mass are selected, then accelerated by several MeV in a tandem van der Graaf accelerator. At the positive high-voltage terminal, they are then passed through a column of Ar gas at low pressure, which does two things; it strips up to several electrons from the negative atomic ions to form multiply-charged positive atomic ions, and it ruptures molecular ions into their constituent atoms in addition to stripping off electrons. As a result, all molecular ions are destroyed so the problem of molecular isobars vanishes. The positive ion beam is then mass-analysed at low resolution.

AUSTRALIS is larger, more complex and more expensive than SHRIMP. In addition, it is one of several projects at North Ryde that will share use of the tandem accelerator, so its capacity for geological analysis will be constrained. There will be the need to correct for variable elemental discrimination during sputtering, because the collected Pb^+/U^+ cannot be normalized to the same UO^+/U^+ in the absence of molecular ions. Only negative secondary ions can be used.

Previous AMS experience has concentrated greatly on low counting-rates, and the use of sophisticated proportional counters that allow each ion to be identified from its charge-state and momentum which gives AMS its unique power for ultra-low trace-elements. In contrast with this, the U-Pb, Rb-Sr, Nd-Sm and oxygen isotope applications for geology demand the use of very high count-rates, to realise enough precision in a reasonable analytical time. AMS will thus have the same high count-rate linearity challenge in the detector as SHRIMP, and rather than detecting ions of 10 keV energy, AMS will need to handle ion energy of several MeV.

Laser-sampling, inductively-coupled plasma ionization mass-spectrometry

At the recent meeting of the ANZSMS in Sydney, G Hieftje from the Department of Chemistry, University of Indiana assessed the present and future status of 'Atomic Mass Spectrometry' (Burgoyne *et al.* 1995). He addressed the question of just how good ICPMS is, as presently available commercially, for making quantitative fast determinations of all the elements and isotopes.

For *in situ* micro-analysis, a succession of pulsed laser shots is fired to ablate the target. This ablated material is swept away in a stream of gas, usually He, then the gas

plus suspended particulate sample introduced to the inductively-coupled plasma to be ionized. Ionization is done with great efficiency hence high sensitivity could be available. Then the ions are extracted and mass-analyzed either on a fast quadrupole analyzer for wide mass-range and speed, or on a double-focussing sector analyzer with multicollector if a relatively small mass range is sufficient.

Hieftje emphasized several practical problems. The laser gives a non-continuous supply of the sample. The intensities of the sample ions rapidly rise with the start of the pulse then decline, and all the isotope and elemental ratios must be measured while this is happening. Because quadrupole mass-analysers measure masses in sequence, the influence of a variable sample signal is difficult to eliminate, and therefore use a time-of-flight mass-analyser which analyzes ions of all masses formed during the same short time-interval was necessary. Currently, the TOF analyser has an efficiency-problem; the heavy ions must travel to the detector before taking another laser pulse. To improve this even to 10% efficient duty-cycle, complex electronic timing and electric field sweeps are necessary. Irrespective of the mass-analyser, isobaric interferences remain even using plasma-ionization. Oxides are present for many elements. The exact species must be known and peak-stripping used if the mass-analyser operates at low resolution, or a high resolution mass-analyser should be used. There are also matrix-effects attributed to space-charge dispersion in high density beam-waists in the plasma; the light ions are spread more than the heavy ions. Overall, Hieftje made the point that present ICPMS instruments have serious deficiencies and that it might be 10 years before the necessary control on TOF analysers has been perfected.

