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/DISTRIBUTIONS OF RARE EARTH ELEMENTS AND OTHER TRACE  
ELEMENTS WITHIN UNMINERALIZED PORTIONS OF THE  
BONNETERRE FORMATION, SOUTHEAST MISSOURI/

by

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## I N T R O D U C T I O N

The Viburnum Trend is part of a zone of metallic mineralization surrounding the St. Francois Mountains in southeast Missouri. Mining of galena, sphalerite, and chalcopryite ore began in 1846 in the Old Lead Belt. By the 1960's the ore in the Old Lead Belt was exhausted, but the mining industry was kept alive by the discovery of another ore zone 77 km to the west, the Viburnum Trend (Fig. 1). Rocks of the Viburnum Trend and the Old Lead Belt formed part of a barrier reef around the St. Francois Mountains during the deposition of the Bonneterre Formation.

The mineralized zone of the Viburnum Trend is contained entirely within the reef facies of the Bonneterre Formation where the ore was deposited as replacement and open-space fillings. The process by which the ores were deposited was extremely complex including several phases of mineral deposition and brecciation, dissolution, and faulting of the host rock (Clendenin, 1977). After years of research a number of questions still persist regarding what effect interaction with the ore bearing fluids had on the Bonneterre Formation. The source of metals and solution pathways of the ore fluids are still unknown. A study of the rare earth element (REE) patterns of the



Figure 1: Location of the Viburnum Trend, southeast Missouri.  
(After Gerdemann and Myers, 1972)

Bonneterre Formation may help to answer these questions.

Graf (1984) determined the REE pattern of the Bonneterre Formation within the ore zones. His work suggested that the ore fluids were depleted in light REE (LREE). Analysis of the REE pattern of the unmineralized sections of the Bonneterre Formation should indicate the extent of ore solution interaction with the host rock. Pinpointing sections of the host rock that have been in contact with the ore fluid, will help delineate the path or paths of ore fluid migration.

#### PURPOSE OF STUDY

This report describes the normal variations of REE and metals found within the unmineralized sections of the Bonneterre Formation in southeast Missouri. Samples from all three facies of the Bonneterre Formation were chosen for analysis to determine what control lithology and facies have on the REE pattern of sedimentary rocks. Analysis of trace metal and REE content may also determine the extent of ore fluid interaction with the host rock. The objectives of this study are to: (1) define the background values and distributions of REE and metals found within portions of the Bonneterre Formation and upper Lamotte Sandstone that do not contain ore mineralization, (2) determine

what effect dolomitization had on the Bonneterre Formation's REE patterns and (3) determine whether the studied rocks could have served as the source rock or solution paths of the ore fluids, assuming the REE and metals had the same source.

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## PREVIOUS INVESTIGATIONS

### Ore Precipitation

In the earliest recorded study of the genesis of ores in southeast Missouri, Whitney (1862) suggested that the ores were deposited by meteoric water that had leached and transported the metals. The theory of meteoric water was disproved by Newhouse (1932) when he analyzed fluid inclusions in galena and found the temperature of the ore solution to be 80° C. Newhouse's research also indicated that the ore solutions were concentrated chloride brines.

During the 1950's extensive research was done by the St. Joseph Lead Company. Their research included mapping and a detailed description of the sedimentary features. During this phase of research, the term "reef" was first applied to the ore-bearing rocks of the lead-zinc district. Lead-isotope studies of the ores also were begun in the 1950's, and by the 1970's, these studies had documented that the lead isotopes of the district

were of the Joplin (J) type, with  $^{206}\text{Pb}/^{204}\text{Pb} > 20$  (Heyl, Landis and Zartman, 1974). These strongly radiogenic leads were inconsistent with a magmatic source. Doe and Delevaux's (1972) lead-isotope studies on galena determined that the lead was derived from the Lamotte Sandstone.

In recent years the analyses of fluid inclusions in sphalerite has yielded some specific information regarding the composition of the ore solutions. The inclusions indicated that the ore fluids had high salinities (20-30 weight percent) and temperatures of  $95-125^{\circ}\text{C}$  (Anderson, 1975). The Bonnetterre Formation was never buried deeply enough to generate temperatures greater than  $100^{\circ}\text{C}$  (Gerdemann and Myers, 1972), suggesting that the ore fluids were generated at greater depths and then migrated up into the Bonnetterre Formation.

The current views of ore deposition involve the metals being transported in Na-Ca-Cl brines that were devoid of sulfide (Anderson, 1975). Field evidence suggests that the ore fluids did dissolve the carbonate rock as the ores were deposited. Sverjensky (1981) suggested that the ore solutions were close to saturation so that the host rock could be dissolved or left undisturbed, depending on the degree of over or under saturation of the ore fluid with respect to dolomite and calcite. The ores were deposited when the brine came in contact with biogenic

sulfide generated at, or near, the ore bodies (Gerdemann and Myers, 1972). Thus, the most important factor governing deposition of the ores was the continued availability of metals and sulfur at the same location (Anderson, 1975).

### REE in Sediments and Sedimentary Rocks

Definition of REE.-- Rare earth elements, lanthanum to lutetium (atomic numbers 57-71) also are commonly called lanthanides. The REE decrease in ionic radius with increasing atomic number; this phenomenon is known as the lanthanide contraction. The lanthanide contraction occurs because, with only one exception, all REE after La promote their last electron into the 4f subshell. Gd promotes its last electron into the 5d subshell in order to achieve the stability of a half-filled subshell (Brady and Humiston, 1975). The inner shell electrons are able to shield the outer 5d electrons so that the 5d electrons experience only a small increase in effective nuclear charge as the f subshell is filled. A small increase in effective nuclear charge across the row, results in only a slight decrease in size for each successive REE. A change in the total amount of electrons in the 4f subshell also does not alter the chemistry of the individual REE (Henderson, 1984). The similar

outer electron configuration for all REE results in a preferred oxidation state of +3. Under normal geologic conditions only Ce and Eu have low enough resistances to be oxidized or reduced to Ce +4 and Eu +2 (Haskin and Frey, 1966). Yttrium is commonly treated along with the REE because it is chemically similar to the lanthanides.

REE constitute almost fifteen percent of all known elements, but the chemical similarity of the REE made analysis of individual REE extremely difficult until the advent of neutron activation analysis. Because the REE behave so chemically alike, it has been postulated that the REE in the whole earth have retained a relative abundance similar to that of REE in the primordial solar-system. The REE pattern of chondrites is assumed to represent the original composition of the primordial solar-system and, therefore, the REE pattern of the primitive earth. Tracing the later fractionation of the REE helps chart the geochemical evolution of the earth (Haskin and Frey, 1966).

Comparison of REE Data.-- When the REE content is plotted against the atomic number, a zig-zag pattern is observed (Fig. 2). This zig-zag pattern is a result of the greater stability of the even-numbered isotopes produced during nucleosynthesis (the Oddo-Harkins rule). To clearly observe the trend of the REE, the amount of each REE is divided by the average amount of that REE

in the stony chondrite. This method is referred to as chondrite normalization (Fig. 2). On a chondrite normalized plot of REE versus atomic number, a sample with amounts of individual REE equal to those of chondrites would plot as a horizontal line equal to one. Individual samples can be enriched or depleted in all, or just groups, of REE. The two most common groups of REE are the light REE (La to Sm) and heavy REE (Gd to Lu) (Henderson, 1984).

Another convenient way to compare the REE data is to look at REE ratios. Typical REE ratios are La/Sm, Sm/Lu, Sm/Yb, and Eu/Sm. REE ratios in this study were not normalized to chondrites but were calculated using the ppm value of the individual REE. Mean chondrite La/Sm, Sm/Yb, Sm/Lu, and Eu/Sm ratios are 1.74, 0.88, 5.73, and 0.37 respectively (Henderson, 1984). Enrichment or depletion in heavy and light REE can be discerned by comparing the REE ratios in the sample with those REE ratios in chondrites. For example, La/Sm and Sm/Lu ratios greater than those in chondrites indicate both LREE enrichment and HREE depletion, respectively. A Eu/Sm ratio less than 0.37 indicates a depletion in Eu relative to chondrites. REE ratios also help to compare the shapes of the REE pattern. The greater the La/Sm ratio the steeper the slope between La and Sm in the REE plot.

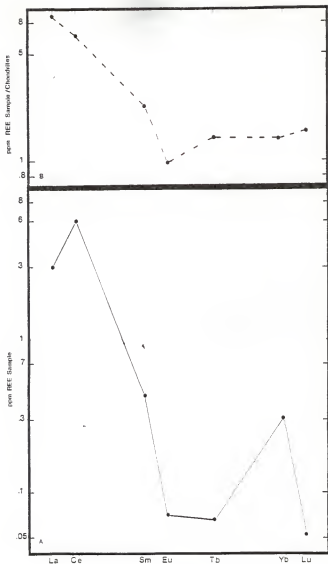


Figure 2: Chondrite normalization. A- REE plot of sample RE1 621 B- REE plot of sample RE1 621 with values normalized to chondrites.

REE in the Sedimentary Cycle.-- The REE pattern of sedimentary rocks reflects the weathering of the earth's crust (Haskin and Gehl, 1962; Haskin and others, 1966; Cullers and others, 1979; Piper, 1974; Ronov and others, 1967; Balashov and Tugarinov, 1976). Although the REE patterns of source rocks may vary, the similarity of REE patterns in sedimentary rocks has been illustrated by various authors (Veizer and Jansen, 1979; Haskin and Frey, 1966; Fryer, 1976; Haskin and others, 1966; 1968; Wildeman and Haskin, 1973; Haskin and Gehl, 1962; Ronov and others, 1967; Wildeman and Condie, 1973; McLennan, 1982; Graf, 1983; 1984). The North American Shale Composite (NASC) is a composite of 40 shale samples whose REE pattern is assumed to represent the average REE pattern of all sedimentary rocks (Haskin and others, 1968). When the NASC is normalized to chondrites, a trend of light REE (LREE) enrichment is observed (Fig. 3). All rocks of the continental crust also exhibit this LREE enrichment (Cullers and Graf, 1984). This enrichment is a result of the differentiation process that resulted in the outer parts of the earth being enriched in the lighter elements (Haskin and Gehl, 1962).

Piper (1974) showed that REE have short residence times and low solubilities in seawater and that the chemical similarity of REE allows for very little fractionation of the REE during the weathering and transportation of sediments into a basin.

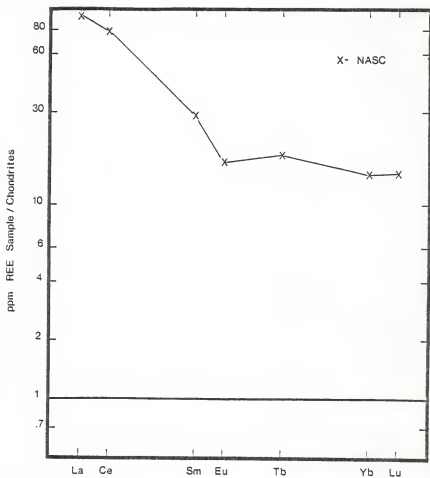


Figure 3: REE plot of North American Shale Composite (NASC). Horizontal line equal to 1 is the chondrite normalized plot

Diagenesis also has very little effect on REE patterns of sedimentary rocks, as the REE are relatively inert during diagenetic changes (Chaudhuri and Cullers, 1978).

A recent study by Veizer and Jansen (1979) described the sedimentary process as "canabalistic". These authors suggested that during a sedimentary turnover approximately 65-85 percent of the existing sedimentary rocks are regenerated as new sedimentary rocks. Nd/Sm age dates older than the stratigraphic age of the sediments support this conclusion (Veizer and Jansen, 1979). The sedimentary process is thus so destructive that varying REE patterns of the source rocks are recycled into one homogeneous REE pattern for all sedimentary rocks.

REE in the Carbonate Rocks and Minerals of Southeast Missouri.-- More recent work on REE patterns in carbonates, specifically those from the Viburnum Trend, was done by Graf (1984). He found a difference in the REE patterns of host-rock dolostones and of those rocks and minerals affected by the ore-bearing solutions. Samples of vug calcite, vug dolomite, and recrystallized dolostone all show a strong depletion in LREE (La/Sm ratios of 0.1-1.2, 0.8-3.1, and 1.9-3.3, respectively) relative to the host rock La/Sm of 5.68, indicating that the ore solutions were significantly depleted in LREE (Graf, 1984). The ore solutions could not have developed LREE depleted patterns

without interacting with rocks and minerals that are depleted in LREE. Sedimentary rocks, feldspars and granitic rocks have La/Sm ratios of 8, whereas amphiboles and pyroxenes have La/Sm ratios of 3. If the ore solution traveled near the basement where mafic and intermediate rocks are present, the fluid could have become depleted in LREE. Thus, Graf (1983) felt that proximity of the ore solution to the basement may have played an important role in determining the REE pattern of the ore fluid.

