



GR focus review

Rare earth elements in sedimentary phosphate deposits: Solution to the global REE crisis?



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ABSTRACT

The critical role of rare earth elements (REEs), particularly heavy REEs (HREEs), in high-tech industries has created a surge in demand that is quickly outstripping known global supply and has triggered a worldwide scramble to discover new sources. The chemical analysis of 23 sedimentary phosphate deposits (phosphorites) in the United States demonstrates that they are significantly enriched in REEs. Leaching experiments using dilute H₂SO₄ and HCl, extracted nearly 100% of their total REE content and show that the extraction of REEs from phosphorites is not subject to the many technological and environmental challenges that vex the exploitation of many identified REE deposits. Our data suggest that phosphate rock currently mined in the United States has the potential to produce a significant proportion of the world's REE demand as a byproduct. Importantly, the size and concentration of HREEs in some unmined phosphorites dwarf the world's richest REE deposits. Secular variation in phosphate REE contents identifies geologic time periods favorable for the formation of currently unrecognized high-REE phosphates. The extraordinary endowment, combined with the ease of REE extraction, indicates that such phosphorites might be considered as a primary source of REEs with the potential to resolve the global REE (particularly for HREE) supply shortage.

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1. Introduction

Rare earth element based technologies underpin an increasingly broad range of industrial sectors (Long et al., 2010; Service, 2010). These elements, grouped because of their chemical and physical similarities, include the 14 naturally occurring lanthanides, and yttrium

(Y) (Long et al., 2010). Here, as increasingly common in the resources discussions, the REEs are informally subdivided into light REEs (LREEs—La through Sm) and heavy REEs (HREEs—Eu through Lu and Y) (Kato et al., 2011). The HREE group is particularly important to emerging technologies in green energy, defense, and electronic industries (Humphries, 2010; Long et al., 2010; British Geological Survey, 2011; Kato et al., 2011).

Currently, more than 95% of the world's REEs are produced from two ore deposit types in China (Humphries, 2010; Long et al., 2010).

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The Bayan Obo deposit, the largest REE deposit, is a high-grade, igneous-related carbonate deposit that sources 80% of the world's LREEs (U.S. Geological Survey, 2011; Kynicky et al., 2012; Verplanck et al., 2014), but as is typical of this deposit type, is low in HREEs. The ion-adsorption clay-type deposits of South China, although small and low grade, dominate the HREE market because they are proportionally HREE enriched and are mined and processed at very low cost (Long et al., 2010; Kynicky et al., 2012).

Meeting the growing need for HREEs seems daunting because efforts to identify additional economically feasible HREE-enriched deposits have generally been unsuccessful (Long et al., 2010; British Geological Survey, 2011). Recent exploration has identified a number of HREE-enriched deposits of various types. However, their exploitation is challenging because REEs reside within a diverse array of fine-grained, refractory minerals that are difficult to physically concentrate (beneficiate) and dissolve. Moreover, high Th and U concentrations in these deposits pose environmental concerns (Long et al., 2010). Recently, deep-sea muds have also been proposed as REE resources (Kato et al., 2011), though their profitable exploitation depends on overcoming the technical and environmental obstacles associated with seafloor mining 3–5 km below the surface (Kato et al., 2011). We report the concentration of REEs in U.S. phosphorites and propose, as a function of predictable variations in REE content through the geologic record, the resource potential of similar deposits elsewhere in the world. Our evaluation of the U.S. deposits indicates that they have REE

concentrations equal to or greater than any known resource, contain readily extractable REEs, and present fewer environmental concerns than most conventional REE deposits.

2. Methods

Samples from 23 sedimentary phosphorites in the United States were collected from outcrop and core (Fig. 1). Regional sequence stratigraphic frameworks for major phosphorite intervals were constructed to constrain their spatial distribution, depositional environment, and to inform genetic models. Chronostratigraphic correlation was established through the integration of published biostratigraphy, carbon isotope stratigraphy, and mapping of sequence boundaries. Phosphate, REE, U, and Th abundances for all bulk-sediment samples were determined by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at the U.S. Geological Survey (USGS). Analyses are within 15% of the accepted values of USGS reference materials, duplicate analyses of selected samples by inductively coupled plasma atomic emission spectrophotometry and mass spectrometry sodium peroxide sinter (SGS Mineral Services, Toronto), and in-house ICP-MS sinter method. Replicate analyses were <3% relative standard deviation (RSD). Francolite separates were analyzed by LA-ICP-MS analysis following the procedures described in Koenig et al. (2009). Calibration curves were constructed for each mass measured by integrating the signal from the USGS microanalytical phosphate reference material

