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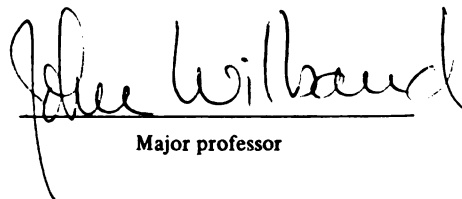
RARE EARTH ELEMENT DISTRIBUTION
OF THE NEEBAUNEE IRON FORMATION,
MARQUETTE DISTRICT, MICHIGAN

presented by

Susan E. Pituskin

has been accepted towards fulfillment
of the requirements for

M.S. degree in Geology


Major professor

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RARE EARTH ELEMENT DISTRIBUTION IN THE
NEGAUNEE IRON FORMATION, MARQUETTE DISTRICT, MICHIGAN

By

Susan E. Tituskin

A THESIS

Submitted to
Michigan State University
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ABSTRACT

RARE EARTH ELEMENT DISTRIBUTION IN THE NEGAUNEE IRON FORMATION, MARQUETTE DISTRICT, MICHIGAN

BY

Susan E. Tituskin

The Negaunee Iron Formation, at the Empire Mine, has several lithologies (oxide, carbonate, and silicate iron formation) dependent upon diagenesis weathering, and metamorphic history. The mineralogic content of primary unit(s) from which these lithologies were derived is controversial.

The REE abundances progressively decrease in the sequence: clastics-oxides-carbonates-chert rich samples. Distribution patterns are variable within groups but show no systematic lateral or vertical trends. This, coupled with anomalous cerium behavior, suggest deposition near a basin margin from a LREE-enriched solution. The effect of alteration on original REE distributions is difficult to assess, but appears to correlate to ore formation through diagenetic diffusion mechanisms whereby the presence of carbonate complexes permit the stabilization of HREE in solution.

The REE trends of chemical sediments are grossly similar to clastic interbeds. This suggests that continental erosion was a major contributor to the solution chemistry and a probable iron source.

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INTRODUCTION

Purpose and Scope of Research

This investigation deals with the distribution of trace elements, specifically the rare earth elements (REE) in the Negaunee Iron Formation (NIF), Marquette District, Michigan. REE's have been extensively used as petrographic indicators in igneous systems, however, several studies have also been carried out on sediments and sedimentary rocks. The behavior of the REE's in sedimentary systems is not as clearly understood, and this includes their precipitation and occurrence in banded iron formations (BIF). Pioneering investigations by Fryer (1977a, b) and Graf (1978) have indicated that REE distribution patterns are useful for placing constraints on the depositional nature of iron formations. It is generally thought that the BIF's formed as chemical precipitates when iron-rich solutions entered the sedimentary environment, therefore, the REE distribution pattern would be effected by: 1) the chemical nature of the sea water, 2) the REE pattern of the iron source solution, 3) the degree of mixing between these solutions, 4) the amount and type of precipitating or detrital phase, 5) the nature of the basin (i.e., shallow versus deep marine), and 6) the mode of precipitation.

The NIF is considered typical of Superior-type Proterozoic iron formations. The Superior-type iron formations in the Marquette-Gogebic ranges have a geological setting for which both turbulent and quiescent conditions of deposition exist. The role of volcanism is uncertain, but most Proterozoic iron formations are not immediately associated with volcanic rocks. This is true of the NIF except for the possible association of the Clarksburg volcanics with the post-Negaunee age iron formations in the Michigamme Formation.

Samples have been collected from the Empire Mine located within the lowest-grade metamorphic zone of the NIF. Because the REE are more resistant to fractionation during metamorphism than other trace elements (Cullers, et al., 1974), they may be considered the most chemically representative of the original unaltered sediments. Therefore, the acquired data will be acceptable for discussing the above six parameters. Trace element data has been collected from 45 core samples. Chert, carbonates, clastics, ores, and the underlying Siamo Slate have been analyzed.

These data will be used to investigate mineralogic, lithologic, and facies controls of the REE's within the Negaunee. This information will be used to infer the chemical nature of the solution from which the NIF was deposited, possible sources of the iron-rich solution, and the environment of deposition. The REE imprint will be compared to similar Proterozoic BIF's.

Geological Setting

The NIF, a member of the Marquette Range Supergroup, consists of a series of metasedimentary rocks occupying the Marquette Trough. This structure is a narrow, westerly trending synclinorium which extends approximately 70 km from the city of Marquette to near the village of Three Lakes. The Empire Mine is located in the south-limb sector in the lowest grade metamorphic zone of the Iron Formation. The south limb folds into a smaller syncline called the Republic Trough in western Marquette County. A second belt trends south from the western portion of the Republic Trough. The Marquette Range extends from Marquette County through Baraga, Iron and Dickinson Counties (Figure 1; Gair, 1975).

The NIF is the upper member of the Menominee Group within the Precambrian X series of metasedimentary rocks. Van Schmus and Woolsey (1975), using whole rock and mineral Rb/Sr studies, determined that the

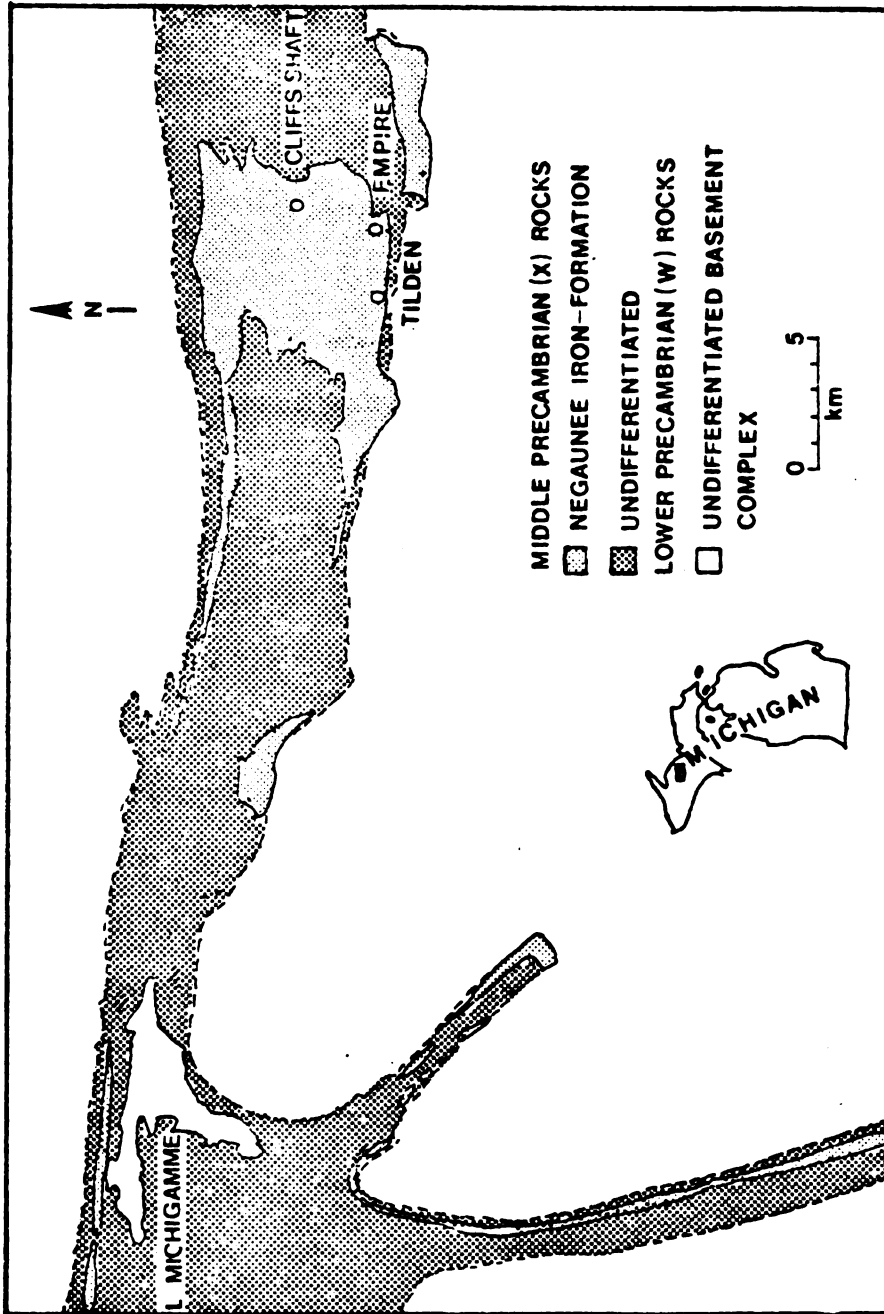


Figure 1. Generalized map of the Marquette District, Michigan (after Gair, 1975).

sediments of the Menominee Group were deposited between c. 1.9 and 2.0 Ga. This series is underlain by Lower Precambrian mafic, metavolcanic, and granitic rocks. The primary members of the basement complex are the Mona Schist, Compeau Creek Gneiss, and the Palmer Gneiss. Age relationships of the Marquette Range Supergroup are summarized by Gair (1975). The deposition of the NIF is assumed to correlate to that of other iron bearing sequences in the Lake Superior District (James, 1955, 1958; Trendal, 1968).

The iron formation consists of three primary facies: carbonate, oxide, and silicate (James, 1954). Maximum thickness reaches approximately 1300 meters. These facies change laterally in thickness and lithology resulting in difficulty in overall stratigraphic correlations. Correlations have been further complicated by post-depositional changes including diagenesis, metamorphism and post-metamorphic oxidation.

The Empire ore body falls stratigraphically in the upper portion of the NIF, where the ore consists predominantly of magnetite with minor hematite. Other common minerals are chert, siderite, iron silicates, and martite. At this location, the NIF reaches a thickness of 900 to 1100 meters. The ore occurs in a monoclinical fold dipping 35° to the northwest. The area is cross-cut by dike-filled transverse faults of Precambrian X and Y ages.

The Negaunee is overlain unconformably by the Goodrich quartzite (Baraga Group) and underlain conformably by the Siamo Slate. Gair (1975) notes that this lower contact is, in places, gradational through a thickness of as much as 30 meters. The Siamo contains slate, sericitic, chloritic, and feldspathic quartzite, and graywacke as the major rock types. The Siamo contact with the underlying Ajibik quartzite is also conformable. This transition through the NIF appears to represent a change from detrital facies to essentially detritus-free (NIF) facies.

Early investigations suggested an east to west transgressive sequence for the formation of middle Precambrian sediments (Tyler and Twenhofel, 1952). More recently, it has been proposed that early deposition occurred within the stable shelf with later strata deposited after mild uplift in a mildly active miogeosynclinal environment (Van Schmus, 1976; Cannon, 1973). The system of troughs appears to be fault controlled based on the lack of evidence for intervening anticlines. Gair (1968) suggests that faulting has influenced sedimentation and was active during deposition.

The area was subsequently metamorphosed and deformed during the Penokean Orogeny (Goldich, et al., 1961) which has been dated to c. $1.9 \pm .05$ Ga. (Van Schmus and Woolsey, 1975). This has resulted in heavy secondary folding to the west (Cannon, et al., 1975) and faulting to the east (Gair, 1975; Cannon, et al., 1975). Metamorphic grade increases from the chlorite facies in the east, near the City of Negaunee to the sillmanite facies in the west near Republic (James, 1955). Haase (1979) suggests that sillmanite grade was barely reached, since only andalusite has been found in situ.

A later swarm of east-west trending Keweenawan dikes (c. 1 Ga) were emplaced during a short-lived rifting interval and intrude the Marquette Supergroup. They are considered to have been emplaced during the early opening phase of rifting (Pesonen and Halls, 1979) based on their remnant polarity.

Stratigraphy and Geochemistry of the Empire Mine

Numerous investigations have been carried out in the Marquette District since the early 1900's because of its economic importance. Early studies by Van Hise and Bayley (1897) and Van Hise and Leith (1911) characterized the sedimentation, stratigraphy, structure, and metamorphism of the Marquette Trough. Subsequent investigations have refined the petrology, chemistry, age, and stratigraphic nomenclature of the district (James, 1955, 1958;

Anderson, 1968; Cannon and Gair, 1970; Gair, 1975; Cannon, 1973; Cannon, et al., 1975; Van Schmus and Woolsey, 1975; Cannon, 1976; and Haase, 1979). The most detailed geochemical studies at the Empire Mine have been conducted by Cleveland Cliffs Iron Company (CCIC) (Han, 1962, in Gair, 1975) which characterize mineralogy and lithology of the primary facies and diagenetic replacement. Haase (1979) has extended James (1955) metamorphic investigation by utilizing mineral assemblages, compositions, and reaction mechanisms to discern metamorphic grade and processes. Initial carbon and oxygen isotope data has also been presented by Haase and Rye (1980).

Han (in Gair, 1975) categorized the three major lithologic groups at the Empire as follows:

Magnetite-carbonate-chert: alternating layers of magnetite chert plus carbonate, and chert plus some carbonate and/or magnetite. At least some of the magnetite is believed to form from the replacement of carbonate.

Magnetite-carbonate-silicate-chert: laminae of concentrated magnetite and alternating layers of silicate-chert, carbonate-chert plus some silicate, and carbonate-silicate-chert.

Carbonate-chert: laminae of carbonate-chert and chert plus some subordinate carbonate, locally containing appreciable magnetite that apparently formed by the replacement of carbonate.

A generalized stratigraphic section of the NIF (Figure 2) at the Empire has been constructed by Boyum (1975). The portion of the formation overlying the Siamo Slate are silicate to silicate-carbonate-oxide types. This is followed stratigraphically by the carbonate-silicate assemblage overlain by the oxide facies. This sequence appears to correlate with the remainder of the formation (Gair, 1975). Han (1978, 1982, personal communication, 1982) believes the "primary precipitates" can essentially be subdivided into two groups: a carbonate (sideritic)-chert association which has altered to the present magnetite-chert "ore facies"; and a hematite-chert association which now is a magnetite + iron-silicate + chert + carbonate (ankerite, siderite) "ore facies".

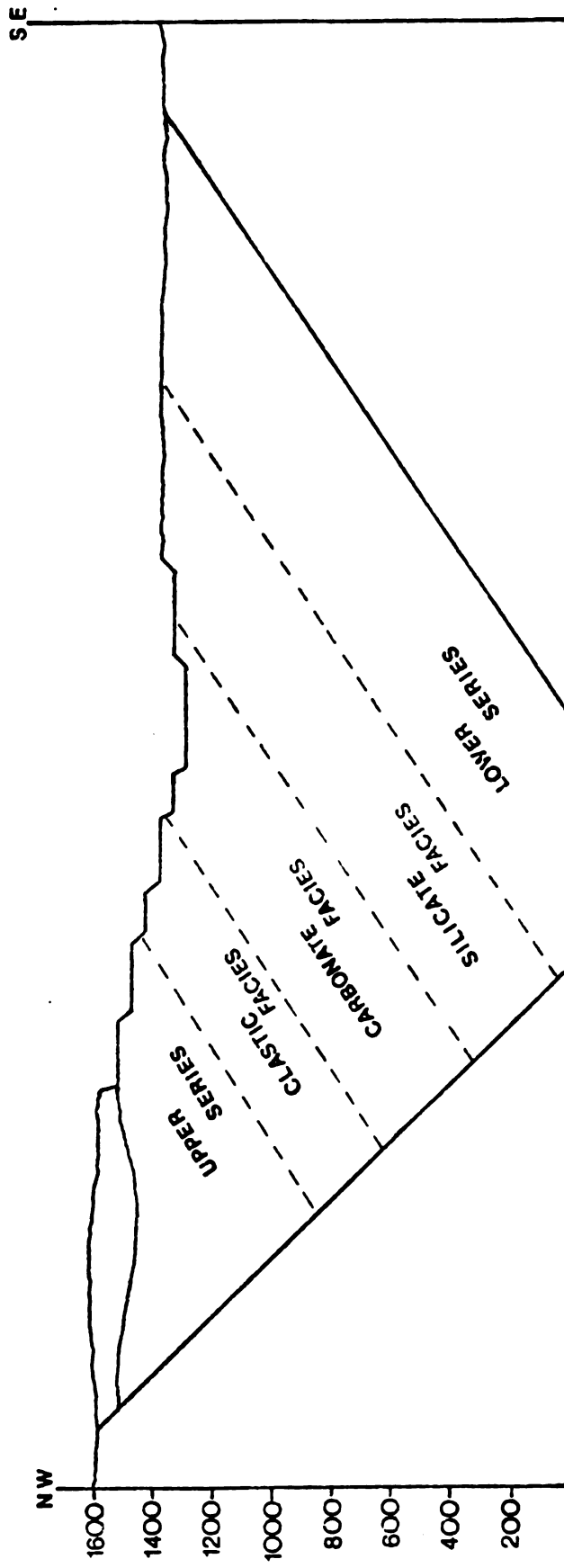


Figure 2. Generalized cross-section of the Negaunee Iron Formation at the Empire Mine, Marquette District, Michigan (after Bogum, 1975). Vertical scale in feet above sea level.

Vertical variation of "ore facies" as seen in drill core are complex and from the limited data, one cannot discern the relationship of the original material. The "ore facies", however, has gross vertical patterns from base to top. The Siamo-BIF base is transitional, marked by a decrease in clastics and increase in BIF. This transition is overlain by carbonate and variable amounts of iron silicates. Some clastic lenses persist. The silicates are overlain by the magnetite-chert-carbonate association which in turn gives way to an iron-silicate rich facies. Clastics are then found and cores reveal that carbonates are present.

The "ore facies" consists of a series of alternating laminae varying in size from meso-banding (5 to 250 mm) to microbands (0.5 to 1.5 mm) defined by variations in mineral abundances. Haase (1979) observed that mesobands in the NIF consist predominantly of quartz, quartz and iron-oxides, carbonates, carbonates and iron oxide, and iron oxide and silicate. Microbands are well developed in the quartz and carbonate mesobands.

The major element geochemistry conducted by CCIC has been summarized by Han:

In general, magnetite-chert-carbonate iron formation contains more Fe_2O_3 , SiO_2 and less FeO , Al_2O_3 , MnO , CaO , CO_2 , P_2O_5 , and S than does the magnetite-carbonate-chert-silicate iron formation. Both types appear to contain less FeO , Al_2O_3 , MgO , and S and more MnO than does the magnetite-silicate-carbonate-chert iron formation that contains clastic beds.

Detailed mineralogic and chemical analyses are presented by Haase.

Han (1962) has characterized diagenetic replacement, and metamorphism observed at the Empire Mine. The major processes noted are: 1) silicification, 2) recrystallization, 3) carbonatization, and 4) magnetitization (diagenetic replacement). These processes appear to have occurred after lithification. "Silicification" to minnesotaite, stilpnomelane, and chlorite is primarily confined

to the upper and lower portion of the formation. Carbonitization is found throughout the formation and may be recognized by the presence of poikiloblasts containing chert, magnetite, silicates, and primary carbonates. "Silicification" is observed primarily in the magnetite-carbon-chert bands by the replacement of earlier carbonates and purification of chert grains. Magnetitization occurs in the magnetite-carbonate-chert facies and is characterized by zonal distribution of minerals, in discrete layers of unreplaced carbonate-chert, a transition zone, and magnetite enriched laminae. This process is believed responsible for the formation of the major ore body.

Haase (1979) and Han (1962) place the Empire in the lower greenschist metamorphic facies. Haase characterizes the lowest metamorphic zone by an abundance of siderite and quartz with minor minnesotaite. His geochemical and petrologic data imply that any mass transport of material is restricted to an individual mesoband and that metamorphic recrystallization appears to have been isochemical except for the loss of volatiles.

PREVIOUS STUDIES

Rare Earth Elements in Sediments and Seawater

Generally, the REE's are trivalent, have decreasing atomic radii with increasing atomic weight and behave chemically similar in the sedimentary cycle. However, two elements, cerium and europium, exhibit common oxidation states other than +3: Ce (+3, +4) and Eu (+2, +3). This variation results in the anomalous behavior of these elements in sea water and sedimentary processes making them of primary interest in the study of REE distributions.

Present day sea water is depleted in Eu by a factor of 0.7 (Wildman and Haskin, 1973) compared to chondritic abundances. Modern sea water also shows a large negative Ce anomaly (Goldberg, et al., 1963). REE contents of clastic sedimentary rocks are likely to reflect changing REE compositions of crustal source regions and may have a wide vertical and horizontal range of REE concentration within a stratigraphic sequence. Chemical precipitates, however, should be less erratic in their distribution patterns and thus provide the best evidence for the behavior of REE in the sedimentary environment. It is logical, therefore, that REE data from Precambrian iron formations, which are composed primarily of chemical sediments, have been used as environmental indicators in an attempt to unravel their genesis.