## REGIONAL SETTING

## STRATIGRAPHY

A generalized stratigraphic column of the rocks in southeast Missouri is shown in Figure 4. Only the stratigraphy of the Lamotte Sandstone and the Bonnetterre Formation will be discussed as these are the two Cambrian units that are possible source rocks and solution pathways for the ore fluids. The Lamotte Sandstone is a supermature quartz arenite with thin hematitic shale partings in the middle and basal sections. It was deposited unconformably on top of Precambrian basement and has a maximum thickness of 114 m. Portions of the Lamotte Sandstone that pinch out against Precambrian knobs are characteristically arkosic (Thacker and Anderson, 1977). The Bonnetterre Formation is the basal formation of the Upper Cambrian Series in southeast Missouri. Two lithologies, limestone and dolostone, are recognized in this formation; dolostone predominates in the ore zones. Maximum thickness of the Bonnetterre Formation is 90 m. Cambrian units deposited above the Bonnetterre Formation are the Davis Formation, Derby-Doerun Dolomite, Potosi Dolomite, and Eminence Dolomite. Total thickness of the Upper Cambrian strata is 610 m.

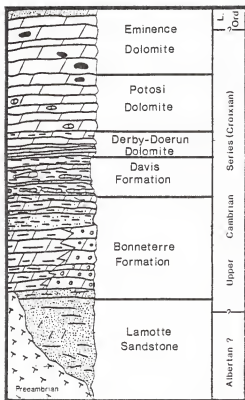


Figure 4: Stratigraphic column.  
(After Thacker and Anderson, 1977)

## DEPOSITIONAL ENVIRONMENT

The southeast Missouri lead-zinc district lies within and around the St. Francois Mountains. The rocks of the St. Francois Mountains were formed during the late Precambrian (1.5 b.y.) (Bickford and others, 1981) and are composed of rhyolitic porphyritic rock intruded by granite (Larsen, 1977). The core of the mountains was subjected to a long period of erosion, which resulted more than 600 m of relief (Snyder, 1968). During the transgression in Middle to Late Cambrian the Lamotte Sandstone was deposited. During the Cambrian the St. Francois highland was located on the edge of an eastward-sloping cratonic shelf that formed the western margin of the Illinois basin (Larsen, 1977). On the western and northern sides of the Precambrian highland, local intracratonic basins formed at the intersection of the westward-dipping slope of the highland and the eastward-dipping slope of the cratonic shelf (Larsen, 1977). The entire area began to subside differentially; eastward toward the Illinois basin, the rate of subsidence was greater as indicated by the marked increase in the thickness of the Bonneterre Formation in this region (Larsen, 1977; Willman and others, 1975). As the entire area subsided, the more rapid eastern subsidence caused the westward-dipping slope of the St. Francois Mountains to flatten (Larsen, 1977). This flattening resulted in the shoaling

of the local intracratonic basins. Thus, although the major transgression was westward out of the Illinois basin, the shoaling of the local intracratonic basins caused a local eastward transgression onto the St. Francois Mountains (Larsen, 1977). The whole environment is therefore a "shelf within a shelf" (Wilson and Jordan, 1983). On a larger scale the deposits in Missouri were formed in a middle shelf environment, but when viewed on a smaller scale the middle shelf deposits are actually shelf facies built out from the local Precambrian highlands (Wilson and Jordan, 1983) (Fig. 5).

Various authors have described the sediments deposited within this environment. Although the published descriptions of the Lamotte Sandstone are fairly consistent, the published descriptions of the Bonnetterre Formation vary according to the authors' classifications of the depositional environments. Larsen (1977) recognized four facies of the Bonnetterre Formation. The planar stromatolite and burrowed lime-mud facies were deposited within the platform environment. A full description of these two facies was given by Howe (1966). Locally, this facies is referred to as "White Rock" because of its light-gray color. Gerdemann and Myers (1972) named the depositional environment of these facies the back-reef (Fig. 6). The low-energy back reef or platform environment developed by a combination of the baffling effect of the Precambrian highland and the sheltering effect of

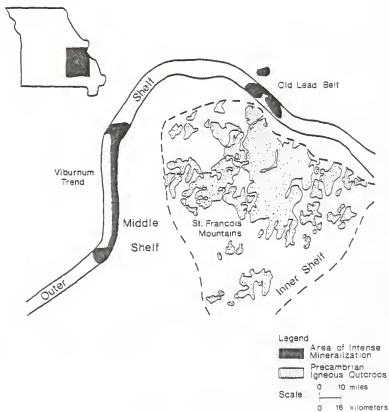


Figure 5: Small shelf system within the large middle shelf environment of the stable Mid-Continent area.  
(After Wilson and Jordan, 1983)

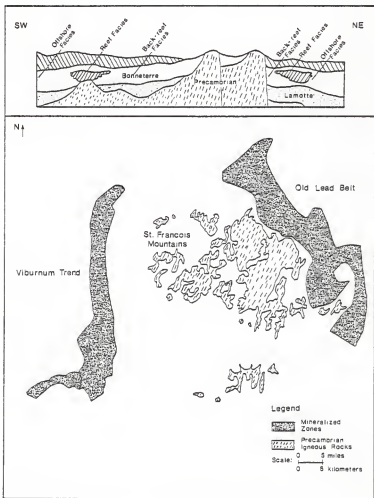


Figure 6: Reef formation in southeast Missouri.  
(After Gerdemann and Myers, 1972).

the reef. Thus, the planar stromatolites grew above wave base in a shallow and restricted basin (Lyle, 1977).

Larsen's (1977) second depositional environment within this complex is the platform margin. The dominant facies resulting from this environment is the digitate-stromatolite facies. This facies represents the reef that surrounded the Precambrian highland on the west and northwest (Gerdemann and Myers, 1972). The reef complex was a high-energy environment that formed above the wave base where both the tidal and wave energies were effective. There were two types of digitate stromatolite reefs: (1) bioherm-like algal heads that grew vertically and (2) biostromal-like algal mats that grew horizontally (Snyder, 1968). Bioherms are found in the Old Lead Belt where the rate of subsidence was great enough to allow consistent upward growth of the stromatolites. In the Viburnum Trend the shallow western slope caused shoaling that forced the stromatolites to grow outward.

Gerdemann and Myers (1972) defined the offshore facies as consisting of fine-grained carbonate and clastic rocks with limestone predominant farthest offshore. Lyle (1977) called the depositional environment of these sediments the fore-reef. Although described differently, this offshore facies is dominantly a low-energy environment formed below wave base (Lyle,

1977). Larsen (1977) defined two depositional environments within the offshore facies. His intracratonic basin with micrite and shale facies is nearly analogous to Lyle's (1977) fore-reef. Larsen's (1977) oolite facies developed in a subtidal zone above wave base that was present along the slope into the basin adjacent to the Viburnum Trend.

#### DOLOMITIZATION

The carbonate rocks of the Bonneterre Formation were originally deposited as limestone and then dolomitized (Gerdemann and Myers, 1972). Only the farthest offshore portions of the Bonneterre Formation have not been altered by the dolomitizing solutions. The exact time of dolomitization is unknown, but regional stratigraphic relationships suggest that dolomitization was a broadly regional process (Howe, 1966). Lyle (1977) showed that dolomitization occurred after lithification of the Bonneterre Formation. Petrographic evidence suggests that pellets, stromatolites, and micrite were selectively dolomitized first, followed by trilobite and echinoderm fragments and interstitial calcite cement (Lyle, 1977). Cross-cutting relationships indicate that there were several phases of dolomitization.

## METHODS OF ANALYSIS

## SAMPLE COLLECTION

Two sets of samples were collected from the southeast Missouri lead-zinc district. One set of samples is from a set of six drill holes located between the Magmont and Viburnum mines (Fig. 7). The U.S. Geological Survey obtained portions of these cores from the Missouri State Geological Survey and separated the cores into three-meter composite samples by crushing representative lithologies of each three-meter interval. Splits of each composite sample were obtained from the U.S. Geological Survey and twenty-one of these samples were chosen for analysis. To check the validity of each three-meter composite sample, nine core samples from within these three-meter intervals were chosen from the core remaining at the Missouri State Geological Survey.

Another set of samples was selected from three drill holes that transect the southern portion of the Viburnum Trend near the Ozark Lead Mine (Fig. 7). Portions of drill core from each of the three drill holes were selected from the core housed at the Missouri State Geological Survey. Twenty samples of core were then selected for further chemical analysis. Drill hole locations are listed in Appendix A. Sample locations and

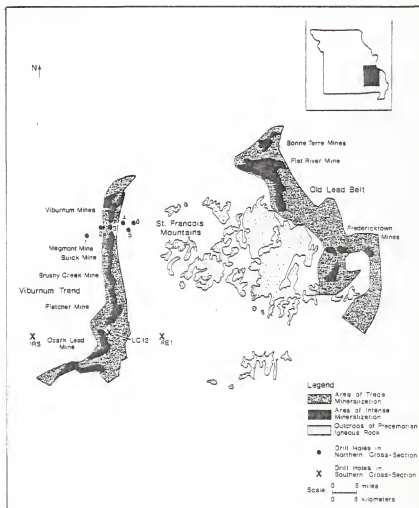


Figure 7: Sample locations across the Viburnum Trend.

insoluble residue descriptions are presented in Appendix B.

#### PETROGRAPHIC TECHNIQUES

Thin sections were made from each of the twenty-nine core samples. Classification of the carbonate rocks was based on Folk's system (Folk, 1974). Calcite was distinguished from dolomite by staining with Alizarin-red S. Petrographic summaries are in Appendix C.

#### CHEMICAL TECHNIQUES

Forty-nine samples were chosen for chemical analysis. Core samples were cut into thirds, and the center section was crushed by a jaw crusher and pulverizer. Further crushing was done by hand using an agate mortar and pestle. Once crushed, these samples and the powdered samples were split and aliquots were analyzed chemically.

Rare earth elements and Fe, Th, Cr, Rb, Zn, Sc, Co, Na, K, Sb, and Ba were determined by Instrumental Neutron Activation (INA) analysis. This method was adopted from Gordon and others (1968). Details of this procedure are given in Appendix D.

The amount of insoluble residue was determined for each sample. Approximately 2-4g ( $\pm 0.0002$ g) of sample was weighed on an analytical balance and transferred to a glass beaker. Thirty to forty ml of 2N HCl was then added to each beaker. The samples remained in the acid overnight to allow for complete dissolution of the carbonate. The solution was then filtered and the residue rinsed with distilled water. Weight of the insoluble residue was determined by subtracting the weight of the filter paper from the weight of the dried filter paper plus the residue. The filtrate was diluted with distilled water to a final volume of one hundred ml and then stored in a sealed container.

Concentrations of Zn, Mn, Fe, Pb, Sr, K, Mg, and Ca in the HCl soluble fraction were determined by Direct-Current Plasma (DCP) analysis. Details of this method are in Appendix E.

## R E S U L T S

## INSOLUBLE-RESIDUE AND ELEMENTAL CONCENTRATION

Elemental concentrations and percent insoluble residue for Bonnetterre Formation samples are listed in Table 1. Table 2 lists the average elemental concentration of each facies. The composition of the insoluble residue, as determined by X-ray and petrographic analysis, was found to be predominantly clay minerals with a minor amount of quartz, feldspar, and sulfide minerals. The elemental concentrations of selected insoluble residues are listed in Table 3. In order to observe the correlations between a clay-rich insoluble residue and the various elements, two Bonnetterre Formation samples with quartz-rich insoluble residues were excluded from the sample set during the calculation of correlation coefficients. These samples are LC12 1167 (sandstone) and 1RS 1198 (quartz-rich micrite).

K, Rb, Sc, Ba, and Th in the unmineralized dolostone and limestone samples correlate positively with each other and with the amount of insoluble residue (significant to the 99 percent confidence level). A strong positive correlation suggests that these elements occur predominantly in the non-carbonate fraction of the host rock. This same positive correlation also is seen

Table 1: Elemental Concentration and Percent Insoluble Residue: Whole Rock  
(concentrations determined by INAA and expressed in ppm)

Sample	IR	TREE	Fe	Th	Cr	Rb	Zn	Sc	Ba	Co	Ca	Na	K	Sb
HOST BONNETTERE FORMATION: Offshore Facies:														
1-940	3.77	9.36	3174	1.09	3.48	--	--	0.52	38.29	0.52	417309	162.1	3992	--
1-1010	23.60	56.0	5930	6.37	8.19	53.72	47.72	2.31	206.2	1.81	355174	318.9	--	0.18
1-1050	17.0	48.0	9130	4.45	10.01	41.73	40.18	2.27	127.9	1.72	10972	370.6	20983	--
1-1170	12.04	29.04	12648	2.52	6.49	19.02	17.73	1.47	49.2	3.90	143169	411.3	14047	0.23
1RS-1198	77.05	94.19	5613	12.84	27.15	132.9	23.08	4.31	--	3.08	57221	463.9	37872	0.31
1RS-1226	6.00	19.38	13204	1.01	3.32	5.97	303.4	0.36	--	0.90	259607	407.5	--	0.21
1RS-1291	20.78	68.35	5889	5.05	5.59	49.49	--	1.57	183.6	1.74	442843	351.2	21138	--
1RS-1365	23.31	63.93	9868	6.87	10.79	67.21	--	3.01	164.32	4.88	351885	427.8	26904	0.24
1RS-1370	15.37	52.60	3767	3.09	3.92	--	--	2.10	99.4	1.37	424384	229.8	19117	--
HMI-945	0.99	8.02	1215	0.32	1.09	--	--	0.21	--	0.22	470191	92.8	--	--
HMI-1052	16.03	43.11	5626	4.73	6.84	42.01	--	1.97	133.7	1.32	369331	295.0	19833	0.12
HOST BONNETTERE FORMATION: Reef Facies:														
3-580	3.41	6.64	4179	0.64	3.19	5.55	--	0.45	--	1.38	256367	374.7	--	0.27
3-610	4.00	8.87	9999	1.10	6.8	6.86	--	0.84	--	3.18	240239	437.9	4266	0.35
3-660	3.19	7.39	8133	0.57	3.36	--	7.13	0.42	--	3.16	244486	317.7	3761	0.42
3-700	1.96	5.66	8059	0.33	1.99	--	--	0.25	--	3.72	258447	454.3	--	0.22
3-750	9.21	30.17	21232	2.48	8.03	17.43	27.42	1.89	--	5.82	214409	575.8	--	0.45
3-790	6.01	22.45	15511	2.45	8.09	--	50.05	1.26	--	8.84	250632	561.4	9478	--
LC12-879	16.06	30.05	14906	2.62	16.91	--	--	2.54	51.9	6.60	366516	338.1	19449	--
LC12-915	6.24	17.19	3932	1.36	6.67	11.44	--	0.89	--	0.69	258357	379.3	7423	--
LC12-988	0.15	14890	0.15	1.82	--	--	--	0.13	--	2.21	267679	449.1	--	0.07