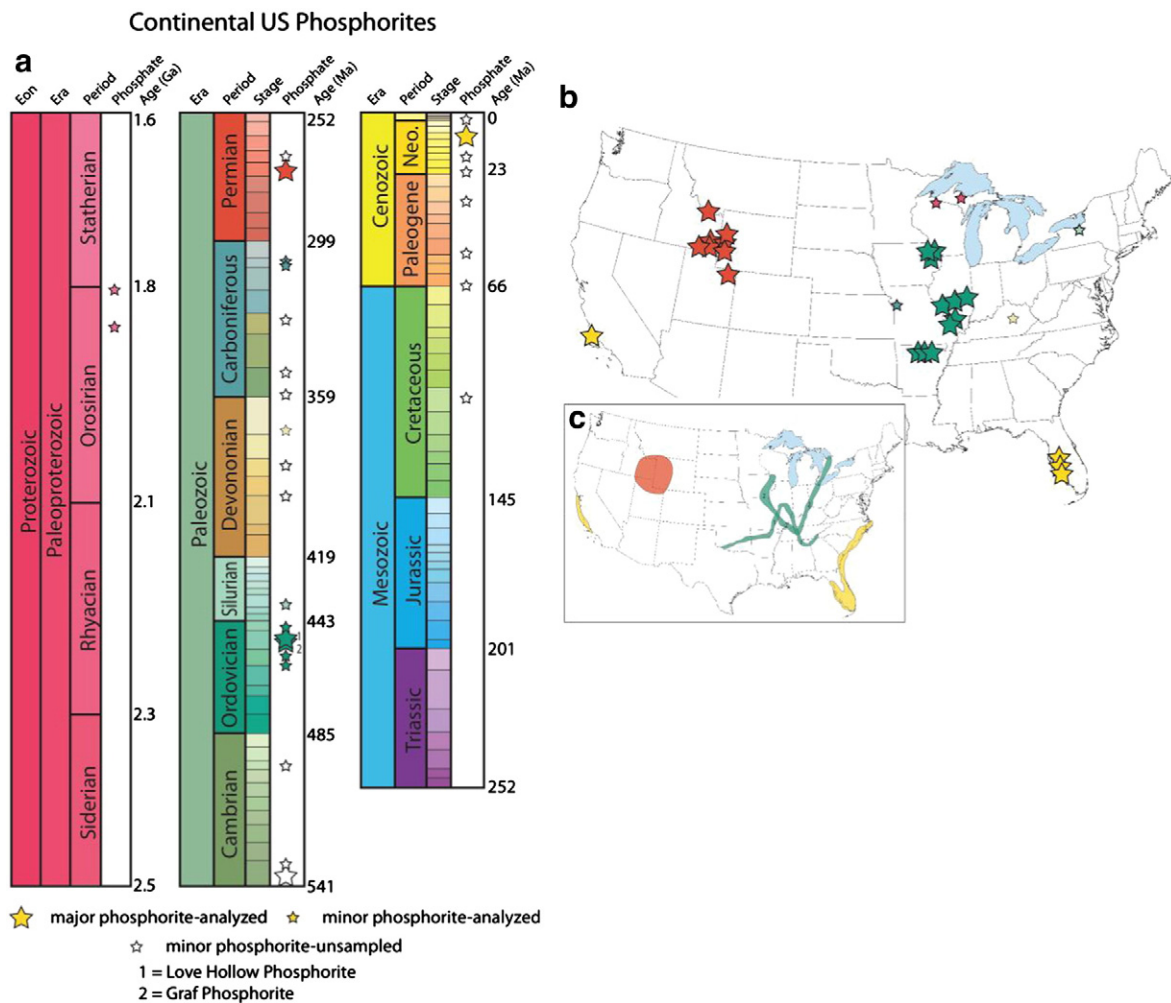


Fig. 1. Localities and stratigraphic age of studied phosphate deposits. Ages and color coding in the stratigraphic chart are adapted from the International Commission on Stratigraphy (www.stratigraphy.org/ICSChart/ChronostratChart2013-01.pdf). a, Temporal distribution of major (i.e., mined) and minor phosphorites in the United States. b, Spatial distribution of phosphorites sampled by this study. c, Distribution of major phosphorite occurrences across the United States (see Fig. 4 for more detail).

(MAPS-4), NIST 612 glass reference material. Replicate analyses were <3% RSD of USGS reference materials were generally 15% of accepted values. Similarly, REE maps were measured and plotted using the procedures described in Koenig et al. (2009).

The REE extraction experiments were conducted on phosphorite samples ground to less than 100 μm . The abundance of apatite was estimated using standard relative intensity ratio methods of powder X-ray diffraction. In addition to apatite, minor constituents within samples included quartz, dolomite, potassium feldspar, illite, chlorite, smectite, and pyrite. Separate 0.1-gram aliquots of each sample were combined with 50 mL of 0.5 N HCl and 0.4 N H_2SO_4 in acid-washed polytetrafluoroethylene beakers, and reacted overnight. High-purity acids were used for the dissolutions. Resulting solutions were passed through a 0.2- μm filter and stored in acid-washed high density polyethylene bottles until analysis. Four procedure blanks were processed for each acid. X-ray diffraction of solid residuals after partial dissolution verified that apatite was completely removed by the acid treatment. Bulk-rock solids and partial leachates were analyzed using procedures described in Verplanck et al. (2004). Analytical uncertainties in REE determinations are generally 3–6% (Verplanck et al., 2004).

3. Sedimentary phosphorites and rare earth elements

3.1. Sedimentary phosphorites

Sedimentary marine phosphorites, the world's principal source of phosphorus fertilizer, were deposited intermittently over geologic time along continental and ocean basin margins. Yearly, the United States produces nearly 30 million metric tons (Mt) of phosphate rock (beneficiated or physically concentrated francolite—a carbonate-rich

fluorapatite), nearly all of which is dissolved in sulfuric acid to produce fertilizer (Jasinski, 2011). Approximately 85% of the U.S. phosphate is sourced from Miocene and Pliocene strata (Hawthorn Group and age equivalent formations) that cover the southeast coastal U.S. region; the remainder is produced from the Permian Phosphoria Formation in Idaho, Utah, Montana, and Wyoming (Fig. 1) (Jasinski, 2011). Mines in Florida alone annually produce about 19 Mt of phosphate rock mined from about 20 km^2 of the Hawthorn Group (Jasinski, 2011). Importantly, Th and U have not been an issue in U.S. phosphate mining (Zielinski et al., 1997).

3.2. Rare earth elements in phosphorites

The enrichment of REEs in francolite, where REE substitutes for Ca in the francolite lattice (Jarvis et al., 1994; Piper, 1999), has been recognized for more than a century (Jarvis et al., 1994). Our work demonstrates that the REEs in phosphate-rich rocks are almost entirely contained in francolite (Fig. 2). Early studies recognized the possibility of byproduct REE extraction during the production of phosphoric acid from Hawthorn and Phosphoria phosphates (McKelvey et al., 1951; Altschuler et al., 1967). However, historically the prime impetus for the study of the REEs in phosphate has been the investigation of phosphate genesis and paleocean chemistry (Jarvis et al., 1994; Piper, 1999; Lécuyer et al., 2004).

Some U.S. phosphorites have HREE contents that are considerably higher than in currently mined REE deposits (Fig. 3; Supplementary Data 1). Pure phosphate ore (and its beneficiated equivalent) from the two U.S. phosphate-producing units, are REE enriched relative to the Chinese clay-type deposits that range from 500 to 2000 ppm total REEs (ΣREE), of which 50–200 ppm are total HREEs (ΣHREE) (Wu

