

RARE EARTH ELEMENT AND Nd ISOTOPIC VARIATIONS IN REGIONALLY EXTENSIVE DOLOMITES FROM THE BURLINGTON-KEOKUK FORMATION (MISSISSIPPIAN): IMPLICATIONS FOR REE MOBILITY DURING CARBONATE DIAGENESIS¹

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ABSTRACT: Marine carbonates of the Burlington-Keokuk Fm. (Miss.) of the midcontinent region have been subject to two major episodes of regionally extensive (100,000 km²) dolomitization. Previous studies of the cathodoluminescent petrography, Sr, C, and O isotopic compositions, and Sr, Fe, Mn, and Ca concentrations of Burlington-Keokuk dolostones outline a diagenetic history in which lime mud was pervasively dolomitized by a seawater-dominated fluid. At many localities, this early dolomite generation (dolomite I) was recrystallized by nonmarine diagenetic fluids at shallow-burial depths to produce dolomite II.

Dolomites I and II have similar rare earth element (REE) patterns and abundances and a narrow range of initial ¹⁴³Nd/¹⁴⁴Nd isotope ratios of 0.511906 ± 0.000025 (1 σ). This consistency in the Nd isotope ratios and REE patterns, along with the presence of anomalously low abundances of cerium in the dolomites, cherts, glauconite pellets, fish apatite, and crinoids, suggests that 1) seawater-derived REE dominated the system, and 2) the extensive water-rock interaction that produced profound textural and compositional changes during the formation of dolomite II did not significantly alter the REE patterns or Nd isotopic signatures of the dolomites. The results of quantitative modeling of isotopic and trace element exchange during water-rock interaction in carbonate systems indicate that extremely large water : rock ratios are required to alter the REE signatures of diagenetic carbonates. Such large water : rock ratios can reflect either 1) large extents of fluid flow during carbonate recrystallization, or 2) minimal interaction between diagenetic fluids and host rocks during carbonate cement crystallization. Late vug-filling calcite and dolomite have low Sm/Nd and high (Ce/Nd)_n ratios relative to the dolostones. Such distinct REE signatures probably reflect limited interaction between late diagenetic fluids and Burlington-Keokuk host rocks.

Penecontemporaneous clastic sediments have similar initial ¹⁴³Nd/¹⁴⁴Nd isotope ratios (0.511857–0.511877) and lower Sm/Nd ratios compared to the dolomites, suggesting 1) a common crustal source of REE for the clastics and carbonates, and 2) REE fractionation during the formation of carbonate, apatite, glauconite, and other authigenic phases in the marine environment.

INTRODUCTION

Geochemical studies of sedimentary carbonates have used variations in the abundances of trace elements such as strontium, iron, manganese, magnesium, and sodium, and the isotopic compositions of oxygen, carbon, and strontium to gain insight into the multivariate processes of diagenesis as well as the chemistry of ancient oceans. Although not as widely applied, the rare earth elements (REE), a coherent group of mainly trivalent elements that include the Sm-Nd isotopic system, have several important applications to understanding the origin and diagenetic history of ancient carbonates.

Carbonate and apatite in living marine organisms have low abundances of the REE, on the order of parts per billion, whereas similar carbonate and apatite in seafloor sediments have much higher abundances on the order of 1–2,000 parts per million (Bernat 1975; Shaw and Wasserburg 1985; Palmer 1985; Elderfield and Pagett 1986). The enrichment of REE in sea-floor sediments apparently occurs during the interaction of sediment with pore and/or bottom waters near the sediment-water interface (Shaw and Wasserburg 1985; Palmer 1985; Palmer and Elderfield 1986). Modern authigenic marine sediments, when compared to clastic sediments such as shales and greywackes (Taylor and McLennan 1981; Bhatia 1985), commonly have distinct REE signatures. These include light

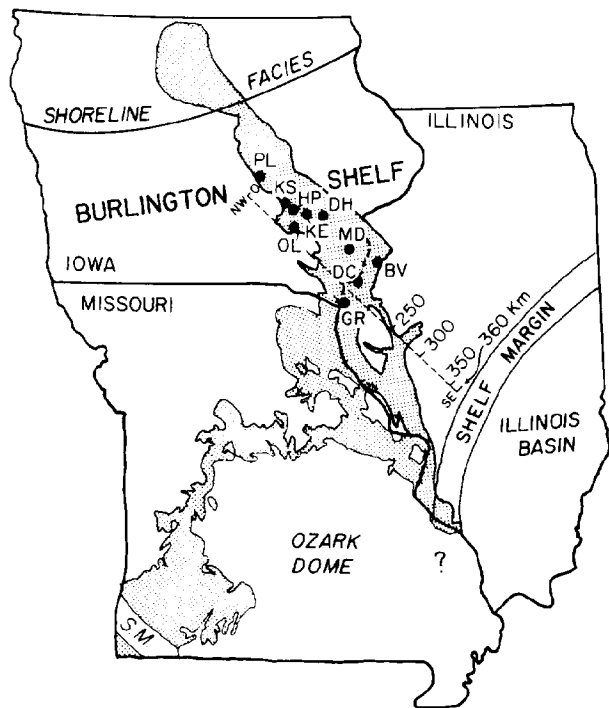
REE (LREE) depletion and, most significantly, anomalously low or high abundances of cerium (negative or positive Ce anomaly). Ce anomalies in seawater and authigenic marine sediments are indicative of the presence of the relatively insoluble Ce⁴⁺ in oxidizing marine environments (Goldberg et al. 1963; Piper 1974; Shimizu and Masuda 1977; deBaar et al. 1985). REE in selected ancient carbonates may therefore provide a trace element and isotopic record of contemporaneous marine water chemistry, and it may be possible to identify marine versus nonmarine sources of REE in ancient carbonates.

Owing to the short oceanic residence time of the REE relative to the mixing time of the world's oceans (Elderfield and Greaves 1982) the ¹⁴³Nd/¹⁴⁴Nd ratios of seawater and modern authigenic marine sediments preserve differences in the Nd isotopic composition of the provenances of the REE between and within different ocean basins (e.g., Piepgras et al. 1979; Piepgras and Wasserburg 1980, 1982, 1985, 1987; Goldstein and O'Nions 1981; Frost et al. 1986; Palmer and Elderfield 1985; Stordal and Wasserburg 1986). Nd isotope studies of ancient marine authigenic sediments may be used to establish variations in seawater ¹⁴³Nd/¹⁴⁴Nd through time, which in turn can be used for paleotectonic reconstructions of the Earth's exposed crust as a function of time (Shaw and Wasserburg 1985). The presence or absence of Ce anomalies in ancient marine authigenic sediments has the potential for establishing paleoredox variations in ancient oceans (Wright et al. 1984).

The REE are greatly enriched in diagenetic carbonates (ppm) relative to natural fluids such as seawater, river water, and groundwater (10⁻⁶ to 10⁻³ ppm; Piepgras and Wasserburg 1980; Hoyle et al. 1984; Banner and Was-

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serburg 1987; Goldstein and Jacobsen 1987), and estimated calcite-fluid exchange K_D s for the REE (e.g., $K_D(Nd/Ca)$) are large, on the order of 100 (Palmer 1985). The results of quantitative modeling of O, Sr, C, and Nd isotopic and trace element variations during water-rock interaction are presented here in order to illustrate important differences in the *relative* water : rock ratios required to change each isotopic parameter in diagenetic carbonates. Relative to other isotopic and trace element systems, extremely large water : rock ratios are needed in order to impose the REE and Nd isotopic signature of diagenetic fluids on carbonate sediments. The REE abundances and Nd isotopic compositions of carbonates, when used in conjunction with other geochemical and petrographic data, may help constrain physical and chemical parameters of diagenetic systems such as the extent of water-rock interaction, fluid composition, and fluid source.

Relatively little is known about the behavior of the REE during the lithification and diagenesis of ancient carbonate sediments. The purpose of this study is to examine the distribution of REE and Nd isotopes among regionally extensive, thick-bedded dolomites from the Mississippian subtidal-shelf carbonates of the Burlington and Keokuk Fm. These finely grained, replacive dolomites offer an opportunity to examine REE behavior during carbonate diagenesis because they occur in two separate major episodes that exhibit distinct textures and compositions on a regional and temporal scale. Dolomite cathodoluminescence, trace element abundances, and O and Sr isotope geochemistry indicate markedly different sources of diagenetic fluid constituents for the two major dolomite generations (Banner 1986; Banner et al. 1988b).

In this study, we present Nd isotopic compositions and REE analyses by isotope dilution for the major dolomite generations from the Burlington and Keokuk Fms. Analyses of glauconite, chert, biogenic apatite, pyrite, calcite, and clastics from these and associated formations were also performed in order to determine the distribution of the REE among the dolomite and nondolomite phases in a sample. This information is essential for determining both the optimum sample preparation method and the extent to which noncarbonate phases control the REE geochemistry of the dolomite phase. The results are interpreted in a diagenetic framework developed from geologic, petrologic, and geochemical data and from quantitative geochemical models for water-rock interaction.

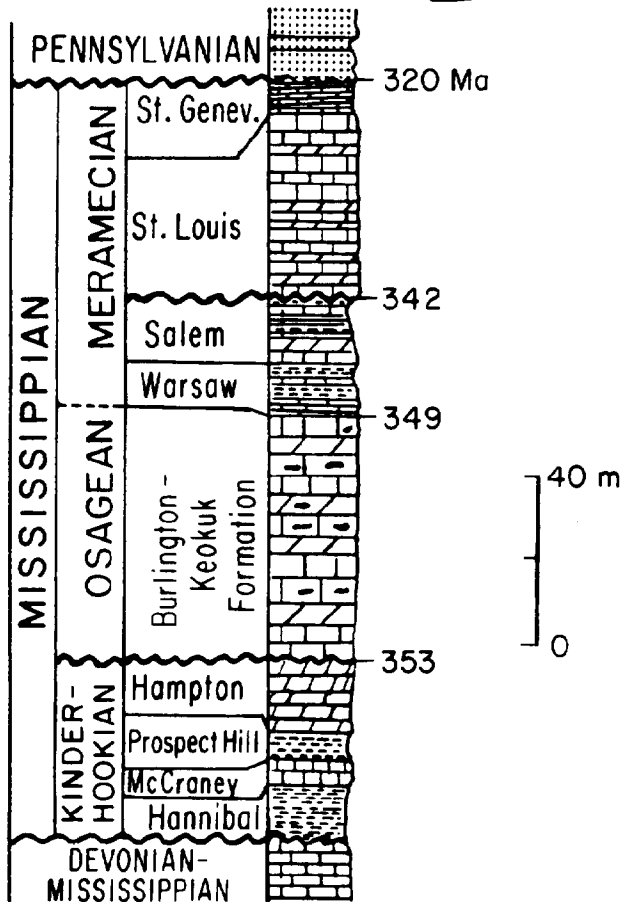


FIG. 1.—Paleogeographic sketch map showing dolostone sample localities in Iowa and western Illinois. Stippled pattern represents outcrop pattern of Mississippian rocks. Paleogeography after Lane and DeKeyser

PETROGRAPHY AND GEOCHEMISTRY OF BURLINGTON-KEOKUK DOLOMITES

The Burlington and Keokuk Formations crop out in Iowa, Illinois, and Missouri as part of the Osage Series

(1980). Inferred shoreline facies after Sixt (1984). Generalized stratigraphic column of Mississippian strata in southeast Iowa and western Illinois after Harris (1982). The Warsaw Fm. represents the westward equivalent of the Borden Fm. of Illinois and Indiana (Lineback 1981). Stratigraphic time scale is after Harland et al. (1982). Samples were analyzed from the following quarries: BV = Biggsville; DC = Dallas City; DH = Don Hays; G = Gray's; HP = Harper; KE = Keota; KS = Keswick; MD = Mediapolis; OL = Ollie; PL = Puls Malcolm.

of the Mississippian system (Fig. 1). These two formations have had similar depositional and diagenetic histories. In Missouri, the formational boundaries are not defined, so these two units will be collectively referred to as the Burlington-Keokuk Fm. The Burlington-Keokuk Fm. was deposited on a broad, shallow, subtidal carbonate shelf on the southeast flank of the Transcontinental Arch and west of the Illinois Basin. The regional distribution of the Borden and Warsaw Fms. indicates that clastic sedimentation was predominantly to the east and increased toward the end of Osagean time and into the Meramecan (Lineback 1981). Stratigraphic reconstructions indicate that the Burlington-Keokuk Fm. was subject to maximum burial depths of less than 500 m in the study area (Cox, unpubl. data). Burlington-Keokuk strata are comprised of medium to thickly bedded, coarse-grained, crinoidal packstones and grainstones interbedded with pervasively dolomitized lime mud in skeletal wackestones and mudstones. Chert lenses and nodules are abundant, especially in the dolomitic portions. Glauconitic and thin, shaly horizons are common. Minor sparry calcite, saddle dolomite, sphalerite, pyrite, and megaquartz are found in solution vugs and fractures.