Table 1: continued  
(concentrations determined by INAA and expressed in ppm)

Sample	IR	TREE	Fe	Th	Cr	Rb	Zn	Sc	Ba	Co	Ca	Na	K	Sb
HOST BONNETERRE FORMATION: Reef Facies cont.:														
LC12-1086	2.89	19.16	6963	0.81	2.38	--	--	0.43	--	2.79	272743	407.9	--	--
LC12-1128	2.12	21.43	10065	1.87	3.93	--	--	0.82	--	0.41	274567	611.2	--	--
LC12-1167	39.58	11.87	11078	0.69	3.1	--	--	0.37	--	5.06	163262	244.7	2479	0.34
8EE-590	1.65	5.88	6443	0.52	2.65	--	--	1.52	0.37	--	255570	396.2	1425	0.39
8EE-758	7.15	12.27	14181	1.51	2.27	12.65	--	1.02	27.41	3.98	231752	664.4	10261	0.32
8EE-793	6.90	22.90	13830	1.89	8.66	14.79	112.0	1.35	39.44	8.78	249305	565.3	9045	0.24
HOST BONNETERRE FORMATION: Back-reef Facies:														
4-621	5.11	46.72	7667	1.71	4.55	6.37	61.38	0.57	--	1.52	251171	538.8	--	0.18
4-640	0.88	4.48	3994	0.33	2.55	--	4.42	0.23	--	0.66	330793	525.7	--	0.49
4-740	2.50	8.65	2709	0.57	2.45	--	--	0.66	--	0.49	282200	699.8	2476	0.28
4-810	2.57	9.65	4434	0.67	3.72	--	--	0.42	--	1.55	274478	437.3	--	0.26
4-850	4.79	15.02	3010	1.39	5.59	9.73	--	0.91	--	0.75	233130	580.33	--	--
5-348	1.11	3.63	4379	0.26	1.63	--	15.77	0.16	--	0.67	237223	393.9	--	0.31
5-420	2.82	10.09	2462	0.66	2.74	--	6.83	0.47	--	0.87	270928	732.1	--	0.24
5-486	16.21	48.30	5303	3.94	10.18	29.81	11.49	2.52	--	1.78	227883	569.7	24375	0.28
6-420	4.00	8.53	3187	0.85	3.36	7.30	18.26	0.58	--	1.82	240121	633.1	5405	0.53
6-460	3.40	15.86	3854	0.93	4.06	9.64	15.42	0.79	--	1.07	272590	621.9	--	0.31
6-500	4.71	18.00	3383	0.97	3.75	7.22	11.40	0.90	--	0.88	205093	462.1	4991	0.10
RE1-426	0.85	4.47	1100	0.37	2.65	--	--	0.31	--	0.32	263523	403.4	--	--
RE1-473	2.41	17.87	1129	0.93	5.59	--	--	0.98	--	0.38	255844	983.6	--	--

Table 1: continued

(concentrations determined by INAA and expressed in ppm)

Sample	*IR	*TREE	Fe	Th	Cr	Rb	Zn	Sc	Ba	Co	Ca	Na	K	Sb
HOST BONNETTERRE FORMATION: Back-reef Facies cont.:														
RE1-621	0.50	9.99	1904	0.32	2.28	--	--	0.29	--	0.51	357256	518.8	256	--
RE1-676	0.95	7.96	833	0.39	2.09	--	--	0.33	--	0.43	313934	658.7	--	--
RE1-721	4.25	10.83	3070	0.66	3.10	--	--	0.47	--	0.50	273422	351.8	2739	--
RE1-898	2.77	16.01	2247	0.94	3.94	6.89	--	1.02	--	0.57	268927	721.8	2241	--
1EE 646	3.87	2.89	6230	0.18	1.69	--	--	0.13	--	0.27	327077	321.8	--	0.29
1EE 745	1.68	4.77	1516	0.29	1.02	--	0.35	0.21	--	0.34	252357	636.6	--	0.14
1EE 814	0.56	6.06	2961	0.33	1.26	--	0.41	0.17	--	0.48	256748	402.0	--	0.11

## LAMOTTE SANDSTONE:

LC12-1186	98.16	19.42	151	1.76	2.77	--	--	0.52	--	0.27	--	53.1	1386	--
IRS-1470	98.46	19.32	334	1.60	3.44	--	--	0.24	--	0.26	--	65.6	--	--
RE1-973	98.42	10.40	285	1.02	1.51	--	4.58	0.23	--	--	--	27.3	1019	--

\* TREE - Total REE Content

IR - Insoluble Residue

Approximate analytical uncertainties are as follows: Fe-1.4%, Th-2.3%, Cr-3.4%, Rb-3%, Zn-7.5%, Sc-1.3%, Ba-4%, Co-3.4%, Na-1.4%, K-2.3%, Sb-5.1%.

Table 2: Distribution by Facies of the Means of Insoluble Residue and Selected Elements: Whole Rock Samples

	<u>Offshore</u>	<u>Reef</u>	<u>Back-reef</u>
IR	13.89 (8.04)	5.07 (4.06)	3.29 (3.39)
Sc	1.58 (0.94)	0.91 (0.67)	0.61 (0.53)
Th	3.55 (2.29)	1.31 (0.84)	0.84 (0.83)
Rb	39.87 (20.91)	11.45 (4.56)	10.99 (8.40)
Ba	125.32 (60.43)	39.59 (12.25)	---
Cr	5.97 (3.10)	5.48 (4.14)	3.41 (2.05)
Fe	7045.43 (4026)	10880.6 (5004)	3269.0 (1748)
Zn	102.27 (134.7)	39.63 (44.75)	14.57 (17.61)
Co	1.83 (1.46)	3.78 (2.76)	0.79 (0.49)
Ca	324486.0 (146406)	260076 (34559)	269734 (37754)
Na	306.71 (112.8)	466.68 (109)	559.68 (159)
K	18002 (7239)	8138.8 (5539)	6069.6 (8257)
Sb	0.19 (0.05)	0.30 (0.11)	0.27 (0.13)

Mean values expressed in ppm. Standard deviation about the mean is given in parentheses below each mean value.

Table 3: Elemental Concentrations in the Insoluble Residue  
(concentrations determined by INAA and expressed in ppm)

Sample	*TREE	Fe	Th	Cr	Rb	Zn	Sc	Ba	Co	Ca	Na	K	Sb
3-750	127.17	11583	9.35	55.24	156.8	--	5.53	145.3	23.65	--	359.2	74752	2.94
HM 1052	117.01	11506	9.41	29.47	261.1	--	3.74	656.3	2.61	--	743.4	103741	0.55
LC12 1086	46.79	15658	2.46	4.51	36.7	--	0.92	88.4	9.60	--	325.7	21977	0.39
LC12 915	40.07	19432	4.79	40.94	150.2	--	2.74	392.4	4.52	--	611.3	86208	0.82
1-1010	117.30	12661	--	22.84	255.48	--	3.2	27.9	1.83	--	696.2	101828	0.53

\*TREE - Total REE Content

Approximate analytical uncertainties are as follows; Fe-1.4%, Th-2.3%, Cr-3.4%, Rb-3%, Zn-7.5%,  
Sc-1.3%, Ba-4%, Co-3.4%, Ca-1.8%, Na-1.4%, K-2.3%, Sb-5.1%

when the three facies of the Bonnetterre are considered individually (Table 4).

Concentrations of Ca, Mg, Sr, Mn, Fe, Pb, Zn, and K in the HCl soluble portion of the samples are given in Table 5. Table 6 lists the average elemental concentrations in the carbonate fraction for each facies. Ca, with a mean value of 348,825 ppm, and Sr, with a mean value of 465 ppm, are highest in the carbonate fraction of samples from the offshore facies (significant to the 99 percent confidence level). The high Ca value is the result of the dominantly limestone lithology in the offshore facies. Sr can substitute more readily into the calcite than into the dolomite structure, accounting for the lower Sr values in the dolostone samples from the reef and back-reef facies.

The Mg/Ca weight ratios also illustrate the carbonate composition of the sample. Four samples-HM1 945, HM1 1052, IRS 1365, and IRS 1370-are nearly pure limestone with Mg/Ca ratio's less than or equal to 0.02. Bonnetterre Formation dolostone samples have very uniform Mg/Ca ratios, averaging 0.59. Viets and others (1983) also noticed this same uniformity in Mg/Ca ratios in dolostone samples from the three-meter composite samples in the northern cross section.

Table 4: Correlation Coefficients for Insoluble Residue versus Elements: All Samples and Individual Facies

	All Samples IR	Offshore IR	Reef IR	Back-reef IR
Sc	0.91*	0.95*	0.95*	0.89*
Th	0.96*	0.97*	0.79	0.95*
Rb	0.96*	0.97*	0.97*	0.97*
TREE	0.91*	0.96*	0.72*	0.78*
Ba	0.89*	0.93*	0.86*	--
Cr	0.73	0.82*	0.89*	0.86*
Fe	0.29	0.21	0.48	0.46
Zn	0.11	-0.71	0.52	0.18
Co	0.32	0.60	0.57	0.60
Ca	0.12	-0.09	0.47	-0.43
Na	-0.27	0.59	0.02	0.01
K	0.98*	0.98*	0.98*	0.99*
Sb	-0.02	-0.05	0.49	-0.001

\* Correlations are significant to greater than the 90 percent confidence level. Correlation coefficients calculated by the Pearson product-moment method.

Table 5: Elemental Concentration of Carbonate: Core Samples Only  
(concentrations determined by DCPA and expressed in ppm)

Sample	Zn	Mn	Fe	Pb	Sr	K	Mg	Ca	*Mg/Ca
HOST BONNETERRE FORMATION: Offshore Facies:									
IRS-1198	95	2100	--	110	130	1380	142	333	0.43
IRS-1226	94	3130	12020	140	45	75	127760	240600	0.57
IRS-1291	37	570	3940	53	360	180	16660	359450	0.04
IRS-1365	32	70	7011	50	610	520	9060	363940	0.02
IRS-1370	30	500	2940	31	650	230	6570	373930	0.02
HMI-945	27	160	552	15	520	40	4780	388100	0.01
HMI-1052	170	365	4410	19	610	450	7960	366930	0.02
HOST BONNETERRE FORMATION: Reef Facies:									
LC12-879	44	590	2450	55	420	300	142550	361650	0.03
LC12-915	53	460	2690	80	69	150	144370	243485	0.59
LC12-988	31	3090	13300	160	57	80	119140	200000	0.59
LC12-1086	23	1400	5250	110	52	86	118700	192780	0.61
LC12-1128	45	1700	5760	110	57	120	121340	204250	0.59
LC12-1167	62	6070	160970	120	47	110	122600	214060	0.57
8EE-590	44	830	4580	160	83	110	116750	191860	0.61
8EE-758	36	5470	12350	103	96	120	133000	232900	0.57
8EE-793	85	3370	7800	780	72	165	122400	211500	0.58

\* Mg/Ca ratio determined using weight percents

Table 5: continued

(concentrations determined by OCPA and expressed in ppm)

Sample	Zn	Mn	Fe	Pb	Sr	K	Mg	Ca	*Mg/Ca
HOST BONNETERRE FORMATION: Back-reef Facies:									
RE1-426	23	160	616	120	108	84	146070	244740	0.59
RE1-473	33	270	820	77	120	210	145380	242230	0.60
RE1-621	21	230	900	63	100	42	148550	248250	0.59
RE1-676	30	230	202	74	140	86	140490	232950	0.60
RE1-721	30	380	2460	133	80	80	143860	242500	0.59
RE1-898	30	370	1000	130	91	150	131400	213610	0.61
1EE-646	50	750	4750	110	69	54	150390	251040	0.59
1EE-745	20	440	850	70	110	100	138890	229710	0.60
1EE-814	24	800	2120	69	68	54	143120	235900	0.61

\*Mg/Ca ratio determined using weight percents

Percent relative standard deviation less than 3% for all elements

Table 6: Means of Carbonate Elemental Concentration By Facies

	Offshore	Reef	Back-reef
Na	553 (184)	600 (111)	538 (197)
Zn	65 (57)	45 (18)	29 (9)
Mn	799 (1157)	2113 (1739)	403 (228)
Pb	51 (46)	194 (239)	94 (28)
Sr	465 (230)	113 (124)	98 (24)
K	249 (196)	141 (70)	95 (53)
Fe	5145 (3967)	6772 (4110)	1524 (1406)
Mg	28798 (48652)	127281 (11134)	143127 (5688)
Ca	348825 (53952)	229803 (56400)	237881 (11467)

Mean values expressed in ppm. Standard deviation about the mean is given in parentheses below each mean value.