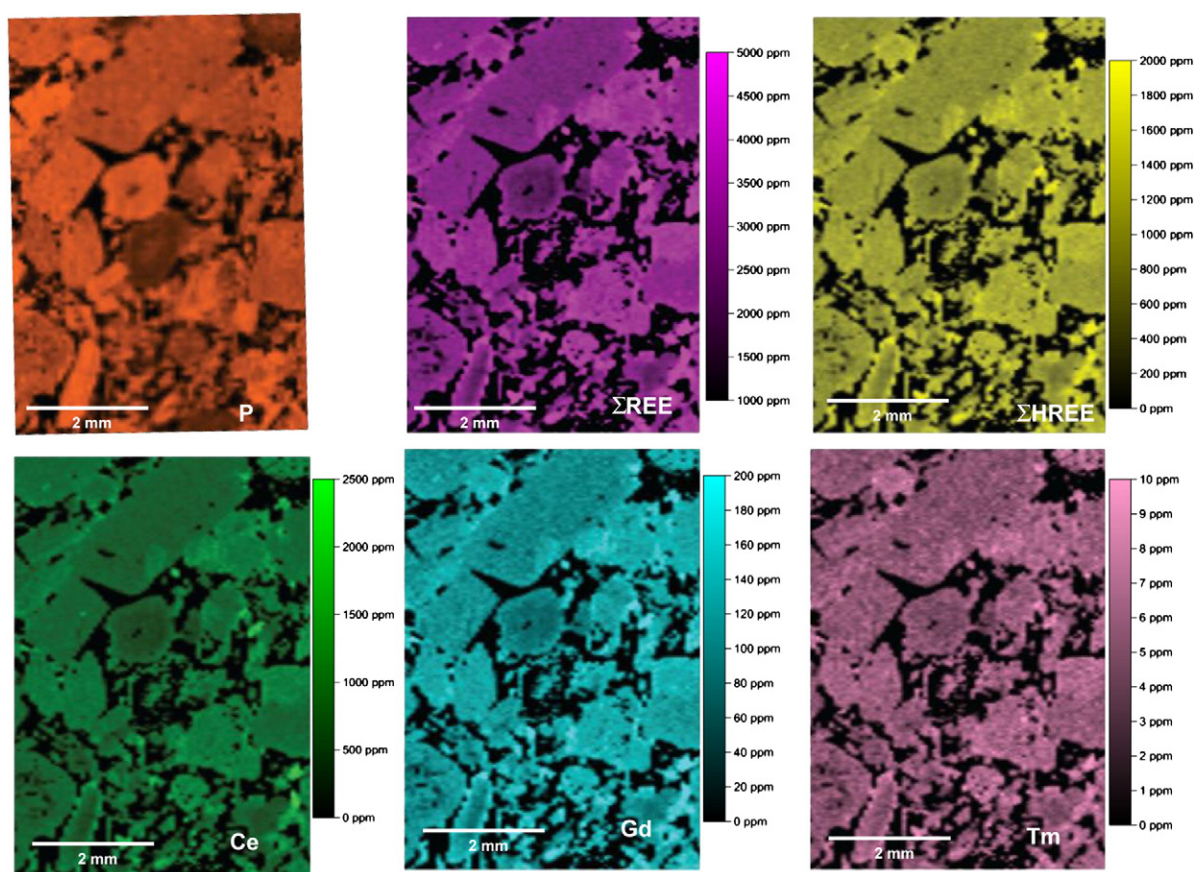


Fig. 2. Element concentration map of P, ΣREE , ΣHREE , and select REEs (Ce, Gd, and Tm) obtained by LA-ICP-MS from the Upper Ordovician Love Hollow phosphorite, Arkansas. Note the uniform REEs distributed in the francolite grains.

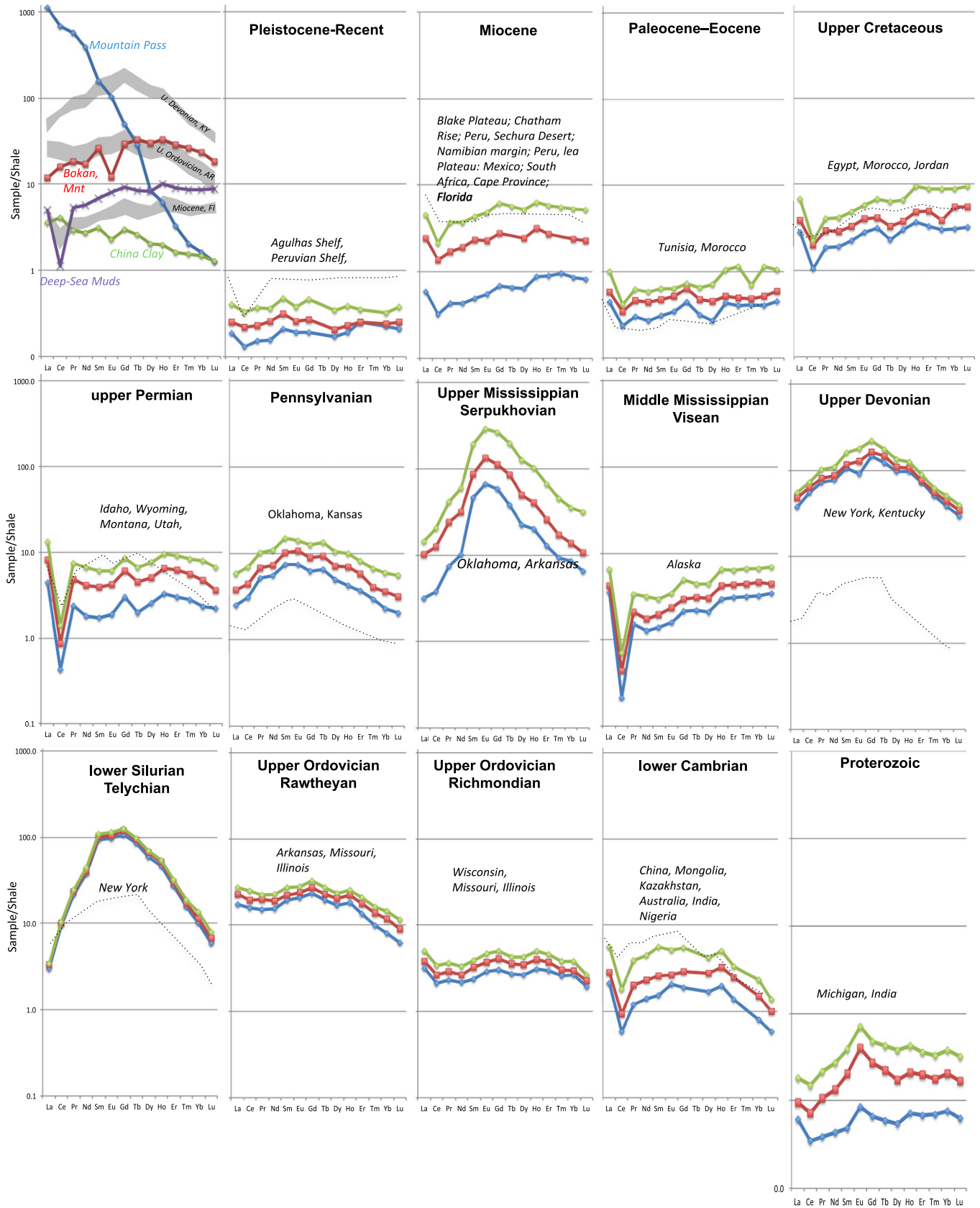


Fig. 3. Shale-normalized REE (NASC, McLennan (1989)) plots for francolite from sedimentary phosphorites, grouped by geologic age. The first panel shows mean REEs of major deposits: deep-sea muds (site 76: Kato et al. (2011)), Bokan Mountain, Alaska (Bentzen et al., 2013), Mountain Pass, California (Haxel, 2005; Long et al., 2010), and China clay-type deposits (Bao and Zhao, 2008) plotted relative to francolite from three U.S. phosphorites. Subsequent panels depict 1st (blue), 2nd (red), and 3rd (green) quantiles of REE abundances of francolite in global phosphorites. Plotted data: whole rock samples with $P_2O_5 > 10\%$ and phosphate grain separates, normalized to pure francolite (see Supplementary Data 1 for data and references). Dotted patterns are median values of coeval biogenic phosphate from Lécuyer et al. (2004). A major finding of this study is that REE patterns are time specific indicating geologic age and is a powerful predictive tool for the exploration of high-REE deposits.