The above problems are greatly reduced if instrumental needs can be restricted to isotopic ratios of single elements within the limited mass-range of multi-collector sector analysers. However, there is one ultimate comparison that should be made between the SHRIMP ion microprobe and all ICPMS instruments, laser-sampling or otherwise. Which method of analysis has the greater intrinsic sensitivity? The fundamental definition of sensitivity for a given element is its *useful yield*, the ratio of ions collected for analysis per second to the number of atoms of that element consumed per second by the sampling process. Here, SHRIMP remains well ahead of ICPMS. For SHRIMP I at $\geq 5000R$, the useful yield for Pb in zircon was measured approximately as 0.7% (Compston & Williams, unpublished), and more accurately for SHRIMP II at $\geq 1.5\%$ (J W K Lee & I S Williams, *pers. comm.*). The only published ICPMS value known to me is 0.22 % for Pb in a standard glass (Walder *et al.* 1993). Even lower values are reported verbally for Pb in zircon, 0.14% (P. Turner, *pers. comm.*). It is therefore quite clear that the *total* sensitivity found for trace elements using laser-sampling ICPMS has been obtained by the use of much greater amounts of sample than SHRIMP. This is consistent with the multiple laser shots used per analysis as well as the hemispherical shape of the laser pits (e.g. 20 μm diameter and 20 μm deep), as compared with single 20 x 25 μm elliptical spots using SHRIMP that are typically only 1 μm deep.

Recent theoretical advances in sector mass analyser design

Advances in ion optical theory have been made by H Matsuda, whose 1974 design we employed for SHRIMP I and II. Matsuda (1990) has now shown that it is possible to design families of double-focussing sector mass-analysers that have strong demagnification of the final image without an equivalent reduction in the mass-dispersion. This means that for a mass-analyser of a given size ('size' means turning radius of the magnet), the mass-resolution at a given object-slit width (which sets the sensitivity) can be increased by a large factor. The particular design selected for the SHRIMP-RG will operate routinely at the same sensitivity as SHRIMP II, but with 4x greater mass-resolution. That in turn means that a number of new and important types of geochemical analyses, not practical for SHRIMP II, could be undertaken using an ion probe based on the post-1990 design.

There are some constraints that accompany the new design. One is that multiple collection can never be used, because the beam must be sent first through the mass-dispersing magnet rather than first through the energy-analyser. This arrangement is known as 'reverse-geometry'. Only one selected mass at a time can be transmitted through the energy analyser to the collector slit, thereby limiting the collection of data to the intrinsic inefficiency of a single collector. On the other hand, the latter has the virtues of equal gain for all masses, simplicity and cheapness. In addition, reverse-geometry is well-known to give much higher abundance-sensitivity than forward-geometry *i.e.* the background of scattered ions will be very small so that low abundance peaks can be measured more accurately.

The new design must be well-corrected for image-aberrations to give highly demagnified images of good quality. The present SHRIMP IIs have low values for all 2nd order aberration coefficients, but the new design requires that several 3rd order coefficients must be low also. As in SHRIMP II, the design itself incorporates the means of nulling the necessary image aberrations through its particular selection of ion optical parameters. We therefore consider that the attainment of good focussing in the new design will be no more difficult than in SHRIMP II.

Practical design problems for a new model SHRIMP

A constraint in the new design is the need for a much wider pole-face area than that used in the SHRIMP II magnet. At its widest, the secondary ion beam will diverge to ± 120 mm within the sector magnet compared with ± 30 mm in SHRIMP II. This places a greater demand on the design and engineering of the magnet, especially for the laminated pole-pieces that are necessary for fast field-switching.

The question arises of whether the theoretical performance of the new designs can be made in practice, bearing in mind the imperfections of fabrication, variable magnetic properties of iron, and small misalignment of components. The same concerns were held for SHRIMP I but proved groundless. In addition, the manufacturer JEOL has successfully produced more than 100 small double-focussing mass spectrometers based on one of Matsuda's new designs, which gives confidence that the theoretical performance can be achieved. We are satisfied

therefore that the necessary low image-aberrations will be achieved at the same level of accuracy in machining and alignment of ion optical components as used in the manufacture of SHRIMP II. Nevertheless we will take the precaution of including at least one ion optical stigmator to compensate empirically for image imperfections.

