

Neutron Activation Analysis: Solving the Mystery of Airborne Rare Earths

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Abstract:

Concentrations of about 35 elements, many of them trace species, can be measured without chemical separations by instrumental neutron activation analysis. Samples are irradiated with neutrons to transform some of the stable isotopes of the elements to radioactive isotopes. Elements are identified and their concentrations are determined by observing energies and half lives of the γ rays emitted by the irradiated samples, as the combination of energies and half life are unique to certain isotopes. Sources of particles in the air can be identified by their detailed composition patterns ("chemical fingerprints"). Studies in Philadelphia revealed concentrations of rare earth elements about forty times greater than expected. The story of the discovery of the sources of these elements illustrates the fact that much scientific progress is made more by accident and chance encounters than is indicated by the classic "scientific method." The trail leads eventually to the possible discovery of a tracer for emissions from motor vehicles, which is needed now that leaded gasoline is nearly phased out.

Introduction

Most of you are familiar with the "scientific method:" make an observation, construct a hypothesis, design and perform an experiment to test the hypothesis and, if the results confirm the hypothesis, elevate it to a theory. There are elements of the classic method in all research breakthroughs, but I have rarely seen science progress in such an orderly fashion. Not only is this true of the minor advances that we ordinary scientists make, but some of the greatest discoveries contain strong elements of chance. An excellent example is Niels Bohr's construction of his theory of atomic structure, as described beautifully in Rhode's *The Making of the Atomic Bomb* (1). My good friend and colleague, the late Charles Coryell, co-discoverer of Promethium, often said that "the scientific method consists of plotting data in various ways until you get a straight line and then figuring out why it works."

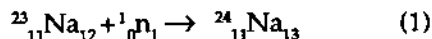
Although I would not compare my discoveries with those of Bohr and Coryell, I want to convey to you the way in which science usually progresses and the excitement and satisfaction that one feels when that light bulb comes on above one's head, and one understands something that no one has ever understood before! As the work I will describe involves the use of neutron activation analysis (NAA), with which not many people are familiar, I must first explain how it works. The use of NAA is critical for my work, as it

allows one to observe extremely small quantities of various trace elements. This is possible because of our ability to observe radioactive decay of individual nuclei because they typically release energy a million times greater than energies involved in chemical reactions.

Neutron Activation Analysis

The only stable isotope of Na is ^{23}Na , whose nucleus consists of 11 protons and 12 neutrons, for a total of 23 "nucleons." To remind us of its composition, we can depict ^{23}Na as $^{23}_{11}\text{Na}_{12}$, where the subscript, 11, is the atomic number, Z , the number of positive charges on all nuclei of the element Na. The other subscript, 12, is the neutron number, N , and the superscript, 23, is the mass number, $A = Z + N$. The concept of a mass number is useful because the proton and neutron have about equal masses, both being about 1800 times that of the electron, so the mass of an atom is largely determined by the numbers of neutrons and protons in its nucleus.

If we irradiate a sample containing Na with neutrons in a nuclear reactor, some stable ^{23}Na nuclei "capture" neutrons, converting the nuclei to ^{24}Na :



The ^{24}Na atom is unstable because its mass is greater than that of ^{24}Mg , so a neutron in the ^{24}Na nucleus converts to a proton and an electron. The electron is ejected from the nucleus with high energy and called a "beta particle" (β) and the process is called " β decay:"



Conversion of a neutron to a proton in the nucleus yields a nucleus containing 12 protons, so the element is now Mg, with atomic number $Z = 12$. The ^{24}Na atoms have a "half life" of about 15 hrs, meaning that half of the remaining atoms decay to ^{24}Mg atoms every 15 hrs. If we started with 1000 atoms of ^{24}Na , 15 hrs later we would have 500 left, after another 15 hrs, 250 atoms and, after a total of 45 hrs, 125 atoms, and so forth.

As in this case, β decay often leaves the final nucleus in an excited nuclear state. The nucleus usually gets rid of the extra energy by emitting gamma rays (γ), a form of electromagnetic radiation like visible light, but with about a million times as much energy (measured in millions of electron volts, MeV, instead of the electron volts, eV, typical of atomic and molecular processes). Just as the visible light emitted by atoms has a spectrum of energies characteristic of an element, the γ rays

emitted by a nucleus have energies quite specific to that nuclide, corresponding to differences in energies between states in the nucleus. Sodium-24 emits γ rays of energies 1.389 and 2.754 MeV.

