

DISCOVERER AND METHODOLOGIST: ALFRED O. C. NIER AND THE INSTRUMENTAL REVOLUTION IN GEOCHEMISTRY, 1935-1948

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Abstract

During the mid-20th century, geochemistry—one of the core Earth sciences—underwent a spectacular transformation as a result of the introduction of high-tech instruments. In this process, mass spectrometry became the workhorse analytical technique in isotope geochemistry. The theme of this essay is the dynamic relationship between discoveries of isotope systems and the variations in their relative abundances, on the one hand—discoveries that became the foundation of isotope geology—and the development of mass spectrometry, on the other. This relationship is illustrated by the career of physicist and instrument-builder Alfred O. C. Nier, who was based at the University of Minnesota in Minneapolis. Nier's 60°-sector mass spectrometer design of 1940 endowed the instrument with powerful new capabilities, as well as facilitated its adoption outside the nuclear physics community. In the course of developing and applying the instrument, Nier also made important discoveries about the relative abundances of isotopes that paved the way for geochemical research on the deep past. My thesis is that Nier's early career, spanning the 1930s and '40s, illustrates a certain dynamic relationship between science and instrumentation, in which instrument development and scientific discovery co-evolved synergistically. This pattern of research spread beyond Nier—who largely moved on from this research after the 1940s—to develop into a research tradition, initially based at the University of Chicago's Institute for Nuclear Studies and then spreading to other institutions, notably Caltech and the University of California, San Diego. This tradition made crucial contributions to the discovery of global warming, of which Nier's career represents an element of the "pre-history."

The following abbreviations are used: NP, Alfred O. C. Nier Papers, University of Minnesota Archives;

1 Introduction

In a letter dated February 16th, 1946, the eminent geologist and pioneer of geochronology, Arthur Holmes, made clear his debt to the addressee, one Alfred Nier, physics professor at the University of Minnesota:

Ever since your isotopic analyses of ore-leads was published I have hoped that it would be possible to calculate from the results the time that has elapsed since the earth's primaeval lead began to be contaminated by radiogenic lead. The acquisition of a calculating machine a few months ago has now made possible the somewhat formidable

calculations and I have just completed the work. The age works out at about 3000 million years by various sets of solutions, the range being about 2750 to 3150 and the average of the best set of solutions ... being 3015. We can, however, afford to neglect the odd 15.! [sic] This looks like being the first really reliable estimate of the age of the earth and I should like to salute your work as the means of making it possible.¹

Holmes had been working on the problem of the earth's age since the beginning of the century. Though Holmes' 1946 estimate was supplanted a decade later by Claire Patterson and colleagues' figure of 4.56 billion years, the currently accepted age, that revision remained dependent on the techniques and data that Nier pioneered and to which Holmes gives so much credit.

Though trained in electrical engineering and physics, Nier was a pioneer in the application of mass spectrometry to geochemistry. In part due to his contributions, geochemistry has become a core Earth science. It has transformed the scientific understanding of Earth processes and the planet's history during the 20th century. Geochemistry studies the exchange of elements between the atmosphere, oceans, land and fossil fuels. The carbon cycle is one of the most studied due to its centrality in climate change: the impact of carbon emissions depends on how far they are absorbed into the cycle and alter its dynamics. To understand how global climate and geochemical cycles are linked, geochemists study the geological record for information about past variations in climate and cycles.² Instrumental methods in geochemistry, like those Nier pioneered, helped 20th-century scientists better understand global lead pollution, plate tectonics, processes of mineral formation relevant for prospecting and mining, the history of the solar system, and the global hydrological cycle on geological timescales. All of this has become central to our understanding of the Earth, and how humans can live upon it productively and sustainably.

The history of geochemistry has been covered by geochemists, with a focus on key discoveries.³ Aspects of the history have been treated by historians, largely in the context of broader studies.⁴

¹ Arthur Holmes to Alfred O. C. Nier, 16th February 1946, NP, Box 3, Folder 50.

² Sundquist, E. T. & K. Visser. (2004). The geologic history of the carbon cycle. In H. D. Holland, K. K. Turekian, & W. H. Schlesinger (Eds), *Treatise on geochemistry: volume 8, biogeochemistry*. Amsterdam: Elsevier.

³ (a) White, W. M. (2018). History of Geochemistry. In W. M. White (Ed.), *Encyclopedia of Geochemistry* (pp. 670-683). Encyclopedia of Earth Sciences Series. Cham: Springer. Fairbridge R.W. (1998). History of geochemistry. In C. P. Marshall & R. W. Fairbridge (Eds) *Geochemistry. Encyclopedia of Earth Science*. Dordrecht: Springer. (c) Gorham, E. (1991). Biogeochemistry: its origins and development. *Biogeochemistry*, 13, 199-239.

⁴ (a) Bowler, P. J. (2000). *The Earth Encompassed: A History of the Environmental Sciences*. London: W. W. Norton & Co. (b) Oreskes, N. (1999). *The Rejection of Continental Drift*. Oxford: Oxford University Press. (c) Weart, S. R. (2008). *The Discovery of Global Warming*. Cambridge, MA: Harvard University Press. (d) Dry, S. (2019). *Waters of the World*. Chicago: University of Chicago Press. (e) Conway, E. (2008). *Atmospheric Science at NASA: A History*. Baltimore: Johns Hopkins University Press. (f) Shindell, M. (2019). *The Life and Science of Harold C. Urey*. Chicago: University of Chicago Press. (g) Ronald E. Doel, "Constituting the Postwar Earth Sciences: The Military's Influence on the Environmental Sciences in the USA after 1945," *Social Studies of Science*, 2003, 33(5), 635-666. (h) Naomi

Instrumentation in the Earth sciences has been the subject of historiographical studies, notably that of Matthew Shindell on the development of isotope geochemistry during the Cold War.⁵ These studies tend to reduce Nier's role to that of instrument inventor. On the other hand, Nier's career has received considerably more attention from mass spectroscopists and geochemists.⁶ These histories focus on Nier's contributions to the development of mass spectrometry and geochronology. In this article, I will highlight how those contributions emerged in the context of two on-going lines of research: mass spectrometric measurement and geologic age determination. These were distinct fields when Nier began his career, the early 1930s. Mass spectroscopists were physicists, without geological expertise and professional interests. Conversely, geologists were not physicists, and so lacked the expertise, and professional interest, to develop mass spectroscopy for geochronological purposes. Though Nier's 60°-sector mass spectrometer is well-known, among geochemists, as the basic design for many of the spectrometers that would go on to be used in geochemistry after World War II, I will argue that beyond particular inventions and discoveries, one of Nier's main contributions was to show how the two activities, mass spectroscopic measurement and geologic age determination, could be united.

One can understand this contribution in terms of historian and philosopher of science Hasok Chang's notion of an 'epistemic activity.' The latter is 'a coherent set of mental or physical actions (or operations) that are intended to contribute to the production or improvement of knowledge in a particular way, in accordance with some discernible rules.' Epistemic activities are generally practiced in relation to others, forming what Chang calls a 'system of practice.' A set of epistemic activities forms

Oreskes and Ronald E. Doel, "The Physics and Chemistry of the Earth" in *The Modern Physical and Mathematical Sciences*, ed. Mary Jo Nye (Cambridge, UK, Cambridge University Press: 2002).

⁵ (a) Caneiro, A. & Klemun, M. (Eds). (2011). Seeing and measuring, constructing and judging: instruments in the history of the Earth sciences. Special issue. *Centaurus*, 53. (b) Schilling, T. (2013). Uranium, geoinformatics, and the economic image of mineral exploration. *Endeavour*, 37(3), 140-149. (c) Shindell, M. (2014). From the end of the world to the age of the Earth: the Cold War development of isotope geochemistry at the University of Chicago and Caltech. In N. Oreskes, J. Krigs (Eds), *Science and Technology in the Global Cold War*. Cambridge, MA: MIT Press.

⁶ (a) Alfred O. Nier, "Some Reminiscences of Isotopes, Geochronology, and Mass Spectrometry," *Annual Review of Earth and Planetary Science*, 1981, 9, 1-17. (b) Alfred O. Nier, "Some Reflections on the Early Days of Mass Spectrometry at the University of Minnesota," *International Journal of Mass Spectrometry and Ion Processes*, 1990, 100, 1-13. For a very informative oral history, see (c) interview by Michael A. Grayson and Thomas Krick at the University of Minnesota, Minneapolis, Minnesota, 7-10 April 1989 (Philadelphia: Chemical Heritage Foundation, Oral History Transcript # 0112), highlights of which are reported in (d) Michael A. Grayson, "Professor Al Nier and His Influence on Mass Spectrometry," *Journal of the American Society of Mass Spectrometry*, 1992, 3, 685-694 (e) John H. Reynolds, *Alfred Otto Carl Nier, 1911-1994* (Washington, D.C., National Academies Press: 1998) (f) Konrad Mauersberger, "Alfred O. C. Nier (28 May 1911 – 16 May 1994)," *Proceedings of the American Philosophical Society*, 1999, 143(4), 686-691. (g) Michael A. Grayson, *Measuring Mass*, (Santa FE, American Society for Mass Spectrometry: 2002). (h) John De Laeter and Mark D. Kurz, "Alfred Nier and the Sector Field Mass Spectrometer," *Journal of Mass Spectrometry*, 2006, 41, 847-854. (i) Keith A. Nier, "Alfred Otto Carl Nier," in *The Encyclopedia of Mass Spectrometry, Volume 9: Historical Perspectives, Part B: Notable People in Mass Spectrometry*, ed. Michael L. Gross and Richard M. Caprioli (Amsterdam, Elsevier: 2016), pp. 167-169.

such a system when they are performed with a view to achieving certain aims. The system is coherent when the constituent activities combine effectively to achieve the aims of the system.⁷ Applying these notions to Nier's career, I argue that he showed how mass spectroscopy and geochronology could be combined to effectively achieve the aim of age determination. In so doing, and to the extent his approach was adopted, geochronology was transformed into a technologically-driven endeavor. Though it is often noted that science and technology have co-evolved synergistically, it is less often noted that that dynamic is not given, but is, rather, an *achievement* that can be more or less successful. Nier helped to establish an extremely successful system of practice in isotope geochemistry in which instrument development and scientific discovery could co-evolve synergistically. In this respect, Nier was an exemplar of a way of conducting geochemical research. His work provided a 'paradigm' of research in the original Kuhnian sense of an exemplary achievement.⁸

Focusing on Nier's early career also puts the impact of the Cold War on the development of geochemistry in perspective. As noted, the latter was the focus of studies by Shindell and Oreskes and Doel. Shindell observes that mass spectrometers

had existed before the [Second World War], but only a few laboratories had had sufficient expertise to build and maintain them. Wartime development of mass spectrometers by US industries under military contract and postwar tinkering by interested engineers, scientists, and oil companies effectively black-boxed the technology (although a trained technician was still required to operate it), increased its precision dramatically, and put it within reach of any university department willing to pay for the still relatively expensive instrument.⁹

Nier's early career, however, suggests that there were important continuities and precursors to the post-war flourishing of mass spectrometry. In this respect, his career supports Mary Jo Nye's thesis, in *Before Big Science*, according to which "[f]or all this seemingly radical change [between pre- and post-WWII science], much remained continuous with the past. Most of the basic presuppositions and fundamental explanatory systems in chemistry and physics changed very little from those of the prewar period, even while postwar instrumentation, much of it computer-driven, became bigger, faster, and more complex."¹⁰ In the case of isotope geochemistry, at any rate, the fundamentals of the instrumentation were also developed before direct US involvement in the war.