Advantages of the SHRIMP-RG

The principal benefit of the SHRIMP-RG would be the removal of isobars, such as hydrides of the heavier elements, that trouble or disallow a number of important geochemical applications. Examples are listed below but there will be many more. Discoveries in research cannot be predicted. In general, mass-resolution should be viewed as a commodity that cannot be overdone. In addition, SHRIMP-RG could be operated with a very wide source slit for other applications, such as stable isotope analysis, that do not demand high mass resolution but are especially susceptible to variable mass discrimination. Discrimination in the secondary ion mass-analyser cannot occur in the absence of beam truncation. In SHRIMP II, truncation occurs both at the source slit (at least 10 % of the beam at resolution 5500) and at other apertures during the transfer of ions from the analysed spot to the source slit. SHRIMP-RG offers the opportunity of improved phase-space matching between the mass-analyser and the analysed spot. If the present truncations can be avoided totally, only the sputtering process itself would remain to cause variable discrimination.

Some geological applications for SHRIMP-RG

Interference between Sr isotopes and Ca isotope dimers, such as $^{44}\text{Ca}^{43}\text{Ca}$ with ^{87}Sr ($m/\Delta m$ of 16000) discourage serious $^{87}\text{Sr}/^{86}\text{Sr}$ fingerprint studies for the above and other Ca rich minerals. Sr isotope 'chemostratigraphy' is plagued by ambiguity caused by diagenetic alteration. Using whole rock samples, it is rarely clear whether a genuine shift in seawater isotope composition has been discovered in a stratigraphic sequence or a zone of later fluid alteration. Ion probe analysis will reveal diagenetic changes in many cases through their variable effects on a 10 micron spatial scale, and preserved areas should be identified.

^{40}K - ^{40}Ca dating of K-rich minerals

There is a moderate prospect that radiogenic ^{40}Ca will be retained more strongly than ^{40}Ar during cooling after igneous emplacement or metamorphism, so that ^{40}K - ^{40}Ca ages of mica and K-feldspar would contribute to cooling history studies. The problem will be to find minerals in which the radiogenic ^{40}Ca is not diluted by common Ca. There are good prospects that *in situ* 10 μm scale analyses will be better in this respect than bulk mineral separates. The very high abundance-sensitivity of SHRIMP-RG would minimize scattering from the adjacent intense ^{39}K peak. In addition, it would be possible to resolve ^{40}K from ^{40}Ca ($m/\Delta m$ of 28000) during analysis so that the ratio $^{40}\text{Ca} / ^{44}\text{Ca}$ would be a direct measure of the radiogenic enrichment without peak-stripping of K isotopes.

^{147}Sm - ^{143}Nd dating and ^{143}Nd isotope labelling of REE-rich minerals. There are at least two problems with ion probe analysis for the above; the need for maximum sensitivity to amass enough counts for worthwhile precision,

and the need for minimum peak-stripping of isobars to keep the analysis process simple. Some minerals such as perovskite have no obvious isobaric interferences other than hydrides, which SHRIMP-RG would remove at resolution 25000. More complex interferences must be expected for silicates and phosphates.

Removal of $^{206}\text{Pb}^1\text{H}$ from ^{207}Pb in the dating of hydrous minerals

The variable water content of pitchblende or any other U-rich hydrous mineral inhibits us from attempting to date such minerals at present. Peak-stripping is unreliable because mass 209 might be occupied by ^{209}Bi as well as $^{208}\text{Pb}^1\text{H}$. The ratio of $^{90}\text{Zr}^1\text{H} / ^{90}\text{Zr}$ could be used for Zr-bearing minerals as shown by Long & Hinton (1984), but this requires very large mass jumps during data-collection. Although large jumps might be practical on SHRIMP II when the laminated magnet poles are fitted, it would be far better to remove the hydrides at resolution 29000 which should be possible for SHRIMP-RG with some loss of sensitivity.