Analytical chemists often use the characteristic visible spectra of atoms to determine which elements are present in a sample and measure their concentrations. This principle is used, for example, in techniques such as atomic absorption spectrophotometry (AAS) and emission spectrometry. Gamma-ray spectra are, likewise, used in NAA. For example, to determine the concentration of Na in a sample, we could irradiate the sample with neutrons in a nuclear reactor to convert some of the stable ^{23}Na atoms to ^{24}Na atoms, whose decay we could observe via its characteristic γ rays. Before about 1965, it was usually necessary to chemically separate the elements of interest from a complex sample before observing the radiations because the detectors available were unable to sort out radiations of the many radioactive species produced from the many elements present. Today, however, we can use semiconductor Ge detectors to observe the γ rays because they yield energy spectra in which the γ -ray lines are so narrow (typically about 0.003 MeV wide) that one can identify γ -rays of twenty or so species in a complex mixture. Thus, we can measure concentrations of about 35 elements in many types of samples (e.g., soil, rocks, coal, airborne particles) by irradiating the samples and taking γ -ray spectra at various times after irradiation. Soon after irradiations, spectra are dominated by γ rays from species with very short half life, e.g., 2.3-min ^{28}Al and 3.8-min ^{52}V . After two or three weeks, the short-lived species will have all decayed, so one can see much longer-lived species such as 5-yr ^{60}Co and 13-yr ^{152}Eu . Examples of typical spectra are shown in Fig. 1.

This completely instrumental method, called "instrumental neutron activation analysis" (INAA), allows us to observe many more elements per unit time and effort than the more laborious, time-consuming radiochemical neutron activation analysis (RNAA).

