

STATE OF ARKANSAS

Arkansas Geological Commission

William V. Bush, Acting State Geologist

INFORMATION CIRCULAR 33

**RARE EARTH ELEMENTS IN THE CASON SHALE OF NORTHERN
ARKANSAS:
A GEOCHEMICAL RECONNAISSANCE**

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Table of Contents

Abstract	1
Introduction	1
Geology of the Cason Shale	2
Rare earth elements in the Cason Shale	3
Geochemical analyses	3
Results and Discussion	3
References	13

List of Figures

Figure 1 - Location map of Cason Formation sample sites.....	4
Figure 2 - Comparison of the lanthanide content of the average crustal shale, the average marine phosphorite, and the average Cason phosphorite sample.....	11
Figure 3 - Comparison of the lanthanide content of some phosphorites to the average Cason phosphorite sample.....	11

List of Tables

Table 1 - Location coordinates, thicknesses sampled, and descriptions of samples collected in 1969 and 1987.....	5
Table 2 - Spectrographic data for samples collected in 1969.....	6
Table 3 - Inductively coupled mass spectrometry (ICP - MS) data for samples collected in 1987.....	7
Table 4 - Comparison of the lanthanide content of the average crustal shale, the average marine phosphorite, the average Cason phosphorite (1987 samples).....	9
Table 5 - Composition of the lanthanides in the average crustal shale, the average marine phosphorite, the average Cason phosphorite, and in samples collected in 1987.....	10
Table 6 - Lanthanide content and composition in some phosphorites elsewhere in the world and the average Cason phosphorite.....	12

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by

A. E. Grosz, A. L. Meier, and B. F. Clardy

ABSTRACT

Geochemical analyses of a suite of samples from the Lower Silurian - Upper Ordovician Cason Shale in northern Arkansas indicate that basal phosphorite contains an average of 1692.2 ppm rare earth elements. This level of concentration is approximately eight times greater than in the average crustal shale, and approximately four times greater than in the average marine phosphorite. The composition of the rare earth elements in the Cason Formation is closer to that in the average crustal shale than to the average marine phosphorite. Cason phosphorite samples contain larger amounts of the light rare earths and lesser amounts of the heavy rare earths than the average marine phosphorite. The data show that the Cason Formation is not sufficiently enriched in rare earths to be considered unusual in the context of the chemistry of phosphorites worldwide. Moreover, as the recovery of these elements from phosphate rock is dependent on byproducts of the fertilizer manufacturing process, the resource potential of the rare earths in the Cason Shale is presently very low.

INTRODUCTION

The rare earth elements comprise the third subgroup of the periodic table of the elements. The term "rare earths" is a misnomer because it describes a group of elements that are more common than rare, and are metals rather than earths. Also referred to as the lanthanides, the rare earth elements (REE) are a group of 15 elements with atomic numbers 57-71. Yttrium (Y), atomic number 39, has similar chemical properties and a close mineralogical association to the REE; it is, therefore, commonly included in a discussions of the REE. The REE are classified into 1) the light REE (LRE) consisting of the first seven lanthanides [lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), and europium (Eu)], and 2) the heavy REE (HRE) consisting of the remaining lanthanides [gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu) and yttrium (Y)]. Promethium (Pm), atomic number 61, is a highly radioactive fission product of uranium with a halflife of only 2.6 years. Its occurrence in nature is questionable.

Lanthanides occur in a variety of geologic settings. Concentrations exist in igneous, metamorphic, and sedimentary rocks; minable concentrations are predominantly in alkaline igneous rocks and carbonatites, and in placer deposits. The REE are present in over 100 mineral species; however, they are recovered from only a few minerals. Principal sources include bastnäsite (CeFCO_3), monazite (Ce,YPO_4), phosphorites and byproduct solutions from processing uranium (Hedrick, 1993).

Fluorapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$, in phosphorite rock is typically enriched in REE, containing an average of 0.1 to 0.8% REE. In contrast to igneous rocks, the REE in phosphorites do not form their own minerals but enter into the crystal lattice of calcium phosphate in isomorphous substitution for Ca^{+2} . Except for a few cases, the REE content of the phosphorite is generally proportional to the P_2O_5 content. Sedimentary phosphorites have a characteristic yttrium enrichment and a cerium deficiency, reflecting the composition of sea water (Altschuler, 1980).

Commercial recovery of REE from phosphorites is potentially feasible during the production of phosphoric acid for fertilizer manufacture--the principal end use for the world production of phosphate rock (Neary and Highley, 1984). During the reaction of phosphorite with sulfuric acid, most of the REE are lost into the phosphogypsum (Ionescu and others, 1980). However, the REE can be completely dissolved in nitric acid and recovery has been carried out on a commercial scale in the former Soviet Union, Poland (Bril, 1964) and in Finland (Lounamaa and others, 1980). Recovery of the REE from phosphorite was achieved successfully in connection with fertilizer manufacturing at Kemira Oy in Finland during 1965-1972 (Habashi, 1985). However, less costly sources of REE are available (heavy mineral sands and basnäsite) so utilization of this resource is unlikely.

Interest in REE-bearing minerals originated in 1883 with the development of incandescent gas mantles containing rare-earth and zirconium oxides. Since then, a wide range of commercial applications for the REE have been developed. Currently Ce, La, Nd, Pr, Sm, Gd, Eu, and a mixture of metallic REE termed mischmetal are of commercial importance. Yttrium is also of considerable commercial interest. The principal uses of REE are: 1) as catalysts in petroleum refining, in some chemical processes, and in pollution control; 2) for metallurgical uses as iron and steel additives and as alloys; 3) in ceramics, glass polishing compounds, and glass additives; and 4) for miscellaneous uses in phosphors, electronics, permanent magnets, lighting, and research (Hedrick, 1993).