A detailed diagenetic history for the Burlington-Keokuk Fm. includes five episodes of dolomitization, two major generations of calcite cementation (early nonferroan and late ferroan), dedolomitization, chertification, and mechanical and chemical compaction. A paragenetic sequence can be correlated over an area of approximately 100,000 km² in Iowa, Illinois, and Missouri using dolomite and calcite zonal stratigraphies based on cathodoluminescent petrography (Harris 1982; Kaufman et al. 1988). Rhombohedral dolomite replaced nearly all lime mud in mudstone through grain-dominated lithologies (Fig. 2a), while skeletal grains are largely undolomitized. Less commonly, dolomite occurs as a cement. Massive dolomites, or dolostones, consist of 50–125-micron rhombs of dolomite with variable proportions of other phases. These include pelletoidal glauconite and more finely dispersed clays, iron oxide coatings on dolomite rhombs, disseminated pyrite, marcasite and pyrrhotite, calcitic fossils (crinoids, brachiopods, bryozoans, corals), chert and quartz cements, siliceous sponge spicules and phosphatic ichthyolith teeth, and fin spines. Rhombs contain variable amounts of one- and two-phase fluid inclusions (Smith 1984) and mineral inclusions. The most common accessory phases in the dolostones are pyrite, calcite, chert, and glauconite.

Two major and three minor dolomite generations can be identified by their cathodoluminescent characteristics (Fig. 2b, c). Dolomite I, the earliest and most ubiquitous dolomite, consists of orange to brown, concentrically zoned rhombs. Dolomite II occurs as a dull red replacement of dolomite I and is more stoichiometric (51–52.5 mole % CaCO₃) than dolomite I (54.5–56.5 mole % CaCO₃; Prosky and Meyers 1985; Prosky et al. 1986). Dolomite II' is less common and occurs as a very dull red to chocolate brown replacement of dolomites I and II. The truncation of the fine-scale growth banding in dolomite I by dull red patches of dolomite II demon-

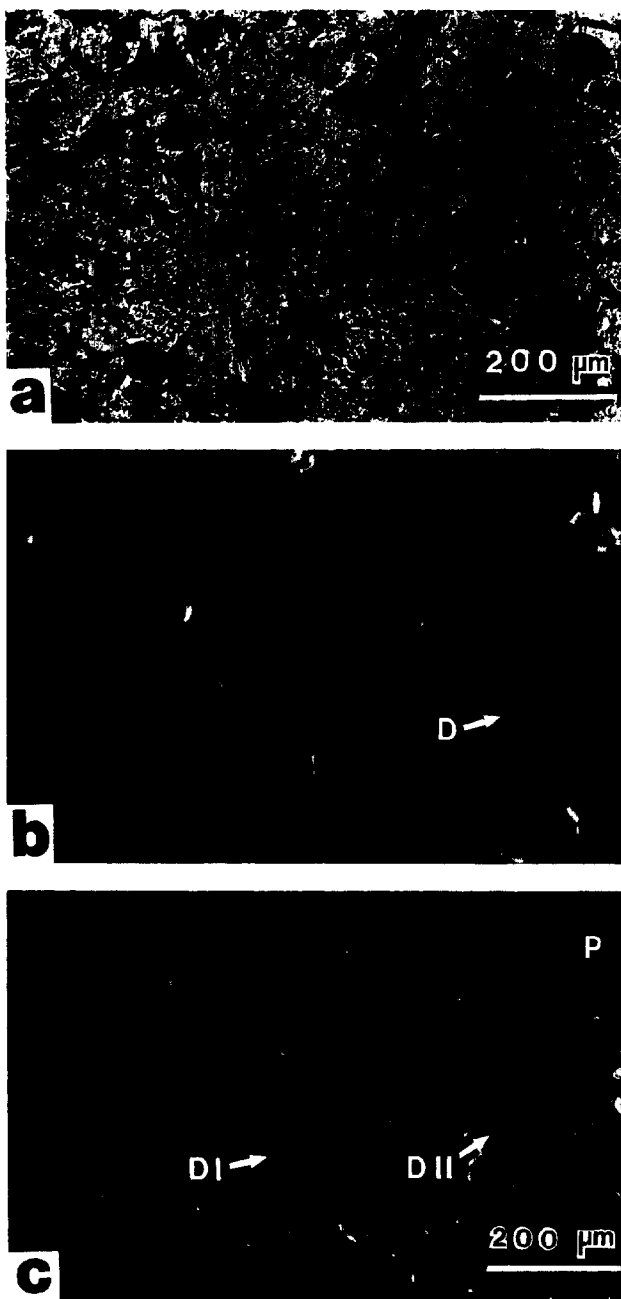


FIG. 2.—Major cathodoluminescent generations of Burlington-Keokuk dolomites. a) Dolomite I sample in plane-polarized light; euhedral to subhedral rhombs. Some larger rhombs have inclusion-rich cores. Finely crystalline iron oxides (goethite) coat many rhombs. Dark circles are bubbles in epoxy. Sample DH-8. b) Same field of view as in (a) under cathodoluminescence. Concentric zonation, fine-scale light and dark growth bands and yellow to light brown luminescence characterize dolomite I. Dissolution of dolomite shown at D. Zonal patterns for dolomite I samples are correlative within a hand sample. c) Dolomite II sample under cathodoluminescence. Dull red luminescence (DII) illustrates preferential replacement of the interiors of precursor dolomite I rhombs, leaving bright yellow rims. Different stages of recrystallization can be observed from unreplaced dolomite I rhomb (DI) to pervasive replacement. P = porosity. Sample KS-6.

TABLE 1.—Ranges of isotopic and trace element data for Burlington-Keokuk dolomites and estimated marine dolomite (EMD)

	EMD	Dolomite I	Dolomite II, II'	Vug Dolomite, Calcite
$\delta^{18}\text{O}$ (‰, PDB)	1.8–2.8	–2.2 to 2.5	–6.6 to –0.2	–11.3 to –5.0
$\delta^{13}\text{C}$ (‰, PDB)	4.0–4.6	–0.9 to 4.0	–1.0 to 4.1	–2.1 to 1.8
($^{87}\text{Sr}/^{86}\text{Sr}$) _i	0.7076	0.70757–0.70808	0.70885–0.70942	0.70987–0.71024
Sr, ppm	>150	104–123	50–63	87–91
Fe, ppm (mean)	40	1,500	3,500	—
Mn, ppm (mean)	20	1,000	1,200	—
mole % CaCO_3	—	54.5–56.5	51–52.5	—

Data and estimates from Banner et al. (1988a, b) and Prosky (pers. comm.). Initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios calculated for the estimated time of diagenesis (342 Ma).

strates the replacement relationship (Banner et al. 1988a). Dolomite III is a younger, nonluminescent cement and replacement (Harris 1982) and is volumetrically minor. Iron concentrations increase through the sequence dolomite I-II-II'-III (Prosky and Meyers 1985). Saddle dolomite is also nonluminescent and fills solution vugs which postdate all other dolomites in the field area. In measured sections that have both dolomites I and II, there is a transition from dolomite II-dominated strata at the bottom to domination by dolomite I higher in the section.

Cathodoluminescence is used to 1) establish the regional and stratigraphic distribution of the different dolomite generations, 2) document deflection geometries and truncation of calcite cement zones around dolomite rhombs, and 3) compare the Burlington-Keokuk calcite zonal stratigraphy with cement sequences in overlying strata that postdate regional unconformities (Harris 1982; Kaufman et al. 1988; Cander et al. 1988; Prosky, unpubl. data). These studies have constrained the following age ranges for the Burlington-Keokuk dolomites: 1) dolomite I: post-Osagean to pre-Pennsylvanian (349–320 Ma), and 2) dolomite II, II': post-dolomite I to pre-Pennsylvanian

or pre-Permian. For the purposes of calculating initial Nd isotopic compositions, an age corresponding to the pre-St. Louis unconformity is used in the analytical section, and the effect of the age uncertainty on these values is discussed.

The major generations of dolomite have significantly different Sr and O isotopic compositions and Sr, Fe, and Ca concentrations (Table 1). Dolomite I samples have isotopic compositions that lie on or near estimated marine dolomite compositions for Osagean time. Compared to dolomite I, dolomites II and II' have significantly higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Fe concentrations, similar $\delta^{13}\text{C}$ values and Mn concentrations and lower $\delta^{18}\text{O}$ values and Sr and Ca concentrations. The late stage vug carbonates have higher $^{87}\text{Sr}/^{86}\text{Sr}$ and lower $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values compared to the two major dolomite generations. The petrography of the dolomites and quantitative modeling of their isotope and trace element geochemistry provide evidence that the two major dolomite generations formed in distinctly different diagenetic environments. A predominantly marine source of diagenetic constituents is indicated for dolomite I, while dolomites II and II' appear to

TABLE 2.—REE abundances (ppm) and Nd isotopic compositions for results of comparative dissolution experiments and mineral separate analysis for Burlington-Keokuk dolostones

	BV-6.8-JGR				BV-6.8-JGF		HP-4GR	
	1	2	3	4	5	6	7	8
Ce	52.3	49.6	20.2	7.75	1,280	9.53	37.2	35.8
Nd	55.9	56.2	20.0	8.80	1,450	8.62	39.2	39.4
Sm	13.0	13.5	4.93	2.25	362	1.87	9.47	9.48
Eu	3.04	3.02	1.10	0.491	74.9	0.449	2.13	2.14
Gd	12.5	12.6	4.40	2.15	345	1.88	10.01	8.98
Dy	8.86	8.87	3.59	1.37	224	1.51	6.19	5.99
Er	3.67	3.50	1.71	0.502	86.4	0.751	2.46	2.41
Yb	2.16	2.01	1.28	0.246	38.3	0.514	1.32	1.25
(Ce/Nd) _n	0.687	0.648	0.742	0.646	0.651	0.812	0.697	0.668
Eu/Eu*	0.724	0.702	0.713	0.680	0.646	0.732	0.671	0.705
$^{147}\text{Sm}/^{144}\text{Nd}$	0.1406	0.1452	0.1490	0.1546	0.1512	0.1311	0.1460	0.1456
$^{143}\text{Nd}/^{144}\text{Nd}$	—	—	0.512230	0.512243	—	0.512252	—	—
2σ	—	—	± 0.000031	± 0.000015	—	± 0.000014	—	—
$\epsilon_{\text{Nd}}(342)$	—	—	–5.9	–5.9	—	–4.7	—	—
T_{CHUR} (Ga)	—	—	0.87	0.87	—	0.76	—	—

(Ce/Nd)_n, Eu/Eu*, $^{147}\text{Sm}/^{144}\text{Nd}$, ϵ_{Nd} , and T_{CHUR} are defined in text. 2σ errors for $^{143}\text{Nd}/^{144}\text{Nd}$ ratios are based on within-run statistics. Detailed petrographic descriptions, localities, and stratigraphic positions for samples in Tables 2–4 are given in Banner (1986) and are available from the authors. Analysis numbers are as follows:

1 through 5: BV-6.8-JGR (Glauconite-apatite-rich layer) — 1) whole rock flux-fusion; 2) whole-rock leach; 3) dolomite separate; 4) glauconite separate; 5) apatite separate.