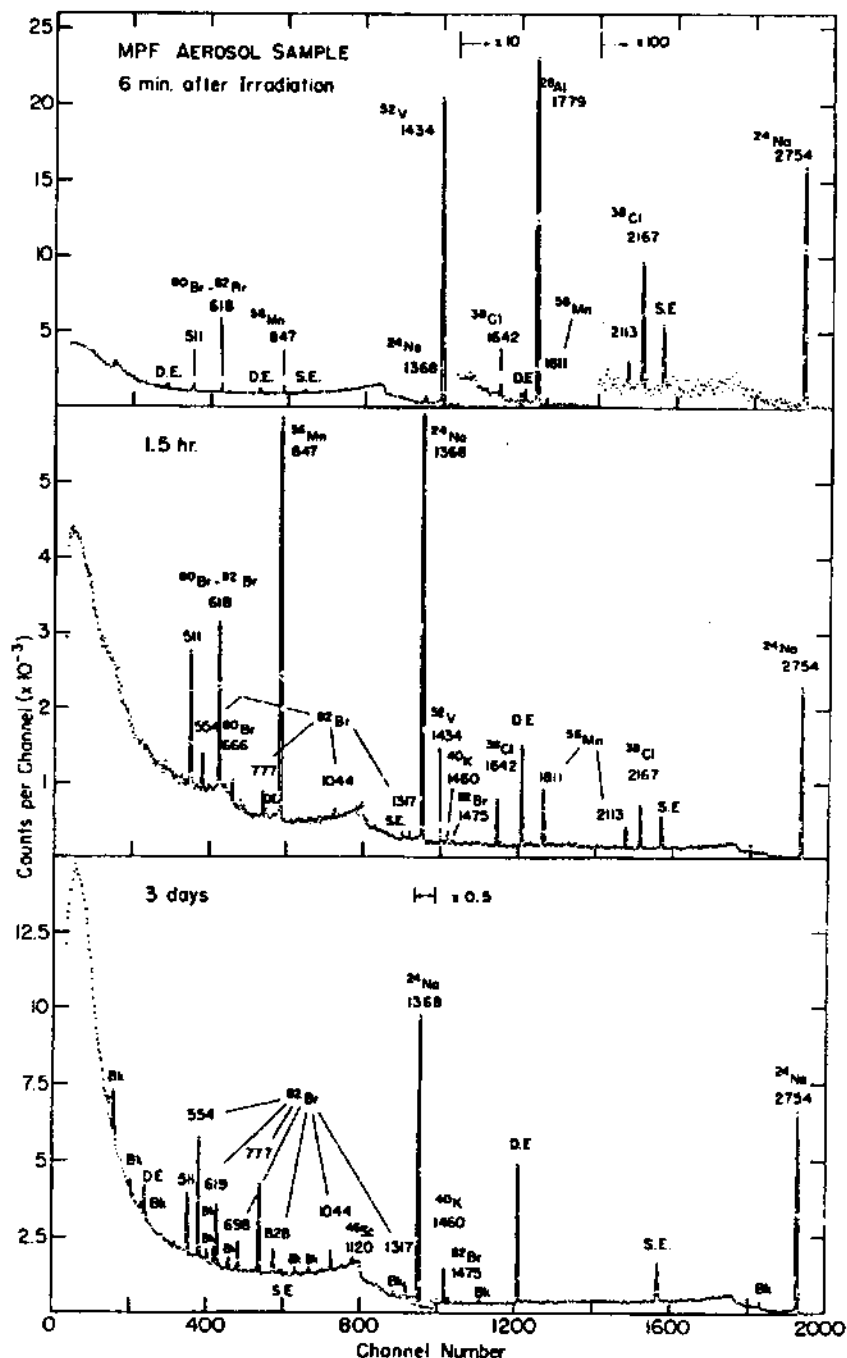


Figure 1. Gamma-ray spectra taken at three times after neutron irradiation of airborne particles collected in Cambridge, MA on a Millipore filter (MPF). Peaks are labelled with the radioactive species and energy in keV (1 keV = 0.001 MeV), approximately proportional to the Channel Number of the x axis. "Bk" indicates peaks in the background (i.e., with no sample present). S.E. and D.E. are peaks produced when γ rays of energy >1.02 MeV produce a positron-electron pair in the detector and one or two of the 511-keV γ rays produced when the positron annihilates is lost from the detector, respectively. For example, loss of one and two 511-keV photons from the ^{24}Na events at 2754 keV yields S.E. and D.E. peaks at about 2243 and 1732 keV, respectively (approx. channels 1200 and 1560). Spectra taken from publication of the first use of Ge detectors for INAA of airborne particles (2).

vehicles. They mainly emit carbonaceous material, but there are many other sources of carbon. (In a later paper in the session, Ann Sheffield will describe the use of the ratio of ^{14}C to ^{12}C to distinguish emissions from diesel engines from those of fire places and wood stoves.)

As noted above, we usually observe the REEs on samples of airborne particles, but until recently, they didn't appear to tell us very much. Airborne particles are commonly collected by pumping air through a filter, which is then subjected to INAA or other analyses. Filters collect particles with diameters up to about 40 μm (where 1 μm = 10^{-6} m). Particles with diameters larger than about 2 μm arise mainly from mechanical processes, e.g., wind erosion of soil and rocks, grinding, abrasion of highways by traffic. In most air-filter samples, the REEs were mostly accounted for by large particles of soil and other crustal material of the earth. This was shown by the fact that ratios of concentrations of prominent rare earths La and Ce to that of the major crustal element, Al, were usually quite similar to the ratios for average crustal material of the Earth, about 0.00037 and 0.000074, respectively (4). People studying other aspects of airborne particles often asked me at conferences, "Why do you keep showing up with this laundry list of obscure elements like rare earths?" I pointed out that "we got their concentrations from the same γ -ray spectra as for the other elements, so it didn't require much extra effort to get them, so we might as well report them in case they became valuable some day."