⁷ Hasok Chang, "Compositionism as a Dominant Way of Knowing in Modern Chemistry," *History of Science* 49 (2011): 247-268, on 250-251.

⁸ Thomas Kuhn, *The Structure of Scientific Revolutions*, 3rd ed. (Chicago: The University of Chicago Press, 1996).

⁹ Shindell, "From the End of the World to the Age of the Earth" (ref. 5c), 109.

¹⁰ Mary Jo Nye, *Before Big Science*, (Cambridge, MA: Harvard University Press, 1996), 226.

The structure of this paper is as follows. In the second section, I give a brief overview of the state of mass spectroscopy and of isotope geochemistry at the time Nier entered graduate school in physics, in 1934. Then, I describe Nier's trajectory in graduate school, his post-doc at Harvard, and his early work as an assistant professor at the University of Minnesota, Minneapolis. Section 4 discusses his contributions to the Manhattan Project and his postwar work to the end of his career. In section 5, I shift focus to the use of mass spectrometers in post-war geochemistry. I will examine some key discoveries that were made by Nier's methodological descendants, and argue that they illustrate a Nierian tradition of research. In section 6, I put these developments in the broader context of technical changes occurring in chemistry as a whole during the period, the so-called "Instrumental Revolution." I conclude with reflections on Nier's significance in history of science.

2 State of instrumentation, and state of isotope geology, in the early 1930s

Nier was trained as an electrical engineer, receiving bachelor's and master's degrees in the subject from the University of Minnesota in the early 1930s. His work on mass spectrometry began during his doctoral studies at the university, which were conducted in the laboratory of physicist John Tate. When Nier entered the field, both mass spectrometry and isotope geology had been developed to some extent, though both were still in their youth. Moreover, mass spectrometry was only just starting to be applied to geological questions. In 1929, Francis Aston at the University of Cambridge had used a mass spectrograph to detect isotopes of lead in radioactive broggerite.¹¹ In a companion article, Rutherford estimated the age of the Earth from Aston's data.¹² One of Nier's main contributions would be to show how the two activities, mass spectroscopic measurement and age determination, could be carried out fruitfully by the same scientist.

2.1 State of isotope field

Isotope geology is based on the possibility of dating processes and events by measuring relative isotope abundances. Such dating became possible with the discovery of isotopes. Recognition that substances with different atomic weights could have the same chemical identity came primarily from two new lines of research. The first was studies of radioactivity; the second was mass spectrometric studies of nonradioactive elements. A key development in the first was the recognition (first put forth by Frederick

¹¹ F. W. Aston, "The Mass-Spectrum of Uranium Lead and the Atomic Weight of Protactinium," *Nature*, 1929, 123(3096): 313.

¹² E. Rutherford, "Origin of Actinium and Age of the Earth," *Nature*, 1929, 123(3096): 313-314. Nier summarized Rutherford's article on an undated sheet (NP, folder XYZ).

Soddy in 1913¹³) that atoms of different mass (and thus atomic weight) and radioactive properties could have essentially the same chemical properties and place in the periodic table. Soddy called these atoms 'isotopes.' In 1919, Aston used a mass spectrograph to show that ordinary neon, a nonradioactive element, is composed of two isotopes of different abundances with masses 20 and 22 respectively, resulting in the chemical atomic weight of 20.2. During the following two decades, Aston and other scientists, notably Arthur Dempster, continued to apply mass spectroscopy to identify the isotopic composition of elements across most of the periodic table. Mass spectroscopy became central to identifying isotopes and to measuring their properties and abundances.

It was quickly recognized that the phenomenon of radioactivity could be used for measuring time. Ernest Rutherford (1906) was the first to propose that the proportion of radioactive atoms that disintegrate in a given time interval is an unvarying constant and therefore a potential clock. A particularly important kind of radioactive decay, in the early 20th century, was that of uranium into lead. Several scientists tried to exploit this process to develop an absolute geological timescale and establish estimates of the age of the Earth. In order to measure the age of a sample, the quantities of both the residual 'parent' atom (e.g. uranium) and the decay product or 'daughter' atom (e.g. lead) had to be measured. Until the 1930s, this was done solely by bulk chemical techniques, involving chemical analysis of the sample followed by gravimetric or volumetric measurements.

The character of the task of radioactive dating was radically transformed by the recognition of the range and complexity of isotopic differences among the elements, largely due to the work of Aston, Dempster and a few others. It became clear that one could no longer hope to simply measure the uranium and lead contents of a sample in order to get an accurate age. Age measurements based on radioactivity would require the measurement of isotopes, not just bulk chemical analysis of the radioactive parent element and its daughter, and this would require mass spectroscopy. In particular, since both parents and daughters might consist of isotopes, each with its own decay properties, it was necessary to be able to accurately measure their relative abundances. In the uranium-lead case, for example, it was necessary to distinguish between two different processes, the decay of ²³⁸U and that of ²³⁵U. Moreover, uranium ore samples were contaminated with non-radiogenic or "common" lead, which also consisted of different isotopes. Though traditional gravimetric methods were initially used to sort some of these isotopic complications out, their inherent sensitivity limits limited the accuracy of this approach, as Nier would famously show (see section 3).

¹³ F. Soddy, "Intra-atomic Charge," *Nature*, 1913, 92: 399-400.

2.2 State of instrumentation

When Nier started working on mass spectroscopy, however, isotopic abundances were poorly known in many cases, and the existence of rare isotopes was uncertain. Mass spectroscopy had been developed concurrently with the discovery and exploration of isotopes. In the 1910s, J. J. Thomson had invented the technique of separating ions according to their mass-to-charge ratio using combinations of electric and magnetic fields.

After Thomson, two instrumental traditions had emerged, which were distinguished according to the method of detection employed. The mass *spectrograph* tradition, inaugurated by Francis Aston's 1919 instrument, sent positive ions through a combination of electric and magnetic fields in such manner as to sort them by their masses. The separated beams of ions were allowed to hit a photographic plate. From measurements of the positions and intensities of the lines found on the plate after development, the masses of the ions and the relative abundances could be determined. The ions themselves were formed in a high-voltage gas discharge tube.

The other tradition originated in the work of Arthur Dempster at the University of Chicago, who focused on the development of mass *spectrometers*. Though Thomson was the first to use electrical detection, he only did so for one apparatus of his design, whereas Dempster made electrical detection his method of choice.¹⁴ His seminal 1918 instrument accomplished mass separation with a magnetic field only.¹⁵ The mass analyzer bent the ions through a 180° semi-circular path, a design that would be standard for spectrometers until Nier introduced the 60° design in 1940. The ion currents were measured by a sensitive current measuring device, the electrometer. Data could thus be obtained in real-time, and the relative abundances of the ions were determined directly rather than through the indirect photographic process. In this tradition, ions were produced either by bombarding the sample with electrons, in the case of gaseous samples, or, in the case of solids, by heating appropriate salts. The techniques of using mass spectrometers and spectrographs are often collectively referred to as 'mass spectroscopy.'

¹⁴ J. J. Thomson, "XIX. Further Experiments on Positive Rays," *Philosophical Magazine*, 1912, 24(140), 209-253.

¹⁵ A. J. Dempster, "A New Method of Positive Ray Analysis," *Physical Review*, 1918, 11, 316-324.

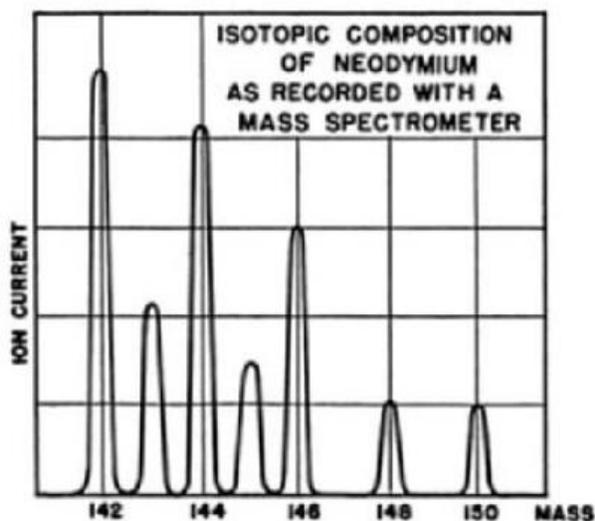


FIG. 16.—The isotopes of neodymium recorded with a recording mass spectrometer. The ion source used for this particular record was the hot anode source.



Figure 1. This figure is from a 1948 book chapter on mass spectrometry by a student of Nier's, Mark Inghram, who would later become an influential figure at the Institute for Nuclear Studies at the University of Chicago. The upper graph is the output of electrical detection, a graph of ion current versus mass for neodymium. The lower image is the photograph of the neodymium spectrum produced by a mass spectrograph. The isotopes 148 and 150, which show up quite clearly by electrical detection, are hardly perceptible photographically. From Mark G. Inghram, "Modern Mass Spectrometry," in L. Marton (Ed.), *Advances in Electronics* (New York: Academic Press, 1948), page 249.

When Nier began his graduate work, almost all known isotope abundances had been measured with mass spectrographs. This method was problematic for several reasons. The glow-discharge method required instruments that could not be baked, which hindered the removal of contaminating gases. Impurities were formed from contaminating water and hydrocarbons present in wax and grease in the joints and stopcocks of the apparatus. Most problematic was the method of photographic detection. Abundances were determined from the blackening of the spectral lines on the plates. The determination was subject to a number of internal problems, such as nonlinear sensitivities of the plates to ions with respect to many variables, as well as errors owing to the development of the plates.¹⁶ For example, lighter particles penetrate further into the film on the plate than heavier ones, if their energies are equal, thus producing more intense lines on the photograph irrespective of the relative abundance.¹⁷

¹⁶ For an overview, see Mark G. Inghram and Richard J. Hayden, *A Handbook on Mass Spectroscopy*, (Washington, D.C., National Academy of Sciences—National Research Council: 1954), pp. 36-39.

¹⁷ J. J. Thomson, *Rays of positive electricity and their application to chemical analyses*, (London, Longmans, Green and Co.: 1921), pp. 120-21.

