Reports

Rare Earths: Atmospheric Signatures for Oil-Fired Power Plants and Refineries

Abstract. *The concentration pattern of rare earth elements on fine airborne particles (less than 2.5 micrometers in diameter) is distorted from the crustal abundance pattern in areas influenced by emissions from oil-fired plants and refineries. For example, the ratio of lanthanum to samarium is often greater than 20 compared to a crustal ratio less than 6. The unusual pattern apparently results from the distribution of rare earths in zeolite catalysts used in refining oil. Oil industry emissions perturb the rare earth pattern even at remote locations such as the Mauna Loa Observatory in Hawaii. Rare earth ratios are probably better for long-range tracing of oil emissions than vanadium and nickel concentrations because the ratios of rare earths on fine particles are probably not influenced by deposition and other fractionating processes. Emissions from oil-fired plants can be differentiated from those of refineries on an urban scale by the much smaller amounts of vanadium in the latter.*

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Concentrations of trace elements on airborne particles serve as indicators of the sources of atmospheric materials and are used in receptor modeling to study the histories of air masses (*1*). For example, most airborne Pb in urban areas originates from combustion of leaded gasoline; V and Ni are indicators of oil combustion; and As, Se, and other chalcophile elements are usually associated with coal-fired plants or sulfide ore smelters (or both). Although receptor models have been most used on an urban scale, they have also been used on a global scale to identify sources of Artic haze on the basis of Mn:V ratios (*2*). Because of uncertainties in models designed to predict the transport, chemical reactions, and deposition of gases and particles containing S and N that are associated with acid deposition (*3*), attempts are being made to develop alternate approaches based on receptor models (*4–6*).

The requirements for tracers on a regional scale are more stringent than for those used on an urban scale. During transit over hundreds of kilometers, tracer particles and gases are subject to wet and dry deposition, chemical reactions, and processing by clouds and fogs; such processes can fractionate materials making up the tracer signature. Thus, there is an intense search for tracers that resist modification (robust tracers).

About half the rare earth elements (REE's) are usually observed by instrumental neutron activation analysis (INAA) of atmospheric particulate matter and source materials such as soil, coal, and fly ash (*7, 8*). Although a basic concept of receptor modeling is that the more species observed, the greater the chance of identifying some associated with certain sources or regions, the REE's have largely been ignored. The REE's are chemically so similar to each other and to other lithophile elements that they are not expected to be fractionated by most environmental and combustion processes. Nevertheless, we have often observed variations of REE patterns, as has Rahn (*9*), who found that light REE's are often more abundant relative to the heavy REE's than is predicted by crustal abundance patterns (*10*), especially among fine airborne particles. Rahn felt that REE anomalies might arise from fractionation during high-temperature processes (such as coal combustion) and attempted, unsuccessfully, to correlate enrichments with boiling points of individual members.

Examination of data for REE's reveals that anomalies can be used as a signature of emissions from the oil industry. Concentration ratios of La to other REE's and to V (Table 1) are about the same for coal and crustal material. Data for crude oils are so limited that about all we know is that, compared to coal and crustal material, there are greater amounts of V relative to La (that is, a lower La:V ratio).

We have observed some discrepancies with the crustal REE pattern from examination of a new source-composition library (*11*) and new data on ambient particles. The REE pattern for particles released by coal-fired plants is approximately the same as the crustal pattern, but patterns for oil-fired plants and refineries are strongly depleted in heavy REE's (Table 2). Refineries and oil-fired plants have recently become major sources of REE's. Concentrations of REE's in crude oil are so low that they are difficult to measure, even by INAA. The probable source of the REE is zeolite cracking catalysts, which have come into wide use over the past 15 years and which typically contain 1 to 3 percent mixed REE oxides (*12*). Many changes have occurred in the oil industry in response to oil crises, requirements for low-sulfur fuels in metropolitan areas, and replacement of alkyl Pb in gasoline by aromatics. Refiners have had to produce different mixes of products with certain compositions, increasing the

Table 1. Concentration ratios of La to other REE's and to V in potential atmospheric source materials. REE values for the earth's crust are based on many crustal samples: North American, Japanese, and European shales, Finnish sediments and Russian platform sediments (*27*), and Chinese soils (*23*). The La:V ratio is derived from compilations of crustal abundance patterns (*10*). Uncertainties are standard errors of the mean values.

