



# ANOMALOUS COMPOSITION OF REE ORTHOPHOSPHATE STANDARDS: WHY ARE THEY ANOMALOUS, AND DO THEY HAVE ANY ROLE IN TRACE ELEMENT ANALYSIS?

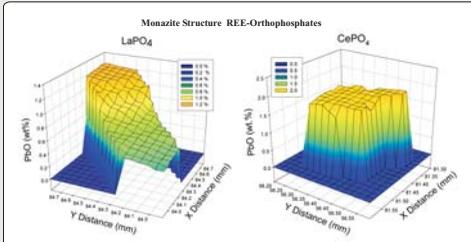
**Philip M. Piccoli**  
Department of Geology, University of Maryland

**John M. Hanchar**  
Department of Earth & Environmental Sciences, The George Washington University

**John J. Donovan**  
Department of Geology, University of Oregon



**Abstract**  
In an effort to obtain accurate analysis by electron probe microanalysis, it is imperative that high-quality analyses of standards are obtained. Any uncertainty in the composition of the standards can be propagated through the analysis of unknowns. Fourteen REE(+Sc,Y)-phosphate standards have been examined for their Pb contents. Some of these standards contain significant quantities of Pb. This is presumably due to the flux, PbPO<sub>4</sub>, used to dissolve the oxide starting materials prior to the crystal synthesis, and to promote large crystal size. The grains selected for this analysis were random, and the locations of the analyzed surface to original crystal faces could not be determined in most cases. The LREE/MREE-PO<sub>4</sub> standards contain significant and variable amounts of Pb. The remaining REE-PO<sub>4</sub> and Se-Y-PO<sub>4</sub> contain Pb in concentrations near or below detection. What is even more striking is that the Pb content varies considerably not only within each grain but even more so from grain to grain. Pb is only present in significant amounts in the monoclinic, monazite structure (LaPO<sub>4</sub>, GdPO<sub>4</sub>) phosphates, and is absent, or nearly so, in the tetragonal, xenotime structure (TbPO<sub>4</sub>, LuPO<sub>4</sub>, ScPO<sub>4</sub>, YPO<sub>4</sub>) phosphates. This is consistent with a distinct structural change from monoclinic to tetragonal in the high-temperature forms of these orthophosphates that occurs between GdPO<sub>4</sub> and TbPO<sub>4</sub>. These results suggest that accurate determination of Pb contents of REE-PO<sub>4</sub> standards is imperative if accurate determination of REE concentrations in LREE-rich phases is necessary (e.g. monazite, xenotime).

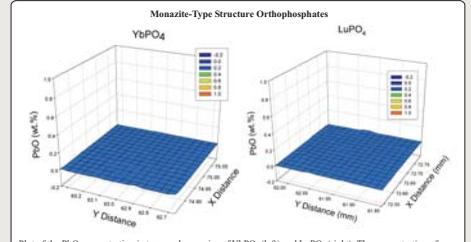


Plot of the PbO concentration in two random grains of LaPO<sub>4</sub> (left) and CePO<sub>4</sub> (right). The concentration of PbO in all of the monazite structure REE-orthophosphates are high (relative to xenotime structure REE-orthophosphates). Furthermore, the grains within a given sample are highly variable in composition, and individual grains often show considerable variation (for example, LaPO<sub>4</sub> at left).

**ANALYSES**  
Analyses of Pb were performed on a JEOL 8900 Superprobe. X-ray fluxes of Pb were obtained using an accelerating voltage of 20 keV, and a cup current of 150 nA (1.5E-7A). Count times were 60 seconds on the peak, and 30 seconds on the background on each side of the peak. Pb was analyzed using a PETH crystal, at a position of 169.307 mm (L-value: λ = 5.2860Å; E = 0.4264 keV), and background positions of +4 mm (L=173.307Å; = 5.4013Å) and -3 mm (L=166.307Å; = 5.1828Å). Natural cerussite (PbCO<sub>3</sub>) from Tsumeb, Namibia, was used as a standard for Pb (83.53 wt. % PbO). The Pb-Mn was used for all analyses, with the exception of Y (Mb). REE and phosphate were not measured, but were incorporated into the ZAF algorithm in order to account for atomic number, absorption and fluorescence effects.

