

Rare-earth element chemistry of Mississippian-age phosphate nodules in the Fayetteville Shale of Oklahoma and Arkansas

Ranjini Murthy, David Kidder, Royal Mapes, and Robyn Hannigan

ABSTRACT

Phosphate nodules from marine black shales and nonmarine gray shales from the Mississippian Fayetteville Shale of north-central Arkansas and northeastern Oklahoma are strongly enriched in middle rare-earth elements (MREEs) as is common in Paleozoic phosphate deposits. The nodules commonly preserve conspicuous europium anomalies that are not typical of phosphate deposits elsewhere in the geologic record, suggesting extremely reducing diagenetic conditions. Contrastingly, minor cerium anomalies imply oxidizing conditions that are not unexpected in the light to medium gray nonmarine host shales. The most likely explanation for the Ce anomalies in the marine phosphate nodules is that bottom waters in the marine environment reverted from the anoxic waters that probably characterized the basal Fayetteville Formation to weakly oxidizing waters that permitted survival of the fauna that occurs in a well-defined zone. All of the Ce anomalies probably formed during an earlier diagenetic stage than the Eu anomalies that developed later, as decaying organic matter consumed what little oxygen was available.

INTRODUCTION

Phosphate nodules are concretions that are formed during early diagenesis (processes associated with the compaction and lithification of sediments). The phosphate nodules studied are from the late Mississippian (~340 m.y.) and were collected from north-central Arkansas and northeastern Oklahoma. Nodules formed under marine conditions are found throughout central Arkansas and northeastern Oklahoma. Nonmarine nodules are found only in the vicinity of the Lincoln Dam section of the Fayetteville Formation in north-central Arkansas (Figure 1). The cores of the marine phosphate nodules are commonly coprolitic, and they can contain exceptionally well-preserved cephalopod mandibles in a fauna that is dominated

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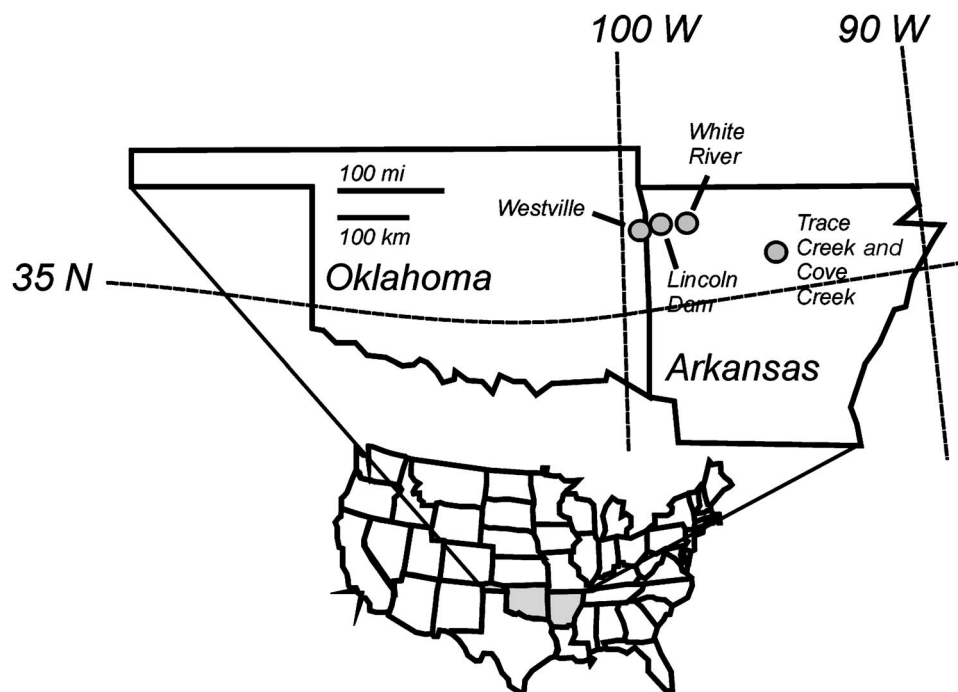
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Figure 1. Index map of sample localities in Arkansas and Oklahoma from where nodules were obtained. Marine and non-marine nodules of Carboniferous age have also been found in Texas, Kansas, and Ohio. In this study, nodules collected from the Lincoln Dam are considered nonmarine based on sedimentologic and paleontologic reconstructions (Kidder, 1985).



by ammonoid, bactritoid, coleoid, and nautiloid cephalopods (Gordon, 1964; Mapes, 1987; Tanabe and Mapes, 1995). The phosphate nodules bear lesser numbers of arthropods and invertebrate debris (Mapes, 1987). In addition to cephalopods, carbonate concretions in close stratigraphic proximity to the marine phosphate nodules preserve sponge spicules, brachiopods, and pelecypods (Zangerl et al., 1969). Non-marine nodule cores contain only plant fossils. These include delicate fern foliage and lycopod leaves, which could not withstand transportation from a terrestrial to a marine environment. The nonmarine phosphate nodules overlie interbedded coaly layers and shales; some of the latter bear in-situ root casts. The cores of both marine and nonmarine nodules are enclosed by a distinct phosphatic rind (Figure 2).

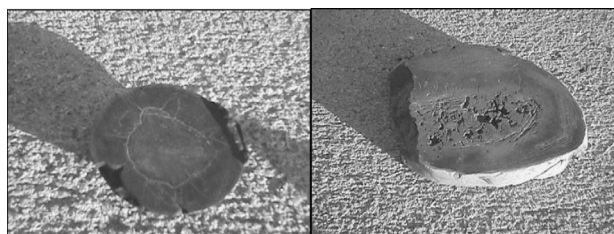


Figure 2. Phosphate nodules from the Fayetteville Formation. Left: a typical marine nodule (5 cm [2 in.] across). The boundary between the coprolitic core and phosphatic rim is distinct. Right: a typical nonmarine nodule showing the oxidized core and distinct phosphatic rim (12 cm [5 in.] across).

Exceptional preservation of fossils, such as soft parts from nektic cephalopods, suggests that these nodules formed during early diagenesis of the host sediment (Mapes, 1987). This interpretation is consistent with the early diagenesis common in many phosphogenic settings (e.g., Bentor, 1980). Early lithification can preserve the original sedimentary fabric as well as inclusions, such as body fossils, coprolites, peloids, etc., with minimal overprint (Kidder, 1985). The types of fossils found in the cores of these nodules provide information concerning the depositional environment and provide significant insight into the early diagenetic history of these nodules. For example, disarticulated cephalopod jaws and shell fragments preserved in the coprolitic cores of marine nodules (Mapes, 1987) not only indicate the presence of a carnivorous predator that ate cephalopods, but also help constrain the paleo-environment in terms of factors such as distance to the shore and oxygen conditions (Cuomo and Bartholomew, 1991). The chemical composition and paleontology of these nodules, then, have the potential to provide significant information regarding the processes that occurred during the time of nodule formation.