## REE DATA

The concentrations of REE and La/Sm, Sm/Yb, Sm/Lu, and Eu/Sm ratios are listed in Table 7. The means and standard deviations of the REE ratios are given in Table 8. Figures 8 through 10 are representative REE patterns for the three facies of the Bonnetterre Formation. These plots indicate that, although the amount of REE may vary, the shapes of the REE patterns remain constant (i.e. REE patterns are parallel). The shape of the REE patterns, and the REE ratios, of the Lamotte Sandstone are similar to the average REE pattern of the Bonnetterre Formation (Fig. 11). The REE concentrations and La/Sm, Sm/Lu, Sm/Yb, Eu/Sm of selected insoluble residues are given in Table 9.

## INSOLUBLE RESIDUE AND TOTAL REE CONTENT

The amount of insoluble residue (IR) also correlates with the total REE (TREE) content of the Bonnetterre Formation (correlation coefficient of 0.91). A correlation between IR and TREE is also observed within each of the three facies (significant to the 99 percent confidence level). Although the TREE content correlates with the amount of IR, no correlation was observed between the amount of IR and REE ratios.

Table 7: REE Data

(concentrations determined by INAA and expressed in ppm)

Sample	La	Ce	Sm	Eu	Tb	Yb	Lu	La/Sm	Sm/Lu	Sm/Yb	Eu/Sm
HOST BONNETTERRE FORMATION: Offshore Facies:											
1-940	2.43	5.96	0.51	0.07	0.08	0.23	0.08	4.80	6.32	2.23	0.15
1-1010	16.95	33.32	3.02	0.45	0.52	1.50	0.23	5.61	12.79	2.01	0.15
1-1050	14.35	29.23	2.46	0.42	0.46	1.06	0.18	6.08	12.95	2.21	0.18
1-1170	8.82	17.14	1.61	0.24	0.25	0.84	0.14	5.48	11.76	1.92	0.15
IRS-1198	18.64	65.40	3.70	0.86	2.58	2.64	0.37	5.04	9.94	1.39	0.23
IRS-1226	5.27	12.22	0.93	0.17	0.14	0.55	0.10	5.69	9.18	1.67	0.18
IRS-1291	17.12	44.53	3.44	0.49	0.57	1.89	0.28	4.98	12.32	1.82	0.15
IRS-1365	19.51	38.99	2.55	0.41	0.57	1.63	0.25	7.64	10.26	1.56	0.16
IRS-1370	12.58	34.46	3.11	0.50	0.40	1.34	0.19	4.04	15.78	2.31	0.16
HMI-945	2.01	5.18	0.39	0.05	0.03	0.21	0.05	5.34	8.04	1.84	0.14
HMI-1052	13.28	25.93	1.98	0.31	0.38	1.05	0.16	6.68	12.51	1.88	0.15
HOST BONNETTERRE FORMATION: Reef Facies:											
3-580	1.72	4.02	0.44	0.05	0.07	0.28	0.04	3.86	10.13	1.56	0.12
3-610	2.25	5.30	0.59	0.14	0.11	0.38	0.08	3.78	7.18	1.54	0.23
3-660	2.37	4.16	0.39	0.04	0.07	0.28	0.05	6.01	7.45	1.42	0.11
3-700	1.62	3.37	0.33	0.05	0.08	0.18	0.03	4.91	9.45	1.85	0.14
3-750	9.73	18.03	1.28	0.16	0.20	0.65	0.12	7.57	10.89	1.97	0.12
3-790	6.99	13.09	1.05	0.17	0.21	0.80	0.12	6.62	8.58	1.31	0.16
LC12-879	9.73	17.58	1.24	0.31	0.25	0.80	0.14	7.85	8.72	1.54	0.25
LC12-915	4.65	11.02	0.77	0.15	0.13	0.39	0.06	5.99	11.59	1.97	0.19
LC12 988	0.92	--	0.31	0.02	0.04	0.12	0.02	2.95	12.52	2.65	0.07

Table 7: REE Data continued  
(concentrations determined by INAA and expressed in ppm)

Sample	La	Ce	Sm	Eu	Tb	Yb	Lu	La/Sm	Sm/Lu	Sm/Yb	Eu/Sm
HOST BONNETTERRE FORMATION: Reef Facies cont.:											
LC12-1086	6.18	11.54	0.77	0.15	0.11	0.34	0.06	8.02	12.64	2.24	0.20
LC12-1128	5.43	13.46	1.38	0.22	0.22	0.61	0.10	3.94	13.39	2.25	0.16
LC12-1167	3.76	6.66	0.70	0.11	0.12	0.44	0.08	5.38	8.61	1.57	0.16
8EE-590	1.56	3.51	0.39	0.04	0.07	0.25	0.04	3.92	8.67	1.57	0.10
8EE-758	7.99	2.60	0.93	0.04	0.05	0.57	0.08	8.57	11.66	1.63	0.04
8EE-793	7.22	13.54	1.02	0.15	0.19	0.68	0.10	7.09	10.08	1.48	0.14
HOST BONNETTERRE FORMATION: Back-reef Facies:											
4-621	12.38	29.79	2.59	0.39	0.33	1.06	0.16	4.76	15.65	2.45	0.15
4-640	1.34	2.65	0.27	0.04	0.03	0.12	0.03	4.91	9.44	2.32	0.14
4-740	2.61	5.24	0.42	0.07	0.08	0.19	0.03	6.18	12.41	2.22	0.17
4-810	2.74	5.94	0.60	0.05	0.05	0.20	0.05	4.53	12.62	2.98	0.09
4-850	4.69	8.91	0.72	0.13	0.17	0.35	0.05	6.49	12.89	2.06	0.18
5-348	1.02	2.19	0.22	0.03	0.03	0.11	0.02	4.70	8.38	2.01	0.15
5-420	2.64	6.43	0.58	0.06	0.08	0.25	0.04	4.57	13.76	2.35	0.11
5-486	13.97	29.61	2.47	0.35	0.46	1.21	0.22	5.65	11.39	2.03	0.14
6-420	2.34	5.11	0.50	0.07	0.10	0.30	0.09	4.64	5.60	1.65	0.15
6-460	4.39	9.61	1.08	0.14	0.14	0.43	0.06	4.04	17.82	2.52	0.13
6-500	5.02	10.87	1.18	0.18	0.17	0.49	0.07	4.25	16.40	2.37	0.15
RE1-426	1.40	2.75	0.16	0.03	0.03	0.07	0.02	8.66	9.00	2.16	0.19
RE1-473	4.93	11.91	0.57	0.10	0.07	0.23	0.04	8.67	15.37	2.41	0.18

Table 7: REE Data continued  
(concentrations determined by INAA and expressed in ppm)

Sample	La	Ce	Sm	Eu	Tb	Yb	Lu	La/Sm	Sm/Lu	Sm/Yb	Eu/Sm
HOST BONNETTERRE FORMATION: Back-reef Facies cont.:											
RE1-621	3.01	6.05	0.43	0.07	0.06	0.31	0.05	6.95	8.17	1.40	0.16
RE1-676	2.16	5.17	0.31	0.05	0.05	0.18	0.03	7.03	9.59	1.67	0.18
RE1-721	2.91	6.98	0.48	0.08	0.08	0.25	0.04	6.02	12.71	1.95	0.17
RE1-898	4.85	9.59	0.83	0.11	0.13	0.42	0.07	5.81	11.76	1.98	0.13
1EE 646	0.73	1.77	0.22	0.03	0.02	0.09	0.02	3.39	9.00	2.40	0.14
1EE 745	1.46	2.92	0.23	0.03	0.03	0.08	0.01	6.34	16.50	2.71	0.12
1EE 814	1.46	4.08	0.30	0.03	0.03	0.11	0.03	4.83	10.92	2.56	0.09
LAWOTTE SANDSTONE:											
LC12-1186	5.16	12.83	0.79	0.15	0.15	0.67	0.11	6.56	7.02	1.18	0.19
IRS-1470	5.23	12.92	0.56	0.07	0.11	0.37	0.05	9.37	10.33	1.49	0.14
RE1-973	2.89	6.74	0.39	0.06	0.08	0.20	0.04	7.44	9.70	1.96	0.16

Approximate analytical uncertainties are as follows; La-2.8%, Ce-2%, Sm-2.1%, Eu-3.2%, Tb-3.6%, Yb-4.8%, Lu-3.5%.

Table 8: Means of REE Ratios in Sample Groups

	<u>La/Sm</u>	<u>Sm/Lu</u>	<u>Sm/Yb</u>	<u>Eu/Sm</u>
HOST BONNETERRE FORMATION (45)	5.68 (1.5)	11.23 (2.8)	2.01 (.39)	0.15 (.04)
FACIES:				
Offshore (11)	5.63 (1.0)	11.19 (2.7)	1.94 (.25)	0.15 (.02)
Reef (14)	5.79 (1.8)	10.21 (1.9)	1.78 (.38)	0.15 (.06)
Back-reef (20)	5.62 (1.4)	11.96 (3.3)	2.21 (.38)	0.15 (.03)
LAMOTTE SANDSTONE (3)	7.79 (1.4)	9.02 (1.7)	1.54 (.39)	0.16 (.03)

Number of samples in each sample group given in parenthesis after group name. Standard deviation about the mean is given in parentheses below each mean value.

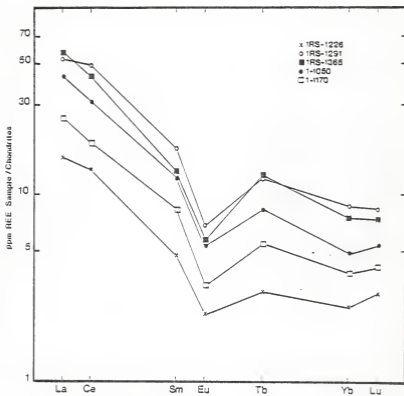


Figure 8: REE patterns of the Bonnetterre Formation, offshore facies.

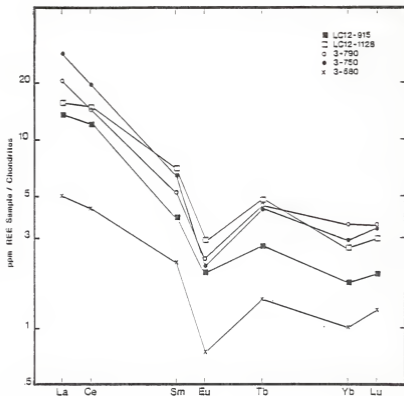


Figure 9: REE patterns of the Bonnetterre Formation, reef facies.

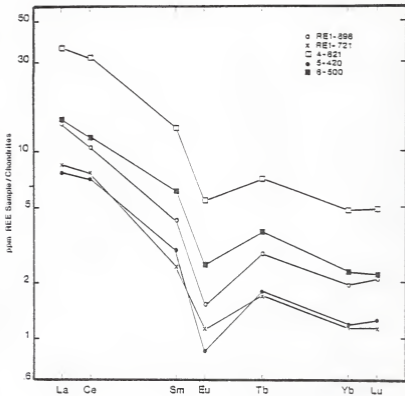


Figure 10: REE patterns of the Bonnetterre Formation, back-reef facies.

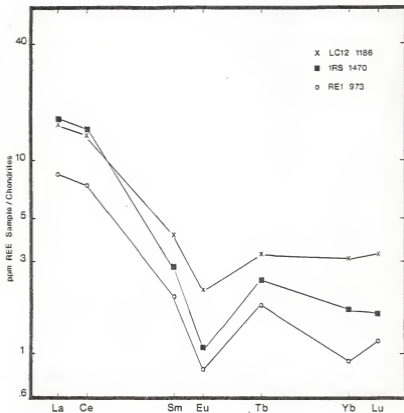


Figure 11: REE patterns of the Lamotte Sandstone.

Table 9: Insoluble Residue REE Data

(concentrations determined by INAA and expressed in ppm)

Sample	La	Ce	Sm	Eu	Tb	Yb	Lu	La/Sm	Sm/Yb	Sm/Lu	Eu/Sm
3-750	52.61	67.76	1.78	0.49	0.33	2.76	0.46	29.42	0.65	3.88	0.27
HM1 1052	42.95	67.41	1.97	0.79	0.42	2.79	0.44	21.75	0.46	4.55	0.40
LC12 1086	15.82	28.62	1.08	0.18	0.18	0.59	0.14	14.61	1.81	7.65	0.16
LC12 915	13.99	21.82	0.90	0.47	0.16	1.87	0.45	15.48	0.48	2.02	0.53
1-1010	44.17	65.43	1.91	0.25	0.48	3.46	0.51	23.05	0.55	3.74	0.13

Approximate analytical uncertainties are as follows; La-2.8%, Ce-2%, Sm-2.1%, Eu-3.2%, Tb-3.6%, Yb-4.8%, Lu-3.5%.