6: BV-6.8-JGF (Glauconite-apatite-poor layer) — dolomite separate (whole-rock leach analysis given in Table 3, analysis 19).

7 through 11: HP-4GR (Glauconite-apatite-rich layer) — 7) whole-rock flux-fusion; 8) whole-rock leach; 9) dolomite separate; 10) 1–15 μ fraction of dolomite separate; 11) glauconite separate.

preserve a record of the extensive recrystallization of dolomite I by extraformational subsurface fluids at shallow-burial depths (Banner 1986; Banner et al. 1988b).

ANALYTICAL METHODS

In order to evaluate the utility of weak HCl as a leaching agent for dolostones, complete and partial dissolutions were carried out on samples with a range of nondolomite constituents. All whole-rock and mineral separate samples were ground to less than 200 mesh. Samples undergoing partial dissolution, designed to selectively decompose only dolomite, were leached in 30 mL of 1.25 N HCl or HNO₃. For complete dissolution, sample powders were fused with 800 mg of purified LiBO₂ flux in graphite crucibles at 1,050–1,100°C and then dissolved in 30 mL 1 N HNO₃. Enriched REE spikes were added to the acid prior to the addition of the sample. After each of the dissolution procedures, the dissolved sample was filtered and then processed through cation exchange columns.

Mineral separates were prepared using heavy liquids, a Franz magnetic separator, sieving, and hand picking. In an effort to further purify some dolomite separates of small inclusions and coatings on rhombs, separates were ultrasonically disaggregated and separated in a settling column to obtain the 1–15- μ fraction. REE abundances were determined on the whole-rock fusions and leaches, and REE abundances and Nd isotope ratios were determined on mineral separates. The results are given in Table 2 and Figures 3 and 5.

A suite of whole-rock dolostones was selected which was comprised of nearly pure dolomite of more than 90 percent of one cathodoluminescent type, and which contained only minor amounts of other phases. HCl insoluble

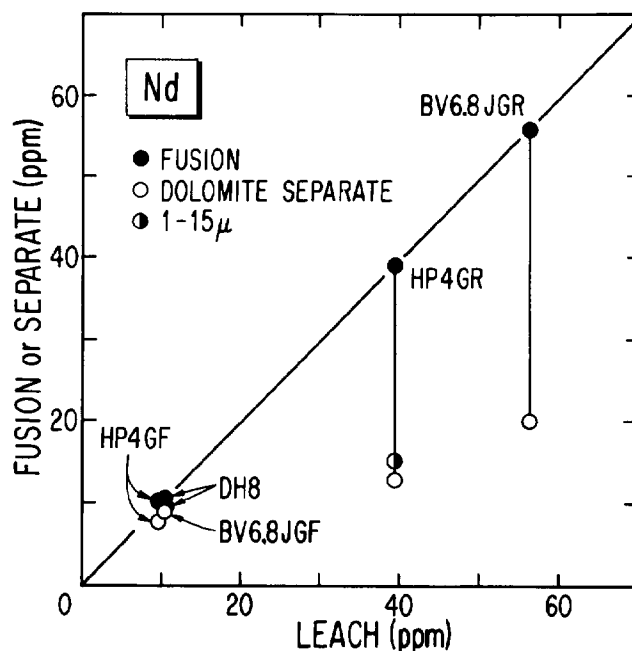


FIG. 3.—Comparison of Nd abundances in selected dolostones obtained by fusion with LiBO₂ flux, leaching with 1.25 N acid, and analysis of physically separated dolomite. BV-6.8-JGR is a glauconite-apatite-rich dolomite I sample, and BV-6.8-JGF is a glauconite-apatite-poor dolomite I sample above BV-6.8-JGR (Fig. 4). HP-4GR and HP-4GF are dolomite II samples that stratigraphically correlate to this same horizon at another locality. DH8 comprises dolomite I rhombs that are commonly coated with iron oxides (Fig. 2). Lines connect analyses from the same sample. Half-filled circles are analyses of the 1–15-micron fraction of the dolomite separate.

TABLE 2.—Continued

HP-4GR			HP-4GF		DH8			Chondrites	BCR-1	Mean Dev. (%)
9	10	11	12	13	14	15	16	17a	17b	17c
12.2	14.5	36.5	10.7	7.75	7.69	6.72	6.60	0.813	53.7	2.7
12.9	15.12	41.6	10.1	7.66	10.4	10.2	9.22	0.597	28.9	0.8
3.06	3.58	10.4	2.30	1.73	2.44	2.40	2.20	0.192	6.57	0.9
0.719	0.838	2.25	0.550	0.433	0.580	0.563	0.545	0.0722	1.94	0.5
3.29	3.61	9.67	2.56	2.04	2.56	—	—	0.259	6.34	2.3
2.61	3.10	5.77	2.53	2.36	2.44	2.32	—	0.325	6.43	0.8
1.38	1.50	1.88	1.36	1.32	1.31	1.29	—	0.213	3.67	1.6
0.911	0.961	0.813	0.952	0.943	0.958	0.932	—	0.208	3.34	2.5
0.696	0.702	0.644	0.772	0.743	0.542	0.483	0.526	—	—	—
0.695	0.712	0.681	0.700	0.713	0.712	—	—	—	—	—
0.1440	0.1432	0.1509	0.1373	0.1366	0.1416	0.1420	0.1443	—	—	—
—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—

12: HP-4GF (Glauconite-apatite-poor layer) — whole-rock flux-fusion (whole-rock leach given in Table 3, analysis 24).
 14 through 16: DH8 — 14) whole-rock flux-fusion (whole-rock leach given in Table 3, analysis 22); 15) dolomite separate; 16) 1–15 μ HNO₃ fraction of dolomite separate.
 17a: Chondrite-normalizing values from Hanson (1980).
 17b: Average REE concentrations in BCR-1 standard determined at Stony Brook (Vocke et al. 1987).
 17c: Mean deviation, in percent, for flux-fusion and acid leach analysis of four whole-rock dolostones: BV-6.8-JGR, HP-4GR, HP-4GF, and DH-8.

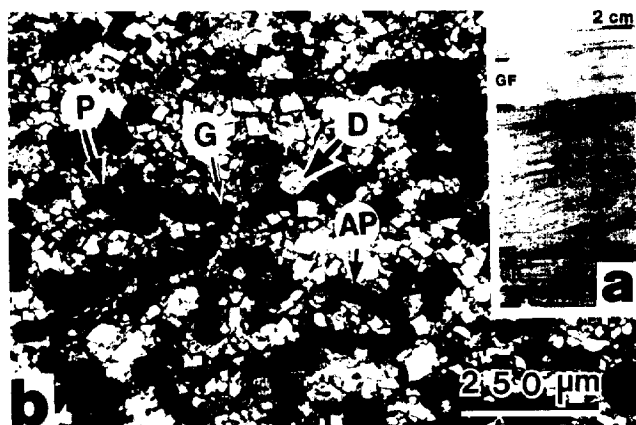


FIG. 4.—Sample BV-6.8-J. a) Dolostone specimen with layers of varying amounts of dark (deep green) glauconite pellets. Stratigraphic up is to the top of the photograph. Whole-rock samples and mineral separates were obtained from a glauconite-apatite-rich layer (GR) and a glauconite-apatite-poor layer (GF). BV-6.8-JGR, shown in (b), is composed of 83% dolomite (D), 13% glauconite (G), 3% biogenic apatite (AP), and less than 1% each of pyrite (P), calcite, and siliceous sponge spicules. BV-6.8-JGF is composed of 97% dolomite I, 2% glauconite, and less than 1% each of apatite, pyrite, calcite, and siliceous sponge spicules. Cathodoluminescent zoning is the same within each layer. REE analyses from sample BV-6.8-J are presented in Figures 5 and 6.

residues were determined for several samples and were less than or equal to five percent by weight. These samples were leached in 30 mL of 1.25 N HCl or 1.25 N HNO₃. REE abundances and Nd isotope analyses for these samples are presented in Table 3 and Figure 7.

After the particular dissolution procedure was complete, the REE were separated using three cation exchange columns using HNO₃, HCl, and 2-methylactic acid (Shirley et al. 1987). The REE were separated into four fractions for analysis on the mass spectrometer: Yb-Er-Dy, Gd, Eu-Sm-Nd, and Ce. Each fraction was loaded on single Ta filaments as phosphates. Ratios were measured on a 15-cm radius of curvature, NBS-design surface emission mass spectrometer. Complete replicate analyses by the same dissolution procedure indicate that precision is generally better than $\pm 1\%$. Replicate trace element and isotopic data are given in Banner (1986).

For the determination of Nd isotopic compositions, separate aliquots of the same sample powders used for isotope dilution analysis were dissolved in an identical manner. Similar cation exchange procedures were used to separate Nd from the other REE. Triple Re filament assemblies were used to analyze masses 143, 144, 146, and 147 with a 30-cm radius, NBS instrument. ¹⁴³Nd/¹⁴⁴Nd ratios are normalized to ¹⁴⁶Nd/¹⁴⁴Nd = 0.72190. Sixteen analyses of the UCSD Nd₂O₃ standard during the course of this study gave a mean value of 0.511759, with a value for one standard deviation of any given analysis of ± 0.000025 . Ten samples of dolomites I and II (Tables 2 and 3) give a mean value of 0.511906 for their initial ¹⁴³Nd/¹⁴⁴Nd ratio (342 Ma), with a value for one standard deviation of any given analysis of ± 0.000025 . Thus, the dolomites have Nd isotopic compositions that vary within the analytical precision. All analyses presented here

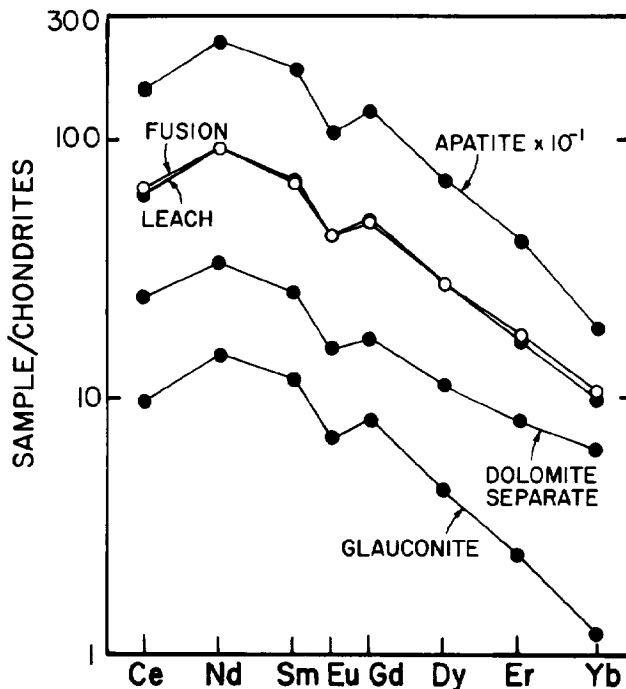


FIG. 5.—Chondrite-normalized REE patterns for whole-rock and mineral separates for sample BV-6.8-JGR. Whole-rock patterns refer to dissolution by fusion with LiBO₂ flux and leaching with 1.25 N HCl.

are adjusted to a value of 0.511858 for the UCSD Nd₂O₃ standard (Lugmair and Carlson 1978). Procedural blanks for the REE are less than 2 ng using the flux dissolution and less than 0.3 ng without flux and were insignificant for the samples analyzed in this study. Details of these procedures are presented in Shirley and Hanson (1986) and Vocke et al. (1987).

