MINERAL CHEMISTRY OF HEAVY MINERALS IN THE OLD HICKORY DEPOSIT,

SUSSEX AND DINWIDDIE COUNTIES, VIRGINIA

by

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# MINERAL CHEMISTRY OF HEAVY MINERALS IN THE OLD HICKORY DEPOSIT, SUSSEX AND DINWIDDIE COUNTIES, VIRGINIA

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(ABSTRACT)

The Old Hickory is the largest of a series of Pliocene (?) age heavy mineral sand deposits in Virginia and North Carolina. The high density of heavy minerals allows for selective concentration during transport and deposition. Under the right conditions, placers of considerable size can be formed. The elliptically shaped ore body of the Old Hickory Deposit extends in a North - South direction and is approximately 13 km (8 miles) long and up to 2.5 km (1.5 miles) wide, with an average thickness of 6.5 m (20 feet). The deposit lies along the Fall Zone, where a thin wedge of Cenozoic Coastal Plain sediments unconformably overlies the older rocks of the Piedmont.

The principal minerals of economic interest found in the heavy mineral sands at the site are ilmenite ($FeTiO_3$), leucoxene ($Fe_{2-x}Ti_{3+x}O_{9+x/2}$) where x $\geq$ 2, rutile (TiO_2), and zircon ($ZrSiO_4$). An important focus of this study is the alteration of ilmenite by leaching away of iron, which results in enrichment in titanium. Titanium metal is highly valued for its light weight and high strength. In terms of total economic value, however, the use of titanium dioxide pigments for paint, coated paper, and other products is far more important. As the value of the ore is heavily dependent on the titanium content, the weathering process is a matter of considerable interest to the mineral industry.

Analysis of ilmenite grains using reflected light microscopy revealed a wide range of alteration textures. Quantitative analysis and mapping of trace elements showed altered areas with enrichment in Ti and depletion in Fe, Mn, Mg, and Cr. It is believed that the weathering process took place in a reducing environment prior to final deposition according to the reaction:

$$Fe^{2+}TiO_3 + 2H^+ \rightarrow Fe^{2+} (aq) + TiO_2 + H_2O$$
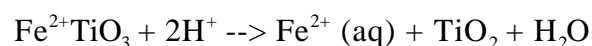
Reducing environments are found in water-logged soils such as floodplains and other low-lying areas. Repeated cycles of burial and exhumation during transport would have created conditions ideal for the removal of iron from the ilmenite.

ACKNOWLEDGMENTS

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INTRODUCTION

Titanium, long classed as a strategic metal, is also a material whose compounds are used in vast array of products which serve modern civilization in forms as diverse as white paint, jet engines, and the powdered coating on doughnuts. Pure titanium dioxide is extensively used in the manufacture of pigments as well as for the production of titanium metal. Such metal is highly valued in the aerospace and chemical processing industries for its combination of light weight, strength, high melting temperature, and excellent corrosion resistance. In terms of quantity and total economic value, however, the use of titanium dioxide pigments for paint, coated paper, and other products is far more important. In 1996, the United States produced over 1.2 million metric tons of titanium and titanium dioxide pigment. This represents about one-fourth of total world output. Other major world producers include Australia, Brazil, Canada, India, Norway, South Africa, and Sri Lanka (Gambogi, 1997).

The element titanium was first discovered near England in 1790 after dark beach sands containing the mineral now known as ilmenite were experimentally treated with acid, removing the iron (Barksdale, 1966). Titanium is found in nature in both oxide and silicate minerals. Ilmenite ($FeTiO_3$), leucoxene ($Fe_{2-x}Ti_{3+x}O_{9+x/2}$) where $0 < x$ 2, and rutile (TiO_2) are all important ore minerals which respectively contain titanium in progressively increasing amounts. In general, the higher the titanium content of the feedstock, the greater the value of the ore.

Historically, titanium has been extracted from both hard rock (igneous and metamorphic) deposits and placer or residual sedimentary deposits. Hard rock rutile deposits in Roseland, Virginia, mined at the turn of the century, were among the first major sources of titanium for industrial purposes. Production from beach sand deposits in India, Brazil, and Australia ensued shortly thereafter. The search for additional domestic sources of titanium was stimulated by the onset of World War II and led to discoveries of placer deposits in Florida and elsewhere (Gillson, 1959). While total reserves of hard rock deposits are much greater overall, sedimentary deposits make up a disproportionate amount of annual production worldwide. These sedimentary deposits can be quite large in terms of their total titanium

contents; furthermore their near surface and unconsolidated nature allows for easy, economic, and environmentally "friendly" extraction.

Placer deposits form by the concentration of high-density minerals in a variety of sedimentary environments and are best known as sources of gold ore (e.g. the California Gold Rush, the Yukon and Klondike in Alaska, and the Witwatersrand paleoplacer in South Africa). Today, however, placer deposits are also essential to the worldwide production of a number of other heavy minerals including those containing titanium. By definition, heavy minerals are generally considered to be those having a specific gravity of 2.9 or greater. (This value was not chosen arbitrarily but rather due to the fact that liquid bromoform, often used for separation purposes, has a specific gravity of 2.89). While many minerals from the commonplace to the exotic fall under this broad classification (See Table 1), they are usually only minor constituents of most rock types. In placer deposits, however, it is possible for such heavy minerals to be selectively concentrated during transport and deposition of unconsolidated sediments because of their high density. Thus it should be no surprise that placers play an important role in modern day mining activities for those heavy minerals with commercial value.

The densities of these heavy minerals relative to that of the more abundant quartz commonly results in their selective concentration during fluvial and/or marine transport. Most deposits, though, even if highly enriched in heavy minerals, are too small to justify the initial investment involved in establishing an active mine. Occasionally, however, geological processes have acted either over long periods or with such intensity that deposits measured in the millions of tons of heavy minerals have been created. Such is the case at the Old Hickory Deposit located in Sussex and Dinwiddie Counties in southeastern Virginia (See Figure 1). The elliptically-shaped ore body extends in a North-South direction and is approximately 13 km (8 miles) long and up to 2.5 km (1.5 miles) wide, with an average thickness of some 6.5 meter (20 feet). It lies directly along the Fall Zone (historically known as the Fall Line) which marks the boundary between the Piedmont and the Coastal Plain.

The Old Hickory Deposit is a stranded beach terrace, with sands unusually rich in heavy minerals. The repeated action of the waves on the former shore concentrated heavy mineral grains high on the beach face. Over time, through selective sorting of the sediments and breakdown of minerals less resistant to weathering, a heavy mineral deposit of considerable size was formed. Among the ore minerals found in particular abundance are ilmenite, leucoxene, rutile, and zircon.

Zircon, although it contains no titanium, is still an important byproduct with commercial value of its own. It is used both as foundry sand and in the ceramics industry because of its refractory properties. Zirconium metal alloys are also used as casings for nuclear fuel rods. Other heavy minerals found at the site include staurolite, kyanite, tourmaline, and monazite but these are all of little economic importance. Monazite can be used as a source of rare-earth elements, however, it is present only in very small amounts.

Along with the discovery of the Old Hickory Deposit in 1987, several similar smaller deposits have been found in a narrow belt extending southward along the Fall Zone through much of North Carolina. Among the largest of these are the Brink, Aurelian Springs, and Bailey Deposits. While these heavy mineral placers may have initially extended linearly over much greater distances, erosion and dissection by streams has left only the small, isolated remnants found today. Commercial interest in all of these heavy mineral sand deposits is high although actual mining operations have been limited to date with the exception of the Old Hickory Deposit. Mineral rights to the deposit have been secured by the Mineral Sands Division of Renison Goldfields Consolidated (RGC) Limited. Full-scale production began in the Fall of 1997. Estimates place the total reserves of heavy minerals there alone at some 8 to 10 million metric tons!

In spite of its considerable commercial promise, however, little detailed mineralogical work about the site has been published. This paper contains an examination of the complete suite of heavy found at the Old Hickory Deposit, with an emphasis on those of economic importance. The processes governing the formation of such marine strand-line placers are reviewed and comparisons with other deposits of a similar nature are made where appropriate. The geologic setting of the site is outlined and the probable provenance of the

heavy minerals discussed. Mineral morphology and textures are given special attention, along with an analysis of mineral compositions. In particular, the process of titanium enrichment of ilmenite through the removal of iron is of major economic interest and is explored here in detail as the primary focus of the study. Based on the textural evidence and a consideration of the environmental factors needed for chemical weathering of ilmenite, it is hypothesized that much of this alteration took place under reducing conditions prior to deposition at the site. Such a multi-faceted approach is intended to provide not only valuable insights into the history of this particular deposit but also to allow a better understanding of other deposits of this type in general and to aid in future exploration effort.

Table 1 - Specific gravity of selected heavy minerals. Modified after Klein and Hurlbut, 1993.

Mineral	Composition	Specific Gravity
Monazite	$(Ce,La,Y,Th)PO_4$	4.6 - 5.4
Magnetite	Fe_3O_4	5.18
Ilmenite	$FeTiO_3$	4.7
Zircon	$ZrSiO_4$	4.68
Chromite	$FeCr_2O_4$	4.6
Rutile	TiO_2	4.18 - 4.25
Spinel	$MgAl_2O_4$	3.5 - 4.1
Corundum	Al_2O_3	4.02
Anatase	TiO_2	3.9
Staurolite	$Fe_2Al_9O_6(SiO_4)_4(O,OH)_2$	3.65 - 3.75
Kyanite	Al_2SiO_5	3.55 - 3.66
Sphene	$CaTiO(SiO_4)$	3.40 - 3.55
Hypersthene	$(Mg,Fe)SiO_3$	3.4 - 3.5
Epidote	$Ca_2(Al,Fe)Al_2O(SiO_4)(Si_2O_7)OH$	3.35 - 3.45
Augite	$(Ca,Na)(Mg,Fe,Al)(Si,Al)_2O_6$	3.2 - 3.4
Hornblende	$(Ca,Na)_{2-3}(Mg,Fe,Al)_5Si_6(Si,Al)_2O_{22}(OH)_2$	3.0 - 3.4
Sillimanite	Al_2SiO_5	3.23
Apatite	$Ca_5(PO_4)_3(F,CL,OH)$	3.15 - 3.20
Biotite	$K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$	2.8 - 3.2