## PETROGRAPHY

Composition summary charts for each drill hole are provided in Tables 10-15. The offshore facies is predominantly a trilobite-echinoderm biomicrite. Sample LRS 1198 is a silty algal biomicrite and LRS 1226 is a medium crystalline dolomite. Within the reef facies, the dominant lithology is medium crystalline dolomite. Only sample LC12 879, a dolomitized algal biomicrudite, contains limestone. Samples collected from the back-reef facies are composed of medium and coarsely crystalline dolomite and dolomitized sparite.

Generalized Stratigraphic Column

Depth below surface is listed in feet

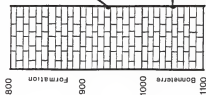


Table 10: Composition of Samples from Drill Hole HMI. Abundance of components reported in percent with size in millimeters listed in parentheses below.

Sample Number	Framework Components					Matrix Components			Replacement Minerals		Misc Minerals
	Intracrystals	Bioclastic Components			Quartz Sand	Mollusks	Microcrinoids	Spar	Dolomite	Pyrite	Glaucodite
		Envolutions Fragments	Visible Fragments	Stromatolite Fragments							
HM1	28.4	5.1	13		11	30	17			5.4	
945	(1.95)	(0.85)	(18)		(0.04)					(0.11)	
HM1	6.5	6.5	13	7	3.1	25	12		2.4	2.2	0.7
1052	(1.25)	(0.95)	(1.06)	(15)	(0.02)				(0.16)	(0.14)	(0.2)

Generalized Stratigraphic Column

Depth below surface is listed in feet

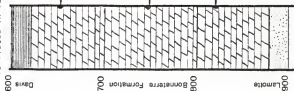


Table 11: Composition of Samples from Drill Hole 1EE. Abundance of components reported in percent with size in millimeters listed in parentheses below.

Sample Number	Framework Components				Matrix Components			Replacement Minerals	
	Skeletal Components	Framework Components			Micrites	Matrix Components		Dolomite	Pyrite
		Grainstone Fragments	Pellets	Quartz Sand		Microspar	Spar		
1EE 646	10 (0.12)		4 (0.11)	1 (0.05)		35 (0.07)		50 (0.1)	
1EE 745								98 (0.77)	2 (0.03)
1EE 814								97 (0.12)	3 (0.04)

Table 12: Composition of Samples from Drill Hole 8EE. Abundance of components reported in percent with size in millimeters listed in parentheses below.

Sample Number	Framework Components		Replacement Minerals	
	Skeletal Components Stromatolite Fragments	Quartz Sand	Colomite	Pyrite
8EE 590	9 (10)	1.5 (0.01)	89.5 (0.11)	
8EE 758			98.5 (1.16) & (0.48)	1.5 (0.01)
8EE 793			84 (0.40)	16 (0.07)

Generalized Stratigraphic Column

Depth below surface is listed in feet

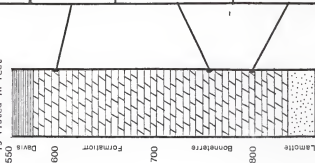


Table 13: Composition of Samples from Dr-111 Hole IRS. Abundance of components reported in percent with size in millimeters listed in parentheses below.

Sample Number	Framework Components				Matrix Components			Replacement Minerals		Misc Minerals	
	Intracracks	Skeletal Components			Quartz Sand	Mica	Microspar Spar	Biotite	Pyrite	Glauconite	Calcite
		Framework Fragments	Isolated Fragments	Wedge-like Fragments							
IRS 1198				15 (11)	40 (0.02)	41			4 (0.01)		
IRS 1226				45.1 (8)	10.8 (0.05)			42.3 (0.24)	1.6 (0.02)	0.4 (0.03)	
IRS 1291	12.8 (3.25)	5.6 (0.7)	7.8 (1.3)	4.5 (9)	4.5 (0.01)	20	22	10.5 (0.09)	2.5 (0.01)	10 (0.03)	
IRS 1365	1.04 (3.15)	2.5 (0.6)	10.4 (1.5)	11.8 (8.5)	5 (0.01)	20	30	8.6 (0.04)	1 (0.01)	1.8 (0.02)	0.4 (0.2)
IRS 1370	50.2 (4.17)	3.8 (0.88)	4.2 (1.4)	3.8 (5)		13	14.5	0.8 (0.08)	0.8 (0.03)	4.2 (0.03)	
Sample Number	Framework Components			Matrix Components							
	Common	Quartz			Clay						
IRS 1470	98 (0.43)				2						

Generalized Stratigraphic Column

Depth below surface is listed in feet

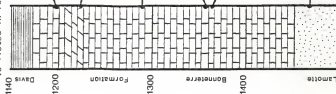


Table 14: Composition of Samples from Drill Hole LC12. Abundance of components reported in percent with size in millimeters listed in parentheses below.

Sample Number	Framework Components					Stroniatites	Matrix Components		Replacement Minerals		Misc Minerals		
	Intracrystals	Bacterial Components			Quartz Sand		Murchie	Microspiral Spar	Dolomite	Pyrite	Glauconite	Chertite	
		Relictive Fragments	Isolate Fragments	Wormlike Fragments									
LC12 879		3 (0.55)	2.3 (1.25)	2.5 (5)	0.9 (0.04)	25 (15)	45	4.7		10 (0.21)	3.8 (0.02)		3.3 0.03
LC12 915				7.5 (4)	2	30 (14)				56 (0.14)	4.5 (0.02)		
LC12 988										94 (0.34)	6 (0.03)		
LC12 1086				4.6 (7)						93.4 (0.19)	2 (0.02)		
LC12 1128	60.1 (1.26)	3.2 (0.82)								26.7 (0.23)	8.3 (0.03)	1.7 (0.03)	
LC12 1167					42.6 (0.25)					54.2 (0.09)	3.2 (0.02)		
Sample Number	Framework Components			Matrix Components									
	Common	Quartz			Clay								
LC12 1186	97.5	(0.28)			2.5								

Generalized Stratigraphic Column

Depth below surface is listed in feet

B40

Days

Formation

Bonneville

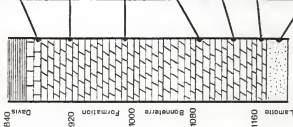
1080

1160

Lamotte

Generalized Stratigraphic Column

Depth below surface is listed in feet



Generalized Stratigraphic Column

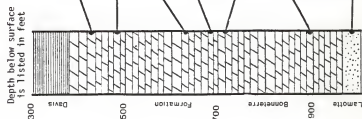


Table 15: Composition of Samples from Drill Hole RE1. Abundance of components listed in percent with size in millimeters listed in parentheses below.

Sample Number	Framework Components			Matrix Components			Replacement Minerals		Misc Minerals
	Skeletal Components		Stromatolite Fragments	Quartz Sand	Micrite	Microspar	Spar	Dolomite	Pyrite
	Epilobium Fragments								
RE1 426								100 (0.07)	
RE1 473			8 (10)					92 (0.32)	
RE1 621		7.5 (1.06)						92 (0.08)	0.5 (0.03)
RE1 676								100 (1.26)	
RE1 721				6 (0.03)	10		12	72 (0.02)	
RE1 898								100 (0.96) 8 (0.22)	
Sample Number	Framework Components		Matrix Components						
	Common	Quartz	Clay						
RE1 973	96.5 (0.29)		3.5						

## DISCUSSION

## INSOLUBLE RESIDUE AND K, Rb, Th, Sc, Cr AND Ba.

The Bonnetterre Formation, when considered as a whole, shows positive correlations between the amount of IR and K, Rb, Th, Sc, and Ba. Rb and Th are commonly associated with the IR of carbonate rocks, and the K content of carbonate rocks is usually considered a function of the clay content of the carbonate rock (Wedepohl, 1983). Th and Rb normally are found in the clay fraction of carbonate rocks because Rb and Th are most abundant in micas (Wedepohl, 1983). Sc is associated with the clay fraction of carbonate rocks but is present only in very small amounts, whereas Ba in carbonate rocks is directly associated with the amount of detrital clay (Wedepohl, 1983).

The correlations between IR and Sc, Th, Ba, Rb, and K also are substantiated by the INA analysis data from the IR (Table 3). The IR of several samples were analyzed and all IR samples showed an increase in the ppm value of the previously mentioned elements compared to the values in the whole rock. Of these elements, Rb and K showed the strongest enrichment in the IR, with an average enrichment factor of six.

Each of the three facies of the Bonneterre Formation has some elements that correlate positively with the IR. The offshore facies shows correlations between IR and Cr and all the previously mentioned elements; the reef facies exhibits correlations between the IR and Sc, Rb, Ba, K, and Cr; and the back reef facies shows correlations between IR and Sc, Th, Rb, K, and Cr.

The Bonneterre Formation as a whole exhibits a much lower correlation between IR and Cr than any of the facies. The reef and back-reef facies are represented by samples with Cr values less than 11 ppm and IR values less than 9 percent. The offshore facies is represented by samples with Cr values less than 11 ppm and IR values greater than 10 percent. When all the data are combined, there is a lower correlation between IR and Cr because some samples have different values of IR and similar values of Cr. This relationship indicates that Cr is not directly associated with the non-carbonate fraction of a sedimentary rock.

The lower correlation coefficient between IR and Th within the reef facies is the result of changes in the composition of the IR. The reef facies contains limestone and dolostone with clay-rich IR and dolostone with clay minerals and sulfide minerals in the IR. The samples without sulfides exhibit a fairly high correlation between IR and Th, but samples with sulfides have

higher amounts of IR and low Th values because only the clay is contributing Th.

In all three facies the correlation between IR and K remains constant (correlation coefficient of 0.99). This stable correlation indicates that K is the only element that truly parallels the amount of clay-rich IR in these carbonate rocks. This relationship is substantiated by the carbonate and IR data. The K content in the soluble portion of the rocks is much lower than the K value in the whole rock, and the IR is enriched in K relative to the whole rock. Thus, the majority of K in carbonate rocks is contained within the clay-rich IR.

#### ELEMENTAL CONCENTRATION WITHIN FACIES

The offshore facies whole-rock samples contain a statistically significantly higher amount of Sc, Th, Rb, Ba, K, and Ca than either the reef or back-reef facies samples. The large amount of Ca within the offshore facies is the result of limestone being the dominant lithology of the offshore facies. The maximum values of Sc, Rb, Th, Ba, and K are a direct result of these elements' parallel relationship with the maximum amount of clay-rich insoluble residue present in the offshore facies. The observed differences in Zn values among facies are not

statistically significant.

The reef facies contains a significantly higher amount of Fe and Co than either the offshore or back-reef facies. Both Fe and Co are generally associated with sulfide minerals in carbonate rocks. Although this section of the reef is unmineralized, some samples have traces of sulfide minerals in their IR's. Thus, all reef rocks that have had some interaction with the ore fluid have higher values of Fe and Co than rocks in other facies.

The back-reef facies contains a significantly greater amount of Na than the offshore or reef facies. The restricted environment of the back-reef facies results in evaporation and concentration of salts in the water. The limestone samples that are deposited within this environment are enriched in Na relative to the other facies.

#### INSOLUBLE RESIDUE AND REE PATTERN

A positive correlation exists between the amount of IR and the TREE content. Each facies of the Bonnetterre Formation also exhibits a correlation between IR and TREE content (significant to the 99 percent confidence level). A correlation between IR and TREE content indicates that the bulk of the REE are carried

within the clay or non-carbonate fraction of carbonate rocks.

The lower correlation coefficients between IR and TREE content in the reef and back-reef facies are the result of a poorer dispersion of IR values in these two facies. Plots of IR versus TREE content for all three facies have similar slopes, but the abundance of samples with small amounts of IR and TREE content in the reef and back-reef facies generates lower correlation coefficients for these two facies.

Because clays contain the majority of REE found in sedimentary rocks (Clark, 1984), even a trace amount of clay in a carbonate rock may dominate the REE pattern of the rock. Evidence provided by this study does not support this conclusion. When the amount of insoluble residue is plotted against REE ratios, no correlation is observed (Fig. 12) (correlation coefficients less than 0.5). REE ratios illustrate the shape of the REE pattern, and their lack of correlation with a clay-rich insoluble residue indicates that the amount of clay is not wholly responsible for a carbonate rock's REE pattern.

Although the amount of clay does not alter the shape of a sedimentary rock's REE pattern, on a chondrite-normalized plot samples with greater TREE contents plot above those samples with lower TREE contents. The TREE content is determined by the amount of clay in the sedimentary rock. The effect of variances

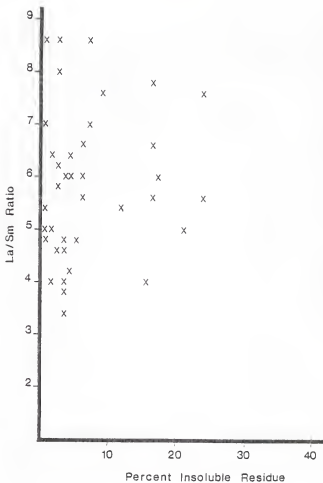


Figure 12: Insoluble residue versus La/Sm ratio.

in the amount of clay on a sedimentary rock's REE pattern is reflected by a series of parallel, similarly shaped REE patterns. Those samples with greater amounts of clay will plot above those samples with lower values of clay-rich IR.

