

Invention of Lunatic I Mass Spectrometer and the Lunatic Industrial Revolution, M. Sharma. Department of Earth Sciences, 6105 Fairchild Hall, Dartmouth College, Hanover, NH 03755,

Introduction: The advent of reliable high precision isotope ratio measurements of trace elements began with the invention of the Lunatic I thermal ionization mass spectrometer [1]. This opened the way to understand early solar system and planetary evolution at an unprecedented precision. Precise isotope measurements using Lunatic I also permitted to look for nucleosynthetic anomalies in meteorites and their components. In the years that followed the flexibility of the mass spectrometer allowed precise isotope measurements of a large number of elements (Rb-Sr, Sm-Nd, Ba, Gd, Mg, Ca, Pd-Ag, U-Th-Pb, Ti, Cr, Fe, Zn, B, Re-Os, Ir) that addressed numerous geochemical and cosmochemical problems. Nobu Shimizu has affectionately called this the “Lunatic Industrial Revolution”.

The decade before Apollo missions had seen rapid growth in using ^{87}Rb - ^{87}Sr isotope system to date terrestrial and extra-terrestrial rocks. However, the existing mass spectrometers permitted determination of initial Sr isotope composition to a precision typically worse than 0.3%. Using Lunatic-I Papanastassiou and Wasserburg [2] were able to obtain a precision that was a factor of 10 better.

Following the landmark papers on stellar nucleosynthesis and the discovery of radiogenic ^{129}Xe by John Reynolds, the decade before the Apollo missions also saw intense searches for isotope anomalies of Ag, Mo, Ba and Li isotopes. These studies yielded conflicting results [3]. Using the instrument Eugster et al. [3] showed that Ba isotopic composition of stony meteorites, silicate inclusions within iron meteorites and terrestrial standard were uniform to a level of 0.1%.

Lunatic I was used to obtain precise Rb-Sr ages of the Apollo samples and also to meas-

ure Gd and Sm isotopes that allowed calculation the irradiation history of lunar regolith (e.g., [4-8]).

Invention of Lunatic-I was accompanied by development of clean laboratory chemistry [9] and improvements in sample preparation [10] and sample loading technology that allowed precise and accurate measurements of a few milligrams of mineral separates from Lunar samples. Development of chemistry to separate Gd from other REEs led to Sm-Nd isotope dating, which combined with U-Th-Pb isotope systematics set the stage to understand in detail crust-mantle evolution within the paradigm of Plate Tectonics [11-15].

Immediately following Lunatic-I's success home-built and commercially available mass spectrometers were modified to have a programmed magnetic field and digitized output where the mass spectrum was scanned by varying the magnetic field stepwise at predetermined values using a Hall effect probe (e.g., Thomson-C.S.F., [16, 17]; [18]). Commercial production of reliable thermal ionization mass spectrometers soon followed and began to be used to understand mainly terrestrial geochemical problems (e.g., VG Micromass 30 ([19])). The next improvement in the design of thermal ionization mass spectrometers was the development of multi-collection, which was immediately followed by variable multi-collection whereby ion beams with different mass to charge (m/z) ratios were detected by an array of Faraday collectors placed in the focal plane. Multi-collection not only improved the duty cycle (total amount of time a single isotope is counted) it also reduced noise due to ion beam instability. In addition to Faraday collectors that were typically connected to 10^{11} ohm resistors, mass spectrometer were equipped with a single secondary electron multiplier (SEM)

or a Daly photomultiplier. Commercial variable multi-collector mass spectrometers became available in the mid-1980s (e.g., Finnigan MAT 261 [20]) leading to an explosion in the field of isotope geochemistry. This revolution continues to the present-day: innovations in multi-collector mass spectrometry are permitting ultra-high precision isotope ratio measurements that continue to re-shape our understanding of our origins.

Instrument development has gone hand-in-hand with innovations in miniaturized low-blank high-yield chemical techniques needed to isolate the relevant trace elements for thermal ionization mass spectrometry. While increasingly sophisticated instruments such as multi-collector ion probes and multi-collector inductively thermal plasma mass spectrometers have allowed us to obtain, respectively, spatially resolved isotope analyses and isotope analyses of difficult to ionize elements, thermal ionization mass spectrometry remains the “gold standard” for obtaining the most reliable isotope measurements for a large number of trace elements. This is because of the requirement of chemical separation and purification of typically a single element to be thermally ionized. This requirement permits high ionization efficiency (ratio of ions obtained to atoms loaded) and determination of relative isotope abundances of a given element that are free from molecular and isobaric interferences. Combined with a high ion transmission, thermal ionization instruments have ion yields varying from 1% to 50% [21]. In comparison, while the ionization in an ICP-MS is nearly 100% the transmission efficiency from the plasma through the skimmer is quite low. As a result, the ion yield of a modern ICP-MS is that is combined with a high efficiency nebulizer is only 0.03% to 0.05%.

References:

[1] Wasserburg G.J. et al. (1969), *Rev. Sci. Instr.*, **40**, 288-295.
 [2] Papanastassiou D.A. and Wasserburg G.J. (1969), *Earth Planet. Sci. Lett.*, **5**, 361-376.
 [3] Eugster O. et al. (1968), *J. Geophys. Res.*, **74**, 3879-3908.

[4] Eugster O. et al. (1970), *Earth Planet. Sci. Lett.*, **8**, 20-30.
 [5] Papanastassiou D.A. and Wasserburg G.J. (1971), *Earth Planet. Sci. Lett.*, **12**, 36-48.
 [6] Papanastassiou D.A. and Wasserburg G.J. (1971), *Earth Planet. Sci. Lett.*, **11**, 37-62.
 [7] Papanastassiou D.A. et al. (1970), *Earth Planet. Sci. Lett.*, **8**, 1-19.
 [8] Papanastassiou D.A. and Wasserburg G.J. (1970), *Earth Planet. Sci. Lett.*, **8**, 269-278.
 [9] Sanz H.G. and Wasserburg G.J. (1969), *Earth Planet. Sci. Lett.*, **6**, 335-345.
 [10] Wasserburg G.J. et al. (1969), *Earth Planet. Sci. Lett.*, **7**, 33-42.
 [11] Wasserburg G.J. and DePaolo D.J. (1979), *Proceedings of the National Academy of Sciences of the United States of America*, **76**, 3594-3598.
 [12] DePaolo D.J. and Wasserburg G.J. (1979), *Geochimica Et Cosmochimica Acta*, **43**, 615-627.
 [13] DePaolo D.J. and Wasserburg G.J. (1976), *Geophys Res Lett*, **3**, 743-746.
 [14] DePaolo D.J. and Wasserburg G.J. (1976), *Geophys Res Lett*, **3**, 249-252.
 [15] Gancarz A.J. and Wasserburg G.J. (1977), *Geochim. Cosmochim. Acta*, **41**, 1283-1301.
 [16] Birck J.L. and Allegre C.J. (1973), *Earth Planet. Sci. Lett.*, **20**, 266-274.
 [17] Birck J.L. and Allegre C.J. (1973), *Geochimica Et Cosmochimica Acta*, **37**, 2025-2031.
 [18] Bogard D.D. et al. (1975), *Earth and Planetary Science Letters*, **26**, 69-80.
 [19] Onions R.K. and Pankhurst R.J. (1973), *Earth Planet. Sci. Lett.*, **21**, 13-21.
 [20] Loveridge W.D. (1986), *Int. J. Mass Spec. & Ion Proc.*, **74**, 197-206.
 [21] Birck J.L. (2001), *Geostandard Newslett*, **25**, 253-259.