Old Hickory Deposit
Outline Map

C5

Route 40 ———————————————————————————— Route 40

Dinwiddie
County

Bolsters
Store

C4

Sussex
County

C2 C3

*

C1

Virginia

1000 ft
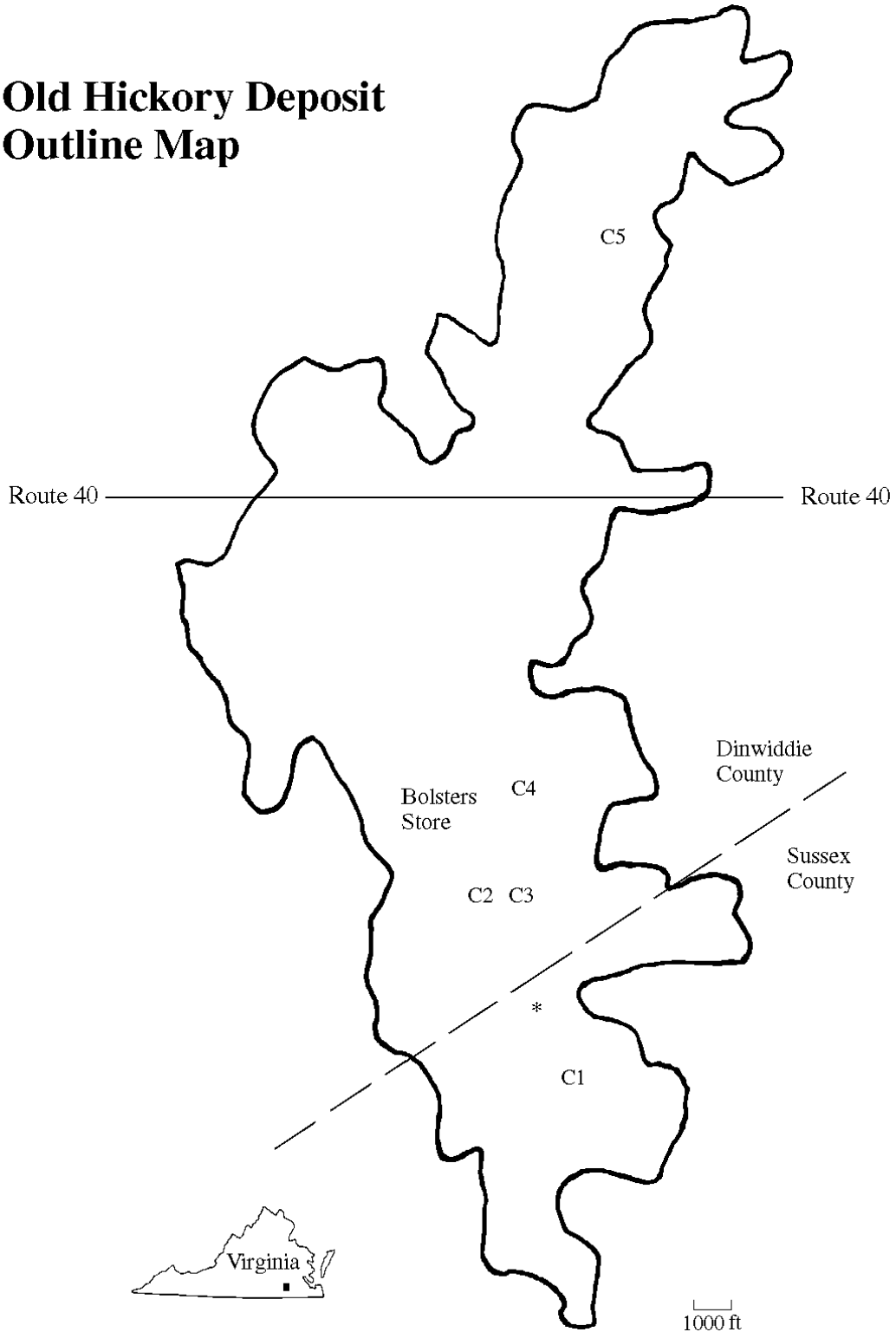
Figure 1 - Outline map of the Old Hickory Deposit, southeastern Virginia showing the 2% cutoff grade for heavy minerals, adapted from materials provided by RGC. Locations C1-C5 mark where heavy mineral concentrate samples were taken. The star identifies where a drill core was analyzed. Figure 17 shows the other deposits which lie along the Fall Zone.

6

PREVIOUS WORK

Background

The long axis of the Old Hickory Deposit lies along the Fall Zone in northwestern Sussex and southeastern Dinwiddie counties and is centered near the small community of Bolster's Store, southwest of Richmond. Although the unlithified heavy mineral sands of the deposit generally are found at or very near the surface of this primarily agricultural area, their potential value went apparently unnoticed until observed by C. R. Berquist, Jr. of the Virginia Division of Mineral Resources. Berquist (1987) first published reports about heavy minerals in the area following reconnaissance sampling of the region. During previous fieldwork and mapping, he had noted the presence of mineral "slicks" in many farm fields and drainage ditches, with the dark coloration of many of the heavy mineral grains resembling an oil slick. He later returned to the area to conduct a more systematic analysis (Berquist, personal communication). Examining samples collected from road cuts and by hand auger, he did, in fact, find unusually high levels of heavy minerals, with an average of 4.46 wt. % total heavy minerals and one sample testing at over 14 wt. %! (Berquist, 1987). Subsequent exploration following this initial report, much of it done by commercial interests, has uncovered a series of similar sandy deposits enriched in heavy minerals extending along the Fall Zone from Virginia to North Carolina and defined the areal extent of the larger deposits such as the Old Hickory. Geologic mapping by Mixon and others (1989) in the Fall Zone of Virginia guided exploration both there and in North Carolina.

Formation of Marine Placers

The deposition and sorting of heavy mineral grains in fluvial and marine environments is controlled primarily by grain size, shape, and density. Placer deposits form where the conditions selectively favor the deposition and concentration of heavy minerals. Titanium is reported to be the ninth most abundant crustal element at an average of 0.57% (Mason and Moore, 1982). Although widely distributed, titanium minerals are present only in small amounts in most source rocks. Mafic and intermediate igneous rocks generally contain more TiO_2 than ultramafic or silicic rocks although variations are subtle (Force, 1976).

Interestingly, analysis of samples from the Apollo 11 lunar mission revealed titanium concentrations in the moon rocks an order of magnitude higher than those typically found in terrestrial rocks (Engel and Engel, 1970).

Gillson (1959) observed that the early geologic histories of all titanium sand deposits share certain fundamental features. He noted that whereas each deposit is unique, they all shared igneous or metamorphic rocks from continental land masses in the "hinterland" as the original source. None of these granites and gneisses initially were particularly rich in ilmenite or rutile. Over time, however, weathering broke down these crystalline rocks leading to the formation of a soil zone. During this period, easily weathered minerals such as magnetite and feldspar quickly decomposed whereas more durable ones such as ilmenite, rutile, zircon, and quartz were comparatively unaffected. Finally, after erosion, selective concentration processes active during transport and deposition of this sediment served to concentrate the heavy mineral fraction and form a placer.

Beyond these initial similarities, however, the geologic history of each heavy mineral sand deposit can vary significantly. Such placers can form in fluvial, littoral, and even eolian environments. Marine placers are the primary focus of the present study, and, in particular, strand-line deposits such as the Old Hickory. Heavy mineral enrichment in marine placers is due to several factors. Sediments in a high-energy beach environment are constantly being reworked, causing considerable mechanical weathering and abrasion, resulting in the breakdown of many less durable minerals such as feldspar. More important is the fact that the action of the waves on the shore can serve as a very effective means of winnowing away minerals of low density, such as quartz (specific gravity = 2.65), while leaving heavy minerals behind. This selective concentration of heavy minerals is thought to take place through a combination of hydraulic sorting mechanisms. To better understand how these mechanisms operate it is necessary to look at three main elements including settling velocity, entrainment, and differential sediment transport.

The concept of hydraulic equivalence was first applied to heavy mineral deposition by Rubey (1933) and by Rittenhouse (1943) and is now well established in the geological literature. Stokes' Law states that the settling velocity of spherical particles from

suspension varies in relation to both the density and the square of the particle diameter and inversely with the viscosity of the fluid. Thus heavy minerals, because of their higher density, as a whole would tend to be proportionately finer grained than quartz or feldspar sediments deposited in the same bed. It is important to realize that this fact by itself does not necessarily imply that any enrichment of heavy minerals has taken place, merely that there will tend to be a difference in the average grain size of the two populations. However, several subsequent studies have shown that the difference is settling rates alone is not sufficient to explain observed grain-size distributions in the case of many heavy mineral marine placers. Instead, heavy minerals tend to be finer (i.e. have slower settling velocities) than would be predicted by the simple settling velocities under Stokes' Law of the low density minerals with which they are found (Hand, 1967; Lowright et al., 1972).

The reason for this apparent anomaly becomes evident as one looks closer at the nature of the depositional environment. Stokes' law applies to simple settling of fine-grained particles in a static column of water. While suspension equivalence as outlined above does primarily govern deposition from a wave breaking over a beach face, the backwash of the same wave has an erosive effect. Now a different set of processes which regulate particle motion are in effect, most significantly the entrainment of grains by the returning flow. Small grains may "hide" in the interstices between larger ones, making them less likely to be caught up and carried back as the wave ebbs seaward (Force, 1991). Being smaller, the heavy mineral grains are thus progressively concentrated in the swash zone by the repeated action of the waves on the shoreline as larger grains are carried offshore (See Figure 2). The "modified equivalence" concept of Hand (1967) was the first attempt to take this factor into account in a model of marine placer deposition. By shifting the settling velocity curves of higher density minerals downward towards lower velocities, he found that the empirical data fit the predicted grain size distribution values much more closely. Understanding of the entrainment process has been further refined by Lowright et al. (1972), Slingerland (1977), and Komar and Wang (1984).