Rare-earth elements (REEs) are uniquely suited to the study of a variety of geological processes. The distinctive chemistry of the REEs across the series from La to Lu has been applied to sediment provenance (Taylor and McLennan, 1985; Cullers, 1994, 1995; Wombacher and Muenker, 2000; Ding et al., 2001; Nyakairu and Koeberl, 2001), chemical weathering

(Morey and Setterholm, 1997; Viers et al., 1997; Land et al., 1999; Hannigan and Sholkovitz, 2001), and groundwater chemistry (Smedley, 1991; Johannesson et al., 1996; 1997a, b; 1999; Dia et al., 2000). The relative abundance of the REEs in marine and nonmarine nodules of the Fayetteville Formation is used here to investigate the processes controlling diagenesis of these nodules.

In sedimentary rocks, the chief host of REEs are clay minerals such as illite (Kidder, 1985; Hannigan and Basu, 1998). Additional mineral hosts in phosphate nodule-bearing shales include diagenetic apatite and calcite cements (Kidder, 1985; Kidder and Eddy-Dilek, 1994). Rare-earth elements are predominantly trivalent and are commonly associated with phosphate in aqueous solutions (e.g., Brookins, 1989; Byrne et al., 1996; Hannigan and Sholkovitz, 2001). Laboratory experiments and REE speciation calculations all point to inorganic phosphate as an important control on the fractionation of REE in natural waters (Wood, 1990; Byrne and Kim, 1993; Byrne et al., 1996). A good example comes from the laboratory experiments of Byrne et al. (1996), which show that the precipitation of phosphates from seawater results in the preferential removal of dissolved middle rare-earth elements (MREEs) and the formation of MREE-enriched precipitates and phosphatic salts at neutral to high pH (Byrne and Kim, 1993; Johannesson et al., 1995). Eu and Ce are two of the REEs that exhibit redox behaviors in geological systems. Ce can be oxidized and reduced, depending on conditions, in low-temperature systems such as marine depositional environments. Although Eu also exhibits redox behavior, there is no convincing evidence that Eu^{2+} occurs in low-temperature settings. Certainly, in magmatic and geothermal systems, there is no evidence to suggest that Eu^{3+} reduces to Eu^{2+} with these high-temperature settings (Sverjensky, 1984). When phosphatic minerals are present in sediments, they commonly contain high concentrations of REEs, with the MREEs (Sm to Dy) particularly enriched (e.g., Wright et al., 1984, 1987; Elderfield and Pagett, 1986; Grandjean and Albarède, 1989; Grandjean-Lécuyer et al., 1993; Kidder and Eddy-Dilek, 1994; Ilyin, 1998; Ogihara, 1999; Kidder et al., 2003; Lécuyer et al., 2004), although the enrichment is less common in post-Paleozoic phosphates (McArthur and Walsh, 1984). In addition, depending on the conditions of deposition, the nodules may preserve Ce anomalies characteristic of the depositional/diagenetic conditions (oxidizing vs. reducing). The chemical affinity between the trivalent REEs and the phosphate anion was used to understand

diagenetic processes responsible for nodule formation in the Fayetteville Shale, particularly in nonmarine formations.

GEOLOGIC SETTING

The nodules we studied are from the late Mississippian (~350 m.y.) Fayetteville Formation of northern Arkansas and eastern Oklahoma (Figure 1). The Fayetteville Formation is considered to rest conformably on the Batesville Sandstone (and Hindsville Member; Figure 3), although at places, it unconformably overlies the Boone chert (Handford, 1986). Samples for this study were collected from the transgressive marine facies near the

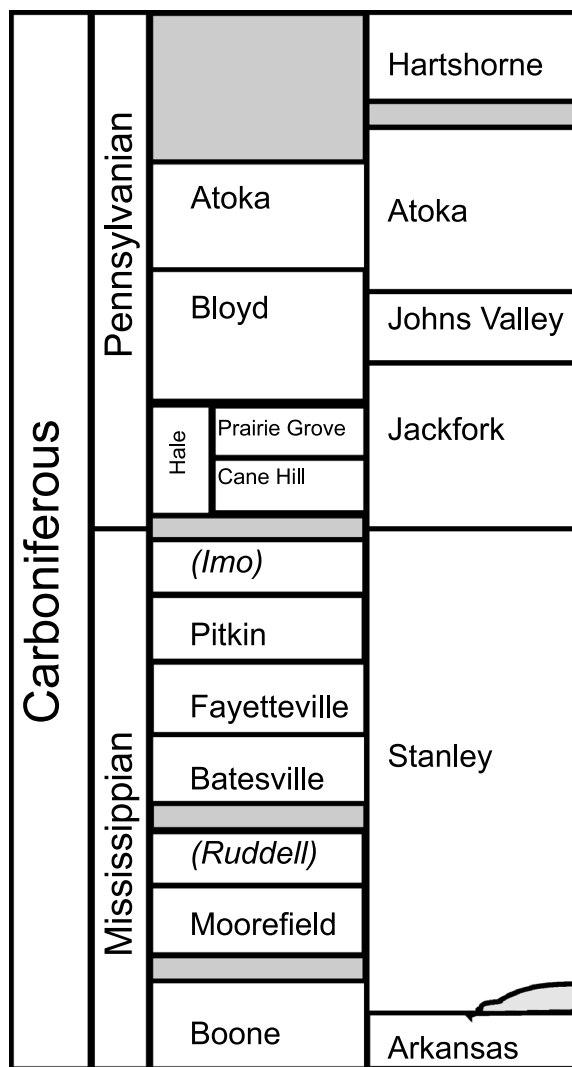


Figure 3. Stratigraphic column showing the conformable relationships between the Fayetteville and the Batesville formations (AGC, 2003).

base of the formation in Arkansas and Oklahoma and from the younger nonmarine strata in the Lincoln Dam section of Arkansas (Figure 1). At the base and in the middle of the Fayetteville Shale, the unit is a dark-gray to black, fissile, concretionary, clay shale. The Wedington Sandstone Member is in the upper third of the Fayetteville Formation in northwestern Arkansas and is absent in northeastern Oklahoma and north central Arkansas. Most exposures of the member are composed of gray to brown, fine-grained, sometimes calcareous sandstone, and in some places, like the Wedington Dam section, the sandstone is split by a bed of nonmarine, brown, clay shale. In north-central Arkansas and north-eastern Oklahoma, the upper part of the Fayetteville Formation is composed of thin-bedded, dark-gray, fine-grained limestones that are commonly interbedded in the black, fissile marine shales. Septarian concretions are more common in the lower beds of the Fayetteville, but they may be found throughout the formation. Fossils are abundant in some intervals and in local areas. Most of the fauna recovered from the dark-gray and black shales are partly to completely pyritized; some are three-dimensionally preserved, but most are crushed. Phosphate nodules in the gray nonmarine and black marine host shales range from spheroidal to platy in shape (Figure 2). The marine nodules are typically about 5 cm (2 in.) in maximum dimension, and nonmarine nodules commonly reach 25 cm (10 in.) in maximum dimension (Table 1).

