Lanthanoid geochemistry of urban atmospheric particulate matter

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ABSTRACT. Relatively little is known about the lanthanoid element (La to Lu) chemistry of inhalable urban atmospheric particulate matter (PM). PM samples collected during an air sampling campaign in the Mexico City area contain lanthanoid concentrations of mostly 1-10 ng m⁻³, increasing with mass where resuspension of crustal PM is important (low PM_{2.5}/PM₁₀), but not where fine emissions from traffic and industry dominate (high PM_{2.5}/PM₁₀). Samples show anthropogenic enrichment of lighter over heavier lanthanoids, and Ce enrichment relative to La and Sm occurs in the city centre (especially PM₁₀) possibly due to PM from road vehicle catalytic converters. La is especially enriched, although many samples show low La/V values (<0.11), suggesting the dominating influence of fuel oil combustion sources rather than refinery emissions. We use La/Sm v La/Ce, LaCeSm, and LaCeV plots to compare Mexico City aerosols with PM from other cities. Lanthanoid aerosol geochemistry can be used not only to identify refinery pollution events, but also as a marker for different hydrocarbon combustion emissions (e.g. oil or coal power stations) on urban background atmospheric PM.

INTRODUCTION

Fractionation of the lanthanoid elements (La to Lu) has been widely used to investigate geochemical processes in the lithosphere and hydrosphere, but relatively few publications have dealt with the signature of these elements in atmospheric particles. Early interest in the lanthanoid content of atmospheric PM was stimulated by the discovery that emissions from oil refineries using zeolitic fluid catalytic converters (FCC) were enriched in La due to the use of La-concentrates (derived from the ore minerals bastnasite and monazite) within the FCC structure (1-6). The La is released into the atmospheric environment not only directly in FCC regenerator flue gas emanating from the refinery, but also from smokestack emissions when La-contaminated oils are burnt at power stations (7-8). Other documented artificial sources of lanthanoid atmospheric pollution include the manufacture and use of fertilizers (9-10), fugitive dusts from mines (11), steelworks emissions (12), and the use of catalytic converters in road traffic (5, 13-16). Once released from their various sources, such aerosols will join the natural continental background of lanthanoid-bearing atmospheric particles derived from the weathering

44 of rocks and soils (mostly silicate, non-silicate oxide and phosphate minerals). Lanthanoid-bearing, non-
45 marine atmospheric PM will therefore comprise a mixture of crustally-derived minerals and
46 anthropogenic compounds sourced from differing geochemical pathways.

47 Despite the considerable interest demonstrated by the recent publications mentioned above, there
48 remains only limited geochemical information published on lanthanoid-bearing aerosols in urban
49 settings sited away from obvious specific industrial contamination hotspots such as refineries. In this
50 context, we report on the lanthanoid concentrations and fractionation patterns of atmospheric particulate
51 matter collected from the Mexico City area during a sampling campaign in March 2006, and use these
52 data to investigate further the processes that control lanthanoid content of urban aerosols. Note that we
53 use the term lanthanoid elements (La to Lu: as recommended by IUPAC) rather than the commonly used
54 but anachronistic “rare earth elements” (REE, they are neither especially rare nor earths), or
55 “lanthanides” (the suffix “-ide” generally indicates negative ions). By analogy with the accepted notation
56 for REE we further subdivide the lanthanoids into light (LLoid: La to Eu), middle (MLoid: Sm to Ho)
57 and heavy (HLoid: Gd to Lu).

58

59 **EXPERIMENTAL SECTION**

60 The data reported here were collected as part of the Megacity Initiative: Local and Global Research
61 Observations (MILAGRO) project, one of the main objectives of which was improved characterisation
62 of the atmospheric pollution plume emanating from Mexico City (17-22: these references include
63 meteorological details during sampling). The sampling campaign focused in particular on PM₁₀ and
64 PM_{2.5} at three sites named T0, T1 and T2 (Supporting Information Figure S1). T0 lies inside the Mexico
65 City Metropolitan Area (MCMA) on the roof of the Instituto Mexicano del Petróleo (13.5 m high;
66 19°29′22″N, 99°08′22″W, 2243 masl), whereas T1 is just outside the metropolitan limit at Universidad
67 Tecnológica de Tecamac (12m high; 19°42′14″N, 98°57′45″W, 2270 masl), and rural site T2 (PM₁₀
68 only) is at Rancho La Bisnaga (2m high; 20°01′14″N, 98°54′09″W, 2542 masl (21). Sampling period
69 lasted for 12 hours (08-20.00 and 20.00-08.00 local time), with average PM₁₀ day/night levels being