et al., 1996; Bao and Zhao, 2008; Kato et al., 2011). The median Σ REE values of pure francolite in U.S. phosphate deposits is comparable (900 ppm, Hawthorn, and 1200 ppm, Phosphoria), and the Σ HREE are enriched (400 ppm and 600 ppm, respectively) relative to the clay-type deposits and approximately equivalent to those in high-grade deep-sea muds (1100 ppm Σ REE and 600 ppm Σ HREE; high-grade site #76, Kato et al., 2011). Importantly, some other U.S. phosphorites have HREE contents that are greater than any recognized REE deposit (Fig. 3). In particular, Upper Devonian and Mississippian phosphorites contain francolite with startlingly high concentrations (18,000 ppm

Σ REE, 7000 ppm Σ HREE), and are from strata of large but incompletely known extent. The informal Upper Ordovician unit, the Love Hollow phosphorite, that occurs within the Fernvale Limestone, underlies >1800 km² in northern Arkansas and contains an average thickness of 1.5 m of high-grade phosphate ore (Branner and Newsom, 1902; Grosz et al., 1995) and extends for >400 km into central Illinois (Figs. 4 and 5). Francolite from this unit, over a 100 km² area in Arkansas and localities in Missouri and Illinois (Fig. 4), averages 5400 Σ REE and 1600 ppm Σ HREE. These concentrations are more than ten times those characteristic of clay-type deposits. They are also similar to those of

