Contamination in the Rare-Earth Element Orthophosphate Reference Samples

1. Introduction

Highly accurate analyses from the electron microprobe analyzer (EMPA) are only (but not solely) obtainable through the use of well-characterized and stable standards containing a major and/or known concentration of the element in question. For the rare earth elements (REE) this goal has, until recently, been elusive due to the lack of specimens exhibiting these vital properties.

The lanthanide orthophosphates, consisting of compounds with the stoichiometry LnPO₄ where Ln represents any of the REE in the series extending from La to Lu (plus the related compounds YPO₄ and ScPO₄), are...
chemically durable and radiation resistant refractory materials. During the early 1980s a variety of single crystal rare earth orthophosphate samples were synthesized at Oak Ridge National Laboratory and the structures determined from x-ray refinements [1, 2, 3, 4, 5, and 6]. The primary purposes of these studies were varied, but they included nuclear and actinide waste disposal and scintillator material research as well as fundamental materials characterization investigations. The crystals were synthesized using a high-temperature solvent (flux-growth) technique, the details of which are available from the original papers, and a good overview of the development of these orthophosphates is discussed in Boatner and Sales [7], and references therein.

One interesting fact is that although the starting materials were carefully selected to be free from REE impurities, they were grown in a lead pyrophosphate (PbHPO₄) flux. Pb contamination was not a concern for the original purposes of those experiments, however its presence was detected early on, and the solid state chemistry (but not the concentration) of Pb in the orthophosphate was characterized by means of electron paramagnetic resonance spectroscopy (EPR) [8]. Subsequently, these materials were investigated for possible use as standards for EPMA by the Smithsonian Institution [9], and put through a series of tests. These included homogeneity testing and a comparison to the commonly used REE doped aluminum silicate glass standards of Drake and Weill [10] using the EPMA, and a check of 10 selected REE contaminants on 7 of the compounds using instrumental neutron activation analysis. The materials appeared to be robust under electron bombardment, did not oxidize or seem hygroscopic, and no serious contamination or inhomogeneities were noted at the time and these efforts were followed by a general distribution of the material to interested parties.

In the late 1990s it was reported to one of us (JJD) that at least one investigator (E. J. Essene, University of Michigan, personal communication) had raised the issue of the role of the Pb impurity in some of the REE phosphate standards. The Pb impurity is exceptionally significant in the CePO₄ crystals whose black coloration is consistent with possible mixed valence (Ce³⁺ – Ce⁴⁺) effects—the presence of which could alter the high-temperature solid-state chemical properties and lead to an enhanced incorporation of Pb during the crystal-growth process. Subsequent investigations of the materials revealed Pb ranging in concentration from less than 0.01 mass fraction to more than 0.04 mass fraction in the CePO₄, depending on the specific grains analyzed. It is the intent of this paper to characterize the extent of the Pb contamination in these otherwise extremely useful standards for EPMA.

2. Experimental Methods

Quantitative wavelength dispersive spectrometry (WDS) analyses for the REEs Sc, Y, and Pb in each of the 16 orthophosphate samples were done using a Cameca SX-51¹ electron microprobe at 20 keV, 20 nA (2.0 × 10⁻⁸ A), using a 10 μm beam diameter at UC Berkeley. In addition, one of the Drake and Weill REE glasses [10], and two other REE doped calcium aluminum silicate discussed in Roeder [11] and Roeder et al. [12] were analyzed. For quantitative analyses, the Kα x-ray line was used for Sc, La, Ce, Pr, Nd, Sm, Dy, Ho, Er, Yb, and Lu, and the Drake and Weill REE-1 glass was used based on published concentrations for Eu, Gd, Tb, and Tm [10]. For all rare-earth elements, the relative differences obtained when comparing the secondary standards to the primary standard is better than 10 % at the 0.01 mass fraction to 0.04 mass fraction concentration levels and better than 6 % in all but three cases (Pr, Sm and Lu).