La: element	Earth's crust	U.S. coals (*28*)		Crude oil (*29*) (n = 6)	Monazite (*30*) (n = 122)	Bastnäsite (*16*) (n = 15)
		Eastern (n = 14)	Western (n = 22)			
Ce	0.50 ± 0.04	0.63 ± 0.02	0.54 ± 0.05		0.51	0.67 ± 0.05
Nd	0.84 ± 0.08				1.3	2.9 ± 0.5
Sm	4.9 ± 0.4	6.1 ± 0.3	9 ± 1	12 ± 16	7.7	26 ± 3
Yb	12 ± 1	20 ± 2	14 ± 1		>240	165
Lu	70 ± 8	90 ± 11	59 ± 5		>240	
V	0.13 ± 0.06	0.45 ± 0.05	0.48 ± 0.04	$(3 \pm 2) \times 10^{-5}$		

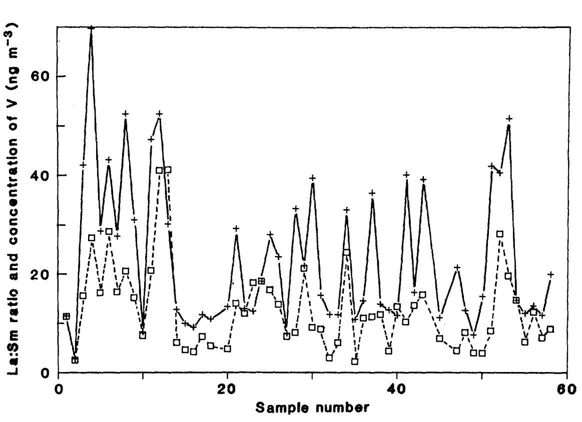

Fig. 1. Concentration of V and La:Sm ratio in 55 successive 12-hour samples of fine particles (<2.5 μm) collected in Camden, New Jersey, from 14 July to 28 August 1982 (*15*). Symbols: (□) V, (+) La:Sm.

need for cracking and reforming of hydrocarbon molecules at the same time that properties of zeolite catalysts were being improved. Most petroleum products now contain some components that have been subjected to the zeolite catalysts.

Although the catalyst is repeatedly recovered and regenerated, an estimated 2000 tons of catalyst material is lost per day by U.S. oil refineries (*13*); some escapes from refinery stacks and some, apparently, is incorporated into petroleum products. These losses account for the estimated 7600 tons of REE's used by the industry yearly (43 percent of the total U.S. use) (*14*). The unusual REE pattern of refinery emissions and of affected petroleum products results not from fractionation during a process but rather from the composition of the REE source material. The two major commercial sources of REE's are monazite and bastnäsite (Table 1), both of which have REE patterns that are different from the crustal ratios. Bastnäsite, a $(Ce,La)CO_3(F,OH)$ mineral, is the major source of REE in zeolite catalysts, and its REE pattern is similar to that of emissions from oil-fired plants and refineries. There is an apparent depletion of Ce (increased La:Ce ratio) in particles from refineries and oil-fired plants relative to bastnäsite, and preliminary analyses of catalyst samples also reveal an increased ratio with considerable fluctuation (3.7 ± 3.6). Perhaps there is some exclusion of Ce during synthesis of the zeolites related to the fact that Ce can have a 4+ oxidation state, whereas other REE's (except Eu) have only 3+.