Sediment transport is controlled by many of the same variables which govern settling and entrainment of grains. For particles of equal size and shape, the ones with higher density will be harder to carry in suspension and will tend to hit bottom more frequently during
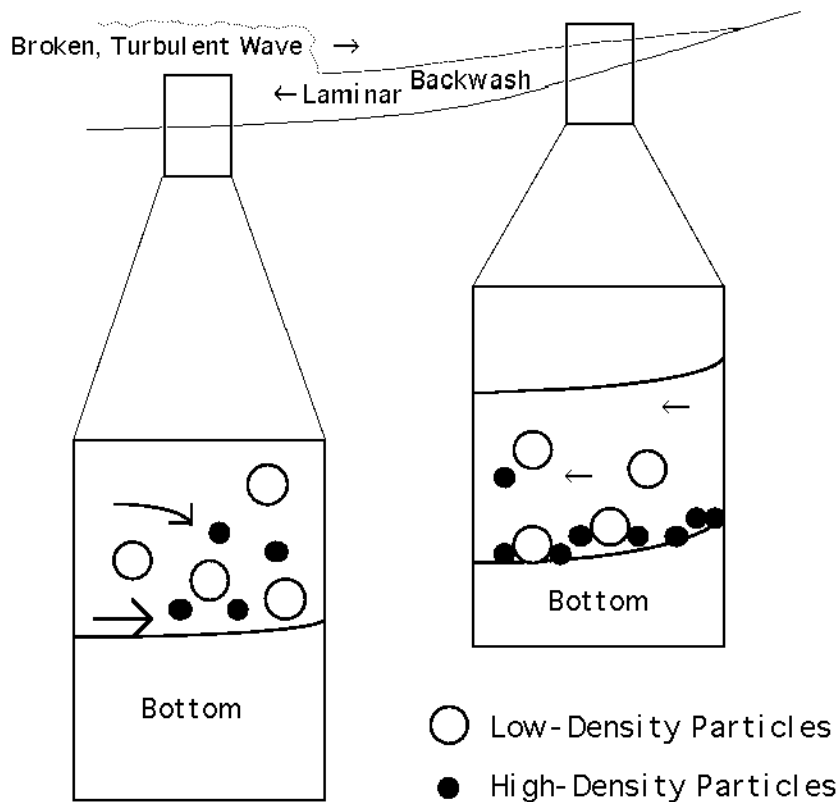
Figure 2 - The above diagram schematically shows the process by which heavy minerals are selectively concentrated on the shore. As they lose energy, the incoming waves deposit sediment in the swash zone according to suspension equivalence. The returning laminar backwash tends to pluck the larger particles off of the bottom because they protrude further into the returning flow. In contrast, smaller, high-density particles tend to "hide" behind the larger ones where they are more protected. Over time this phenomenon can result in the concentration of significant quantities of heavy minerals. Modified after Force, 1991.

saltation, thereby slowing their movement. This differential is especially important at low fluid velocities with highly discontinuous grain motion (Steidtmann, 1982). Consequently, as might intuitively be expected, the lighter minerals would generally move farther in the same amount of time. In the case of beach deposits, lighter minerals could thus be preferentially transported offshore while the heavies are left behind as a lag. Also important, however, is the role that differences in grain size also play in determining transport distances. Flume tests conducted by Meland and Norrman (1966) showed that, on average, larger grains always moved faster that smaller ones for any given particle size, shear velocity, and degree of bed roughness within the range of their experiments. Although they did not include density as one of their parameters, the significance of these findings to heavy mineral sorting should be readily apparent from the discussion above. Clearly both the relative densities of the minerals involved along with their respective differences in grain size are important factors which contribute to the enrichment of the heavy mineral fraction in marine placer deposits.

Shoreline morphology has also been shown to greatly affect heavy mineral deposition in marine environments. Pioneering aerial reconnaissance efforts by McKelvey and Balsley (1948) along the southeast Atlantic coast revealed not only that black sand deposits of heavy minerals were much more common than previously believed but also that their distribution was closely related to the shape of the shoreline. In more detailed work along the coast of Oregon, it was found that heavy mineral concentration varied significantly along short distances (1-2 km) of uninterrupted beaches, implying that composition was primarily controlled by localized sorting processes rather than by regional variations in source mineralogy (Peterson et al., 1987). In particular, the study noted, each of the segments of greatest heavy mineral enrichment was located to the south of a prominent headland. Extending into the sea, these headlands cause a deceleration of the northward-flowing longshore currents at the point of inflection along the shoreline, leading to the preferential deposition of high-density minerals there. Weather and seasonal variations can also play an important role in placer formation as found by Komar and Wang (1984). Strong waves associated with storms can move heavy minerals from the swash zone high up onto the shoreface where they are more protected. Winds may blow this material further inland, forming heavy-mineral rich dunes. These factors are especially important because

beach erosion during periods of intense storm activity can transport large quantities of material offshore.

Taken together, these many different methods of selective concentration outlined above can prove very effective. Fluid-sediment interactions at the microscale act as a natural "dressing mill," separating the heavier ore minerals from the lighter tailings (Slingerland and Smith, 1986). Although these sorting mechanisms act grain by grain, the net result over time can be surprising. Studies of modern beach placers in Oregon by Komar and Wang (1984) have shown that the "concentration factor", the ratio of the concentration of different minerals from the backshore to that found at 50 meters offshore, varied systematically with density and ranged from in excess of 1000 for ilmenite and zircon to less than one for quartz! The results of this natural beneficiation of the ore with respect to heavy minerals clearly dramatizes why such marine placers are so important to the minerals industry.

Geologic Setting

Given the general means by which marine placers are formed as described above, one may then ask what are the specific features which characterize the Old Hickory heavy mineral deposit? A complete description first requires an understanding of the stratigraphy and the geologic history of the area. As previously stated, the Old Hickory Deposit lies along the Fall Zone, where the outer edge of the Piedmont Region and the western margin of the Atlantic Coastal Plain meet. Looking quickly over the site, however, it might be easy to miss this important boundary between the two physiographic provinces given the poor exposure and minimal topographic relief there. Within southeast Virginia, the Piedmont Region in characterized by a complex suite of Paleozoic igneous and metamorphic rocks coupled with Triassic rift basin deposits. Extensive weathering and erosion has produced a gently rolling landscape. The warm, humid climate of the area has also led to considerable chemical weathering beneath the surface and the formation of a thick saprolite layer which often reaches to depths of 30 to 40 feet (Berquist and Goodwin, 1989). Even at roadcuts, the rock often crumbles at the slightest touch. Exposures of solid rock are rare and are limited primarily to stream channels.

The thin wedge of Coastal Plain sediments found on the eastern side of the Fall Zone in the study area unconformably overlies the older crystalline rocks of the Piedmont. Research has shown, though, that the rock types found in the Piedmont Region extend far seaward under this surficial drape of Coastal Plain sediments (Mixon et al., 1989).   The Cenozoic formations of the Middle and Upper Coastal Plain are generally preserved as tabular sheets which record a series of marine transgressions. The relatively uneroded aggradational surfaces which remain have produced a distinctive "stair-stepped" topography. In contrast to the gently rolling landscape of the Piedmont, the Coastal Plain Region is marked by a succession of flat-lying plains with intervening scarps that decrease in elevation seaward (Johnson et al., 1987).

The Piedmont crystalline basement complex of the study area is by no means uniform. Borehole data and regional geologic mapping indicate that under much of the Old Hickory Deposit lies a large mass of late Mississippian Petersburg Granite in fault contact with some felsic gneiss (Raleigh Terrane?). This mass is bounded to the west by a Mesozoic (?) normal fault from low-grade metavolcanic and metasedimentary rocks which may be a northern extension of the eastern Carolina Slate Belt . The fault scarp is of particular significance in that the irregular basement surface which it created likely contributed to the localization of heavy mineral deposition during the subsequent Pliocene transgression (Berquist and Goodwin, 1989; Berquist, 1991).

Within the Upper Coastal Plain sediments of the study area, preliminary stratigraphic investigations recognized two distinct lithologic units. Correlation of these units with other named units, however, has proved difficult.   Following earlier workers, Berquist and Goodwin (1989) designated these units simply as G1 and G2. The older of them, G1, lies unconformably atop the Piedmont basement rock. The younger G2 sediments either overlay the G1 sediments or were deposited directly over basement highs. Their combined thickness is about 15 meters (50 feet) on average (Berquist 1991). Piedmont windows which outcrop within the ore body may have been offshore islands at the time of deposition. Berquist and Goodwin (1989) also reported evidence in many places of an erosional scarp marking an ancient shoreline between 240 and 250 feet in elevation separating the two units. Locally this scarp is known as the Chippenham but it is more commonly referred to as the

Orangeburg Scarp. Similarly, to the east, they noted, another erosional scarp is found at approximately 175 feet above sea level, which divides the G2 sediments from those of the still younger Bacon's Castle Formation (See Figure 3).

The tidal prism sands and mud of the G1 unit are readily identifiable by a basal gravel lag of fluvial (?) origin. This lag is composed predominately of quartz pebbles and cobbles up to 15 cm (6 inches) in length. These clasts are a mixture of hard vein quartz and less-competent quartzose sandstone. Most, though not all, of these quartz clasts are well-rounded. Cobbles and boulders up to 150 cm (5 ft.) of iron-cemented sand are also present near the scarp. These quartz and ironstone clasts were reworked from older materials during the initial transgression associated with the formation of the Old Hickory Deposit. Above this flaser bedding, which often has evidence of bioturbation, clay lenses can also be observed.

It is the G2 terrace sediments, however, which are the richest in heavy minerals. The G2 unit is a fine-grained quartzose sand which is rich in dispersed clay, probably in part as a result of in-situ weathering of feldspar. The G2 unit is well-sorted, and generally lacks the coarse sand, gravel, and clay beds found in the G1 unit. The two units are one of the oldest in a series of beach terrace deposits found in the Coastal Plain, each the result of a marine transgression at successively lower elevations which led to the "stair-stepped" topography of the region (Berquist and Goodwin, 1989). The G1 and G2 units have been mapped by Mixon et al. (1989) as Tmsg (Miocene sand and gravel) and Tpsg (Pliocene sand and gravel) respectively. Subsequent reevaluation of their age, however, led to the combination of the two units under the single designation psg (Pliocene sand and gravel) on the 1993 Geologic Map of Virginia (Virginia Division of Mineral Resources, 1993). Furthermore, observations in the exposures created by mining will likely result in stratigraphic refinement or redefinition of these sediments.

Carpenter and Carpenter (1991) conducted a thorough review of the stratigraphy of the Upper Coastal Plain sediments of Virginia and North Carolina, supplementing existing studies with drilling data from nearly 2,500 auger holes. They also recognized the two distinctive lithologic units found in the region which they termed the "lower unit" and the

West

East

Orangeburg Scarp

Broad Rock Scarp

___
300 ft

G2

HM   HM

G1   G1

___
200 ft

Eastern Slate Belt
Metavolcanics

HM

G2

G2

Bacon's Castle
Formation

Petersburg Granite &
Raleigh Belt Gneiss

G1 – Transgressive lag gravel, overlain by tidal prism sands.