The difficulty of dealing with interfering elements for REE analyses using the Lα x-ray lines is painfully evident in even cursory WDS spectral scans on these samples and can only be overcome by careful and consistent application of an automatic correction scheme. Table 2 shows the REEs that interfere with the analyzed elements. These were interferences quantitatively corrected for using the iteration method of Donovan et al. [13], that is especially well suited for using large magnitude interferences for trace element determinations. For the Pb analyses, the Mα line was used with a quantitative interference correction for Y (possible high order interferences from La and Tb were not observed). Standard

¹ NIST disclaimer: Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.
Table 1. Analytical setup and measured differences between the secondary standards and the primary standard for REE quantitative analysis

| Element | Spect. setup | Primary standard | Secondary standard | Relative diff. |
|---------|--------------|------------------|-------------------|---------------|
| Sc Kα  | LiF (FPC-2)  | YPO₄ (syn.)      | YAG (stoic.)      | +0.368, +0.82 % |
| La Lα  | LiF (FPC-2)  | LaPO₄ (syn.)     | S-254 (1.04 nom.) | −0.020, −1.92 % |
| Ce Lα  | LiF (FPC-2)  | CePO₄ (syn.)     | S-254 (1.04 nom.) | −0.010, −0.95 % |
| Pr Lα  | LiF (FPC-2)  | PrPO₄ (syn.)     | S-254 (1.04 nom.) | −0.103, −9.95 % |
| Nd Lα  | LiF (FPC-2)  | NdPO₄ (syn.)     | S-254 (1.04 nom.) | −0.007, −0.70 % |
| Sm Lα  | LiF (FPC-2)  | SmPO₄ (syn.)     | S-254 (1.04 nom.) | −0.055, −5.27 % |
| Eu Lα  | LiF (FPC-2)  | EuPO₄ (syn.)     | REE-1 (3.63 pub.) | +0.069, +1.90 % |
| Gd Lα  | LiF (FPC-2)  | GdPO₄ (syn.)     | REE-1 (3.87 pub.) | −0.012, −0.31 % |
| Tb Lα  | LiF (FPC-2)  | TbPO₄ (syn.)     | REE-1 (3.78 pub.) | −0.116, −3.08 % |
| Dy Lα  | LiF (FPC-2)  | DyPO₄ (syn.)     | S-254 (1.04 nom.) | −0.035, −3.35 % |
| Ho Lα  | LiF (FPC-2)  | HoPO₄ (syn.)     | S-254 (1.04 nom.) | −0.041, −3.92 % |
| Er Lα  | LiF (FPC-2)  | ErPO₄ (syn.)     | S-254 (1.04 nom.) | −0.047, −4.51 % |
| Tm Lα  | LiF (FPC-2)  | TmPO₄ (syn.)     | REE-1 (3.81 pub.) | −0.127, −3.33 % |
| Yb Lα  | LiF (FPC-2)  | YbPO₄ (syn.)     | S-254 (1.04 nom.) | −0.047, −4.53 % |
| Lu Lα  | LiF (FPC-2)  | LuPO₄ (syn.)     | S-254 (1.04 nom.) | −0.103, −9.94 % |
| PbMα  | PET (FPC-1)  | PbCO₃ (Tsumeb)   | PbSiO₃ (stoic.)   | +0.550, +0.75 % |

*Analytical spectrometer setup (flow proportional detectors: FPC-1 indicates 1 atm P-10 and FPC-2 indicates 2 atm P-10) for REE elements (plus Sc, Y, and Pb) and results of secondary standard measurements (algebraic difference and relative difference) performed at UC Berkeley. All elements were measured at 20 keV, 20 nA (150 nA for the four grain map), 10 s each. Count times were 60 s on peak, and 30 s for off-peak except for Pb which was counted for 40 s on-peak and 20 s on each off-peak position (240 s on-peak and 120 s on each off-peak position for the four grain map in Fig. 5). Each result shown is the average of 10 measurements.