DATA REPRESENTATION

In order to facilitate comparison of REE patterns for different samples, the abundances of the individual REE in samples are divided by the abundances in chondritic meteorites (Hanson 1980). Comparisons with shale REE abundances are made in Figures 9 and 10. Ratios of elemental abundances are compared for different samples by their chondrite-normalized abundances (e.g., (Ce/Nd)_n) and their isotopic abundances (¹⁴⁷Sm/¹⁴⁴Nd). The ¹⁴⁷Sm/¹⁴⁴Nd ratio of a sample is proportional to the Sm/Nd (ppm) ratio, depending on the isotopic composition of Nd in the sample. For the samples in this study, these ratios are related by ¹⁴⁷Sm/¹⁴⁴Nd = 0.6045(Sm/Nd). The initial ¹⁴³Nd/¹⁴⁴Nd ratio of a sample at a given time, *T*, is expressed as a deviation from a chondritic uniform reservoir (CHUR) standard value using the ϵ notation of DePaolo and Wasserburg (1976):

$$\epsilon_{Nd}(T) = \left[\frac{(^{143}\text{Nd}/^{144}\text{Nd})_{\text{sample at } T}}{(^{143}\text{Nd}/^{144}\text{Nd})_{\text{CHUR at } T}} - 1 \right] \times 10^4, \quad [1]$$

where $(^{143}\text{Nd}/^{144}\text{Nd})_T = (^{143}\text{Nd}/^{144}\text{Nd})_{\text{today}} - ^{147}\text{Sm}/^{144}\text{Nd}(e^{\lambda_{\text{Sm}} T} - 1)$, the present-day ¹⁴³Nd/¹⁴⁴Nd value of

CHUR is 0.512638 (Jacobsen and Wasserburg 1980), and the decay constant for the decay of ¹⁴⁷Sm to ¹⁴³Nd is $\lambda_{Sm} = 6.54 \times 10^{-12}/yr$. Eu anomalies are expressed as $Eu/Eu^* = Eu_n/[0.5(Sm_n + Gd_n)]$, where Eu/Eu^* values of unity represent no anomaly.

RESULTS

Distribution of REE between Dolomite and Nondolomite Phases in Dolostones

The results of comparative dissolution experiments are presented in Table 2. Nd abundances analyzed on whole-rock fusions, 1.25 N acid leaches, dolomite separates, and the 1-15-micron fractions of the separates are compared in Figure 3. Complete dissolution by flux fusion gives essentially identical results to acid leaching for the four dolostones analyzed by both methods. For example, Nd, Sm, Eu, and Dy abundances determined by acid leaching are reproducible to within $\pm 1\%$ of the values determined by flux fusion for the same samples (Fig. 3; Table 2). Results for the other REE give a mean deviation of less than $\pm 3\%$ for the two methods. Physically separated dolomite can have REE abundances that are as much as a factor of three lower than the whole rock. The dolostones which have a larger noncarbonate component (BV-6.8-JGR, HP-4GR) also have the larger differences between whole-rock and dolomite separate REE abundances. The results for the dolomite separates indicate that a significant proportion of the REE must be associated with the noncarbonate portions of the rocks and that REE from these noncarbonate phases are leached by 1.25 N HCl and HNO₃.

Sample BV-6.8-JGR, a glauconite-apatite-rich dolostone (Fig. 4), has whole-rock REE abundances that are markedly higher than the whole-rock analyses of the nearly pure dolostones (Fig. 3), indicating that dolostone mineralogy plays an important role in determining whole-rock REE abundances. REE patterns for physically separated apatite and glauconite are similar in shape to the whole-rock analyses, but the apatite has a factor of 30 higher REE abundances, while the glauconite has a factor of seven lower REE abundances (Fig. 5). The dolomite rhombs have a factor of three lower abundances than the leach analysis of the whole rock, demonstrating the significant effect that leaching has in removing REE from the noncarbonate phases. The results of mass balance calculations suggest that both glauconite and apatite release REE into 1.25 N HCl. Thus, for impure carbonates, it may be necessary to physically separate the carbonate for analysis, or to rigorously evaluate any leaching method to ensure that it will attack only the phase of interest (e.g., Palmer 1985). It was also found that 1.25 N HCl leaches Rb and Sr from the minor silicate components of the dolostones (Banner et al. 1988a).

The separated dolomite from the two REE-rich whole-rock samples have Nd abundances of 12.9 and 20.0 ppm (Fig. 3). These abundances are higher than those for dolomite separates from purer dolostones that were sampled only centimeters away from each glauconite-apatite-rich

TABLE 3.—REE abundances (ppm) and Nd isotopic compositions in nearly pure whole-rock Burlington-Keokuk dolostone samples

	Dolomite I					Dolomite II					Dolomite II'	
	18	19	20	21	22	23	24	25	26	27	28	
Ce	8.42	11.1	6.43	3.07	7.55	5.59	9.64	1.53	4.99	9.13	7.42	
Nd	8.74	10.2	5.31	4.30	10.3	6.89	9.71	1.42	5.82	10.4	7.46	
Sm	2.03	2.33	1.18	1.04	2.42	1.70	2.24	0.320	1.36	2.48	1.86	
Eu	0.467	0.520	0.277	0.258	0.572	0.413	0.542	0.072	0.303	0.575	0.415	
Gd	2.12	2.28	1.29	—	—	1.90	2.50	0.359	1.44	2.64	2.14	
Dy	1.77	1.74	1.11	1.24	2.41	1.82	2.49	0.280	1.51	2.25	2.09	
Er	0.890	0.817	0.615	0.697	1.27	0.987	1.30	0.138	0.857	1.14	1.11	
Yb	0.707	0.520	0.391	0.519	0.947	0.693	0.896	0.106	0.651	0.792	0.700	
(Ce/Nd) _n	0.689	0.799	0.889	0.524	0.538	0.596	0.729	0.791	0.630	0.642	0.739	
Eu/Eu*	0.1404	0.1381	0.1343	0.1462	0.1420	0.1492	0.1395	0.1362	0.1413	0.1442	0.1507	
¹⁴⁷ Sm/ ¹⁴⁴ Nd	0.512209	—	0.512190	0.512215	0.512224	0.512265	—	0.512168	0.512236	0.512234	0.512278	
2 σ	± 0.000016	—	± 0.000012	± 0.000020	± 0.000027	± 0.000013	—	± 0.000019	± 0.000018	± 0.000017	± 0.000020	
$f_{CHUR}(342)$	-5.9	-6.0	-6.0	-6.0	-5.7	-5.2	—	-6.5	-5.4	-5.6	-5.0	
$f_{CHUR}(Ga)$	0.88	—	0.89	0.89	0.86	0.81	—	0.93	0.83	0.85	0.80	

Whole-rock analyses by leaching with 1.25 N HCl or 1.25 N HNO₃. Notation identical to that used in Table 2. Gd values extrapolated for analyses 21 and 22 for Eu/Eu* calculation. Dolomite I: 18) BV-11; 19) BV-6.8-JGF; 20) HP-18-J; 21) MD-F; 22) DH8. Dolomite II: 23) DC-18; 24) HP-4GF; 25) HP-3-J; 26) HP-10.1-J; 27) KS-8. Dolomite II': 28) HP-15-J.

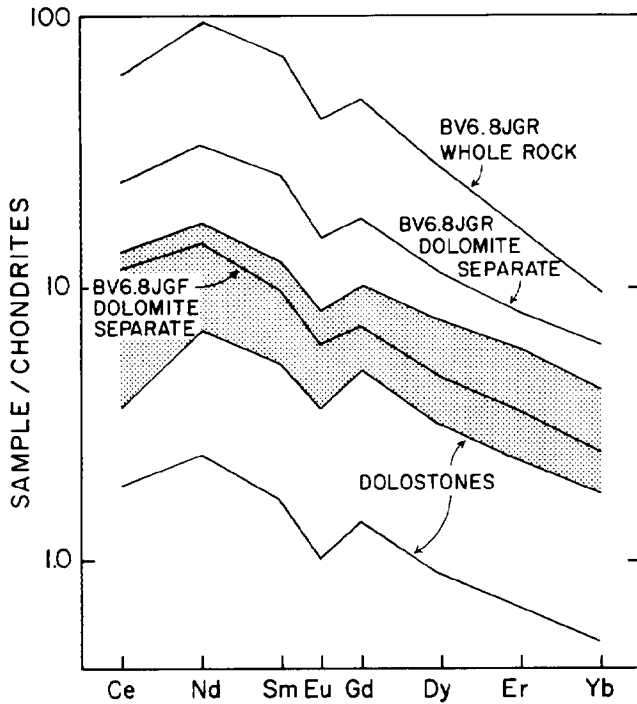


FIG. 6.—REE pattern for dolomite separate from glauconite-apatite-rich horizon (BV-6.8-JGR) compared with field of analyses for nearly pure dolostones (see Fig. 7). Note that the dolomite separate (BV-6.8-JGF) only centimeters from the glauconite-apatite-rich horizon (BV-6.8-JGR) plots within the field of dolomite I samples from other localities.

sample (Fig. 6). These separates and other, nearly pure, dolostones have a range of Nd abundances of 4.3–10.4 ppm (Tables 2 and 3). Therefore, the process by which these dolomites became enriched in REE apparently operated on a small scale (centimeters). The two glauconite-apatite-rich dolomite horizons, BV-6.8-JGR (dolomite I) and HP-4GR (dolomite II), correlate stratigraphically between localities and probably represent a period of sluggish carbonate deposition (Wilson 1975). The similar REE enrichment that occurs in dolomite from stratigraphic horizons with similar depositional histories and distinct

diagenetic histories indicates that the small-scale differences in REE abundances were not significantly altered by the later fluids that formed dolomite II.

REE Geochemistry of Burlington-Keokuk Dolostones

Chondrite-normalized REE patterns for nearly pure whole-rock dolostones from the Burlington-Keokuk Fm. are shown in Figure 7. The patterns for all cathodoluminescent dolomite types are similar, in contrast to the distinct variations in cathodoluminescence, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, $\delta^{18}\text{O}$ values, and Fe and Ca contents. All of the samples show moderate enrichment in the LREE relative to the HREE. Several key trace element ratios illustrate the similarity of the patterns. For example, the range in $^{147}\text{Sm}/^{144}\text{Nd}$ ratios is 0.134 to 0.146 for dolomite I and 0.136 to 0.149 for dolomite II (Table 3). The high $^{147}\text{Sm}/^{144}\text{Nd}$ ratios in the dolomites relative to shales (0.11 ± 0.01) reflect less LREE-enriched patterns. Each sample has anomalously low abundances of Eu and Ce relative to their neighboring REE, as indicated by the values for Eu/Eu^* and $(\text{Ce}/\text{Nd})_n$. $(\text{Ce}/\text{Nd})_n$ ratios vary in a similar fashion to Ce anomalies in seawater, and the values can be used to monitor changes in Ce anomalies in a suite of samples (deBaar et al. 1985). There is greater variation in $(\text{Ce}/\text{Nd})_n$ ratios among the dolostones (0.524–0.889) as compared to the Eu anomaly ($\text{Eu}/\text{Eu}^* = 0.654\text{--}0.717$).

The major differences in REE patterns between the dolostones are among their absolute abundances of the REE. Dolostones from one measured section or even from different portions of a single hand sample show a range of REE abundances nearly as large as the range shown by all the samples. For example, the total range in Nd abundances for all of the nearly pure dolostones is 1.4 to 10.4 ppm. Four dolostones from the HP locality have a range of 1.4 to 9.7 ppm Nd (Table 3). Within sample BV-6.8-J, two layers give whole-rock Nd abundances of 10.2 and 56.2 ppm Nd by acid leaching. Thus, no systematic variations in dolomite REE patterns or abundances are observed as a function of either geographic locality or diagenetic history. Rather, the REE abundances of the dolostones are correlated to sample mineralogy.