The Philadelphia Story

In the summer of 1982, our group participated in a study of the Philadelphia atmosphere along with several other groups in a study organized by Robert Stevens, Thomas Dzubay and others at the EPA laboratory in Research Triangle Park, NC (5). Some groups collected particles at three sites and others analyzed them for elements by XRF (which mainly observes the major elements). If properly done, XRF is gentle enough that it is non-destructive, so we were able to analyze the samples by INAA following XRF. The particles were collected with a device (a "virtual impactor") that sorts them into two size fractions: coarse particles with diam. $>2.5 \mu\text{m}$ and fine particles with diam. $<2.5 \mu\text{m}$ (see Fig. 3). As INAA is expensive and, as the coarse particles are mainly crustal material, which doesn't tell us much, we analyzed only the fine particles. The latter are rich with information, as they contain a lot of the trace elements from high temperature sources such as power plants, incinerators, motor vehicles, etc. They are also of most concern in the atmosphere because they contain most of the acid, sulfate, toxic elements and carcinogenic material, and they cause most of the light scattering that we see as "haze." They are also small enough to be breathed deeply into the lungs and they typically remain airborne for a week or more, so they can travel thousands

of kilometers before coming to ground (6). For these reasons, fine particles are of much more interest and concern than large particles.

When we obtained results, we were quite surprised by the REE concentrations: the La/Al and Ce/Al ratios in the fine particles were often about forty times the crustal ratios! Furthermore, the REE pattern itself was distorted. The REEs are chemically so similar, that the ratios of one REE to another in most samples from the environment are the same as for the average crustal material of the Earth. But in the Philadelphia atmosphere, the light rare earths were enriched, the La/Sm ratio, for example, ranging as high as 70, whereas the ratio is about 6 for crustal material. Thus, there we had to find a source in Philadelphia that was emitting fine particle REEs whose pattern was distorted, favoring light REEs.

Fortunately, the EPA group had also arranged for samples to be taken from the stacks of seven major air pollution sources in Philadelphia and we also analyzed some of these after another group performed XRF (7). One of the sources studied was a fluidized catalytic converter of a refinery. I was not very excited about that, as I thought that refineries would mainly emit hydrocarbons and other carbonaceous materials. Perhaps they might emit some materials used as catalysts, but those would probably be elements such as Pt and Ni, which we wouldn't see via INAA. But, surprise: they were loaded with fine-particle REEs and the light REEs were enriched relative to the heavier ones, the La/Sm ratio typically being about 30. But why would REEs be coming in large amounts from an oil refinery? We knew from other studies that crude oils contain very small amounts of REEs.

Zeolite Catalysts

In March, 1984, I went to Rensselaer Polytechnic Institute to give a seminar and see my good friend, Ivor Preiss. He had recently been using a special form of XRF to observe various elements, including REEs (which are not observed well by the usual XRF method) in many types of samples. During our conversation, I told him about the Philadelphia results. Immediately he pointed out that the REEs were undoubtedly coming from zeolite catalysts. Zeolites are natural minerals having a pore and cavity structure that makes them useful for separating various chemical species because of their size selectivities. Since the 1960's, oil companies have been using artificially prepared zeolite-like materials, which were found to be very effective catalysts for "cracking" large hydrocarbon molecules in crude oils. By making the catalysts artificially, manufacturers can control their properties (e.g., pore sizes) by adjusting their compositions and the process for making them. Most zeolite catalysts contain rare earth oxides in amounts up to several percent, embedded in an aluminosilicate structure having an overall composition