Two schools of thought have arisen to explain changes in the relative abundances of Ce and Eu to other REE in the sedimentary cycle. The first attributes changes in Eu and Ce behavior to an overall decrease in the abundance of these elements in sea water with time (Wildman and Haskin, 1973; Nance and Taylor, 1976; Fryer, 1977a). The second view stresses that the changes in

relative concentrations is controlled by sedimentary and diagenetic processes including; the chemical nature of the solution, the iron source solution, the mixing of these solutions, and the depositional environment, which may serve to mask overall sea water patterns (Graf, 1977, 1978; Shimizu and Masuda, 1977).

Fryer (1977a) is the major advocate for a time dependency of REE, and uses BIF's as his major source of evidence. Fryer attributes the present Ce depletion to the selective removal of Ce by manganese nodules. His data show a normal Ce distribution within the chemical sediments of the Archean, slight enrichment or depletion during the Proterozoic, followed by a depletion trend. This implies the oxidation of cerium to Ce^{+4} in the early Proterozoic. Fryer suggests Ce^{+4} is scavenged from sea water during the formation of Mn-nodules and, in so doing, suggests their existence as early as 2.3 Ga. It is believed that even in a highly oxidizing state, the catalytic effect of Mn is needed to oxidize cerium. The negative europium anomaly is attributed to the oxidation of europium to Eu^{+3} in response to the introduction of free oxygen to the atmosphere at approximately 1 Ga. Fryer, therefore, proposes a time dependence for the anomalous behavior of these elements in iron formations.

Graf (1978) tested this hypothesis by comparing the REE distribution of Archean Algoma type and Ordovician iron formations (IF). His data show that Archean and Ordovician IF show a positive anomaly and concludes, in contradiction to Fryer, that Eu cannot be used as an outgassing indicator but reflects the specific environment of the particular basin in which the IF form. REE patterns of iron formations are dependent upon the nature of source solution, the degree of mixing of iron source solution and sea water, geological setting, and the amount and type of precipitating or detrital phase. His data also indicate that overall absolute REE concentrations are related to mineralogic

components and sedimentary processes rather than a function of time as has been previously suggested (Nance and Taylor, 1976).

Graf's speculations were alluded to in 1973 by Wildman and Haskin when the application of REE to sediments, and particularly iron formations, was at an early stage of development. Although their data also show a predominant Eu enrichment for Precambrian sediments, interpretations of igneous, metamorphic, and sedimentary processes associated with these samples could not account for a decrease in the overall concentration of Eu in sea water. Early investigations were hampered by a lack of data for REE in recent sediments. Although the data bank is still minimal, the parameters set forth by Graf may be applied to varying degrees. First, it is necessary to evaluate the scope of the investigations which have been conducted to date.

The REE imprint may be indicative of the source of the iron solution, specifically, volcanic exhalation (Graf, 1977) versus a terrestrial origin (Wildman and Haskin, 1973). The data indicate that a magmatic source would result in the enrichment of LREE, overall high concentrations, and would not show a Ce depletion relative to chondrite data. This model has been applied by Graf (1977) where REE's were used as hydrothermal tracers in massive metal-sulfide deposits. Eu behavior would also be affected by a magmatic origin. For example, feldspars selectively concentrate Eu over other REE (Haskin, 1966). As a result, fractional crystallization of a rock containing feldspars will produce a liquid deficient in Eu relative to REE patterns. The resultant feldspar rich solid would be preferentially enriched in Eu. Subsequent melting of a feldspar-rich rock would result in an Eu enriched liquid. Sediments derived from a feldspathic rich source would contain a large positive Eu anomaly. Conversely, a terrestrial source is indicated by the lack of, or slightly positive Ce anomaly, based on the North American Shale Composite (NASC). The associated chemical sediment

REE patterns would also be similar to those of accompanying clastic material. Therefore, a correlation between clastic and chemical sediments has been assumed to be indicative of crustal source regions (McLennan, et al., 1979; 1980).

The source solution may interact with sea water. This mixing may serve to mask the overall REE pattern. Although mass balance calculations are possible, at this point, there is no adequate method to determine the degree of mixing of these solutions for Precambrian sediments. Therefore, the REE pattern of the BIF may not be representative of the original source area.

REE in Chemical Sediments

Goldberg, et al. (1963) stressed the role of separate mineral components in REE studies of sediments. Chert and carbonates are of primary concern in the evaluation of REE data from iron formations. Because Ce is subject to selective removal relative to other REE, it is evident that the absence or presence of a Ce anomaly and the extent of deviation can be a good indicator of aqueous environment of formation for cherty rocks. Cherts generally exhibit overall low REE concentrations and primarily act as a diluent when interbedded with other lithologies. Shimizu and Masuda (1977) compared deep sea cherts (Deep Sea Drilling Project) to "terrestrial" cherts, including the Gunflint Formation. Samples of both cherty rocks and siliceous microfossil separates from radiolarian oozes were analyzed. Deep sea cherts tended to show a large Ce depletion similar to modern sea water, while terrestrial samples were slightly positive or show no Ce anomaly at all. All samples show a small Eu anomaly. The absolute concentrations of the REE within the cherts is extremely variable and appears to be a function of the degree of diagenesis. They conclude that the lack of a Ce anomaly within terrestrial cherts can be interpreted as suggesting that they formed in coastal areas, marginal seas, and land enclosed seas. They reason that Ce in these environments is mostly involved in suspended solid particles and

behaves in the same fashion as other REE's, while in the deep seas, Ce is subject to selective removal by Mn-nodules.

Two major theories, biogenic and volcanic, have been advocated to explain the genesis of cherty rocks. If volcanic activity is directly responsible for chert formation, the rocks so formed should not show a negative Ce anomaly because it is expected to be introduced and adsorbed within the sediments in the Ce^{+3} state, rather than being scavenged in the oxidized state (Ce^{+4}). Predicted REE abundances in biogenic chert are not conclusive; however, in carbonates formed in organic rich environments there are indications that the HREE's are enriched in organic (bacterial) rich environments (Scherer and Sertiz, 1980).

Although REE distribution patterns in carbonates are poorly understood, theoretically, substitution of REE^{+3} for Ca^{+2} and Fe^{+2} could be expected. It has also been suggested that the REE's are adsorbed onto the surface of carbonate minerals rather than incorporated into the crystal structure (Haskin, et al., 1966). Most previous investigations have shown rather low REE concentrations in carbonate rocks (Haskin, et al., 1966; Jarvis, et al., 1975). McLennon, et al. (1979) found that the distribution of REE in carbonates of the Espanola Formation (Huronian) is similar to clastics of post-Archean age. Ce does not behave anomalously. In more extensive studies a distinct depletion of Ce was noted in marine carbonates. They suggest that this anomaly is inherited from sea water. HREE depletion and LREE enrichment is likely in carbonate minerals. HREE depletion may be explained by the tendency of these elements to form soluble complexes in solutions (Piper, 1974; Parekh, et al., 1977).

It has been demonstrated (Scherer and Seitz, 1980) that REE are partitioned differently by different phases of carbonate minerals. Scherer, et al. (1980) studied REE's in Pleistocene and Holocene corals. Their data show variations in distribution coefficients for both aragonite and magnesium calcite.

Therefore, it appears that carbonate phases must be treated independently when studying REE distribution patterns. Analysis of the carbonates of the NIF have been conducted by Haase (1979). This work indicates that the carbonates exhibit a solid-solution from ankerite to siderite. A detailed study of the effects of the carbonate components on REE patterns may explain the sporadic distributions found by previous investigators.

Clastic Sediments

The REE content of shales is strongly affected by parent lithology, local volcanism, weathering rates, and depositional environment (Goldberg, et al., 1966; Piper, 1974; Dypvik and Brunfeld, 1976). Weathered rocks are generally enriched in total REE compared with original unweathered rocks. Strong weathering of the source rocks and later reworking of the sediments result in consistent REE patterns over a large regional area. Conversely, rapid tectonic activity will result in variations in clay patterns. Measured abundances of REE in clay minerals indicate that they can be a significant sink for REE's primarily through adsorption processes (Roaldset, 1973). Therefore, REE patterns in shales are both the result of detrital or authigenic processes.

Effects of Metamorphism

The effects of metamorphism on sedimentary rocks must also be taken into consideration. It is generally accepted that REE distribution is not altered at least through the greenschist facies (Cullers, et al., 1974; Herrmann, et al., 1976; Menzies, et al., 1979). The most extensive study has been conducted by Ronov, et al. (1977). Their data show that in progressive regional metamorphism of sedimentary rocks, REE concentrations decrease by less than 10%. Ronov further suggests regional metamorphism is an open system only for the volatiles, to some extent sulfur, chlorine, boron, mercury and uranium, and to a very slight

extent the heavy lanthanides. Therefore, Ronov, et al. conclude the regional metamorphism is isochemical and does not distort primary chemical trends of sedimentation.

Sokoman Iron Formation

The most extensive study of a BIF was conducted by Fryer (1977b) on the Sokoman Iron Formation, Labrador, and its associated sediments. His primary observations are: 1) absolute REE abundances of the iron formation are much lower than the associated shales, 2) the iron formation shows a HREE and Eu enrichment while shales exhibit a HREE and Eu depletion compared to NASC, 3) REE patterns normalized to the average slate composite for the iron formation show no relationship to clastic sediments of the same age, and 4) within the formation, different REE abundance patterns can be correlated with sedimentary facies and mineralogy.

Fryer's (1977b) primary observations were as follows. The iron-silicate-carbonate facies show relatively little fractionation of the LREE compared to associated shales. HREE enrichment was noted with HREE preferentially incorporated into the "dark" silicates and siderite. The absolute REE abundance is inversely proportional to chert content, indicating that chert acts as a dilutant of trace elements. The oxide facies is enriched in the HREE relative to NASC, with enrichment of iron, although trace element patterns are widely variable. The Fe-rich oxide facies samples also show variable REE behavior. This led Fryer to conclude that REE's are adsorbed onto the surface of oxides rather than incorporated into the lattice. Variations are also attributed to: 1) differing rates of precipitation of scavenging iron hydrates, 2) changing pH, 3) post-depositional processes, and 4) a highly unstable chemical system. Therefore, Fryer suggests REE's adsorbed onto iron oxide hydrates abundances may have changed when incorporated into the crystal structure. He also concluded that

there is an increasing stability of REE in carbonate complexes with increasing atomic number associated with migration and concentration of iron during diagenesis. These results are consistent with petrographic interpretations of formation.

Summary of Constraints of REE Studies in Sediments

An experimental data base, such as exists for magmatic rock-forming minerals, is urgently needed in sedimentary and natural hydrothermal minerals. Morgan and Wandless (1980) have investigated hydrothermal mineral systems and suggest that the relative pattern in a hydrothermal mineral is strongly influenced by the respective sizes of major and trace cations. They further suggest that, for continental regions, the REE pattern in hydrothermal fluids may closely resemble the light REE-enriched character of crustal rocks, both igneous and sedimentary. If one is allowed great liberal extrapolation, any "exhalative" solutions associated with BIF environments could be expected to be different from the hydrothermal "exhalations" generated along mid-ocean ridges. For example, mixing of seawater with exhalations along mid-oceanic ridges will show REE patterns consistent with mantle derived material, while those generated with the formation of BIF's in restricted basins will be more typical of continental trace element compositions.

LOCATION AND SAMPLE DESCRIPTION

Core samples were taken from seven diamond drill holes during the Summer, 1980. All samples are from the Empire Mine located in Palmer, Michigan, operated by the Cleveland-Cliffs Iron Company (CCIC). All selected diamond drill holes fall approximately along two north-south lines for a distance of 1050 meters (Figure 3). For the purpose of this investigation, the drill holes are labelled alphabetically from north to south. Thirty-nine samples representative of the dominant lithologies and facies were analyzed for seven REE's using instrumental neutron activation analysis. Twelve carbonate samples were analyzed for major elements using an electron microprobe. Analytical methodology and sample descriptions are presented in Appendices A and B, respectively. Samples were selected from the following lithologic groups: carbonates, ores, chert, and clastics. Whenever possible, at least one lithologic sample was selected from each facies in order to develop stratigraphic control.

In addition, six samples of the underlying Siamo Slate were also analyzed for REE content. Data for the Siamo Slate is only available from two diamond drill holes.

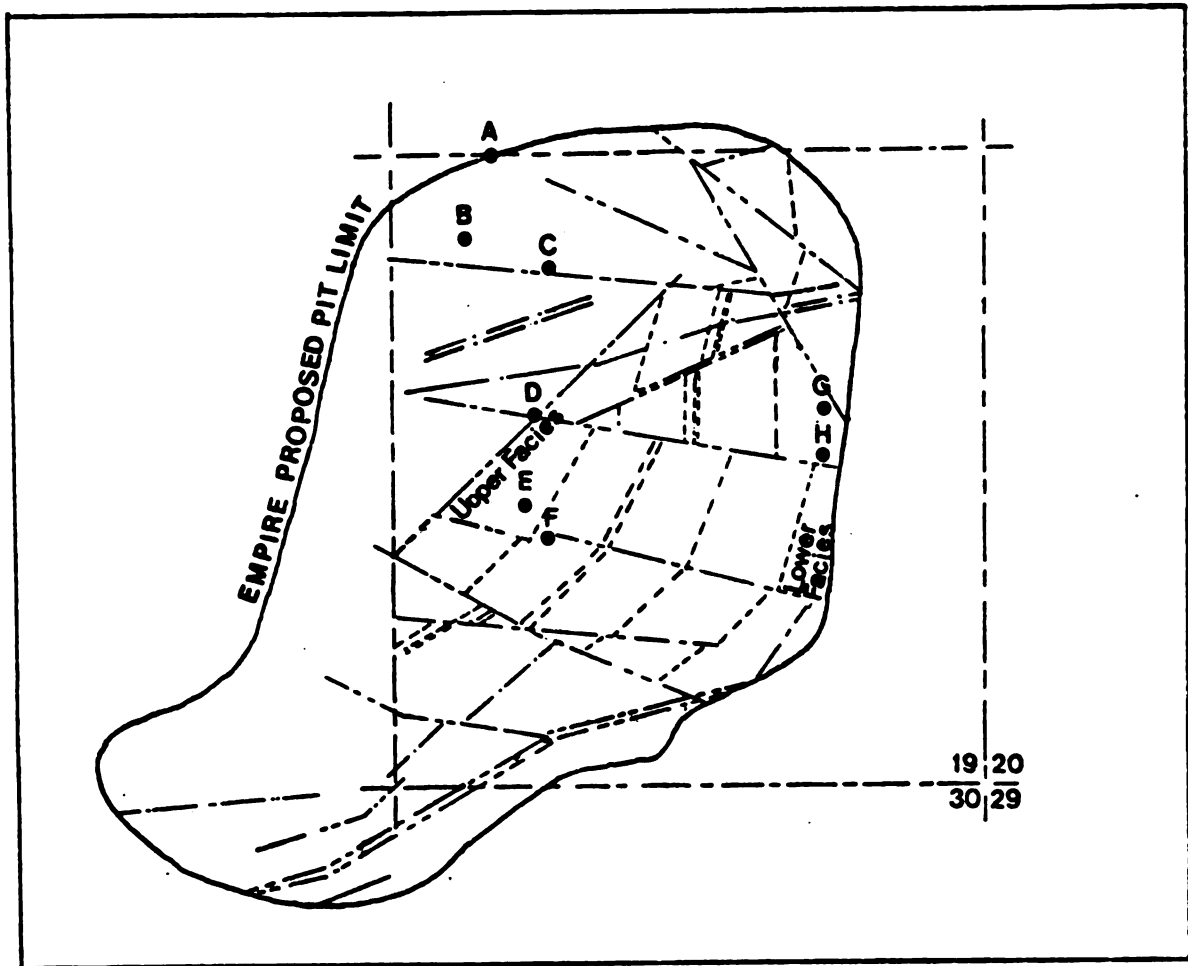


Figure 3. Study diamond drill hole locations, Empire Mine, sec 19, T47NR26W, Marquette District, Michigan.

1. Die folgenden Aussagen sind wahr oder falsch? Begründen Sie!
a) Die Funktion $f: \mathbb{R} \rightarrow \mathbb{R}$ ist durch $f(x) = x^2 + 1$ gegeben.

PETROLOGY

The dominant mineralogies of the samples collected at the Empire Mine consist of carbonates, chert, and magnetite with minor hematite, jasper, chlorite, and stilpnomelane. Samples are generally well banded with laminae varying from micro- to mesobands, while magnetite ore samples are massive. In places laminae have been disrupted by a series of post-depositional features including fractures, veins, and faults (Figure 4).

The major mineral/lithologic assemblages included in this study are: 1) carbonate with minor chert, 2) magnetite-carbonate-chert, 3) magnetite-silicate, 4) clastics interbedded with silicate, 5) clastics interbedded with carbonate-ore, 6) chert with minor carbonate, and 7) the underlying Siamo Slate. Magnetite is present to some extent in virtually every sample. A thorough discussion of the major lithologic groups is presented by Han (in Gair, 1975). Samples which contain one dominant mineralogy were chosen for this investigation (Appendix B).

Carbonates

Carbonate samples consist of alternating laminae of both meso- and microbands of chert and carbonate. Analysis was conducted on those samples which contained at least 70% carbonate and less than 5% magnetite based on hand sample and thin section examination (Appendix C). Carbonate bands contain small percentages of chert (Figure 5), while magnetite is predominant in the silicate rich laminae.

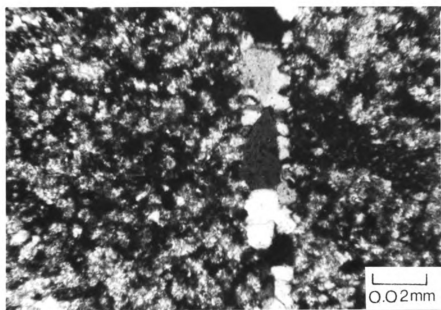


Figure 4. Fine grained, anhedral siderite matrix with minor chert. Note fracture filled with secondary quartz.

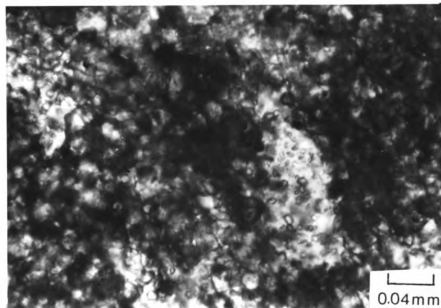


Figure 5. Typical siderite mosaic. Anhydrous, fine grained.

Generally, siderite is very fine to fine-grained (0.005 to 0.01 mm) anhedral equant crystals (Figure 6). Ankerite is coarser grained (0.01 to 0.05 mm) and ranges from anhedral to euhedral crystals. In most cases, ankerite is found coexisting with siderite in alternating laminae, or filling cross-cutting fractures with magnetite (Figure 7). Ankerite appears to be a diagenetic replacement of siderite. Often, it is associated with coarse grained recrystallized quartz. Two samples show minor oxidation.

Chert

Chert-rich samples chosen consist predominantly of quartz, with minor magnetite. Thin laminae rich in carbonate may be locally present. These samples consist of both microcrystalline quartz (0.002 to 0.01 mm) and minor recrystallized quartz (0.01 to 0.25 mm). Grains are anhedral forming an interlocking mosaic pattern. In carbonate laminae chert is scattered throughout the band. Minor magnetite is generally present as euhedral to subhedral crystals.

Magnetite

Representative samples of magnetite ore consist of magnetite coexisting with chert, or with chert and less than 10% carbonate. Samples are either massive with intergranular chert or iron-silicates or contain microbands of silicate and carbonate. Magnetite is generally euhedral to subhedral ranging in size from 0.1 to 0.5 mm (Figure 8). In the more massive samples, grains may become anhedral forming a mottled appearance. Coexisting carbonate and chert remain equant and anhedral and are sometimes enclosed by magnetite porphyroblasts. Han (1975) has identified ilmenite as the core of some porphyroblasts. Magnetite appears to replace both carbonates and chert (Figure 9). Hematite is present in minor amounts, generally enclosed in quartz or jasper and closely associated with magnetite.

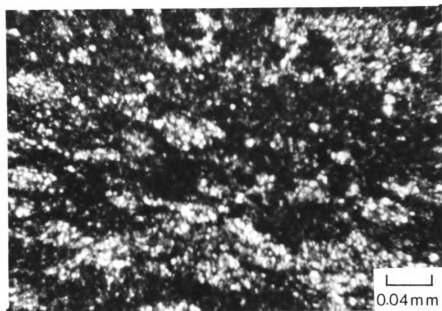


Figure 6. Carbonate-rich section with chert laminae and some intergranular chert.