Much evidence suggests that REE's in catalysts affect the atmospheric REE pattern. Figure 1 shows ratios of La to Sm for a series of samples collected with a dichotomous sampler in Camden, New Jersey, during July and August 1982 (*15*) (a site frequently downwind of refineries and oil-fired power plants in the Philadelphia area) and analyzed by INAA. Although the data in Table 2 indicate that La:Yb and La:Lu ratios would reflect the oil influence more sensitively than the La:Sm ratio, we used the latter because Sm can be measured more reliably than Yb and Lu. Also, a small amount of crustal material with normal ratios of Lu and Yb to La would obliterate signals based on those elements. The La:Sm ratio in Camden usually fluctuates between the crustal ratio of about 5 and the bastnäsite value, which is 36 for ore mined at Mountain Pass, California (*16*). Many La:Sm peaks are accompanied by peaks in the V concentration (Fig. 1), indicating emissions from oil-fired plants; others are not because little V is released by refineries. We focused on fine particles in Philadelphia because about 95 percent of the particulate mass emitted from these sources is in the fine fraction (<2.5 μm in diameter). The coarse fraction would obscure the signal because of REE's from crustal material.

Many data sets provide evidence for the anomalous pattern of REE's. Average La:Sm ratios on air filters collected throughout the Washington, D.C., area in 1976 ranged from 7.0 to 9.2 (*7*). To determine size distributions of particles bearing various elements, Kowalczyk (*17*) collected 17 sets of cascade-impactor data. Coarse particles (>2 μm in diameter) yielded the crustal ratio, but the fine fraction yielded a La:Sm ratio of 17. As part of a receptor model test conducted in Houston, Texas, in 1980 (*18*), Hopke examined particulate samples by INAA that had been previously analyzed by x-ray fluorescence. In Houston, where many refineries are located, Sm was not measured but the La:Al ratio in the fine fraction was 0.012, whereas the crustal ratio is 0.00056. Samples from Shenandoah Valley (*5*) have shown La:Sm ratios of 19 when wind trajectories are from the southeast and of 10 when trajectories are from other directions. Enrichments of V in air masses from the southeast confirmed the influence of oil combustion in that area.

There is also evidence that the REE signature can be used to trace air masses on a global scale. Transport of large amounts of Asian dust to Mauna Loa Observatory in Hawaii has been observed between February and early July of every year since 1979 (*19*). The dust usually has an approximately crustal composition and arises from dust storms in China. However, during 8 weeks in the spring of 1980, dust with an unusually high La concentration was collected. The REE ratios for normal Asian dust are similar to crustal ratios (Table 3), but those observed during 1980 were similar to those associated with petroleum burning. The REE oil signature may have resulted from contamination of the Asian dust by catalysts from industrial areas of Asia. Ten-day back-trajectories were obtained for this period (*19*), but these were uncertain by the time they reached Japan and the coast of Asia. The V concentration was not elevated, suggesting that the material originated from refineries rather than oil-fired plants; however, fraction-

Table 2. Concentration ratios of La to other REE's and to V in particles emitted by three types of sources (*11*). Concentrations are for released particles of all sizes, but there is little variation in the ratios for particles of different size from these sources. For power plants, the results are based on studies of seven coal-fired and eight oil-fired plants, and the number of reported values for each element is listed in parentheses after the concentration. Uncertainties are standard errors of the mean values based on plant-to-plant variations, which are usually much greater than analytical uncertainties, except when a value is available for only one plant, for which sample-to-sample variation or analytical uncertainty is listed. The refinery data are based on analyses of three fine and three coarse particle samples, and uncertainties are standard errors of the mean values.

La: element	Power plants		Refinery
	Coal-fired	Oil-fired	
Ce	0.51 ± 0.04 (7)	1.8 ± 0.2 (8)	1.25 ± 0.01
Nd	1.6 ± 0.15 (2)	2.9 ± 1.9 (2)	1.83 ± 0.02
Sm	5.2 ± 0.5 (6)	28 ± 4 (3)	20 ± 1
Yb	18 ± 4 (4)	135 ± 50 (1)	950 ± 50
Lu	80 ± 17 (3)	1000 ± 500 (1)	5400 ± 350
V	0.30 ± 0.08 (7)	0.045 ± 0.015 (8)	20 ± 3

Table 3. Concentration ratios of La to other REE's and to V in airborne particles collected at Mauna Loa Observatory (*19*). Uncertainties are standard errors of the mean values. Asian dust 1 has the composition of dust normally observed each year from about February to early July; Asian dust 2 has a distinctly different composition and was observed only for an 8-week period during the spring of 1980.