The REE data from the clay-rich IR are difficult to interpret. The IR has much higher La/Sm ratios and lower Sm/Lu and Sm/Yb ratios than the whole rock, indicating an overall enrichment in both light and heavy REE. Mass balance equations indicate that the La/Sm ratios of the carbonates based on the La/Sm ratio of the whole rock and IR range from 0.03-7.82. However, these ratios are inconsistent with whole-rock La/Sm ratios. If the higher La/Sm ratios are correct, there should be a much greater spread in La/Sm ratios for the whole rocks, and a much better correlation between IR and La/Sm ratio than those observed.

There are two possible explanations for the observed IR REE ratios. The IR could have become relatively enriched in some REE during the dissolution process if the solution transferred REE to the clays, or if Sm was removed from clays and transferred to the solution. Further analysis with lower strength HCl is needed before any conclusions can be drawn about the REE patterns of the IR.

## LITHOLOGY AND REE PATTERN

Although previous authors have demonstrated that diagenesis has very little effect on a sedimentary rock's REE pattern (Chaudhuri and Cullers, 1978), it was originally postulated that dolomitization of the carbonate rocks may have altered their REE patterns. Analysis of dolostone and limestone REE patterns has indicated that dolomitization did not change the shape of the rock's REE patterns; offshore limestone samples and reef and back-reef dolostone samples have similar REE ratios. As previously stated, the main differences among REE plots are caused by variances in the TREE content. Analysis has shown that limestone and dolostone samples with equal amounts of IR contain similar amounts of TREE. Dolomitization does not change the TREE content of a carbonate rock, and is therefore not able to alter the REE pattern of the original sedimentary rock.

## REE PATTERN

## Comparison of REE Ratios

The La/Sm, Sm/Lu, and Sm/Yb ratios of the Bonneterre Formation statistically are equivalent to those REE ratios in the NASC. Both the Bonneterre Formation and the NASC show a LREE enrichment relative to chondrites. Each of the three Bonneterre Formation facies also has La/Sm, Sm/Lu and Sm/Yb ratios similar to the NASC. The similarity of the Bonneterre Formation's REE ratios with those of the NASC further illustrates the small role gross-sediment composition has on a sedimentary rock's REE pattern. The La/Sm, Sm/Lu and Sm/Yb ratios of the Bonneterre Formation remain constant regardless of composition (dolostone or limestone) and amount and composition of IR in the sample.

Only the Eu/Sm ratio in the Bonneterre Formation is significantly different from the Eu/Sm ratio in the NASC. Both the NASC and the Bonneterre Formation sample sets exhibit a negative Eu anomaly with respect to chondrites, but the Bonneterre Formation samples have a larger negative anomaly. The Bonneterre Formation's depletion in Eu is not unusual. All sedimentary rocks of post Archean age exhibit a depletion in Eu, whereas Archean rocks have normal to slightly enriched Eu values.

Because REE are normalized to Archean chondrites, all younger sedimentary rocks will exhibit a Eu depletion relative to chondrites. The exact reason for the enlarged negative Eu anomaly in the Bonnetterre Formation is still unknown. It may be a result of the low-temperature solution geochemistry of Eu for which very little published data exist.

#### Scatter of REE Ratio Data

The La/Sm, Sm/Yb and Sm/Lu ratios of the Bonnetterre Formation exhibit a remarkable similarity in the scatter of their data points. Approximately 70 percent of the samples have REE ratios that are within one standard deviation of their respective means, 15 percent of the samples have REE ratios between one and two standard deviations lower than their respective means, and another 15 percent of the samples have REE ratios that are between one and two standard deviations higher than their respective means. The symmetry of the scatter of the data points about the mean for all three REE ratios suggests that the variances in the Bonnetterre Formation's ratios are part of a normal distribution of REE values in sedimentary rocks.

More evidence that the scatter in REE ratios data is part of a normal variance comes from other authors' data. Haskin and Frey

(1966) analyzed 34 sedimentary rocks and found only seven that were identical to the average within experimental error. These authors (1966, p. 305) concluded that "... most REE patterns of an individual sedimentary rock differ by 15 percent or more from the average pattern, but that only about one in 20 shows a deviation from the average as great as 50 percent." None of the REE ratios for the Bonnetterre Formation deviates by more than 30 percent from its respective mean. The Bonnetterre Formation's REE ratios therefore show no greater scatter than other sedimentary rocks.

Although gross sediment composition does not affect the REE pattern, local composition changes can alter the REE pattern of the rock. Balashov and others (1964), in their study of the Russian platform, found that when sedimentation occurred under arid conditions there were slight differences in the relative amount of REE present in the clay. The Bonnetterre Formation's REE ratios are similar to those of other sedimentary rocks, but the close proximity of the granitic basement and the presence of ore mineralization may have altered the REE ratios. Haskin and others (1966) found that the observed differences in individual samples' REE patterns are the result of a number of different effects, including the mixing of the sediment. In some instances, a sample with an anomalous REE pattern could be traced back to its original source.

### Proximity of Granitic Basement

During the deposition of the Bonneterre Formation the Precambrian highland stood out as a positive feature. The Precambrian highland was therefore able to contribute detritus directly to the region as the Bonneterre Formation was deposited. Thus, the sedimentary cycle was reworking this detritus only once or twice before it was incorporated into the Bonneterre Formation's carbonate rocks. Because these sediments were not reworked numerous times, the imprint of a granitic source rock may still be present in some of the samples.

Granitic rocks are enriched in the LREE (Koljonen and Rosenberg, 1974; Clark, 1984; Bickford and others, 1981). Any Bonneterre Formation sample that incorporated a portion of granitic rock into its composition would have a higher La/Sm ratio. Only seven Bonneterre Formation samples have slightly higher La/Sm ratios (La/Sm of 7.57-8.65) relative to the mean La/Sm ratio. These higher La/Sm ratios are what would be expected for sediments locally derived from the granitic Precambrian basement. Although the granitic basement rock did alter the La/Sm ratios of the Bonneterre Formation, the granitic rock's influence was slight, as the majority of La/Sm ratios are within one standard deviation of the mean.

The Lamotte Sandstone's REE pattern also was slightly influenced by the granitic source rock. Three samples of the Lamotte Sandstone were analyzed and all samples show a slight LREE enrichment (La/Sm ratios of 6.56-9.37). These La/Sm ratios are similar to the higher La/Sm ratios observed in the Bonnetterre Formation. The Lamotte Sandstone was not completely derived from the St. Francois Mountains; some of the quartz rich detritus was derived from the Precambrian rocks of the Great Lakes area (Houseknecht and Ethridge, 1978). The samples of Lamotte Sandstone that were analyzed exhibit the slightly enriched La/Sm ratios that are characteristic of a granitic source rock.

#### Effects of Interaction with Ore Fluids

Although the samples chosen for analysis are unmineralized, it is possible that the migrating ore fluids did alter the REE patterns of the host rock. Graf (1984) analyzed samples of host rock, vug calcite and vug dolomite and determined that the ore fluids were depleted in LREE (La/Sm ratio of 0.3-0.78) relative to the host rock. Field evidence has shown that the ore fluids were able to dissolve the Bonnetterre Formation during deposition of the ore minerals. If the ore fluids migrated through the Bonnetterre Formation and dissolved part of the carbonate rock,

REE from host rock and brine could mix. The interaction between the host rock and the ore fluid would result in an initial increase in the LREE content of the ore fluid and an initial decrease in the LREE content of the host rock. With continued interaction between host rock and ore fluid, the host rock would develop a REE pattern approaching that of the ore fluid. Thus, any section of the Bonnetterre Formation that was dissolved as the ore fluid passed through it, should develop a low La/Sm ratio as a result of this interaction.

LREE Depleted Samples.-- Assuming that interaction with the ore fluid would lower the La/Sm ratio of the Bonnetterre Formation, only seven samples could be thought of as having come in contact with the ore fluid. These seven samples do not have anomalously low La/Sm ratios, but rather form the low end of a La/Sm distribution plot. If these samples did interact with the ore fluid, their trace-metal content should be greater than the surrounding rocks.

Trace Metal Content.-- Previous workers found an increase in the Fe and Mn contents of the carbonate portion of the host rock within the Viburnum Trend (Viets and others, 1983). Samples from drill hole 3, although unmineralized, lie within the trend and have an average Mn value of 1800 ppm, enriched when compared with samples from drill holes that constitute the rest of the cross section (Viets and others, 1983). In the southern cross section, the greatest amount of Fe and Mn are also found within the reef facies, drill hole LC12. The average values of Mn and Fe in the reef are 2113 and 6772 ppm, respectively. Both of these values are significantly higher than the corresponding values in the back-reef facies (significant to the 90 percent confidence level). The offshore facies contains an anomalously high value of Fe. This high mean value is dominated by the 12,020 ppm Fe value of sample LRS 1226. This dolostone sample contains pyritic stromatolites, thus increasing the Fe content of the sample. Without this sample the mean Fe content of the offshore facies is 3700 ppm. Samples from the southern cross section also exhibit a significantly higher amount of Pb within the reef facies (significant to the 90 percent confidence level). An ore fluid rich in Fe, Mn and Pb could easily substitute these ions into the dolomite lattice because of the similarity of the ionic radius size of Fe, Mn, Pb and Mg. The amount of Zn in the samples is not a good indication of mineralization as both the carbonate and

non-carbonate fraction of the rock contain Zn.

The high contents of Mn, Fe, and Pb within the reef facies in both the northern and southern cross sections suggest the entire reef facies interacted with the ore fluids. If interaction with the ore fluid is capable of producing LREE-depleted host rocks, then the entire reef facies should have low La/Sm ratios. Only seven samples have low La/Sm ratios, and of these samples only four are located in the reef facies. The La/Sm ratios of the other reef samples are varied and show no relation to the high trace-metal contents. Therefore, the Mn and Fe contents of the carbonate phase are much more sensitive indicators of trace mineralization than small changes in the La/Sm ratios.

Further evidence that interaction with the ore fluids did not alter the REE pattern of the host rock comes from Graf (1984). He found the REE ratios of the host rock within mineralized sections of the reef to be similar to the REE patterns of the rest of the host rock (average La/Sm approximately 5.4). Only the samples of recrystallized dolostone, vug calcite and vug dolomite, which were directly affected by the ore fluid, exhibit La/Sm ratios less than three. All evidence at this time suggests that minor interaction with the ore fluid does not alter a sample's REE pattern but may enrich the samples in Fe, Mn, and Pb.

Although these data do not support the conclusion of LREE-depleted host-rock samples pinpointing areas of ore fluid interaction, the data do not completely rule out this theory. Sample LC12 988 has a La/Sm ratio of 2.95 and high values of Fe and Mn. Further research may find other samples with high Fe and Mn contents and low La/Sm ratios. If more samples with La/Sm ratios less than three are discovered, these REE ratios will no longer fit into the low end of a La/Sm distribution plot but will be anomalously low. At this time there is no evidence to suggest that the low La/Sm ratios observed in a few samples are anything other than the low end of a normal REE-distribution pattern.

#### SOLUTION PATHWAYS

The samples that developed a high Fe and Mn content as the result of interaction with the ore fluid, help delineate the migration paths of the ore fluid. All the samples with high trace-element contents are in the reef facies. This distribution indicates that the reef was the main pathway for the ore solutions.

The exact path the ore fluids traveled to reach the Bonnetterre Formation's reef facies is unclear, but the Fe and Mn data

indicate that there was very little interaction with the ore fluid outside of the reef facies. These data are consistent with previous authors' interpretations that the solution pathways of the ore fluids were outside of the Bonneterre Formation. Doe and Delevaux (1972) felt that the ore fluids traveled through the Lamotte Sandstone and then migrated updip into the reef facies of the Bonneterre Formation.

High Fe and Mn values in the reef facies shown in both northern and southern cross section of the Bonneterre Formation indicate that the ore solutions migrated through the entire length of the Viburnum Trend. If further analysis shows that low host-rock La/Sm ratios developed through interaction with the ore fluid, then the presence of only four samples in the reef facies with low La/Sm ratios indicates that the ore fluids traveled very selective paths within the reef facies. Only those samples that were dissolved as the ore fluids traveled through them would develop a low La/Sm ratio. Thus, high Fe and Mn values indicate trace mineralization, but anomalously low La/Sm ratios may pinpoint the specific pathways of ore-fluid migration along the Viburnum Trend. At this time the only specific conclusions that can be drawn regarding the solution pathways are: (1) the ore fluids were generated outside of the Bonneterre Formation and (2) the ore fluids did not migrate through most of the Bonneterre Formation.

## C O N C L U S I O N S

INA analysis of the whole rock samples indicated that the offshore facies of the Bonneterre Formation contains the maximum amount of IR, Sc, Th, Rb, K, and Ba; the reef facies contains the maximum amount of Fe and Co; and the back-reef facies contains the maximum amount of Na. The high mean values of Sc, Th, Rb, K, and Ba in the offshore facies are the direct result of the strong correlations between the IR and these elements (significant to the 99 percent confidence level). The composition of the IR as determined by petrographic and X-ray analysis is predominantly clay minerals, with minor amounts of quartz and feldspar. The concentrations of Sc, Th, Rb, K, and Ba in a carbonate rock therefore are a function of the clay content of the carbonate rock. High concentrations of Fe and Co in the reef facies are the result of the presence of sulfide minerals in some of the reef-facies samples, and the high Na value in the back-reef facies developed because of the ability of the restrictive environment of the back-reef facies to concentrate salts.