MATERIALS AND METHODS

All REE analyses were performed using Perkin Elmer's ELAN 9000 inductively coupled plasma mass spectrometer (ICP-MS). Phosphate analyses were performed by ion chromatography (IC) after leaching and oxidation of the samples (Aspila et al., 1976). To prepare nodules for analysis, the central part of the core and the rim were mechanically reamed as powdered samples with a carbide-tipped engraver. The carbide tip was rinsed between samples with 18.2 Mohm water to avoid cross-contamination. A longitudinal set of samples across the core and rim of two nodules was also collected to explore heterogeneity in composition across the nodules. After samples of rims and cores were reamed with a carbide-tipped engraver, approximately 0.250 g of the powdered samples were digested under clean room conditions in concentrated ultrapure HNO₃ and ultrapure HF in tightly sealed 15-mL Teflon Tetrafluoroethylene screw-cap bombs by heating on a

Table 1. Sample Identification, Collection Location, and Nodule Type

Sample Identification	Sample Location	Type of nodule (Marine or Nonmarine)
IWR-2	White River, Arkansas	marine
WR-A	White River, Arkansas	marine
ICC-1	Cove Creek, Arkansas	marine
ICC-2	Cove Creek, Arkansas	marine
ITC-10	Trace Creek, Arkansas	marine
ITC-11	Trace Creek, Arkansas	marine
WRP-1	White River, Arkansas	marine
TC-9	Trace Creek, Arkansas	marine
TC-1	Trace Creek, Arkansas	marine
WOKP-1	Westville, Oklahoma	marine
WOKP-2	Westville, Oklahoma	marine
CC-10	Cove Creek, Arkansas	marine
CC-7	Cove Creek, Arkansas	marine
NM-1	Lincoln Dam, Arkansas	nonmarine
NM-2	Lincoln Dam, Arkansas	nonmarine
NM-3	Lincoln Dam, Arkansas	nonmarine
LDP-1	Lincoln Dam, Arkansas	nonmarine
LDP-A	Lincoln Dam, Arkansas	nonmarine
LDP-B	Lincoln Dam, Arkansas	nonmarine
LDP-C	Lincoln Dam, Arkansas	nonmarine
LDP-D	Lincoln Dam, Arkansas	nonmarine
LDP-E	Lincoln Dam, Arkansas	nonmarine
LDP-F	Lincoln Dam, Arkansas	nonmarine

hot plate at 80°C for 24 hr. The final solutions were prepared by adding the internal standard (2 ppm ¹¹⁵In) and diluting the samples with 2% ultrapure HNO₃. External precision was calculated using external standardization based on measurements of a range of REE standards (0.1 and 0.5 ppm and 0.10, 0.20, and 0.40 ppb). All calibrations were better than 0.9995. External precision was monitored using U.S. Geological Survey Devonian Oil Shale (SDO)-1 with measured values better than 5% for all REE. Rare-earth element data are shown in Table 2.

To determine the total phosphate concentration, samples were prepared according to the method of Aspila et al. (1976). After samples of cores and rims were isolated using a carbide-tipped engraver, 0.250-g sample aliquots were transferred into numbered crucibles. About 1 mL of 50% magnesium nitrate was added to each crucible to ensure that the sample was completely wet and to prevent loss because of volatilization. The wet samples were then placed in an oven at 110°C until dry. The dry samples were ashed in a muffle

furnace for 2 hr at 550°C. We ashed the samples to convert organic phosphorus into inorganic phosphorus through dry oxidation at high temperatures. After the jars were cooled, 25 mL of 1 M hydrochloric acid (HCl) into 100-mL Pyrex jars was added to allow the resuspension of the sample. A spatula was used to scrape ashed samples from jar walls and bottom to achieve resuspension. The Pyrex jars were closed securely and placed on shaker table for 16 hr, adjusting shaker table speed so that the samples remained suspended. After 16 hr extraction, the supernatants were transferred into 50-mL centrifuge tubes. The samples were centrifuged at 2500 rpm for 10 min. The supernatant was then decanted and filtered with 0.45- μ m filter attached to a luer tip. The first 5 mL was discarded through the filter, and the remaining sample collected in a vial for phosphate analysis using the IC (Dionex 120).

RESULTS AND DISCUSSION

Analysis of Pennsylvanian-age phosphate nodules by Kidder and Eddy-Dilek (1994) showed the MREE enrichments typical in reworked phosphatic material hosted by black shale. The Mississippian-age nodules studied here also showed the MREE enrichment when concentrations were normalized to the upper continental crust (UCC; Condie, 1991) (Figures 4, 5). We will use the convention of normalizing the measured REE concentrations (Table 2) to UCC throughout this discussion.

A variety of processes can influence the relative abundances of the different REEs. Specific depositional environments of shales or nodules can be deduced from the REE chemistry (Murray et al., 1990; MacLeod and Irving, 1996). The variable degree of MREE enrichment in mid-continent Pennsylvanian nodules resulted from differing levels of terrigenous detrital influence that, in turn, may have been related to thickness of host shale, perhaps reflecting changes in detrital clay input (Kidder and Eddy-Dilek, 1994). Most of the samples analyzed in our study show strong MREE enrichment (Figures 4, 5). There are many possible reasons for this pattern, some of which can be ruled out as unlikely in the Fayetteville Formation. Hannigan and Basu (1998) attributed the MREE enrichment to thermal maturation. However, this cannot be applied to our study, as thermal maturation occurs during late diagenesis, which would not have allowed the perfect preservation of fossils such as molluscan shell material (made of aragonite) and the cellulose of vascular plant material. Hannigan and Shol-

kovitz (2001) found that MREE enrichment can result from acidic pH and chemical weathering based on measurements of waters draining phosphatic and organic shales. There is no evidence for a phosphatic provenance in the Fayetteville Formation, and the potential for survival of dissolved MREEs through estuaries is limited (Hannigan and Sholkovitz, 2001) and hence does not account for the MREE enrichment in marine phosphate nodules specific to this study, but perhaps may have been a factor in the nonmarine phosphates. The deposition and diagenesis of both marine and nonmarine nodules are very different from that observed in shales, and therefore, the chemistry is expected to be different as well.