GEOLOGY OF THE CASON SHALE

The Cason Shale was named by H.S. Williams (1900) from exposures at Cason tract in the manganese district, near Batesville, Independence County, Arkansas. The unit is as much as 23 feet (7 m) thick and is exposed in Independence, IZard, Stone, Newton, and Searcy Counties. The formation is absent in many places due to erosion or nondeposition; the Cason Shale disconformably overlies the Fernvale or Kimmswick limestones of Ordovician age and is unconformably overlain by Silurian to Mississippian age strata. Originally considered entirely Upper

Ordovician by Williams and many later workers, the upper shaly portion of the formation has been shown by Craig (1984) to be Lower Silurian.

Fossils are locally abundant in the Cason Shale, although much of the formation is nonfossiliferous. *Girvanella*, a genus of fossil algae, is present in Williams' type section of the formation. The fossil algae are round in their maximum dimension (1 inch/2.5 cm) and oval in their minimum dimension (0.5 inch/1.3 cm). They resemble buttons, and the local term for the beds in which they occur is "button shale". The *Girvanella*, along with several other species of macrofossils, indicated to early workers a Late Ordovician age for the Cason Shale. Many of the "buttons" are completely replaced by manganese oxide. Craig has demonstrated that some of the manganese buttons retain a relic cellular structure typical of blue-green algae, not *Girvanella*. Conodont collections from the "button shale" support the contention that the upper portion of the Cason Shale extended into the Lower Silurian (Craig, 1984).

The units presently mapped as the Cason Shale consist of varying amounts of shale, phosphorite, sandstone, conglomerate, and manganese and iron oxides. The shale is generally calcareous and fissile. Its color is variable, being either greenish gray, bluish gray, dark gray, brown, or black. Greenish-gray and bluish-gray shale predominates, which, upon weathering, becomes greenish yellow and noncalcareous. Dark-gray, brown, and black shale intervals are ferruginous and manganeseiferous. Phosphate rock in the Cason Shale is either massive, gray to brown, conglomeratic phosphorite, or gray, shaly, pebbly phosphorite. Local beds of sandstone are greenish gray to yellowish brown and contain grains of quartz, phosphorite, and glauconite.

Conglomerate commonly occurs at the base of the formation. Phosphorite pebbles and cobbles, manganese nodules, and iron nodules make up the coarse-grained constituents of the conglomerate. The fine-grained constituents of the conglomerate are clay, phosphorite grains, quartz sand, and earthy iron and manganese oxides. Manganese and iron oxides are abundant in the Cason Shale. In the Batesville district, these oxides occur in beds

and as agglomerated masses resting on the Fernvale Limestone where they have been mined as manganese ore (Straczek and Kinney, 1950).

RARE EARTH ELEMENTS IN THE CASON SHALE

Reports of rare earth elements in the Cason Shale provided impetus for D. F. Holbrook, geologist from the Arkansas Geological Commission, to collect a suite of samples for follow-up analyses (Figure 1). Ten samples from the Cason Shale were collected in the Spring of 1969 and analyzed in July of 1969 by a semiquantitative spectrographic method (Grimes and Marranzino, 1968) at the U.S. Geological Survey laboratories in Denver, Colorado under the direction of A.P. Marranzino (Marranzino, unpublished open-file data, Arkansas Geological Commission). Location coordinates, thicknesses sampled, and descriptions of the 1969 samples are given in Table 1; the geochemical data are given in Table 2. The spectrographic data indicate high concentrations of La and Y in a number of the samples. Two additional phosphorite samples from the Cason Shale were collected in the Fall of 1969 and analyzed subsequently by D. Adams (U.S. Geological Survey, Denver, Colorado). Adams reported the following analyses of the samples collected at Love Hollow Quarry, Izard County (SE 1/4 Sec. 4, T. 14 N., R. 8 W.):

	<u>Sample A</u>	<u>Sample B</u>
CaO	13.91%	12.73%
Ce	1500ppm	1500ppm
Yb	30ppm	30ppm
Nd	700ppm	700ppm
Sm	50ppm	200ppm
Y	700ppm	700ppm
La	700ppm	700ppm

Researchers' efforts in 1987 in making superconductor ceramic bodies, which contain La and Y as important constituents, encouraged geologists of the Arkansas Geological Commission to conduct a reconnaissance sampling program of the Cason Shale to evaluate the REE potential of the formation. Thirteen phosphorite-bearing samples from the Cason Shale were collected by B.F. Clardy and J.M. Howard (Arkansas Geological Commission) and analyzed by

A.L. Meiser (USGS, Denver) for this reconnaissance study (Figure 1). A phosphorite-bearing sample from the Mississippian age Pitkin Formation was also included for comparison. Locations of samples, thicknesses sampled, and descriptions of the 1987 samples are given in Table 1; geochemical data are given in Table 3.

Samples 87-1A through 87-1E, 87-2, and 87-C were collected by cutting 1 inch X 1/2 inch (2.5 X 1.3 cm) channels into the outcrops. Samples 87-2AGC, 87-LCD, 87-LCM, 87-SC, and 87-PC were collected by selecting the highest grade phosphorite available at the collection sites. Samples 87-PH is a composite sample collected by random sampling of a phosphorite outcrop. Sample 87-#2AGC is a heavy-mineral concentrate of sample 87-2AGC prepared by grinding to -20 mesh and separating the minerals using S-tetrabromoethane (S.G.= 2.96).