Element	Asian dust 1 composition (n = 20)		Asian dust 2 composition (n = 7)	
	Absolute (parts per million)	Relative (La:element)	Absolute (parts per million)	Relative (La:element)
La	50	1.00	370	1.00
Ce	84	0.64 ± 0.04	95	4.0 ± 0.3
Sm	7.2	6.8 ± 0.3	17	22 ± 1
Yb	3.3	18 ± 1.5	2.2	145 ± 30
Lu	0.54	92 ± 7		1200 ± 400
V	114	0.43 ± 0.03	110	3.4 ± 0.2

ation of V from REE's may have occurred during the long transit time to Mauna Loa. The samples were collected at the observatory with filters; however, virtually all particles that survived deposition during transit had diameters less than 3 μm, allowing the REE signature to be observed. Although high La:Sm ratios were most persistent during the spring of 1980, they were occasionally seen at other times, especially during the summers of 1979 and 1981 (*20*) (these last events were not necessarily due to Asian dust transport).

In support of this interpretation, a feasibility calculation showed that the rate of release of REE-bearing catalyst from Japan or other areas of Asia at about one-third of the rate from the United States could account for the La concentration observed at Mauna Loa Observatory during the spring of 1980. At monitoring stations along the east coast of Japan, the average La:Sm ratio of airborne particles with diameters up to 10 μm rose from 8 in April 1979 to 16 in early 1984 (*21*), suggesting increased release of catalyst. If the upper cutoff diameter were smaller, as for the data of Fig. 1, the ratio would presumably be higher. In contrast, the La:Sm ratio at stations on the west coast of Japan, which is less industrialized and the first to receive dust from China, increased only from 6 to 9 over the same period.

A possible explanation for the abnormal REE pattern is that soil of an unusual composition may occasionally be entrained in China, particularly because a large deposit of bastnäsite is located at Paot'ou, Inner Mongolia, about 500 km west of Beijing, China (*22*). However, there were no abnormal REE patterns among airborne particles from a dust storm on 18 April 1980 that originated in Inner Mongolia, or in soils over which the storm passed on the way to Beijing (*23*). We examined data for many soils, coals, and airborne particles from the Beijing area, including 15 airborne particle samples analyzed in our laboratory, and found no evidence for unusual REE patterns.

In summary, the REE pattern provides an excellent tracer for emissions from oil-fired plants and refineries. Ratios of REE's on fine particles should be a more robust tracer over long distances than those used in the past, because REE's are chemically similar to each other and arise from the same sources. In contrast, for other elemental ratios proposed as regional tracers (*6*), elements in the numerator are chemically different and may originate from sources different from those of the element in the denominator. The REE signature is most useful when size-segregated samples are used to remove crustal particles that would obscure the signature. We attempted to observe the oil signature in air-filter data by subtracting a crustal component, using Al as a measure of crustal material. Statistically significant amounts of noncrustal La were obtained, but differences for Sm were rarely significant and often negative. Furthermore, samples must be analyzed by INAA because other methods are not sensitive enough for accurate REE measurements.

Emissions from other petroleum products, such as diesel fuel, gasoline, home heating oil, rubber, plastics, and petrochemicals, may carry the REE signature. Tires and motor oil display the catalyst signature, but no statistically significant REE's could be associated with motor-vehicle emissions in the Baltimore Harbor tunnel (*24*) or the Allegheny Mountain tunnel (*25*). Thus, it is unlikely that motor-vehicle emissions seriously affect the REE pattern in areas along the east coast of the United States, which are heavily influenced by oil-fired power plants, but the signature could arise from the other sources in western areas. Also, contributions from iron and steel mills must be examined in areas where extensive related industrial sources exist locally. The steel industry uses amounts of REE's comparable to those used by the petroleum industry; however, data from areas strongly affected by iron and steel (*26*) reveal no REE anomalies.

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31. We thank I. L. Preiss for advice about the composition of catalysts containing rare earths, and T. G. Dzubay, R. K. Stevens, and J. A. Cooper for helpful discussions and for permission to quote data on rare earth and V concentrations prior to joint publication. Supported in part by NSF grant ATM-82-19020 and by EPA cooperative agreement CR-806263.

21 March 1985; accepted 9 July 1985