Meanwhile, the Dempster method had been significantly developed in the Tate lab. The latter had become interested in mass spectroscopy as a means for studying electron impact phenomena, for example measuring the ionization potentials of atoms and molecules. It developed expertise in the construction of apparatus, as well as in high vacuum techniques (the latter were not widespread in academia at the time).¹⁸ The lab had made a few key improvements in the mass spectrometer that Nier was able to take advantage of. First, graduate student Walker Bleakney had figured out a method for creating ions by bombarding the sample with electrons of controlled energy, known as the “electron impact” method. Descendants of this method are still widely used today. Second, Tate and graduate student P. T. Smith had come up with a novel design that isolated the ionization process from the mass analyzer section of the instrument. This design made it possible to construct instruments with larger magnetic analyzers than before, which made higher mass resolution possible. Third, the use of larger analyzers required the use of larger magnets, and it so happened that Nier was able to take advantage of a larger solenoid magnet than had been used before in mass spectroscopy, and which had been constructed for unrelated cloud chamber studies. The larger magnet also contributed to enhanced resolving power. Fifth, graduate student Merrill Distad and post-doc John Williams had designed and constructed a novel detector, consisting of an electrometer vacuum tube amplifier of extremely high sensitivity.¹⁹

3 Early Academic Career

Alfred Nier was born in 1911 in St. Paul, Minnesota, of German immigrants. After graduating high school in 1927, he earned both a bachelor’s (1931) and master’s (1933) degree in electrical engineering. In his 1989 interview with Grayson and Krick, Nier states that he took mainly graduate physics courses for the master’s degree, due to the very slim graduate offerings in electrical engineering at the time. He was thus theoretically well-prepared for his subsequent doctoral studies in physics. His master’s thesis was devoted to an analysis of how the magnetic flux changes in an iron bar when the latter is placed inside a variable magnetic field.²⁰ Nier shows how equations previously used to model current in an electrical transmission line could be applied, by analogy, to the magnetic flux changes. He

¹⁸ Alfred O. C. Nier, Grayson-Krick interview (ref. 6c), 15.

¹⁹ Alfred O. Nier, “Some Reflections on the Early Days of Mass Spectrometry at the University Of Minnesota,” *International Journal of Mass Spectrometry and Ion Processes*, 1990, 100, 1-13.

²⁰ This phenomenon is related to the Barkhausen effect, the noise produced in wires of certain materials when they are placed inside a varying magnetic field. The noise arises from discontinuous changes in the magnetic flux as the field is varied. This effect can be exploited to assess the quality of materials. See K. J. Sixtus and L. Tonks, “Propagation of Large Barkhausen Discontinuities”, *Physical Review*, 1931, 37, 930-959, cited in Nier, “The Magnetic Transmission Line,” Master’s Thesis (Minneapolis, University of Minnesota: 1933).

also criticizes previous investigators of the phenomenon for misapplying such equations to it. This knowledge of the interplay between theory and apparatus would serve Nier well in the Tate lab: his first paper there reports the invention of a device to stabilize the magnetic field of a mass spectrograph, based on consideration of the mass-to-charge equation used to determine the values of the magnetic and electric fields in the instrument. Nier credits the idea for a key component of the device to his master's advisor.²¹

From the beginning of his physics career, Nier's approach consisted of pushing the instrumentation to its limits in order to detect extremely low abundance isotopes or abundance variations. Nier begins his dissertation (1936) by reviewing the progress made in the study of isotopes since J. J. Thomson's discovery of the isotopes of neon in 1912.²² He laments that "[u]nfortunately, the apparatus employed by the experimenters mentioned above [Thomson, Aston, Dempster, Bainbridge, Boltwood, and Soddy] is not well adapted to this type of work. The sensitivity is not great enough to detect very weak isotopes; the possibility that one may confuse an impurity for a weak isotope is always a source of apprehension."²³ He states the purpose of the dissertation as being to describe a mass spectrometer that overcomes this deficiency.

Thus in 1935, he modified a 180° magnetic sector instrument design previously used to study ionization potentials to investigate the isotopes of potassium. The instrument combined the five improvements, described above, with a device, invented by Nier, for compensating the instability of the magnetic field through feedback control, a novel concept in electrical engineering at the time. The instability was due to that of the motor generator that was used to produce the large amount of power, 5 kW, required to run the solenoid.

Though Nier initially applied the instrument to the study of organic compounds, he quickly moved to that of isotope abundances, which were of growing interest in nuclear physics, itself an increasingly hot field. Tate, as editor of *Physical Review*, was keenly aware of this trend and interested in

²¹ Professor H. E. Hartig. See Nier, "Device to Compensate for Magnetic Field Fluctuations in a Mass Spectrograph," *Review of Scientific Instruments*, 1935, 6, 254-255. See Nier, interview by Michael A. Grayson and Thomas Krick, (ref. 6c), p. 17.

²² There is some ambiguity regarding who is the true discoverer of the isotopes. Thompson first detected neon-22 in the mass spectrum of pure neon in 1913, but thought it was an impurity. Aston identified it as an isotope of neon six years later. See *The Encyclopedia of Mass Spectrometry, Volume 9, Part A, "The Development of Mass Analyzers,"* by Michael A. Grayson.

²³ Alfred O. Nier, "A Mass Spectrographic Study of the Isotopes of Argon, Potassium, Rubidium, Zinc, and Cadmium," Doctoral Thesis (Minneapolis, University of Minnesota: 1936), p. 2.

getting into it himself. So Nier turned his attention to the study of the potassium isotopes, which were of particular interest because of the observed, but unexplained, radioactivity of potassium.²⁴

With this instrument in hand, Nier was able to detect the extremely low abundance ^{40}K isotope that was suspected to exist based on the observed radioactivity. Earlier analyses of the isotopes of potassium by Dempster, Aston and Keith Bainbridge at Harvard had not detected this isotope. Nier's discovery would later serve as the starting point for the development of the important K-Ar dating method, when in 1948 he suggested this method as a possible application of his discovery (with graduate student L. T. Aldrich) that ^{40}K decays to ^{40}Ar .²⁵

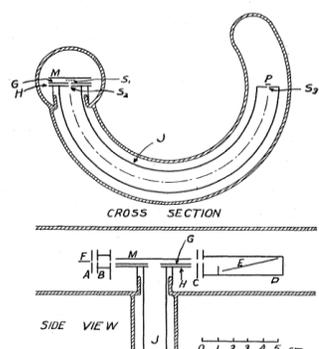


FIG. 1. Diagram of apparatus used for the study of potassium, rubidium, zinc and cadmium. Slit $S_1=0.25$ mm; Slit $S_2=0.15$ mm; Slit $S_3=0.15$ mm for K, 0.07 mm for Rb, Zn and Cd.

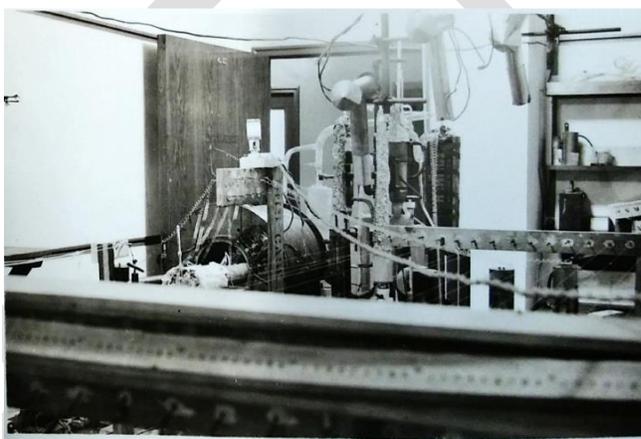


Figure 2. The left-hand image is a schematic of Nier's 1935 instrument. The cross section is of the mass analyzer. Note the 180° path. The diagram below it illustrates the electron-impact method of ionization. From Alfred O. Nier, "A Mass-Spectrographic Study of the Isotopes of Argon, Potassium, Rubidium and Zinc," *Physical Review*, 1936, 50: 1041. Despite Nier's use of the term 'mass-spectrographic,' this instrument had an electrometer detector. The photograph on the right is from the Nier Papers, University of Minnesota Archives, box 34, folder 4, and is labelled "1935 MS of AOCN." The cylinder on the left is the magnet; the mass analyzer sits inside.

In graduate school, however, Nier was not yet interested in geochronology. This came during his subsequent post-doc at Harvard in the laboratory of Keith Bainbridge from 1936 to 1938. Bainbridge was a respected physicist working on precision measurements of atomic masses with mass spectrographs. Nier's graduate work had attracted considerable attention due to the power of his technique. On graduating in 1936, Nier won a coveted National Research Council Fellowship in physics, one of two awarded that year. Bainbridge thought Nier's precision measurement of isotope abundances

²⁴ Nier, interview by Michael A. Grayson and Thomas Krick, (ref. 6c), 14, 20.

²⁵ Alfred O. Nier, "Evidence for the Existence of an Isotope of Potassium of Mass 40," *Physical Review*, 1935, 48, 283-284; L.T. Aldrich and Alfred O. Nier, "Argon 40 in Potassium Minerals," *Physical Review*, 1948, 47(8), 876-877; and Nier, "Some Reflections," (ref. 6b), for Nier's account of the background to, and his design of, the 1935 instrument.

could complement his on-going research, and offered Nier \$5000 (1936 dollars) in lab funds, free access to Harvard's excellent facilities and shop-work, and freedom of research. Nier accepted.²⁶

At the time, Harvard was the world leader in precision atomic weight measurements by chemical analysis. The Chemistry Department was home to Gregory P. Baxter, who carried on the "Harvard method" of making such measurements developed by his predecessor T. W. Richards.²⁷ The atomic weights measured by Richards, Baxter and others had revealed a difference between the atomic weights of what was called "common" lead, on the one hand, and radiogenic lead from the decay of uranium and thorium, on the other. Common lead is lead found in non-uranium or thorium ores. It was recognized that this difference could be used for dating purposes, namely by correcting the age of a sample for contamination by common lead.

Cambridge was also home to Alfred Lane, a professor emeritus at Tufts. Lane was chairman of the National Research Council Committee on the Measurement of Geological Age, and was excited at the possibility, raised by Nier's graduate work, of accurate isotope measurements of lead samples. Lane's influence on Nier's work should not be underestimated. Reminiscing years later, Nier regretted that he had not followed up more on his post-doctoral discoveries, citing lack of knowledge in geology as the main reason.²⁸ According to Nier, Lane "was one of the very few persons in this country interested in quantitative geological age measurements" at the time.²⁹ In a letter of 1976, Nier recalls that Lane was "intensely interested in the geological age question" and credits him with providing moral support during the post-doc.³⁰ Nier's papers contain an agenda for a meeting of Lane's committee in Boston in 1937, according to which various radioactive decay dating methods were to be discussed at the meeting, and also the "[i]mportance of work of A.O. Nier."³¹ Lane's letters to Nier also exhibit

²⁶ Grayson, "Professor Al Nier," (ref. 6d), 688.

