Presidential Address

A New Era for Isotope Geochemistry

FRANCIS ALBAREDE

Ecole Normale Supérieure, Lyon 69007, France (albarede@ens-lyon.fr)

Until the advent of multiple-collector inductively-coupled plasma mass spectrometry (MC-ICP-MS), only a small fraction of the periodic table was liable to precise isotopic analysis, and even then for most of the elements only the radiogenic, cosmogenic or nucleosynthetic part of isotopic variability was accessible. It was widely held that most heavy elements, with the exception of Se, were isotopically homogeneous and that most elements with only two isotopes such as Cu or Ga remained out of reach.

MC-ICP-MS started in the mid-90s under unfavourable auspices. Ion yields of about 50 ions per million atoms, a precision of hardly 0.02 percent, abundance sensitivity of several ppm and isobaric interferences deterred many users from shifting from TIMS to MC-ICP-MS. Over the following five years, this situation dramatically evolved: ion yields up to a few percent, precision down to 30 ppm or even better, and interference control improved through collision cells, high-resolution devices, or, simply, efficient chemical separation tipped the balance between the two techniques. New specifications on abundance sensitivity will very soon bring the isotope geochemistry of actinides within reach.

New radioactive isotopic systems benefited from this major technological advance: the revival of the ^{176}Lu-^{176}Hf chronometer with novel applications to the dating of garnet-bearing rocks (eclogites, garnet peridotite) and phosphates is particularly important because of the apparently high closure temperature of the Lu-Hf system. A decisive advantage of this chronometric system in planetary sciences is that it is the only system together with Sm-Nd for which both the parent and the daughter nuclides are incompatible lithophile refractory elements which allows planetary mass balance to be evaluated with more confidence than with for example U-Pb, Rb-Sr, or Re-Os. Application of this principle to the differentiation of the Earth, the Moon, Mars, and the eucrite parent body has proved to be particularly fruitful. A few radioactive systems involving extinct nuclides with refractory progeny also greatly benefited from the expansion of MC-ICP-MS. After the early success of ^{182}Hf-^{182}W that helped clarify the chronology of core-mantle segregation in different planets, we are seeing a growing number of publications on ^{97}Tc-^{97}Mo, ^{92}Nb-^{92}Zr, ^{107}Pd-^{107}Ag, and now ^{146}Sm-^{142}Nd.

The old U-Th-Pb system received a significant face lift: the precision of MC-ICP-MS Pb isotope data is currently better than 30 ppm for all ratios that do not involve ^{204}Pb and of 100-200 ppm for those that do, as a probable result of the poor abundance sensitivity of all the first-generation machines. This is, however, enough to demonstrate that the precision advertised so far for TIMS Pb isotope measurements was far too optimistic. It can be predicted that in the near future, MC-ICP-MS precision will break even with that of triple spike techniques (<100 ppm), thus paving the way for further improvement in U-Pb geochronology.

Some important principles underlying TIMS isotopic measurements do not transpose to the new technique. Since MC-ICP-MS is a steady-state instrument and samples are normally bracketed by standards, accuracy is no longer a pre-requisite. In this respect, MC-ICP-MS isotope measurements borrow their principles from conventional stable-isotope techniques. A huge advantage is that mass discrimination can be precisely monitored even for elements with only two isotopes. This technique leads to considerable improvement on the precision on Lu (and presumably on Rb and Re) for chronology and for Cu stable isotope geochemistry.

A new stable isotope geochemistry is born for a number of elements whose isotopic abundances so far remained poorly known or known only within the limits of double-spike measurements. It is remarkable that for decades stable isotope geochemistry had been largely restricted to the right-hand side of the periodic table. The isotopic compositions of metals such as Cu, Zn, Fe, Mg, are Mo are now routinely analyzed in several laboratories with a precision of 0.04 delta units. Mass-dependent Zn and Fe isotopic fractionation is well-behaved. In meteorites, these elements show amazingly large metal-silicate isotopic differences, while Cu may reveal some unsuspected nucleosynthetic effects. Seawater and biogenic carbonates are revealing isotopic variability for a number of elements such as Zn, Cu, Fe, and Mo. Exciting controversies are popping out about possible isotope fractionation mechanisms, notably the potential of Fe isotope geochemistry to fingerprint biological effects. New experimentally controlled determinations of isotopic fractionation are desperately needed in large numbers. Modellers need to catch up with analysts to ‘predict’ these unpredicted phenomena.

The future of coupling laser ablation with MC-ICP-MS is hard to forecast. The statistics of measurements necessarily limit precision for small impacts and we may not expect particularly precise in situ Nd or Fe isotope measurements in any foreseeable future. In contrast, the prospect for the U-Pb dating of zircons is bright. In general, it seems wise to keep matrix-spewing laser ablation applications separate from those needing clean instruments for solution work.

Isotopic tracers are simpler and more amenable to modelling and prediction than chemical tracers. We can anticipate that we are only seeing the beginning of the isotopic revolution. First, biology is not expected to remain immune to a new isotope geochemistry so obviously capable of establishing the economy and dynamics of metals in many living “things” at all scales of living biota. Second, painstaking isotopic measurements on rock samples that used to be the privilege of a few specialized laboratories are bound to become abundant and their quality, probably after a teething period, to improve drastically. The new frontiers are the sample size (sensitivity) and the elimination of isobaric interferences, notably in the perspective of the return of planetary samples.