G2 – Medium-grained well-sorted sands.

HM – Heavy mineral concentration varies across the deposit but
is richest at higher elevations and at the toe of the scarp.
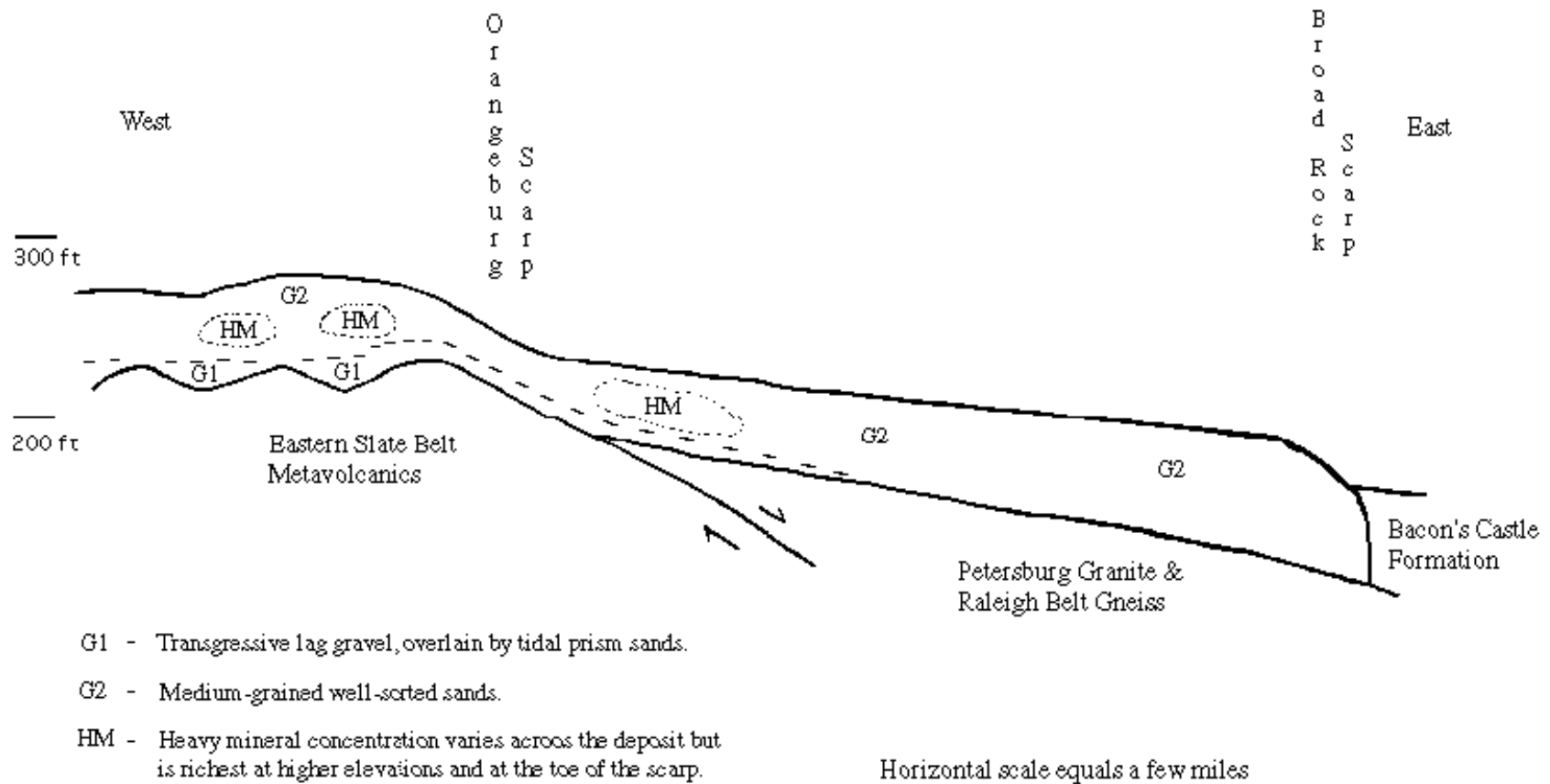
Horizontal scale equals a few miles

Figure 3 - Generalized cross-section of the Old Hickory Deposit, modified after Berquist, 1989, Carpenter and Carpenter, 1991 and unpublished material provided courtesy of RGC Minerals Sands Limited.

"upper unit." Somewhat confusingly, however, their upper unit corresponds to the lower-elevation G2 unit of Berquist and Goodwin (1989) described above.
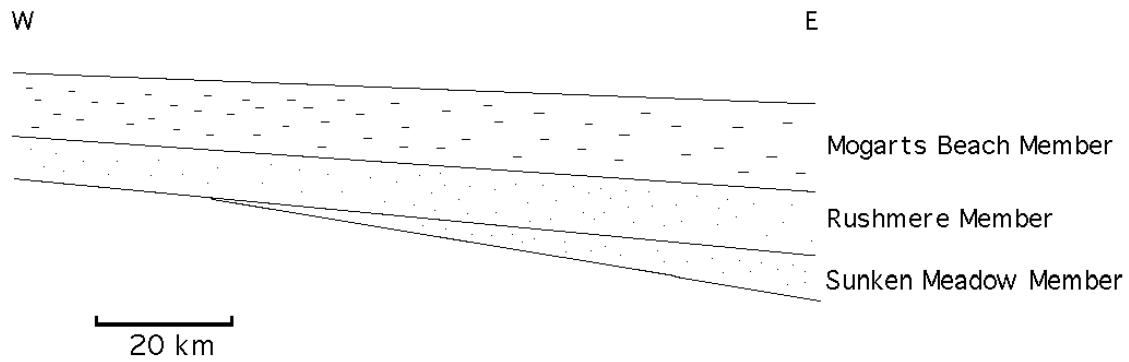
Carpenter and Carpenter (1991) interpreted the two units to be updip, near-shore equivalents of the Yorktown Formation. After a thorough review of the geologic history of the Yorktown in northeastern North Carolina, Bailey (1987) had determined that it was deposited as a result of a major transgressive-regressive event during the Pliocene which, at its peak, pushed the sea westward to slightly beyond the present Fall Zone. Based on biostratigraphy and other lithologic evidence, he prepared a detailed reconstruction of the depositional history of the formation (See Figure 4). According to Bailey's interpretations, the well-sorted sands of the lowermost Sunken Meadow Member comprise a winnowed sand sheet which formed by shoreface erosion and reworking of older sediments during the early stages of the transgression. These basal sands were in turn overlain by the shell-rich Rushmere Member, which formed in a lower-energy, shallow-to-intermediate shelf setting. Finally, the thick overlying sequence of thinly laminated silts of the Mogarts Beach Member, Bailey hypothesized, formed during a regression as estuarine basins to the west were filled in and more sediment was passed on directly to the shelf.

The model described above provides a useful framework for understanding the depositional history of the Coastal Plain sediments found further inland in the area of the Old Hickory Deposit. Based on paleontological evidence, Cronin and others (1984) determined that the age at the base of the Yorktown to be about 4.0 m.y. with a maximum age of 4.8 m.y. According to Carpenter and Carpenter (1991), the two lithologic units found there along the Fall Zone can be correlated with the upper two members of the Yorktown Formation. During the initial stages of the transgression, when the Sunken Meadow Member was being deposited to the east, the sea had not yet reached the area of the Fall Zone. Rather it is the later Rushmere Member of the Yorktown Formation which marks the maximum extent of the transgression. Hoffman and Carpenter (1992) estimated that at its peak this transgression reached to an elevation of at least 280 to 290 feet. Based on the presence of basal gravel in the lower unit coupled with a general rise in the elevation of this unit towards the west, Carpenter and Carpenter (1991) interpreted the lower unit to be a near-shore equivalent of the Rushmere Member. The finer-grained and better-sorted upper unit in

turn was believed to be an updip equivalent of the retrogradational facies of the Mogarts Beach Member. Extended periods of stillstand provided the time needed for heavy minerals to be concentrated on the beachface (Hoffman and Carpenter, 1992).

The Old Hickory and related deposits along the Fall Zone in Virginia and North Carolina, are not the only heavy mineral placers thought to have formed as a result of a major transgression-regression during the Pliocene. In fact several major deposits of this type are believed to have formed along coastlines in various parts of the world during this time. These include Trail Ridge, Florida; Lakehurst, New Jersey; and Enneaba, Australia among others (Force and Rich, 1989; Carpenter and Carpenter, 1991).

Yorktown Formation, NE North Carolina

W   E

Mogarts Beach Member

Rushmere Member

Sunken Meadow Member

20 km

Unit		Sea Level		Descriptive Notes
		Rising	Falling	
Y o r k t o w n F o r m a t i o n	Mogarts Beach Member			Thin laminated silts, formed from sediment bypassed from the west.
	Rushmere Member			Fossiliferous sands, formed in low-energy shelf setting.
	Sunken Meadow Member			Basal sands, formed by shore-face erosion and reworking of older sediments.

Figure 4 - Generalized cross-section and stratigraphic column of the Yorktown Formation in northeastern North Carolina with details of the depositional history. The upper two units of the Yorktown as found there have been interpreted as distal equivalents of the Old Hickory Deposit. Modified after Bailey, 1987.

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METHODS OF STUDY

During survey work undertaken by RGC, cores were taken by truck mounted auger at regular intervals in a systematic grid pattern with a minimum spacing of 62 m (200 feet) East - West and 308 m (1000 feet) North - South across the entire study area. Horizons were separated visually and logged by the operator during drilling until basement was reached. For this study, bulk heavy mineral concentrates from five different sites across the deposit were examined. In addition to these bulk samples, known depth samples from drill hole 552462 situated in one of the richer zones of the deposit were also studied. After a light pounding to break up dried clumps of material, initial separation of the heavy mineral fraction from the lighter minerals and fine-grained clay was done using a gold pan. Ultrasonic cleaning was used to help remove any surficial clay coatings from the heavy mineral grains. Settling of the remaining material in a solution of sodium polytungstate was used to complete the separation process. This heavy liquid is much safer to work with than the more traditional bromoform or tetrabromethane preparations, both of which are toxic (Callahan, 1987). Samples were then washed in distilled water and allowed to air dry. Polished sections 2.5 cm (1 inch) in diameter were then prepared using standard techniques (Craig and Vaughan, 1994). Because of the loose, disaggregated nature of the sample material, vacuum impregnation was used during casting in an attempt to improve the effectiveness of the epoxy resin and reduce the number of air pockets. By subdividing each of the polished sections into quarters using small plastic dividers, it was possible to put up to four separate samples of mineral sand into each one, saving time during sample preparation and reducing the volume of material needed.