51/50 $\mu\text{g m}^{-3}$, 94/66 $\mu\text{g m}^{-3}$ and 36/31 $\mu\text{g m}^{-3}$ at T0, T1 and T2 respectively (21). Sites were equipped with high volume samplers fitted with cutoff inlets for PM_{10} (Wedding, 68 $\text{m}^3 \text{h}^{-1}$) and $\text{PM}_{2.5}$ (MCV, 30 $\text{m}^3 \text{h}^{-1}$), and samples were collected on quartz micro-fiber filters with high collection efficiency, which were conditioned ($50 \pm 4\%$ humidity and 22 ± 3 °C for 48 h) prior to gravimetric determination of PM mass. Filters were Pallflex rectangular (203 mm x 254 mm) in all cases except for $\text{PM}_{2.5}$ collection at T0 where they were QF20 Schleicher&Schuell circular filters (150 mm). Trace element concentrations were determined in bulk sample acidic digestions ($\text{HF}:\text{HClO}_4:\text{HNO}_3$) using ICP-MS (details in 23). In order to check data quality, relative analytical errors were estimated using small amounts (5 mg) of the NIST-1633b (fly ash) reference material loaded on a 1/2 quartz micro-fibre filters. In addition four blank filters were analysed every 30 samples. Thus relative errors reached values of 10% for most elements, with the exception of P and K (15%).

81

82 RESULTS AND DISCUSSION

83 **Lanthanoid concentrations and sample mass.** Concentrations of total lanthanoid (ΣLoid) in our PM
84 samples mostly lie within the range 1-10 ng m^{-3} (Supporting Information Table S1), with the higher
85 values ($>5 \text{ ng m}^{-3}$) occurring in the coarser fraction (PM_{10}) at T1 but in examples of both coarser and
86 finer PM at the city centre site T0 (Figure 1). Lanthanoid element concentrations in the T0 $\text{PM}_{2.5}$
87 samples show wide variation from <1 to $>10 \text{ ng m}^{-3}$, whereas at T1 the $\text{PM}_{2.5}$ concentrations are usually
88 much lower and the range more limited (1-4 ng m^{-3}) than PM_{10} . Thus, whereas there is no correlation
89 between ΣLoid concentration and particle size or sample mass at T0 (Figure 1a), at T1 the coarser
90 samples (PM_{10}) normally have both higher mass (due to more soil exposed, the slightly lower sampling
91 height off the ground, and stronger afternoon winds) and higher lanthanoid content (Figure 1b). Plotting
92 the limited PM_{10} data from site T2 reinforces the trend on Figure 1b, these rural samples usually being
93 low in mass and therefore lying at the lower end of the PM_{10} range. The T2 sample with the highest
94 mass (60 $\mu\text{gPM}_{10} \text{ m}^{-3}$) was collected on a day when this site received a direct intrusion of the MCMA
95 plume from the city centre to the south (21).

96 The observation that lanthanoid concentrations in PM_{2.5} can range up to > 10 ng m⁻³ at T0 is
97 presumably linked to the fact that at this site PM_{2.5}/PM₁₀ ratios are typically high both during the day
98 (0.81) and night (0.77), indicating a permanent dominance of fine particles in the city centre (21, 23). In
99 contrast, at T1 average PM_{2.5}/PM₁₀ values lie below 0.5, being lowest during the day when high PM
100 mass levels are commonly generated by afternoon aeolian resuspension of local surface sediments
101 (mostly clays and other silicates) at this suburban site (21). Thus we attribute the link between ΣLoid
102 concentrations and mass at T1 as due primarily to the resuspension of lanthanoid-bearing PM, whereas
103 at T0 it appears that fine anthropogenic primary emissions have a greater influence on lanthanoid
104 abundance.