Removal of hydrides in Hf isotope ratio measurement

At present, peak-stripping must be used to remove ^{18}O , Yb, Lu and hydrides. Moreover, the hydrides of Yb and Lu differ in proportion to that of Hf. There is only one independent Hf isotope ratio left after the stripping to judge the veracity of the process, which is dangerous. The absence of the need to strip hydrides would be an enormous advantage, and it would be routinely possible to operate SHRIMP-RG at the necessary 22000 mass-resolution.

Easy separation of light REE oxides from heavier REE metal ions

Our REE measurement procedure is presently limited by the need to select the best mass-channels to avoid oxide overlaps. The routine operating resolution for SHRIMP-RG would remove these and other isobaric interferences that will arise when different minerals and REE levels are attempted. When trace-elements are present at the ppb level, many new possibilities exist for isobaric interferences that can be neglected at the ppm level. Examples are low abundance combinations of very light nuclides (e.g. boron) which have nuclidic mass 'surpluses' with oxides of heavier nuclides which have mass deficiencies. If geochemistry is to examine trace-elements in minerals at such levels, that problem must be faced.

Meteoritic isotope anomalies

SHRIMP-RG could resolve isobars in the Fe-group of elements, such as ^{58}Ni and ^{58}Fe , which opens the way for specialised cosmogenic isotope studies in addition to high-quality terrestrial geochemical/isotope analyses.

Concluding Remarks

A new Australian manufacturing company now exists to build SHRIMPs, Australian Scientific Instruments (ASI), in response to several requests made to the ANU for commercial sales. I wish to acknowledge here the very important role played by John de Laeter in precipitating our decision to participate in this commercial venture.

De Laeter formed the view that more than one SHRIMP was needed in Australia; one should also be located in Perth, for geological research at two Universities and to aid geological mapping by the State Geological Survey and by the mining industry. He also believed, and stated persuasively, that he could raise the necessary money for its purchase. At the same time, the demand for access to the ANU SHRIMP had become excessive, both from internal ANU projects, from visiting scientists and from the Commonwealth Bureau of Mineral Resources. It became clear that a second and hopefully improved ANU SHRIMP could be built as a commercial prototype, followed by manufacture by ASI from this prototype and with the Perth Consortium led by John de Laeter as the first customer. Happily, this desirable course of events came to pass.