²⁷ For accounts of this method, see: Theodore William Richards, "Atomic Weights and Isotopes," *Chemical Reviews*, 1924, 1(1), 1-40; Arthur F. Scott, "Critique of the Harvard Method for Determining Atomic Weights," *Analytical Chemistry*, 1961, 33(9), 23A-31A; George Fleck, "Theodore William Richards," in *Nobel Laureates in Chemistry 1901-1992*, ed. Laylin K. James (American Chemical Society and Chemical Heritage Foundation: 1993), pp. 100-107; Keith Nier, "The Transformation of Atomic Weight: New Instrumentation and Objective Progress," in *5th International Conference on the History of Chemistry — "Chemistry, Technology and Society" — Proceedings*, ed. Isabel Malaquias, Ernst Homburg, M. Elvira Callapez (Sociedade Portuguesa de Quimica: 2005), pp. 231-240.

²⁸ (a) Henry Faul to Alfred O. C. Nier, 3rd November 1976, NP, Box 3, Folder 21. (b) Alfred O. C. Nier, Grayson-Krick interview (ref. 6c), 60-61, 259-260.

²⁹ Alfred O. C. Nier, Grayson-Krick interview (ref. 6c), 54. Nier adds that Lane's interest was "[n]ot just stratigraphy, but numbers," alluding to the distinction between the relative chronology afforded by rock strata and the fossil record and the absolute chronology afforded by isotope dating.

³⁰ Alfred O. C. Nier to Henry Faul, 3rd November 1976, NP, Box 3, Folder 21.

³¹ NP, Box 11, Folder "Harvard, research data, 1938." The extent of Lane's influence is also suggested by Nier's recollection that the former "was very interested in my work, and tried to promote it, getting samples and things

enthusiasm about his results.³² It seems possible, therefore, that without Lane's enthusiasm and expertise Nier's work might have taken a different direction.

It was in this context that, with Bainbridge's assistance, Nier designed an improved mass spectrometer with higher resolution. Resolution is mass-dependent, and so a higher-resolution instrument would enable accurate abundance measurements on lead, uranium, and other heavy elements. To improve the resolution relative to the 1935 instrument, Nier decided to double the radius of the mass analyzer and increase the strength of the magnetic field. This modification required a much larger magnet. According to Nier, the use of a larger solenoid would have been impractical, and so he and Bainbridge decided to replace it with a two-ton electromagnet, with the analyzer now sandwiched between the poles.³³ This modification produced a field approximately four to five times stronger than the solenoid without increasing the power requirement, though the latter (5 kW) remained high. The magnet was still unstable, however, but the stabilizing device Nier had invented in Minnesota would not work with the new design. So Nier had to invent a new compensating device that stabilized the power supply to the magnet rather than the field itself, an approach that was actually facilitated by the switch to an electromagnet.³⁴ (I mention these details because they are important for understanding the design of the later 60° sector instrument).

Initially, Nier focused on measuring the isotope abundances of several elements, justifying his research by appeal to the growth of nuclear physics and the power of his instrument for discovering rare isotopes and measuring relative abundances.³⁵ Under the influence of Baxter and Lane in particular, and with encouragement from Bainbridge, Nier shifted towards applying the new spectrometer to geochronology.³⁶ As a result of the work of Richards, Baxter and colleagues, the Harvard chemistry

for me to work on. So I spent most of my time, or a very large part of it, working on things related to geochronology" (Grayson-Krick interview, (ref. 6c), 54)

³² Alfred Lane to Alfred O. C. Nier, 7th January and 10th March 1939, and 13th May 1940, Box 3, Folder 30.

³³ Nier, "Some Reflections," (ref. 6b), 9.

³⁴ Nier, Grayson-Krick interview, (ref. 6c), 50-51. In 1935, Nier had not deemed direct stabilization of the power supply feasible.

³⁵ (a) Alfred O. Nier, "The Isotopic Constitution of Osmium," 52 (1937), 885; b) Alfred O. Nier, "A Mass-Spectrographic Study of the Isotopes of Hg, Xe, Kr, Be, I, As, and Cs," *Physical Review*, 52 (1937), 933-937; (c) Alfred O. Nier, "The Isotopic Constitution of Calcium, Titanium, Sulphur and Argon," *Physical Review*, 53 (1938), 282-286; Alfred O. Nier, "The Isotopic Constitution of Strontium, Barium, Bismuth, Thallium and Mercury," *Physical Review*, 53, 275-278.

³⁶ Nier, Grayson-Krick interview, (ref. 6c), 53ff. In the latter, Nier states that Bainbridge introduced him to Baxter. He sometimes makes it sound as if Bainbridge might have suggested geochronology as a potential application. See (a) Alfred O. Nier, "Some Reminiscences of Mass Spectrometry and the Manhattan Project," *Journal of Chemical Education*, 66 no. 5, (1989), 385-388, on 385; and (b) Nier, "Some Reflections," (ref. 6b), 9. In his letter of November 3, 1976 to the geologist Henry Faul, Nier "suspected" it had been Bainbridge who had informed him of the possibility of working on lead at Harvard: Nier to Faul, 3rd Nov 1976, NP (ref. 11).

department had accumulated a large number of lead samples of high purity, which Baxter made available to Nier. Baxter's willingness to help Nier can be understood by considering the state of radioactive dating at the time. The latter was dependent on chemical atomic weight determinations to estimate isotopic composition, which limited the accuracy of the technique. For example, it was assumed at the time that common lead is of constant isotopic composition, because its atomic weight was always found to have a value very close to 207.21. In order to determine the age of a sample, the atomic weight of the lead in it was measured, and the amount of common lead contamination estimated in light of the result. For instance, the closer the weight approached 206, the greater the purity of the sample in ^{206}Pb . This method was less than optimal, however, both because it is an indirect measure of isotopic purity, and also because the chemical methods employed were time-consuming. In contrast, the mass spectrometric approach potentially offered a direct measure, as well as faster through-put. According to Nier, "I could do in an hour for which [*sic*] the chemists, in making atomic weight measurement, needed weeks." Baxter appears to have been especially excited by the speed of the mass-spectrometric analysis.³⁷

For historical studies in isotope geology, three key results came out of Nier's research with this new and improved mass spectrometer:

- I. Nier discovered that common lead consists of a mixture of isotopes the relative abundance of which varies by sample source. This was a great surprise, given the constancy of atomic weights observed in all previous measurements, and given that that constancy is not to be expected if the relative abundances vary. Nier's discovery had three important consequences for geochronology. First, it showed that U-Pb dating would have to be corrected for the isotopic composition of the common lead that is co-present in samples of radiogenic lead. Second, the variations gave insight into the age and origin of the different lead ores. They were therefore useful data for historical research. Thirdly, it showed that mass-spectrometric measurements were superior to chemical methods for detecting small variations in isotope abundances.³⁸

³⁷ (a) Nier, Grayson-Krick interview, (ref. 6c), 55-56; (b) Nier, "Some Reminiscences of Isotopes, Geochronology, and Mass Spectrometry," *Annual Review of Earth and Planetary Sciences*, 1981, 9, 1-17, on 5-6.

³⁸ Alfred O. Nier, "Variations in the Relative Abundances of the Isotopes of Common Lead from Various Sources," *Physical Review*, 1938, 60, 1571-1576; helpful explanations of the significance of the variations can be found in Alfred O. Nier, "Some Reminiscences of Isotopes," (ref. 38b), 1-17 and in Nier, Grayson-Krick interview, (ref. 6c), esp. 53-63.

- II. His results revealed the diverse relations of the four stable isotopes of lead and showed how their ratios and their relations to thorium and uranium could be used to measure geological time with unprecedented precision. He made the most precise measurements of the decay constants of ^{235}U and ^{238}U to date. He also measured the abundance ratio of the two isotopes. This latter quantity allowed him to develop an “internal” method for dating radiogenic lead samples that dispensed with the need to measure the absolute quantities of uranium and lead (*vide supra*). Instead, the age of a sample could be inferred from the ratio of ^{206}Pb to ^{207}Pb . This method obviated the need for chemical analysis. In addition, Nier showed that mass spectrometric data could be used to compute ages from the decay of ^{238}U to ^{206}Pb and from that of thorium to ^{208}Pb , thus yielding three independent methods for determining the age of a sample. It is worth noting that these methods depended on knowledge of the isotopic variations in common lead, and hence built on the first discovery. This work showed that certain minerals were over two billion years old, which challenged various prior estimates of the age of the earth and even of the universe as a whole.³⁹
- III. Though discoveries I and II were contributions to radiogenic isotope geochemistry, Nier also made an important discovery for stable isotope geochemistry during his post-doc. Together with Earl Gulbransen, an instructor at Tufts University, Nier discovered (1939) that the ratios of the two stable isotopes of carbon, ^{13}C and ^{12}C , vary by up to 5 percent depending on the sample source, with limestone-derived samples having the largest amount of ^{13}C and plant-derived the least. They suggested that the variation may be related to the process of formation of the sample.⁴⁰ Though Nier and Gulbransen were not the first to observe stable isotope variations—variations in the oxygen isotopes had

³⁹ (a) Alfred O. Nier, “The Isotopic Constitution of Uranium and the Half-Lives of the Uranium Isotopes. I,” *Physical Review*, 55, (1939), 150-153; (b) Alfred O. Nier, “The Isotopic Constitution of Radiogenic Leads and the Measurement of Geological Time. II,” *Physical Review*, 55, (1939), 153-163. In the latter paper, Nier computes an age for a uraninite sample, based on the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio, of 2.2×10^9 years, “a value greater than the present assumed *age of the Earth*” (p. 163, italics in the original). Nier hypothesizes that this calculation underestimates the sample’s age, due to error introduced by alterations of the mineral since its formation. In a footnote, he cites the third edition of Arthur Holmes’ classic work *The Age of the Earth* (London, Thomas Nelson & Sons Ltd: 1937). In the preface to this work, one can read: “The fact that the earth’s oldest-known rocks approach an age of 2,000 million years suggests that we may have nearly reached the beginning of things ... Most exciting of all in its far-reaching implications is the conclusion, based on the recent discovery of the expansion of the universe, that the age of the universe itself may be limited to about 2,000 million years” (p. vi).