GEOCHEMICAL ANALYSES

Geochemical analyses of samples collected in 1987 were determined by inductively coupled plasma mass spectrometry (ICP-MS), using a modification of the method reported by Lichte and others (1987). A sodium peroxide sintering technique was used to render the REE soluble. In this technique, 0.1 gram samples are mixed with 0.4 gram sodium peroxide. The mixture is heated in a furnace at 430°C for 30 minutes. The resulting sinter is dissolved in water, acidified with nitric acid, and diluted to 20 ml. The solution is analyzed directly by ICP-MS. The average relative standard deviation for all the REE by this method is about 3 percent. The geochemical data, along with REE, LRE, HRE, and LRE/HRE for samples collected in 1987 are given in Table 3.

RESULTS AND DISCUSSION

It is important to note that none of the samples, collected in 1987 and discussed below, contain REE values as large as those reported by Adams for the 1969 A and B samples (values given above).

Geochemical data indicate that the Cason phosphorite samples (87-2, 87-2AGC, 87-C,

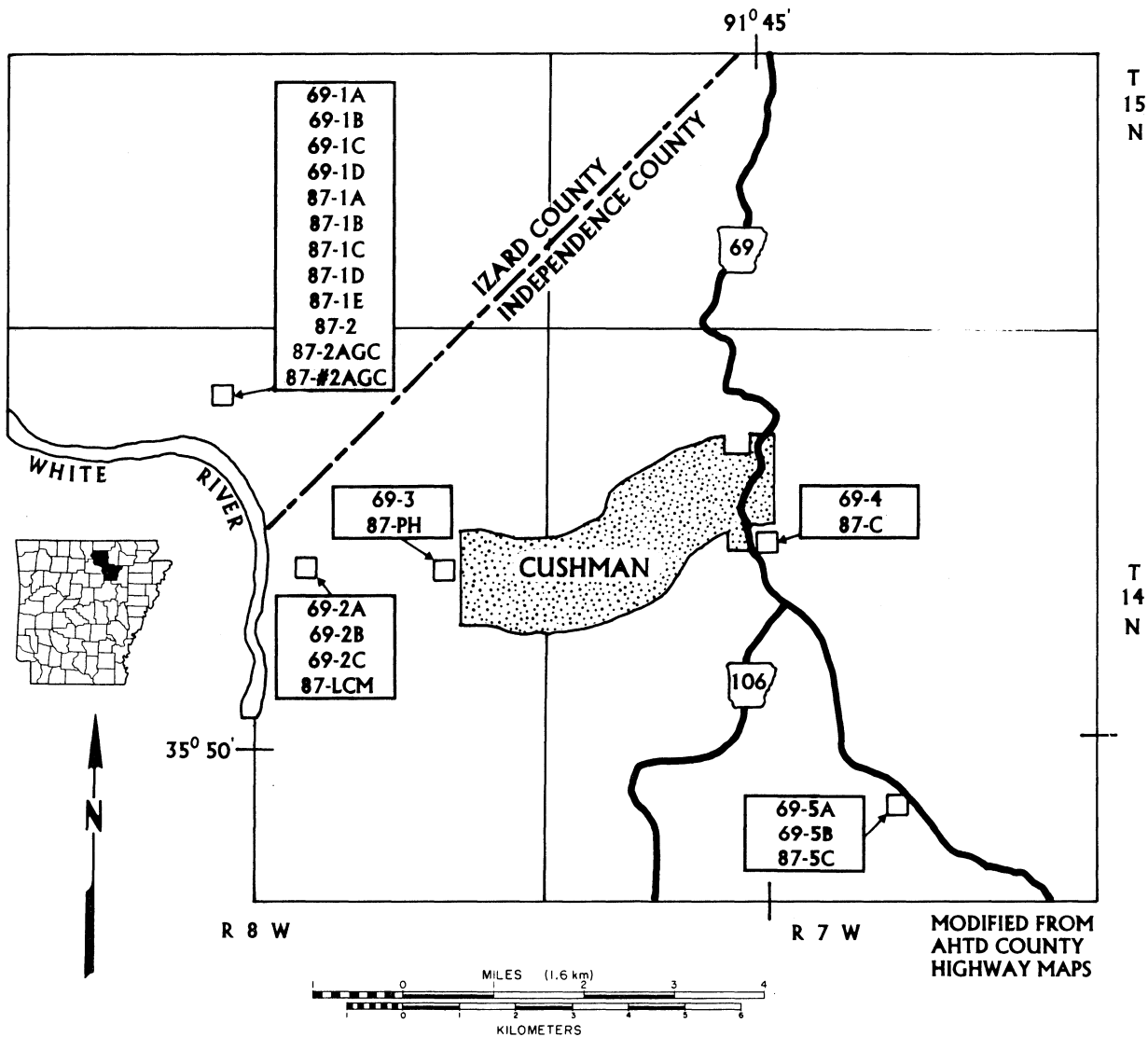


FIGURE 1 - Location map of Cason Formation sample sites.

TABLE 1 - LOCATION COORDINATES, THICKNESSES SAMPLED, AND DESCRIPTION OF SAMPLES COLLECTED IN 1969 AND 1987.