	Average (wt.%)	Std. Dev.	Minimum	Maximum
Grain #1	2.68	0.45	2.04	3.47
Grain #2	2.55	0.16	2.33	2.83
Grain #3	1.54	0.04	1.48	1.59
Grain #4	3.64	0.46	3.08	4.50

Concentration of PbO (wt.%) in a secondary mount of CePO<sub>4</sub>. This demonstrates that variations in PbO between grains of CePO<sub>4</sub> can be considerably more than within individual grains.



Plot of the PbO concentration in two random grains of YbPO<sub>4</sub> (left) and LuPO<sub>4</sub> (right). The concentration of PbO in the xenotime-structure REE-orthophosphates are low, and are generally at or below the detection limit for Pb (approximately 140 ppm at the 99% confidence interval, given the operating conditions employed here).

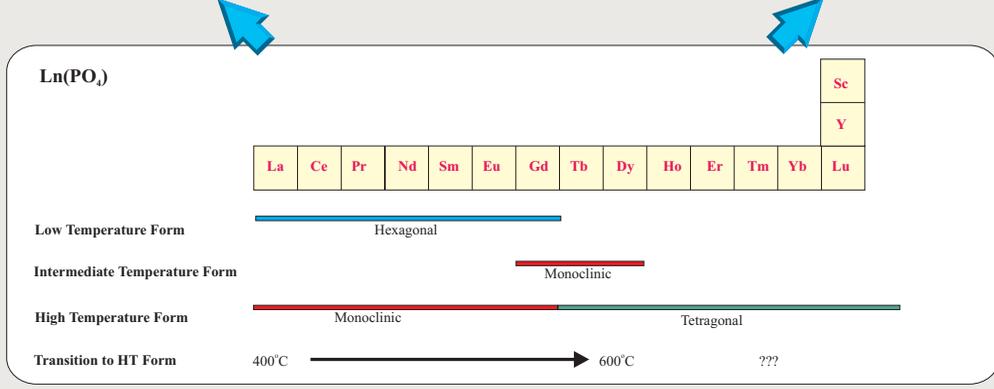
**Primary Effects of Using These Standards for EPMA Work**  
The LaPO<sub>4</sub> standards that exhibit a monazite structure (La-Gd) contain between 0 (i.e. below detection) and 4.5 wt. % PbO, depending on the grain within a mount, and location within a grain. As a first order estimate, when using these as standards for the REE analyses, the concentration of REE in the standard is overestimated, and this produces an overestimation of REE concentration in unknown specimens (up to approximately 4.5% [relative]). The remaining LuPO<sub>4</sub> standards (Tb-Lu, and Y and Sc) have been found not to contain significant Pb and can be used without problem.

**Secondary Effects of Using These Standards for EPMA Work**  
Consider a monazite with the following composition: 50,608 ppm Th, 3,883 ppm U, and 6,587 ppm Pb (15.0 La<sub>2</sub>O<sub>3</sub>; 29.9% Ce<sub>2</sub>O<sub>3</sub>; 3.0% Pr<sub>2</sub>O<sub>3</sub>; 11% Nd<sub>2</sub>O<sub>3</sub>; 1.5% CaO; 30.0% PbO). This yields an age of 2,160 Ma assuming stoichiometric LaPO<sub>4</sub> standards. When Pb in the standards is taken into account, the concentration of the REE change considerably, but the concentration of Th, U and Pb change by less than 5 ppm, producing an identical age (within 1 Ma). In short, in monazite geochronology, uncertainties from counting statistics (primarily from Pb) exceed uncertainties introduced from the Pb substituting for the REE in the orthophosphates. The modified stoichiometries of the orthophosphates will generally not affect quantitative results beyond the analytical sensitivity of most measurements.