All polished sections thus obtained were initially examined using reflected light with a Lietz polarizing microscope. A substantial amount of useful information could be gathered even by this comparatively simple approach. Grains showing evidence of textural features of interest were marked for further study. A CamScan Series II scanning electron microscope (SEM), equipped with an energy dispersive system spectrometer, was then used for more detailed examination, including analyzing the degree of ilmenite alteration. Finally, a Cameca Camebax SX 50 electron microprobe was used for quantitative mineral analysis of selected grains, both to determine precise mineral compositions and for mapping of minor and trace elements.

MINERALOGICAL CHARACTERIZATION

Overview

The four principal minerals of economic interest found at the Old Hickory site are ilmenite, leucoxene, rutile, and zircon. Several other heavy minerals including staurolite, kyanite, tourmaline, and monazite are also present. Total heavy mineral concentrations vary widely across the deposit with the remainder of the material composed mainly of quartz and clay. Figure 5 shows a sample of heavy mineral concentrate after initial separation. The photomicrographs in Figures 6 through 9 show examples of the four major minerals of economic interest as they appear in polished section. Quartz grains average about 0.25 mm in diameter, with ilmenite grains about half of that. This size differential is a direct result of the sorting mechanisms described earlier. Zircon grains at the site are commonly elongated and grains of all types show evidence of substantial mechanical weathering and abrasion.

Mineralogy of the Iron-Titanium Oxides

Ilmenite, leucoxene, and rutile comprise nearly 70% of the total heavy mineral assemblage. The physical properties of the major titanium oxide minerals are summarized in Table 2. Taylor (1964) experimentally determined the phase relations within the system FeO - Fe_2O_3 - TiO_2 at high temperature, documenting the three major solid solution series which are present (See Figure 10). Elsdon (1975) provides a detailed review of the mineralogy of these phases. A thorough knowledge of these minerals and the relationships between them is helpful to those studying rock magnetism. Furthermore, in petrologic studies, the iron-titanium oxide minerals can provide important paragenetic information on oxygen fugacities in igneous melts as well as serve as a useful geothermometer (Buddington and Lindsley, 1964; Powell and Powell, 1977).

Ilmenite ($FeTiO_3$) is a common accessory mineral in igneous and metamorphic rocks where it is often associated with hematite or magnetite. It is opaque, with a deep blue to black color and metallic to submetallic luster. Grains at the Old Hickory site are sub-rounded to rounded, reflecting the high-energy depositional environment (See Figure 6). Ilmenite has a

Figure 5 - Sample of heavy mineral concentrate from the Old Hickory Deposit after the initial separation by the spirals. Elongate, clear to whitish grains are zircon. Darker grains are primarily a mix of ilmenite in various stages of alteration along with a small amount of rutile. Note the high degree of rounding throughout. Field of view equals 3.5 mm.
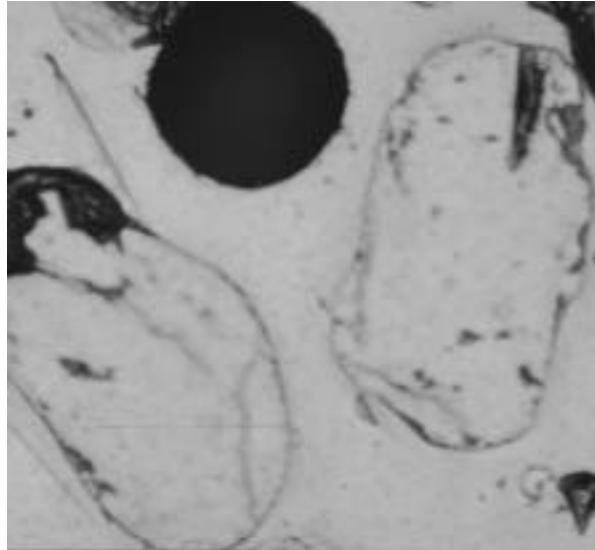
Figure 6 - Photomicrograph of two typical ilmenite grains from the Old Hickory Deposit as seen in polished section. (The large black circle at the top is a hole in the surface of the sample.) These grains are relatively unaltered but, as will be shown later, a wide variety of alteration textures can be observed among the ilmenite grains. Field of view equal 0.4 mm.
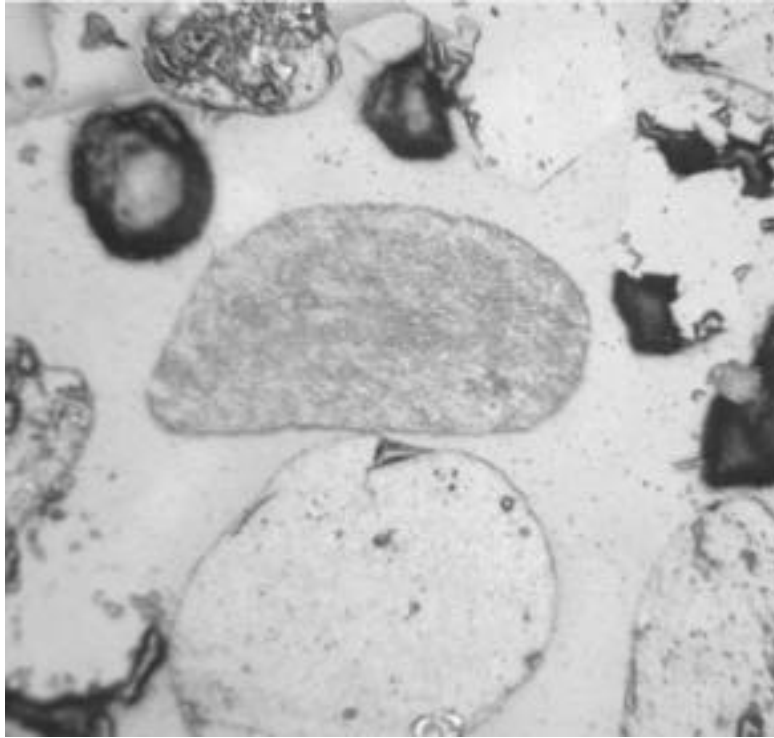
Figure 7 - Photomicrograph of a typical leucoxene grain from the Old Hickory Deposit. (The mottled grain in the center.) Leucoxene is a finely crystalline aggregate. Under crossed polars it resembles a dirty snowball in appearance. Field of view is 0.6 mm.
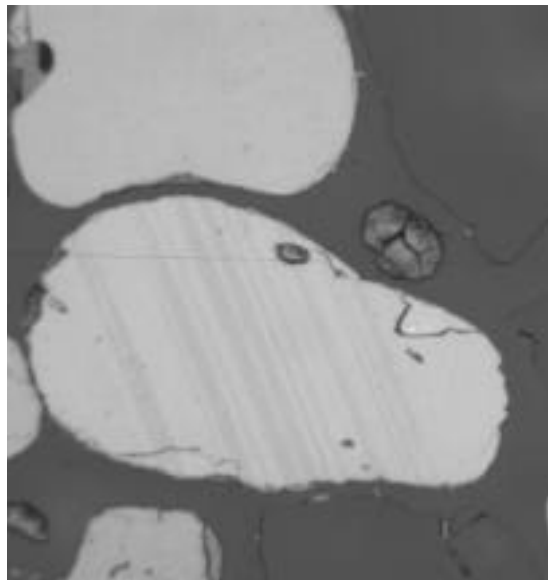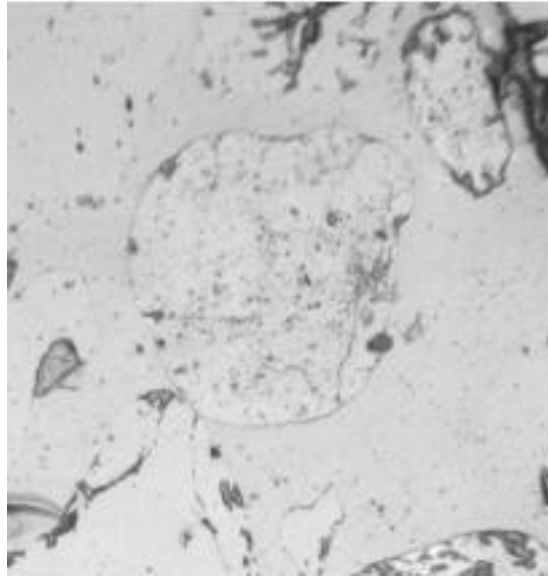
Figure 8 - The top photomicrograph is of a typical rutile grain from the Old Hickory Deposit. (The clear grain in the center.) Rutile is primary in origin, in comparison to leucoxene which is a secondary mineral that forms by weathering of ilmenite. Even though their composition is similar, their appearance is quite different. Rutile grains also exhibit uniform extinction and may show twinning as in the bottom photograph. These features can further serve to differentiate the two. Field of view equals 0.4 mm for both.
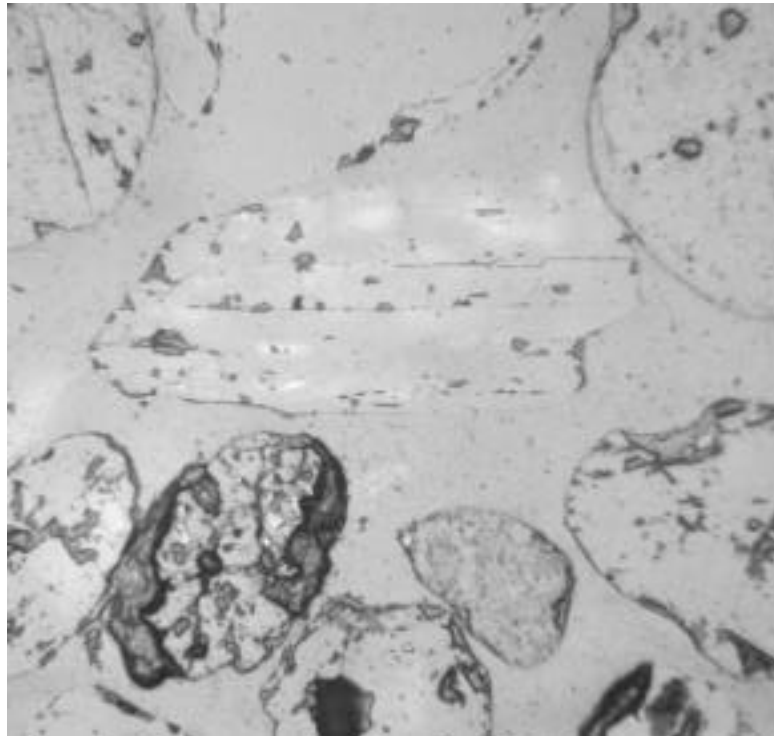
Figure 9 - Photomicrograph of a typical zircon grain from the Old Hickory Deposit. (The elongate grain in the center.) The zircon grains as a whole tend to be much more angular than most of the other minerals present. Note also the strong internal reflections. Field of view equals 0.6 mm.