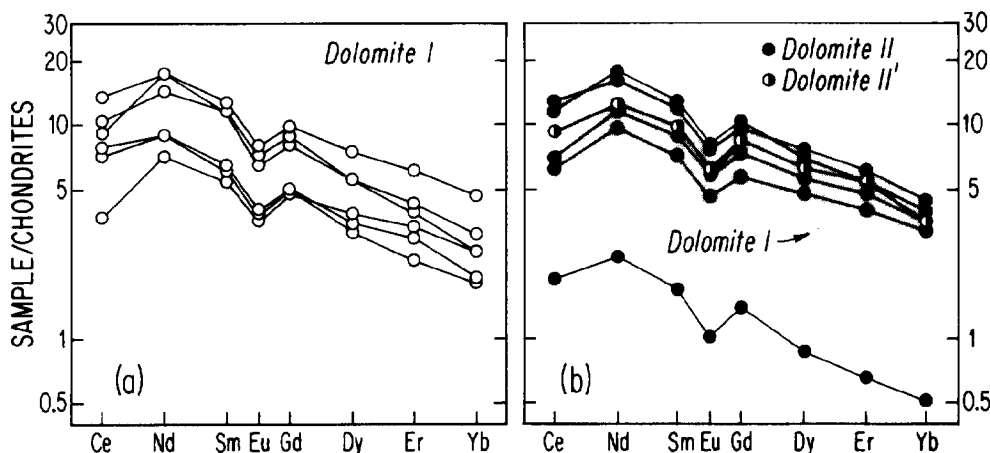


FIG. 7.—REE patterns for nearly pure dolostones. a) Dolomite I; b) Dolomites II and II'. A pattern for an oxide-clay-rich dolostone (dolomite I; analysis 45, Table 4) is also included in (a).

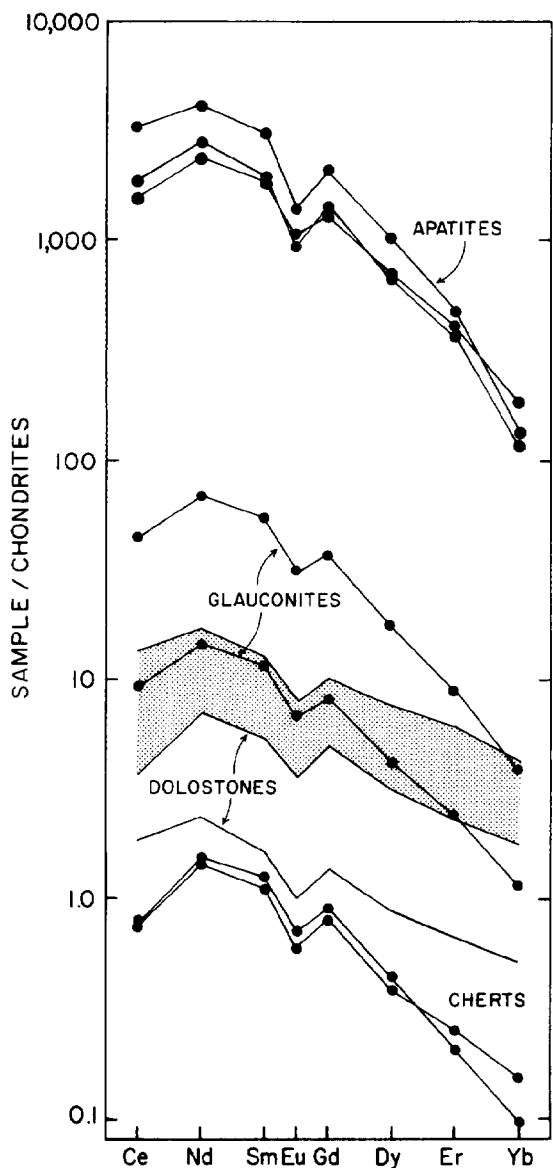


FIG. 8.—REE patterns for various diagenetic and depositional phases from the Burlington-Keokuk Fm. illustrating large range in REE abundances and similarity in REE patterns among the different phases. Dolostones shown are those from Figure 7.

REE in Other Phases from the Burlington-Keokuk Formation

Modern marine carbonates often have negative Ce anomalies and REE abundances in the ppb to ppm range (Shaw and Wasserburg 1985; Palmer 1985), and ancient carbonates analyzed to date have much higher REE abundances in the 1–100 ppm range and often lack a Ce anomaly (Graf 1984; Jarvis et al. 1975; Parekh et al. 1977). The absence of a Ce anomaly and high REE abundances in these carbonates are most likely due to the influence of detrital components during any of the following: 1) deposition, whereby local seawater attains a LREE-enriched signature; 2) diagenesis and incorporation of mo-

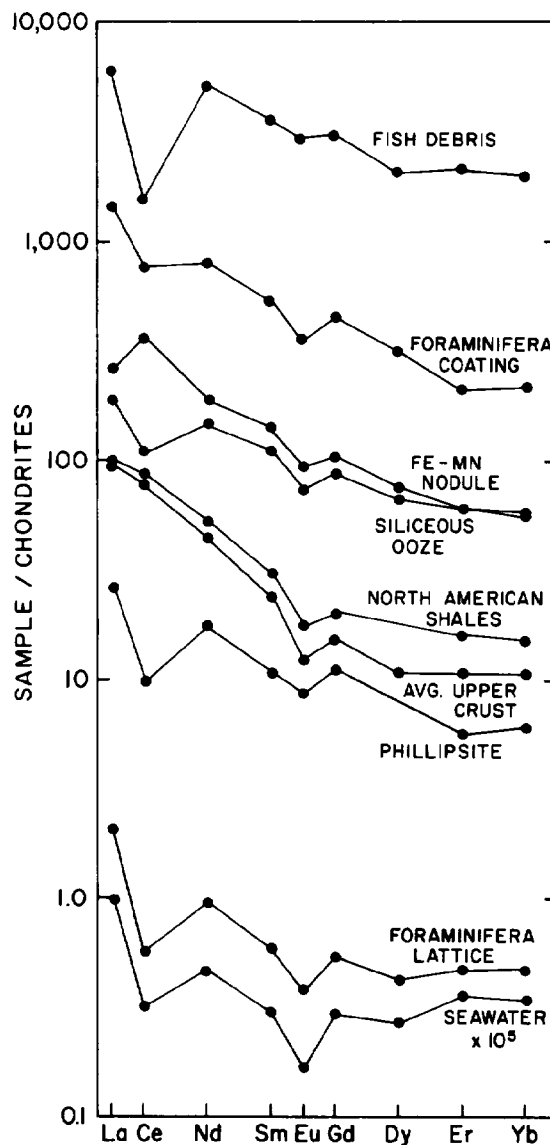


FIG. 9.—REE patterns for sedimentary rocks, minerals, and seawater samples. Data from Haskin et al. (1966); Piper (1974); Bernat (1975); Elderfield et al. (1981); Taylor and McLennan (1981); Elderfield and Greaves (1982); Palmer (1985). All authigenic phases shown here are from modern marine environments.

bilized REE from local detrital phases into diagenetic carbonates; or 3) analysis, whereby REE from detrital phases affect the apparent carbonate composition. Alternatively, the lack of a Ce anomaly in ancient carbonates may be indicative of anoxic marine waters, or formation by nonmarine diagenetic fluids with no Ce anomaly.

Chert nodules, fish apatite and glauconite pellets from Burlington-Keokuk strata all have REE patterns with similar shapes but the different phases have significantly different abundances (Fig. 8). The low $(Ce/Nd)_n$ ratios (0.504–0.821), moderate LREE enrichment and negative Eu anomalies in these phases are characteristic of the dolostones, although the slope of the HREE is steeper compared to the dolostones. The apatite, chert and glau-

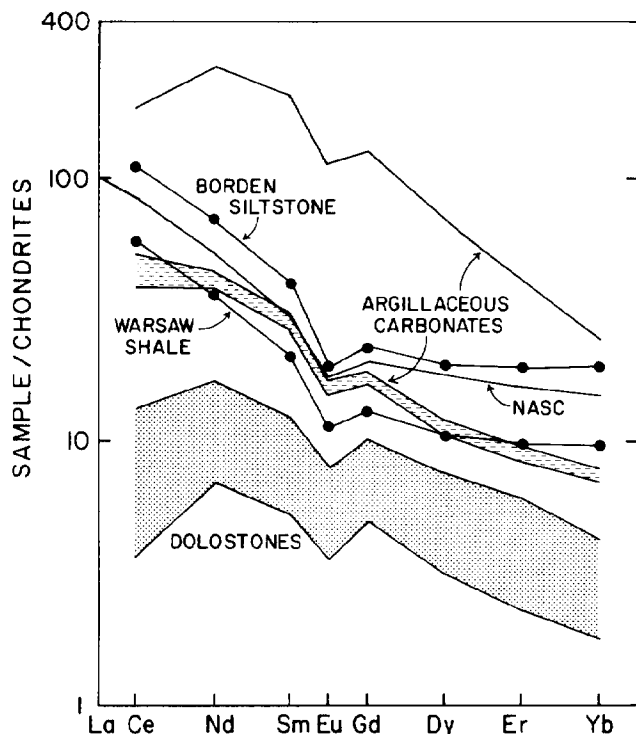


FIG. 10.—REE patterns for clastic sediments from the Warsaw and Borden Fm and argillaceous carbonates from the Burlington-Keokuk Fm. Compare to North American shales (NASC) and with dolostones.

conite also have similar REE patterns and steeper HREE slopes compared to their modern counterparts (Fig. 9). Separated crinoid ossicles composed of recrystallized low magnesium calcite from Burlington-Keokuk limestones

have similar REE patterns to those for the dolostones (Chyi et al., unpubl. data).

Clastic sediments from the Warsaw and Borden Fms. were deposited during and shortly after the deposition of the Burlington-Keokuk Fm. (Fig. 1) and have REE patterns typical of shales (Fig. 10). They are LREE-enriched and have high $(Ce/Nd)_n$ ratios (1.58–1.59). Argillaceous carbonates from the Burlington-Keokuk Fm. have REE patterns that lie between the shale and dolomite patterns in both shape and abundance. Sr isotopic data indicate a significant detrital component in these samples (Chyi et al. 1985), and their REE patterns are consistent with this (Fig. 10).

REE patterns that are distinctly different from the dolostones are observed for vug-filling calcite and dolomite samples (Fig. 11). The crystallization of these phases postdates the formation of apatite, chert, glauconite pellets, and dolomites I, II, and II'. The calcite spar is LREE-enriched with a $(Ce/Nd)_n$ ratio of 1.20 and a $^{147}Sm/^{144}Nd$ ratio of 0.101 (Table 4), more similar to the ratios for typical clastic sediments. The saddle dolomite also has a fairly high $(Ce/Nd)_n$ value of 0.924 and low $^{147}Sm/^{144}Nd$ value of 0.137. Significant differences are also seen between the REE patterns of gangue carbonates associated with Mississippi Valley-type mineralization and their host-rock marine carbonates in the Viburnum Trend of south-east Missouri, although in this case the gangue carbonates are LREE-depleted relative to the host rocks (Graf 1984).

In contrast to the considerable variation in abundances in the authigenic phases of the Burlington-Keokuk Fm. (Fig. 8), all apatite, glauconite, chert, and dolomite samples have similar low $(Ce/Nd)_n$ and high Sm/Nd ratios when compared to the clastic sediments (Fig. 12). In addition to the characteristic Ce anomaly, many modern marine authigenic sediments also have high Sm/Nd ratios

TABLE 4.—REE abundances (ppm) and Nd isotope compositions for various diagenetic and depositional phases of the Burlington-Keokuk and associated formations

	Apatites		Cherts		Warsaw Shale	Borden Siltstone
	29	30	31	32	33	34
Ce	1,500	2,730	0.610	0.635	48.2	92.9
Nd	1,670	2,440	0.872	0.928	22.1	43.3
Sm	369	595	0.216	0.244	4.19	7.93
Eu	67.7	101	0.043	0.051	0.836	1.42
Gd	370	534	0.211	0.232	3.46	6.15
Dy	218	335	0.124	0.140	3.50	6.47
Er	78.1	102	0.053	0.045	2.12	4.17
Yb	24.5	28.5	0.032	0.019	2.01	4.11
$(Ce/Nd)_n$	0.660	0.821	0.513	0.502	1.59	1.58
Eu/Eu*	0.559	0.541	0.611	0.651	0.658	0.605
$^{147}Sm/^{144}Nd$	0.1336	0.1474	0.1497	0.1589	0.1141	0.1107
$^{143}Nd/^{144}Nd$	0.512292	0.512273	0.512270	—	0.512132	0.512105
2σ	± 0.000012	± 0.000012	± 0.000032	—	± 0.000021	± 0.000018
$\epsilon_{Nd}(342)$	-4.0	-5.0	-5.1	—	-6.3	-6.6
T_{CHUR} (Ga)	0.70	0.79	0.81	—	0.91	0.94

29) BV-F-J: Apatite separate from chondrichthyan fin spine.