Sample number	Latitude Deg. Min. Sec.	Longitude Deg. Min. Sec.	General Land Office Survey	Thickness Feet (cm)	Formation, lithology, and site, description
1969					
69-1A	35 53 20	91 51 36	NW 1/4 SE 1/4 Sec. 4, T14N, R8W	2.5 (76)	Cason Formation gray-green shale (Love Hollow quarry, Izard Co.)
69-1B	35 53 20	91 51 36	NW 1/4 SE 1/4 Sec. 4, T14N, R8W	1.5 (46)	Cason Formation dark red shale (Love Hollow quarry, Izard Co.)
69-1C	35 53 20	91 51 36	NW 1/4 SE 1/4 Sec. 4, T14N, R8W	1.7 (52)	Cason Formation play reddish-brown to gray-green shale (Love Hollow quarry, Izard Co.)
69-1D	35 53 20	91 51 36	NW 1/4 SE 1/4 Sec. 4, T14N, R8W	3.0 (91)	Cason Formation phosphorite, dark gray (Love Hollow quarry, Izard Co.)
69-2A	35 51 46	91 50 29	SE 1/4 NW 1/4 Sec. 15, T14N, R8W	GRAB*	Cason Formation phosphorite (dump, Lafferty Creek mine, Independence Co.)
69-2B	35 51 46	91 50 29	SE 1/4 NW 1/4 Sec. 15, T14N, R8W	GRAB*	Cason Formation shale (dump, Lafferty Creek mine, Independence Co.)
69-3	35 51 40	91 48 49	SE 1/4 NE 1/4 Sec. 14, T14N, R8W	GRAB*	Cason Formation shale (road ditch outcrop, Independence Co.)
69-4	35 51 54	91 45 10	NE 1/4 NW 1/4 Sec. 16, T14N, R7W	GRAB*	Cason Formation shale (Ark. Hwy. 69, road ditch outcrop, Independence Co.)
69-5A	35 49 30	91 43 23	SE 1/4 SE 1/4 Sec. 27, T14N, R7W	GRAB*	Cason Formation phosphorite (dump, test pit southwest of Spring Creek, Independence Co.)
69-5B	35 49 30	91 43 23	SE 1/4 SE 1/4 Sec. 27, T14N, R7W	GRAB*	Cason Formation shale (dump, test pit southwest of Spring Creek, Independence Co.)
1987					
87-1A	35 53 20	91 51 36	NW 1/4 SE 1/4 Sec. 4, T14N, R8W	0.66 (20)	Cason Formation unconsolidated, banded, reddish-orange clay (east end Love Hollow quarry, Izard Co.)
87-1B	35 53 20	91 51 36	NW 1/4 SE 1/4 Sec. 4, T14N, R8W	0.75 (23)	Cason Formation hematitic and manganese, shaly, dark maroon mudstone (east end Love Hollow quarry, Izard Co.)
87-1C	35 53 20	91 51 36	NW 1/4 SE 1/4 Sec. 4, T14N, R8W	0.50 (15)	Cason Formation upper 2 in. shaly, pebbly, fossiliferous tan mudstone; lower 4 in. massive, phosphatic, pebbly gray mudstone (east end Love Hollow quarry, Izard Co.)
87-1D	35 53 20	91 51 36	NW 1/4 SE 1/4 Sec. 4, T14N, R8W	0.75 (23)	Cason Formation upper 4 in. pebbly, greenish-gray mudstone with MnOx staining; middle 3 in. thinly laminated brown mudstone; lower 2 in. oxidized, brown earthy material (east end Love Hollow quarry, Izard Co.)
87-1E	35 53 20	91 51 36	NW 1/4 SE 1/4 Sec. 4, T14N, R8W	3.3 (102)	Cason Formation phosphorite; upper 12 in. massive, gray to brown, with small pebbles; middle 3 in. shaly, laminated; lower 25 in. massive, gray to brown, with 3 in. shaly zone near base (east end Love Hollow quarry, Izard Co.)
87-2	35 53 20	91 51 36	NW 1/4 SE 1/4 Sec. 4, T14N, R8W	4.2 (128)	Cason Formation phosphorite, massive with thin shaly zones (southeast end Love Hollow quarry, Izard Co.)
87-2AGC	35 53 20	91 51 36	NW 1/4 SE 1/4 Sec. 4, T14N, R8W	GRAB*	Cason Formation phosphorite (southeast end Love Hollow quarry, Izard Co.)
87-#2AGC	35 53 20	91 51 36	NW 1/4 SE 1/4 Sec. 4, T14N, R8W	concentrate	Heavy mineral fraction of phosphorite sample 87-2AGC (southeast end Love Hollow quarry, Izard Co.)
87-C	35 51 54	91 45 10	NE 1/4 NW 1/4 Sec. 16, T14N, R7W	0.83 (25)	Cason Formation phosphorite, (Ark. Hwy. 69, east side road ditch, Independence Co.)
87-PC	35 47 15	92 32 10	NW 1/4 NW 1/4 Sec. 12, T13N, R15W	12.0 (366)	Pitkin Formation phosphorite (chip composite, Peyton Creek mine, Van Buren Co.)
87-PH	35 51 40	91 48 49	SE 1/4 NE 1/4 Sec. 14, T14N, R8W	4.0 (122)	Cason Formation phosphorite (chip composite from Pine Hollow road ditch outcrop, Independence Co.)
87-SC	35 49 30	91 43 23	SE 1/4 SE 1/4 Sec. 27, T14N, R7W	GRAB*	Cason Formation phosphorite (dump, test pit southwest of Spring Creek, Independence Co.)
87-LCD	35 51 46	91 50 29	SE 1/4 NW 1/4 Sec. 15, T14N, R8W	GRAB*	Cason Formation phosphorite (dump, Lafferty Creek mine, Independence Co.)
87-LCM	35 51 46	91 50 29	SE 1/4 NW 1/4 Sec. 15, T14N, R8W	GRAB*	Cason Formation phosphorite (outcrop and talus, Lafferty Creek mine, Independence Co.)