Table 2 - Physical properties of the major titanium oxide minerals.

Mineral	Formula	Crystal System	Density	Remarks
Ilmenite	$FeTiO_3$	Trigonal	4.7	Pinkish tint, strong pleochroism and anisotropism
Pseudorutile	$Fe_2Ti_3O_9$	Hexagonal	4.2-4.5	Metastable, higher reflectivity than ilmenite
Leucoxene	$Fe_{2-x}Ti_{3+x}O_{9+x/2}$	Transitional	3.9-4.2	Amorphous to finely crystalline
Rutile	TiO_2	Tetragonal	4.18-4.25	Strong internal reflections, may be twinned
Anatase	TiO_2	Tetragonal	3.9	Low-temperature polymorph of rutile

Note: In general, reflectivity tends to increase and both specific gravity and magnetic susceptibility tend to decrease with increasing degrees of ilmenite alteration. Table compiled in part from data in Klein and Hurlbut (1993), Grey and Reid (1975), Craig and Vaughan (1994), and Wort and Jones (1980).
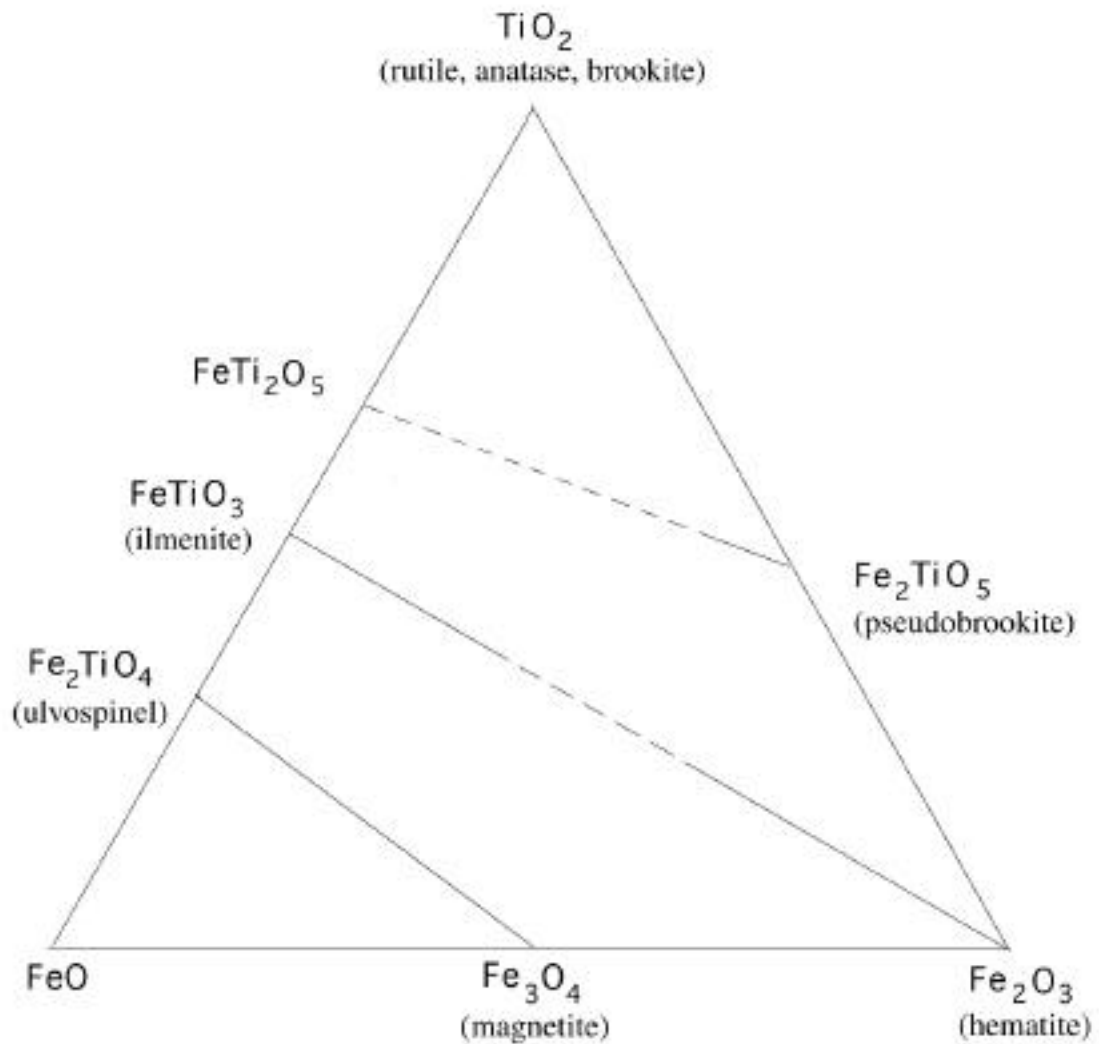
Figure 10 - Ternary diagram showing the three major solid solution series within the system
FeO - Fe_2O_3 - TiO_2. Modified after Klein and Hurlbut, 1993.

rhombohedral structure similar to that of corundum, with Fe and Ti in alternate octahedrally coordinated layers perpendicular to the c-axis. The oxygen framework is slightly distorted from true hexagonal closest packing. Two-thirds of the available interstitial sites are occupied by cations. Within this structure a number of substituents are possible, most notably Mn and Mg (Lindsley, 1976; Klein and Hurlbut, 1993, p.380-381). It is well known that iron can exist in nature in multiple valence states and the same is true of titanium. Based on a study of X-ray adsorption edges, Hamos and Stscherbina (1933) determined that ilmenite must be $Fe^{2+}Ti^{4+}O_3$ and not $Fe^{3+}Ti^{3+}O_3$ even though both formulas were theoretically possible based on chemical considerations alone.

Stoichiometric ilmenite contains 52.7 wt. % TiO_2. However natural ilmenites can vary widely in their actual titanium concentrations from this theoretical ideal. The reasons for this fact can be found both in the way in which ilmenite crystallizes from a melt and in the effect that weathering reactions can have on it after it has formed. At high temperatures, ilmenite forms a complete solid solution with hematite. As a result the TiO_2 content of most primary ilmenite is actually lower than the molecular formula would suggest. On cooling the two components unmix to create an intergrowth of two phases (See Figure 11) consisting of ilmenite with a small amount of hematite in solution and vice versa (Dimanche and Bartholome, 1976). For the sake of simplicity, hereafter these two phases are referred to by the dominant component. The remains of thin lenses of hematite which form parallel to the basal plane (0001) of ilmenite during exsolution can readily be observed in many grains in samples from the Old Hickory Deposit. The hematite in these lamellae has been selectively leached away, leaving a series of empty pits (See Figure 12). The same was found to be true in the case of ilmenite from modern beach sediments at Emerald Isle, North Carolina (See Figure 13). These hematite exsolution lamellae can still be seen, though, in similar samples of detrital ilmenite grains from fluvial deposits at Lilesville, North Carolina which are not as heavily altered. Even there, however, it is evident that hematite has already been leached away from the outer portions of the ilmenite grains (See Figure 14).