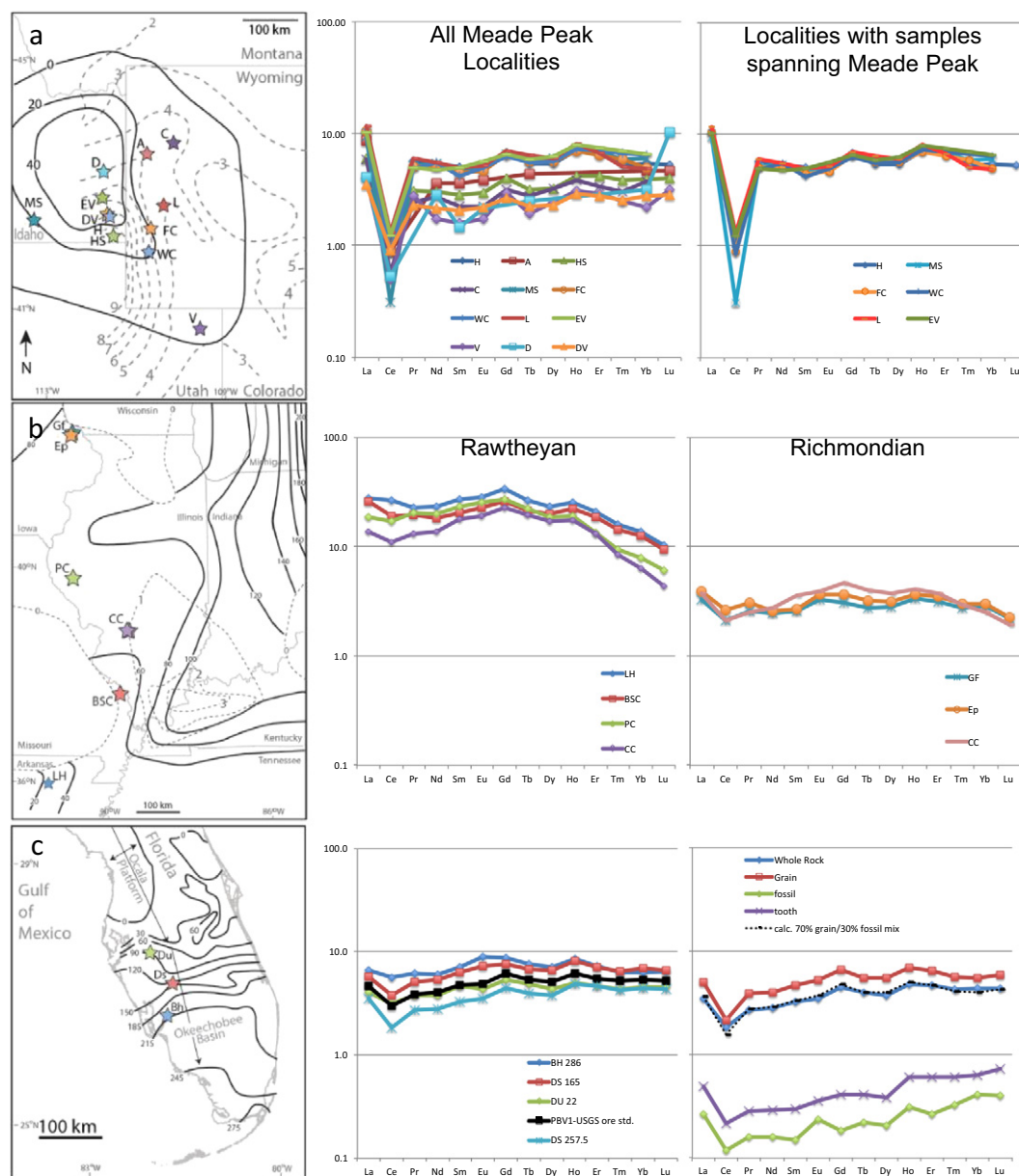


Fig. 4. Shale-normalized REE (NASC) plots showing the homogeneity of francolite REE contents in three major U.S. phosphorite regions regardless of local depositional environments and post-depositional burial histories. Sample locations (stars) plotted on isopach (solid lines in meters) maps of phosphorite-hosting units and estimated maximum burial depths (dashed lines, in kilometers). The REE values normalized as in Fig. 3. a, Map of the Permian Meade Peak Member of the Phosphoria Formation after Hiatt and Budd (2001). a1, Mean REE patterns, by location (see Supplementary Data 1 for data and references). a2, Sections where samples span the entire thickness of this long-ranging formation (Roadian to Capitanian). Note patterns from these localities are indistinguishable. b, Isopach map of Richmondian and younger Ordovician units (from our study) and burial depths from Root and Onasch (1999). b1, REE contents of phosphate from Rawtheyan Love Hollow and stratigraphically equivalent units. b2, REEs from the Ordovician Richmondian Maquoketa Group. Note distinct REE contents of Rawtheyan versus Richmondian phosphate, despite sample separated, in some cases, by only a few meters of stratigraphic section. c, Isopach map and basin facies of the shallowly buried upper Hawthorn Group samples after Scott (1988). c1, REE patterns from the Hawthorn Group from across central Florida. c2, REE patterns demonstrate that fossil phosphate has markedly lower REE contents than granular phosphate from the same sample (sample DS 257.5). Correspondence between the whole rock composition and a calculated 70:30 mixture of fossil and granular phosphate (consistent with petrographic observation), suggests that variation in values between samples in c1 may reflect different mixtures of granular and fossil phosphate. The striking correspondence of REE contents from equivalent horizons within each of the three broad regions despite highly variable burial depths suggests that the REE content of phosphate is controlled by broadly consistent ocean chemistry and depositional processes rather than by post-burial modification.

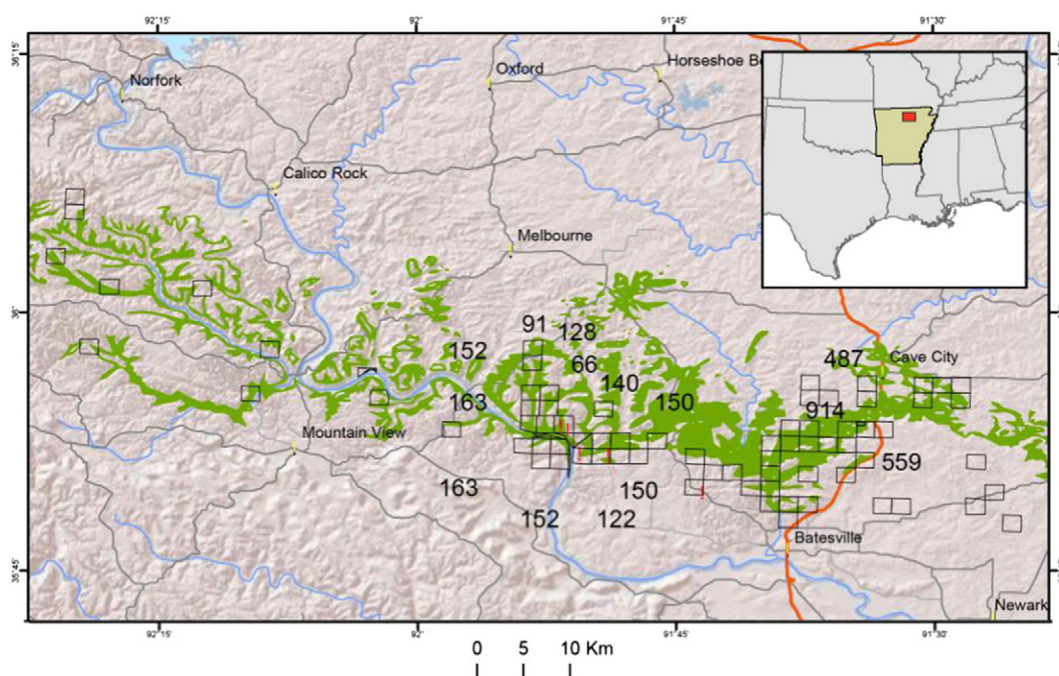


Fig. 5. Geologic map of northern Arkansas showing distribution of the Upper Ordovician Fernvale Limestone (green), host for the Love Hollow phosphorite (Haley et al., 1993). Black rectangles identify sections within which the Love Hollow phosphorite (Branner and Newsom, 1902) has been recognized; numbers indicate phosphate thickness (in cm) (Branner and Newsom, 1902; Wells, 1949; Grosz et al., 1995) and this study. Inset index map shows the location of the geologic map (red) in Arkansas.

Bokan Mountain prospect ore (Fig. 2), the peralkaline-type deposit in southeastern Alaska that is one of the largest, high-grade HREE resources known in the United States and has an inferred resource of 5.2 Mt of ore containing 5482 ppm Σ REE and 2113 ppm Σ HREE (Bentzen et al., 2013).

3.3. Extraction of REEs from phosphorites

The viability of REE resources is heavily dependent on the cost of beneficiation and chemical REE extraction. Global domination of HREE production by the small, low-grade South China clay-type deposits, for example, reflects the simplicity of liberating REEs adsorbed on clay surfaces using a simple acid leach (Humphries, 2010; Long et al., 2010; Chakhmouradian and Wall, 2012; Mariano and Mariano, 2012). Similarly, ease of beneficiation and chemical dissolution of sedimentary francolite allows the world's fertilizer industry to produce 150 Mt/yr of inexpensive phosphate fertilizer (Zhang et al., 2006). For example, the Hawthorn Group remains a premier phosphate source because cost-effective beneficiation allows upgrading ore as low as 3% P_2O_5 to nearly pure francolite (>30% P_2O_5) (Zhang et al., 2006). More than 90% of U.S. phosphate rock is dissolved in sulfuric acid to produce phosphoric acid that is mainly used in the production of fertilizer, animal feed, and various phosphorus chemicals (Zhang et al., 2006). Importantly, a similar dissolution of francolite contained in phosphate ores from the Hawthorn, Phosphoria, and Love Hollow strata, using dilute H_2SO_4 (0.4 N) and HCl (0.5 N), extracted 100% (within analytical error of $\pm 6\%$) of their total REE content (Fig. 6). These results demonstrate that the extraction of REEs from phosphorites is not subject to difficulties faced by many traditional REE prospects where REEs residing in fine-grained, refractory minerals that are cost-prohibitive to physically beneficiate and dissolve.