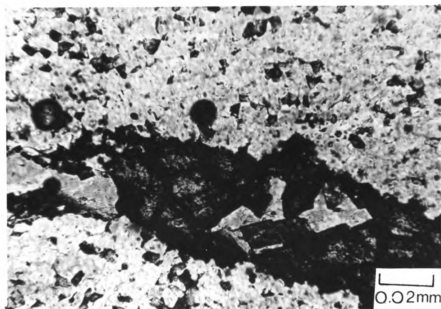


Figure 7. Typical siderite mosaic with minor chert. Note fracture partially filled with coarse grained anhedral ankerite.

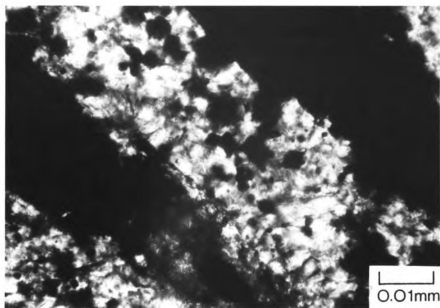


Figure 8. Magnetite ore in carbonate-chert matrix. Note some grains magnetite euhedral, others elongate.

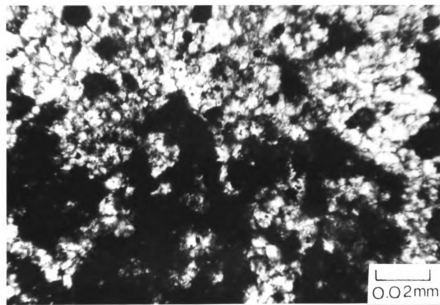


Figure 9. Magnetite ore replacing siderite with nonexisting chert.

Clastics

Clastic material was noted both as discrete layers or lenses or as scattered grains in the NIF. Microscopic examination indicates that this material consists predominantly of quartz (0.1 to 0.35 mm) and minor magnetite (0.05 to 0.15 mm). Only major clastic lenses were considered for chemical analysis in this study (Figure 10). Detrital quartz grains are poorly sorted, angular to subangular fragments comprising 60 to 70% of the sample, occasionally being rounded and moderately well sorted. Detrital magnetite consists of poorly sorted subhedral fragments. Two primary matrices are associated with clastic material: 1) carbonate with magnetite, and 2) iron silicates with minor magnetite. The carbonate-magnetite matrix is generally associated with carbonate or magnetite laminae devoid of clastics. Carbonate is anhedral and fine grained, while magnetite is subhedral to euhedral and medium grained. Iron silicate matrices consist of chlorite and stilpnomelane. Minnesotaite has also been reported (Han, 1975; Haase, 1979).

Bedding is lacking in this lithologic grouping, although occasionally large quartz fragments are concentrated in discrete layers. Stilpnomelane may comprise up to 25% of the sample. It exists as small blades, generally at random orientations or in rosette structures. In one more altered sample (Figure 11), stilpnomelane blades penetrate quartz grains. This sample illustrates a more advanced degree of oxidation than most clastic samples with a large amount of alteration of magnetite to hematite. Chlorite matrix is either platy or bladed, at random orientations, and generally concentrated into patches.

Iron Silicates

Quartz and magnetite are occasionally associated with minor silicates in both carbonate and chert samples (Figure 12). Common habits of chlorite and stilpnomelane are similar to those described above. Haase has also reported

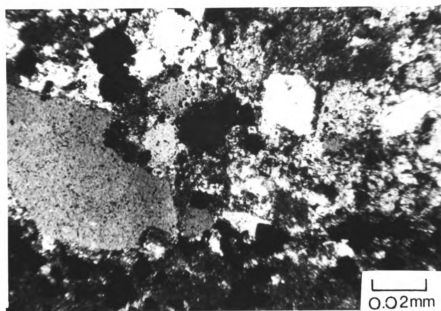


Figure 10. Interformational clastic lens. Predominantly poorly sorted detrital quartz in carbonate matrix.

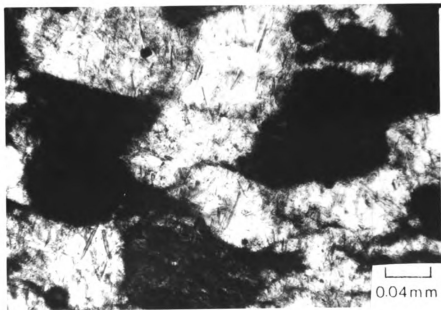


Figure 11. Detrital quartz grains. Note bladed stilpnomelane penetrating quartz.

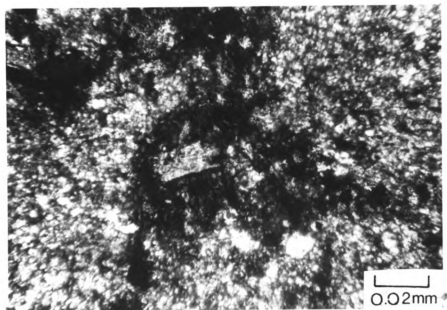


Figure 12. Bladed/platy iron-silicates in chert-carbonate matrix with minor magnetite.

minnesotaite, biotite, and riebeckite. Stilpnomelane may occur as an intergrowth with chlorite such that positive optical identification cannot be made. Iron silicates are assumed to be an alteration of Fe-rich muds (Han, 1975).

Siamo Slate

Samples of slate were selected from the upper unit of the Siamo formation. The upper portions are primarily massive with occasional mesobands of chert or coarse grained clastic material. Samples of both the massive slate and coarse grained laminae were analyzed for REE concentrations (Appendix D).

The massive unit can be classified as a graywacke. It is comprised of 45 to 60% detrital quartz grains with minor plagioclase, granular magnetite, and discrete chloritic concentrations which are interpreted to be mafic interclasts (Figure 13). The matrix is primarily chlorite, although traces of biotite, muscovite, and sericite are present. Samples vary from well sorted and well rounded quartz grains (0.2 to 0.35 mm) to moderately sorted smaller subangular quartz grains (0.1 to 0.06 mm). Evidence of strain and compaction are illustrated by a small portion of quartz fragments. A trace of cryptocrystalline rounded chert fragments were also noted. Plagioclase grains are anhedral and serrated with alteration to sericite along twin planes. The composition ranges from $Ab_{92}An_{05}$ to $Ab_{100}An_0$, although this is based on a limited number of grains. Mafic clasts are well rounded with slightly serrated edges and are heavily altered composed predominantly of chlorite, biotite, and possibly epidote (Figure 14). Alignment of the platy minerals is marked and different from that of the chlorite matrix. The chlorite matrix is very fine grained and fibrous showing only limited lineation of elongate minerals. Chlorite may penetrate quartz grains, and this penetration shows a definite orientation.

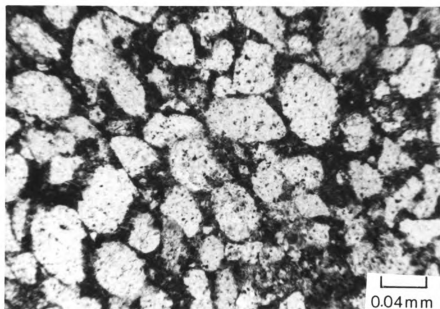


Figure 13. Typical quartzite of Siamo Slate. Note moderately well sorted and rounding of quartzite grains in chlorite matrix.

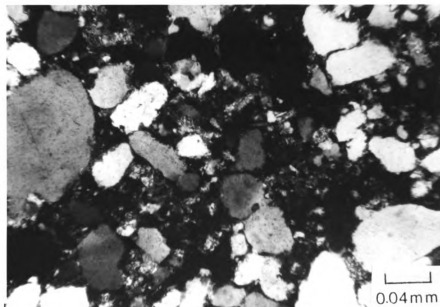


Figure 14. Typical graywacke of Siamo Slate. Poorly sorted subrounded to subangular detrital quartz in chlorite matrix.

The coarse grained clastic lenses in the Siamo are distinguished by a higher percentage of detrital quartz (70–80%) approaching a quartzite composition. They are more poorly sorted, and contain higher percentages of mafic interclasts (5 to 10%) and cryptocrystalline quartz (Figure 15). Muscovite is also higher in these samples (approximately 1%). Although lamination is not apparent, chlorite is concentrated in zones.

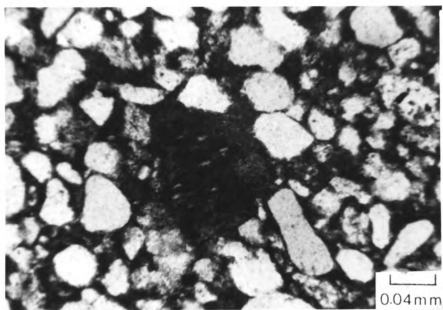


Figure 15a. Mafic fragments in Siamite Slate. Note variation in grain size and orientation from surrounding chlorite matrix.

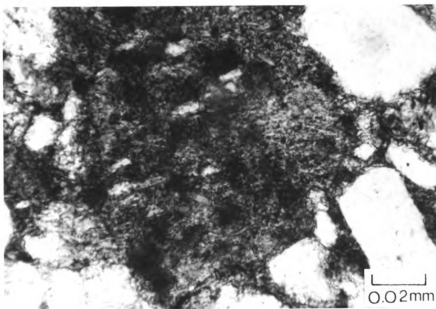


Figure 15b. Same as Figure 15a under higher magnification.

MAJOR ELEMENT GEOCHEMISTRY

Whole rock analysis for total iron content (reported as percent Fe_2O_3) was determined for carbonate, chert, and magnetite-rich samples using X-ray fluorescence. Ca, Fe, and Mg were determined for the carbonates by electron microprobe analysis (Appendix A).

Analysis of carbonate grains indicate that although both ankerite and siderite are present in the Empire samples, siderite is predominant. This is in agreement with Han (1972) and Haase (1979). In some cases, ankerite coexists with siderite. Chemical analysis are presented in Table 1. Siderite consists of $\text{Fe}_{.76-.91}\text{Mg}_{.03-.21}\text{Ca}_{.004-.04}\text{CO}_3$ and ankerite of $\text{Fe}_{.03-.09}\text{Mg}_{.37-.46}\text{Ca}_{.39-.55}\text{CO}_3$. No intermediate members appear to be present.

Total iron content, reported as Fe_2O_3 is presented in Table 2. Large variations are seen in all samples. Higher concentrations in chert rich samples are due primarily to carbonate contamination. Similarities in the variations of concentrations in magnetites and carbonates is attributed to iron present in the siderite lattice. Therefore, iron content does not appear to be a good indicator of ore content. Trace element data presented in the following sections appears to be more chemically diagnostic of percent ore present.

Table 1. Microprobe analyses of carbonates.

Sample Number	CaCO ₃		MgCO ₃		FeCO ₃	
	Average	Range	Average	Range	Average	Range
A/517.5	(11) 1.43	1.19-1.62	15.13	19.44-11.67	83.42	78.99-86.87
A/582	(5) 2.33	2.15-2.59	10.86	9.12-11.87	86.65	85.79-88.3
B/278.5	(7) 0.41	.08-.68	9.98	9.63-10.77	89.61	89.36-90.03
C/41	(14) 53.33	50.20-57.24	43.49	38.17-48.15	3.32	0.66-6.03
	(3) 3.43	3.09-3.77	4.52	2.18-6.86	92.42	89.97-94.88
C/1042	(8) 55.06	49.19-57.96	41.39	34.21-48.44	2.57	0.61-5.97
C/1386	(8) 0.93	0.29-1.51	19.17	16.15-27.10	79.90	72.50-82.01
D/126	(8) 53.06	49.12-57.90	37.24	34.08-49.54	9.15	1.10-16.25
	(8) 2.46	1.78-3.23	3.36	3.00-3.62	94.17	93.34-94.73
D/878.5	(12) 0.54	0.15-1.27	3.15	0.78-7.73	96.32	91.89-98.29
D/1210	(10) 39.64	32.95-45.82	45.86	39.35-50.13	14.49	5.97-25.72
F/8	(8) 0.76	0.29-2.17	3.38	0.38-8.70	95.86	90.80-99.29
G/578.5	(5) 0.81	0.44-1.02	14.07	12.25-14.28	85.09	82.56-87.31
H/448.5	(7) 0.75	0.31-0.98	8.64	6.73-12.41	92.51	87.65-95.42
H/805.5	(9) 1.21	0.74-1.55	21.15	19.35-22.64	77.67	76.52-79.22

Table 2. Total iron content reported as percent Fe_2O_3 .

Carbonates		Chert		Ores	
Sample Number	Fe_2O_3	Sample Number	Fe_2O_3	Sample Number	Fe_2O_3
A/517.5	32.99	D/88.2	25.64	C/87	27.96
A/582	26.01	D/752	9.24	C/582	36.36
B/278.5	34.80	D/958	12.63	C/929	37.96
C/41	27.26	F/76	33.91	C/1042	38.61
C/1386	32.28	F/225	5.98	D/518	49.23
D/126	24.01	F/297	29.31	D/733.5	26.97
D/878.5	34.79	G/845	17.37	E/70.5	22.34
D/1210	11.80			F/695	43.81
F/8	32.75			F/1119	25.02
G/578.5	28.68			G/761.5	39.31
H/448.5	29.34			H/710.5	22.01
H/805.5	31.02			H/849.5	37.48

TRACE ELEMENT GEOCHEMISTRY

The REE's (La, Ce, Sm, Eu, Tb, Yb, and Lu), thorium, and chromium of samples from the NIF and Siamo Slate were determined by nondestructive instrumental activation analysis. Concentrations, measured in ppm compared against liquid and U.S.G.S. rock standards (see Appendix A), are presented in Table 3. It is standard procedure to normalize REE concentrations to chondrite values or to the North American Shale Composite (NASC) (Haskin, et al., 1968). For simplicity, values quoted in this investigation will be chondrite normalized unless otherwise stated.

Absolute concentrations of REE vary with lithology, but all rock types show a marked fractionation of the LREE. Overall variations with respect to Eu and Ce behavior vary between lithologic groups although all show an Eu depletion compared to chondrite. LREE to HREE ratios and Eu observed to Eu predicted are presented in Table 4.

Carbonates

Twelve carbonate samples from the Empire Mine were analyzed. Chondrite normalized values are plotted in Figure 16a. The carbonate sediments exhibit an average LREE value of 20 times chondrite with a range of values from approximately 4 to 40x. HREE are enriched an average of 2.5 times chondrite, with values ranging from 1 to 4x. The highest abundances are observed in samples containing considerable amounts of magnetite, iron silicates, or hematite. Ankerite samples are depleted compared to siderite and show a substantially smaller enrichment of the LREE. All samples exhibit an europium

Table 3. Absolute Rare Earth Element concentration (ppm).

Sample Number	CARBONATES									
	La	Ce	Sm	Eu	Tb	Yb	Lu	Th	Cr	
A/517.5	6.30	7.12	0.64	0.19	0.13	0.47	0.04	1.44	3.94	
A/582	2.62	4.19	0.45	0.14	0.16	0.34	0.24	1.77	6.67	
B/278.5	4.07	9.53	0.58	0.11	0.22	0.73	0.06	0.53	8.68	
C/41	5.91	13.29	0.69	0.14	0.13	0.49	0.06	1.70	6.59	
C/1386	7.14	13.24	0.85	0.18	0.09	0.53	0.09	3.93	9.87	
D/126	2.90	4.37	0.24	0.08	0.14	0.39	0.02	1.63	8.00	
D/878.5	10.57	18.62	1.46	0.32	0.21	1.13	0.08	8.27	12.29	
D/1210	3.13	4.36	0.35	0.10	0.09	0.48	0.05	1.87	31.09	
F/8	5.82	6.23	0.54	0.16	0.06	0.46	0.04	2.08	6.10	
G/578.5	11.92	16.59	1.86	0.56	0.45	1.10	0.11	3.41	11.30	
H/448.5	8.56	19.47	1.18	0.28	0.19	0.69	0.08	4.59	6.60	
H/805.5	10.64	16.24	1.16	0.29	0.25	0.75	0.09	4.08	11.85	
Average	6.59	11.10	.833	.21	.18	.63	0.63	2.94	8.35	
St. Dev.	3.27	5.82	.487	.13	.10	.26	.027	2.09	2.64	

Table 3 (Continued).

Sample Number	CHERT									
	La	Ce	Sm	Eu	Tb	Yb	Lu	Th	Cr	
D/882	4.79	2.49	0.56	0.14	0.13	0.43	0.04	0.68	6.82	
D/752	3.79	3.62	1.73	0.08	0.14	0.23	0.03	1.31	4.57	
D/958	2.55	1.26	1.46	0.07	0.19	0.20	0.03	0.81	4.94	
F/76	6.06	10.99	0.67	0.18	0.23	0.46	0.04	3.32	5.25	
F/225	0.61	1.63	0.10	0.03	0.15	0.15	0.05	0.47	4.58	
F/297	5.93	12.19	0.69	0.13	0.12	0.37	0.06	3.86	5.81	
G/845	6.43	4.40	0.93	0.23	0.24	0.51	0.08	3.62	9.69	
Average	4.31	5.23	0.50	0.12	0.16	0.15	0.05	2.01	5.95	
St. Dev.	2.14	4.49	0.29	0.69	0.34	0.02	0.02	1.52	1.82	

Table 3 (Continued).

Sample Number	ORE								
	La	Ce	Sm	Eu	Tb	Yb	Lu	Th	Cr
C/87	6.50	9.80	0.73	0.21	0.14	0.76	0.05	1.88	7.18
C/582	5.72	17.01	0.84	0.08	0.25	0.82	0.08	3.69	12.73
C/929	8.23	17.09	1.27	0.25	0.24	0.75	0.05	5.34	17.02
C/1042	6.57	12.58	0.79	0.16	0.11	0.54	0.06	3.21	10.12
D/518	5.79	11.11	0.68	0.10	0.05	0.52	0.04	1.70	7.81
D/733.5	5.70	10.62	0.61	0.15	0.09	0.50	0.06	3.79	6.32
E/70.5	3.63	11.53	0.66	0.14	0.05	0.55	0.06	2.37	7.12
F/695	6.39	11.87	0.72	0.20	0.11	0.70	0.06	6.95	9.04
F/1119	31.27	59.82	4.29	0.66	0.39	2.66	0.26	40.67	23.26
G/761.5	12.24	20.02	1.23	0.22	0.18	0.93	0.08	10.04	15.02
H/710.5	20.03	30.77	2.64	0.47	0.25	1.70	0.17	16.76	18.29
H/849.5	10.42	19.39	1.30	0.15	0.18	0.93	0.13	4.05	16.73
Average	10.21	19.30	1.31	0.23	0.17	0.94	0.09	8.03	12.92
St. Dev.	7.94	14.07	1.09	0.16	0.10	0.63	0.06	11.14	5.36

Table 3 (Continued).

Sample Number	CLASTICS									
	La	Ce	Sm	Eu	Tb	Yb	Lu	Th	Cr	
C/412.8	23.22	35.62	3.10	0.25	0.50	1.82	0.24	25.25	13.76	
E/595.5	5.13	11.43	0.63	0.14	0.08	0.67	0.03	1.98	6.94	
E/649.5	9.89	22.21	1.32	0.36	0.43	1.24	0.16	6.50	9.04	
E/1126.5	80.05	111.46	7.37	0.95	1.92	5.06	0.51	64.94	27.20	
F/419	6.31	10.25	0.68	0.32	0.26	0.73	0.07	3.91	6.57	
F/585.5	5.13	11.43	0.63	0.15	0.08	0.67	0.03	1.98	9.36	
G/285.5	42.79	71.32	4.27	0.39	0.94	2.68	0.23	30.60	12.92	
H/593	41.69	87.89	4.64	0.54	0.86	2.87	0.31	31.24	31.36	
Average	27.15	45.00	2.88	0.40	0.64	1.99	0.20	21.90	14.64	
St. Dev.	26.31	38.96	2.42	0.25	0.60	1.51	0.15	21.07	9.45	

Table 3 (Continued).