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References

- Andersen C A & Hinthorne J R 1972 U, Th, Pb and REE abundances and $^{207}\text{Pb}/^{206}\text{Pb}$ ages of individual minerals in returned lunar material by ion microprobe mass analysis. *Earth & Planetary Science Letters* 14:195-200.
- Andersen C A & Hinthorne J R 1973 Thermodynamic approach to the quantitative interpretation of sputtered ions in mass spectra. *Analytical Chemistry* 45:1421-1438
- Bowring S A, Williams I S & Compston W 1989 3.97 Ga gneisses from the Slave province, Northwest Territories, Canada. *Geology* 17:971-975.
- Burgoyne T W, Chambers D M, Heintz M A, Hieftje G M, Li G, Mahoney P P, Myers D P, Ray S J & Ross-Buckley B S 1995 Atomic mass spectrometry: the next generation. Australian and New Zealand Society for Mass Spectrometry Fifteenth Conference, Sydney NSW, WeO-01.
- Camacho A, Compston D, Compston W, Fanning C M, Sircombe K N & Williams I S 1993 U-Th-Pb dating of baddeleyite, rutile and monazite using SHRIMP II. Research School of Earth Sciences Annual Report, 93-94.
- Clement S W J, Coles J, Compston W, Kerr D & Newstead G 1978 High resolution ion microprobe. Research School of Earth Sciences Annual Report, 172-174
- Clement S W J, Coles J, Compston W, Schram N, Foster J J & Newstead G 1979 High resolution ion microprobe. Research School of Earth Sciences Annual Report, 159-161.
- Clement S W J, Compston W, Dabrowski R, Foster J J, Reinfrank R F & Williams I S 1992 SHRIMP II performance, isotopic mapping with SHRIMP II. Research School of Earth Sciences Annual Report, 70-72.
- Coles J, Compston W & Foster J J 1980 Microanalysis of Pb and S isotopes in galena. Research School of Earth Sciences Annual Report 175-179.
- Compston W, Foster J J, Williams I S, Coles J N & Heydegger H R 1981 Ti isotopic composition using the ion microprobe. Research School of Earth Sciences Annual Report, 212-217.
- Compston W, Kinny P, Williams I S & Foster J J 1982 Hafnium isotopes in zircons. Research School of Earth Sciences Annual Report, 249-252.
- Compston W, Williams I S, Bristow J & Ireland T R 1985 Measurement of U-Pb ages of kimberlitic perovskite by ion microprobe. Research School of Earth Sciences Annual Report, 82-83.
- Compston W, Williams I S, Froude D & Foster J J 1982 U-Pb dating of zircons from lower Palaeozoic tuffs using the ion microprobe. Research School of Earth Sciences Annual Report, 244-246.
- Compston W, Williams I S, Froude D O, Ireland T R, Kinny P D & Foster J J 1982 Ion microprobe (SHRIMP) research and development. Research School of Earth Sciences Annual Report, 110-116.
- Compston W, Williams I S & Meyer C 1983 Ages determined on lunar zircons in thin section. Research School of Earth Sciences Annual Report, 116-119.
- Compston W, Williams I S & Meyer C 1984 U-Pb geochronology of zircon from lunar breccia 73217 using a sensitive high mass-resolution ion microprobe. *Journal of Geophysical Research* 89: Supplement B525-B534.
- Compston W, Williams I S & Meyer C 1988 A new insight into the early history of the moon. Research School of Earth Sciences Annual Report, 73-74.
- Compston W, Williams I S & Meyer C 1991 Initial Pb isotopic compositions of lunar granites as determined by ion microprobe. *Stable Isotope Geochemistry: A Tribute to Samuel Epstein* (eds H P Taylor, J R O'Neil & I R Kaplan). The Geochemistry Society Special Publication 3:473-486.
- Compston W & Williams I S 1992 Ion probe ages for the British Ordovician and Silurian stratotypes. In: *Global Perspectives on Ordovician Geology* (eds B D Webby & J R Laurie). Proceedings of the 6th International Symposium on the Ordovician System, Sydney, 59-67.
- Compston W, Williams I S, Kirschvink J L, Zhang Zichao & Ma Guogan 1992. Zircon U-Pb ages for the Early Cambrian time-scale. *Journal of the Geological Society of London* 149:171-184.
- Eldridge C S, Compston W & Williams I S 1985 Determination of sulphur isotopic composition by ion microprobe. Research School of Earth Sciences Annual Report, 83-84.
- Eldridge C S, Compston W, Williams I S & Walshe J L 1987 *In situ* microanalysis for $^{34}\text{S}/^{32}\text{S}$ ratios using the ion microprobe SHRIMP. *International Journal of Mass Spectrometry and Ion Processes* 76:65-83.
- Froude D O, Ireland T R, Kinny P D, Williams I S, Compston W, Williams I R & Meyers J S 1983 Ion microprobe identification of 4,100-4,200 Myr-old terrestrial zircons. *Nature* 304:616-618.
- Ireland T R & Compston W 1987 Large heterogeneous ^{26}Mg excesses in a hibonite from the Murchison meteorite. *Nature* 327:689-692.
- Ireland T R, Compston W & Heydegger H R 1985 Titanium isotopic anomalies in hibonites from the Murchison carbonaceous chondrite. *Geochimica et Cosmochimica Acta* 49:1989-1993.
- Ireland T R & Wlotzka F 1992. The oldest zircons in the solar system. *Earth and Planetary Science Letters* 109:1-10.
- Kinny P D, Wijbrans J R, Froude D O, Williams I S & Compston W 1990 Age constraints on the geological evolution of the Narryer Gneiss Complex, Western Australia. *Australian Journal of Earth Sciences* 37:51-69.
- Kinny P D, Compston W, & Williams I S 1991 A reconnaissance ion-probe study of hafnium isotopes in zircons. *Geochimica et Cosmochimica Acta* 55:849-859.
- Lee J K W, Williams I S & Ellis D J 1995 Pb, U and Th diffusion in zircon. Research School of Earth Sciences Annual Report, 105-106.
- Long J V P & Hinton R W 1984 The intensity of metal hydride peaks in secondary positive-ion spectra from silicates. *International Journal of Mass Spectrometry and Ion Processes* 55:307-318.
- Maas R, Kinny P D, Williams I S, Froude D O & Compston W 1992 The Earth's oldest crust: A geochronological and geochemical study of 3900-4200 Ma old zircons from Mt Narryer and Jack Hills, Western Australia. *Geochimica et Cosmochimica Acta* 54:2535-2547.
- Matsuda H 1974 Double focussing mass spectrometers of second order. *International Journal of Mass Spectrometry and Ion Physics* 14:219-233.