3.4. Quantity of REEs in phosphorites

Our detailed stratigraphic analysis allowed the sampling of individual phosphate beds over strike lengths of hundreds of kilometers and

areas of thousands of square kilometers (Fig. 4). Phosphate beds in age-equivalent horizons show strikingly similar REE contents despite being deposited across a wide range of sedimentary environments and in different sedimentary rock types. For example, the Hawthorn Group deposited in marginal marine to deeper-water environments, has uniform REE concentrations, as does the Love Hollow phosphorite along a 400 km transect between Arkansas and Illinois. The REE concentrations of the Phosphoria Formation from Utah, Idaho, and Wyoming are strikingly similar (Fig. 3). Uniform REE contents of individual phosphate beds allow U.S. phosphate production data to be used in estimating the amount of REEs contained, but not recovered, from phosphate ore produced from U.S. mines. Measured REE contents suggest that 15% of Σ REE and more than 65% of the Σ HREE projected global demand for 2014 is mined, beneficiated, and put into solution by the U.S. phosphate industry annually (Table 1). Significantly, the monetary value of phosphate fertilizer-contained REEs (Humphries, 2010) rivals that of the fertilizer itself. Accordingly, REE contents of some phosphate occurrences suggest that they could be economically mined primarily for REEs.

The areal distribution and therefore the volume of the most REE-enriched (but not mined) Paleozoic phosphate deposits in the United States remain undocumented. However, the REE endowment of Love Hollow phosphorite in Arkansas can be estimated to illustrate the potential of these deposits. Using the average measured phosphate of 23% P_2O_5 and assuming a density of 2.8 g cm^{-3} , the 1.5-m-thick horizon distributed over 100 km^2 contains roughly 235 Mt of phosphate rock that contains 1.3 Mt of extractable Σ REE, of which 0.37 Mt are Σ HREE; this is nearly twice the Σ HREE estimated for the South China clays and 60 times that contained in the Bokan Mountain deposit (Table 1). Mining 1 km^2 of this horizon (about 5% of the area mined annually for phosphate in Florida), where the thickest beds are 9 m, would yield an amount of Σ REE approximately equivalent to five times that contained in the entire Bokan Mountain deposit, or equivalent to 50% of the Σ REE projected global annual demand and more than 150% of the current Σ HREE demand (Table 1).

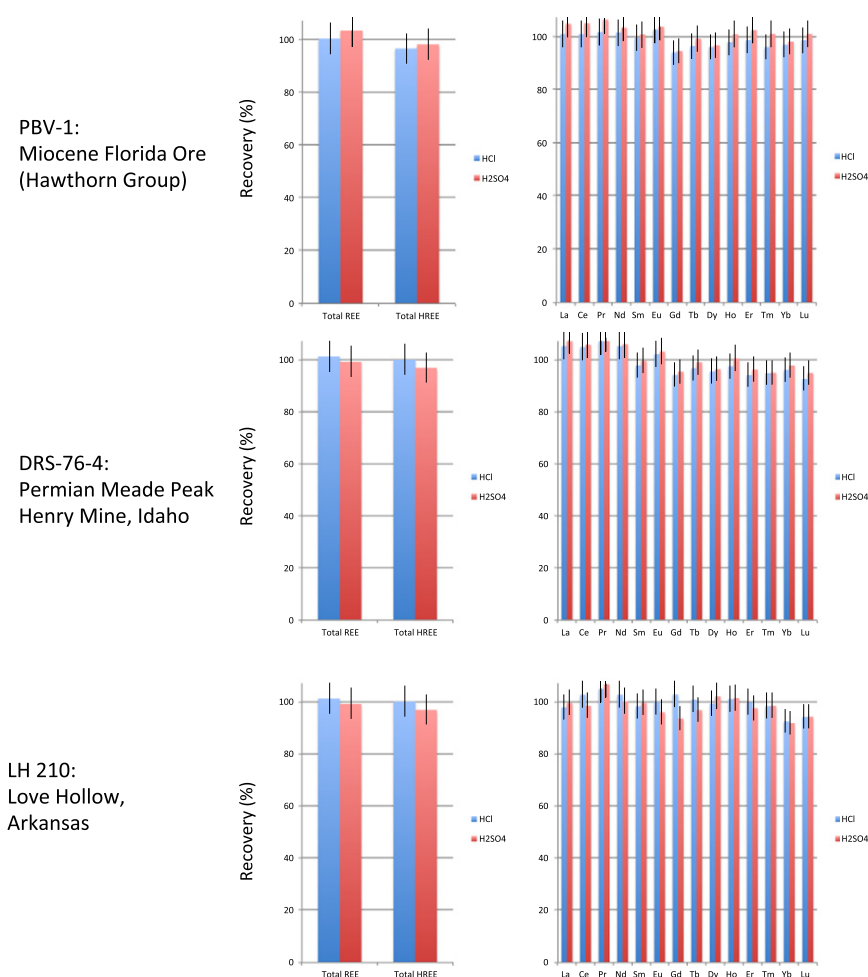


Fig. 6. Results of REE extraction experiments on phosphorite samples from the Miocene Hawthorn Group, Permian Meade Peak Member of the Phosphoria Formation, and the Upper Ordovician Love Hollow Formation. Results of bulk-rock solids and partial leachates (using 0.5 N HCl and 0.4 N H₂SO₄ as outlined in the [Methods](#) section), analyzed using procedures described in [Verplanck et al. \(2004\)](#). Column graphs that compare percent recovery of the total REEs (Σ REE), total heavy REEs (Σ HREE) and individual rare earth elements relative to bulk-rock abundance using the indicated acid extractions. See Supplementary Data 2 for data. Error bar indicates 6% analytical uncertainties reported for the analytical technique ([Verplanck et al., 2004](#)).

3.5. Secular variation of REEs in phosphorites

Our data suggest that REE concentrations in phosphate rock are uniform within a geologic time interval, but have varied by as much as three orders of magnitude among geologic periods. This compositional variability is an important exploration consideration and is evaluated by a temporal comparison of shale-normalized REE compositions of sedimentary phosphate grouped by geologic age ([Fig. 3](#)). Modern phosphates are low in REEs and have patterns that mirror the distinctive pattern of modern seawater, indicating that REEs were minimally fractionated during their incorporation into francolite from seawater ([Elderfield and Pagett, 1986; Wright et al., 1987; Jarvis et al., 1994; Lécuyer et al., 2004](#)). Miocene phosphorites are more REE enriched, but their REE patterns are similar to those of modern occurrences. Early Cenozoic and late Mesozoic phosphorite REE contents are also grossly similar to those of the Miocene. In contrast, REE contents of Paleozoic phosphorites are distinct relative to those of late Mesozoic and younger deposits. REE contents among Paleozoic phosphorites vary by as much as a thousand-fold and some of these deposits have distinctive middle REE-enriched, concave-down shale-normalized REE patterns ([Lécuyer et al., 2004](#)). The REE contents of Early Cambrian phosphorites are markedly lower and resemble those of Miocene phosphorites. Finally, Paleoproterozoic phosphorites have the lowest REE contents and distinctive patterns, which include positive Ce and Eu anomalies.