and background intensities along with the calculated \( P/B \) (peak to background) for each line in its associated primary standard are shown in Table 3. Under the analytical conditions which were utilized at Berkeley, the minimum detection limits for both single analyses calculated from Love and Scott [14], and for the average of 10 replicate analyses based on Goldstein et al. [15], are shown in Table 4. Minimum detection limits for 10 replicate analyses based on the actual measured standard deviation are about 3.0 \( \times 10^{-4} \) mass fraction to 6.0 \( \times 10^{-4} \) mass fraction for all elements in all matrices although only values for CePO₄ or GdPO₄ are shown in Table 4. A measured detection limit of 3 \( \times 10^{-4} \) mass fraction to 6 \( \times 10^{-4} \) mass fraction for the average of 10 replicates at 99% confidence level was typical for the REE analyses under these conditions. The Pb detection limit at a 99% confidence level was about 4.5 \( \times 10^{-4} \) mass fraction.

Another set of measurements, for the analysis of Pb homogeneity only, were also done on the same grains, but in a different area from the REE and Pb measurements done at UC Berkeley. These measurements were made for each REE orthophosphate using a JEOL 8900 Superprobe at the University of Maryland-College Park. X-ray intensities of Pb were obtained using an accelerating voltage of 20 keV, and a beam current of 150 nA. Count times were 60 s on peak, and 30 s for backgrounds on each side of the peak. Pb was analyzed using a PETH (which utilizes a smaller diameter Rowland Circle allowing for higher count rates, but has poorer wavelength resolution) crystal, and background positions of +4 mm (\( L = 173.307 \) mm or 5.4013 Å) and −3 mm (\( L = 166.307 \) mm or 5.1828 Å). Natural cerussite (PbCO₃) from Tsumeb, Namibia, was used as a standard for Pb (0.8393 mass fraction PbO). It should be noted that although cerussite is a carbonate mineral it did not appear to degrade under the electron beam during the analyses. The Pb Mα x-ray line was used for all analyses, with the exception of YPO₄, where Mβ was used due to an interference from YI₂ on Pb Mα. For these Pb homogeneity measurements, the REE and phosphate concentrations were not measured but were incorporated as stoichiometric proportions into the ZAF algorithm in order to approximately account for matrix effects. The single analysis detection limit at a 99% confidence level for Pb under these analytical conditions was about 1.4 \( \times 10^{-4} \) mass fraction Pb based on a standard count rate of 263.9 cps/nA and a background of 0.8 cps/nA measured on CePO₄.

Measurements were done on two different sets of REE orthophosphate samples. The first set consists of material for 16 orthophosphates, including Sc and Y obtained from one of us (JMH) and mounted along with primary and secondary standards for analysis and interference corrections. These materials were mounted in a 25 mm diameter acrylic mount approximately 1.5 cm deep using a cold set epoxy and circulated to both laboratories. This sample will be referred to as the “Round Robin” mount in the discussion that follows.
Table 2. Quantitative interferences. Also listed are the wavelengths (in Å) of the x-ray lines