Particle Size Spectrum

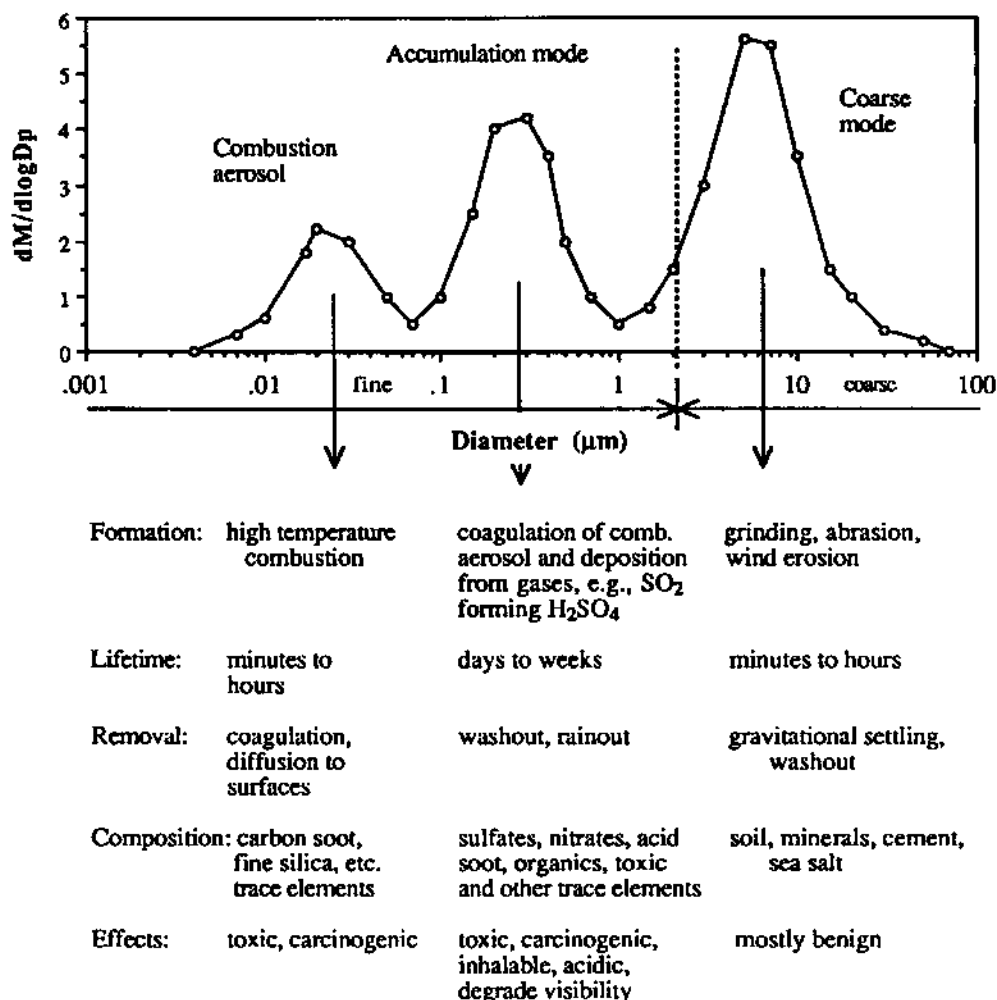


Figure 3. Schematic graph of particle size spectrum based on Fig. 1-6 of Ref. 6. The y-axis shows the mass per uniform interval of the logarithm of diameter. ($1 \mu\text{m} = 10^{-6} \text{m}$).

of about 30% Al₂O₃ and 45% SiO₂ (8). We obtained samples of zeolite catalysts, which we confirmed were loaded with REEs, with the light rare earths being enriched.

This finding did not fully explain the story. First, in chemistry textbooks it says that catalysts "participate in the reaction, but are not consumed." So why were they getting out of the plant? Second, why were they on fine particles? I thought they would be grinding against each other in the oil or against the container walls and, thus, release coarse particles. Third, why were the light REEs enriched relative to the heavy ones?

My research associate, Ilhan Olmez, now at the M.I.T. reactor, and I looked into these questions and found that the surfaces of the catalyst particles build up carbon deposits, so they have to be periodically "regenerated" in a catalyst-regenerating tower, in which the carbon is burned out, which probably takes some of the catalyst along. As that is a high temperature process, it presumably produces fine particles. Although the

plants do regenerate the catalyst many times, in the real world, small amounts of catalysts are lost up the stack. Also, some appears to get into the petroleum products, as we found smaller, but significant amounts of REEs being emitted by oil-fired power plants in the Philadelphia area. Regarding the distorted pattern, there are two major REE ores: monazite and bastnasite. The former has a normal REE pattern, but the latter is enriched in light REEs. The major domestic source of REEs is the Molycorp, Inc., which mines REEs from a bastnasite deposit at Mt. Pass, CA. The La enrichment is enhanced because some companies use a combination of rare earth oxides and a "La concentrate" produced by Molycorp (9). It should be noted that the petroleum industry is a major consumer of rare earth oxides, as it has accounted for about 40% of the total consumption of the oxides over the past two decades (10,11). Olmez and I submitted this information to *Science* in May, 1985, and it was published in Sept., 1985 (12).