Basin position can be related to the magnitude of MREE enrichment (Hannigan and Basu, 1998). If basin position was related to MREE enrichment (proximity to phosphorus-rich parent material), then a systematic variation would be seen in nonmarine nodules and the deeper marine nodules in Arkansas and Oklahoma. There is no systematic variation in either marine or nonmarine nodules, and hence, basin position does not account for the MREE enrichment observed in phosphate nodules that we studied. However, the greater degree of MREE enrichment in Fayetteville phosphate nodules relative to those in the Pennsylvanian of the mid-continent (Kidder et al., 2003) is consistent with a lower level of terrigenous detrital influence in the marine Fayetteville phosphates, but not with the nonmarine ones, which are closely associated with terrigenous detrital sources.

MREE enrichment because of algae and biogenic processes is one possible explanation for the MREE relationships seen in the Fayetteville phosphate nodules (Stanley and Byrne, 1990; Kidder and Eddy-Dilek, 1994). For example, fish consumption of certain algae, which are capable of incorporating MREE from the water column, can potentially deliver MREE-enriched fecal matter to the sediment, thereby explaining the trend observed in our data (Figure 6) (Kidder and Eddy-Dilek, 1994). A second potential mechanism for delivering MREE-enriched detritus to bottom sediments is in organic and oxyhydroxide grain coatings (Elderfield et al., 1990). In addition, MREE enrichment can happen in the sediment as concretionary phosphate nodules form. This is supported by experimental work (Byrne et al., 1996) that documented preferential removal of MREE from water during coprecipitation of REE with apatite. We do not know which of these three processes was dominant, but all may have contributed to MREE enrichment.

Table 2. Rare-Earth Element and Phosphate Concentrations of the Marine and Nonmarine Nodules*

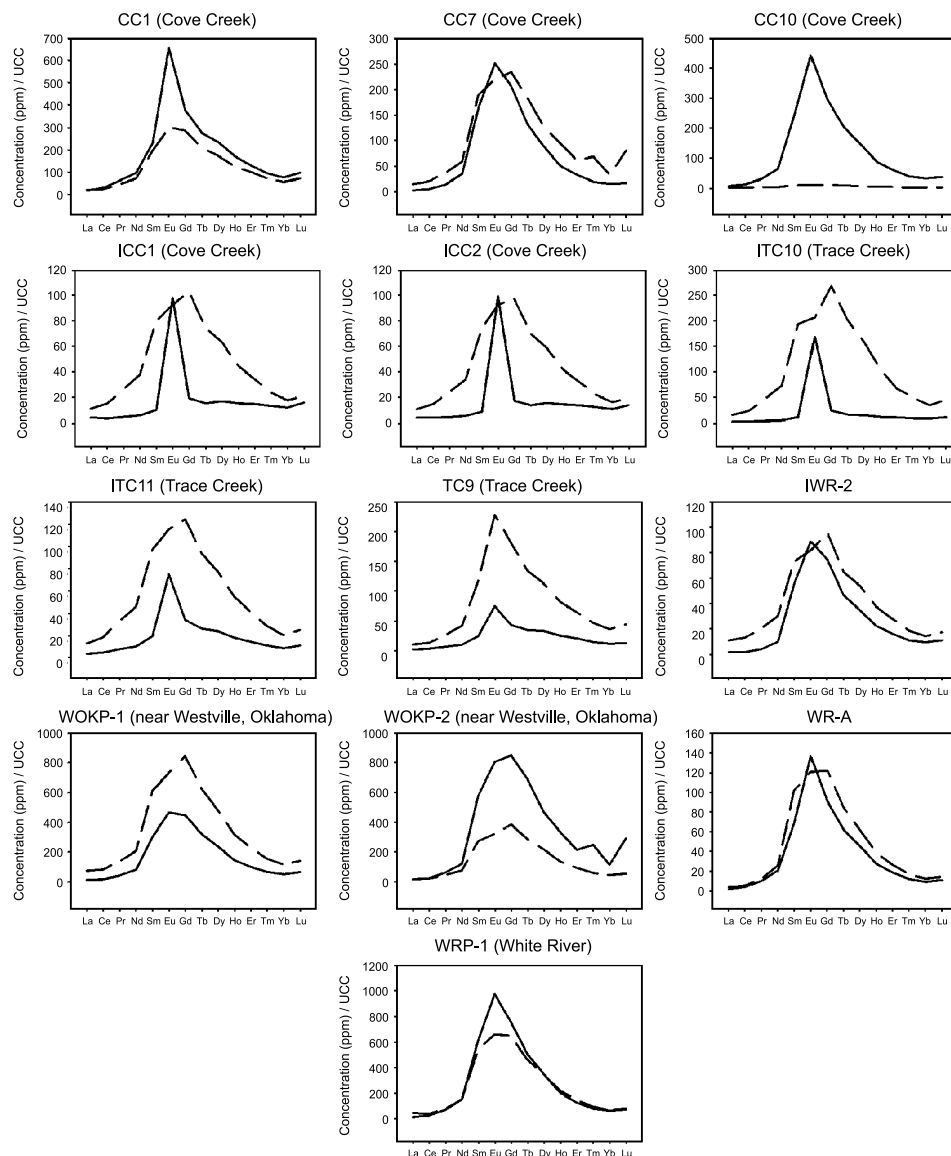
Marine Nodules	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	PO ₄ ³⁻	Ce/Ce*	Eu/Eu*
IWR-2	core	58.4	129	30.1	263	249	77.9	282	29.7	121	17.9	37.9	21.7	2.5	525.3	0.7	0.98
	rim	339	872	147	788	328	71.8	364	41.3	188	30	63.6	32	3.9	126.8	0.89	1.38
WR-A	core	55.3	272	72.6	532	310	120	345	39.8	158	22	42.1	20.7	2.4	1251.5	0.98	1.08
	rim	111	364	88.7	664	458	106	463	54.1	216	30.9	60	27.4	3.2	282.9	0.84	1.72
ICC-1	core	128	222	34.5	154	45.8	86.2	74.4	10	59.9	12.4	34.6	26.8	3.5	43.4	0.76	6.94
	rim	336	986	188	988	360	81.7	390	47.7	221	35.8	78.9	39.1	4.7	228.3	0.87	1.02
ICC-2	core	129	249	32.7	142	39.8	87.3	66.6	9	55.6	11.7	32.3	23.9	3.1	249.8	0.89	7.97
	rim	328	950	172	885	333	81.8	369	44.7	204	33.3	73.4	36.1	4.3	71.3	0.91	1.1
ITC-10	core	76.2	152	26.4	134	50.2	148	91.3	10.7	53.6	9.7	24.1	18.3	2.5	195.4	0.77	10.27
	rim	463	1510	335	1900	869	182	1020	129	556	84.3	154	76.1	10.2	282.1	0.87	0.91
ITC-11	core	97.2	282	53.5	261	87.2	65.8	128	16.7	82.9	14.4	32.8	18.4	2.4	328.8	0.89	2.93
	rim	380	1180	232	1190	435	101	471	59.9	269	43.6	94	44.5	5.5	300.8	0.91	1.05
WRP-1	core	272	1490	486	4000	2760	856	2850	323	1220	159	290	135	15.6	392.6	0.93	1.43
	rim	1320	2320	557	3900	2430	581	2460	294	1200	172	335	145	17.5	118.5	0.62	1.12
TC-9 TCC	core	64.9	224	49.4	270	112	65.8	163	22.2	116	20.5	48.3	25.9	2.9	297.6	0.9	2.29
	rim	315	859	193	1080	527	200	686	85.9	394	65.3	148	78.7	9.7	194	0.79	1.56
TC-1	core	523	1990	445	2500	1040	577	1440	177	824	138	299	168	21.5	146	0.94	2.22
	rim	605	1600	330	1880	875	265	1080	133	606	101	229	122	15.7	1078.8	0.82	1.28
CC10	core	207	760	210	1630	1100	388	1120	130	512	70.1	137	67	7.7	223.3	0.83	1.64
	rim	18.4	55.8	10.7	71.1	38.7	9	39.4	4.6	20.3	2.7	5.6	2	0.1	1097	0.91	1.08
CC7	core	69.7	320	102	899	737	221	783	84	308	40.4	75.4	34.2	3.7	130.4	0.87	1.37
	rim	453	1300	262	1530	850	193	888	117	444	75.4	141	72	17.6	114.3	0.86	1.04
WOKP1	core	420	1190	300	2120	1360	411	1700	206	827	117	230	112	14.1	568.9	0.76	1.27
	rim	2220	5300	985	5380	2750	643	3210	401	1680	255	525	254	31.1	1302.5	0.82	1.02
WOKP2	core	573	1570	448	3180	2610	710	3230	442	1640	268	492	252	64.2	422.7	0.71	1.15
	rim	517	1540	320	1990	1230	283	1460	184	755	109	215	98.3	11.8	146.1	0.86	0.99
UCC		30	64	7.1	26	4.5	0.88	3.8	0.64	3.5	0.8	2.3	2.2	0.32			