| Element | On peak interferences | Å | Å |
|---------|-----------------------|---|---|
| ScKα at 3.0320 | ErLγ (II) at 3.0284 |   |   |
| YLLα at 2.6657 | LaLγ (III) at 6.4260 (not observed) |   |   |
| LaLγ at 2.6657 | NdLα (I) at 2.6766 |   |   |
| CeLα at 2.5615 | PrLα at 2.4630 | LaLγ (I) at 2.4595, 2.4595 | SmLα (I) at 2.4826 |
| NdLα at 2.3704 | CeLγ (I) at 2.3566, 2.3499 |   |   |
| SmLα at 2.1998 | CeLα (I) at 2.2092 | PrLα (I) at 2.2175 (not observed) |   |
| EuLα at 2.1209 | NdLγ (I) at 2.1273 |   |   |
| GdLα at 2.0468 | CeLβ (I) at 2.0489 | LaLγ (I) at 2.0462, 2.0415 | NdLγ (I) at 2.0365 |
| TbLα at 1.9765 | LaLα (I) at 1.9834 | PrLα (I) at 1.9614 (not observed) | SmLα (I) at 1.9627 (not observed) |
| DyLα at 1.9088 | EuLγ (I) at 1.9207, 1.9258 | YbLγ (I) at 1.8946 (possibly observed) |   |
| HoLα at 1.8450 | GdLγ (I) at 1.8472, 1.8543 | LuLα (I) at 1.8362 (not observed) |   |
| ErLα at 1.7842 | TbLγ (I) at 1.7770, 1.7867 | NdLγ (I) at 1.8015, 1.7968 |   |
| TmLα at 1.7268 | DyLγ (I) at 1.7110, 1.7212 | GdLγ (I) at 1.7457 |   |
| YbLα at 1.6718 | EuLβ (I) at 1.6577 | SmLα (I) at 1.6608 | TbLα (I) at 1.6834 |
| LuLα at 1.6195 | HoLβ (I) at 1.6580 (possibly observed) | YKγ (II) at 1.6580 (possibly observed) | HoLγ (I) at 1.6597 (not observed) |
| PbMα at 5.2860 | YLα (I) at 5.2848 | LaLγ (I) at 5.3326 (not observed) | TbLα (II) at 5.3310 (not observed) |

* Analyzed elements and interfering elements were quantitatively corrected by using the iteration method of Donovan et al. [12]. Many of these interferences are 1st order interferences and therefore are the same energy as the interfering line, and hence, cannot be reduced by the use of pulse height analysis (PHA). Selection of alternative (beta) lines is sometimes possible, but the resulting reduction in intensity will also reduce sensitivity.

The “Round Robin” mount was carefully analyzed for Pb at both Berkeley and College Park to check for inter-laboratory differences since the analytical results of trace element measurements are extremely sensitive to differences in spectrometer resolution and placement of off-peak intensity measurement positions. Homogeneity measurements were also done on this mount at College Park to check for possible Pb variations within this material itself.

Additional Pb measurements were performed at UC Berkeley on other material that was originally resident in the laboratory standard collection to check for possible inter-batch differences in Pb contamination some of the material had been produced in several runs at Oak Ridge under possibly different growth conditions. Analyses on this material will be referred to as the “Berkeley” REE mount.
Table 3. Standard peak and background intensities (linear interpolation method) *

| Element | Peak intensity (cps/nA) | Background intensity (cps/nA) | Peak/Background |
|---------|-------------------------|-------------------------------|-----------------|
| ScK     | 49.3 (ScPO₄)           | 0.2                           | 246.5           |
| YL      | 68.3 (YPO₄)            | 0.5                           | 136.6           |
| LaL     | 38.5 (LaPO₄)           | 0.3                           | 128.3           |
| CeL₆₇   | 45.4 (CePO₄)           | 0.5                           | 90.8            |
| Pr₆     | 55.1 (PrPO₄)           | 0.6                           | 91.8            |
| NdL₆₇   | 64.9 (NdPO₄)           | 0.6                           | 108.1           |
| SmL₆₇   | 80.8 (SmPO₄)           | 1.3                           | 62.2            |
| EuL₆₇   | 89.6 (EuPO₄)           | 1.1                           | 81.5            |
| GdL₆₇   | 95.2 (GdPO₄)           | 1.2                           | 79.3            |
| TbL₆₇   | 101.9 (TbPO₄)          | 1.3                           | 78.4            |
| DyL₆₇   | 107.8 (DyPO₄)          | 1.5                           | 71.9            |
| HoL₆₇   | 113.6 (HoPO₄)          | 2.2                           | 51.6            |
| ErL₆₇   | 119.5 (ErPO₄)          | 2.1                           | 56.9            |
| TmL₆₇   | 122.9 (TmPO₄)          | 2.5                           | 49.2            |
| YbL₆₇   | 128.0 (YbPO₄)          | 2.6                           | 49.2            |
| LuL₆₇   | 131.3 (LuPO₄)          | 3.4                           | 38.6            |
| PbM₆₇   | 72.0 (PbCO₃)           | 0.6                           | 120.0           |

* Average peak and background intensities measured on the primary standards for the analyzed elements along with calculated peak to background ratios. Off-peak positions were based on high-resolution spectral scans of the low to high off-peak regions of each REE element and Pb in each of the REE phosphates. The purpose was to avoid off-peak interferences as much as possible.