4. Sources and processes of REE enrichment in phosphorites

The geologic processes that control REE contents in phosphorites are intensely debated. Many researchers interpret normalized REE patterns that resemble modern seawater as primary ([Elderfield and Pagett, 1986; Wright et al., 1987; Piper et al., 1988; Picard et al., 2002; Martin and Scher, 2004](#)); whereas deviations from the modern are considered, by some, the product of post-depositional alteration where redistribution of REEs among detrital and authigenic phases occurs during diagenetic equilibration of phosphate solids with pore water ([McArthur and Walsh, 1984; Ilyin, 1998; Shields and Stille, 2001; Shields and Webb, 2004; Bright et al., 2009](#)). Variations in francolite REE abundances have been attributed to facies, grain size, duration and depth of burial ([McArthur and Walsh, 1984; Ilyin, 1998; Shields and Stille, 2001; Shields and Webb, 2004](#)). Alternatively, deviations in REE abundance in phosphate phases have been interpreted to be primary, a direct result of secular variations in ocean chemistry ([Wright et al., 1987; Picard et al., 2002; Lécuyer et al., 2004](#)).

Our synthesis favors secular variations in ocean chemistry. Analyses of many phosphorites show that there is no systematic trend of increasing REE content with age ([Fig. 3](#)). In fact, the oldest phosphorites (Cambrian and Proterozoic) have significantly lower REE contents than younger phosphorites. Our carefully collected sample suites (Supplementary Data 1; [Fig. 4](#)) also demonstrate that individual phosphate beds over regions as large as thousands of square kilometers

Table 1

The REE contents of world-class REE deposits compared with the estimated REE potential of sedimentary phosphate deposits.

	Projected demand (t)	Mountain pass total (t)	Mountain pass annual (t)	China clay total (t)	Bokan Mountain total (t)	Bokan Mountain annual (t)	Miocene annual (t)	Phosphoria Fm. annual (t)	L. hollow 100 km ² (t)	L. hollow 1 km ² (t)
Lanthanum (La)	43,521	743,495	37,175	164,536	1714	156	2718	1382	200,900	12,355
Cerium (Ce)	53,542	1,042,279	52,114	253,849	5293	481	3655	358	443,543	27,278
Prasodymium (Pr)	6581	88,027	4401	33,550	648	59	549	196	40,740	2506
Neodymium (Nd)	29,931	247,033	12,352	115,949	2521	229	2329	735	182,148	11,202
Samarium (Sm)	1198	18,913	946	32,901	665	60	465	118	36,900	2269
Europium (Eu)	707	2350	118	2975	65	6	115	27	8370	515
Gadolinium (Gd)	1995	4701	235	25,758	675	61	537	157	41,760	2568
Terbium (Tb)	480	351	18	3641	116	11	77	32	5494	338
Dysprosium (Dy)	1777	765	38	20,030	775	70	516	160	32,981	2028
Holmium (Ho)	44	90	4	4291	130	12	114	35	6477	398
Erbium (Er)	831	136	7	12,599	340	31	340	108	17,150	1055
Thulium (Tm)	44	46	2	1803	43	4	45	14	1934	119
Ytterbium (Yb)	44	46	2	9442	225	20	293	80	10,328	635
Lutetium (Lu)	44	27	1	1431	22	2	45	579	1215	75
Yttrium (Y)	9528	2642	132	147,387	3766	342	4737	2310	242,496	14,914
ΣREE	150,267	2,150,900	107,545	830,143	16,998	1545	16,536	6291	1,272,437	78,255
ΣLREE	134,774	2,139,747	106,987	600,786	10,841	986	9717	2789	904,232	55,610
ΣHREE	15,493	11,153	558	229,357	6157	560	6819	3503	368,205	22,645

Projected 2014 global REE demand from the [British Geological Survey \(2011\)](#). REEs contained in Mountain Pass, California, and the South Chinese deposit from [Long et al. \(2010\)](#) and Bokan Mountain, Alaska, from [Bentzen et al. \(2013\)](#). Annual REEs mined from Mountain Pass and Bokan Mountain estimated using anticipated ore mined and its average REE content. Estimate does not include the rate of recovery of REEs, if any. Potential annual REE production from operating phosphate mines is calculated using our mean phosphate REE concentration (Supplementary Data 1) and the annual phosphate produced from Miocene phosphate (Florida + Carolina = 25.5 Mt) and Phosphoria Formation (4.5 Mt) ([Jasinski, 2011](#)). Estimated REE content of the Love Hollow Formation, Arkansas, inferred from its areal distribution, thickness, and REE content (see discussion in text). These estimates are not intended as formal REE ore-reserve estimations, but rather as rough approximations to illustrate the relative potential of phosphorite-hosted REEs.

have similar REE contents, this despite deposition in shallow marginal marine to deeper basinal environments, different sedimentary host rock compositions, different grain morphologies and sizes, and burial depth differences spanning 10 km ([Fig. 4](#)). These observations are incompatible with explanations that phosphorite REE contents are determined by the depth and duration of burial, depositional setting, phosphate grain morphology, or host rock composition. The temporal correspondence of REE concentrations and patterns in coeval deposits, widely separated across continents ([Fig. 3](#)), are best explained by the variation of ocean REE compositions through time.

The accumulation of REEs in biogenic (skeletal) and sedimentary francolite on the modern seafloor has been intensely studied. Researchers of modern environments generally agree that REEs are incorporated into francolite during the earliest diagenesis, which faithfully records the REE composition of seawater at the time of deposition ([Elderfield and Pagett, 1986](#); [Wright et al., 1987](#); [Piper et al., 1988](#); [Picard et al., 2002](#); [Lécuyer et al., 2004](#); [Martin and Scher, 2004](#)). A recent study of REE contents and Nd-isotopic compositions for biogenic francolite determined that REE concentrations acquired during recrystallization on the seafloor, are very high relative to concentrations surrounding pore fluids during later diagenesis ([Martin and Scher, 2004](#)). Consequently, REE compositions are not easily altered during later burial and diagenesis ([Martin and Scher, 2004](#)). It has been suggested that granular phosphorites better preserve the original seawater REE compositions than biogenic phosphate, largely because anomalous REE compositions have not generally been recognized in the phosphorites ([Jarvis et al., 1994](#); [Ilyin, 1998](#); [Shields and Stille, 2001](#); [Shields and Webb, 2004](#)) and because some ancient intervals, like the lower Cambrian, have values similar to those of modern seawater ([Shields and Stille, 2001](#); [Shields and Webb, 2004](#)). Yet, a comparison of coeval biogenic and phosphorite data shows that they have similar REE patterns ([Fig. 3](#)), and anomalous patterns (unlike modern seawater) are most conspicuous in the sedimentary phosphorites ([Fig. 3](#)).