Nonmarine
Nodules

Nodules		La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	PO ₄ ³⁻	Ce/Ce*	Eu/Eu*
LDP-1	core	202	487	99.8	796	781	516	1450	149	502	62.2	106	9.4	55.1	6.6	1613.6	0.78	2.28
	rim	383	947	170	1200	1040	441	1850	195	682	91	165	14.4	78.3	9.2	1283.6	0.85	1.49
	core	6	27.8	8.8	81.3	79.6	39.6	118	12.8	39.3	4.4	7.8	0.6	6.5	0.7	772	0.88	1.92
	rim	51.2	156	33.9	229	170	68	237	27.7	95.9	12.3	24.6	2	16	1.8	538.9	0.85	2
NM-2	core	6.6	13.5	7.5	66.4	58.8	27	78.9	8.2	24.2	2.7	4.7	0.4	3.9	0.4	1363.4	0.44	1.86
	rim	13.9	40.2	11.8	98.7	94.6	40.4	143	15.9	50.2	5.9	10.8	0.8	8.3	0.9	586	0.72	1.59
	core	93.3	223	31.1	206	157	69.9	270	26.7	97.9	15.5	30.1	4.1	17	3.1	1123.3	0.94	1.6
	rim	23.7	64.9	14	126	114	66.3	213	19.6	69.6	9.1	16.2	1.4	7.5	0.8	153.4	0.81	1.63
LDP-A	core	8.2	12.3	4.2	35.1	32.4	13.8	48.3	5.4	17.2	2.1	4	0.3	3.1	0.3	1103	0.48	1.64
	rim	28.1	75.9	12.9	71.1	43.4	16.4	64.8	7.6	27.8	3.9	8.2	0.7	5.2	0.6	369	0.91	1.45
	core	10.9	32.2	6.6	44	30.3	24.5	53.5	6.4	24.1	3.3	6.9	0.6	4.6	0.5	308	0.86	2.86
	rim	29.7	42.4	13.3	71.8	41.3	27.8	59.8	7.1	24.6	3.3	6.9	0.7	4.7	0.6	363.6	0.49	2.63
LDP-B	core	13	19.2	3.9	27.1	22	10.8	35.3	3.9	12.4	1.8	3.6	0.4	2.6	0.4	1018	0.62	1.82
	rim	24.2	48	9.6	55.1	34.8	14.6	50.6	5.8	20.5	2.8	6	0.6	4.1	0.5	411.8	0.72	1.63
	core	2.8	11.6	4	32.5	28.9	19.4	48.6	5.5	18.3	2.2	3.9	0.3	2.8	0.3	461.6	0.79	2.43
	rim	86	187	31.6	172	81.5	30	132	15	57.7	8.6	19	1.7	11.2	1.4	597.5	0.82	1.36
LDP-D	core 1	7.4	22.5	8.6	73.1	63.8	30.5	85.2	9.2	26.9	2.8	4.9	0.3	4	0.4	132.7	0.64	1.94
	core 2	5	22.2	6.5	60	56.8	29.2	85.5	9.3	42.6	3	5.2	0.4	4.4	0.5	395.4	0.89	1.97
	rim 1	36.7	82.1	15.9	103	75.3	31.7	111	12.6	28.2	5.7	11.6	1.1	8.1	1	1414.5	0.78	1.63
	rim 2	16.5	42.3	8.9	70.4	66.4	30.2	111	12.3	40.3	5.1	9.7	0.8	7	0.8	175.6	0.8	1.65
LDP-E	rim 3	6.4	19.7	5.2	47.5	48.2	23.6	79.9	8.9	28.3	3.4	6	0.5	4.5	0.5	1827.1	0.78	1.79
	rim 4	4.1	15.3	5.8	50.9	47.1	22.3	68.9	7.4	22.3	2.5	4.4	0.3	3.4	0.3	672.7	0.71	1.84
	core 1	25.2	128	37.5	330	318	173	501	57.7	180	19.8	33.4	2.6	27	2.9	453.6	0.95	2.04
	core 2	1.7	4.5	2.4	21.9	20	8.6	26.9	2.8	101	0.9	1.5	0.1	1.3	0.1	866.5	0.51	1.75
LDP-F	rim 1	45.3	123	24.6	183	165	66.9	269	30.4	8.4	13	24.8	2.1	17	2	749.8	0.84	1.49
	rim 2	17.1	54	13	111	117	50.6	187	21.3	67.7	8.1	14.5	1.2	10.4	1.2	301.7	0.83	1.61
	UCC	30	64	7.1	26	4.5	0.88	3.8	0.64	3.5	0.8	2.3	0.33	2.2	0.32			

All concentrations are in parts per million. UCC = upper continental crust values from Condie, 1991; Ce/Ce = (Ce_N)/{(La_N) × (Pr_N)^{0.5}}, Eu/Eu* = Eu_N/(Sm_N × Gd_N)^{0.5}.