Sample Number	SHALE									
	La	Ce	Sm	Eu	Tb	Yb	Lu	Th	Cr	
G/923A	5.65	10.57	0.83	0.66	0.73	0.54	0.07	12.77	19.54	
G/923B	24.99	39.75	3.79	0.66	0.73	2.08	0.31	12.77	67.32	
H/865.5	6.13	11.23	0.90	0.18	0.26	0.57	0.05	3.49	14.19	
H/867.5	33.95	68.44	4.32	1.00	0.75	2.61	0.30	14.23	56.48	
H/906	5.53	14.57	0.49	0.12	0.07	0.35	0.02	2.39	7.87	
H/916	10.28	24.48	1.28	0.37	0.19	0.85	0.12	12.46	31.87	
Quartzite Average	29.47	54.10	4.09	0.83	0.74	2.35	0.31	13.5	61.9	
St. Dev.	6.34	20.29	0.42	0.24	0.01	0.37	0.01	1.03	7.67	
Graywacke Average	6.90	15.21	0.88	0.22	0.17	0.58	0.07	8.68	18.22	
St. Dev.	2.27	6.42	0.32	0.11	0.08	0.21	0.04	6.83	9.93	

Table 4. Rare Earth Element ratios.

Sample Number	LREE/HREE	LREE/HREE	Eu/Eu	Eu/Eu
	(chondrite normalized)	(shale normalized)	(chondrite normalized)	(shale normalized)
Carbonates				
A/517.5	4.882	1.048	0.84514	1.23104
A/582	2.418	0.572	0.73463	1.07051
B/278.2	2.612	0.580	0.43847	0.63868
C/41	5.276	1.119	0.59204	0.86273
C/1386	5.738	1.192	0.74905	1.09115
D/126	2.459	0.533	0.66744	0.97245
D/878.5	4.912	1.081	0.69999	1.01969
D/1210	2.831	0.600	0.75208	1.09522
F/8	5.829	1.197	1.03132	1.50240
G/578.5	3.564	0.832	0.80855	1.17782
H/448.5	4.047	1.210	0.72983	1.06321
H/805.5	4.874	1.048	0.69775	0.86273
Chert				
D/88.2	3.274	0.733	0.68056	0.99158
D/752	3.455	0.738	0.56291	0.81990
D/958	2.791	0.612	0.64163	0.93473
F/76	4.129	0.911	0.64205	0.93530
F/225	0.786	0.179	0.43808	0.63884
F/297	5.778	1.223	0.56489	0.82272
G/845	2.960	0.692	0.94691	0.65005
Ore				
C/87	4.227	0.905	0.83479	1.21594
C/582	3.509	0.771	0.23867	0.34770
C/929	4.975	1.136	0.57409	0.83619
C/1042	5.668	1.204	0.65381	0.95253
D/518	7.011	1.460	0.58759	0.85567
D/733.5	5.295	1.098	0.77862	1.13437
E/70.5	4.975	1.072	0.83884	1.22207
F/695	4.843	1.107	0.86961	1.26666
F/1119	6.375	1.372	0.57262	0.83403
G/761.5	6.152	1.286	0.56802	0.82735
H/710.5	5.858	1.262	0.65363	0.95210
H/849.5	4.942	1.047	0.37314	0.54364

Table 4 (Continued).

Sample Number	LREE/HREE	LREE/HREE	Eu/Eu	Eu/Eu
	(chondrite normalized)	(shale normalized)	(chondrite normalized)	(shale normalized)
Clastics				
C/412.8	4.776	1.049	0.24793	0.36113
E/595.5	5.395	1.146	0.79254	1.15466
E/649.5	3.117	0.681	0.66336	0.96621
E/1126.5	5.052	1.074	0.33776	0.49197
F/419	3.093	0.668	1.08514	1.58052
F/585.5	5.196	1.109	0.61366	0.89390
G/285.5	5.834	1.251	0.25314	0.36872
H/593	6.030	1.285	0.34161	0.49756
Siamu				
G/923A	4.046	0.915	0.76630	1.11622
G/923B	4.358	0.963	0.50460	0.73503
H/865.5	3.685	0.847	0.50624	0.73750
H/867.5	5.416	1.179	0.68700	1.00071
H/906	5.412	1.935	0.78405	1.14197
H/916	5.586	1.178	0.91371	1.33077

depletion ($\text{Eu}/\text{Eu}^* = 0.84\text{-}0.43$). Cerium values range from slightly negative to slightly positive, while the average shows no anomalous activity.

Normalized to the North American Shale Composite, carbonate samples exhibit an overall depletion compared to the average shale (Figure 17b). Generally, ankerite is HREE enriched, while siderite is HREE depleted, to slightly enriched. Compared to NASC, both Eu and Ce are anomalous varying from slightly negative to slightly positive. The average of the carbonates exhibit a slight negative Ce and slight positive Eu anomaly.

Chromium values in carbonates are relatively constant. Values range from 11.85 to 3.94 ppm. One anomalous sample has a value of 31.09 ppm. Omitting this sample, the carbonates show a mean chromium value of 8.35 ppm (standard deviation = 2.69). Thorium values are constant with a mean of 2.94 (standard deviation = 2.09).

Cherts

This group may be divided into two classifications: 1) chert (1 sample), and 2) chert-carbonate (6 samples). Both trace element and Fe concentrations are substantially lower in the chert sample. Chert has an Fe value of 6% Fe_2O_3 , while chert-carbonate have an average of 18.33%. All samples show an enrichment compared to chondrite values. Carbonate-chert LREE vary from 8 to 10 times while average cherts are approximately 1.5x (Figure 16b). HREE values vary from comparable to chondrite to 3 times enriched. LREE are 3 to 5 times enriched over HREE. Cerium anomalies are variable for chert-carbonate and positive for chert. All europium values are negative.

NASC normalized values are depleted compared to the average shale (Figure 17b). Samples show a HREE enrichment or values comparable to LREE. Cerium shows no anomaly to negative behavior, while europium does not act anomalously.

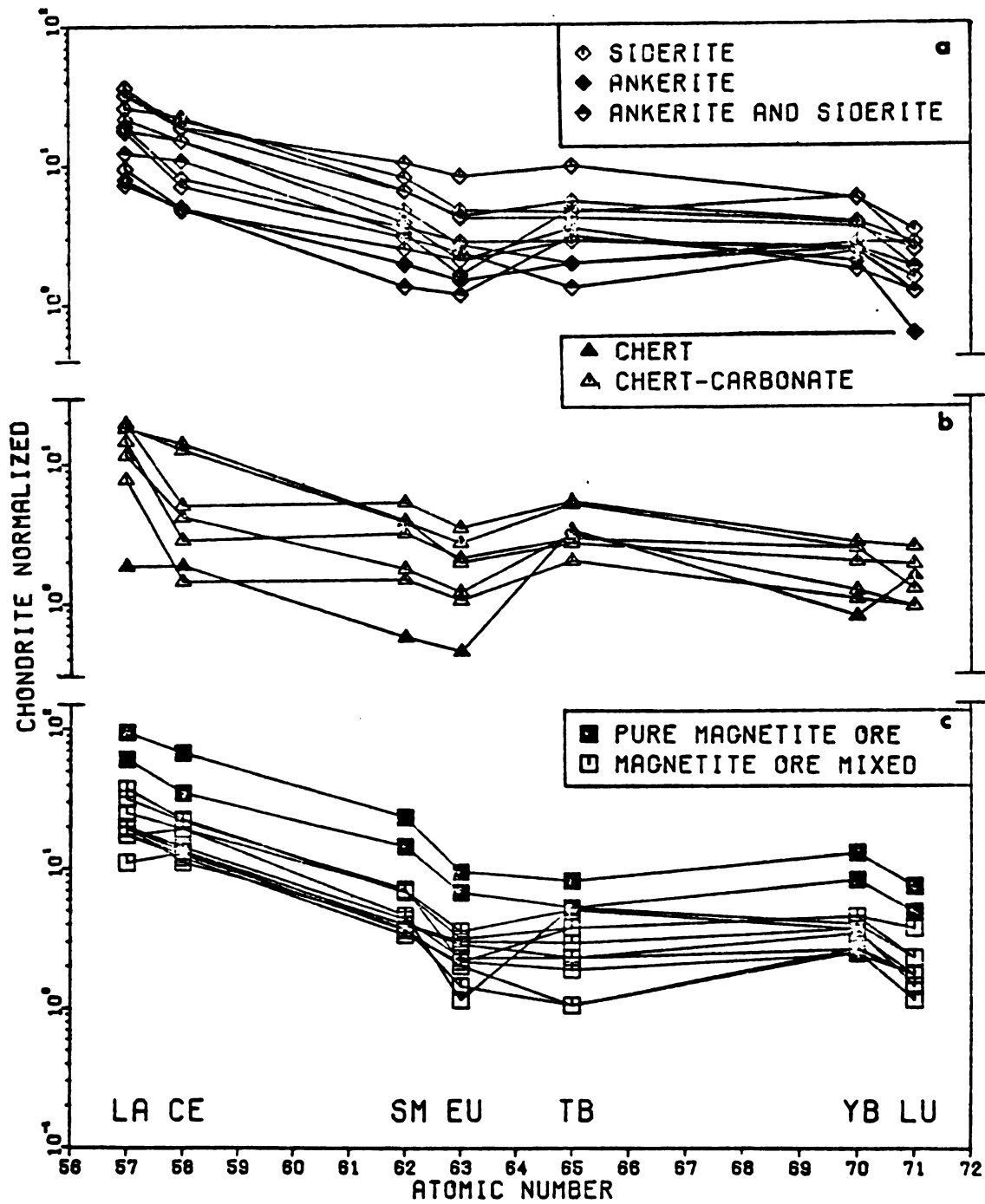


Figure 16. Chondrite normalized REE abundances of: a) carbonates, b) cherts, c) magnetite ores, d) clastic interbeds, and 3) Siamu Slate.

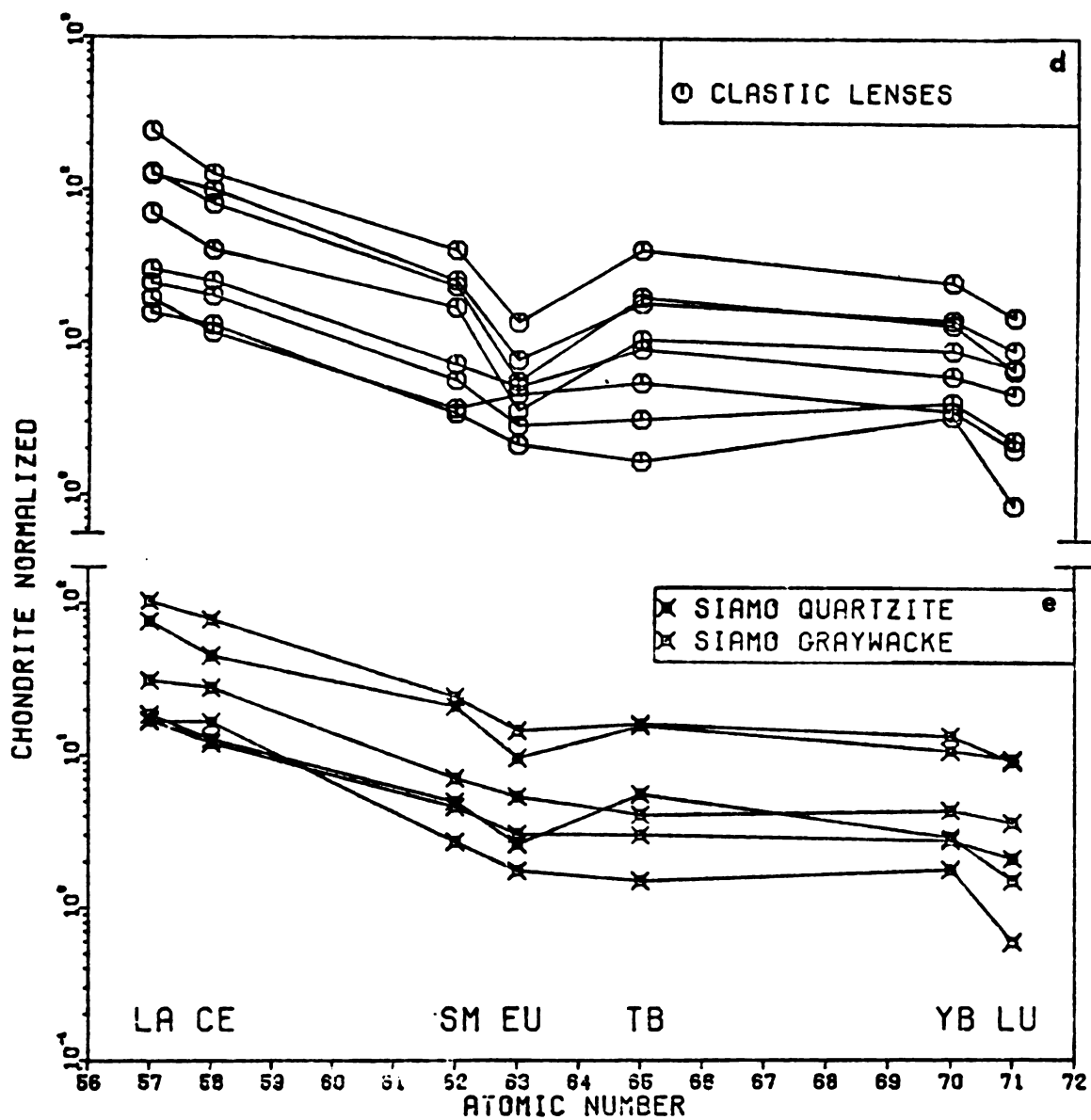


Figure 16 (continued).

Chromium and thorium exhibit average values of 5.95 ppm (standard deviation = 1.828) and 2.01 ppm (standard deviation = 1.52), respectively, showing minimal variation between samples. Chromium values are approximately one half those of carbonates and may be used to differentiate these rock types.

Magnetite Ores

Twelve ore samples were analyzed. Ores from the Empire exhibit extreme REE enrichment trends up to a factor of 100 times chondrite values for LREE with a 20 to 100 range (Figure 16c). Average LREE enrichment is 22 and HREE enrichment 15 times chondrite. A marked Eu depletion is found in all samples and variation is seen in Ce behavior. A slight Yb enrichment is found in some samples. Both hand sample and thin section examination revealed samples with lower concentrations contain higher proportions of carbonate and/or chert.

Ore samples are depleted compared to NASC although highest concentrations approach that of the average shale (Figure 17c). The overall trends are relatively flat. Cerium has normal to slightly enriched abundances; Eu varies from positive to negative, and an Lu depletion is evident. Some samples exhibit slight LREE enrichment.

Average thorium values are 8.03 ppm (standard deviation = 11.14). Chromium values range from 23.26 to 6.32 with average values of 12.92 (standard deviation = 5.36) and are correlative to magnetite content. Chromium does not directly correlate to total rock Fe_2O_3 content because of the presence of siderite (up to 48 mole % Fe) and iron silicates which are Cr depleted compared to magnetite.

Clastic Interbeds

Eight samples of clastic layers collected at the Empire Mine show similar, but significantly enriched, distribution patterns to carbonates and cherts

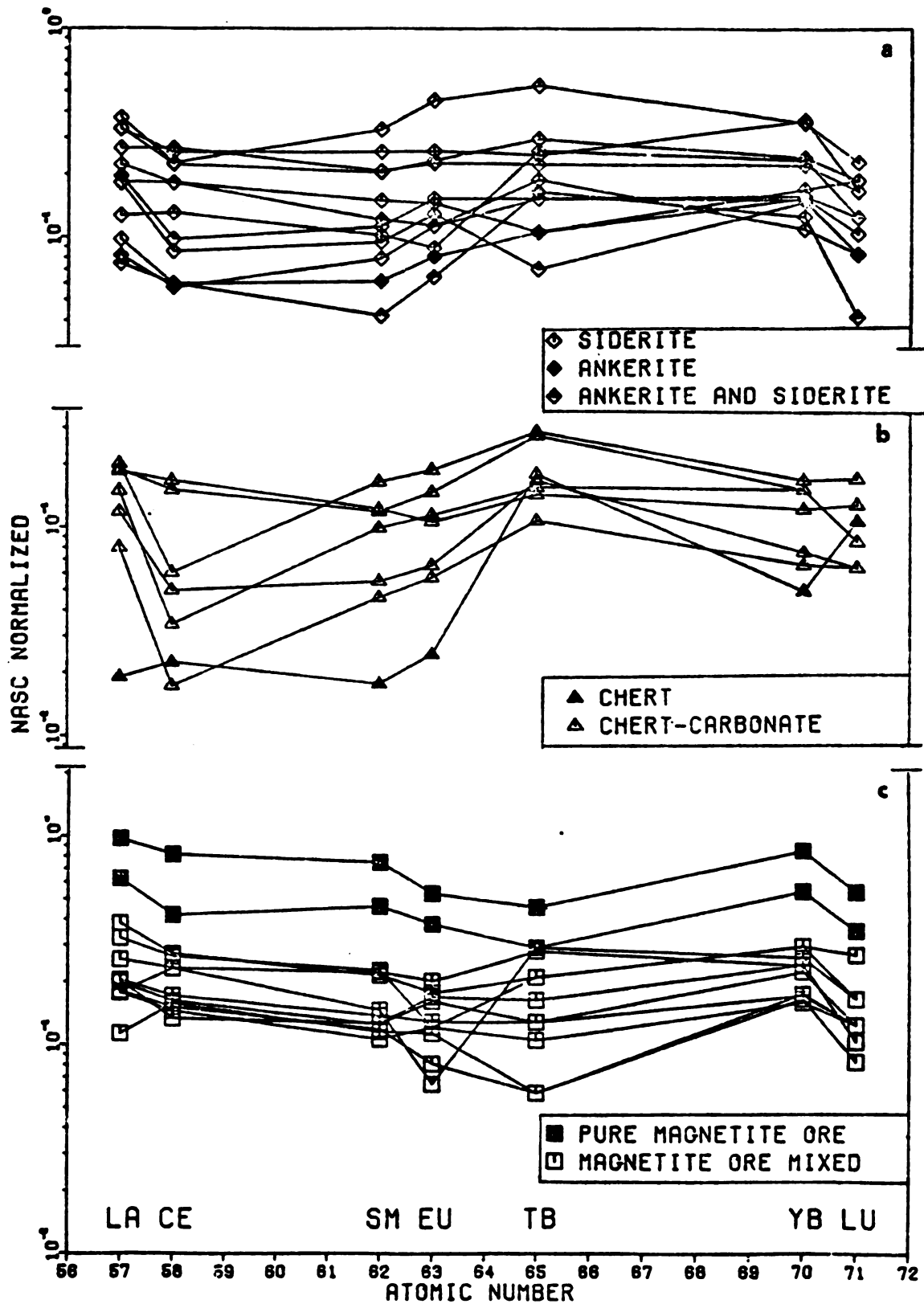


Figure 17. NASC normalized REE abundances of: a) carbonates, b) cherts, c) magnetite ores, d) clastic interbeds, and e) Siamu Slate.

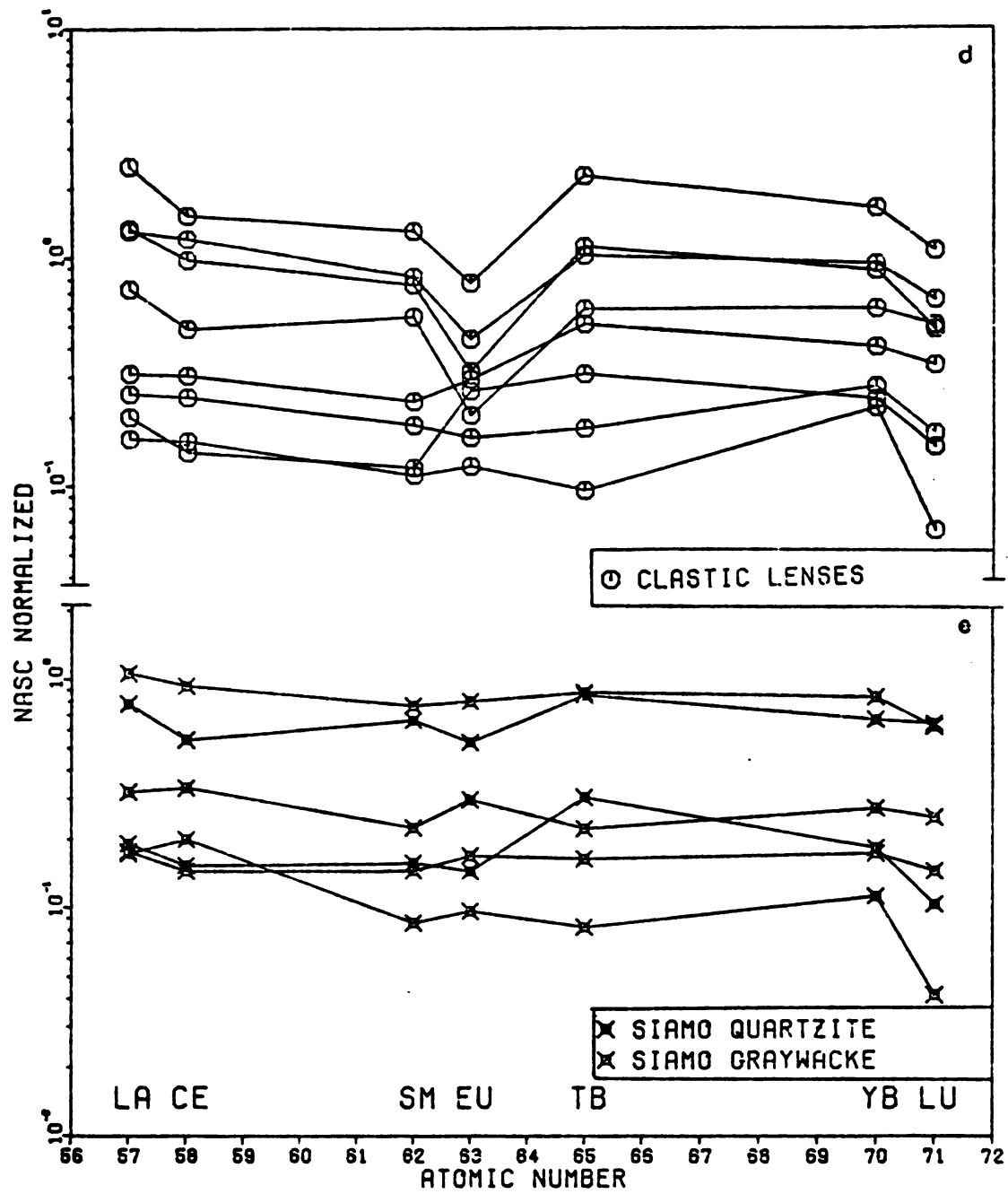


Figure 17 (continued).