Table 4. Typical single analysis and average (replicate) detection limits *

| Element | Detection limit (single point) (mass fraction × 10⁻² in CePO₄) | Detection limit (avg. of 10) (mass fraction × 10⁻² in CePO₄) |
|---------|--------------------------------------------------------------|---------------------------------------------------------------|
| ScK₆₇  | 0.058                                                        | 0.018                                                         |
| YL₆₇   | 0.103                                                        | 0.024                                                         |
| LaL₆₇  | 0.187                                                        | 0.045                                                         |
| CeL₆₇  | 0.147 (in GdPO₄)                                            | 0.050 (in GdPO₄)                                             |
| Pr₆     | 0.104                                                        | 0.058                                                         |
| NdL₆₇  | 0.111                                                        | 0.068                                                         |
| SmL₆₇  | 0.103                                                        | 0.042                                                         |
| EuL₆₇  | 0.137                                                        | 0.052                                                         |
| GdL₆₇  | 0.097                                                        | 0.125                                                        |
| TbL₆₇  | 0.139                                                        | 0.046                                                         |
| DyL₆₇  | 0.100                                                        | 0.033                                                         |
| HoL₆₇  | 0.140                                                        | 0.042                                                         |
| ErL₆₇  | 0.097                                                        | 0.042                                                         |
| TmL₆₇  | 0.139                                                        | 0.033                                                         |
| YbL₆₇  | 0.139                                                        | 0.038                                                         |
| LuL₆₇  | 0.142                                                        | 0.043                                                         |
| PbM₆₇  | 0.077 (in GdPO₄)                                            | 0.045 (in GdPO₄)                                             |

* Single point analysis detection limits in a matrix of CePO₄ at a 99 % confidence level (CL). A GdPO₄ matrix for Ce and Pb was used since Ce is a major element in CePO₄ and Pb was determined to be inhomogeneous in the CePO₄ CL and averaged detection limits for the same matrices at 99 % confidence interval based on the actual measured standard deviation of 10 measurements on each standard are reported.

* Gd is possibly present as very small, widely dispersed concentrations in the CePO₄ which could explain this unusually high calculated detection limit (for example the calculated average detection limit for GdL₆₇ in DyPO₄ is 0.07 mass fraction × 10⁻²).

3. Results and Discussion

3.1 REE Impurities in the Orthophosphate Standards

Table 5 shows the trace REE elements measured in each of the orthophosphates at UC Berkeley on the “Round Robin” mount. One can see that as stated in the original paper by Jarosewich and Boatner [9], the material is generally very pure based on quantitative results from instrumental neutron activation analysis (INAA). The only statistically significant REE contamination anomalies we observed were the presence of approximately 9 × 10⁻⁴ mass fraction Eu in GdPO₄ (Jarosewich...
Table 5. Trace Pb and REE concentrations in the REEPO₄ standards* (concentrations and uncertainties in mass fraction × 10⁷)