Figure 4. Upper continental crust-normalized REE patterns for the marine phosphate nodules analyzed in this study. Solid line represents the core concentrations, and dashed line represents the rim concentrations. Note the pronounced MREE enrichment in some of the samples and the variable positive Eu anomalies. Both the MREE enrichment and Eu anomalies may provide insights into the complexation of the REE during deposition and diagenesis.



Positive europium anomalies are present in all marine and nonmarine samples (Table 2; Figures 4, 5). All samples, both marine and nonmarine, preserve a weak negative cerium anomaly (Table 2). Both Eu and Ce exhibit redox behavior dependent on the oxidation state of the fluid medium. Unlike the other REEs, Ce and Eu may exist in a valence state other than +3, and the presence of reduced or oxidized forms of these elements can be used to describe paleodepositional and diagenetic conditions in low-temperature systems (Ce) and oxygen fugacity conditions in high-temperature, high-pressure systems (Eu). Evidence clearly suggests that the REE occur in the trivalent state in low-temperature aqueous systems with the exception of Ce, which may oxidize to Ce^{4+} and be subsequently removed by coprecipitation with an Fe/Mn oxyhydroxide or by precipitation of

CeO_2 . Therefore, if Ce^{3+} predominates, there should be no Ce anomaly observed on the normalized REE plot. A positive anomaly does not necessarily indicate a reducing system but may suggest reductive dissolution of minerals containing relatively more Ce than would be expected compared to La and Pr. The relative enrichment or depletion in Ce relative to La and Pr is expressed as the Ce anomaly and is quantified as the ratio $\text{Ce}/\text{Ce}^* = (\text{Ce}_N)/[(\text{La}_N) \times (\text{Pr}_N)]^{0.5}$, where N represents normalized values. Samples with Ce/Ce^* values greater than 1 are considered to have a positive cerium anomaly and suggests deposition under low-oxygen conditions, or the reduction dissolution of Ce-bearing phases and samples with values less than 1 are said to have a negative cerium anomaly (deposition under oxidizing conditions).

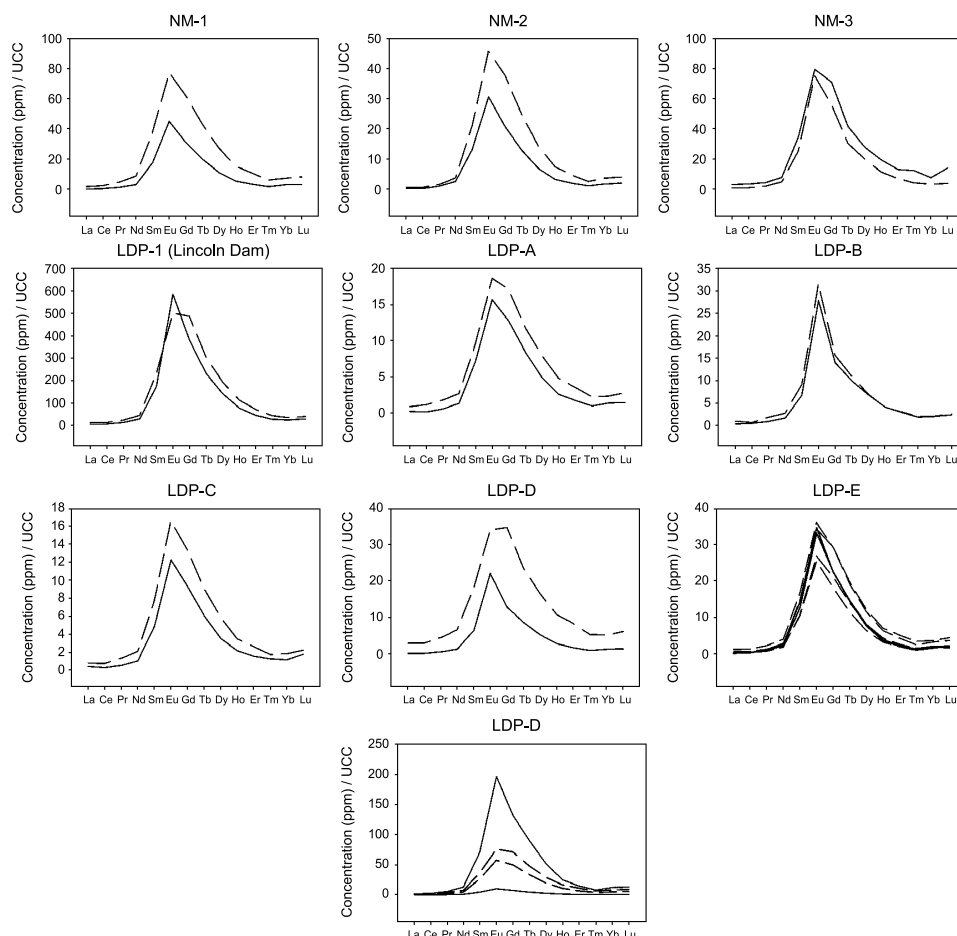


Figure 5. Upper continental crust-normalized REE patterns for the nonmarine phosphate nodules analyzed in this study. Solid line represents the core concentrations, and dashed line represents the rim concentrations. Samples were collected across the surface of samples labeled LDP-E and LDP-F to explore REE heterogeneity in the samples.