(Figure 16d). A LREE enrichment of as much as 300 times chondrite and HREE enrichment between 2 and 20 times chondrite normalization can be seen. Average values of enrichment are 15 (HREE) and 50 (LREE). Samples show a marked Eu negative anomaly but lack a cerium anomaly.

The REE abundances in the clastics vary from enriched to depleted with respect to NASC (Figure 17d). A slight LREE enrichment is noted. No cerium anomaly is present. In individual clastic samples Eu does not act anomalously, or shows negative values, although the average value indicate a distinct Eu depletion relative to adjacent REE's.

Chromium and thorium concentrations show a wide range of variation significantly higher than the chemical precipitates. Average chromium concentrations are 21.90 ppm (standard deviation = 21.07) and thorium concentrations of 14.64 ppm (standard deviation = 9.45).

Siamo Slate

Chondrite normalized values of the Siamo Slate yield two distinctive patterns (Figure 16e). Both groups show a LREE enrichment of 20 to 100 times chondrite and HREE enrichment of 11 to 20x. The two groups have no cerium anomaly. They may be distinguished by the extent of the Eu anomaly. The first group corresponds to quartzite samples and possesses a marked negative Eu anomaly. The graywackes show only slightly anomalous Eu behavior.

Normalized to NASC (Figure 17e), all samples show distributions similar to the shale composite. Concentrations range from equal to NASC to 0.2 times depleted. Some samples exhibit a slight HREE depletion. Quartzites have a slight negative and negative Ce and Eu anomaly, respectively. Graywackes lack, or have slightly positive Ce and Eu anomalies. A composite of Siamo Slate normalized to NASC has an average value of approximately 0.5 depletion, lacks both Ce and Eu anomalies and shows a slight HREE depletion.

Quartzite samples of the Siamo have an average Cr of 61.90 (standard deviation = 7.66) and thorium values of 13.50 (standard deviation = 1.032). The graywackes show an average Cr of 18.23 (standard deviation = 9.93) and Th of 8.68 ppm (standard deviation = 6.83). Both groups show a substantial range of variation compared to the chemical precipitates.

DISCUSSION

REE data may be used as evidence to interpret the formation of extensive iron-rich deposits. Data from the Empire will be used to evaluate the controls on the distribution of REE and infer the depositional parameters of the NIF as well as possible post-depositional alteration. Comparisons are drawn to other iron formations, specifically, the Sokoman (Fryer, 1977b), the Gunflint and Vulcan (Slaughter, et al., 1981), and Algoma-type iron formations summarized by Graf (1978).

The overall distribution of REE's for the average chemical sediments and clastics have patterns which are, in general, intuitively expected. These patterns, normalized to chondrite concentrations (Figure 18), are similar with LREE enrichment and small Eu depletions. With decreasing REE abundance, the patterns of lithologies analyzed are subdued replicas as follows: clastics - Siamo slate - "ores" -carbonate facies - chert. This subparallel order is maintained for NASC normalized averages (Figure 19). The only noteworthy Eu depletion compared to NASC occurs in the clastic lenses. The similarity between the detrital patterns (clastic lenses and Siamo) and the chemical sediment averaged patterns is noteworthy.

The prime difficulty in any interpretation of REE patterns in Proterozoic BIF's is rooted in the fact that one cannot be sure if the analyzed specimens or mineral separates are pure authigenic phases. It is clear that all Precambrian BIF have undergone post authigenic changes to various extents.

There are several controls which determine the abundance of REE's in chemical sediments and clastic rocks. These can be broadly subdivided into primary and secondary factors, i.e., depositional and authigenic REE uptake

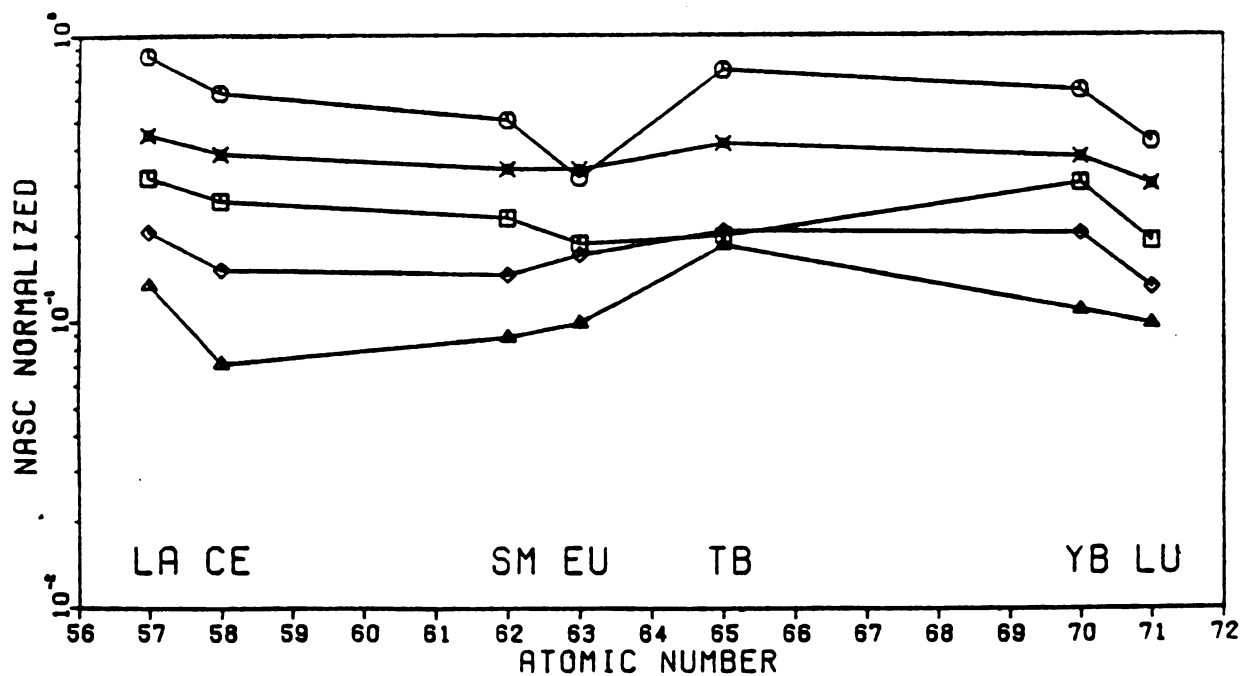
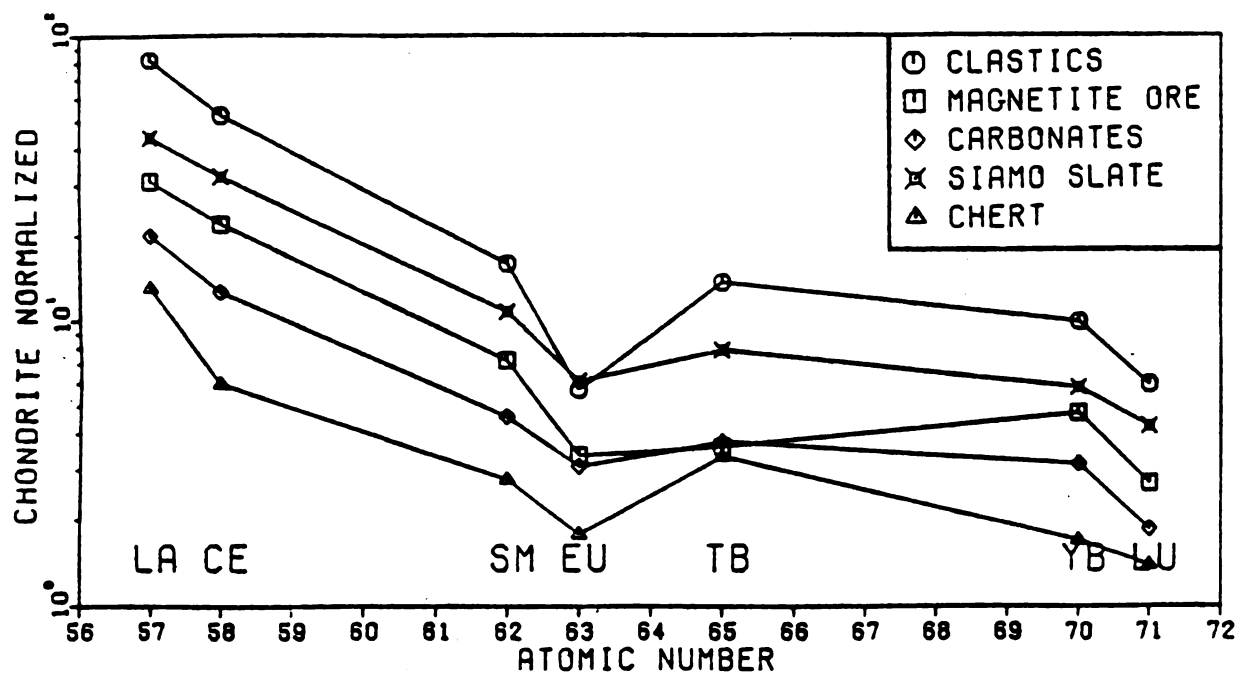


Figure 18. Average REE concentrations for chemical sediments and associated clastics normalized to chondrite values.

Figure 19. Average REE concentrations for chemical sediments and associated clastics normalized to NASC.

which represent the depositional environment such as source area (clastics) and solution; and those post depositional factors which may act to modify the primary REE abundances and ratios. It is common practice in igneous systems to use whole rock REE analysis to propose constraints on the crystallization sequence and nature of the source material. This is possible because there is enough of a data base available for coexisting minerals in igneous systems to permit such modelling. There are very few systematic laboratory studies on sedimentary systems. Therefore, most investigations are of an empirical nature based on untested hypotheses. For quantitative interpretation of REE abundances, an experimental data base similar to that existing for magmatic rock forming minerals is urgently needed.

The discussion which follows cannot address quantitative modelling of the distribution patterns due to the wide number of parameters controlling REE partitioning. Instead, the observations are incorporated into a somewhat qualitative theoretical framework based on the "state of the art" for sedimentary REE investigations. The discussion will focus on the inter- and intra-group REE abundance variations of lithologic units.

CONTROLS OF REE DISTRIBUTION

Mineralogy and Diagenesis

It is accepted that the mineral phases present will affect the concentration and distribution of REE. The predominant phases at the Empire are chemically precipitated carbonate and chert, and magnetite, attributed to either diagenetic (Han, in Gair, 1975) or metamorphic origin (Haase, 1979). Primary REE abundances are based on a crystallographic or adsorption control. The amount and type of clay minerals present in a sediment have a distinct positive correlation to REE abundances and it is generally considered that adsorption is the primary method of REE fixation. On the other hand, if pure carbonate phases are investigated, one may intuitively expect that Ca^{+2} ($1.08 \text{ \AA}$) favors replacement by the largest (lightest REE) ions, whereas smaller substitutional sites such as that occupied by Fe^{+2} ($0.69 \text{ \AA}$) prefer smaller (heavier REE) ions.

When both processes are operative, it is often difficult to assess which factor was dominant because the clay mineral phases are recrystallized. However, certain trends may be useful in interpreting REE abundances. For example, Fryer (1977b) noted the similarity between the Attikomagen slate and Denault Dolomite REE patterns in Labrador. He suggests that the lower but similar pattern of the dolomite is due to the incorporation of the REE's into minor amounts of clay minerals which has effected REE trends (the lithologies are in gradational contact). Stated otherwise, the dolomite acted as a dilutant without imposing its own unique signature on the REE pattern. Several other investigators have also described dilution effects (Graf, 1978; Dypvik, 1979; Haskin, 1974).

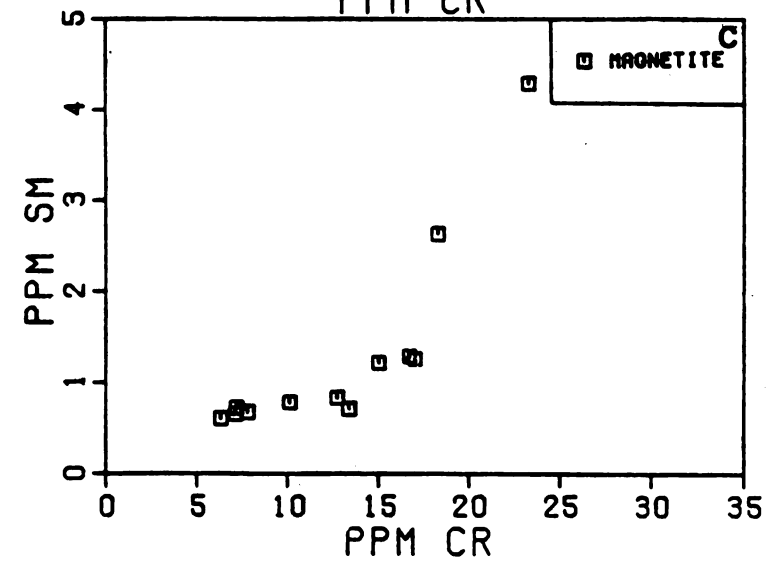
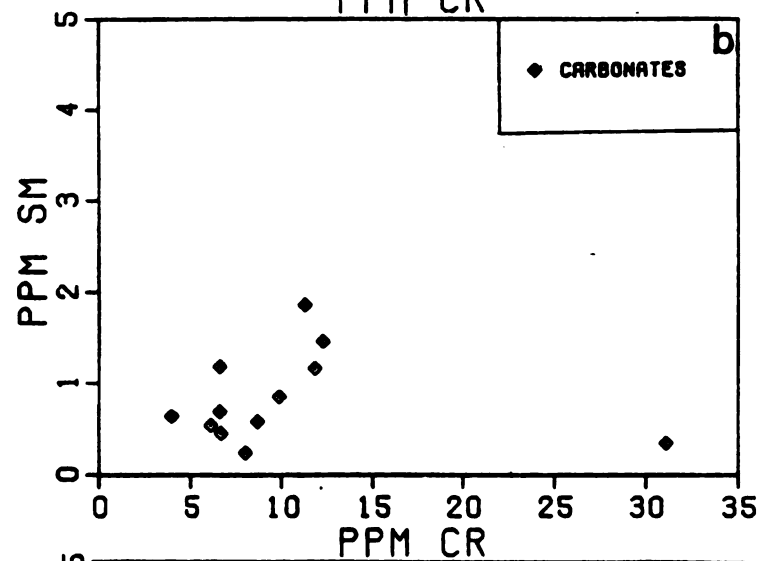
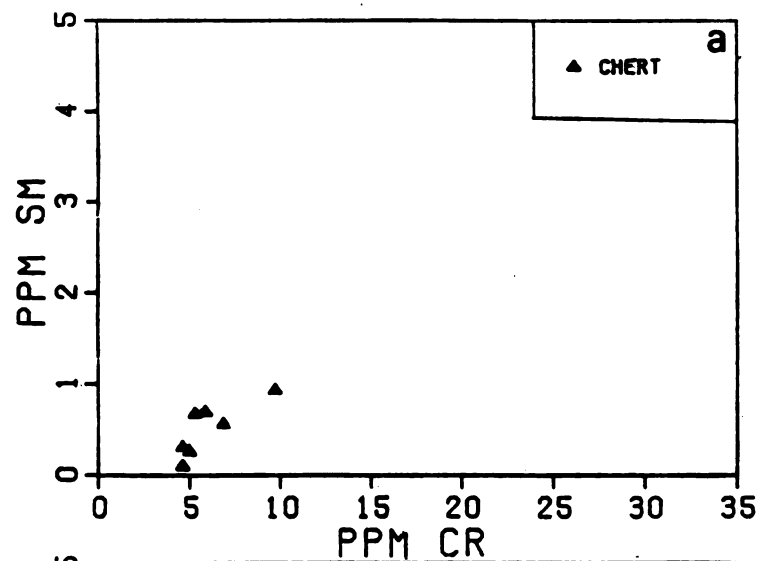
NIF chert values coincide with the assumptions made in the above investigation. Sample (F/225), which may be considered nearly a pure chert,

shows substantially lower concentrations of REE, Fe, and Cr than chert-carbonates analyzed in this study. Therefore, chert does act primarily as a dilutant of other mineralogies, and chert REE imprints may be masked in chert-carbonate samples by trace elements associated with carbonate and/or magnetite minerals.

The so called Negaunee ore samples, which contain greater than 50 percent magnetite (+ hematite), have relatively similar REE patterns, but whose abundances seem to be related to dilution by chert (Figures 16c and 17c). Magnetite acts as the largest sink for the REE with concentrations which approach clastic values but are 2 to 3 times carbonate, and 15 to 30 times chert values. In nearly pure magnetite lenses (Samples F/1119 and H/710.9), the REE abundances are higher than samples with magnetite-chert which in turn have similar patterns but greater REE abundances than pure chert samples (i.e., sample F/225, Figures 16b and 17b). Pure carbonate samples from the Negaunee BIF have similar patterns but lower abundances than the pure ores. There is predictably considerable overlap of the carbonates with other lithologies as the magnetite (+ hematite) and/or chert contents vary (Figures 16b and 17b). The lower concentrations of the chemical precipitates may reflect: 1) overall low concentrations in source solution, or 2) the lack of appropriate lattice positions for REE occupation.

The Negaunee carbonates (A/517.5, C/1386, and H/805.5, most siderite-rich) are relatively uniform in abundance and pattern with respect to depth. In addition, Cr abundances in the carbonates and chert are similar (Figure 20a, b). This would support their formation as crystalline precipitates under similar conditions. The regular abundances observed may be attributed to the incorporation of trace elements into the carbonate crystalline structure in equilibrium with sea water in contrast to Fryer's observations for the Sokoman

Figure 20. Correlation of chromium to REE content (Sm) in Negaunee samples for: a) chert, b) carbonates, and c) magnetite ore.



BIF. Changes in REE concentrations between ankerite and siderite may also be due to incorporation into the crystal structure rather than adsorption onto the surface. Therefore, the carbonates appear to regulate the REE concentrations observed.

Chromium may occur in the +3 and +6 oxidation state. In the reduced form, it has a similar atomic radius (0.64 versus 0.69) to Fe^{+3} . The major cations in carbonates occur in the +2 state. Therefore, theoretically, Cr may be predicted to be more abundant in magnetite enriched samples. Positive correlation of Cr content to REE concentration (Figure 20c) occurs in samples composed predominantly of magnetite. Therefore, it may be assumed that Cr concentration reflects Fe oxide content. Fe content (Table 2) does not appear to be a worthwhile index of magnetite content due to the high abundance of Fe in the siderite structure. Correlation of REE content to Cr concentration also suggests the incorporation of REE into the lattice of magnetite, but cannot be adequately tested without more detailed trace metal chemistry of ore samples. Microprobe data of Han (1975) has shown that both ilmenite and magnetite are present at the Negaunee as oxides. REE patterns may be influenced by the composition and crystal system of oxides present which may reflect the magnetite/ilmenite ratio.