| USNM # | ScPO₄ | YPO₄ | LaPO₄ | CePO₄ | PrPO₄ | NdPO₄ | SmPO₄ | EuPO₄ |
|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| 168495 | .01 ± .01 | .01 ± .02 | .01 ± .01 | .01 ± .01 | .01 ± .01 | .01 ± .01 | .01 ± .01 | .00 ± .00 |
| 168499 | .01 ± .02 | .01 ± .01 | .01 ± .01 | .00 ± .01 | .02 ± .03 | .01 ± .02 | .00 ± .00 | .00 ± .00 |
| 168490 | .01 ± .01 | .02 ± .03 | .00 ± .00 | .03 ± .05 | .02 ± .04 | .03 ± .03 | .01 ± .01 | .00 ± .00 |
| 168484 | .01 ± .01 | .02 ± .03 | .00 ± .00 | .03 ± .04 | .03 ± .04 | .02 ± .02 |
| 168493 | .01 ± .01 | .02 ± .03 | .00 ± .00 | .03 ± .04 | .03 ± .04 | .02 ± .02 |
| 168492 | .01 ± .01 | .02 ± .03 | .00 ± .00 | .03 ± .04 | .03 ± .04 | .02 ± .02 |
| 168494 | .01 ± .01 | .02 ± .03 | .00 ± .00 | .03 ± .04 | .03 ± .04 | .02 ± .02 |

| USNM # | GdPO₄ | TbPO₄ | DyPO₄ | HoPO₄ | ErPO₄ | TmPO₄ | YbPO₄ | LuPO₄ |
|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| 168488 | .01 ± .01 | .00 ± .00 | .01 ± .01 | .01 ± .01 | .01 ± .01 | .01 ± .01 | .01 ± .01 | .01 ± .02 |
| 168496 | .01 ± .02 | .01 ± .02 | .07 ± .05 | .02 ± .03 | .02 ± .03 | .01 ± .01 | .04 ± .03 | .03 ± .03 |
| 168495 | .01 ± .02 | .01 ± .02 | .02 ± .04 | .03 ± .04 | .01 ± .02 | .01 ± .01 | .03 ± .05 | .02 ± .03 |
| 168490 | .01 ± .02 | .01 ± .03 | .01 ± .02 | .02 ± .02 | .01 ± .03 | .03 ± .04 | .01 ± .01 | .01 ± .02 |
| 168484 | .01 ± .02 | .01 ± .03 | .02 ± .03 | .02 ± .03 | .01 ± .03 | .02 ± .05 | .01 ± .01 | .00 ± .00 |
| 168493 | .01 ± .02 | .02 ± .03 | .01 ± .03 | .03 ± .04 | .03 ± .04 | .01 ± .01 | .01 ± .02 | .01 ± .02 |
| 168492 | .01 ± .02 | .02 ± .03 | .01 ± .03 | .03 ± .04 | .03 ± .04 | .01 ± .01 | .01 ± .02 | .01 ± .02 |
| 168494 | .01 ± .02 | .02 ± .03 | .01 ± .03 | .03 ± .04 | .03 ± .04 | .01 ± .01 | .01 ± .02 | .01 ± .02 |
| 168498 | .01 ± .02 | .02 ± .03 | .01 ± .03 | .03 ± .04 | .03 ± .04 | .01 ± .01 | .01 ± .02 | .01 ± .02 |
| 168497 | .01 ± .02 | .02 ± .03 | .01 ± .03 | .03 ± .04 | .03 ± .04 | .01 ± .01 | .01 ± .02 | .01 ± .02 |
| 168498 | .01 ± .02 | .02 ± .03 | .01 ± .03 | .03 ± .04 | .03 ± .04 | .01 ± .01 | .01 ± .02 | .01 ± .02 |

* Average trace analyses of REE elements plus Sc, Y, and Pb for the USNM REE phosphates in the “Round Robin” mount measured at Berkeley. The quoted uncertainty is the measured one standard deviation value for 10 measurements.

** Large magnitude interference corrections resulting in increasing uncertainty at trace levels. The apparent concentrations and large standard deviations for these three cases could be greatly reduced by using longer acquisition times on the unknown and the standard used for the interference correction.