30) HP-F-J: Apatite separate from ichthyolith tooth.

31) OL-13: Bedded chert.

32) BV-5: Bedded chert.

33) GR-3-J: Dolomitic shale, Warsaw Fm.

34) MKU12-J: Siltstone, Borden Formation, Millport Knob roadcut, Indiana (Stop 4 from Kammer et al. 1983).

35) GR-6: Sparry, ferroan calcite filling solution vug in crinoidal grainstone.

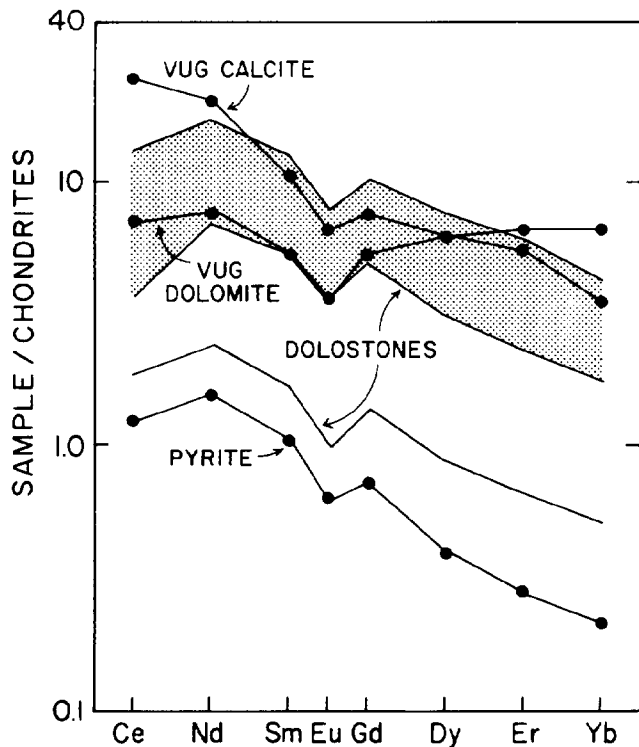


FIG. 11.—REE patterns for late-stage vug-filling carbonates and fracture-filling pyrite and field of dolostone analyses. All data from Burlington-Keokuk Fm.

mixtures of 5–10 percent of a detrital component with a dolomite with low $(Ce/Nd)_n$ and high Sm/Nd could account for this trend (Fig. 12). However, nearly pure dolostones and mineral separates were used for this study, and the samples show no correlation between REE abundances and either Rb or Sr concentrations or insoluble residue contents. This $(Ce/Nd)_n$ - Sm/Nd trend most likely reflects dolomite chemistry rather than a physical mixture involving detrital and carbonate and/or apatite end members. This does not exclude the derivation of REE from detrital phases during the formation of either dolomite generation or their calcium carbonate precursors. On the other hand, the similar $(Ce/Nd)_n$ - Sm/Nd correlation shown by the argillaceous carbonates is most likely the result of such a physical mixing process (Fig. 12).

Eu^{3+} is probably the dominant valence under most diagenetic conditions (Sverjensky 1984), and, as a consequence, negative Eu anomalies in seawater and modern marine sediments are mostly a function of the crustal source of the REE. Similar Eu/Eu^* values for average upper crust (0.65 ± 0.05 ; Taylor and McLennan 1981), and in samples of Burlington-Keokuk dolostones ($0.65-0.73$) and the Warsaw and Borden Fms. ($0.61-0.66$) imply that Eu fractionation during the formation and recrystallization of the carbonates has not been significant.

Nd Isotopes

The Nd isotopic compositions of the Burlington-Keokuk dolostones show a small range of values (Fig. 13) similar to the REE abundance data and in contrast to the large Sr isotope variations. Based on petrographic constraints reviewed above, the major episodes of dolomitization probably occurred prior to Pennsylvanian time. An age of 342 Ma was used to calculate $\epsilon_{Nd}(T)$ for the

(Goldstein et al. 1984; Shaw and Wasserburg 1985). The various diagenetic phases in the Burlington-Keokuk Fm. display an inverse correlation between their $(Ce/Nd)_n$ and Sm/Nd ratios, with the exception of the apatites. Physical

TABLE 4.—Continued

Vug Phases			Argillaceous Carbonates				Oxide-Clay-Rich Dolostone
35	36	37	38	39	40	41	42
19.8	5.70	1.01	33.1	42.1	31.9	154	5.84
12.1	4.53	0.954	23.6	27.0	22.1	161	5.39
2.03	1.03	0.206	5.36	6.01	4.94	40.9	1.25
0.468	0.265	0.046	1.16	1.12	1.02	8.41	0.271
1.97	1.38	—	4.78	4.63	4.29	33.5	1.30
2.04	2.01	0.137	3.86	3.60	3.38	22.3	1.02
1.18	1.38	0.063	1.96	1.77	1.83	8.86	0.486
0.720	1.34	0.045	1.64	1.60	1.45	5.02	0.378
1.20	0.924	0.777	1.03	1.14	1.06	0.705	0.794
0.714	0.687	—	0.694	0.676	0.668	0.680	0.650
0.1014	0.1374	0.1305	0.1373	0.1346	0.1351	0.1536	0.1402
0.512205	—	—	—	—	—	—	0.512247
± 0.000021	—	—	—	—	—	—	± 0.000029
-4.3	—	—	—	—	—	—	-5.2
0.73	—	—	—	—	—	—	0.81

- 36) GR-F-1: Saddle dolomite lining solution vug in argillaceous dolostone.
- 37) OL-8.9-J: Pyrite filling fracture in dolostone.
- 38) MD-17.5-J: Argillaceous carbonate.
- 39) OL-8.9-J: Argillaceous carbonate.
- 40) HP-4.2-J: Argillaceous carbonate.
- 41) KE-8.5-J: Apatite-rich argillaceous carbonate.
- 42) PL-J-22: Iron oxide-clay-rich dolostone (dolomite I).

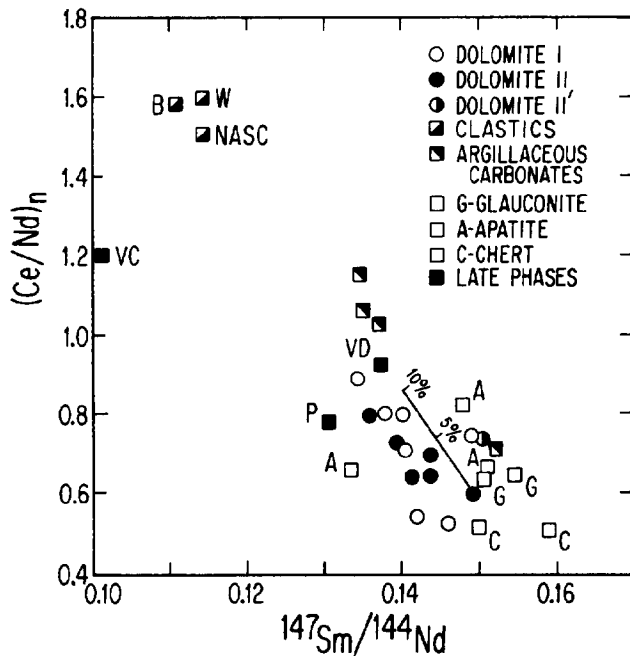


FIG. 12.— $(\text{Ce}/\text{Nd})_n$ versus $^{147}\text{Sm}/^{144}\text{Nd}$ for various diagenetic and depositional phases associated with the Burlington-Keokuk Fm. Nearly pure dolostones and dolomite separate data are shown (Tables 2 and 3). W = Warsaw; B = Borden. Line indicates compositions of physical mixtures of up to 10% Warsaw shale with a high $^{147}\text{Sm}/^{144}\text{Nd}$, low $(\text{Ce}/\text{Nd})_n$ dolomite. Late phases include the following: P = fracture-filling pyrite; VD = vug-filling dolomite; VC = vug-filling calcite.

dolostones. $\epsilon_{\text{Nd}}(342)$ for five dolomite I samples range from -5.2 to -6.0 , and a sixth sample has an $\epsilon_{\text{Nd}}(342)$ of -4.7 , with a typical analytical uncertainty of $\pm 0.5 \epsilon$ units at the $2\text{-}\sigma$ level (Fig. 13). Four dolomite II samples also have a narrow range of $\epsilon_{\text{Nd}}(342)$ from -5.2 to -6.5 , while a dolomite II' sample has an $\epsilon_{\text{Nd}}(342) = -5.0$. In all, ten of eleven dolomite analyses fall in the narrow range of -5.0 to -6.5 . As discussed in Banner et al. (1988a), dolomites II and II' may have formed as late as Pennsylvanian time, while dolomite I is constrained to be of Mississippian age. An age uncertainty ranging from the pre-St. Louis unconformity (342 Ma) to the middle Pennsylvanian (312 Ma) would correspond to a difference in $\epsilon_{\text{Nd}}(T)$ of $0.25\text{-}\epsilon$ units. Thus, dolomites I, II, and II' have indistinguishable ranges of initial Nd isotopic compositions.

Such negative values of $\epsilon_{\text{Nd}}(T)$ in the dolostones are indicative of an older crustal source for the REE with low Sm/Nd relative to CHUR (DePaolo and Wasserburg 1976). The narrow range of Nd isotopic compositions for the major dolomite generations are consistent with the similar REE patterns and are invariant with respect to locality and diagenetic history. A glauconite separate, bedded chert, and the Warsaw and Borden clastic sediments all have $\epsilon_{\text{Nd}}(342)$ in the narrow range displayed by the dolostones (Fig. 13). The biogenic apatites and vug calcite range to slightly more radiogenic Nd isotopic compositions compared to the average Nd isotopic compo-

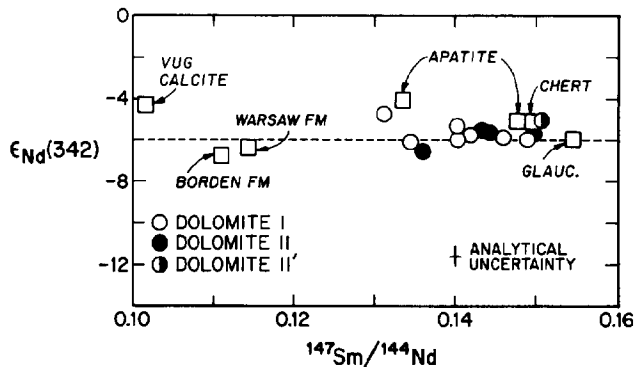


FIG. 13.—Nd isotopic compositions, expressed as $\epsilon_{\text{Nd}}(342)$, versus $^{147}\text{Sm}/^{144}\text{Nd}$ for dolomites I, II, and II', biogenic apatite, glauconite pellets, and chert from the Burlington-Keokuk Fm., and associated clastic sediments from the Borden and Warsaw Fms. Dashed line at $\epsilon_{\text{Nd}}(342) = -6$ for reference.

sition of the dolostones. Although there is no data for Osagean samples on the "seawater ϵ_{Nd} " curve of Shaw and Wasserburg (1985), their data for older Mississippian conodonts show a narrow range of $\epsilon_{\text{Nd}}(T)$ of -8 to -6 , which overlaps the isotopic data for the Burlington-Keokuk dolostones.

DISCUSSION

Two end-member hypotheses are considered to explain the REE and Nd isotope distributions in the dolostones: 1) the REE patterns of the rocks may represent the patterns obtained during the enrichment of the REE in the carbonate precursors to dolomite during syndepositional interaction with seawater near the sediment-water interface, as proposed for modern marine carbonates (Shaw and Wasserburg 1985; Palmer 1985); or 2) the REE patterns may represent regionally pervasive overprinting by nonmarine diagenetic fluids. Several lines of evidence suggest that the REE in the dolostones are inherited from the Mississippian marine environment and that later fluids did not significantly change the REE patterns or Nd isotopic compositions.