Europium also exhibits a redox behavior where the soluble Eu^{3+} can be reduced to soluble Eu^{2+} under extremely reducing conditions. The Eu anomaly was calculated as $\text{Eu}/\text{Eu}^* = \text{Eu}_N / (\text{Sm}_N \times \text{Gd}_N)^{0.5}$. Eu/Eu^*

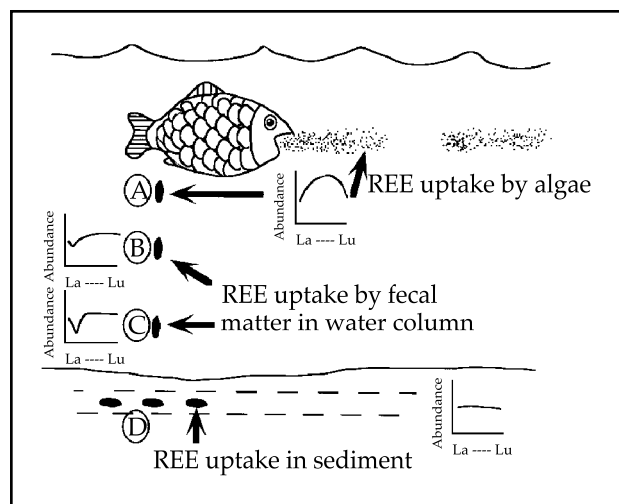
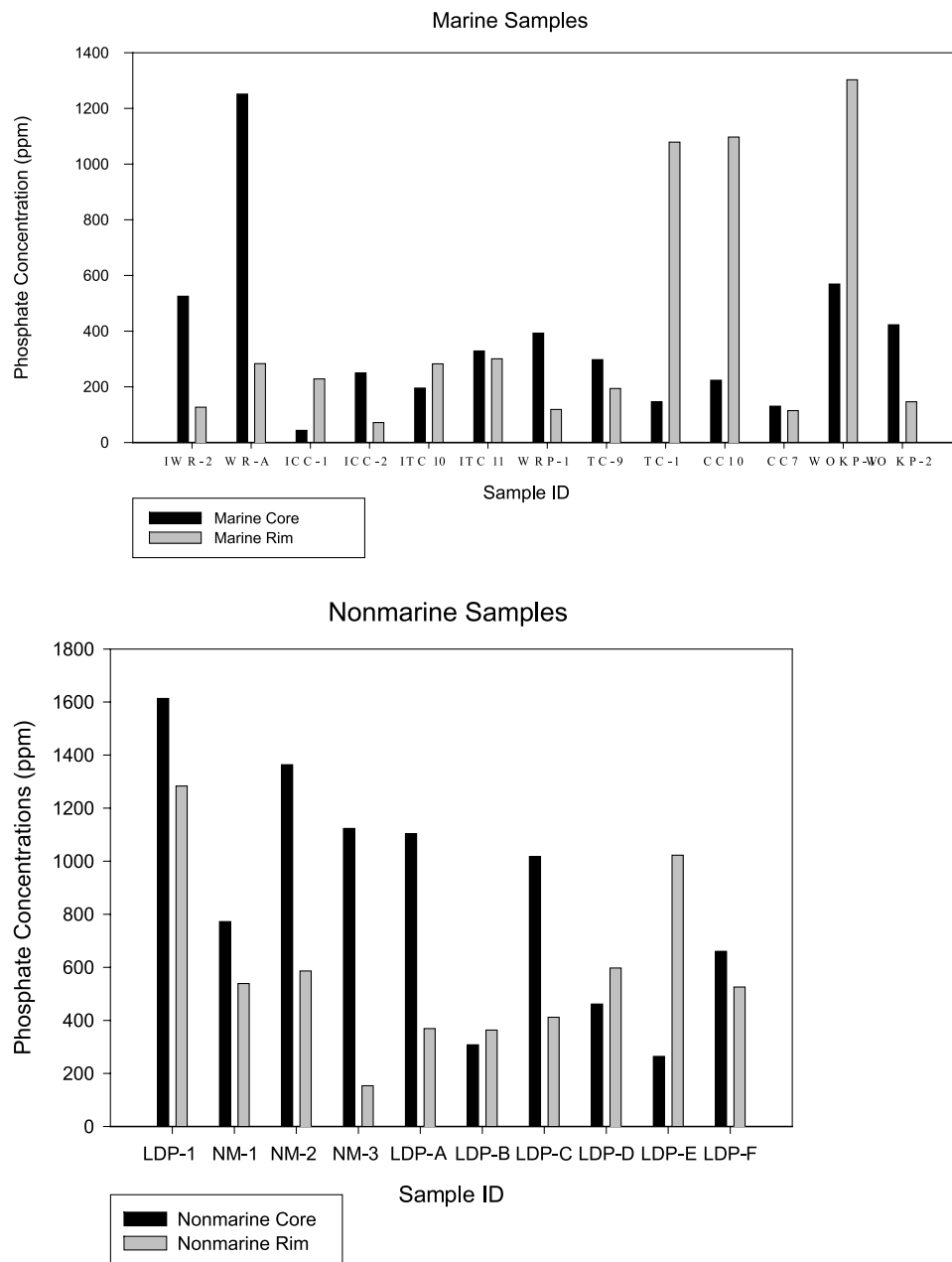


Figure 6. Flow diagram of REE uptake at different water column depths and associated REE patterns (modified from Kidder and Eddy-Dilek, 1994).

values greater than 1 are indicative of reducing conditions where Eu^{2+} is more abundant than Eu^{3+} . This positive anomaly is generally associated with the presence of a calcium-bearing igneous mineral such as plagioclase where Eu^{2+} has substituted for Ca^{2+} in the mineral matrix under the low-oxygen fugacity conditions of the Earth's mantle. Eu^{2+} is not known to occur in low-temperature environments (Sverjensky, 1984). A negative Eu/Eu^* (less than 1) may suggest the preferential loss of Ca-bearing minerals during weathering and deposition or the provenance of the sediments under investigation.

The phosphate concentration of the cores and rims of both the marine and nonmarine nodules was expected to correlate linearly or positively with the total concentration of REEs, specifically MREEs, as the nodules were expected to be primarily phosphatic. In marine samples, there was no correlation between MREE and phosphate ion ($R^2 = 0.1848$). Rare-earth elements' relative abundances are controlled by other factors such as remobilization, redox conditions, or diagenesis. In nonmarine samples, there is a moderate correlation between MREE and the phosphate ion

Figure 7. Phosphate concentration in cores and rims of marine and nonmarine nodules. Note that there is no systematic relationship between the phosphate concentrations of the marine cores and rims, with each equally likely to have a higher concentration than its counterpart. In the nonmarine samples, the cores are generally more enriched in phosphate than the rims.



($R^2 = 0.3877$). These relations are not strong enough to support our assertion that MREE enrichment is caused by complexation by phosphate ion. The work of Byrne et al. (1996) also argues that in the presence of a high degree of solution complexation of the REEs (which will be the case for all but acidic solutions), phosphate scavenging of REEs via coprecipitation leads to a heavy rare-earth element (HREE) (Dy to Lu) enrichment relative to the light rare-earth elements (LREEs) (La to Nd). Therefore, the geochemical signature preserved in these nodules may reflect the competitive scavenging of the MREEs via coprecipitation leading variable enrichments in the HREE. The

relative enrichments in HREE and MREE and the lack of correlation between MREE and the phosphate ion in nodules suggest that REE precipitation may be the results of complexation by ligands other than phosphate as shown by Lee and Byrne (1992) and Byrne et al. (1996).