Lanthanides prefer the +3 oxidation state and have a radius approximately equal to 1.0. Substitution for Ca^{+2} , Mg^{+2} , or Fe^{+2} in carbonates will cause an electronic imbalance. But, the spinel structure of magnetite will easily accommodate the REE's. Europium will behave differently due to its ability to be reduced to the +2 state. In previous work by Schock (1979) on volcanic magnetites, a marked Eu depletion was noted as well as an enrichment in the larger radii, light REE's. In contrast, carbonates of hydrothermal origin (Morgan and Wandless, 1980) show an affinity for the smaller radii HREE. The data of both studies suggest an europium depletion. In this investigation, REE patterns

of carbonates are subdued replicas of the LREE enriched magnetites suggesting Eu depletion and LREE enrichment are inherent from the solution rather than a product of crystallographic control.

Distinct diagenetic alteration of mineral components can be recognized at the Empire Mine. A major process in the formation of massive iron deposits is attributed to magnetization or diagenetic enrichment (Han, 1962). This process proceeds by the replacement of carbonate-chert by magnetite-chert. Petrographic evidence indicates that the formation of ankerite is due to the diagenetic replacement of siderite, although siderite may also be secondary. Ankerite is porphyroblastic, euhedral, and generally associated with recrystallized quartz and magnetite. Similar observations were made by Haase (1979) and Han (in Gair, 1975). Han suggests that the growth of ankerite occurred by the uptake of some of the CO_2 released by the conversion of siderite to magnetite.

Scherer and Seitz (1980) noted that diagenesis results in LREE enrichment in modern carbonates. Although the data is somewhat limited and hampered by the fact that ankerite generally coexists with siderite, in this study, a LREE depletion and slight HREE depletion was noted for ankerite (C/41, D/126 and D/1210) relative to siderite samples (Figures 16a and 17a, Table 4). This pattern becomes more evident when ankerite samples are normalized to the average siderite from this study (Figure 21). In absolute concentrations, ankerite has a mean La concentration of 2.01 ppm and a mean Lu concentration of 0.035 ppm, whereas these elements have mean values of 7.36 and 0.06 ppm in siderite enriched samples. Although, theoretically, REE would preferentially substitute for Ca^{+2} in ankerite rather than Mg^{+2} or Fe^{+2} in siderite, it appears that the REE are preferentially incorporated into the magnetite lattice position or adsorbed onto the surface during magnetite and ankerite formation.

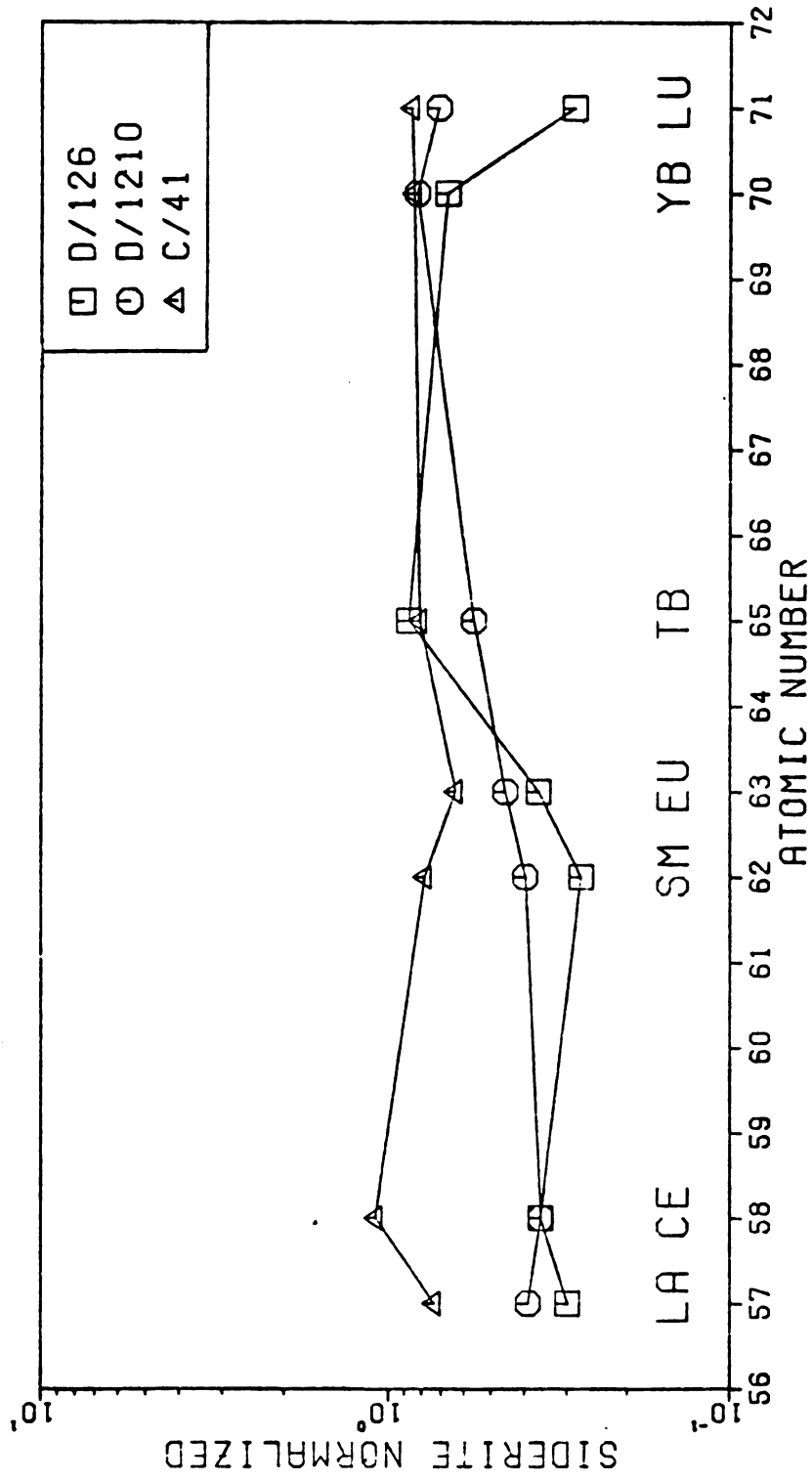


Figure 21. Ankerite (D/1210) and ankerite and siderite mixed samples (D/126, C/41) normalized to the average Empire siderite.

Scherer and Seitz also established two main trends during diagenesis; a strong increase in REE/Ca ratios and a shift towards lighter REE's. They further noted that the highest contents of REE's are present in magmatic and hydrothermal carbonates and that both are enriched in the LREE's. A similar plot for $\text{Yb/Fe}_2\text{O}_3$ versus Yb/La of NIF carbonates (Figure 22) indicates the reverse trend (i.e., HREE enrichment), although data is not conclusive, again illustrating the effect of magnetite formation in the system.

It was also found (Scherer and Seitz, 1980) that REE's have a greater distribution coefficient for Mg-calcite than aragonite. Their conclusions support theoretical predictions that the REE's can substitute more readily for calcium in the calcite structure than for Ca^{+2} in the orthorhombic structure of aragonite. Therefore, both crystallographic influences and the formation of new minerals during diagenetic processes may cause minor reequilibration of REE's during alteration.

Recent work by Chaudhuri and Cullers (1979) indicates moderate REE enrichment with depth in Gulf Coast sediments. They conclude that these changes are primarily in response to changes in source provenance, and diagenesis plays only a minor role. Variations in REE concentrations noted in this study, by Scherer and Seitz, and by Chaudhuri and Cullers may indicate that diagenesis does have at least a minor effect on REE concentration. Based on these preliminary observations, interpretations of anomalous REE behavior appear applicable to trace element studies, but interpretations of concentrations with respect to ancient sea water and comparisons between iron formations will be more meaningful with accurate distribution coefficients for carbonate phases and the determination of their mobility during diagenetic processes. Therefore, modern analogs, or an experimental data base are needed to fully evaluate this problem.

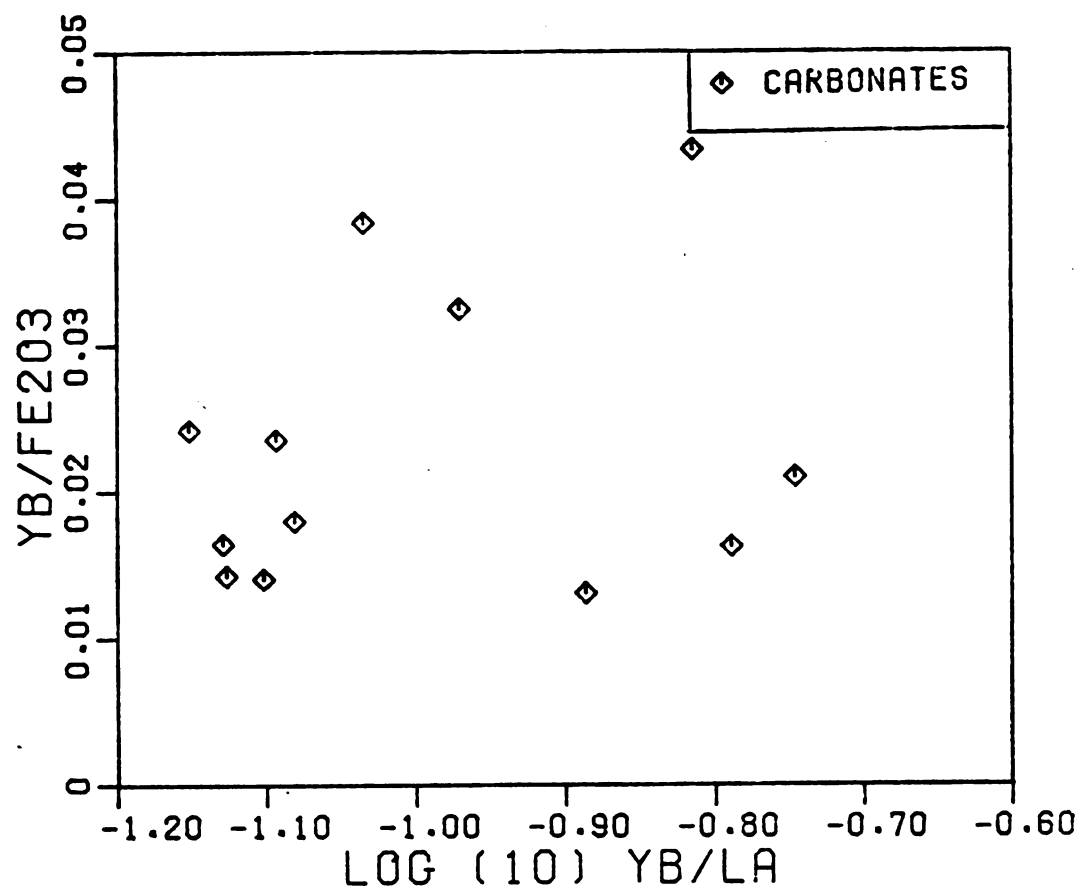


Figure 22. Plot of Yb/La versus Yb/Fe₂O₃ for Empire carbonate-rich samples.

Metamorphism

Possible controls of metamorphism on REE distribution cannot adequately be evaluated based on this investigation alone. Samples were collected from the lowest metamorphic grade of the Negaunee. Therefore, correlations between metamorphic facies cannot be considered. Previous investigations indicate that metamorphic alteration of sediments has little effect on REE distribution through the green schist facies. Ronov, et al. (1977) data indicate that metamorphic processes may result in a slight HREE depletion. HREE depletion is noted in this study, but appears to be both a product of mineralogic control and the chemical character of the primary solution. Generally, carbonates, oxides and cherts are depleted in HREE (Scherer and Seitz, 1980; Schock, 1979; Goldberg, 1963).

Some samples show a more marked HREE depletion which may be enhanced by the loss of volatiles during low grade metamorphism or diagenesis. Since the mobility of REE's have not been fully addressed in sediments, it is possible that the REE's become less mobile with time. Vulcan IF samples show decreased concentrations suggesting increased mobility with metamorphic grade (Slaughter, et al., 1981). But, this problem cannot be totally evaluated with the present data.

Haase (1980) has done preliminary carbon and oxygen isotope studies on Negaunee carbonates. These data show that homogenization during diagenesis and low grade metamorphism was limited and that magnetite formation had no noticeable effect on the isotope geochemistry. Fryer has observed inconsistent patterns in Cr content of oxides in the Sokoman iron formation. He has attributed these fluxuations to the migration of desorbed ions during post-depositional processes. In Negaunee samples, a positive correlation is observed between the REE and chromium concentrations. This appears to follow

increased oxide content of the rock samples based on hand sample and thin section examination. If Fryer's assumptions are correct, the Negaunee oxides have not been sufficiently altered during post-depositional or metamorphic processes. One sample (G/578.5) shows minor recrystallization to chlorite which appears to have enhanced REE concentrations similar to iron-silicates of the Sokoman.

Oxidation

Post-metamorphic alteration has resulted in oxidation of magnetite to goethite and iron carbonates to hematite in the Negaunee. These processes have occurred locally at the Empire and are attributed to the downward circulation of groundwater along fractures, contacts between dikes and iron formations, bedding surfaces, and pore spaces (Han, in Gair, 1972). These processes are more extensive in the "hard ores" of the Negaunee. Samples analyzed from the Empire are primarily from the unoxidized portions of the formation. Two carbonate samples (C/1386 and F/578.5) show minor alteration from siderite to hematite and chert to jasper. Oxidation has resulted in a slight overall depletion. Reverse patterns have been found for the hard ores of the Tilden mine, Negaunee Iron Formation and are plotted in Figure 23 (Slaughter, et al., 1981). The high proportion of jasper in these two samples may explain the conflicting results.

Summary

Experimental determinations of crystallographic versus adsorption controls are urgently needed to access REE behavior in sediments. The effects of post-depositional processes (diagenesis, metamorphism, and oxidation) may be substantially different for each type of REE fixation. Until such an experimental data base has been obtained, investigations such as this, of natural sedimentary systems, will remain of an empirical nature.

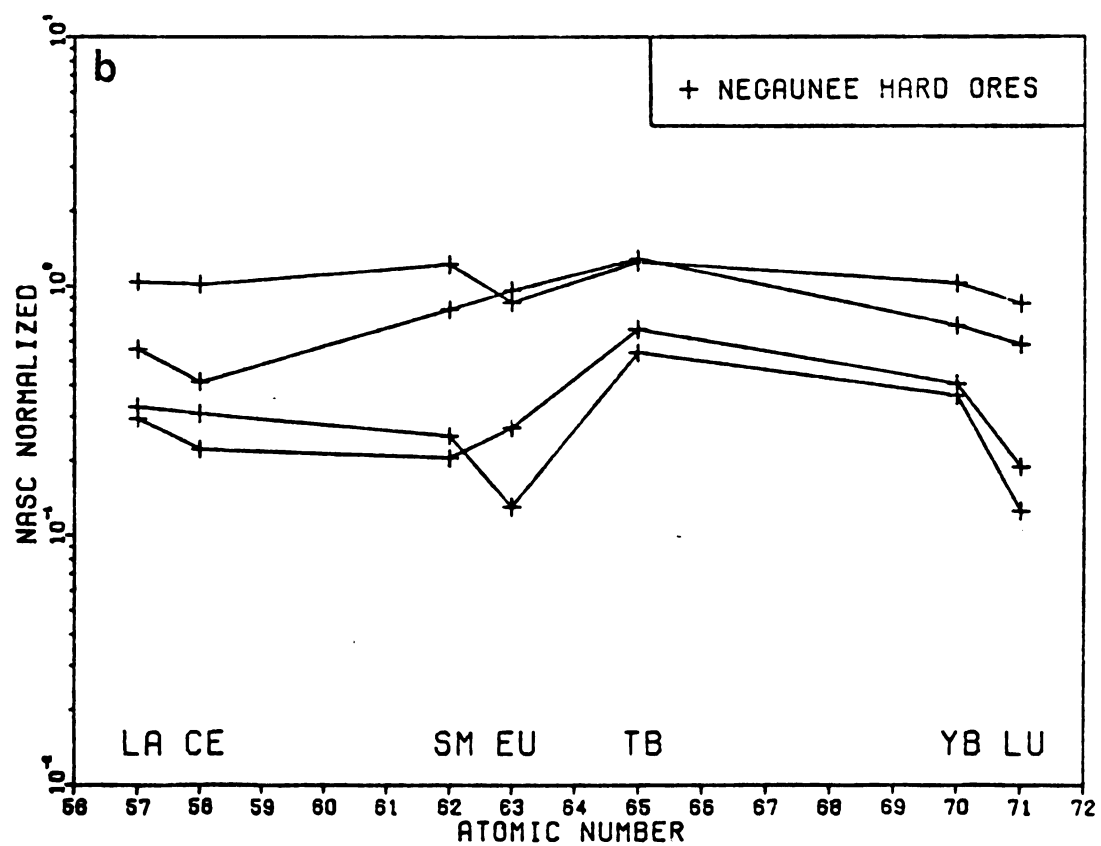
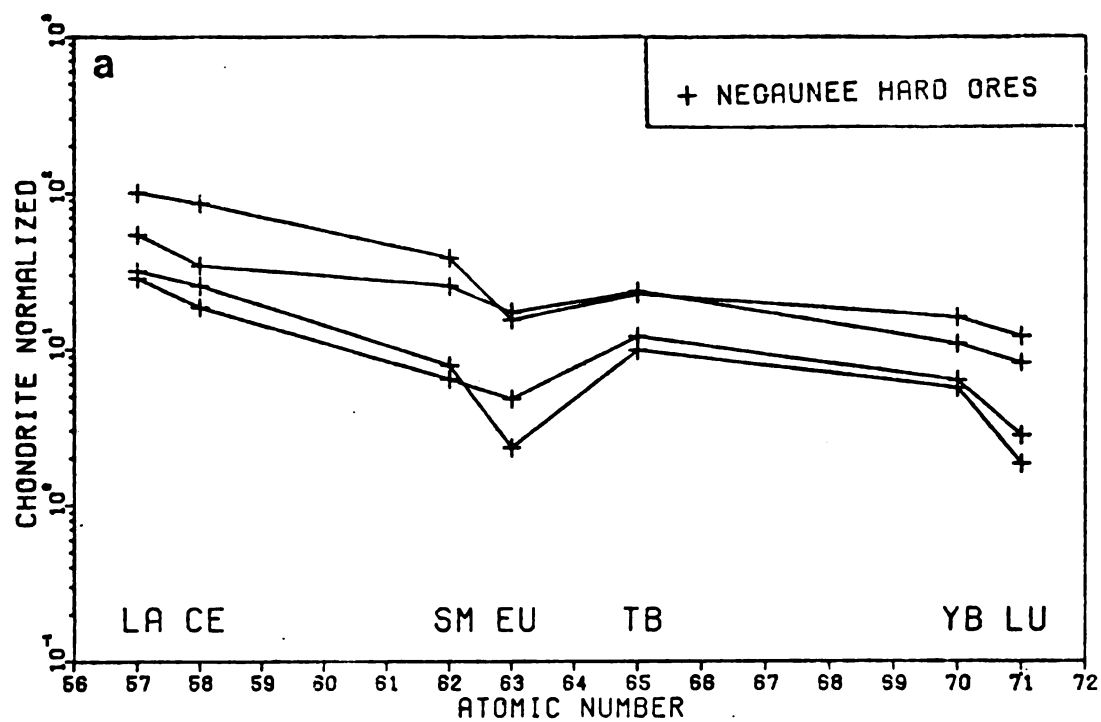


Figure 23. REE concentrations for Negaunee hard ores normalized to: a) chondrite and b) NASC.

IMPLICATIONS OF REE CONCENTRATIONS ON CHANGING SEA WATER COMPOSITION WITH TIME

Assuming that the above processes have not significantly altered REE concentrations, the chemical precipitates may be used to evaluate the chemical characteristics of the solution from which the NIF was deposited. From these data, we may then infer possible conditions of formation of the NIF.

It has been proposed that the chemical composition of sea water has changed through time by several investigators. Sandberg (1975) and Wilkenson (1975) both support an increase in the Mg/Ca ratio with time. It also appears that O^{18}/O^{16} values have increased to the present (Veizer and Hoef, 1976). Therefore, it would logically follow that trace element, specifically REE concentrations in sea water may also be time dependent. These geochemical trends will be reflected in chemical precipitates such as carbonates and chert, while clastic sediments will reflect the composition of the continental crust (Taylor, 1964; Haskin, et al., 1966; Piper, 1974).

Two different trends are noted for Eu behavior of the NIF chemical sediments relative to NASC. Chert and chert-carbonate samples show a marked negative Eu anomaly while carbonate-rich samples are close to predicted values or slightly depleted. Negative values are observed for all samples in this study compared to chondrite. Ankerite samples generally show a stronger Eu depletion compared to siderite-rich samples.