The results of model calculations simulating isotopic and trace element exchange during the recrystallization of carbonate sediments illustrate the relative changes in O, Sr, C, and Nd isotopic compositions in the diagenetic products (Fig. 14). Owing to the differences in the concentrations of these elements in diagenetic fluids and carbonates, there are significant differences in the water:rock ratios required to alter the isotopic composition of each element from the original rock composition. For example, as a result of 1) the low REE concentrations relative to O and Sr concentrations in fluids, and 2) the large values of estimated REE/Ca exchange $K_{D,s}$ (Palmer 1985), several orders-of-magnitude-larger extents of water-rock interaction are needed to change the Nd isotopic composition of a carbonate rock during recrystallization compared to its O and Sr isotopic composition (Fig. 14).

The Sr, O, and C isotopic compositions of Burlington-

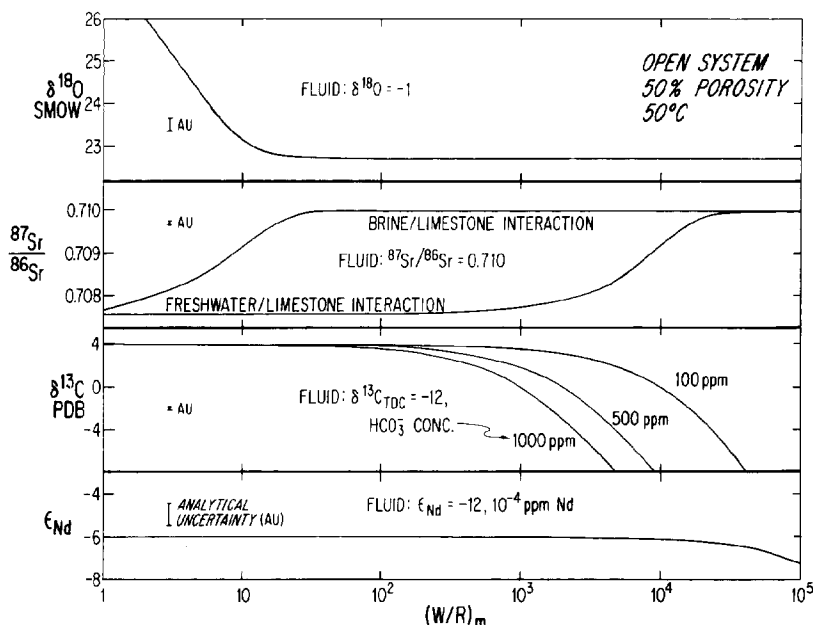


FIG. 14.—Simultaneous variations in the isotopic composition of O, Sr, C, and Nd during open-system recrystallization of limestone as a function of increasing molar water : rock ratio, $(W/R)_m$. In this model, a fluid of given composition flows through a given volume of rock in increments. Each increment of fluid fills the available porosity and recrystallizes calcite until isotopic equilibrium between fluid and calcite is attained. The resulting changes in the rock's isotopic and trace element composition are calculated using mass balance relationships derived in Banner (1986; see also Taylor 1979; and Land 1980). Each new fluid increment displaces the previous one, and the process is repeated. The curves represent the changes in the rock's composition as a function of the total molar water : rock ratio (i.e., the sum of the increments). Initial isotopic compositions of limestone are $\delta^{18}\text{O} = 28\text{‰}$ SMOW, $^{87}\text{Sr}/^{86}\text{Sr} = 0.7076$, $\delta^{13}\text{C} = 4.0\text{‰}$ PDB, and $\epsilon_{\text{Nd}} = -6.0$, 10 ppm Nd. Fluid isotopic compositions are as follows: $\delta^{18}\text{O} = -1.0\text{‰}$ SMOW, $^{87}\text{Sr}/^{86}\text{Sr} = 0.710$, $\delta^{13}\text{C} = -12\text{‰}$ PDB, $\epsilon_{\text{Nd}} = -12$, $T = 50^\circ\text{C}$; porosity = 50%. Two cases illustrated for Sr isotopes are 1) the interaction between a diagenetic carbonate with 200 ppm Sr and a brine with 100 ppm Sr and 20,000 ppm Ca, and 2) the interaction between a marine carbonate with 1,345 ppm Sr and a freshwater carbonate with 0.5 ppm Sr and 20 ppm Ca. Calcite-water exchange $K_D(\text{Sr}/\text{Ca}) = (m_{\text{Sr}}/m_{\text{Ca}})_{\text{calcite}}/(m_{\text{Sr}}/m_{\text{Ca}})_{\text{water}} = 0.05$, where m_{Sr} , m_{Ca} represent molar concentrations. The water-rock interaction pathways for carbon isotopes demonstrate the effects of dissolved bicarbonate concentrations (in ppm) on the rate at which the recrystallizing limestone's $\delta^{13}\text{C}$ value changes. Note large differences in the water : rock ratios at which the O and C isotopic signatures significantly deviate from the original rock composition. Sr isotopic compositions respond at much more variable rates, depending on the fluid and rock concentrations. For Nd isotopes, no significant changes from the original rock composition are obtained at water : rock ratios of up to 5×10^4 using a value of $K_D(\text{Nd}/\text{Ca}) = 100$, and fluid concentrations of 0.0001 ppm Nd and 1,500 ppm Ca. For oxygen isotopes, we use the relationship $\Delta_{\text{calcite water}} = 2.78 \times 10^{-6} T^{-2} (^\circ\text{K}) - 2.89$ (Friedman and O'Neil 1977). Model calculations for dolomite recrystallization give very similar results to those shown here for calcite.

Keokuk dolomite I samples are indicative of predominantly marine-derived diagenetic constituents (Table 1). Early diagenetic processes in the marine environment can modify REE distributions in deep-sea carbonates, but case studies indicate that Ce anomalies and Nd isotopic compositions are not significantly affected (Palmer 1985; Palmer and Elderfield 1986). Although REE distributions in modern shallow, carbonate-forming environments have not been examined in detail, the low $(\text{Ce}/\text{Nd})_n$ ratios of most modern seawater samples (Fig. 15) apparently were also characteristic of North American epeiric seas during Mississippian time, as inferred from REE abundances in conodonts (Wright et al. 1984). The low $(\text{Ce}/\text{Nd})_n$ ratios of dolomite I are therefore consistent with the derivation of the REE in dolomite I from Mississippian seawater or marine porewaters. REE enrichment could have occurred during interaction between seawater and the lime mud precursors to dolomite, or during dolomitization. In either case, a marine REE signature is retained in dolomite I.

Compared to dolomite I, dolomites II and II' have

similar Nd and C isotopic compositions, REE patterns, and concentrations, and distinctly different Sr and O isotopic compositions and Sr, Fe, and Ca concentrations. Quantitative diagenetic models involving the recrystallization of dolomite I by nonmarine subsurface fluids of extraformational origin can account for the geochemical characteristics of dolomites II and II' (Banner et al. 1988b). Subsurface brines with the requisite $^{87}\text{Sr}/^{86}\text{Sr}$ ratios to produce dolomites II and II' may have been derived from interactions with silicates either in detrital sediment components or crystalline basement (McNutt et al. 1984; Stueber et al. 1984; Chaudhuri et al. 1987). Such brines would probably acquire shale-like REE patterns with no Ce anomaly from these sources, and Ce is likely to remain in the trivalent state in subsurface environments.

Quantitative models of water-rock interaction suggest that nearly complete exchange of Sr occurred between dolomite I and the fluids that formed dolomite II (Banner et al. 1988b). These same diagenetic fluids have had an insignificant effect on the REE patterns and Nd isotope

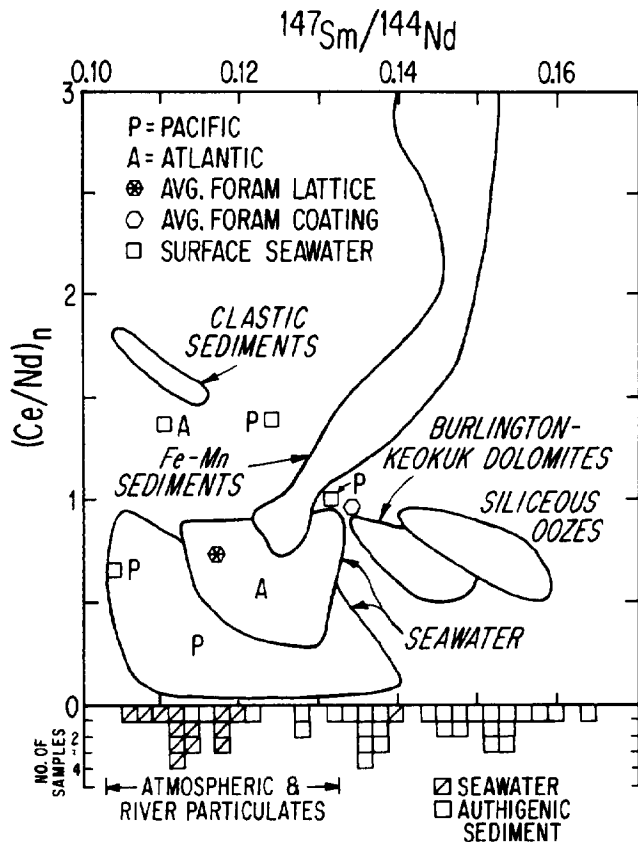


FIG. 15.— $(\text{Ce}/\text{Nd})_n$ versus $^{147}\text{Sm}/^{144}\text{Nd}$ and histogram of $^{147}\text{Sm}/^{144}\text{Nd}$ values for seawater, modern authigenic marine sediments (ferromanganese sediments, carbonates, and siliceous oozes), various crustal erosion products, and Burlington-Keokuk dolomites and associated clastics. Surface-seawater data are for 0–15 m depth. Clastic sediment field encompasses analyses of samples from the Warsaw and Borden Fms., North American Shale Composite (Haskin et al. 1966), and an estimate for average upper crust (Taylor and McLennan 1981), all of which lack a Ce-anomaly in their REE patterns (data sources: Piepgras et al. 1979; Piepgras and Wasserburg 1980; Elderfield and Greaves 1981, 1982; Elderfield et al. 1981; Klunkhammer et al. 1983; Goldstein et al. 1984; Shaw and Wasserburg 1985; Palmer 1985; deBaar et al. 1985; Stordal and Wasserburg 1986). Histogram shows samples for which only Sm and Nd concentrations were measured. One analysis for Atlantic seawater at $^{147}\text{Sm}/^{144}\text{Nd} = 0.18$ and $(\text{Ce}/\text{Nd})_n = 1.01$ was omitted from the diagram. Range for atmospheric and river particulates includes 33 analyses from Goldstein et al. (1984); two analyses from their study at $^{147}\text{Sm}/^{144}\text{Nd} = 0.082$ and 0.146 are omitted here. Note high $^{147}\text{Sm}/^{144}\text{Nd}$ ratios of most authigenic sediments relative to seawater and crustal erosion products, and low $(\text{Ce}/\text{Nd})_n$ ratios of most authigenic sediments (exclusive of Fe-Mn sediments) relative to crustal erosion products.

compositions of dolomites II and II'. This may be explained by either 1) REE and Nd signatures in the dolomite II-forming fluids similar to those of dolomite I, or 2) inheritance of dolomite I REE by dolomites II and II'. In the first hypothesis, the fluid is required to have a similar REE and Nd isotopic signature to dolomite I. The fluid is unlikely to have obtained such a signature from the silicate sources as discussed above, but it may have obtained REE from interaction with carbonates extraformational to the Burlington-Keokuk Fm. Even in this scenario, it would be improbable that dolomites II and

II' would attain narrow ranges of $(\text{Ce}/\text{Nd})_n$, $^{147}\text{Sm}/^{144}\text{Nd}$, and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios and REE abundances similar to the values for dolomite I. A more likely scenario involves the inheritance of dolomite I REE by dolomites II and II' with concomitant large-scale exchange of Sr and O between fluid and dolomite (hypothesis 2) as a result of 1) the low REE/Ca concentration ratios of natural fluids, 2) the high carbonate-fluid exchange K_D s for the REE, and 3) moderate water : rock ratios during dolomite II formation (Fig. 14).