* GRAB samples taken when exposure was not available to provide a channel sample or a composite sample of chips.

TABLE 2. - SPECTROGRAPHIC DATA FOR SAMPLES COLLECTED IN 1969.
A. P. MARRANZINO, USGS, ANALYST.

SAMPLE No.	69-1A	69-1B	69-1C	69-1D	69-2A	69-2B	69-3	69-4	69-5A	69-5B
Fe %	5	15	10	3	5	15	15	7	10	15
Mg %	3	2	2	1.5	1.5	2	1	0.15	1	2
Ca %	10	10	10	20	>20	15	15	2	15	10
Ti %	0.3	0.3	0.3	0.2	0.15	0.2	0.2	0.2	0.3	0.5
Mn ppm	> 5000	> 5000	2000	> 5000	> 5000	5000	> 5000	5000	1500	1000
Ag ppm	N	N	N	N	N	N	N	N	N	N
As ppm	N	N	N	N	N	N	N	N	N	N
Au ppm	N	N	N	N	N	N	N	N	N	N
B ppm	70	70	100	70	15	70	50	70	70	150
Ba ppm	500	2000	1000	700	200	500	700	1500	1000	700
Be ppm	1.5	2	3	3	1	5	3	3	1.5	5
Bi ppm	N	N	N	N	N	N	N	N	N	N
Cd ppm	N	N	N	N	N	N	N	N	N	N
Co ppm	300	20	70	30	30	50	200	30	20	50
Cr ppm	30	50	150	100	100	100	100	20	70	150
Cu ppm	30	10	50	20	30	50	200	10	10	50
La ppm	50	70	200	500	1000	500	500	100	200	70
Mo ppm	N	N	N	N	N	N	N	N	N	N
Nb ppm	15	15	20	20	10	15	15	10	15	15
Ni ppm	150	70	100	50	50	70	150	50	50	100
Pb ppm	700	150	70	100	70	200	150	10	20	15
Sb ppm	N	N	N	N	N	N	N	N	N	N
Sc ppm	15	15	20	15	15	15	15	5	10	15
Sn ppm	N	N	N	N	N	N	N	N	N	N
Sr ppm	100	150	700	1000	1000	700	500	500	500	500
V ppm	100	70	200	150	150	150	150	100	150	150
W ppm	N	N	N	N	N	N	N	N	N	N
Y ppm	50	70	> 200	> 200	> 200	> 200	> 200	150	> 200	150
Zn ppm	N	N	N	N	N	N	N	N	N	N
Zr ppm	150	100	150	200	100	100	100	700	700	200

TABLE 3. - INDUCTIVELY COUPLED MASS SPECTROMETRY (ICP - MS) DATA FOR SAMPLES COLLECTED IN 1987. A. L. MEIER, USGS, ANALYST.

SAMPLE No.	87 - 1A	87 - 1B	87 - 1C	87 - 1D	87 - 1E	87 - 2	87 - 2AGC	87 - #2AGC	87 - C	87 - PC	87 - PH	87 - SC	87 - LCD	87 - LCM
SiO ₂ %	62.70	43.20	37.50	41.10	30.20	34.90	22.20	6.61	39.90	21.40	14.90	45.40	18.40	17.80
Al ₂ O ₃ %	15.50	9.00	7.81	11.80	4.55	4.52	4.41	1.78	3.76	2.82	3.13	3.73	3.63	4.14
Fe ₂ O ₃ %	6.32	26.20	16.40	13.80	10.80	8.58	7.09	2.88	17.70	7.09	9.52	8.97	8.38	8.84
MgO %	0.96	1.59	2.00	2.21	1.37	1.16	1.21	0.62	0.66	0.91	1.39	0.75	1.60	1.68
CaO %	0.93	1.17	16.20	11.50	27.60	25.40	33.90	48.20	18.00	36.90	34.70	19.90	36.70	34.90
Na ₂ O %	<0.15	0.16	0.22	0.23	0.21	0.20	0.20	0.25	0.25	0.24	0.22	0.21	0.28	0.21
K ₂ O %	1.77	2.58	1.37	2.88	0.99	1.04	0.86	0.33	1.24	0.10	0.85	0.86	0.52	0.68
TiO ₂ %	0.69	0.67	0.61	0.57	0.28	0.28	0.27	0.11	0.25	0.10	0.14	0.34	0.16	0.19
P ₂ O ₅ %	0.27	0.27	10.90	7.60	19.10	17.60	23.60	34.00	13.40	21.90	24.20	14.50	23.40	19.50
MnO %	0.83	7.13	0.31	0.20	0.61	0.55	0.49	0.12	1.21	0.05	5.01	0.24	0.39	0.59
LOI 900°C	9.17	7.70	6.70	7.52	3.89	4.58	4.82	2.86	2.95	6.24	5.02	2.90	4.38	9.49
La ppm	110	72	200	170	340	320	400	490	280	140	360	240	420	380
Ce ppm	180	860	480	320	680	650	780	920	600	150	730	500	850	850
Pr ppm	31.0	15	45	34	68	67	82	96	57	27	71	50	86	80
Nd ppm	140	53	190	130	280	280	340	410	240	110	300	210	360	350
Sm ppm	31	10	39	28	60	58	72	83	51	22	63	45	77	76
Eu ppm	7.2	2.1	9.2	6.1	14.0	13.0	17.0	20.0	12.0	5.3	15.0	10.0	17.0	17.0
Gd ppm	31.0	8.1	40.0	27.0	64.0	63.0	77.0	91.0	55.0	23.0	68.0	49.0	83.0	81.0
Tb ppm	4.8	1.1	6.1	4.2	9.5	9.2	11.0	14.0	8.3	3.5	10.0	7.3	12.0	12.0
Dy ppm	26.0	6.3	36.0	25.0	55.0	53.0	67.0	78.0	48.0	22.0	57.0	43.0	69.0	72.0
Ho ppm	5.2	1.3	7.0	4.9	11.0	11.0	13.0	16.0	10.0	4.7	12.0	8.6	14.0	15.0
Er ppm	14.0	4.1	18.0	13.0	27.0	26.0	33.0	38.0	26.0	13.0	28.0	22.0	35.0	36.0
Tm ppm	1.90	0.64	2.40	1.70	3.40	3.30	4.00	5.00	3.30	1.90	3.50	2.90	4.50	4.60
Yb ppm	12.00	4.00	14.00	9.40	19.00	18.00	22.00	27.00	18.00	12.00	18.00	16.00	24.00	25.00
Lu ppm	1.50	0.62	1.70	1.20	2.30	2.00	2.60	3.20	2.10	1.60	2.20	2.00	2.80	2.90
SUM REE	595.6	1038.3	1088.4	774.5	1633.2	1573.6	1920.6	2291.2	1410.7	536	1737.7	1205.8	2054.3	2001.5
SUM LRE	499.2	1012.1	963.2	688.1	1442	1388	1691	2019	1240	454.3	1539	1055	1810	1753
SUM HRE	96.4	26.2	125.2	86.4	191.2	185.5	229.6	272.2	170.7	81.7	198.7	150.8	244.3	248.5
LRE / HRE	5.2	38.7	7.7	8.0	7.5	7.5	7.4	7.4	7.3	5.6	7.7	7.0	7.4	7.1