and Boatner reported 1.9 × 10⁻⁵ mass fraction Eu in GdPO₄ using INAA), 1.1 × 10⁻³ mass fraction Ho and 7 × 10⁻³ mass fraction Y in the DyPO₄ (Jarosewich and Boatner reported 2.47 × 10⁻³ Ho in DyPO₄ using INAA, Y was not analyzed by INAA), and approximately 1.1 × 10⁻³ mass fraction Er in the TmPO₄ (Er was not analyzed by Jarosewich and Boatner with INAA). It is difficult to obtain commercially available REE oxide materials that are completely free of other REE impurities due to the nature of the starting materials (REE-rich phosphate and carbonate minerals) that must be processed to extract individual REEs. The apparent concentration of 0.0009 ± 0.0007 mass fraction Lu in GdPO₄ is possibly due to an interference of Gd L₁ at 1.5928 Å and the 0.0003 mass fraction Dy in YbPO₄ is possibly due to an interference of Y L₁ at 1.8946 Å and finally the 0.0004 ± 0.0003 mass fraction Yb in YPO₄ is possibly due to an interference of Y Kα₁ (II) at 1.658 Å. No other interferences could be invoked to explain the other apparent REE concentrations shown in bold in the table.
3.2 Pb Impurities in the Orthophosphate Standards

The results for Pb in the last row of Table 5 reveal that Pb is present from almost 0.02 mass fraction down to about 0.005 mass fraction element in seven of the REE orthophosphates in the “Round Robin” mount (in order of decreasing concentration: CePO$_4$, LaPO$_4$, SmPO$_4$, PrPO$_4$, NdPO$_4$, EuPO$_4$, and GdPO$_4$). The remaining REE orthophosphates did not contain Pb concentrations above the UC Berkeley detection limit of 4.5 \times 10^{-4} mass fraction. These measurements consisted of a 10-point traverse on a single grain of each REE orthophosphate. Table 6 shows the Pb homogeneity measurements on the same “Round Robin” mount but performed in College Park with increased sensitivity (longer count times and higher beam currents). The two data sets agree well considering the apparent inhomogeneity of the Pb contaminated materials.

What is striking is that the Pb content varies considerably not only within each grain, but even more so from grain to grain, as seen in Table 7 where a number of Pb measurements (13-16) over the face of the four CePO$_4$ grains in the “Berkeley” mount show tremendous variation between grains from about 0.015 mass fraction to 0.045 mass fraction element.

3.3 Crystal Structure and Pb Contamination

Lead is present in significant amounts only in the monoclinic, high-temperature, monazite-structure orthophosphates (LaPO$_4$ through GdPO$_4$), and is absent, or nearly so, in the tetragonal, xenotime-structure, compounds (TbPO$_4$ through LuPO$_4$ and ScPO$_4$ and YPO$_4$) as can be seen in Fig. 1, where Pb concentration is plotted as a function of REE atomic number. Boatner and Sales [7] showed that there is a distinct structural change (monoclinic to tetragonal) between GdPO$_4$ and TbPO$_4$ which suggests that the incorporation of Pb in the monazite structure, and the lack of Pb incorporation in the xenotime structure orthophosphates, is related to this change in structure. The so-called lanthanide contraction is a continuous decrease in size across the REEs, and may also play a role in this, however, there are no abrupt decreases in the trivalent ionic radii across the REE series (including from Gd to Tb). Our data suggest that the exclusion of the large (e.g., 1.29 Å in eight coordination, [16]) divalent Pb$^{2+}$ ion is limited by the space available in the heavy REEO$_8$ (HREEO$_8$) polyhedra and that the divalent Pb ion, or the trivalent HREEs, will not fit easily into the xenotime structure. For the monoclinic orthophosphates, the light REEO$_9$ (LREEO$_9$) polyhedra is much larger and can accommodate the divalent Pb$^{2+}$ ion into the xenotime structure [16].