105 **Lanthanum enrichment.** The atomic number of the lanthanoid elements increases progressively
106 from 57 (La) to 71 (Lu), accompanied by a contraction of the ionic radii and by the filling of the 4f
107 electron shell (as far as Yb). The subtle geochemical differences between the lighter and heavier
108 lanthanoids have concentrated the former in the Earth's crust, so that in crustal materials the light
109 lanthanoids Ce and La are respectively 10 and 5 times more common than Sm, which is in turn nearly
110 twice as abundant as Yb (8). Another key difference between the lanthanoids is that odd-numbered
111 elements are less abundant than their even-numbered neighbours (the Oddo-Harkins Rule), explaining
112 why Ce (atomic number 58) is twice as common as La (atomic number 57). Thus in most crustal
113 materials, such as natural dusts, the commoner lanthanoids occur in the following order of abundance:
114 Ce > La > Nd > Sm > Yb. An immediate indication that lanthanoid abundances in our samples are not
115 entirely "natural" in origin is demonstrated by the fact that not all show this crustal order of abundance.
116 Instead, La values are commonly elevated, in several cases to the point where this element is actually
117 more abundant than Ce (around 20% of samples in Supporting Information Table S1).

118 Lanthanum is even more enriched with respect to each of the other, heavier lanthanoids (see Figure
119 S2a-c in Supporting Information), in a small minority of PM₁₀ samples this enrichment being extreme
120 and accompanied by La concentrations rising to over double those of Ce (Table S1). Figures 2Sa-c also
121 show that the La/Ce value of these samples tends to deviate slightly less from the crustal trend than do

La/Sm and La/Yb. This is especially the case with the data from the city centre site T0, around half of which show La/Ce values <0.6 (Supporting Information Table S1). The deviation from crustal La/Sm and La/Yb values in these samples (with ratios ranging from 10.1-16.6 and 0.6-1.1 respectively) demonstrates a clear fractionation of LLoid over the MLoid and HLoid elements in our atmospheric PM data, in comparison with lithospheric compositions.

Cerium enrichment. The fractionation of LLoid elements in the MCMA atmosphere, shown so clearly for La, is also demonstrated by Ce with respect to the heavier lanthanoids. Thus the T1 samples show a clear separation between PM₁₀ and PM_{2.5} when comparing Ce with Nd, Sm and Yb (see Figure 2Sd-f in Supporting Information), whereas this is lacking at T0. There is also a tendency towards favouring Ce over other lanthanoids in the PM₁₀ samples from T0. This Ce-enrichment with respect to its LLoid neighbour La at T0 is further discernable on Figure 2 which plots the lanthanoid ratios La/Sm and La/Ce for all samples. A majority of T0 points plot above and/or to the left of the area containing samples from T1. Another difference between T1 and T0 data shown on Figure 2 is that at T0 the coarser samples (PM₁₀) mostly show greater La enrichment with respect to Sm than do the finer samples (PM_{2.5}). Overall our plots suggest that atmospheric PM in the city centre site tends to contain more Ce relative to La, and more Ce relative to Sm in the PM₁₀ fraction, than at the more peripheral site T1. In several cases this relative Ce enrichment is enough to reduce La/Ce values below natural crustal values. Also shown on Figure 2 are published lanthanoid data from four other urban-industrial areas (Philadelphia (3, 7), Washington (24), Houston (6), and Delft (25)). These data spread from near-crustal compositions, such as the pre-FCC refinery Washington data, to highly La-enriched refinery-contaminated PM in recent data from Houston. The Mexican data show a similar trend and range, although with the slight displacement towards lower La/Ce values.