87-PH, 87-SC, and 87-LCM) contain larger average concentrations of REE than the average crustal shale and the average marine phosphorite. A comparison of the lanthanide content of the average crustal shale, the average marine phosphorite, and the average Cason phosphorite is given in Table 4. Turekian and Wedepohl (1961) showed that the average crustal shale contains 207.2 ppm REE. The Cason phosphorite, where sampled, contains an average of 1692.2 ppm. This average value represents an approximately 8-fold enrichment of REE in the Cason phosphorite with respect to the average crustal shale. However, this enrichment factor is, at least in part, controlled by the presence of phosphorite in the Cason Shale. Altschuler (1980) shows that the average marine phosphorite contains 461.7 ppm REE. With respect to the average marine phosphorite, the values for the Cason phosphorite represent nearly a 4-fold enrichment.

The composition of the lanthanides (individual elements expressed as percentages of the REE) in the average crustal shale, in the average marine phosphorite, in the average Cason phosphorite, and in the samples collected in 1987 are given in Table 5. A comparison of the distribution of REE in the average crustal shale, the average marine phosphorite, and in the Cason phosphorite is shown in Figure 2. All of the individual REE are more abundant in the average Cason phosphorite; however, La, Ce, and Nd are substantially more abundant. A notable exception to this pattern is found in sample 87-1B, a dark maroon mudstone sample (not included in the average Cason phosphorite). This sample is highly enriched in Ce with respect to all other samples analyzed in this study.

Sample 87-#2AGC, a heavy-mineral concentrate of a phosphorite sample (87-2AGC), has the highest absolute concentrations of REE in the sample suite suggesting that the lanthanides are associated primarily with phosphorites. Supporting evidence for this association is also provided

by a systematic increase of the REE with increasing CaO content. A level of enrichment commensurate with a concentrate, however, is not evident, suggesting that the REE are not associated exclusively with phosphorites. A positive correlation of REE with MnO suggests that adsorption(?) of REE onto manganese oxides and hydroxides may account for some of the REE. Iron oxides and hydroxides as REE carriers are not supported by the data as an inverse relationship exists between these. The composition of the lanthanides in sample 87-#2AGC (heavy mineral concentrate) is identical to that of most of the other Cason phosphorite samples, the exception being sample 87-1B (a dark maroon mudstone).

Within the group of samples analyzed for this study, sample 87-1B is distinctly anomalous with respect to LRE enrichment over HRE. The sample has a LRE/HRE of about 39, in comparison to a LRE/HRE of about 7 in the phosphorite samples. The sample of Mississippian age Pitkin Formation phosphorite (87-PC) contains substantially lower absolute values of REE. However, the HRE comprise a larger amount of the REE than in the Cason samples.

The lanthanide content and composition of worldwide phosphorites (modified from Habashi, 1985) and of the Cason phosphorites is given in Table 6. The composition of lanthanides (Cason Shale from Arkansas compared to worldwide samples) is shown graphically in Figure 3. The data in Table 5 and 6 and Figure 3 demonstrate that REE content and composition of Cason phosphorite samples are comparable to other phosphorites. Table 6 illustrates that in comparison to other phosphorites the Cason is among the more LRE-enriched, HRE-depleted phosphorites.

Insofar as the commercial viability of lanthanide recovery from phosphorites is dependent on the production of phosphoric acid for fertilizer manufacturing, the resource potential of rare earth elements in the Cason Shale phosphorites is presently very low.