### Table 6. Pb (mass fraction \times 10^{-3}) in the “round robin” mount measured in College Park

| Compound | PbM$_\text{av}$ |
|----------|----------------|
| ScPO$_4$ | .00 ± .00 |
| YPO$_4$  | .00 ± .00 |
| LaPO$_4$ | .90 ± .32 |
| CePO$_4$ | 1.90 ± .07 |
| PrPO$_4$ | .92 ± .04 |
| NdPO$_4$ | .86 ± .17 |
| SmPO$_4$ | .86 ± .13 |
| EuPO$_4$ | .64 ± .16 |
| GdPO$_4$ | .39 ± .16 |
| TbPO$_4$ | .00 ± .00 |
| DyPO$_4$ | .00 ± .00 |
| HoPO$_4$ | .00 ± .00 |
| ErPO$_4$ | .00 ± .00 |
| TmPO$_4$ | .00 ± .00 |
| YbPO$_4$ | .00 ± .00 |
| LuPO$_4$ | .00 ± .00 |

* Averaged mass fraction \times 10^{-3} results of Pb contamination measurements performed in College Park on the “round robin” mount. The mass fraction detection limit (99% confidence level) was approximately 140 \times 10^{-6}. Note that the measured Pb standard deviations for the uncontaminated materials are significantly smaller than the measurements performed at Berkeley. These results are due to the increased beam current and counting time used at College Park.

### Table 7. Pb grain to grain variation within the CePO$_4$ material in the “Berkeley” mount

| Grain | Average (concentrations in mass fraction \times 10^{-3}) | Standard deviation | Minimum | Maximum |
|-------|--------------------------------------------------------|-------------------|--------|--------|
| #1    | 2.68                                                   | 0.45              | 2.04   | 3.47   |
| #2    | 2.55                                                   | 0.16              | 2.33   | 2.83   |
| #3    | 1.54                                                   | 0.04              | 1.48   | 1.59   |
| #4    | 3.64                                                   | 0.46              | 3.08   | 4.50   |

* Average and standard deviations (13-16 points over the face of each grain) of four grains from the “Berkeley” mount mapped in Fig. 1 in elemental mass fraction \times 10^{-3}. Analytical conditions were 20 keV, 150 nA, and a 10 µm diameter beam. Each analysis is the average of 13 to 16 measurements distributed over the face of each grain. Only grain #3 was relatively homogeneous in Pb.
Characterizing the exact Pb contamination within a given orthophosphate is problematic because of the degree to which the Pb concentrations vary, not only within a single grain but also from grain to grain. For this reason it is recommended that each laboratory perform systematic x-ray mapping for Pb of their “in-house” REE orthophosphates grains to determine the actual extent and variation of Pb contamination in their own mounts. As can be seen in Table 7 (e.g., grain #3), it may be that the Pb contamination is homogeneous enough that some portion or another of the material may be suitable for use as a quantitative standard for major element concentrations of the REE in question. Once the Pb concentration for a homogeneous grain is known and the position noted, the measured Pb can be proportionally subtracted from the ideal REEPO₄ composition and entered into the laboratory’s standard compositional database for general use.

Regarding which REEPO₄ material should be used for P as an EMPA standard, we suggest that one of the tetragonal orthophosphates should be used to minimize any nonstoichiometry introduced by Pb impurities.

4. Conclusions

Due to their qualities of robustness under the electron beam, resistance to oxidation, and REE purity, the REE orthophosphate standards remain a valuable set of standards for EPMA despite significant Pb contamination in at least 7 of the 16 samples examined. Of those with measurable Pb contamination, only the monoclinic CePO₄ and possibly the LaPO₄ and SmPO₄ contain enough Pb to noticeably affect the stoichiometry for use as a primary standard for major element quantitative analysis (approximately 2 % to 4 % relative differences from their theoretical compositions). None of the tetragonal, xenotime structure orthophosphates (Gd-LuPO₄ and ScPO₄ and YPO₄) contain appreciable Pb.

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About the authors: John J. Donovan is a research assistant with the University of Oregon, John M. Hanchar is a assistant professor of geochemistry at The George Washington University, Phillip M. Picolli is a research scientist at the University of Maryland, Department of Geology, Marc D. Schrier is as staff scientist at Quantum Dot Corporation, Lynn A. Boatner is a corporate fellow in the Solid State Division at Oak Ridge National Laboratory and Eugene Jarosewich is a research chemist (emeritus) at the Department of Mineral Sciences, the Museum of Natural History, Smithsonian Institution.