⁴⁰ Alfred O. Nier and Earl A. Gulbransen, “Variations in the Relative Abundance of the Carbon Isotopes,” *Journal of the American Chemical Society*, 1939, 61: 697-698.

been discovered by bulk density measurements a few years before⁴¹—this work demonstrated the discriminating power of mass spectrometry for the study of these variations. Indeed, testing the power of the technique seems to have been part of the motivation for the study, in addition to theoretical anticipations of carbon variations.⁴² This potential was later recognized by chemist and Nobel laureate Harold Urey. In his 1947 paper, “The Thermodynamic Properties of Isotopic Substances”, Urey developed a statistical mechanical theory to show why, on theoretical grounds, isotope fractionations (the term for changes in isotope ratios arising from some chemical or physical process) could be expected, in the course of which he also suggested that these fractionations could provide useful geologic information. Nier’s carbon studies⁴³ provided some of the initial empirical evidence for Urey’s theory. Moreover, on the basis of these results, Urey suggested that Nier’s 60° sector spectrometer could be used to measure oxygen isotope ratios, and that the latter would allow the temperature at which the samples were formed to be inferred.⁴⁴ Urey would go on to pioneer paleoclimate studies at Chicago, using mass spectrometers based on Nier’s design.⁴⁵

At the end of his post-doc, Nier was offered three jobs, one at the Westinghouse corporation, another as instructor at Harvard (with possibility of tenure), and a third as assistant professor at his *alma mater*. Nier chose the third, largely to be closer to family and because the tenure prospects were better than at Harvard.⁴⁶ Though the discoveries Nier made in graduate school and during his post-doc were certainly important empirical contributions to isotope geology, it was upon his return to the University of Minnesota (1938) that he made his most important *instrumental* contribution to the field.

⁴¹ Malcolm Dole, “The Relative Atomic Weight of Oxygen in Water and in Air,” *Journal of the American Chemical Society*, 1935, 57, 2731 and “The Relative Atomic Weight of Oxygen in Water and in Air,” *Journal of Chemical Physics*, 1936, 4: 268-275.

⁴² Nier, “Some Reminiscences of Isotopes,” (ref. 38b), 7-8.

⁴³ Besides the work with Gulbranson, in 1941 Nier published a paper, co-authored with graduate student Byron Murphey, confirming and extending the 1939 results with the newly invented 60° sector instrument. See Byron F. Murphey and Alfred O. Nier, “Variations in the Relative Abundance of the Carbon Isotopes,” *Physical Review*, 1941, 59: 771-772.

⁴⁴ Namely, by providing observational values for the equilibrium constants Urey calculated for the exchange reaction $\frac{1}{2}\text{C}^{13}\text{O}_2 + \frac{1}{3}\text{C}^{12}\text{O}_3^{2-} = \frac{1}{2}\text{C}^{12}\text{O}_2 + \frac{1}{3}\text{C}^{13}\text{O}_3^{2-}$ by treating the molecules as harmonic oscillators. See Harold C. Urey, “The Thermodynamic Properties of Isotopic Substances,” *Journal of the Chemical Society*, 1947, 562-581, especially pp. 576-578.

⁴⁵ Urey’s work on paleoclimatology will be discussed further in section 5. For a comprehensive study of Urey’s career, see Matthew Shindell, *The Life and Science of Harold C. Urey*, (Chicago: University of Chicago Press, 2019), especially ch. 6.

⁴⁶ Nier, Grayson-Krick interview, (ref. 6c), 66-67.

The instrument he used at Harvard suffered from the magnet design which, in addition to being heavy, also came with exceptional power requirements. On his return to Minnesota, Nier became interested in the preparative separation of isotopes in the context of a collaboration with biologist John Bardeen, who needed carbon enriched in ^{13}C for biological tracer studies. (Nier would also later oversee the ^{235}U enrichment program of the Manhattan project). For preparative purposes, however, more mass spectrometer capacity would be required than for measurement.⁴⁷

The Harvard magnet design was impractical for the capacity needed, and so Nier set out to develop a more economical system. In 1936, Bainbridge had published the use of a 60° sector magnet as a component of a mass spectrograph built for the precision determination of atomic masses.⁴⁸ Bainbridge's instrument was double-focusing, meaning it had an electrostatic analyzer followed by a magnetic one. This design yielded high resolution, which was especially important for the measurement of atomic masses. However, the dual-analyzer design did not work well with electrical detection at the time, which was an important feature for the accurate measurement of isotope ratios (*vide supra*). Basing himself on theoretical considerations, Nier realized that the 180° sector magnet of the Harvard instrument could be replaced with a 60° magnet without negatively affecting resolution.⁴⁹ So, he combined the 60° sector feature of the Bainbridge design—divorced from the electrostatic analyzer—with the electrometer tube amplifier feature of Nier's Harvard instrument. The result was a new instrument with greatly reduced magnet size, power requirements, and cost, and of simpler design, but with comparable resolution and sensitivity.⁵⁰ For comparison, whereas the earlier magnet weighed 4000 pounds and required a 5 kW generator, the new instrument featured a magnet of a few hundred pounds, powered by several automobile batteries.

The title of Nier's report on the instrument was tellingly titled "A Mass Spectrometer for *Routine* Isotope Abundance Measurements" (emphasis added). The design was significant in part because it allowed the mass spectrometer to become more accessible to non-specialists, i.e., scientists outside nuclear physics who had neither the know-how nor the resources to build and operate the kinds of instruments Nier and his colleagues had been working with.⁵¹ This pay-off was crucial for the

⁴⁷ Nier, "Some Reflections," (ref. 6b), 11-12.

⁴⁸ Kenneth T. Bainbridge and Edward B. Jordan, "Mass Spectrum Analysis. 1. The Mass Spectrograph. 2. The Existence of Isobars of Adjacent Elements," *Physical Review*, 1936, 50, 282-296.

⁴⁹ Nier, "Some reflections," (ref. 6b), 11-12 and Nier, Grayson-Krick interview, (ref. 6c), 84-85.

⁵⁰ Alfred O. Nier, "A Mass Spectrometer for Routine Isotope Abundance Measurements," *The Review of Scientific Instruments*, 1940, 11: 212-216.

⁵¹ In his interview with historian Michael Grayson, Nier reflected back on this aspect of the instrument design: "If you could make these tools available to other people, who didn't necessarily have to know how a mass

widespread adoption of mass spectrometry in geology. More strongly, the development of isotope geology as a discipline independent of physics, i.e. one that was pursued by specialists rather than physicists with an interest in geology, depended on having instruments that were simple and reliable enough to be black-boxed for use by non-specialists. Moreover, the compact magnet made it more feasible to increase magnet size in future studies, thereby making progress in resolution more attainable. Conversely, it also made miniaturization more feasible, a feature Nier would exploit in his later work on space exploration (see below). After the war, Nier returned to tracer work and published an improved design that *inter alia* modified the detector electronics so as to allow for the simultaneous measurement of two ion currents, thus reducing imprecision resulting from fluctuations in current magnitude.⁵² The design was subsequently manufactured by the Consolidated Electrodynamics Company for biochemical research.⁵³

4 Manhattan Project and Post-War Work

Once the US entered the war in December 1941, Nier's expertise and instruments were enlisted for uranium analysis and separation in the Manhattan Project. Harold Urey was his supervisor. Though the Project was based at Columbia, Nier remained at Minnesota. Nier made several important contributions to the Project. One of the better known is the separation of ^{235}U from ^{238}U in February 1940, which permitted the identification of ^{235}U as the source of fission. At the behest of Enrico Fermi and John Dunning, the director of Columbia's cyclotron, he accomplished the separation by means of a 180° analyzer instrument, similar to the one he used at Harvard (the 60° instrument was still in development).⁵⁴ In 1941, the Office of Scientific Research and Development, which oversaw the Manhattan Project, commissioned Urey's uranium program to construct mass spectrometers for uranium analysis. Nier's group built seven new 60° instruments in 1942 specifically for the uranium effort. Several methods for the preparative separation of ^{235}U were being considered, and Nier's group established the effectiveness of the gaseous diffusion method. The famous K-25 separation plant in Oak Ridge, Tennessee was constructed to put the method into effect. In 1943, Nier moved to New York to head an instrument laboratory involved in the plant's construction. Two contributions of his, that are

spectrometer worked, but could use it, they could apply it to problems in their fields. I think that this is one of the very important developments of our time." Nier, Grayson-Krick interview, (ref. 6c), 267.

⁵² Alfred O. Nier, "A Mass Spectrometer for Isotope and Gas Analysis," *The Review of Scientific Instruments*, 1947, 18(6): 398-411.

⁵³ Nier, Grayson-Krick interview, (ref. 6c), p. 156.

⁵⁴ Nier, Grayson-Krick interview, (ref. 6c), pp. 73-82.

worth noting here, were prototype mass spectrometers for the plant. One was a portable mass spectrometer to serve as an extremely sensitive leak detector for the air-sensitive uranium separation process. General Electric would make many hundreds of these spectrometers based on this prototype. The other was a system for monitoring the separation process in over 50 locations throughout the process stream. To this end, over 100 instruments were built by General Electric, again based on a prototype provided Nier. The recording output of each instrument was transmitted to a central control room, so that “the entire huge plant could be monitored by a single individual.”⁵⁵

These contributions shed light on the question, raised in the introduction, of continuity, or lack thereof, between pre- and post-war science. Both the leak detector and the recording spectrometer were novel instruments. Moreover, they were black-boxed, mass-produced and, in the case of the recording spectrometer, partially automated for the war effort. The latter also exposed more scientists and engineers to mass spectroscopy than hitherto, when it had been used largely by physicists and the petroleum industry.⁵⁶ Nevertheless, all the instruments built by Nier for the war were based on the 1940 sector design which, as discussed earlier, was itself the fruit of Nier’s research in the 1930s.

Nier’s work after the war moved away from geochronology.⁵⁷ Besides continuing to work on the K-Ar dating system, mentioned earlier, his post-war work in this field largely consisted of collaborations with geologists, like Arthur Holmes at the University of Edinburgh or Samuel Goldich at Minnesota, in which Nier’s role was to build instrumentation and conduct isotopic analyses. Perhaps the most important geochronological result involving Nier, but indirectly, was the independent estimate, by Holmes, Erich Gerling of the Radium Institute of the Academy of Sciences of the USSR, and F. G. Houtermans at the University of Göttingen, of the age of the Earth based on data Nier had published in the pre-war research discussed above.⁵⁸ All three arrived at an age of about 3 billion years, as indicated in Holmes’ case by the letter quoted at the beginning of this article, a figure shortly to be improved upon by Patterson and colleagues.

⁵⁵ Alfred O. Nier, “Some Reminiscences of Mass Spectrometry,” (ref. 37a), 385-388.

⁵⁶ Alfred O. Nier, “Mass Spectroscopy—An Old Field in a New World,” *American Scientist*, 1966, 54(4), 359-384. For a historiographical study of the early use of the technique in the petroleum and chemical industries and its subsequent diffusion into academic chemistry, see Carsten Reinhardt, “The Chemistry of An Instrument: Mass Spectrometry and Structural Organic Chemistry,” in Peter J. T. Morris (Ed.), *From Classical to Modern Chemistry: The Instrumental Revolution*, (London, Science Museum: 2002), pp. 229-247.

⁵⁷ In his interview with Michael Grayson, Nier attributes the shift to the intervention of the war and his involvement in the Manhattan Project, as well as having been discouraged by unnamed others from venturing into a field, geology, outside his specialty. Nier, Grayson-Krick interview, (ref. 6c), 60-61, 259-260.