TABLE 4. - COMPARISON OF THE LANTHANIDE CONTENT OF THE AVERAGE CRUSTAL SHALE (TUREKIAN AND WEDEPOHL, 1961), THE AVERAGE MARINE PHOSPHORITE (ALTSCHULER, 1980), (AND THE AVERAGE CASON PHOSPHORITE (THE AVERAGE OF SAMPLES 87-1E, 87-2, 87-2AGC, 87-C, (87-PH, 87-SC, 87-LCD, AND 87-LCM).

ELEMENT	AVERAGE CRUSTAL SHALE (ppm)	AVERAGE MARINE PHOSPHORITE (ppm)	AVERAGE CASON PHOSPHORITE (ppm)
La	92.0	133.0	342.5
Ce	59.0	104.0	705.0
Pr	5.6	21.0	70.1
Nd	24.0	98.0	295.0
Sm	6.4	20.0	62.8
Eu	1.0	6.5	14.4
Gd	6.4	12.8	67.5
Tb	1.0	3.2	9.9
Dy	4.6	19.2	58.0
Ho	1.2	4.2	11.8
Er	2.5	23.3	29.1
Tm	0.2	1.2	3.7
Yb	2.6	12.6	20.0
Lu	0.7	2.7	2.4
SUM REE	207.2	461.7	1692.2
SUM LRE	188.0	382.5	1489.8
SUM HRE	19.2	79.2	202.4
LRE/HRE	9.8	4.8	7.4

TABLE 5. - COMPOSITION OF THE LANTHANIDES IN THE AVERAGE CRUSTAL SHALE, THE AVERAGE MARINE PHOSPHORITE, THE AVERAGE CASON PHOSPHORITE, AND IN SAMPLES COLLECTED IN 1987.

ELEMENT	AVERAGE CRUSTAL SHALE		AVERAGE MARINE PHOSPHORITE		AVERAGE CASON PHOSPHORITE		87-1A	87-1B	87-1C	87-1D	87-1E	87-2	87-2AGC	87-#2AGC	87-C	87-PC	87-PH	87-SC	87-LCD	87-LCM
	%		%		%															
La	44.4	28.8	20.2	18.5	6.9	18.4	21.9	20.8	20.3	20.8	21.4	19.8	26.1	20.7	19.9	20.4	19.0			
Ce	28.5	22.5	41.7	30.2	82.8	44.1	41.3	41.6	41.3	40.6	40.2	42.5	28.0	42.0	41.5	41.4	42.5			
Pr	2.7	4.5	4.1	5.2	1.4	4.1	4.4	4.2	4.3	4.3	4.2	4.0	5.0	4.1	4.1	4.2	4.0			
Nd	11.6	21.2	17.4	23.5	5.1	17.5	16.8	17.1	17.8	17.7	17.9	17.0	20.5	17.3	17.4	17.5	17.5			
Sm	3.1	4.3	3.7	5.2	1.0	3.6	3.6	3.7	3.7	3.7	3.6	3.6	4.1	3.6	3.7	3.7	3.8			
Eu	0.5	1.4	0.8	1.2	0.2	0.8	0.8	0.9	0.8	0.9	0.9	0.9	1.0	0.9	0.8	0.8	0.8			
Gd	3.1	2.8	4.0	5.2	0.8	3.7	3.5	3.9	4.0	4.0	4.0	3.9	4.3	3.9	4.1	4.0	4.0			
Tb	0.5	0.7	0.6	0.8	0.1	0.6	0.5	0.6	0.6	0.6	0.6	0.6	0.7	0.6	0.6	0.6	0.6			
Dy	2.2	4.2	3.4	4.4	0.6	3.3	3.2	3.4	3.4	3.5	3.4	3.4	4.1	3.3	3.6	3.4	3.6			
Ho	0.6	0.9	0.7	0.9	0.1	0.6	0.6	0.7	0.7	0.7	0.7	0.7	0.9	0.7	0.7	0.7	0.7			
Er	1.2	5.0	1.7	2.4	0.4	1.7	1.7	1.7	1.7	1.7	1.7	1.8	2.4	1.6	1.8	1.7	1.8			
Tm	0.1	0.3	0.2	0.3	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.4	0.2	0.2	0.2	0.2			
Yb	1.3	2.7	1.2	2.0	0.4	1.3	1.2	1.2	1.1	1.1	1.2	1.3	2.2	1.0	1.3	1.2	1.2			
Lu	0.3	0.6	0.1	0.3	0.1	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.3	0.1	0.2	0.1	0.1			
SUM REE	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0			
SUM LRE	90.7	82.8	88.0	83.8	97.5	88.5	88.8	88.3	88.2	88.0	88.1	87.9	84.8	88.6	87.5	88.1	87.6			
SUM HRE	9.3	17.2	12.0	16.2	2.5	11.5	11.2	11.7	11.8	12.0	11.9	12.1	15.2	11.4	12.5	11.9	12.4			
LRE/HRE	9.8	4.8	7.4	5.2	38.7	7.7	8.0	7.5	7.5	7.4	7.4	7.3	5.6	7.7	7.0	7.4	7.1			