During weathering, ilmenite loses iron, becoming progressively enriched in titanium. Taken to completion, the end result is almost pure TiO_2. Because of the gradational nature of this
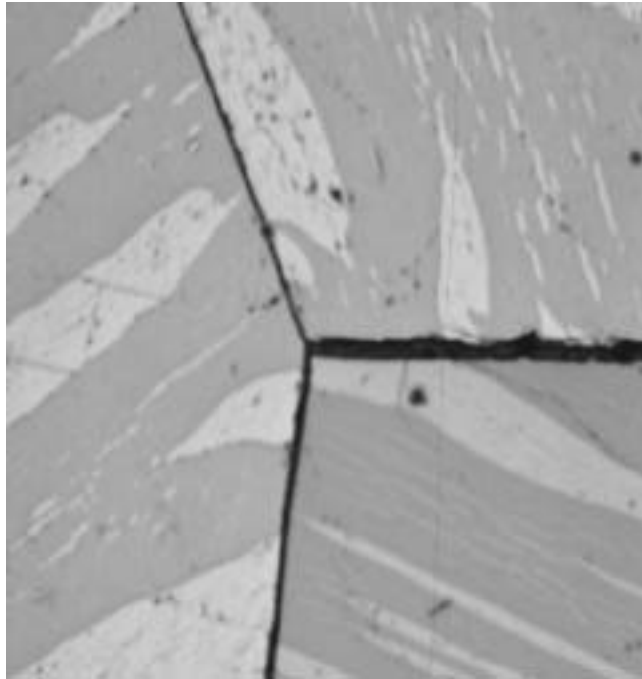
Figure 11 - A close-up of primary ilmenite from Lac Tio, Quebec showing hematite exsolution lamellae (light gray) in a darker matrix of ilmenite. The triple junction and large, coarse exsolution lamellae seen here are characteristic of a metamorphic source rock. Field of view equals 0.6 mm.
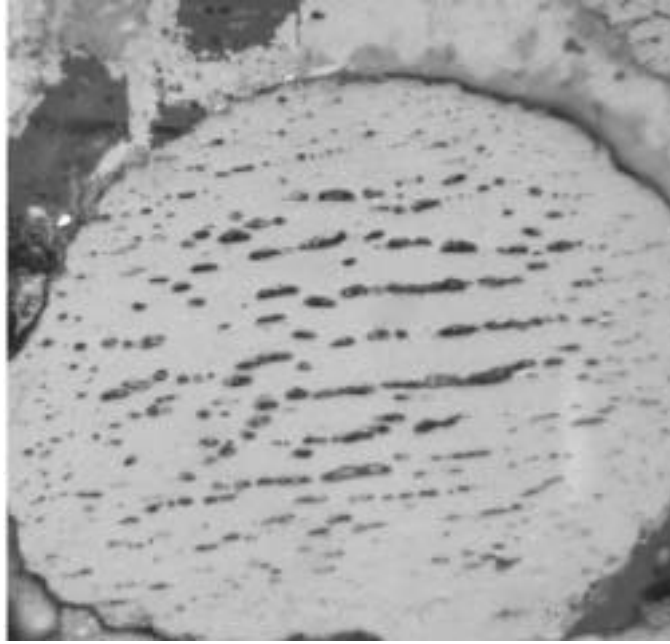
Figure 12 - Photomicrograph of a detrital ilmenite grain from the Old Hickory Deposit showing the rows of subparallel pits left by leaching out of the hematite exsolution lamellae. As shown in this polished section, even lamellae in the interior of the grain have been leached away. Field of view equals 0.24 mm.
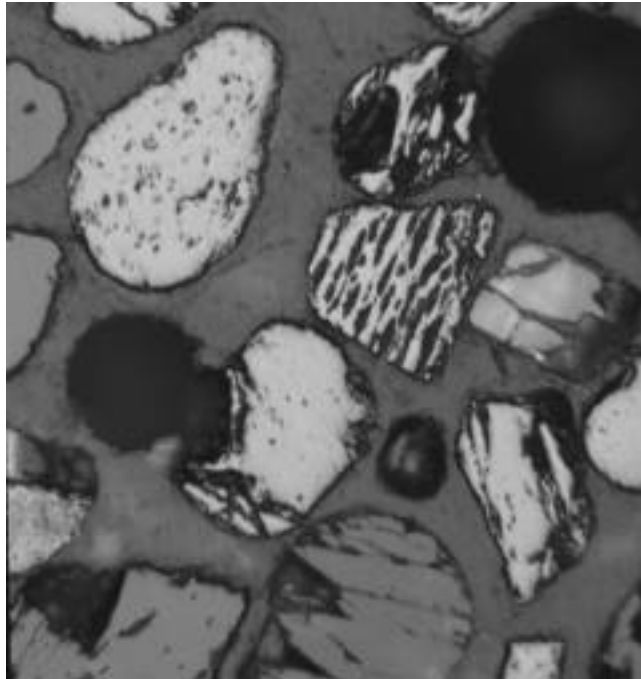
Figure 13 - Photomicrograph of modern beach placers from Emerald Isle, North Carolina. The ilmenite grain near the center shows pits left by the removal of hematite as observed in samples from the Old Hickory Deposit. One difference, though, is that overall grains from the modern beach sediments shown above are significantly more angular. Field of view equals 0.6 mm.
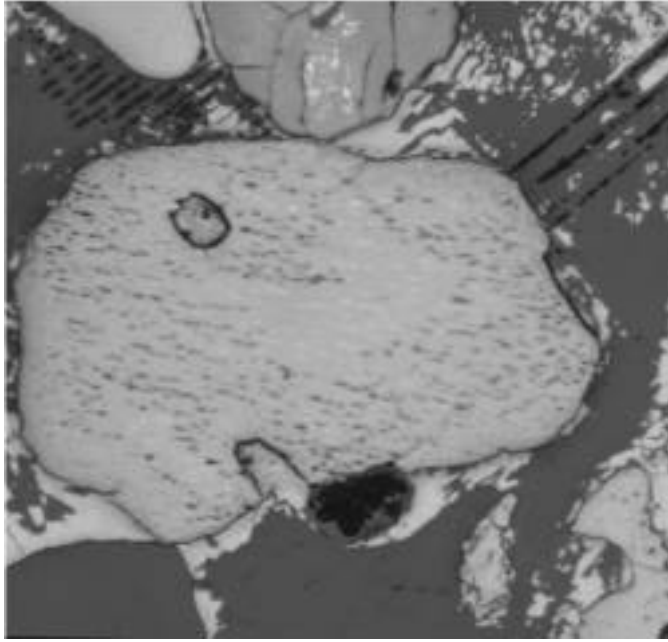
Figure 14 - Detrital ilmenite grain from Lilesville, North Carolina. As the photograph shows, hematite exsolution lamellae are still present in the interior of the grain even though they have been leached away around the perimeter. Field of view equals 0.24 mm. Element concentration maps and backscattered electron images of this same grain are shown in Figures 20 and 21 respectively .

process, the nomenclature of the alteration products of ilmenite has been a source of considerable controversy (Lynd, 1960a; Golding, 1961). The alteration of ilmenite occurs through leaching and progressive removal of iron, primarily along grain boundaries and internal discontinuities. Hematite lenses, when present, may commonly be dissolved first due to their greater solubility under certain conditions. (See following sections for additional details.) The result is subparallel pits on the surface of the ilmenite grains where the hematite has been leached away. Under natural conditions, the reaction kinetics involved in the alteration of ilmenite are slow and multiple states of alteration may often be seen in a single grain (Bailey et al., 1956). When viewed under polarized light, changes in reflectivity and color are evident as a result of alteration. With a loss of iron from the ilmenite lattice, the grains become more porous, with a granular texture (See Figure 30). Magnetic susceptibility has also been found to vary, generally decreasing as alteration progresses (Wort and Jones, 1980). The space created in the internal crystal structure by the removal of iron allows further and deeper oxidation to occur (Temple, 1966). As the value of the ore is heavily dependent on the titanium content, the weathering process of ilmenite is a matter of considerable interest to the mineral industry.

The question naturally arises as to whether this progressive alteration produces any distinct secondary mineral phases intermediate between ilmenite and rutile. Arizonite, a monoclinic (?) mineral described by Palmer (1909) having the composition $Fe_2O_3*3TiO_2$ was later disputed by Overholt et al. (1950) as being a mixture of hematite, ilmenite, anatase and rutile. This view was substantiated by a systematic investigation of titaniferous beach sands undertaken by Lynd et al. (1954) using reflected light microscopy coupled with x-ray examination. Debate about arizonite continued in the literature, however, for a number of years (Flinter, 1959; Karkhanavala, 1959) in part because of the ambiguous results of the powder x-ray diffraction techniques used in the analyses. Teufer and Temple (1966), though, positively identified a new alteration mineral of the same composition, $Fe_2Ti_3O_9$, as had Palmer by using a more precise single crystal x-ray diffraction approach in their analysis. However, the new mineral, which they named pseudorutile, was found to have hexagonal symmetry. Several of the interplanar d-spacings of pseudorutile are very close to those of ilmenite and rutile, no doubt contributing to some of the earlier confusion. Grey and Reid (1975) were able to show that the structure of pseudorutile consisted of a

hexagonally-closest packed oxygen lattice with local metal ordering in the octahedral sites. They also noted that all of the iron in the mineral has been oxidized to the trivalent state and that its composition corresponds to the maximum extent of iron removal from the ilmenite structure without concomitant removal of oxygen.

The mineral pseudorutile therefore serves as a useful reference point in seeking to gain a better understanding of the alteration process of ilmenite. Using nomenclature based on that of Temple (1966), low-Ti alteration products which have not yet reached the composition of pseudorutile may simply be termed "altered ilmenite." The continued alteration by further removal of both iron and oxygen, which destroys what remains of the original structure, will eventually result in nearly pure TiO_2 with minor other impurities. The term leucoxene is commonly used for these finely-crystalline, high-Ti alteration products although exact definitions vary. Such a distinction is also useful in the commercial sense. There are two main ways in which titanium oxide minerals are processed, sulfanation and chlorination. Altered ilmenite, which is still high in iron, is used in the sulfate process of pigment manufacture. Leucoxene, in contrast, with its high titanium and low iron content, may simply be chlorinated like rutile. The resulting titanium tetrachloride can then be reduced with sodium or magnesium to make titanium metal (Gillson, 1959; Temple, 1966). This difference is significant because chlorination is both less costly and less environmentally disruptive than treatment with sulfuric acid. Attempts have also been made to upgrade low-Ti feedstock by leaching with concentrated acid at elevated temperatures and other treatments designed to selectively remove iron (Mackey, 1974; Lynd, 1983). RGC, which has leased the land at the Old Hickory Deposit and has other heavy mineral sand operations in Florida and Australia, utilizes a two-stage proprietary process for the conversion of ilmenite to higher-valued synthetic rutile.

Naturally occurring rutile (TiO_2) is also found at the Old Hickory site in addition to the other titanium minerals. Like ilmenite, rutile is also a common accessory minerals in igneous and metamorphic rocks although known reserves are considerably less. It is reddish-brown to black in color with an adamantine luster (See Figures 5 and 8). The structure of rutile is composed of chains of oxygen octahedra, each with a Ti^{4+} cation at the center, which run parallel to the c-axis. Twinning is common. Rutile has two comparatively rare naturally-

occurring polymorphs, anatase and brookite. In anatase, the TiO_6 octahedra share four edges, in brookite three edges, and in rutile they share only two (Klein and Hurlbut, 1993). Brookite is believed to be metastable and of secondary origin. The free energy of formation for both rutile and for anatase are both very close at -888.8 and -883.2 kJ/mol respectively at 298.15^0 K and 1 bar (Robie and Hemingway, 1995). Experiments by Dachille and others (1968) determined rutile to be the high-temperature, high-pressure phase relative to anatase. The experiments also revealed a fourth polymorph TiO_2 (II) which is stable only at high pressures (See Figure 15).

Leucoxene, as described above, approaches TiO_2 in its final composition. In fact, the leucoxene found in the altered beach sands is actually composed largely of very fine crypto- to microcrystalline rutile ± anatase, intermixed with other residual minerals from the weathering process. The textural differences of leucoxene from primary rutile grains (See Figures 7 and 8) are readily apparent, however, as can be seen in the photographs.