The cause(s) of REE compositional variations through time is unknown. Alleged secular REE variations have been strongly criticized for the lack of a theoretical basis for seawater REE composition shifts ([Shields and Webb, 2004](#)). In contrast, more than 30 years of intensive study of modern ocean chemistry has documented the mass balance, cycling, and fractionations of REEs that accompany marine geochemical

cycles ([Elderfield and Greaves, 1982](#)). Considered with global seawater chemical variations over geologic time, secular REE variation is expected. The dominant control on REE composition in the modern ocean is adsorptive scavenging of REEs by particles (dominantly Fe–Mn-oxyhydroxides) that settle through the water column and sequester REEs in marine sediments ([Elderfield and Greaves, 1982](#); [Sholkovitz, 1994](#)). Preferential removal of Ce and LREEs by oxyhydroxide particles is responsible for distinctive REE patterns characteristic of modern seawater ([Sholkovitz, 1994](#)). Resulting REE patterns are markedly different from those of comparatively LREE- and middle REE (MREE)-enriched contributors (e.g., riverine, hydrothermal, aeolian, and diagenetic inputs) to ocean composition ([Elderfield and Greaves, 1982](#); [Elderfield et al., 1990](#); [Mitra et al., 1994](#)). Adsorptive scavenging limits the REE concentration and, thus, residence time of REEs in the ocean. Despite having concentrations 10 to 100 times greater than those of seawater, more than 70% of riverine ([Elderfield et al., 1990](#)) and nearly 100% of midocean hydrothermal REE fluxes ([Mitra et al., 1994](#)) are quickly adsorbed to settling oxyhydroxide particles. The dissolution of the adsorbing oxyhydroxides in modern dysoxic and anoxic water columns can locally increase seawater REE concentrations by as much as ten times ([German et al., 1991](#)). Moreover, reductive dissolution of oxyhydroxides in anoxic sediments generates large benthic fluxes of Mn, Fe, and REEs ([Elderfield and Greaves, 1982](#); [Elderfield et al., 1990](#); [Sholkovitz et al., 1992](#)) that in anoxic/dysoxic environments are also transferred into the overlying water column. In the modern ocean, local dysoxic environments contribute to relative increases in dissolved LREE and pronounced MREE and Ce enrichments ([De Baar et al., 1985](#); [Elderfield et al., 1990](#)).

Ocean redox conditions and carbon cycles have varied significantly throughout geologic time ([Jenkyns, 2010](#); [Gill et al., 2011](#); [McLaughlin et al., 2012](#); [Harper et al., 2014](#)). Large Mesozoic and Paleozoic positive carbon isotope excursions, for example, are now generally accepted as a consequence of periods of global anoxia that have had profoundly affected ocean and marine biologic systems ([Jenkyns, 2010](#); [Gill et al., 2011](#); [McLaughlin et al., 2012](#); [Liu et al., 2013](#); [Harper et al., 2014](#); [Kaiho et al., 2014](#)). Importantly, nearly all of these processes foster relative increases in dissolved Ce, LREEs, and MREEs. Previously, we documented a dramatic increase in ocean Fe and P concentrations during two Silurian C-isotope events ([McLaughlin et al., 2012](#)). Modern analogs

suggest that a net decrease in the formation and burial of REE scavenging oxyhydroxides dramatically increases ocean REE concentrations and that resulting oceanic REE patterns would have elevated Ce, LREE, and MREE abundances (Elderfield and Greaves, 1982; Elderfield et al., 1990; Mitra et al., 1994). Similarly, transitions from oxic to anoxic oceanic conditions can trigger massive shifts in the cycling of Fe–Mn oxyhydroxides sequestered in shallow sediments causing a benthic flux of REEs, with relative abundances similar to those observed in modern anoxic pore waters, which would greatly increase the flux of MREE and Ce to the ocean (Elderfield and Greaves, 1982; Elderfield et al., 1990; Sholkovitz et al., 1992; Nozaki et al., 1999). By example, Nd isotope data for samples across a Mesozoic anoxic event (OAE II) demonstrate a dramatic ocean-wide shift in Nd composition attributed to a change in the relative contributions of diverse REE sources (MacLeod et al., 2008; Martin et al., 2012).

The coincidence of anomalous REE patterns/abundances and phosphorites is a potentially important relationship. Whereas formation of phosphate deposits has generally been ascribed to deep, cold, phosphate-rich marine water upwelling along continental margins, such a model is inconsistent with the intermittent distribution of giant phosphate deposits in the secular stratigraphic record (Glenn et al., 1994). As with REEs, adsorptive scavenging of phosphorous by oxyhydroxides is the primary control on its oceanic abundance (Van Cappellen and Ingall, 1994; Ingall and Jahnke, 1997; Palastanga et al., 2011). Thus, the coincidence of REE patterns distinct from modern seawater and sedimentary phosphate deposits in the geologic record raises the tantalizing possibility that, in fact, the causative processes are linked and reflect fundamental transitions from oxic to anoxic marine conditions (Van Cappellen and Ingall, 1994; Ingall and Jahnke, 1997; Palastanga et al., 2011). This hypothesis is further supported by the previously recognized coincidence of giant phosphorites and ferruginous sediments (Glenn et al., 1994).

5. Conclusion

Collectively, these data and process-based dynamics strongly support the long-debated suggestion that oceanic REE contents vary in a secular fashion as a result of changes in the redox conditions of the oceans. Consequently, the hypothesis that the relative abundances of REEs are a proxy for redox cycling of metals, and may indicate episodes of phosphogenesis merits additional study. Of particular significance to REE exploration, however, is the consistency of REE abundances within individual time horizons and that these may identify time periods, like the Late Mississippian, Devonian, and Ordovician, that were favorable for the formation of phosphorites with high-REE abundances.

Our evaluation indicates that the concentrations and quantities of HREEs in U.S. phosphorites exceed those of all known resources. Their contained REEs are entirely hosted in francolite and, are nearly 100% recoverable, using the same process currently used to leach and produce the world's phosphate supply. The beneficiation, dissolution, and production of sedimentary phosphate is sufficiently low-cost to produce enough phosphate to fertilize the fields that feed the world's population. In addition, the REE content in even the lowest grade of these deposits exceeds the current value of the phosphate itself. Thus, the extraordinary endowment of easily extracted REEs hosted in environmentally friendly phosphorites indicates they are a REE source with the potential to meet the global REE demand.

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