⁵⁸ G. Brent Dalrymple, “The Age of the Earth in the Twentieth Century: A Problem (Mostly) Solved,” in *The Age of the Earth: from 4004 BC to AD 2002*, ed. C. L. E. Lewis and S. J. Knell (London: The Geological Society, 2001), 205-222, on 211-212. Gerling published his estimate in 1942, Holmes and Houtermans theirs in the period 1946-1948.

Nier shifted to disseminating mass spectrometry across the sciences, making further design improvements, and applying the technique to atmospheric and space exploration, as well as atomic weight determination.⁵⁹ The miniaturization of the spectrometer was an important contribution from this period, for it was essential for sending spectrometers into flight.⁶⁰ Overall, his research approach consisted in leveraging and enhancing his ability to measure isotope variations in order to study the composition of various objects, such as meteorites or the atmospheres of the Earth, Mars and Venus. Similar in this respect to Nier's early study of carbon isotope variations, these investigations continued to be of historical relevance because they provided information on the origin and mode of formation of their objects, as indicated by a report he co-authored on the "Isotopic Composition of Nitrogen: Implications for the Past History of Mars' Atmosphere," which discusses results of the Viking mission.⁶¹

It is worth noting that the topical shift was accompanied by a shift in the sources of funding. As determined from his publications, before the war, Nier was funded by the University of Minnesota, the Milton fund (a Harvard bequest fund), the Rockefeller Foundation and the National Research Council (NRC; his post-doc was funded by an NRC Fellowship in physics). After the war, his papers acknowledge the Office of Naval Research (ONR), the Atomic Energy Commission (AEC), and the Committee on Growth of the NRC, which was a funding arm of the American Cancer Society (ACS). For obvious reasons, the ONR was interested in projects relating to nuclear physics, and Nier's work on spectrometers for precision measurements of atomic masses was relevant.⁶² The ACS funding was motivated by the use of isotopes as tracers for biological studies.⁶³ Nier's work on atmospheric and space exploration would receive funding from NASA and the NSF.⁶⁴

5 The Nierian tradition in isotope geology

Beyond Nier's own research, the post-war period was an exciting one for geochemistry. Highlights from this period include: the flourishing of stable isotope geochemistry, which had not been a priority since Nier's early work on $^{13}\text{C}/^{12}\text{C}$ ratios due to the intervention of the war; its application to paleoclimate studies, through studies of fossils, ocean sediments and polar ice cores, among other phenomena; the continued development of radiogenic isotope geochemistry to encompass more

⁵⁹ Along with fellow mass spectroscopist Josef Mattauch, Nier was one of the key players in the unification of chemical and physical scales of atomic weights, based on the standard $^{12}\text{C} = 12$. For a technical account, see J. R. De Laeter, "Al Nier's contribution to atomic weights," *International Journal of Mass Spectrometry*, 1998, 178, 1-7.

⁶⁰ Grayson-Krick interview, (ref. 6c), 177-215.

⁶¹ Co-authored with Michael B. McElroy and Yuk Ling Yung. *Science*, 1976, 194, 70-72.

⁶² Grayson-Krick interview, (ref. 6c), 142, 230.

⁶³ Grayson-Krick interview, (ref. 6c), 156.

⁶⁴ Grayson-Krick interview, (ref. 6c), 233.

isotope systems, beyond the U-Th-Pb system⁶⁵; the extension of geochemistry to studies of the solar system (cosmochemistry); the discovery of plate tectonics; space exploration, crucially dependent on geoscientific equipment like mass spectrometry; the confirmation of a correlation between variations of past climate conditions with variations of Earth's orbit and rotation, known as Milankovic cycles; knowledge of how the carbon cycle changes over geologic time, and the influence of climate on those changes; and the discovery of an iridium anomaly in the boundary between the Cretaceous and Paleogene periods of the stratigraphic column, key evidence for the asteroid impact hypothesis explaining the extinction of the dinosaurs. In addition, the period saw a flourishing of instrumental methods, of which mass spectrometry was just one of the most important; I will return to this phenomenon later.

Nier's scientific descendants made important contributions to these advances. The pattern of research Nier exemplified in the 1930s and '40s, involving a co-evolution of instruments and knowledge of isotope systems, had a lasting impact on isotope geology. This impact was mediated, in part, by a lineage of mass spectrometrists, descending from Nier, who promoted the application of mass spectrometry to geology.

As with much else in post-WWII science, the experience of the war played a key role in this process. As noted in the introduction, the impact of the war and the Cold War on the development of the Earth sciences, including geochemistry, has been studied by professional historians. In these studies, Nier appears mainly as the inventor of the instrument designs the post-war scientists depended on. In this section, I will argue that Nier played a more significant intellectual role on the course of post-war geochemistry by way of the dissemination of his approach through his students.

Through the Manhattan Project, Nier had got to know Arthur Compton, the head of the Metallurgical Lab at the University of Chicago (established as part of the Manhattan Project, and which would become the Argonne National Laboratory at the end of the war). The Chief Physicist at the Lab was Arthur Dempster (*vide supra*). One of Dempster's graduate students was one Mark Inghram. Compton sent him to Minnesota to learn as much as possible from Nier about the instrument and the methods of analysis. Inghram was then sent to Columbia, with two of Nier's instruments, to work on uranium enrichment.⁶⁶ After the war, Inghram became a physics instructor at Chicago. The University of

⁶⁵ The geologist James M. Mattinson estimated about 40 decay systems had become available by 2013. See Mattinson, "The Geochronological Revolution," in *The Web of Geological Sciences: Advances, Impacts, and Interactions*, ed. Marion E. Bickford (Boulder: The Geological Society of America, 2013), 303-320, on 312.

⁶⁶ On these moves of Inghram and the instruments, see Nier, Grayson-Krick interview, (ref. 6c) , 98 and John H. Reynolds, *Alfred Otto Carl Nier, 1911-1994*, (Washington, D.C.: National Academies Press, 1998), 8 and 10 (though

Chicago managed Argonne National Laboratory, which possessed some of Nier's 60° sector instruments. Inghram was able to work with those instruments upon returning to Chicago.⁶⁷ After the war, the university had founded the Institute for Nuclear Studies (INS), at least in part at the urging of Compton, who wanted to maintain the concentration of scientists who had worked in the Metallurgical Lab.⁶⁸ The INS was led by Manhattan Project alumni Urey, Harrison Brown, and Willard Libby, and attracted a number of students who would become prominent figures in isotope geochemistry. During the late 1940s and throughout the 1950s, Inghram advised or influenced a number of these students, including Clair Patterson, who would become famous for the first accurate determination of the age of the Earth; Gerald Wasserburg, who would become famous for the invention of the Lunatic I, the first fully digital mass spectrometer; George Tilton, John Reynolds, George Wetherill, and others. These students would go on to set up their own labs and train further generations of students. Their contributions were made possible by a deep knowledge of mass spectrometry, combined with a strong interest in applying it to geological problems. To support this claim, I will now examine a few of these contributions.

Clair Patterson's first experience with mass spectrometry was on the Manhattan Project, working on uranium separation at Oak Ridge, though in a different plant than Nier. After the war, he earned a Ph.D. in 1951 at the University of Chicago. His advisor there was nuclear chemist Harrison Brown, who had published a design for a mass spectrometer in 1941 that cited Nier's 1940 design. Brown had also worked at Oak Ridge, on the separation of plutonium in the same plant as Nier (though I am not aware of any contact between them there). Patterson's Ph.D. work focused on determining the lead isotopic composition of zircons, a kind of crystal found in granite. For dating purposes, zircons have the advantage that when they crystallize, they contain uranium but no lead. Hence they are not contaminated with non-radiogenic lead (see section 3), an attractive quality for age measurement. On the other hand, the quantities of uranium they contain are minute, and so are the resulting quantities of lead. According to an interview Patterson gave in 1995, the amounts of lead were 1,000 times smaller than anything that had been measured before.⁶⁹ The attempt to meet this sensitivity requirement revealed to Patterson that his samples were being contaminated by exogenous lead, a discovery that

Reynolds' corroboration should be taken with a grain of salt, since Reynolds, himself a geochronologist and graduate of Chicago from this generation, might have got the information from Nier or even the interview).

⁶⁷ Nier, Grayson-Krick interview, (ref. 6c) ,126 and Albert Parr and Roger Stockbauer, "Mark G. Inghram," in *The Encyclopedia of Mass Spectrometry, Volume 9: Historical Perspectives, Part B: Notable People in Mass Spectrometry*, ed. Keith A. Nier, Aldred L. Yergey, and P. Jane Gale (Amsterdam: Elsevier, 2015).

⁶⁸ Shindell, *Harold C. Urey*, (ref. 4f), 108.

⁶⁹ Clair C. Patterson, interview by Shirley K. Cohen. Pasadena, California, March 5, 6 and 9, 1995. Oral History Project, California Institute of Technology Archives, on 14 and 17.

forced him to develop new methods for avoiding such contamination, notably the use of a rigorously decontaminated “clean lab,” which was a novelty at the time.⁷⁰ He put these techniques to good use for his post-doc, also with Brown, when he determined the age of the Earth based on the comparison of lead isotope ratios in meteorites and terrestrial samples. Importantly, Patterson depended on a mass spectrometer developed by Inghram and colleagues at Argonne National Laboratory, a modified version of Nier’s 60° sector design.⁷¹ These techniques together were essential for allowing Patterson to settle the question of the Earth’s age.⁷²

According to a biographical memoir of Nier by the physicist and geochronologist John H. Reynolds, Nier’s student L. T. Aldrich, mentioned earlier, might have played a disseminating role also: “Around 1950 Aldrich moved to the Department of Terrestrial Magnetism of the Carnegie Institution and established there a geochronology laboratory, which played a prominent role in the development of the rubidium-strontium dating method. Aldrich’s colleagues in turn left Washington to establish other sites for geochronological work.”⁷³ INS alumni George Tilton and George Wetherill would do post-docs in that department of the Carnegie Institution in the 1950s, Tilton arriving in 1951 and Wetherill in 1953. Wetherill would then move to UCLA in 1959, and Tilton to UCSB in 1965.

Both Tilton and Wetherill worked with Aldrich while at Carnegie. This group was expressly aimed at overcoming a severe obstacle for historical research using Nier’s method of age determination. A problem with the U-Pb system was that it required samples containing large amounts of uranium, e.g. uranium ores, and these are rare on the Earth’s surface. This scarcity was compounded by a second kind, which is that the abundance of a sample is inversely proportional to its age. So the farther researchers sought to go back in Earth’s history, the less sample was available to them. The combination of these two scarcities posed a major impediment for historical research. Work towards overcoming it was initiated by Harrison Brown, who assigned the zircon work to Patterson (zircons are present in granites and hence are much more common than uranium ores). The Aldrich group developed a number of techniques for dating minerals in ordinary granitic rocks. They then applied them to creating a

⁷⁰ Ibid., 19. See also Doug MacDougall, *Nature’s Clocks*, (Berkeley: University of California Press, 2008), 110. George R. Tilton, Claire Patterson, Harrison Brown, Mark Inghram, et al., “Isotopic Composition and Distribution of Lead, Uranium, and Thorium in a Precambrian Granite,” *Bulletin of the Geological Society of America*, 66 (1955), 1131-1148 provide a detailed description of the procedures used.