**BACKGROUND**  
Fourteen batches of rare-earth element (plus Sc and Y) orthophosphate standards were grown at Oak Ridge National Laboratory in the 1980s, and were widely distributed by the Smithsonian Institution's Department of Mineral Sciences for use as electron microprobe standards (Jarosewich and Boatner, 1991). Some of the material is significantly contaminated by Pb. The origin of this impurity is the Pb<sub>2</sub>O<sub>3</sub> flux that is derived from the thermal decomposition of PbHPO<sub>4</sub>. The flux is used to dissolve the oxide starting materials at elevated temperatures (~1360°C) prior to the crystal synthesis. Because these rare-earth element standards are extremely stable under the electron beam and considered homogeneous, they have been of enormous value to the technique of electron probe microanalysis (EPMA) whenever rare earth elements (and Sc, Y, and P) are to be analyzed.  
The lanthanide orthophosphates are chemically durable and radiation resistant refractory materials. Their structures were determined in order to explore their use in nuclear and actinide waste disposal, scintillator material research, as well as materials characterization investigations. Subsequently, these materials were investigated for possible use as standards for EPMA by the Smithsonian Institution (Jarosewich and Boatner, 1991), and put through a series of tests. The materials were shown to be extremely robust under electron bombardment, did not oxidize, were not hygroscopic, and no serious contamination or inhomogeneities were noted at the time. These efforts were followed by a general distribution of the material to interested parties.

Monazite-Structure REE(PO <sub>4</sub> )		PbO Concentration (wt.%)	
Material	UC/Berkeley	Std. 1	Std. 2
<b>La Mount</b>	87	10	10
N	0.888	1.120	1.138
Std	0.319	0.184	0.198
<b>Ce Mount</b>	87	10	10
N	1.804	1.813	1.827
Std	0.069	0.074	0.091
<b>Pr Mount</b>	93	10	10
N	0.859	0.828	0.824
Std	0.037	0.048	0.072
<b>Nd Mount</b>	99	10	10
N	0.859	0.843	0.847
Std	0.100	0.030	0.064
<b>Sm Mount</b>	100	10	10
N	0.881	1.064	1.026
Std	0.131	0.072	0.052
<b>Gd Mount</b>	100	10	10
N	0.843	0.587	0.555
Std	0.106	0.068	0.059
<b>Tb Mount</b>	98	10	10
N	0.389	0.323	0.513
Std	0.158	0.072	0.043

Analyses were performed on two different mounts, consisting of grains from two sources, using two different sets of operating conditions. Detection limits at the 99% significance level are 140 and 450 ppm Pb, at Maryland and Berkeley, respectively.



Monazite-Structure REE(PO <sub>4</sub> )		PbO Concentration (wt.%)	
Material	UC/Berkeley	Std. 1	Std. 2
<b>Tb Mount</b>	72	10	10
N	0.007	0.018	0.004
Std	0.008	0.020	0.006
<b>Dy Mount</b>	100	10	10
N	0.000	0.024	0.022
Std	0.000	0.027	0.022
<b>Ho Mount</b>	85	10	10
N	0.000	0.017	0.016
Std	0.005	0.028	0.021
<b>Er Mount</b>	84	10	10
N	0.004	0.019	0.006
Std	0.009	0.026	0.016
<b>Tm Mount</b>	81	10	10
N	0.000	0.010	0.000
Std	0.004	0.022	0.018
<b>Yb Mount</b>	100	10	10
N	0.001	0.018	0.030
Std	0.001	0.031	0.044
<b>Lu Mount</b>	94	10	10
N	0.000	0.041	0.014
Std	0.004	0.044	0.026

Details of the analyses can be found above and at left. All analyses (Avg) of xenotime-type orthophosphates yield Pb concentrations at or below the detection limit.

Monazite-Structure (Y,Sc)(PO <sub>4</sub> )		PbO Concentration (wt.%)	
Material	UC/Berkeley	Std. 1	Std. 2
<b>Sc Mount</b>	74	10	10
N	0.002	0.003	0.006
Std	0.003	0.004	0.011
<b>Y Mount</b>	100	10	10
N	0.002	0.009	0.009
Std	0.002	0.015	0.016

**REFERENCES**  
Boatner, L.A. and Sales, B.C. (1988) Monazite. In: Radioactive waste forms for the future. Lutz, W. and Ewing, R.C., (eds.), p. 495-568.  
Jarosewich, E. and Boatner, L.A. (1991) Rare-earth element reference samples for electron microprobe analysis. Geostandards Newsletter, 15, 397-399.

**ACKNOWLEDGMENTS**  
The JEOL 8900 Superprobe at the University of Maryland was purchased with funds from the National Science Foundation (NSF EAR 9810244), the Department of the Army (DAAG559710383), and the University of Maryland.