DCP analysis of the carbonate portion of these Bonneterre Formation samples indicated that the reef facies contains the highest mean values of Pb, Mn, and Fe. These high values developed through interaction with the ore fluid; as the ore

fluid migrated through the Bonnetterre Formation, the fluid was able to substitute Fe, Mn, and Pb into the dolomite lattice. High mean values of Mn, Pb, and Fe therefore are good indicators of trace mineralization in the Bonnetterre Formation.

Petrographic analysis of the Bonnetterre Formation has shown that it is composed of two lithologies: limestone in the offshore facies and dolostone in the reef and back-reef facies. DCP analysis also supports these findings. The amounts of Ca and Sr in the carbonate portion of the samples are highest in the offshore facies, indicating the predominance of limestone. A consistent Mg/Ca ratio of 0.59 in the reef and back-reef facies reflects the dominantly dolostone lithology of these two facies.

Analysis of the REE contents of the Bonnetterre Formation yielded a mean La/Sm of 5.68, a mean Sm/Lu of 11.23, a mean Sm/Yb of 2.01, and a mean Eu/Sm of 0.15. These ratios are similar to the REE ratios of other sedimentary rocks. The enlarged negative Eu anomaly in the Bonnetterre Formation may be the result of the low-temperature solution geochemistry of Eu. The REE ratios of the Bonnetterre Formation were not significantly altered by the presence of a granitic basement or by the migration of a LREE-depleted ore solution. Dolomitization also had no effect on the REE patterns, in as much as both limestones and dolostones have similar REE ratios.

Although the shapes of the REE patterns, as evidenced by the REE ratios, remain consistent for the entire Bonneterre Formation, those samples with greater amounts of TREE plot above those samples with a lower TREE content. The TREE content is a function of the clay content of the carbonate rock as evidenced by the strong correlation between IR and TREE content (significant to the 99 percent confidence level). Although the amount of IR correlates with the TREE content, there is no relationship between the IR and the REE ratios. Thus, the clay content of a carbonate rock may dominate the TREE content of the sample, but it does not dominate the REE pattern of the carbonate rock. All samples regardless of their clay contents produce similarly shaped REE patterns.

Seven of the Bonneterre Formation samples that were analyzed exhibit a slight depletion in LREE compared to the entire sample set. These samples are not anomalous; they form the low end of a La/Sm distribution plot. Although these seven samples show no correlation with high trace-metal contents, it is possible that further research will show that low La/Sm ratios are an indication of interaction with a LREE-depleted ore fluid. Those samples with high-trace metal contents and low La/Sm ratios would help pinpoint the specific solution pathway(s) of the ore fluids.

This study has not determined the exact fluid-migration path,

but it has substantiated earlier suggestions. The high trace-metal content in the carbonate portion of the reef facies, the lack of high trace-metal contents in the carbonate portion of samples from the offshore and back-reef facies, and the concentration of low La/Sm ratios in the reef facies indicate that there was very little interaction with ore fluids outside of the reef facies. Previous workers (Doe and Delevaux, 1972; Ohle and Brown, 1954) have shown that the ore fluids originated outside of the Bonnetterre Formation, migrated updip in the Lamotte Sandstone, and then traveled through the channelways in the reef facies, depositing ore minerals where the porosity and source of sulfur were available.

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 APPENDIX A: DRILL-HOLE LOCATIONS
 

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## Northern Cross Section

Core Label	U.S.G.S. Label	Facies	Location
HM1	Hole # 1	Offshore	T34N R3W Sec26
8EE	Hole # 3	Reef	T34N R1W Sec6
1EE	Hole # 4	Back-reef	T34N R1W Sec4
10EE	Hole # 5	Back-reef	T34N R1W Sec3
12EE	Hole # 6	Back-reef	T34N R1W Sec2

## Southern Cross Section

Core Label	Facies	Location
1RS	Offshore	T31N R4W Sec30
LC12	Reef	T31N R2W Sec2
RE1	Back-reef	T31N R1E Sec2

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APPENDIX B: SAMPLE LOCATIONS AND INSOLUBLE RESIDUE DESCRIPTIONS

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HOST BONNETERRE FORMATION: Offshore Facies

1-940.- Limestone sample from drill hole HML, located T34N, R3W, Sec 36. USGS Composite sample covering interval 940-950 feet. Insoluble residue-quartz, clay minerals, opaques.

1-1010.- USGS Composite sample covering the interval 1000-1010 feet in drill hole HML. Insoluble residue-mostly clay minerals, some quartz.

1-1050.- USGS Composite sample covering the interval 1050-1060 feet in drill hole HML. Insoluble residue-mostly clay minerals, some quartz.

1-1170.- USGS Composite sample covering the interval 1170-1180 feet in drill hole HML. Insoluble residue-quartz, clay minerals, chlorite.

HML 945.- Sample from drill hole HML, about 95 feet below top of Bonnetterre Formation. Insoluble residue-quartz, clay minerals.

HML 1052.- Sample from drill hole HML, about 208 feet below top of Bonnetterre Formation. Insoluble residue-mostly clay minerals, minor quartz, trace of feldspar.

1RS 1198.- Sample from drill hole 1RS, T31N, R4W, Sec 30, about 38 feet below top of Bonnetterre Formation. Insoluble residue-mostly quartz, clay minerals.

1RS 1226.- Sample from drill hole 1RS, about 66 feet below top of Bonnetterre Formation. Insoluble residue-quartz and clay minerals.

1RS 1291.- Sample from drill hole 1RS, about 131 feet below top of Bonnetterre Formation. Insoluble residue-quartz, some clay minerals, minor glauconite.

1RS 1365.- Sample from drill hole 1RS, about 205 feet below top of Bonnetterre Formation. Insoluble residue-mostly clay minerals, minor quartz, glauconite.

1RS 1370.- Sample from drill hole 1RS, about 210 feet below top of Bonnetterre Formation. Insoluble residue-clay minerals, quartz, trace of pyrite, chlorite.

HOST BONNETTERRE FORMATION: Reef Facies:

3-580.- USGS Composite sample of dolostone from a weakly mineralized interval within the Viburnum Trend, drill hole 8EE, T34N, R1W, Sec 6, 570-580 feet. Insoluble residue-quartz, clay minerals.

3-610.- USGS Composite covering the interval 610-620 in drill hole 8EE. Insoluble residue-quartz, clay minerals, trace of sulfides.

3-660.- USGS Composite covering the interval 660-670 feet in drill hole 8EE. Insoluble residue-clay minerals, quartz, trace of sulfides.

3-700.- USGS Composite sample covering the interval 700-710 feet in drill hole 8EE. Insoluble residue-clay minerals, minor quartz.

3-750.- USGS Composite sample covering the interval 750-760 feet in drill hole 8EE. Insoluble residue-clay minerals.

3-790.- USGS Composite sample covering the interval 790-800 feet in drill hole 8EE. Insoluble residue-clay minerals, quartz, pyrite.

8EE 590.- Sample from drill hole 8EE, about 25 feet below top of Bonnetterre Formation. Insoluble residue-quartz, clay minerals.

8EE 758.- Sample from drill hole 8EE, about 193 feet below top of Bonnetterre Formation. Insoluble residue-mostly quartz, clay minerals.

8EE 793.- Sample from drill hole 8EE, about 228 feet below top of Bonnetterre Formation. Insoluble residue-quartz, clay minerals, trace of sulfides.

LC12 879.- Sample from drill hole LC12, about 17 feet below top of Bonnetterre Formation, located T31N, R2W, Sec 23. Insoluble residue-mostly clay minerals, quartz, trace of chalcopyrite.

LC12 915.- Sample from drill hole LC12, about 53 feet below top of Bonnetterre Formation. Insoluble residue-clay minerals, quartz, feldspar, pyrite.

LC12 988.- Sample from drill hole LC12, about 126 feet below top of Bonnetterre Formation. Insoluble residue-clay minerals.

LC12 1086.- Sample from drill hole LC12, about 224 feet below top of Bonnetterre Formation. Insoluble residue-quartz, clay minerals, trace of sulfides.

LC12 1128.- Sample from drill hole LC12, about 266 feet below top of Bonnetterre Formation. Insoluble residue-quartz, clay minerals.

LC12 1167.- Sample from drill hole LC12, about 305 feet below top of Bonnetterre Formation. Insoluble residue-mostly quartz.

HOST BONNETTERRE FORMATION: Back-reef Facies:

4-621.- USGS Composite sample from drill hole 1EE, T34N, R1W, Sec 4, 420-430 feet. Insoluble residue-mostly quartz, clay minerals.

4-640.- USGS Composite sample covering the interval 640-650 feet in drill hole 1EE. Insoluble residue-quartz, clay minerals.

4-740.- USGS Composite sample covering the interval 740-750 in drill hole 1EE. Insoluble residue-clay minerals, trace of chalcocopyrite.

4-810.- USGS Composite sample covering the interval 810-820 in drill hole 1EE. Insoluble residue-clay minerals.

4-850.- USGS Composite sample covering the interval 850-860 in drill hole 1EE. Insoluble residue-clay minerals.

5-348.- USGS Composite sample from drill hole 10EE, T34N, R1W, Sec 3, 348-360 feet. Insoluble residue-clay minerals.

5-420.- USGS Composite sample covering the interval 420-430 feet in drill hole 10EE. Insoluble residue-clay minerals.

5-486.- USGS Composite sample covering the interval 486-498 feet in drill hole 10EE. Insoluble residue-clay minerals, quartz.

6-420.- USGS Composite sample from drill hole 12EE, T34N, R1W, Sec 2, 420-432 feet. Insoluble residue-clay minerals, quartz, minor feldspar.

6-460.- USGS Composite sample covering the interval 460-470 in drill hole 12EE. Insoluble residue-clay minerals, quartz.

6-500.- USGS Composite sample covering the interval 500-510 feet in drill hole 12EE. Insoluble residue-clay minerals.

1EE 646.- Sample from drill hole 1EE, about 26 feet below top of Bonnetterre Formation. Insoluble residue-clay minerals.

LEE 745.- Sample from drill hole LEE, about 125 feet below top of Bonneterre Formation. Insoluble residue-clay minerals.

LEE 814.- Sample from drill hole LEE, about 194 feet below top of Bonneterre Formation. Insoluble residue-clay minerals, quartz.

REL 426.- Sample from drill hole RE, T31N, R1E, Sec 27, about 26 feet below top of Bonneterre Formation. Insoluble residue-quartz, clay minerals.

REL 473.- Sample from drill hole REL, about 73 feet below top of Bonneterre Formation. Insoluble residue-clay minerals.

REL 521.- Sample from drill hole REL, about 221 feet below top of Bonneterre Formation. Insoluble residue-clay minerals.

REL 676.- Sample from drill hole REL, about 276 feet below top of Bonneterre Formation. Insoluble residue-clay minerals.

REL 721.- Sample from drill hole REL, about 321 feet below top of Bonneterre Formation. Insoluble residue-clay minerals, minor quartz.

REL 898.- Sample from drill hole REL, about 498 feet below top of Bonneterre Formation. Insoluble residue-clay minerals.

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APPENDIX C: PETROGRAPHIC SUMMARIES

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HML 1052 Dolomitized Trilobite-Echinoderm Biomicrite I Ib:DLa

Thin section HML 1052 is a dolomitized fine-grained limestone. The carbonate matrix is composed of micrite and microspar. In increasing abundance the major constituents are: glauconite, pyrite, quartz; stromatolites, echinoderms, trilobites (allochems); dolomite, calcite (orthochems). The dolomite occurs in patches: in small rhombs (0.16 mm) within the stromatolites and as a replacement for the calcite in the echinoderm skeleton. A hash of randomly oriented trilobite and echinoderm fragments cuts into the horizontally laminated planar stromatolites.

HML 945 Trilobite-Echinoderm Biointramicrudite I Ib:Lr

Thin section HML 945 is an intraclastic, fossiliferous limestone with a carbonate matrix composed of micrite and microspar. In increasing abundance the major constituents are: quartz, pyrite; echinoderms, trilobites, intraclasts (allochems); calcite (orthochems). The intraclasts (1.95 mm) show no preferred orientation and in many places cut across fossil fragments. The smaller intraclasts are composed of micrite that is being selectively replaced by pyrite, whereas the larger intraclasts (greater than 2 mm) are composed of pellets.

IRS 1198 Silty Algal Biomicrite TzI Ib:La

Thin section IRS 1198 consists of horizontal laminations composed of fine-grained calcite (0.05 mm) and quartz (0.02 mm) grains. Horizontally oriented planar stromatolites occupy the bottom fourth of the thin section. Pyrite (0.01 mm) is randomly scattered throughout the matrix.

IRS 1226 Medium Crystalline Biogenic Dolomite Yb:D4

Thin section IRS 1226 is a medium crystalline (0.24 mm) dolomite containing 15 percent stromatolite fragments. Both quartz (0.01 mm) and pyrite (0.02 mm) are randomly scattered within the stromatolites.

IRS 1291 Dolomitized Trilobite-Echinoderm Intrabiomicrite  
Iib:DLa

Thin section IRS 1291 is a dolomitized intraclastic fossiliferous limestone. The intraclasts (3.25 mm) are composed of micrite that has been partly replaced by dolomite (0.09 mm). Micrite, microspar and sparry calcite constitute the carbonate matrix. The sparry calcite forms a geopetal structure beneath some intraclasts and trilobite fragments. Quartz and pyrite are scattered within the stromatolites. A hash of trilobite and echinoderm fragments are within the carbonate matrix.