⁷¹ Patterson, interview by Shirley K. Cohen, 21; Tilton et al., “Isotopic Composition and Distribution,” (ref. 71), 1137-1138.

⁷² Claire Patterson, “Age of Meteorites and the Earth,” *Geochimica et Cosmochimica Acta*, 10, (1956), 230-237.

⁷³ Reynolds, *Alfred Otto Carl Nier, 1911-1994*, (ref. 67), 10.

geochronological map of Precambrian regions of parts of Canada the US, that is, regions originating in Earth's early history extending back from 600 million years ago.⁷⁴

Gerald Wasserburg may serve as another example of the kind of research pattern Nier pioneered. Wasserburg earned a PhD in geology in 1954 at Chicago under the joint supervision of Inghram and Urey.⁷⁵ He went on to champion geochronology at Caltech. In the late 1960s, he and his colleagues invented a new 60° sector mass spectrometer, partially in anticipation of the analysis of lunar samples, and baptized the “Lunatic I.” An important problem in mass spectrometry is the instability of the ion beam, which fluctuates over time. This instability erodes the resolution of isotope ratio measurements. For example, with a single-detector spectrometer (i.e., no simultaneous detection of beams) the ion currents must be measured sequentially by varying either the voltage used to accelerate the ions or the strength of the magnetic field. In the time interval between the measurement of one current and another, the intensity of the beams might fluctuate, and hence the ratios of the measurements (i.e. the isotope ratio) will fluctuate as well from one set of measurements to another. Wasserburg's solution was to make the Nier design fully digital, which allowed the magnetic field to be switched rapidly via computer programming. This greatly reduced the time interval between measurements, thereby greatly decreasing the error induced by beam instability, with the precision approaching the limits of counting statistics in many cases. This technique then permitted measurement of extremely small isotopic differences on very small samples of many elements. Wasserburg applied this capability *inter alia* to the study of solar system history. For example, the Lunatic I was used to determine the ages of lunar rocks from the Apollo missions and the Soviet Luna 16 and 20 missions. These studies established the time scales for lunar evolution. One remarkable discovery, inferred from a combination of U/Pb and Rb/Sr measurements, was the so-called “terminal lunar cataclysm,” a large-scale bombardment of the Earth-Moon system by small planetary bodies that occurred 500 million years after the formation of that system due to disturbances in the asteroidal belt. Wasserburg's student R. Lawrence Edwards went on to develop the Lunatic I system, and related techniques, for U/Th dating,

⁷⁴ For this work, see George W. Wetherill, “Contemplation of Things Past,” *Annual Review of Earth and Planetary Science*, 1998, 26, 1-21. See also Macdougall, *Nature's Clocks*, (ref. 71), ch. 5 for an interesting discussion of zircons in geochronology.

⁷⁵ G. J. Wasserburg, “Isotopic Adventures—Geological, Planetological, and Cosmic,” *Annual Review of Earth and Planetary Science*, 2003, 31: 1-74.

which he then used to study climate history, leading to greater insight into the causes of ice age terminations, as well as techniques for calibrating ^{14}C ages, among other discoveries.⁷⁶

Urey's pioneering work on paleoclimate history was also indebted to Nier. As noted above, in 1947 Urey had claimed that past temperatures could be inferred from oxygen isotope ratios, and suggested that a Nier-type spectrometer could provide the requisite data. In the late 1940s, however, the commercial production of a Nier-type spectrometer was still in development, and so Urey decided to build his own. To this end, Urey recruited two young scientists with experience in mass spectroscopy. One was an electrical engineer, Charles R. McKinney, who had maintained Nier's spectrometers at Oak Ridge during the war. Another was Samuel Epstein, a Canadian post-doctoral fellow who had worked as a graduate student with the Canadian mass spectroscopist Harry Thode. By February 1949, Urey's group had constructed two mass spectrometers, based on Nier's design.⁷⁷ Their work with these instruments resulted in a series of foundational papers in paleoclimatology. In his 1947 paper, Urey had calculated the temperature dependence of oxygen isotope fractionation between calcium carbonate and water and proposed that the isotopic composition of carbonates could be used as a paleothermometer. Epstein, McKinney and other members of Urey's group tested Urey's idea by growing mollusks, whose shells are composed of calcium carbonate, in water of various temperatures. They discovered an empirical relationship, the carbonate-water temperature scale, allowing the temperature, at which the shells had grown, to be inferred from the relative O^{18} abundance in the calcium carbonate of the shell.⁷⁸ This work required the optimization of the Nier 60° sector instrument for the measurement of the very small isotope effects involved in fractionation.⁷⁹ One of the first papers in the series was devoted to describing these improvements.⁸⁰

As a final example, the Nier tradition also made an important contribution to the plate tectonics revolution, albeit indirectly. John Reynolds was a student of Inghram's who accepted an assistant

⁷⁶ On ^{14}C , see, for example, Hai Cheng et al., "Atmospheric $^{14}\text{C}/^{12}\text{C}$ changes during the last glacial period from Hulu Cave," *Science*, 362, (2018), 1293-1297. On ice age terminations, see, for example, Hai Cheng et al., "Ice Age Terminations," *Science*, 326, (2009), 248-252.

⁷⁷ Shindell, *Harold C. Urey*, (ref. 4f), 131-136.

⁷⁸ J. M. McCrea, "On the Isotopic Chemistry of Carbonates and a Paleotemperature Scale," *The Journal of Chemical Physics*, 18 no. 6, (1950), 849-857; H. C. Urey et al., "Measurement of Paleotemperatures and Temperatures of the Upper Cretaceous of England, Denmark, and the Southeastern United States," *Bulletin of the Geological Society of America*, 62, (1951), 399-416; Samuel Epstein et al., "Carbonate-Water Isotopic Temperature Scale," *Bulletin of the Geological Society of America*, 62, (1951), 417-426; and Samuel Epstein et al., "Revised Carbonate-Water Isotopic Temperature Scale," *Bulletin of the Geological Society of America*, 64, (1953), 1315-1326.

⁷⁹ Samuel Epstein, interview by Carol Bugé. Pasadena, California, December 19 and 26, 1985, and January 10, 1986. Oral History Project, California Institute of Technology Archives, on 22-23.

⁸⁰ C. R. McKinney et al., "Improvements in Mass Spectrometers for the Measurement of Small Differences in Isotope Abundance Ratios," *The Review of Scientific Instruments*, 21 no. 8, (1950), 724-730.

professorship in the physics department at UC Berkeley in 1950. He began his career there by improving the technique of potassium-argon dating. This technique had previously been limited to rocks older than 10 million years, because the instruments used to measure argon were contaminated with small amounts of argon from the atmosphere. Since young rocks contained particularly small amounts of argon, the latter would be overwhelmed by the atmospheric argon released from the inner surfaces of the instrument. To circumvent this problem, Reynolds built an all-glass, 60°-sector spectrometer that could be heated while under vacuum to drive off the absorbed atmospheric argon. This procedure allowed extremely minute amounts of radiogenic argon to be measured very accurately. The Reynolds spectrometer was then used by Garniss Curtis and Jack Evernden, of the Berkeley geology department, in collaboration with Reynolds graduate student Joseph Lipson, for the dating of young volcanic rocks. Their data, together with those of other researchers, would allow changes in the polarities of volcanic rocks to be dated. The reversals of polarity would provide key evidence for the reality of sea-floor spreading. Isotope measurements using the Reynolds spectrometer were crucial for establishing the chronology of the sequence of reversals. That made it possible, by 1966, to identify and correlate the patterns of remnant magnetism in the ocean floors precisely enough to document movements of oceanic crust outward from mid-oceanic rifts and ridges. Subsequently, dating of samples from deep cores, starting with those drilled in the Atlantic in 1970, directly showed that oceanic crust is older the farther it is from the mid-ocean rift and ridge yet is nowhere older than the Mesozoic era.⁸¹

I will mention two more of Reynolds' contributions. In 1963-1964, Reynolds and colleagues set up a K-Ar laboratory at the University of São Paulo, the first geochronology lab in South America. Using his spectrometer, the group measured ages of Brazilian rocks that fit with age patterns seen along the coast of Africa. This provided evidence that South America had separated from Africa. Among geochemists, however, Reynolds is perhaps best known for the discovery of extinct radioactive nuclides. In 1960 Reynolds discovered evidence of extinct ¹²⁹I in the form of an anomalous excess of ¹²⁹Xe in a meteorite. He again used his spectrometer design, known as a 'static mode' instrument, and which is suitable for noble gases in general. Subsequent research revealed the previous existence of many other, now extinct radionuclides. Many of the extinct nuclides were short-lived, a feature which cosmochemists have exploited to reconstruct the history of the early solar system.⁸²

⁸¹ The role of Reynolds and his spectrometer in confirming the theory of plate tectonics is described in detail in William Glen, *The Road to Jamarillo*, (Stanford, Stanford University Press: 1982).

⁸² For background see Alan P. Dickin, *Radiogenic Isotope Geology*, 3rd ed., (Cambridge: Cambridge University Press, 2018), ch. 15.

6 An Instrumental Revolution in Geochemistry?

The history related in this paper was, arguably, part of a bigger change sweeping chemistry and geochemistry. Historians of chemistry have identified an “Instrumental Revolution” in chemistry during which the methods of the experimental branches saw significant change, picking up steam in the 1940s and stabilizing in the late 1960s.⁸³ This episode saw the rise of “instrumental methods” in chemistry, involving high-tech instrumentation, many of them based on physical principles. Examples are mass spectrometry, nuclear magnetic resonance, infrared, ultraviolet, Raman and other spectroscopies, as well as chromatographic techniques like high-performance liquid chromatography or gas chromatography. The plethora of instrumental methods complemented or replaced traditional chemical ones. For example, organic structural analysis through degradation reactions was largely replaced by spectroscopic methods.