- Matsuda H 1990 High performance mass spectrometers of magnetic section type. *International Journal of Mass Spectrometry and Ion Processes* 100:31-39.
- Nutman A P, Kinny P D, Compston W & Williams I S 1991 SHRIMP U-Pb zircon geochronology of the Narryer Gneiss Complex, Western Australia. *Precambrian Research* 52: 275-300.
- Sie S H & Suter G F 1994 A microbeam AMS systems for mineralogical applications. *Nuclear Instruments and Methods in Physics Research B* 92:221-226.
- Walder A J, Abell I D, Platzner A I & Freeman P A 1993 Lead isotope ratio measurement of NIST 610 glass by laser ablation inductively coupled plasma mass spectrometry. *Spectrochimica Acta* 48B:397-402.
- Williams I S & Claesson S 1987 Isotopic evidence for the Precambrian provenance and Caledonian metamorphism of high grade paragneisses from the Seve Nappes, Scandinavian Caledonides. II. Ion microprobe zircon U-Th-Pb. *Contributions to Mineral Petrology* 97:205-217.
- Williams I S, Compston W, Black L P, Ireland T R & Foster J 1984 Unsupported radiogenic Pb in zircon: a cause of anomalously high Pb-Pb, U-Pb and Th-Pb ages. *Contributions to Mineral Petrology* 88:322-327.
- Williams I S, Compston W, Collerson K D, Arriens P A & Lovering J F 1983 A reassessment of the age of the Windmill Metamorphics, Casey Area. In: *Antarctic Earth Science* (eds R L Oliver, P R James & J B Jago). Australian Academy of Science, Canberra, 73-76.
- Williams I S, Shah J S & Stowe S 1996 Elemental and isotopic microanalysis of zircons and backscattered electron contrast: Surface and Interface Analysis: in press.
- Williams I S, Black L P & Compston W 1983 Excess radiogenic Pb in zircons from Mt Stones, Antarctica. *Research School of Earth Sciences Annual Report*, 1390131.
- Williams I S, Black L P, Foster J J, Coles J N, Kinny P & Compston W 1982 Ancient zircon from the Fyfe Hills, Enderby Land, Antarctica. *Research School of Earth Sciences Annual Report*, 205-208.
- Williams I S, Compston W & Coles J N 1981 Zircon U-Pb geochronology using the ion microprobe. *Research School of Earth Sciences Annual Report*, 217-221.
- Williams I S, Harrison T M & Compston W 1988 Depth profiling by ion microprobe: a study of the diffusion of Pb, U and Th in zircon. *Research School of Earth Sciences Annual Report*, 72.
- Williams I S, Stowe S & Shah J S 1995 Microbeam imaging of zircon growth structure. *Research School of Earth Sciences Annual Report*, 106-107.
- Zeitler PK, Sutter J F, Williams I S, Zartman R & Tahirkheli R A K 1989. Geo-chronology and temperature history of the Nanga Parbat-Haramosh massif, Pakistan. *Geological Society of America, Special Paper* 23:1-22.