IRS 1365 Trilobite-Echinoderm Algal Biomicrite Iib:La

Thin section IRS 1365 consists of a micritic carbonate matrix containing stromatolites and a hash of trilobite and echinoderm fragments. In increasing abundance the major constituents are: pyrite, glauconite; intraclasts, echinoderms, trilobites, stromatolites (allochems); dolomite, calcite (orthochems). The planar stromatolites are horizontally oriented and contain (0.04 mm) dolomite rhombs. The skeletal debris lacks orientation and forms a fossiliferous hash within the matrix.

IRS 1370 Trilobite-Echinoderm Intrabiomicrite Iib:La

Thin section IRS 1370 is an intraclastic, fossiliferous limestone. The intraclasts (4.2 mm) are composed of micrite and algal laminations. The smaller intraclasts (less than 1 mm) contain small dolomite rhombs (0.08 mm). The carbonate matrix consists of micrite, microspar and sparry calcite. Sparry calcite occurs as a geopetal structure on the bottom of the intraclasts and trilobite fragments. Fractures filled with sparry calcite cut into and across some of the intraclasts. A few stromatolitic laminations are also present.

IRS 1470 Medium Sandstone Supermature Quartz Arenite

Thin section IRS 1470 consists of well-rounded medium-grained (0.43 mm) quartz grains. The quartz grains contain vacuoles and are in grain-to-grain contact. Approximately 15 percent of the grains have quartz overgrowths. Clay encloses some quartz grains.

8EE 590 Medium Crystalline Biogenic Dolomite Vb:D4

Thin section 8EE 590 is a medium-grained (0.11 mm) dolomite, containing approximately 9 percent stromatolites. The stromatolites are randomly oriented throughout the dolomite.

Quartz (0.01 mm) and pyrite (0.015 mm) are concentrated within the stromatolites.

8EE 758 Coarsely Crystalline Dolomite V:D5

Thin section 8EE 758 is composed of coarse-grained (0.48 mm) dolomite. Approximately 15 percent of the thin section contains randomly scattered patches of very coarse-grained dolomite (1.18 mm). Minor pyrite (0.02 mm) is scattered throughout the dolomite.

8EE 793 Coarsely Crystalline Dolomite V:D5

Thin section 8EE 793 is composed of 84 percent coarsely crystalline (0.40 mm) dolomite and 16 percent pyrite. The pyrite is disseminated throughout the dolomite, in veins, and as a coating around the dolomite rhombs. In some instances the pyrite is replacing the dolomite.

LC12 879 Dolomitized Algal Biomicrudite IIB:DLR

Thin section LC12 879 has a micritic carbonate matrix containing a hash of trilobite and echinoderm fragments. In increasing abundance the major constituents are: chlorite, pyrite, trilobites, echinoderms, stromatolites (allochems); dolomite, calcite (orthochems). The planar stromatolites are horizontally laminated and are located throughout all of the thin section. All dolomite rhombs (0.21 mm), quartz and chlorite are concentrated within the stromatolites. Pyrite (0.025 mm) is also located within the stromatolites and in small patches scattered throughout the micrite.

LC12 915 Medium Crystalline Biogenic Dolomite Vb:D4

Thin section LC12 915 is composed of medium-grained (0.15 mm) dolomite and horizontally laminated planar stromatolites. Dolomite rhombs (0.07 mm) and pyrite (0.02 mm) are scattered within the stromatolites.

LC12 988 Coarsely Crystalline Dolomite V:D5

Thin section LC12 988 is composed of coarse-grained (0.34 mm) dolomite. A horizontally oriented 0.18 mm wide vein of pyrite cuts across the dolomite. Euhedral rhombs of dolomite (0.12 mm) are scattered within the pyrite vein.

LC12 1086 Medium Crystalline Dolomite V:D4

Thin section LC12 1086 is a medium-grained (0.19 mm) dolomite containing 5 percent stromatolite fragments. The stromatolites are randomly oriented within the dolomite. Pyrite (0.02 mm) is located within both the stromatolites and the dolomite.

LC12 1128 Medium Crystalline Intraclastic Dolomite Vi:D4

Thin section LC12 1128 is composed of randomly oriented dolomitic intraclasts (1.26 mm) cemented by medium-grained (0.22 mm) dolomite. Pyrite (0.03 mm) and chlorite (0.05 mm) are concentrated within the intraclasts.

LC12 1167 Medium Sandstone Dolomitized Supermature Glauconite bearing Quartz Arenite

Thin section LC12 1167 is a dolomitized supermature quartz arenite. In increasing abundance the major constituents are: dolomite (orthochems); glauconite, pyrite, and terrigenous quartz. The quartz grains contain vacuoles, are well rounded and cemented with euhedral dolomite (0.08 mm). Dolomitization occurred after deposition of the sandstone. Pyrite (0.02 mm) and glauconite (0.03 mm) are randomly scattered throughout the dolomite.

LC12 1186 Medium Sandstone Supermature Quartz Arenite

Thin section LC12 1186 consists of well-rounded medium-grained (0.28 mm) quartz grains. The quartz grains contain vacuoles and are in grain-to-grain contact. Approximately 10 percent of the grains contain quartz overgrowths. A trace amount of clay encloses some quartz grains.

LEE 646 Dolomitized Biopelsparite Ibp:DLA

Thin section LEE 646 is a mixture of fine-grained calcite (0.07) and dolomite (0.10). Echinoderms and small pellets (0.11 mm) (originally ooids?) are randomly scattered within this carbonate matrix.

LEE 745 Coarsely Crystalline Dolomite V:D5

Thin section LEE 745 is a coarse-grained (0.77 mm) dolomite. Minor pyrite (0.02 mm) is disseminated throughout the dolomite.

LEE 814 Medium Crystalline Pyritic Dolomite V:D4

Thin section LEE 814 is a medium-grained (0.12 mm) dolomite. Pyrite (0.03 mm) is randomly scattered throughout the dolomite.

REL 426 Medium Crystalline Dolomite V:D4

Thin section REL 426 is composed entirely of medium-grained (0.07 mm) dolomite.

REL 473 Medium Crystalline Biogenic Dolomite Vb:D4

Thin section REL 473 is a medium grained (0.32 mm) dolomite, containing 8 percent stromatolite fragments. The stromatolites contain (0.12 mm) dolomite rhombs.

REL 621 Medium Crystalline Biogenic Dolomite Vb:D4

Thin section REL 621 is composed of medium-grained (0.08 mm) dolomite and echinoderm fragments. Dolomite has begun to replace the echinoderms but most of the fragments are still composed of calcite. Many echinoderm fragments contain calcite overgrowths.

REL 676 Coarsely Crystalline Dolomite V:D5

Thin section REL 676 is composed entirely of coarse-grained (1.26 mm) dolomite.

REL 721 Dolomitized Sparite I:D4a

Thin section REL 721 is composed of 72 percent dolomite (0.02 mm) and 22 percent calcite (0.03 mm). Minor quartz (0.03 mm) is scattered throughout the matrix.

REL 898 Coarsely Crystalline Dolomite V:D5

Thin section REL 898 is composed of 87 percent coarse-grained (0.96 mm) dolomite and 13 percent medium grained (0.22 mm) dolomite. The smaller dolomite rhombs are scattered within the matrix of coarse-grained dolomite.

REL 973 Medium Sandstone Supermature Quartz Arenite

Thin section REL 973 consists of well-rounded medium-grained (0.29 mm) quartz grains. The quartz grains contain vacuoles and are in grain-to-grain contact. Approximately 14 percent of the grains have quartz overgrowths. Clay encloses some quartz grains.

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#### APPENDIX D: NEUTRON ACTIVATION ANALYSIS

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Approximately 0.3-0.7g ( $\pm 0.0002$ g) of powered sample was weighed on an analytical balance and transferred to clean plastic vials. The vials were sealed with a soldering iron in order to prevent reactor water from leaking into the vial during the irradiation. An iron wire was wound around the plastic vial to serve as a monitor of the neutron flux.

Sets of seven samples and a standard (SO3) were irradiated for four hours in a Triga Mark II experimental reactor with a flux of  $10^{13}$  neutrons/cm<sup>2</sup>/sec. Four to five days after irradiation the vials were rinsed with distilled-deionized water and the iron wires cut off and taped in the center of index cards.

Samples and standards were radioassayed for gamma radiation using a 25cm<sup>3</sup> Ge(Li) detector and a Canberra 8180 multichannel analyzer with a 4096 channel memory. The gamma ray given off by the decaying radionuclide has a specific energy and wavelength. The detector is calibrated such that each of the 4096 channels is assigned to a specific gamma ray energy. Proper calibration is achieved using an Eu standard so that 122, 344, and 1408 Kev correspond to 261, 736, and 3004 channels, respectively. The detector counts the number of gamma rays at each channel, thus

creating a spectrum of 4096 numbers. The spectrum of each sample is then transferred to a magnetic tape for computer processing.

The output of the computer program yields the area under each peak and its associated error. The cards printed from the "peak seek" program are then rearranged and run with the concentration program. Elemental values for each sample are listed in ppm.

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#### APPENDIX E: DIRECT-CURRENT PLASMA ANALYSIS

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The concentrations of Ca, Mg, Sr, Cr, K, Pb, Fe, Zn, and Mn in the HCl-soluble portion of the samples were determined by direct-current argon plasma (DCP). Apparatus for the DCP consists of three electrodes (one tungsten cathode and two graphite anodes) that are surrounded by argon gas. Ignition of the Plasma occurs spontaneously as the electrodes are withdrawn after being brought in contact by argon-actuated pistons. The argon gas creates an inert atmosphere, thus reducing the probability of metal-oxide formation. The liquid sample is aspirated through a glass tube and brought in contact with the plasma. Temperatures greater than 6000° C vaporize and excite the sample to the point of light emission. The emission spectrum that is generated is focused onto a spectrophotometer's entrance slit, where the spectrum is dispersed into its component parts. Twenty photomultiplier tubes record the light emission given off by the sample. Since each element gives off energy at a particular wavelength, the use of twenty photomultiplier tubes allows for the detection of twenty elements simultaneously.

The quantity of each element present in the sample is determined by a comparison between a set of known standards and

the samples. A Li buffer was added both to the sample and standard in order to reduce matrix effects and to suppress ionization. The 100 ml stock solution was run directly for all elements except Ca, Mg, and Fe. These three elements required further dilution to 10,000 ml in order to read within the range of the equipment. The ppm value of each element in the sample is printed out by computer within minutes of the sample run.

DISTRIBUTIONS OF RARE EARTH ELEMENTS AND OTHER TRACE  
ELEMENTS WITHIN UNMINERALIZED PORTIONS OF THE  
BONNETERRE FORMATION, SOUTHEAST MISSOURI

by

Lorraine J. Alcott

B.S. Grand Valley State Colleges, 1981

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AN ABSTRACT OF A MASTER'S THESIS

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requirements for the degree

MASTER OF SCIENCE

Department of Geology

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## ABSTRACT

A total of 45 drill core and three-meter composite samples from all three facies of the Bonneterre Formation were analyzed for their REE and trace-element contents. Instrumental neutron activation analysis and direct-current plasma analysis were used to test the whole rocks, insoluble residues, and carbonate portions. The whole-rock samples from the offshore facies contain the maximum mean values of insoluble residue, Sc, Th, Rb, K, and Ba; the reef facies samples contain the maximum mean values of Fe and Co; and the back-reef facies samples contain the maximum mean value of Na. The maximum mean values of Sc, Th, Rb, K, and Ba in the offshore facies are the direct result of the strong correlations between the clay-rich insoluble residue and these elements (significant to the 99 percent confidence level).

Thin-section descriptions of core samples have shown the lithology of the Bonneterre Formation consists of limestone in the offshore facies, and dolostone in the reef and back-reef facies. High mean values of Ca and Sr in the carbonate portion of samples from the offshore facies also support this conclusion. The high mean values of Fe, Mn, and Pb in the carbonate portion of rocks from the reef facies are good indicators of trace mineralization.

Instrumental neutron activation analysis yielded an average La/Sm ratio of 5.68, an average Sm/Yb ratio of 2.01, and an

average Sm/Lu ratio of 11.23. All samples have negative Eu anomalies with an average Eu/Sm ratio of 0.15. The shape of the REE patterns, as indicated by the REE ratios, is not related to lithology or to facies; limestone and dolostone samples and samples from each of the facies all show the same ranges of REE ratios. The total REE content of the samples correlates positively with the amount of insoluble residue, but there are no correlations between the REE ratios and the amount of insoluble residue.

Previous work in and around the ore zones has indicated that the mineralization process produced carbonate rocks and minerals with La/Sm ratios much lower than those of unmineralized rocks and suggested that the ore fluids were significantly depleted in LREE. Only seven of the samples in this study exhibit a moderate degree of LREE depletion (La/Sm ratios between 2.95 and 4.04 relative to the mean La/Sm ratio of 5.68). The majority of samples with low La/Sm ratios occur in the reef facies where the Fe, Mn, and Pb contents also are at a maximum. The concentration both of low La/Sm ratios and of high trace-metal contents in the reef facies suggests that the reef was the main solution pathway for the ore fluids. These data are consistent with other authors' interpretations that the ore fluids originated outside of the Bonnetterre Formation, traveled through the Lamotte Sandstone, and migrated updip into the reef facies of the Bonnetterre Formation (Doe and Delevaux, 1972; Ohle and Brown, 1954).