Something similar appears to have happened in geochemistry. Mass spectrometry was only one, albeit particularly important, method among many others to become employed in geochemical research. Examples include ¹⁴C dating, atomic absorption spectrophotometry (AAS), X-ray fluorescence spectrometry (XRF), instrumental neutron activation analysis (NAA), inductively coupled plasma-atomic emission and –mass spectrometry (ICP-AES and –MS), and various forms of mass spectrometry (e.g. thermal ionization (TIMS), gas source (GSMS), secondary ionization (SIMS)).⁸⁴ Moreover, historical questions are only one such that these techniques can help answer. For example, they are used to identify unknown natural materials, verify the quality of synthetic materials, test for contamination, investigate the course of geochemical processes, determine composition, map the spatial distribution of substances, and monitor the efficiency of experimental or industrial processes.⁸⁵ Like the Instrumental

⁸³ George Borg, “On ‘the Application of Science to Science Itself:’ Chemistry Instruments and the Scientific Labor Process,” *Studies in History and Philosophy of Science*, 79, (2020), 41-56; José A. Chamizo, “About Continuity and Rupture in the History of Chemistry: the Fourth Chemical Revolution (1945–1966),” *Foundations of Chemistry*, 21 no. 1, (2019), 11-29; Apostolos Gerontas, “Creating New Technologists of Research in the 1960s: The Case of the Reproduction of Automated Chromatography Specialists and Practitioners,” *Science and Education*, 23, (2014), 1681-1700; Carsten Reinhardt, *Shifting and Rearranging*, (Sagamore Beach: Science History Publications, 2006); Peter J. T. Morris, ed., *From Classical to Modern Chemistry*, (Cambridge: Royal Society of Chemistry in association with the Science Museum, London and the Chemical Heritage Foundation, 2002).

⁸⁴ Philip J. Potts, “Geoanalysis: Past, Present and Future,” *Analyst*, 122, (1997), 1179-1186; Philip J. Potts et al., “Advances in Analytical Technology and its Influence on the Development of Modern Inorganic Geochemistry: a Historical Perspective,” in *Magmatic Processes and Plate Tectonics*, eds. H. M. Prichard et al. (London : Geological Society, 1993).

⁸⁵ Robin Gill and Michael H. Ramsey, “What a Geochemical Analysis Means,” in *Modern Analytical Geochemistry*, ed. Robin Gill, (London: Routledge, 1997), 1-11, on 1.

Revolution in basic chemistry, many of these methods were introduced over the course of the second half of the 20th century.⁸⁶

The overall change, as far as geochemical techniques are concerned, may be characterized as a relative de-centering of chemical techniques, as in basic chemistry. Traditional geochemical techniques involved a battery of chemical manipulations, purifications, and volumetric and gravimetric measurements. Consider, for example, Henry S. Washington's classic treatise *The Chemical Analysis of Rocks*. In the fourth, last edition of 1930, the table of contents lists as needed apparatus: balances, weights, platinum utensils, glass, fused silica, porcelain, rubber, and metal, in addition to reagents for chemical transformation. The book also describes various lab operations, including pulverization, weighing, decomposition, precipitation, filtration and washing, drying and ignition of precipitates, and titration. A long list of methods, each involving a specific combination of apparatus, reagents and operations, follows.⁸⁷

On the other hand, these methods are virtually absent in the 1997 primer *Modern Analytical Geochemistry*. Though some manual and chemical operations are still required for sample preparation, the bulk of the textbook is given over to instrumental techniques: ICP-AES and –MS, AAS, XRF, NAA, TIMS, GSMS, SIMS, and others. There is also an appendix on vacuum technology (see section 2.2 above).⁸⁸ Other analytical primers display a similar structure.⁸⁹ In contrast to the bulk methods of “classical” geochemistry, and like the instrumental methods of basic chemistry, the new geochemical methods operate on the microscopic level and presuppose physical theory. Also like the basic chemistry methods, they presuppose a great deal of technological know-how. For example, Nier's championing of electronic detection was part of a more widespread move away from photographic detection.⁹⁰

⁸⁶ Some geochemists locate the beginning of the “revolution” in the 1960s. See Potts et al., “Advances in Analytical Technology,” (ref. 85), 503; Mattinson, “The Geochronological Revolution,” (ref. 66), 307; Clark M. Johnson et al., “Smaller, Better, More: Five Decades of Advances in Geochemistry,” in Bickford, ed., *The Web of Geological Sciences*, (ref. 66), 259-302, on 261. The history related in this paper may be viewed as a pre-history to this period.

⁸⁷ Henry S. Washington, *The Chemical Analysis of Rocks*, (New York: John Wiley & Sons, 1930), xiii-xvi. See also W. F. Hillebrand, “The Analysis of Silicate and Carbonate Rocks,” *United States Geological Survey Bulletin*, 700, 1-285.

⁸⁸ Gill, ed., *Modern Analytical Geochemistry*, (ref. 86).

⁸⁹ Jan Schwarzbauer and Branimir Jovančičević, *Introduction to Analytical Methods in Organic Geochemistry*, (Cham: Springer Nature, 2020); Kliti Grice, ed., *Principles and Practice of Analytical Techniques in Geosciences*, (Cambridge: The Royal Society of Chemistry, 2015).

⁹⁰ In 1958, the physical chemist and instrument developer S. Z. Lewin, writing in *Analytical Chemistry*, claimed that “[m]odern electronic detectors of radiation have increased the range of spectrometers enormously, and their utilization in place of the photographic plate has been directly responsible for the current vigorous flowering of the fields of microwave, infrared, near-infrared, Raman, visible, ultraviolet and x-ray spectrometry.” S. Z. Lewin, “Trends in Laboratory Instrumentation for Analysis,” *Analytical Chemistry*, 30, (1958), 19A-29A, on 20A.

Looking back over the changes in geoanalytical techniques brought about over the course of the 20th century, geochemists Potts et al. (1993) credited von Laue's discovery, in 1912, that the crystal lattice of a solid can diffract X-rays, with being "a critical step in the development of the geochemistry, since early results demonstrated that minerals could be distinguished on structural as well as chemical characteristics."⁹¹ Indeed, perhaps the basic effect wrought by the instrumental revolution in geochemistry is that it multiplied the ways in which minerals could be distinguished, to include not just chemical and structural but also atomic (e.g., absorption and emission spectra) and nuclear characteristics. This led to a corresponding expansion of the questions that could be answered empirically, of which those concerning early solar system history, climate change or plate tectonics are but a few particularly spectacular examples.

7 Conclusion



Figure 3. Alfred Nier in the late 1940s, working at a version of his 60-degree sector field mass spectrometer. Note the 60° inflection of the mass analyzer tube as it passes between the poles of the magnet at the center of the photograph. Unlabelled photograph from the Nier Papers, box 34, letter box 1, University of Minnesota Archives.

⁹¹ Potts et al., "Advances in Analytical Technology," (ref. 85), 502.

In the introduction, I claimed that Nier was the founder of a system of practice. I use the term ‘system of practice,’ rather than just ‘technique,’ because modern geochronological studies are based on two intertwined streams of activities: the development of mass spectrometry, on the one hand, and the development of geochronological techniques, on the other. For example, geochemists typically talk of dating by means of a specific target system—an isotope pair, or a type of mineral or element—as a geochemical method, which is coupled with mass spectrometric techniques: rhenium-osmium with TIMS or SIMS, uranium-lead or potassium-argon with GSMS, ^{14}C with accelerator mass spectrometry, zircons with sensitive high-resolution ion microprobes, or noble gases with static gas-mode instruments. Besides the instruments and the target systems there are, in addition, techniques of data analysis and a wealth of geochemical background knowledge that are necessary for applying the instruments and interpreting their outputs.

While of course Nier himself only initiated these developments, his work established that, and how, those two rich streams could be brought together and co-developed to answer geochemical questions, and pose new ones. In the 1930s and ‘40s, he built a succession of spectrometers, each one improving on the other, and culminating in a design that could routinize isotope abundance measurements. Concurrently, he used these instruments to make discoveries of great significance for the emerging field of isotope geochemistry. He was able to engage in this interplay because he was uniquely positioned to combine multiple lines of research and kinds of knowledge: atomic and nuclear physics; radiometric dating; chemical analysis (though he did not perform the analyses himself); mass spectroscopy, and spectrometry in particular; electrical engineering; and vacuum technology. In this sense he illustrates a noted pattern of scientific innovation, that it often involves the creative integrations of ideas and practices from multiple fields.⁹² A condition for him to be in such a position was that those lines of research and kinds of knowledge were sufficiently developed so that ‘the right person at the right time’ could combine them effectively. Instrument development tends to be especially holistic, for reasons I have discussed elsewhere.⁹³ In brief, instruments embody knowledge of different kinds—such as theoretical or practical knowledge (e.g., glass-blowing skills)—produced by different practices and fields, like theoretical physics and electrical engineering. It is rare for one person to master all the different kinds of knowledge required to construct the instrument. Nier’s intellectual itinerary and personal

⁹² Oren Harman and Michael R. Dietrich, *Dreamers, Visionaries, and Revolutionaries*, (Chicago: The University of Chicago Press, 2018), 9-10.

⁹³ George Borg, “Discovery and instrumentation: how surplus knowledge contributes to progress in Science,” *Perspectives on Science*, 27 no. 6, 861-890 and “Science, Labor, and Scientific Progress” (PhD dissertation, University of Pittsburgh, 2020), ch. 8.

aptitudes allowed him to approach this ideal. He acquired an unusual skill set that combined mastery of physical theory, experimental techniques, and engineering know-how. This skill set corresponded well to the holistic requirements of instrument development. Moreover, he grasped the geochronological problem sufficiently well to be able to apply that skill set to it. Finally, the basic design principle of mass spectrographs and spectrometers, which Nier inherited, proved versatile enough to allow an extended series of variants to be derived from it.⁹⁴

My treatment of Nier's career may be contrasted with Carsten Reinhardt's seminal book on the Instrumental Revolution in chemistry, *Shifting and Rearranging*. Reinhardt focuses on the role of "method makers" in the transfer of physical theory and instrumentation to new fields. Reinhardt shows, for the case of chemistry, that this process involved the adaptation of the theory and instrumentation to the needs, knowledge and practices of the importing field, and so was hardly a mere case of "applied physics." Though Nier was clearly a "method maker," my focus has been on the epistemic pre-requisites for a system of practice to come together rather than on the problem of knowledge transfer. While I am sympathetic to the late physicist John de Laeter's claim that "[t]his two-way interaction exhibited by geochronology on the one hand, and mass spectrometric instrumentation on the other, is an exemplar of the manner in which science progresses,"⁹⁵ Nier's career shows that that dynamic is itself an achievement not to be taken for granted. Its occurrence, or not, depends on a convergence of objective and subjective factors. Nier's early career also indicates, by their absence, what factors are needed for that dynamic to proceed on a social scale, namely the institutional, technical and financial conditions for the widespread use of high-tech scientific instruments by non-specialists. Certainly, these missing factors would emerge during and after the war. That said, his designs, results and intellectual influence, via his students and colleagues, furnished important elements for progress on that scale.

8 Acknowledgments

⁹⁴ In this sense, it provided a particularly fruitful *scaffold*, a concept I discuss in the works cited in footnote 94.

⁹⁵ John R. de Laeter, "Mass Spectrometry and Geochronology," *Mass Spectrometry Reviews*, 17, (1998), 97-125.