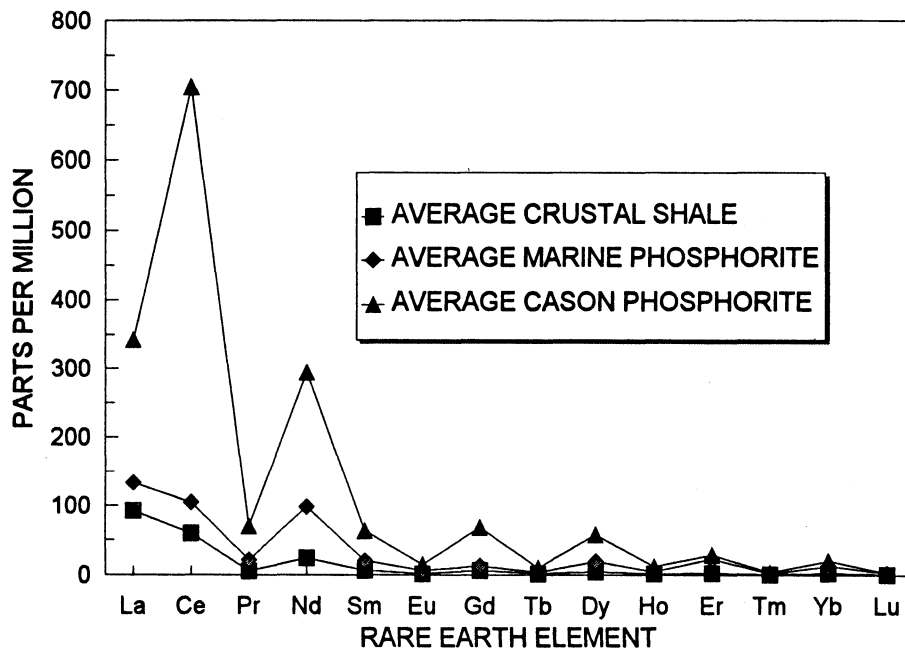


Figure 2 - Comparison of the lanthanide content of the average crustal shale, the average marine phosphorite, and the average Cason phosphorite sample.

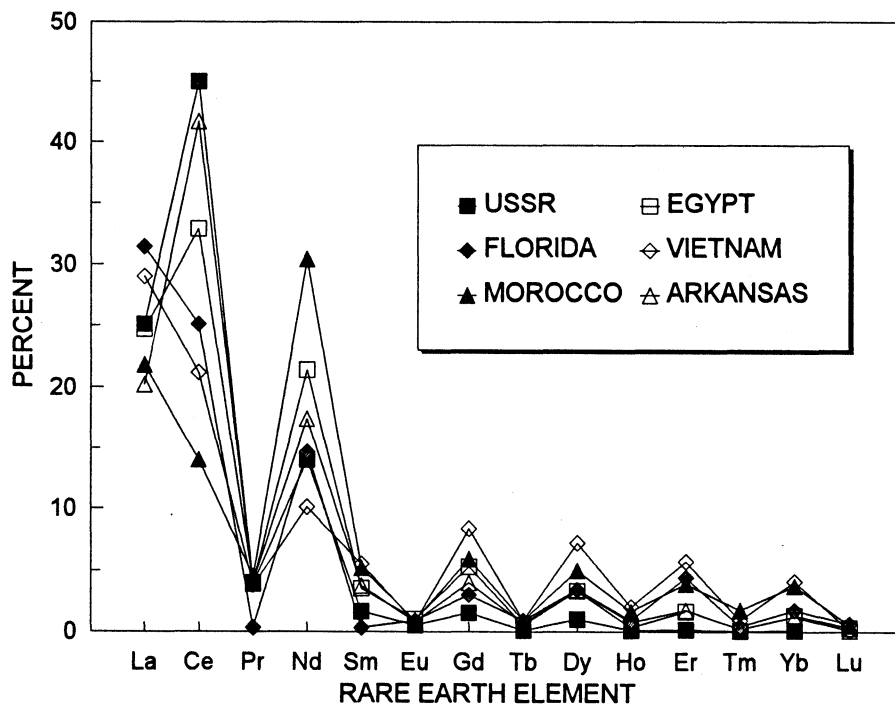


Figure 3 - Comparison of the lanthanide content of some phosphorites to the average Cason phosphorite sample.

TABLE 6. - LANTHANIDE CONTENT AND COMPOSITION IN SOME PHOSPHORITES ELSEWHERE IN THE WORLD AND THE AVERAGE CASON PHOSPHORITE. (MODIFIED FROM HABASHI, 1985).

ELEMENT	KOLA USSR	FLORIDA USA	KHOURIGBA MOROCCO	AL-MAHAMEED EGYPT	LAO-KAI VIETNAM	CASON PHOSPHORITE
	%	%	%	%	%	%
La	25.1	31.4	21.8	24.7	29	20.2
Ce	45	25.1	14	32.9	21.2	41.7
Pr	3.9	0.3	4.5	4	3.8	4.1
Nd	14	14.7	30.4	21.4	10.1	17.4
Sm	1.6	0.3	5.2	3.5	5.5	3.7
Eu	0.5	0.9	0.9	1	0.7	0.8
Gd	1.5	3	5.9	5.3	8.4	4.0
Tb	0.1	0.9	0.9	0.5	0.9	0.6
Dy	1	3.4	5	3.3	7.2	3.4
Ho	0.10	0.9	1.6	0.3	2	0.7
Er	0.15	4.4	3.9	1.6	5.7	1.7
Tm	0.02	0.4	1.7		0.9	0.2
Yb	0.08	1.7	3.7	1.3	4.1	1.2
Lu		0.6	0.5	0.3	0.1	0.1
REE CONTENT (ppm)	8000 - 10000	600 - 2900	1400 - 1600	280	310	1205.8 - 2054.3
SUM REE	93.1	88.0	100.0	100.1	99.6	100
SUM LRE	90.1	72.7	76.8	87.5	70.3	88
SUM HRE	3.0	15.3	23.2	12.6	29.3	12
LRE/HRE	30.5	4.8	3.3	6.9	2.4	7.4

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