These observations do not correspond to Fryer's results. He attributes the positive europium anomalies in Archaean iron formations to the preferential incorporation of Eu^{+2} in sediments. Therefore, Archaean iron formations formed before the oxidation of Eu^{+2} to Eu^{+3} with the introduction of oxygen into the

atmosphere. The Sokoman shows fluxuations in Eu (chondrite normalized) behavior which Fryer would interpret as deposited during the transition period. The NIF which was precipitated at approximately the same time as the Sokoman shows negative values suggesting the presence of an aerobic atmosphere or seawater at this time. It has also been suggested (Eriksson and Triswell, 1978) that an oxygenated sea during the formation of Lake Superior-type iron formations resulting in the precipitation of iron in the +3 state and consequently allowed the segregation of iron and manganese. Therefore, it appears that other chemical constituents have influenced REE values observed in the ore body and it does not necessarily represent overall sea water composition of the time. Instead variations in Eu anomalies appear to be the result of different conditions of formation as proposed by Graf (1978), i.e., in response to phases precipitated and the chemical nature of the solution from which the sediments were derived.

Clastics and chemical sediments have also been utilized to relate REE compositional changes to crustal evolution. McLennan, et al. (1979) found a decrease of La/Th from 3.6 to 2.7 from Archaean to post-Archaean times in clastic sediments. This is assumed to reflect a change in overall continental crust from a more mafic composition. Similar ratios obtained from the Empire (Table 5) have maximum values comparable to those of post-Archaean sediments for the interbedded clastics. But, in general, clastic interbeds and the Siamu Slate have ratios substantially lower than those observed by McLennan. The chemical sediments also show a similar trend. However, increased Th directly relates to increased REE in all samples (Figure 24). Therefore, if the major source of total REE in sea water is considered to be from continental erosion, data from the NIF does not adequately support a model of REE evolution of the crust with time.

Table 5. Lanthanum-Thorium Ratios.

Carbonates			Chert		Ore		Clastics		Slate	
Sample Number	Ratio	Sample Number	Ratio	Sample Number	Ratio	Sample Number	Ratio	Sample Number	Ratio	
A/517.5	4.375	D/88.2	7.044	C/87	3.457	C/412.8	0.920	G/923A	1.957	
A/582	1.480	D/752	2.893	C/582	1.550	E/595.5	2.591	G/923B	0.345	
B/278.5	7.679	D/958	3.148	C/929	1.541	E/649.5	1.523	H/865.5	1.756	
C/41	3.476	F/76	1.825	C/1042	2.047	C/1126.5	1.233	H/867.5	2.386	
C/1386	1.817	F/225	1.28	D/518	3.406	E/419	1.634	H/906	2.314	
D/126	1.472	F/297	1.536	D/733.5	1.504	F/585.5	0.747	H/916	0.825	
D/878.5	1.278	G/845	1.776	E/70.5	1.532	G/285.5	1.398			
D/1210	1.674			F/695	2.266	H/593	1.335			
F/8	2.798			F/1119	0.769					
G/578.5	3.496			G/761.5	1.220					
H/448.5	1.865			H/710.5	1.120					
H/805.5	2.608			H/849.5	2.573					

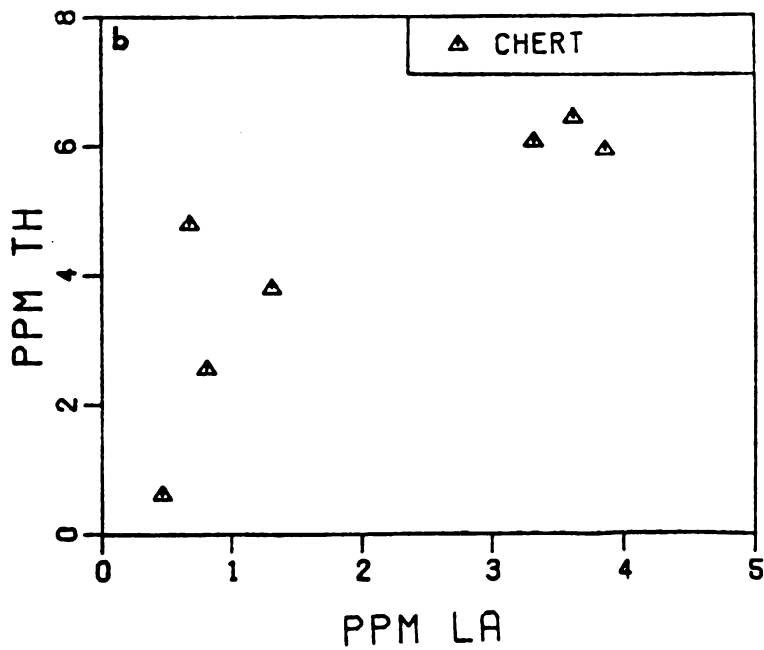
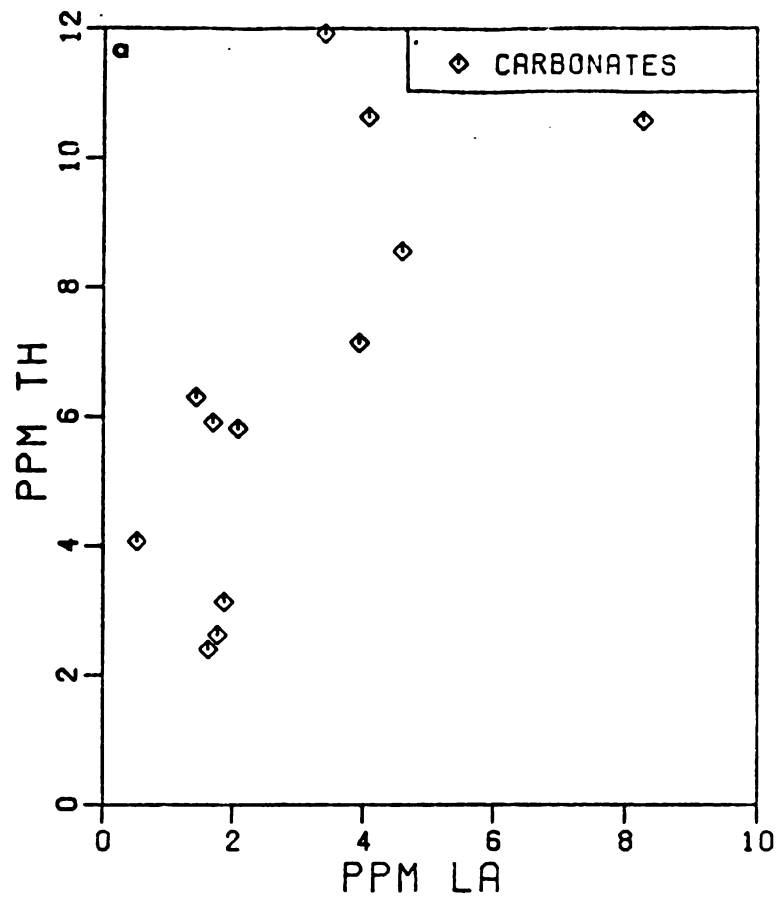


Figure 24. Plot of Th versus La for: a) carbonates, b) chert, and c) magnetite-ore.

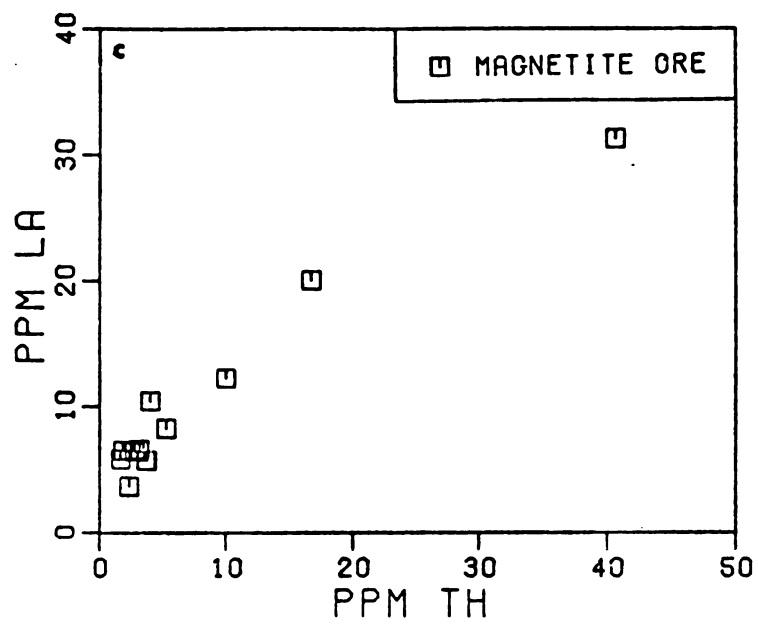


Figure 24 (continued).

Fryer also indicates an increase of REE concentrations of shales with time. Data from the Siamo show values comparable to those of NASC for quartz-rich samples, and slightly depleted for graywackes. It therefore appears that absolute REE concentration in sediments is dependent on mineral phases present and degree of weathering and transport rather than age. The NIF is of a comparable age to the Sokoman, and shows substantially higher concentrations. Therefore, BIF's do not reflect an increase in the REE concentration, although this may also be a reflection of mixed mineralogies used in both of these studies.

Three major conclusions may then be reached: 1) the geochemical nature, specifically relative REE concentrations have not changed through time, 2) post-depositional processes have since altered the concentrations of the REE in the Negaunee, or 3) banded iron formations are not representative of the overall chemical nature of sea water during the Precambrian.

The first and second conclusion cannot be adequately evaluated by this study alone, although it appears that oxidation and diagenesis affect overall concentrations in at least minimal amounts. Recent Nd isotope studies in sea water (Hooker, et al., 1981) provide evidence that metalliferous chemical precipitates dated at 490 m.a. have comparable Nd values to those of modern sea water. This is in direct contrast to the implications of major element systems presented by Wilkenson and Sandberg, although major and trace element systems may act independently. These data may also not reflect any changes which are postulated to be in response to the introduction of oxygen into the atmosphere during the Precambrian. The most conclusive proposition concerning BIF's specifically are those presented by Graf (1978). The presence of a major iron-rich ore bodies suggests geochemical properties and sedimentological processes different from those of a normal sea water system. This is supported by evidence that similar iron formations have like REE imprints and formed under

analogous sedimentary systems regardless of age. It is this conclusion which is supported in this investigation.

INFERENCES OF TRACE ELEMENT DATA ON THE FORMATION OF THE NIF AND COMPARISON TO OTHER IRON FORMATIONS

REE patterns observed in this study are substantially different than those found for other iron formations, specifically the Sokoman (Fryer, 1977b) and Algoma-type iron formations (Graf, 1978). Therefore, it is proposed that the NIF was deposited under different sedimentary conditions. Post depositional alteration processes may also have varied between provenances.

The chemical precipitates of the Negaunee show a marked Eu depletion or compatible values compared to NASC while the Sokoman shows an Eu enrichment trend compared to slates. Generally, the Sokoman has a negative Ce anomaly while those of the NIF are variable. NIF chemical precipitates and oxides have similar distribution patterns compared to associated clastic sediments, or are slightly HREE enriched (Figure 18), while Sokoman samples show extreme fractionation and anomalous Eu behavior compared to associated detrital materials. Algoma-type iron formations have similar distribution patterns to Empire samples, but have an extreme Eu enrichment.

Cerium data in cherts has been used as an indicator of sedimentary environment. Cherts analyzed from the Empire show low absolute abundances compared to all other lithologies (Figure 19). Significantly, the cherts do not have the Ce depletion characteristic of present day sea water but have patterns which Shimizu and Masuda (1977) describe as being "terrestrial", i.e., formed in coastal areas, marginal seas, or within land enclosed areas. Similar patterns have also been found in a chert sample from the Gunflint Formation (Slaughter, et al., 1981).

Haase (1980) found both lateral and vertical variations in carbon and oxygen isotope values in carbonates at the Empire Mine. These observations, complemented by the complex facies changes which exist, led Haase to suggest that deposition of the BIF occurred close to the paleomargin of a depositional basin. In addition, the REE data, unlike that of the Sokoman BIF, do not appear to be strongly controlled by major facies changes. For example, carbonate mesobands from the silicate facies have similar patterns to carbonate mesobands from the oxide facies. Generally, distribution patterns in the NIF show minor fluxuations in comparison to major changes in REE patterns between facies seen in the Sokoman. Therefore, it is possible that the trace element geochemistry of the solution from which the NIF was precipitated changed locally.

This interpretation would lend support to Han's suggestion (personal communication, 1982) that the defined facies at the Empire Mine are primarily mining terminology and may be a result of subsequent alteration (i.e., ore enrichment) rather than a product of major changes in depositional conditions. Therefore, the mineralogy may have originally been much more uniform prior to the occurrence of metamorphic and diagenetic processes. The consistence of REE patterns may be interpreted to mean that primary mineralogic controls of REE uptake dominated the REE abundance at the Empire location and that diagenetic changes or post-metamorphic oxidation have not resulted in significant variation of the original REE imprint. Therefore, it appears from the primary REE patterns that primary mineralogies at the Empire were originally more homogeneous than seen today.

Fryer noted the most consistent REE patterns from the Sokoman oxide facies were from samples which were extensively recrystallized and enriched in iron. These samples show strong HREE enrichment (NASC normalized), whereas other oxides show variable REE patterns (Figure 25). In contrast, the Empire

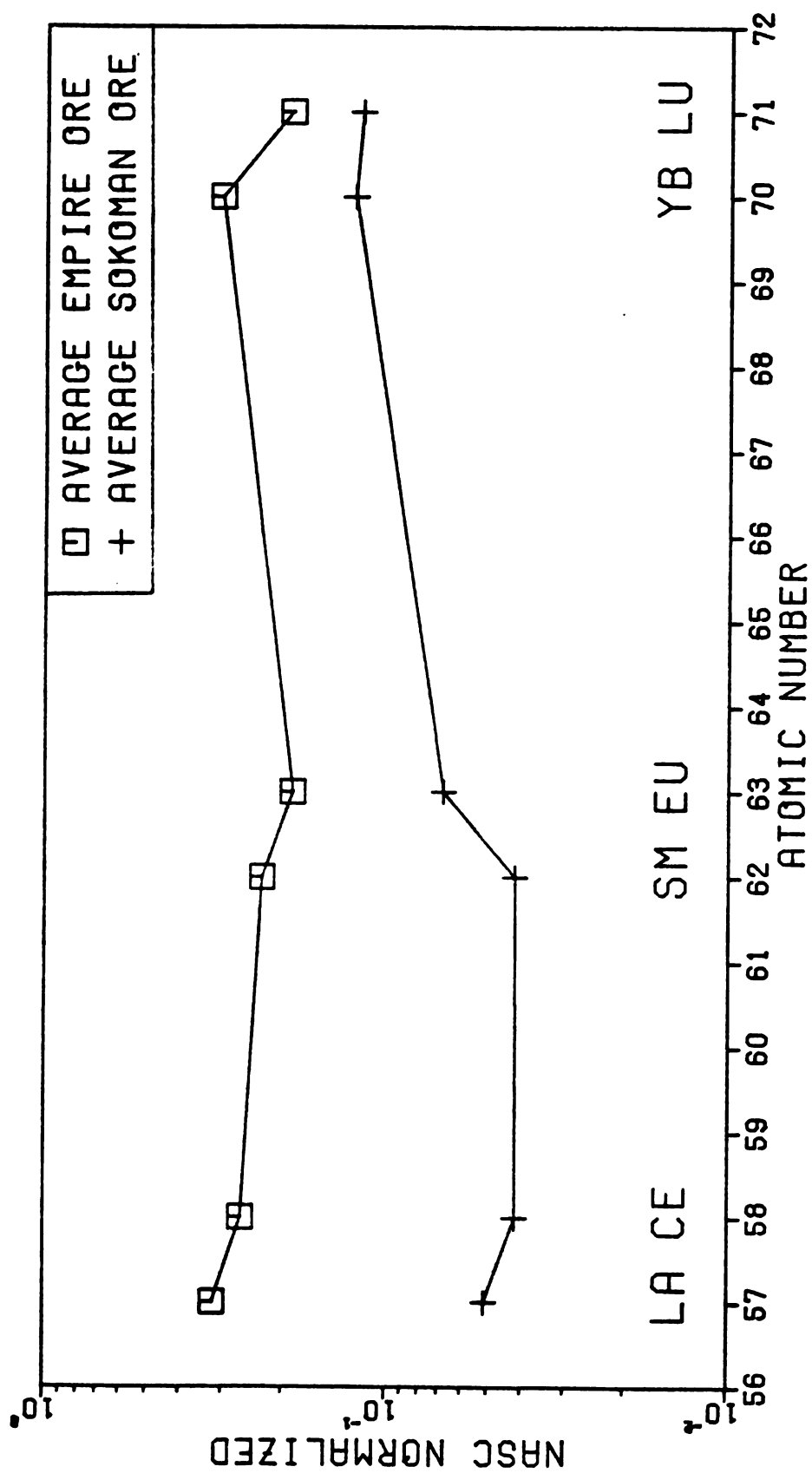


Figure 25. Comparison of REE concentrations for Sokoman and Empire average ores normalized to NASC.

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samples are less variable, have a slight LREE enrichment, and exhibit higher absolute REE abundances relative to the Sokoman oxide facies. Fryer suggests that the variation within the Sokoman oxide facies is related to complex post-depositional behavior during the transition from an adsorption on iron oxide hydrates to crystal structure incorporation. Thus, the processes (post depositional) or solutions operative do not equate to the Negaunee. Indeed, the Negaunee oxides provide evidence that the LREE's behave differently during iron enrichment (siderite to Fe-oxides) than to the iron enrichment process on the Sokoman.

Han (1962) states that magnetization or diagenetic enrichment, a process whereby magnetite-chert slightly to completely replace carbonate-chert is believed to be the most important process in forming the chief ore body at the Empire Mine. He reports all gradations from unreplaced carbonate-chert, a transition zone in which poikiloblasts of Ca-rich carbonate develop, and the enriched magnetite. This change is accompanied by a reduction of thickness and generates new-formed magnetite of unusually uniform size. This process is summarized as follows: elimination of fine-grained magnetite and magnesium iron carbonates; the lowering of chert content; development of calcium-rich carbonate; development of magnetite. The amount of magnetite formed from carbonate-chert layers is less than that formed from primary magnetite bearing chert layers. Han's analysis of unreplaced and enriched portions define the process as an addition of Fe_2O_3 , FeO , CaO , and Al_2O_3 , and appreciable subtraction of MgO , MnO , CO_2 , and SiO_2 . Hence, it may be stated that the magnetization is not a simple diagenetic oxidation of the magnesium iron carbonate but also involves an extensive ionic diffusion and possibly a nucleation of small magnetite during the enrichment stage. Han further suggests (1978) that the interformational structures (i.e., faulting, folding, fracturing, and

brecciation) may have played a major part in channelling oxygen, water, and carbon dioxide through the system.

It is noteworthy that the Sokoman iron enriched samples analyzed by Fryer are devoid of any carbonate, and that the one sample which exhibits LREE (NASC normalized) enrichment and high REE abundances is extensively replaced by carbonate. In addition, it has been suggested that the Sokoman was originally deposited as a gel and iron oxide hydrates (Klein, 1974; Leshner, 1978). Han (1978) proposes that these gels crystallized primarily into iron silicates and hematite. Hydroxides may have also interacted with organic matter resulting in increased mobility during diagenesis and low grade metamorphism. The NIF, on the other hand, appears to have formed directly from precipitated carbonate and/or hematite.

Thus, the carbonate formation appears to be a controlling factor in REE abundances. Transport of Fe, REE's, Ca, etc., could take place in carbonate-rich solutions. Precipitation of the scavenged REE's would be different depending on whether carbonates precipitate (Empire) or not (Sokoman). If the REE's migrate as carbonate complexes the solutions would be enriched in the more stable HREE's and precipitate HREE enriched phases so long as carbonate was not precipitated. It appears likely that the formation of carbonate and magnetite does not favor the enrichment of HREE's at the Empire Mine, and tends to increase the absolute REE abundances.

Hydrothermal alteration has also been suggested by Cannon (1973) as a mechanism for the formation of the Negaunee hard ores. This type of system would allow for the addition of trace elements into the NIF system, or substantial migration of elements within the system which would not be expected by diagenetic or low grade metamorphic processes alone.

Morgan and Wandless' (1980) investigation of hydrothermal minerals concludes that siderite formed during this process will exercise strong crystallographic control over the incorporation of REE. NIF siderite shows distribution patterns markedly different from those expected based on structural considerations. In addition, unpredictable trace element patterns of ankerite also occur. This suggests hydrothermal processes were not operative during formation of Empire carbonates.