The Global Story

In mathematics and theoretical physics, most breakthroughs are made by bright young people, whose minds are least cluttered and most creative. But in fields such as geochemistry and environmental chemistry, success often comes to those who've been in the field long enough to remember many seemingly disconnected observations. In this case, I remembered that Josef Parrington, a student of William Zoller at Maryland, had observed unusual REE concentrations for a several-week period at Mauna Loa Observatory (MLO), on the island of Hawaii in April, 1980 (13). His study was designed as an investigation of particles in global circulation. A major feature of atmospheric particles there is the influx of high concentrations of crustal dust every year from February to June resulting from dust storms in the deserts and loess plains of Asia, more than 6000 km away. At most times these particles have a uniform composition, but for an 8-week period during the spring of 1980, concentrations of La and Sm (the only REEs that could be observed consistently) were abnormally high, as was the La/Sm ratio. I thought that these observations might be a result of emissions from oil refineries in Japan, over which air masses often pass on the way to Hawaii.

In March, 1985, I visited Japan for a series of lectures, during which I mentioned our REE observations, including speculation about REEs' at Hawaii possibly arising from refineries in Japan. The Japanese didn't know about it, but gave me a lot of data from the Japanese air-monitoring network. As far as I know, Japan is the only country in the world that routinely analyzes samples from a network by INAA and, thus, is able to observe REEs on a regular basis. Their data revealed that the La/Sm ratio was rising steadily over the years, as I had expected. However, we still haven't confirmed that refineries in Japan or elsewhere are the source of the Spring, 1980 REEs at MLO. When I carefully examined the Japanese data along with the MLO data, I could not find enrichments of other elements (e.g., Zn and V) that should have occurred if the air masses were contaminated with emissions from typical industrial areas of Japan.

Another Source of Rare Earths?

After my visit to Japan, Akiro Mizohata, at the Osaka Prefecture Radiation Center, analyzed particles collected from catalyst-regeneration towers of two oil refineries and confirmed our results from the Philadelphia refinery (14). This result was very comforting, as a new observation doesn't mean much until another group observes it independently, especially in this case, where our results were based on a single refinery study. Mizohata went further and analyzed fine particles from various areas of Japan. The Japanese network data I had examined are obtained from filters that are placed behind an inlet that excludes

particles of diam. $>10\ \mu\text{m}$. Both Japan and, for the past two years, the U.S. surveillance networks collect particles of that size range, which are considered to be "inhalable" particles, as those of diam. $>10\ \mu\text{m}$ are considered not to be a threat to human health. Particles of $<10\ \mu\text{m}$, called PM10 in the U.S., are not as dominated by large crustal particles as those collected with a bare filter, so I was able to see some change of the La/Sm ratio in the Japanese network data. But Mizohata could observe these effects more strongly by looking only at fine particles of diam. $<1.5\ \mu\text{m}$. He did indeed see some very high La/Sm ratios, up to 42. However, he saw these ratios not only where expected, in areas near refineries, but also in areas that seemed to be dominated by motor vehicle traffic! He confirmed the association by collecting particles upwind and downwind of a high traffic area.

How could REEs be coming from motor vehicles? Surely there wouldn't be enough zeolite catalyst in the gasoline, the most highly refined of the petroleum products, to account for the observation. He did further studies on tailpipes of individual automobiles and confirmed that large amounts of REE were being emitted from vehicles produced since 1982. One brand of Japanese cars emitted large amounts of both La and Ce, whereas most were dominated by Ce. The answer, as he indicated, was that, in order to meet both the older emissions standards for carbon monoxide and hydrocarbons, as well as the newer standards for nitrogen oxides, the manufacturers had introduced "three-way" catalysts that contain rare earth oxides! Cerium oxide is favored by most manufacturers, as Ce has two prominent oxidation states (unlike most other REEs), so the oxide is a mixture of Ce_2O_3 and CeO_2 , and it can take up or release oxygen as needed, depending on the composition of the exhaust gases.