The relative lack of Sm in the coarser fraction and slight enhancement in Ce at T0 is further illustrated by Figure 3. Triangular diagrams such as Figure 3 are commonly used by geologists to depict 3-component variations in lithospheric minerals and rocks, and can equally be employed to illustrate geochemical variations in atmospheric PM (e.g.26). Figure 3 compares La, Ce and Sm, with

148 concentrations adjusted to place crustal abundances of these elements in the centre of the triangle. The
149 anthropogenic nature of LaCeSm compositions are clearly shown by the displacement towards La and,
150 to a lesser extent, Ce on Figure 3a. Figure 3b compares our samples with the aforementioned urban data
151 on Figure 2, adding emissions from refinery FCC (5), coal and oil combustion (4), and compositions of
152 common upper crustal felsic to andesitic igneous rocks and siliciclastic sediments (27) that are
153 ultimately the source of most crustal PM present in the atmosphere. Whereas the latter predictably
154 cluster around the centre of the triangle (close to UCC), the anthropogenically polluted samples spread
155 out towards the La apex. The most extreme La-enrichment is demonstrated by the refinery-influenced
156 samples, but there is overlap between these and emissions from oil combustion: in order to separate
157 these it is necessary to consider V concentrations.

158 **Lanthanum v Vanadium.** Atmospheric particles derived from uncontaminated surface sands, silts
159 and muds would be expected to show La/V values of 0.25-0.5 (27-30). Industrial atmospheric PM
160 emissions, in contrast, commonly show La/V values that deviate strongly from crustal values, mainly
161 due to the combustion of heavy hydrocarbons. The use of high sulphur oils in power plants, for example,
162 produces residual oil fly ashes (ROFA) that can contain over 5 wt% V, which is concentrated by a factor
163 of 3 or more in PM_{2.5} rather than PM₁₀ (31). La/V values in PM_{2.5} emissions from oil power plants are
164 therefore typically extremely low (0.10 or less), as compared to those from coal fired power stations
165 (0.2-0.3: 1, 4) and crustal PM. Vanadium content of atmospheric PM samples offers a possible way of
166 distinguishing between oil power plant emissions and those emanating from refineries because whereas
167 both are enriched in La, PM in FCC refinery regenerator flue gas do not have raised V content. Ambient
168 PM_{2.5} measured in areas directly contaminated by refinery emissions thus show elevated La/V values, as
169 recently demonstrated for example by Kulkarni et al. (6) who recorded average PM_{2.5} La/V values of 1.8
170 at a sampling site lying some 8 km from a refinery in Houston, Texas. Their measurements at this site
171 took place during a prominent FCC emission event, with La values averaging a remarkable 32.5 ng m⁻³.
172 This may be compared to an average La concentration of just 1 ng m⁻³ at our Mexico City T0 collecting
173 site.

Our data from Mexico City show atmospheric La/V values generally well below the “natural” values expected from surface crustal materials, usually being <0.2 , with half of the samples registering 0.10 or less (Table S1). This suggests the dominance of anthropogenic emissions from industries (e.g., oil combustion) releasing low La/V PM rather than from refineries. Even on those days when unusually high La levels were recorded, La/V values usually remained well below any value that might be linked to direct refinery emissions (Table S1). This V enrichment (relative to LLoid elements) can be illustrated using a 3-component LaCeV plot (Figure 4), with lanthanoid values again multiplied so that upper continental crustal compositions plot as equal proportions for all three elements. This plot omits Ce compositions $>50\%$ and is analogous to the clinopyroxene MgCaFe plot used in igneous petrology. For comparison, we have added to this plot published industrial and traffic PM data. Our T0, T1 and T2 data define a field that extends away from crustal compositions at the centre of the triangle towards the V apex, reflecting the contamination by anthropogenic PM with low La/V. Several of the T0 data points define a linear trend consistent with the mixing of crustal and/or traffic PM with oil power station emissions: these are the PM relatively enriched in Ce seen on Figure 2. Other compositions plot away from this linear trend in the direction of La rather than Ce, presumably reflecting other sources such as metallurgical emissions. Lanthanum-bearing steel (added to improve malleability, resistance to impact, and ductility), for example, may explain the raised La content of the electric furnace scrap metal steelworks PM analyzed by Lahd Geagea et al. (12) (Figure 4a). At T1 most of the finer emissions plot towards to the V apex, whereas the coarser fraction contains relatively higher lanthanoid content and plot closer to crustal compositions. The lack of any strong influence from refinery smokestack plumes is again clear, and instead we interpret the distributions on Figure 4a as consistent with a mixture of PM from industries involving hydrocarbon combustion (plus others such as metallurgical plants), crustal background, and traffic emissions. Note that traffic activity produces much resuspension of crustal PM and on this diagram would be expected to produce compositions close to the triangle centre, although perhaps displaced slightly towards Ce due to abrasive loss of Ce-bearing PM from catalytic converters.