The similar REE enrichment in the dolomite separates from the glauconite-apatite-rich horizon at both dolomite I and dolomite II localities (Fig. 3) is consistent with the hypothesis that dolomitization processes did not affect carbonate REE distributions. The high REE contents in these dolomites may reflect either 1) REE remobilization from the nearby REE-rich apatite, or 2) high REE contents of the carbonate precursors to dolomite that resulted from longer seawater-sediment interaction during periods of slow carbonate sedimentation. Both scenarios suggest that mobility of the REE was on a scale of centimeters or less during dolomitization.

Carbon isotopic compositions of diagenetic carbonates will reflect the original rock composition in a similar but less pronounced manner compared to the REE (Fig. 14). The late, vug-filling calcite and dolomite are the only phases that have significantly different C and REE signatures relative to dolomites I, II, and II' (Table 1). The high $(\text{Ce}/\text{Nd})_n$ ratios and negative $\delta^{13}\text{C}$ values of these late phases suggest that they crystallized from extraformational fluids that experienced only minor interaction with the host carbonate.

In light of the above, we propose a model for trace element behavior during deposition and diagenesis of the Burlington-Keokuk Fm. which involves the enrichment of REE in the carbonate sediments during their interaction with seawater and/or pore waters near the sediment-seawater interface. This REE enrichment may take place through the incorporation of REE from Fe-Mn hydroxide phases into the carbonates (Palmer 1985). Later, non-marine diagenetic fluids, which have extensively exchanged extraformational Sr and O with the dolomites, apparently did not affect dolomite REE distributions. Evidence for the importation of REE into the system is found only in late, vug-filling carbonate cements associated with mineralization, suggesting a fluid-dominated environment for the formation of the late calcite and dolomite. This is consistent with their crystallization in solution cavities, which may have occurred with little interaction between fluid and host rock, resulting in high effective water : rock ratios. By contrast, the replacement of dolomite I by dolomite II appears to have proceeded by dissolution-recrystallization, with the fluids extensively interacting with the rock, resulting in lower water : rock ratios.

This model for REE behavior has two important implications:

First is the potential for marine carbonates to serve as indicators of ancient seawater Nd isotopic compositions. This potential lies in well-characterized suites in which

the REE systematics can be demonstrated to be unaffected by postmarine diagenesis.

Second is the conclusion that a nonmarine REE signature in calcite or dolomite in a marine carbonate sequence indicates that the diagenetic system was one in which either 1) extremely limited interaction occurred between host carbonate rocks and nonmarine diagenetic fluids that crystallized carbonate cements, or 2) nonmarine diagenetic fluids recrystallized host carbonates at relatively high water : rock ratios.

REE Fractionation

Critical to tracing the Nd isotope evolution of a rock or mineral is an understanding of the timing of any fractionation between Sm and Nd. Differences in the shapes of the REE patterns among clastic sediments, seawater, and authigenic marine sediments (Fig. 15) can be attributed to fractionation of the REE during various processes. Seawater from both the Atlantic and Pacific oceans have $(Ce/Nd)_n$ ratios (0.05–1.0) that are very different from the values for clastic sediments (1.5–1.8), but the two oceans have similar ranges of $^{147}Sm/^{144}Nd$ (0.10–0.14) compared to typical shales and river and atmospheric particulates (0.10–0.13). This suggests that Sm/Nd fractionation does not occur during the dissolution and residence of transported crustal REE in seawater. Most marine authigenic precipitates have higher $^{147}Sm/^{144}Nd$ ratios than seawater (0.13–0.16) and similar $(Ce/Nd)_n$ ratios (0.5–1.0), indicating that Sm/Nd is fractionated but $(Ce/Nd)_n$ does not change significantly during the formation of these sediments (Fig. 15; see also Goldstein et al. 1984).

Nearly all Burlington-Keokuk carbonates, phosphates, cherts, clays, and sulfides have higher Sm/Nd than typical clastic sediments, seawater, and crustal erosion products. The high Sm/Nd in the Burlington-Keokuk samples is most likely the result of REE fractionation during precipitation of authigenic phases from seawater or other fluids, rather than 1) the inherent signature of nonmarine diagenetic fluids, or 2) the input of a significant component with high Sm/Nd, such as volcanic ash, into the Osagean epeiric sea. If there was significant volcanic activity during the Osage, which is not documented, then the dolomites would be expected to have more radiogenic $\epsilon_{Nd}(342)$ values relative to the penecontemporaneous clastic sediments from the Warsaw and Borden Fms., which have the low Sm/Nd values characteristic of a continental source. A more likely explanation for the high Sm/Nd ratios in the dolomites is Sm-Nd fractionation during deposition of the precursor carbonate and/or early sea-floor diagenesis. The similar Sm/Nd values in dolomites I, II, and II' indicate that dolomite recrystallization did not fractionate Sm and Nd.

While most modern marine precipitates have high Sm/Nd values relative to the seawater from which they form, the chemically separated $CaCO_3$ lattice portions of modern foraminifera tests studied by Palmer (1985) have, on average, Sm/Nd ratios similar to seawater. The Fe-Mn-rich coating phase on the tests has significantly higher REE concentrations than their lattice counterparts. The

coating phase also has higher average Sm/Nd ratios than both the lattice phase and seawater and shows a trend of increasing Sm/Nd ratios with increasing Nd concentrations. The foram data suggest that significant Sm/Nd fractionation may occur during growth of an authigenic Fe-Mn-rich coating rather than during crystallization of a living calcitic test from seawater. Based on the large and similar calcite-fluid exchange K_D s estimated for Sm and Nd (Palmer 1985), no Sm/Nd fractionation would be expected during the precipitation of calcite.

REE Sources

Constraints on the original crustal sources of the REE in the dolostones may be obtained through the calculation of Nd model ages for each dolostone, which represents an average time at which Sm and Nd were fractionated and derived from a mantle source during partial melting and subsequently emplaced in the crust. This age, T_{CHUR} , is the time at which a sample's $^{143}Nd/^{144}Nd$ ratio is equal to the value for CHUR (i.e., $\epsilon_{Nd}(T) = 0$; DePaolo and Wasserburg 1976).

Crustal erosion products may preserve the Nd isotopic compositions and REE patterns of their sources (Goldstein et al. 1984; Basu et al. 1982). The Osagean Warsaw Shale and Borden Siltstone (Fig. 1) represent the westward progradation of a clastic wedge which lapped onto the Burlington-Keokuk shelf (Lineback 1981). Samples from these formations have REE patterns typical of clastic sediments and are therefore distinct from the dolomites. However, $\epsilon_{Nd}(342)$ values for samples of the Warsaw shale and Borden siltstone are similar to the values for the dolostones (Fig. 13). DePaolo et al. (1983) found a similar result for carbonate and detritus in Cretaceous-Tertiary boundary sediments from a locality in Caravaca, Spain. These results suggest that the REE in these penecontemporaneous clastic and carbonate sediments have the same crustal sources.

In order to account for Sm-Nd fractionation in model age calculations, we use dolostone $^{147}Sm/^{144}Nd$ ratios from the present day to the time of deposition and a crustal $^{147}Sm/^{144}Nd$ value (0.11) from deposition to the CHUR evolution curve. It can be seen that such an age represents a minimum residence time of the REE in the Earth's upper crust. Nd model ages calculated in this fashion range from 0.76 to 0.93 Ga for dolomites I and II, and 0.91 and 0.94 Ga for the clastics (Tables 2, 3, 4). A mantle source with a time-integrated LREE depletion may provide a more appropriate representation of the Earth's Nd isotope evolution compared to CHUR (Goldstein et al. 1984). Using such a depleted mantle source increases the Nd model ages to a range of 1.4 to 1.6 Ga.

The dominant REE input into the Osagean epicontinental sea was most likely from detritus associated with the westward-migrating Borden Delta, and the Nd isotopic signatures of the Osagean carbonates and clastics may have been inherited from northeastern North American crustal sources. Water and sediment samples from the Hudson and St. Lawrence rivers may provide representative averages of the Nd isotopic compositions for

two significant portions of northeastern North America that were exposed during Mississippian time. Sediment and water samples show a large range of $\epsilon_{\text{Nd}}(342)$ values and Nd model ages for both the Hudson ($\epsilon_{\text{Nd}}(342)$ of -8.1 and -4.8) and St. Lawrence ($\epsilon_{\text{Nd}}(342)$ of -1.3 and -9.0) rivers (Goldstein et al. 1984; Goldstein and Jacobsen 1987) that reflect variable provenances within each of these drainage systems. The narrow range of initial Nd isotope ratios shown by the Burlington-Keokuk Fm. carbonates and associated clastics may be a consequence of either an isotopically uniform crustal source for Nd, or several distinct sources of Nd that were well mixed by the time they reached the site of deposition.

CONCLUSIONS

Rare earth element and Nd isotopic variations in ancient carbonates can provide important constraints on the physical and chemical parameters of diagenetic systems, such as fluid composition, fluid source, and extent of water-rock interaction. The use of marine carbonates for examining variations in the Nd isotopic composition of ancient seawater relies on an understanding of REE behavior during diagenesis. Among the major findings of our study of the Burlington-Keokuk dolomites are the following:

1) Two major generations of regionally extensive dolomite in the Burlington-Keokuk Fm., dolomites I and II, formed in distinctly different diagenetic environments based on previous studies of the petrography, trace element abundances, and stable and strontium isotopic compositions of the dolomites. Dolomites I and II have similar REE patterns, REE abundances, and Nd isotopic compositions. Dolomite, apatite, glauconite, chert, and early calcite have similar REE patterns with varying abundances. The anomalously low abundances of cerium in all of these phases indicate a predominantly marine source for the REE.

2) Significant enrichments in REE abundances are associated with a glauconite-apatite-rich horizon in the Burlington-Keokuk Fm., both in whole-rock dolostone samples and physically separated dolomite. Whole-rock REE enrichments are the result of high concentrations of REE in the apatite phase, while REE enrichments in the dolomite phase may reflect either 1) remobilization of REE from the apatite during dolomite formation, or 2) longer periods of exposure to and interaction with seawater during the deposition of this horizon. The high REE contents in the dolomite phase from this horizon occur in both dolomite I and dolomite II localities, indicating small-scale mobility of the REE during the major episodes of dolomitization.

3) These results suggest that dolomite I inherited its REE from Mississippian seawater and/or marine porewaters. Dolomite II formed by the subsequent recrystallization of dolomite I by nonmarine diagenetic fluids, which resulted in the extensive exchange of Sr and O between dolomite and fluid. This recrystallization process did not affect the REE patterns or Nd isotopic compositions of the dolomites. The results of quantitative mod-

eling indicate that such differences in the mobility of Sr, O, and the REE during diagenesis may be due to relatively low REE/Ca ratios in diagenetic fluids and high values for carbonate-fluid exchange K_D s for the REE. Late, vug-filling carbonate cements may record an extraformational REE signature (low Sm/Nd, high (Ce/Nd)_n ratios), indicating that extremely limited interaction occurred between late diagenetic fluids and Burlington-Keokuk host rocks.

4) Authigenic sediments from the Burlington-Keokuk Fm. and penecontemporaneous clastic sediments from the Warsaw and Borden Fm have similar initial Nd isotopic compositions. This may reflect common crustal sources of REE for the clastics and carbonates. The high Sm/Nd in authigenic phases in the Burlington-Keokuk Fm. relative to the associated clastics is similar to the Sm/Nd ratios in modern marine precipitates. REE fractionation is indicated during dissolution and residence of transported material into seawater (Ce anomaly) and authigenic precipitation from seawater (high Sm/Nd).

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