To Be Continued

It is often said that good research opens more questions than it answers, and that may be the case here. The atmospheric REE story is not complete yet. We thought we had the answer when we discovered REEs coming in large quantities from oil refineries. Mizohata's finding that they also come from motor vehicles complicates the issue, but also offers opportunities. I noted above that we lost our elemental markers for motor-vehicle emissions with the phase-out of leaded gasoline, so we need something else, which may be the REEs. I have looked for evidence for a motor-vehicle source of REEs in the U.S., but there are very few appropriate data, as one must have fine particles analyzed by INAA in an area affected by traffic since 1982. I looked carefully at data from Philadelphia at a site near the New Jersey turnpike, but couldn't see anything unusual when winds came from the Turnpike. Perhaps in 1982 there were too few vehicles equipped with the new catalysts. (As far as we tell, the Japanese

imports to the U.S. have catalysts similar to those sold in Japan. Also, U.S. car companies tell us that they mainly use Ce oxides in their three-way catalysts.) The only other relevant data are from studies in which we participated at Deep Creek Lake in western Maryland in August, 1983 (15), and simultaneous studies conducted at Allegheny Mt. and Laurel Hill, both in southwestern PA, by a group from the Ford Motor Company (16). These data sets also show no clear evidence for REEs from motor vehicles, perhaps a result of the combination of the sites being too rural and too few motor vehicles being equipped with three-way catalysts by 1983.

Ilhan Olmez and I recently received funding from the Extramural Grants Program of EPA to conduct a two-year study of REEs from motor vehicles. We will collect samples in a highway tunnel, near urban streets with high traffic density and from individual vehicles in an attempt to provide definitive answers. Simply observing that REEs are emitted in large quantities from motor vehicles would not suffice to make them good marker elements for motor vehicle emissions. We would need to have some confidence that the marker has some stability, i.e., that the ratio of Ce and/or La emission to miles driven remains reasonably constant for some years. In the study of trace elements on airborne particles, one must be alert to rapid changes. We've seen that the Pb and Br from motor vehicles has essentially gone away. There have been many other changes, e.g., the concentrations of V and Ni in the air of eastern U.S. cities from oil combustion have dropped by more than an order of magnitude since 1970 as an effect of regulation of sulfur emissions.

Also, we still don't have a definite explanation for the enrichment of REEs observed at MLO in the Spring of 1980. Several groups are conducting studies of airborne particles at remote sites in China, Japan and other areas of the Pacific. Perhaps one day that question will be answered, but how many new questions will open up?

The Nature of Research

I hope that I have been successful in demonstrating that research often proceeds by pathways that are much more random than suggested by the classic "scientific method." In this case, our linking of REEs to refineries would have either not happened or occurred years later if one of the seven sources studied in Philadelphia had not been a refinery. There were more than 50 sources on the initial list considered during design of the study, many of them falling by the wayside because of non-cooperation by the source operators. How long would it have taken us to find out about zeolite catalysts had I not spoken to Ivor Preiss? Probably not long, as a lot of literature exists in that field and our Department had a seminar by a scientist from W. R. Grace Co., a leading manufacturer of the catalysts, at

about that time. Actually, after our *Science* paper was published, John Woodward of Exxon sent me a copy of a short letter that had appeared in *Anal. Chem.* in 1984, in which individual particles from two refineries and ambient particles from air near them were subjected to laser microprobe mass analysis (LAMMA) (17). One refinery apparently included a fluidized catalytic convertor, as the authors saw lines for four REEs and their oxides in the mass spectra along with Al and Si oxides. However, it's hard to imagine how we could have known to look at this paper until we had an idea that refineries were the important source. This illustrates a problem of modern science, namely that there is such a huge volume of research in progress that it is difficult to learn about other work related to your own. In contrast, one of the most striking things to me in Rhodes' book was that, in the early 1900's, most prominent chemists and physicists knew each other and communicated informally a great deal. In those days, physicists could deal with all of physics, as they hadn't become specialized into nuclear, high energy, optical and solid state physicists!

Would the Japanese have gotten interested in the problem if I had not visited there in the Spring of 1985? Probably they would have known about it a few months later when our paper appeared in *Science*. Another unique circumstance was the existence of the Japanese sampling network in which samples are analyzed by INAA. Of course, no one would have known about the REEs in Philadelphia had we not analyzed the samples by INAA, as no other method is sensitive enough to see them even as enriched as they are (although XRF did pick up La in samples taken from the refinery stack).

The other fact about research is that the story never seems to end. As noted above, there are still many dangling questions. When they are answered, new questions will probably arise. That's what makes scientific research both exciting and frustrating.

Acknowledgements

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