199 Finally, Figure 4b shows the compositional fields for our MCMA data and superimposes the
200 published urban-industrial PM data used on Figure 3. Also plotted for comparison are the “asian dust”
201 samples collected on Mauna Loa, Hawai’i by Olmez and Gordon and separated into uncontaminated and
202 La-contaminated subgroups (*I*). The influence of low LaCe/V PM is very clear in the Philadelphia,
203 Washington and Delft data, all of which cluster close to the V apex. Similarly those Houston data less
204 influenced by refinery emissions also plot close to V, whereas those samples collected during the local
205 FCC pollution episode mentioned earlier are drawn towards the La apex on Figure 4b (6).

206 **Controls on urban lanthanoid PM.** The analyses presented in this paper provide, to our knowledge,
207 the largest database published so far on atmospheric lanthanoid concentration measurements in an urban
208 area. These data provide some insight into the controls on trace element geochemistry in such materials.
209 The influence of anthropogenic emissions is obvious: natural crustal ratios between the lanthanoids are
210 strongly perturbed, with a clear preference for the lighter elements in the series. Thus the geochemical
211 fractionation of the more incompatible lanthanoids from asthenosphere to lithosphere continues into the
212 urban atmosphere, increasing L_{Loid}/M_HL_{oid} values above those of lithospheric levels in most of our
213 PM samples. Lanthanum in particular is strongly concentrated relative to the other lanthanoids,
214 sometimes to the point where its concentration exceeds that of Ce. Given the very low La/V values
215 typical of our data, we attribute this pervasive La enrichment of the urban atmosphere primarily to the
216 burning of fuel oils previously contaminated by FCC technology in refineries, rather than to refinery
217 emissions directly (the closest such site being the Tula petrochemical industry around 60 km NNW of
218 MCMA). However, bearing in mind the fact that Baez et al. (32) have recently quoted statistics
219 reporting some 30,000 industries in the area, significant contributions from sources additional to oil
220 fired power stations are likely.

221 In the city centre finer aerosols are more common, presumably due to proximal emissions from local
222 traffic and industry, and diminished resuspended PM₁₀ (especially given the 13.5 m height of the
223 sampling site above street level). The lanthanoid burden of such fine aerosols is highly variable, but can
224 be high, sometimes exceeding 10 ng m⁻³ in PM_{2.5}, whereas away from the city centre at T1 our PM_{2.5}

measurements were always less than half this amount. Instead, lanthanoid content at T1 is broadly proportional to PM mass, a relationship which we attribute to the dominance of resuspension processes. Another difference we detect between T0 and T1 is that the city centre site shows a subtle relative preference for Ce, especially in the PM₁₀ fraction. We suggest that is due to the presence of traffic particles derived from the thermal and mechanical wear of catalytic converters (CAT), already well documented by increased PGE PM in Mexico City (34). Kitto et al. (7) first commented that the La/Ce value in traffic-contaminated PM might be reduced due to CAT emissions, and Gomez et al. (15) have demonstrated a positive correlation between Pt and Ce in airborne PM from Madrid, Spain. CAT particles typically contain extremely low La/Ce values (33), with most of the inhalable fraction being in the coarser PM₁₀ rather than PM_{2.5} fraction, but their presence is masked by road dust resuspension (16). Rather than seeking significant increases in absolute abundances of Ce in road dusts, detection of small increases in lanthanoid-bearing PM emanating from vehicle catalysts has a better chance of success if comparisons are made between lanthanoid elements, using the kind of approach employed in Figures 2-4. In this context, we have also emphasized the slightly higher La/Sm values in the PM₁₀ (mostly >15) as compared to PM_{2.5} (mostly <15) at T0 (Figures 2 and 4c). This may also be due to CAT contamination, given that La/Sm values associated with catalysts and their emissions are greatly elevated above crustal values (5, 13, 16). Although high La/Sm values can also be explained by fuel oil combustion, this would be expected to increase more in the finer not the coarser PM fraction.