Because of the perfect balance of charge between phosphate ion and the trivalent REEs, a positive correlation between concentrations generally exists. However, this depends on the overall chemical matrix of the nodules itself. Figure 7 shows the phosphate concentration in cores and rims of marine and nonmarine nodules.

Europium and cerium anomalies provide important information about the depositional environments. The distinct positive europium anomalies in several of the Fayetteville phosphates (Table 2; Figures 4, 5) could suggest that in initially oxygenated waters overlying the mud that became the Fayetteville Formation, bacteria used most of the oxygen during the decay of organic matter. Consequent extreme low-oxygen conditions reduced Eu that was originally input into the ocean in its oxidized form Eu^{3+} . However, as discussed above and in the studies of Sverjensky (1984) and others, there appears to be no evidence that Eu^{2+} occurs in low-temperature settings or that diagenesis can lead to reduction or oxidation of Eu. Therefore, we suggest that the Eu anomalies preserved in several of these samples reflect the original source material instead of the oxidization of Eu^{2+} to Eu^{3+} during diagenesis. Nodule rims could also inherit the Eu signature of the host muds as they compacted and dewatered around the solidifying nodule. If the positive europium anomaly was inherited from plagioclase-rich parent material, one would expect to find a negative correlation between $(\text{Eu}/\text{Eu})^*_N$ and Sr for cores and rims of both marine and nonmarine nodules. We do not see this correlation; however, a refined study of this hypothesis may refine these relations. An additional explanation for the positive europium anomalies, that isobaric interferences from Ba generated or augmented the Eu concentrations, is not applicable here. Although this could be a plausible explanation, the negative correlation between Ba and Eu anomaly implies that there are no isobaric interferences that could cause the Eu anomaly. In addition, we measured Ba at masses 135 and 137 and Eu at masses 151 and 153 and interferences corrected for mathematically. Therefore, we are confident that the observed Eu anomalies are preserved by the samples and not an artifact of ICP-MS analysis.

Negative cerium anomalies have been reported to be common in Cenozoic phosphates (McArthur and Walsh, 1984; Kidder et al., 2003). Weak cerium anomalies, although sparse, have been documented in Pennsylvanian phosphates (Kidder and Eddy-Dilek, 1994), and comparably weak negative cerium anomalies (Table 2; Figures 4, 5) characterize the Fayetteville phosphates. McArthur and Walsh (1984) analyzed Cenozoic phosphates and attributed negative cerium anomalies to effects of oxygenated seawater. Unlike any other REEs, cerium is capable of undergoing oxidation in seawater from Ce^{3+} to insoluble Ce^{4+} (e.g., Sverjensky, 1984; Moffett, 1990, 1994; DeCarlo et al., 1998, and references therein). The Ce^{4+} occurs as CeO_2 and in Fe/Mn

oxyhydroxides formed in well-oxygenated marine environments (German and Elderfield, 1990; Bellanca et al., 1997; Cullers, 2002). A negative cerium anomaly in marine nodules may correlate to oxidizing conditions thereby recording the original inherited seawater signature as has been suggested for cherts and biogenic phosphates (Murray et al., 1990; Grandjean-Lécuyer et al., 1993). The presence of the Ce anomaly in our marine phosphate nodules is consistent with the presence of the approximately 2-m-thick zone of dark-gray shale that hosts the phosphates as well as the well-preserved fauna. Following a sharp transgression at the base of the Fayetteville Formation, black, platy, generally unfossiliferous shales are found with the interbedded fossiliferous and phosphatic zones, reflecting rapidly changing depositional conditions. A return to black, platy shale that lacks phosphate and well-preserved fossils probably signals a return to more anoxic conditions. Negative cerium anomalies in nonmarine nodules can be attributed to the slightly oxidizing conditions present in the water column or the sediment during the process of diagenesis, perhaps before decay of organic matter has begun to dominate the diagenesis of the phosphatic muds. Positive europium anomalies and negative cerium anomalies represent redox conditions during the diagenesis of phosphate nodules. Ce anomaly and Eu anomaly may be recording different stages of diagenesis. Further experiments are required to explore this possibility. For example, microanalysis of phosphatized skeletal and fecal matter and later phosphatic cements that coat that matter such as that reported by Kidder (1985) could reveal a change from negative Ce depletions to positive Eu enrichments in progressively later phosphate.

The REE concentration in the rims was greater than the REE concentration in the cores of both the marine and nonmarine facies, with the exception of a few nodules (Table 2). The trends may be attributed to the more reducing conditions in the pore waters during rim formation than the waters during the initial coprolite diagenesis, thereby allowing greater mobility of REE toward the rims. In the case of nonmarine nodules, the host sediment pore waters are probably a larger potential source of REEs than are the cores, hence explaining this trend.

CONCLUSIONS

There are three types of REE patterns in Mississippian organic-rich phosphate nodules. Middle rare-earth

element-enriched patterns are common in both marine as well as nonmarine nodules. Negative cerium anomalies and positive europium anomalies were also observed. Negative cerium anomalies are probably caused by inherited seawater signatures and positive europium anomalies inherited from the source material. An interesting question is that if the negative Ce anomaly of the nodules is a direct record of the negative Ce anomaly common to seawater, why do most of these nodules have MREE-enriched patterns and not the HREE-enriched patterns observed in modern seawater? Further investigation of the REE composition of these nodules may reflect what is suggested by Tang and Johannesson (2003) and others that organic ligands play an important role in the complexation of the REE, and that because of the relative abundance of organic matter in the surrounding shales and in the nodules themselves, the REE composition of the nodules may reflect reductive dissolution and complexation of the REE by organic ligands during deposition and diagenesis.

There is no relationship between phosphate-ion concentrations and MREE abundance in most samples. Although the nodules are primarily phosphatic, differences in phosphate abundance do not cause differential uptake of MREEs. Middle rare-earth element-phosphate relationships are not as straightforward as initially hypothesized. Middle rare-earth element enrichments are present in phosphatic material, but not all P_2O_5 is in the form PO_4^{3-} , and therefore, the chemistry of PO_4^{3-} may not be as important as the relative abundance of P_2O_5 . If P_2O_5 is accompanied by hydroxides, oxyhydroxides, and oxides, MREE enrichments could be observed. Diagenesis of nonmarine nodules may either have homogenized the chemistry over time, or the diagenetic history of nonmarine nodules and marine nodules may be quite different.

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