Hard ores (Cliffs Shaft and Cliffs Drive) from the Negaunee (Slaughter, et al., 1981) show extreme REE enrichment compared to Empire samples. No Ce anomaly is observed, and a slight Eu depletion exists normalized to chondrite abundances (Figure 23). Similar trends are noted compared to NASC (Figure 23). Significantly, a HREE enrichment trend is found with concentrations approaching that of the average shale composite.

Cannon (1973) notes that hard ores are located in the upper portions of the NIF. He suggests that fluids, probably derived from dehydration and decarbonization during Penokean regional metamorphism, migrated upwards resulting in the reduction of hematite to magnetite, and the precipitation of magnetite from hydrothermal solution. The REE, and especially the HREE, tend to complex with carbonate ions. Therefore, HREE enrichment trends observed in the NIF hard ores may be explained by their formation by hydrothermal processes.

The presence of slump features and broken laminae in Empire samples indicate that during magnetite formation a reduction of volume did occur (Han, 1978). Therefore, the addition of trace elements, iron, and chromium through hydrothermal processes is not necessary for ore formation. These factors suggest that hydrothermal alteration was not a major factor in Empire ore formation. In addition, the plot of La/Sm vs. Sm/Yb cannot be used as a

discriminatory for rock type or mineral speciation (Figure 26). The overlap may reflect the common origin. Instead, it appears that magnetite enrichment occurred by diagenetic processes whereby the movement of volatiles occurred along structural features allowing for the concentration of Fe, Cr, and REE during oxide formation.

A major controversy remains concerning the source of iron for the formation of massive iron deposits. The two primary theories propose that iron was originally derived from: 1) continental erosion (James, 1954) or 2) subaqueous volcanism (Goodwin, 1956). Presently, each argument has major limitations.

Limited REE data on the Siamo Slate give information concerning the character of the Negaunee. Two major trends are noted in the data. The quartzite samples (G/923B and H/867.5) show a marked Eu depletion while the graywackes show a slight Eu depletion on the order of magnitude found in NASC. This is evidence for two possible source regions for clastic material based on the petrology of the samples. The predominant mineralogies consist of quartz and albite, indicative of a sialic source, and chlorite and mafic rock fragments, probably derived from the weathering of a more mafic terrain. Clastic material is considerably enriched compared to later chemical precipitates. Therefore, a mixing of material from two source regions is implied. Possible origins of this material are the Mona Schist and the Compeau Creek Gneiss of the basement complex. Trace element data are not presently available on these formations to correlate to the Siamo.

Clastic material contained within the Negaunee show similar REE distribution patterns, specifically with respect to Eu behavior, but are slightly REE enriched compared to the Siamo. Again, two distinct patterns in Eu behavior are noteworthy. Specifically, the higher REE concentrations are

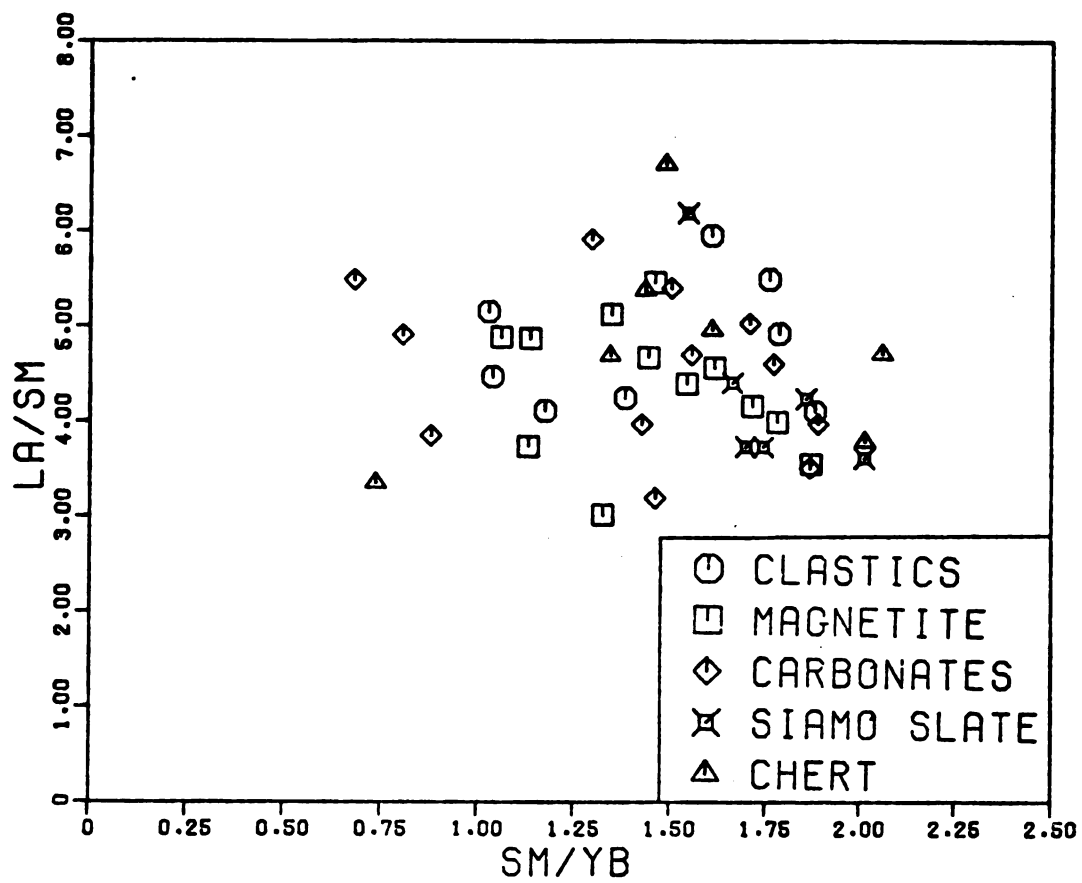


Figure 26. Plot of Sm/Yb versus La/Sm for Empire samples.

observed in clastic samples (C/412.9, E/1126.5, G/285.5, and H/593) which also have a more marked Eu negative anomalies compared to NASC. Mineralogically, samples are also similar, although petrographic data indicate a lower degree of sorting and rounding. Chromium and thorium values are also within the same range. This suggests that the clastic component of the Negaunee has a similar source area to that of previous shale deposits. Therefore, erosional processes were still periodically active in similar lithologic regions during chemical sedimentation. Higher concentrations in erosional products included in the NIF are probable inherent from a short residence time and exchange with sea water. Alternatively, increased concentrations may be due to less alteration in the younger Negaunee interbedded clastic sediments.

REE patterns of the chemical precipitates are at lower concentrations but mimic patterns of clastic material. This is in direct contrast to observations of Fryer (1977b) in the Sokoman iron formation. Therefore, this correspondence indicates that a detrital source for the iron solution cannot be ruled out. Graf reports similar correlation for chlorite-rich New Brunswick Iron Formation. These similarities are not seen in associated iron sulfide deposits presumed to be of hydrothermal origin.

The input of volcanic material in sea water would result in distinct REE patterns of the resultant solution and derived sediments. For example, Graf (1977) suggests that enriched europium values in New Brunswick (Bathurst-New Castle District) Algoma-type iron formations and the Proterozoic Hamersley BIF are the result of the interaction of hydrothermal solutions with felsic material prior to entering sea water. The addition of feldspar-rich material, which preferentially incorporates Eu may cause a change in the chemical character of hydrothermal solutions from which this type of iron formation was formed resulting in distinct Eu enrichment beyond that predicted by crystallographic control.

Although samples of known volcanic origin analyzed by Graf show enriched Eu values, in contrast to the NIF this does not preclude a volcanic origin for Fe-solutions in the Negaunee, as has been suggested by some investigators. Although no known volcanics are associated with the Negaunee, input into the hydrologic system, removed from areas of immediate deposition by volcanic exhalation would affect trace element concentrations of the solution and sediments precipitated. Therefore, analysis of volcanic material in the Lake Superior region may give further insight into this problem.

CONCLUSIONS

The REE data on the Negaunee Iron Formation chemical sediments and associated clastics characterize sedimentary controls and geochemical conditions for its formation during Precambrian times. The following conclusions are drawn from the data:

1. Detrital sediments have marked REE enrichment compared to primary chemical components. Secondary magnetite-rich samples are generally enriched compared to carbonates and chert.
2. Changes in REE distribution patterns between ankerite and siderite and constant chromium content suggest that REE are incorporated into the crystal lattice rather than adsorbed onto the surface. Oxide enriched ores have a wide range of abundances which may reflect original trace element contents were controlled by adsorption processes. The relative REE abundance patterns are grossly similar for all chemical sediments. This may be used to argue for a diagenetic replacement of carbonates as suggested by previous investigators.
3. Metamorphism and post-metamorphic oxidation does not seem to have significantly altered Empire samples. Compared to analyses of samples from the Tilden Mine and Vulcan Iron Formation which illustrate a marked redistribution of REE during these processes, Empire Mine REE patterns are relatively consistent.

4. Comparison of REE data from the Sokoman Iron Formation and Empire Mine shows variations in REE behavior between these time equivalent iron formations. This suggests that trace element imprints are not representative of overall sea water composition of the time. Rather, the chemical character is influenced by the processes of formation and types of precipitating phases. In addition, thorium values from clastic and chemical sediments do not reflect values of continental composition seen in other post-Archean sediments.
5. Anomalous cerium behavior in cherts and minor fluctuations in REE trends, both vertically and laterally, suggest deposition close to the paleo-margin of a depositional basin. This is supported by isotope data of Haase. A facies control is not exhibited by NIF samples. This suggests that the major facies present at the Empire are a result of secondary processes and the original deposition of the NIF was homogeneous throughout.
6. Empire oxides have LREE enriched values (NASC normalized) compared to the HREE enriched character of the Sokoman. It is suggested that the precipitation of carbonate phases is a controlling factor on REE behavior. Or, the presence of carbonate complexes in solution allows for the stabilization of HREE and precipitation of these phases.
7. Hydrothermal alteration does not appear to be a major process in the formation of Empire ores in contrast to the hard ores of the NIF. Instead, it appears that magnetite enrichment is a product of diagenetic enrichment through the movement of volatiles.

8. Similarities of REE imprints of chemical sediments to clastic materials indicate that the erosion of continental material remains a plausible source for iron-rich solutions. However, a volcanic input cannot be ruled out without further data from possible volcanic associations.

SUGGESTED FURTHER RESEARCH

The use of REE as sedimentary indicators appears to be a valid approach to the understanding of the occurrence of banded iron formations. This investigation of the Negaunee has suggested several alternatives to the geochemical conditions of precipitation and alteration. Future research on both the NIF and associated strata may further aid in the evaluation of the occurrence of massive iron ore deposits during Precambrian time. These studies include:

1. Analysis of mineral separates versus whole rock analysis to place constraints on the effects of different mineral phases on REE distribution patterns. These data would aid in further modelling of processes associated with sedimentary systems including source material, crystallographic control, adsorption and diagenetic and post-diagenetic alteration.
2. A better definition of the mobility of REE during diagenetic processes and the relationship to the formation of new minerals using modern analogs.
3. A regional study to quantify trace metal and REE data for the Siamo Slate. Shales are relatively consistent within a single basin unless more than one source of clastic material is present as suggested in this investigation. These data would characterize detrital sedimentation occurring prior to NIF precipitation and give a broader data base for comparison to subsequent chemical precipitation.

4. Trace metal investigation of samples from the Empire to correlate to REE data. These data would further aid in evaluating processes of formations proposed in this study.
5. A detailed trace element study of basement complex (i.e., Mona Schist and Compeau Creek Gneiss) for comparison to clastic and chemical sedimentation.
6. A regional study of the NIF to evaluate the mobility of REE during metamorphism and oxidation.

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APPENDIX A

ANALYTICAL METHODS

Analytical methods used in this study include neutron activation, electron microprobe analysis, and X-Ray fluorescence.

Neutron Activation Analysis

Neutron activation analysis was used to determine whole rock compositions for the rare earth elements La, Ce, Sm, Eu, Yb, and Lu and for Th and Cr. Samples of approximately 1.00000 gm were powdered to pass through a 200 mesh sieve. Powdered samples were placed in polyvinyl vials, sealed, and irradiated at the University Triga Mark I nuclear reactor for six hours. Samples were analyzed at the Michigan State University Department of Geology using a Geli detector coupled with a multichannel analyzer directly tied to the University computer system. Liquid standards and U.S.G.S. rock standards (W-1 and AGV-1) were used for comparison. Liquid standards were prepared by transferring volumetric aliquots of a prepared liquid of known concentration to the polyvinyl sample holders and were allowed to evaporate to dryness by exposure to IR heat lamps.

Electron Microprobe Analysis

An ARL-EMX three spectrometer microprobe was used for individual phase analysis. This instrument is operated and maintained by the MSU Center for Electron Optics. A full-time technician is assigned to the probe for maintenance. The ARL is connected directly to the University computer system. LIF, RAP, and ADP detector crystals were used to measure Fe, Mg, and Ca, respectively. Dolomite and siderite standards were used for comparison.

APPENDIX A (Continued)X-Ray Fluorescence

Total iron content was measured by X-ray fluorescence analysis on magnetite, carbonate, and chert-rich samples. A General Electric XRF X-ray generator and detector panel were used. Data were reduced using Compton's method (Reynolds, 1963) with U.S.G.S. standards BCR-1 and PCC-1. All data are reported as percent Fe_2O_3 .

APPENDIX B
ROCK SAMPLE DESCRIPTIONS

SAMPLE NUMBER	DESCRIPTION	FACIES
A/582	Carbonate with fine chert laminae, minor magnetite veins	Carbonate
A/517.5	Carbonate with fine chert laminae	Carbonate
B/278.5	Carbonate and chert mesobands alternating	Upper series
C/41	Carbonate-chert laminae alternating with chert-magnetite laminae	Upper series
C/87	Magnetite ore with intergranular carbonate	Upper Series
C/412.75	Clastics intergranular with chert	Clastic facies
C/582	Microbands of carbonate with chert and magnetite cross cut by magnetite veins	Carbonate facies
C/929	Magnetite ore with fine laminae of carbonate	Carbonate facies
C/1042	Magnetite ore with intergranular chert and alternating laminae of silicate	Silicate facies
C/1386	Alternating bands of carbonate and chert varying in thickness	Lower series
D/88.2	Chert with minor magnetite some altered to jasper	Upper series
D/126+	Carbonate laminae varying in thickness with chert laminae	Upper series
D/518	Massive magnetite ore	Carbonate facies
D/733.5	Magnetite ore, massive, with minor chert and carbonate laminae	Carbonate facies
D/752	Massive chert, minor carbonate laminae	Carbonate facies

APPENDIX B (Continued)

SAMPLE NUMBER	DESCRIPTION	FACIES
D/878.5	Magnetite ore, massive with carbonate-chert laminae	Carbonate-silicate facies change
D/958	Chert with carbonate microbands	Silicate facies
D/1210	Carbonate with chert microbands	Lower series
E/70.5	Magnetite ore with mesobands of carbonate and jasper	Carbonate facies
E/595.5	Clastics with mesobands locally rich in magnetite and carbonate	Silicate facies
E/649.5	Clastics in magnetite ore matrix	Silicate facies
E/1126.5	Clastics intergranular with chert	Lower series
F/8	Carbonate and chert replacement minor hematite and magnetite	Carbonate facies
F/76	Chert containing microbands locally rich in carbonate	Carbonate facies
F/225	Chert containing microbands locally rich in carbonate	Carbonate facies
F/297	Chert with minor carbonate, replacement features	Carbonate facies
F/419	Magnetite ore containing clastic interbeds	Silicate facies
F/585.5	Alternating bands of magnetite with chert and clastics with chert	Silicate facies
F/695	Alternating bands of magnetite with minor carbonate and carbonate with minor magnetite	Silicate facies
F/1119	Magnetite ore with some magnetite porphyroblasts	Lower series
G/285.5	Clastics interbedded with carbonate, minor magnetite	Lower series

APPENDIX B (Continued)

SAMPLE NUMBER	DESCRIPTION	FACIES
G/578.5	Carbonate with micro- to mesobands of chert	Lower series
G/761.5	Magnetite with chert rich laminae	Lower series
G/845	Chert with thin laminae of carbonate	Lower series Siamo transition
G/923A	Slate	Siamo
G/923B	Slate with bands of quartz	Siamo
H/448.5	Carbonate, predominantly massive locally microbands rich in chert	Lower series
H/593	Arkosic sandstone, chert containing microbands of magnetite	Lower series
H/710.5	Alternating mesobands of chert and magnetite	Lower series
H/805.5	Chert with minor carbonate mesobands	Lower series
H/849.5	Magnetite ore with silicate mesobands	Lower series Siamo transition
H/865.5	Slate containing quartz porphyroblasts	Siamo
H/867.5	Slate	Siamo
H/906	Slate	Siamo
H/916	Slate	Siamo

APPENDIX C

CARBONATE THIN SECTION DESCRIPTIONS

SAMPLE NUMBER	DESCRIPTION
A/517.5	Fine crystalline, anhedral siderite in mesoband coexisting with anhedral quartz and trace euhedral magnetite, minor alteration to chlorite.
A/582	Very fine crystalline anhedral siderite, coexisting with anhedral chert and euhedral magnetite; some alteration to hematite; well banded.
B/278.5	Very fine crystalline, anhedral siderite coexisting with anhedral chert and magnetite, alternating with chert microbands.
C/41	Very finely crystalline, anhedral siderite coexisting with chert and minor magnetite and finely crystalline anhedral ankerite with hematite and minor chert; cross-cut by fractures filled with magnetite and chert.
C/1042	Fine to medium crystalline, anhedral ankerite coexisting with porphyroblastic magnetite; mesoband associated with ankerite chert with minor clastic microbands; cross-cut by fine magnetite filled veins.
C/1386	Very fine to finely crystalline siderite, anhedral, minor subhedral, coexisting with anhedral chert and trace euhedral magnetite surrounded by carbonate porphyroblast; cross-cut by veins filled with quartz and trace chlorite.
D/126	Finely crystalline anhedral siderite with anhedral chert and trace magnetite; some chert-carbonate microbands; cross-cut by fractures filled with anhedral, finely crystalline ankerite.
D/878.5	Massive magnetite ore; subhedral with mesobands containing finely to medium crystalline; anhedral to subhedral siderite; minor chert.
D/1210	Finely crystalline anhedral ankerite coexisting with chert and euhedral magnetite associated with bands of chert and magnetite; fractures partially filled with euhedral ankerite.
F/8	Finely crystalline anhedral siderite coexisting with chert in mesobands alternating with jasper and magnetite; minor alteration to hematite.

APPENDIX C (Continued)

SAMPLE NUMBER	DESCRIPTION
G/578.5	Finely crystalline anhedral siderite coexisting with chert; some porphyroblasts; trace euhedral magnetite associated with chert; minor alteration to chlorite; cross-cut by quartz-filled fractures.
H/448.5	Very fine, anhedral siderite mosaic with microbands chert; trace euhedral magnetite coexisting with chert; trace chlorite in carbonate rich laminae.
H/805.5	Very finely crystalline anhedral siderite coexisting with chert and magnetite in mesobands associated with chert; cross-cut by fractures filled with medium grained anhedral chert.

APPENDIX D

THIN SECTION DESCRIPTION OF THE SIAMO SLATE

SAMPLE NUMBER	DESCRIPTION
G/923A	Moderately to well sorted quartz ($\approx 55\%$) with trace feldspar in matrix of fibrous to platy biotite. Minor muscovite.
G/923B	Poorly to moderately well sorted quartz, minor cryptocrystalline (70-75%) possible mafic fragments, fibrous chlorite and biotite, rounded. Matrix fibrous chlorite and minor platy muscovite.
H/865.5	Poorly sorted detrital quartz ($\approx 70\%$), possible mafic clasts, consisting of chlorite and biotite. Matrix predominantly chlorite with minor biotite and muscovite, all fibrous to platy.
H/867.5	Well rounded, well sorted quartz ($\approx 55\%$) with trace detrital feldspar, possible mafic clastics consisting of chlorite and biotite rounded with serrated boundaries. Matrix predominantly chlorite bladed and fibrous.
H/906	Well rounded, well sorted quartz ($\approx 60\%$) with minor feldspar and trace rounded magnetite. Matrix platy chlorite with trace muscovite. Possible mafic clasts.
H/916	Well rounded, well sorted quartz ($\approx 50\%$) with trace of magnetite. Matrix platy chlorite and minor biotite.