The amount of crustal PM present in urban air will depend on controlling factors such as climate, traffic resuspension, construction activity, dust intrusions blown in from surrounding and more exotic sources, and so on. The data suite from Mexico City is consistent with a crustal influence on lanthanoid geochemistry, but one which is strongly overprinted by anthropogenic emissions. The resulting mixture of crustal and anthropogenic compositions produces a range of trace element compositions that can be illustrated as fields on diagrams such as Figures 3b and 4b. Our compositional field for the Mexico City basin is broad, ranging from crustal compositions to those more typical of coal and oil combustion. Those data plotting close to the V apex seem to be similar to ambient air samples analyzed from North

American and European cities (3, 6, 7, 24, 25), together providing some evidence that fuel oil combustion may have a pervasive influence on urban PM lanthanoid geochemistry worldwide. These low La/V samples are likely to contain large amounts of ROFA particles, which, according to our data set, would be especially common in both the city centre and in the finer (further travelled?) PM collected at T1. In cities where coal rather than oil burning is the dominant form of energy production, such as Beijing, China (34), lanthanoid and La/V values will be more crustal in character, potentially confounding the geochemical separation of anthropogenic and natural PM using LaV plots. Other, more unusual anthropogenic contributions to urban atmospheric PM include those from refinery smoke plumes, detectable from their high La content combined with high La/V, or from other important point sources such as steelworks or ceramic industries. Whatever the mixture of particles in a given urban air sample, we conclude that study of its lanthanoid element geochemistry can provide a useful contribution to understanding the sources of atmospheric pollution.

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SUPPORTING INFORMATION AVAILABLE

Description of the sampling equipment, and methodology used for chemical analysis. One table with all analytical results and two figures: Figure S1 being a map for sampling location, and Figure S2 plotting lanthanoids ratios (La/Ce, La/Sm, La/Yb, Ce/Nd, Ce/Sm, Ce/Yb) for all data in this paper, showing La and Ce enrichments relative to upper crustal ratios. This information is available free of charge via the Internet at <http://pubs.acs.org>.

276

277 **FIGURE 1.** Total lanthanoid concentration versus the mass of sample collected at site T0 (**1a**) and sites
278 T1 and T2 (**1b**). See text for discussion.

279

280 **FIGURE 2.** La/Sm v La/Ce plot for all data in this paper and those published from four other cities (3,
 281 6, 24, 34) comparing them to UCC (Upper Continental Crust, 28), showing the tendency towards Ce
 282 enrichment relative to La at T0, and La enrichment relative to Sm in the coarser fraction (PM₁₀) at T0.
 283 See text for discussion.

284

285 **FIGURE 3.** Three-component CeLaSm plot for all data in this paper (3a) and cities shown on Figure 2
 286 plus common rock types (27) (3b), with values adjusted so that upper continental crustal compositions
 287 (UCC: 28) plot in the centre of the triangle. Note that the Washington data predate the use of FCC in
 288 refineries, and group close to the “crustal” centre. See text for discussion.

FIGURE 4. Three component CeLaV with values adjusted so that upper continental crustal compositions (UCC, 28) plot in the centre of the triangle. **4a:** Data from this paper plus PM compositions published from oil and coal combustion (4), steelworks (12), refinery fluid cracking catalysts (5), and traffic emissions (35), and compositions of fluid catalytic converters (6). **4b:** Comparison of T0, T1 and T2 (shadow area) with data from "asian dust" (1), and the four cities shown in previous figure (3, 6, 24, 34), emphasizing the areas where crustal, refinery and oil related emissions should plot. Note that the Washington data predate the use of FCC in refineries (see Figure 3b).

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