Other Heavy Minerals

The complete suite of heavy minerals at the Old Hickory Deposit contains much more than just the titanium minerals described in the previous section. These other heavy minerals are present in varying amounts, and with the exception of zircon, have little or no economic value. Zircon ($ZrSiO_4$) is often mined as a by-product from titanium minerals sands and comprises 17 to 20% of the heavy mineral assemblage present at the site. Color can vary but the grains from the study area are generally clear to a pale cream with an adamantine luster. The grains are often elongated and tend to be more angular than those of ilmenite due to breakage along cleavage planes during mechanical weathering (See Figures 5 and 9). Dryden and Dryden (1946) found zircon to be highly resistant to weathering, due to its hardness (H = 7.5) and its relative chemical inertness. This accounts in part for its near ubiquity in heavy mineral-bearing sediments. In fact, the percentage of the three minerals zircon, tourmaline, and rutile is used as a measure of the maturity of a heavy mineral assemblage in the ZTR index developed by Hubert (1962).

Zircon has a tetragonal symmetry but its internal crystal structure may often be damaged by bombardment from the decay of radioactive elements present in small amounts in many
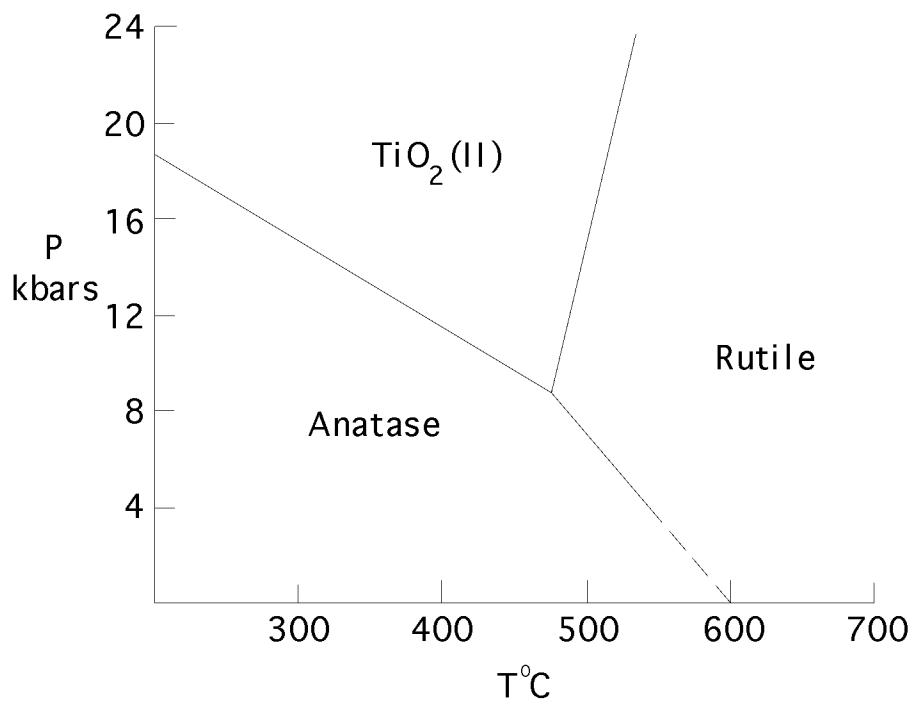
Figure 15 - Pressure-temperature diagram of the three stable polymorphs of TiO_2. Brookite is not shown above because it is metastable. Modified after Dachille, Simons, and Roy, 1968.

zircons (Klein and Hurlbut, 1993). Using polarized light, the grains exhibit strong birefringence and show bright multicolored internal reflections under crossed nichols. The only other mineral present in significant amounts is staurolite ($Fe_2Al_9Si_4O_{22}(O,OH)_2$), which makes up 7 to 10 % of the total heavy minerals. The other heavy minerals that are present include polymorphs kyanite and sillimanite (Al_2SiO_5), tourmaline ($(Li,Mg,Al)(Al,Fe,Mn)_6(BO_3)_3(Si_6O_{18})(OH_4)$), and monazite ($(Ce,La)PO_4$ (Berquist, 1987). Using Back-Scattered Electron (BSE) imaging, the latter stands out clearly because of its high average atomic number.

Non-Heavy Mineral Fraction and Processing Considerations

While it is referred to as a heavy mineral deposit, the majority of the sediment at the Old Hickory Deposit is actually quartz, silt, and clay. The quartz fraction is noticeably coarser in the lower unit, while the upper unit is composed largely of well-sorted fine to medium grained sand. The clay is primarily kaolinite. Some of the dispersed clay found throughout the deposit was clearly codeposited with the sand (e.g. clay drapes in flaser bedding) but much of it is also likely the result of breakdown of feldspar due to chemical weathering.

The clay fraction is problematic for mineral processing as the "slimes" can interfere with mineral separation. After being pumped as a slurry to the wet mill for processing, much of the clay is removed via a large centrifuge or "cyclone." In the remaining sands, the quartz and heavy minerals are then separated out from one another in a bank of spirals (See Figure 16). Land reclamation efforts are also complicated by the need to remix the sand and clay tailings from the different stages of processing in the proper proportions. A flocculant is used to help settle out the finer-grained material from suspension in the tailings ponds.

To better gauge site-specific conditions, a pilot plant was established by RGC in late 1994 and run for several months. Approximately 2,000 tons of heavy mineral concentrate were produced. In general, such pilot plants can provide invaluable test beds to uncover any hidden problems and fine-tune processing techniques before major investments are made. They also provide samples for market research (Macdonald, 1983). In the pilot operation at Old Hickory ore was dug from pits approximately 75 ft. wide by 200 ft. long. The same

general processes is being used in the company's full-scale operation that began in Fall of 1997 with the exception that significantly larger pits are being employed for greater speed and efficiency. RGC currently plans to market three classes of material including ilmenite, zircon, and a "high-Ti" product made up of rutile and leucoxene (L. Clemons, personal communication).
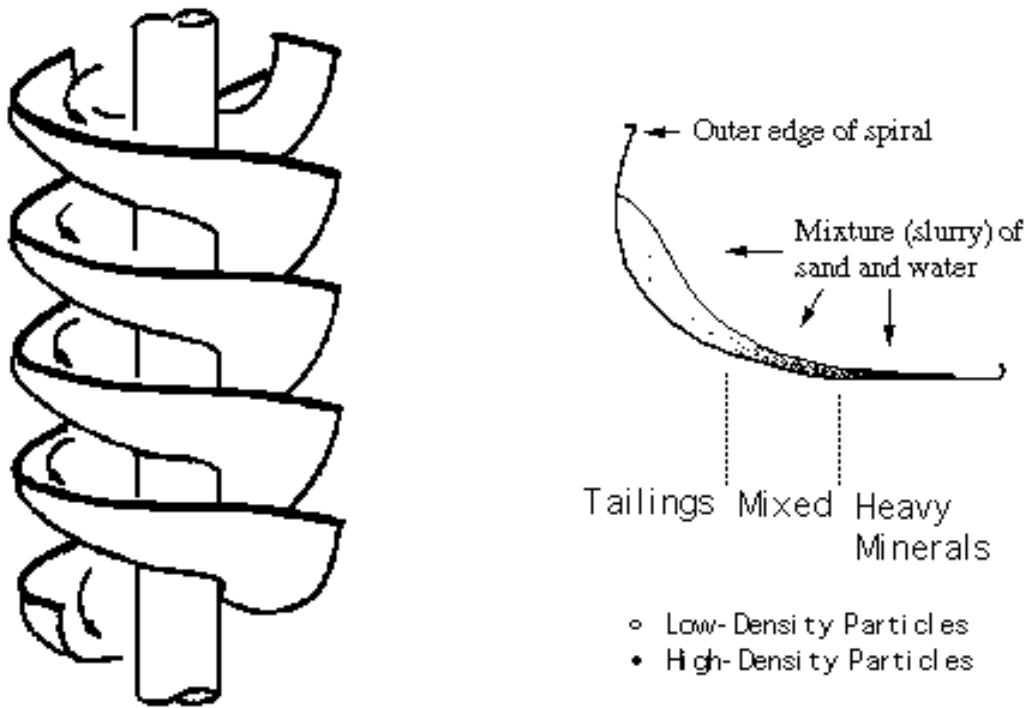
Figure 16 - The left-hand view shows the type of spiral commonly used for initial concentration of heavy minerals. Sand is pumped as a slurry to the top of the spiral and washed downward. In the process, low-density minerals such as quartz are swept to the outside as shown in the enlarged cross-section on the right. The middle fraction, which contains a mixture of both heavy and light minerals is generally sent through the spirals a second time. Modified after Goodall and Bradford, 1983.

RELATED DEPOSITS AND PROVENANCE

Other Related Deposits

The Old Hickory is the largest in a series of stranded beach terrace deposits in Virginia and North Carolina which lie in a narrow belt along the Fall Zone. These were found after reconnaissance reports published by Berquist (1987) of high heavy mineral concentrations in samples from undifferentiated high-level "gravels" in southeastern Virginia. The other major deposits, from North to South, include the Brink, Aurelian Springs, Bailey heavy mineral sand deposits (See Figure 17). Combined with a number of smaller deposits they contain an additional 13 million metric tons of heavy minerals. Erosion and dissection by streams has reduced the original volume of these deposits. Consequently, as shown of the map, several of the above-named deposits are actually composed of two or more distinct areas of identified reserves. Carpenter and Carpenter (1991) provided the most thorough review of the stratigraphy and mineralogy of this series of deposits. They found that the two distinct lithologic units previously discussed were present at each of them. In addition, evidence from field relations suggests that all of the deposits were formed during the same major Pliocene transgressive-regressive event. In general terms, the other characteristics and heavy mineral assemblages are also similar.

There are a few important differences, however. The underlying Piedmont basement rock, for example, varies in character from one deposit to another. Arkosic sands tend to be present in the lower unit wherever it overlies granite, reflecting erosion of basement headlands during the early stages of the transgression. Of the heavy minerals, zircon concentrations tend to vary the most widely between deposits (Geoff Moore, Personal Communication). Carpenter and Carpenter (1991) noted, though, that the most significant difference between the various deposits is in their present-day elevation. The deposits can be found over an elevation range of 53 m (175 feet) to 96 m (315 feet). The richest heavy mineral reserves, however, tend to be those above 73 m (220 feet) in elevation. This suggests that while the above deposits may have all been formed as a result of the same transgressive-regressive event, that they formed at different stages in the process as the sea alternately advanced and then retreated.
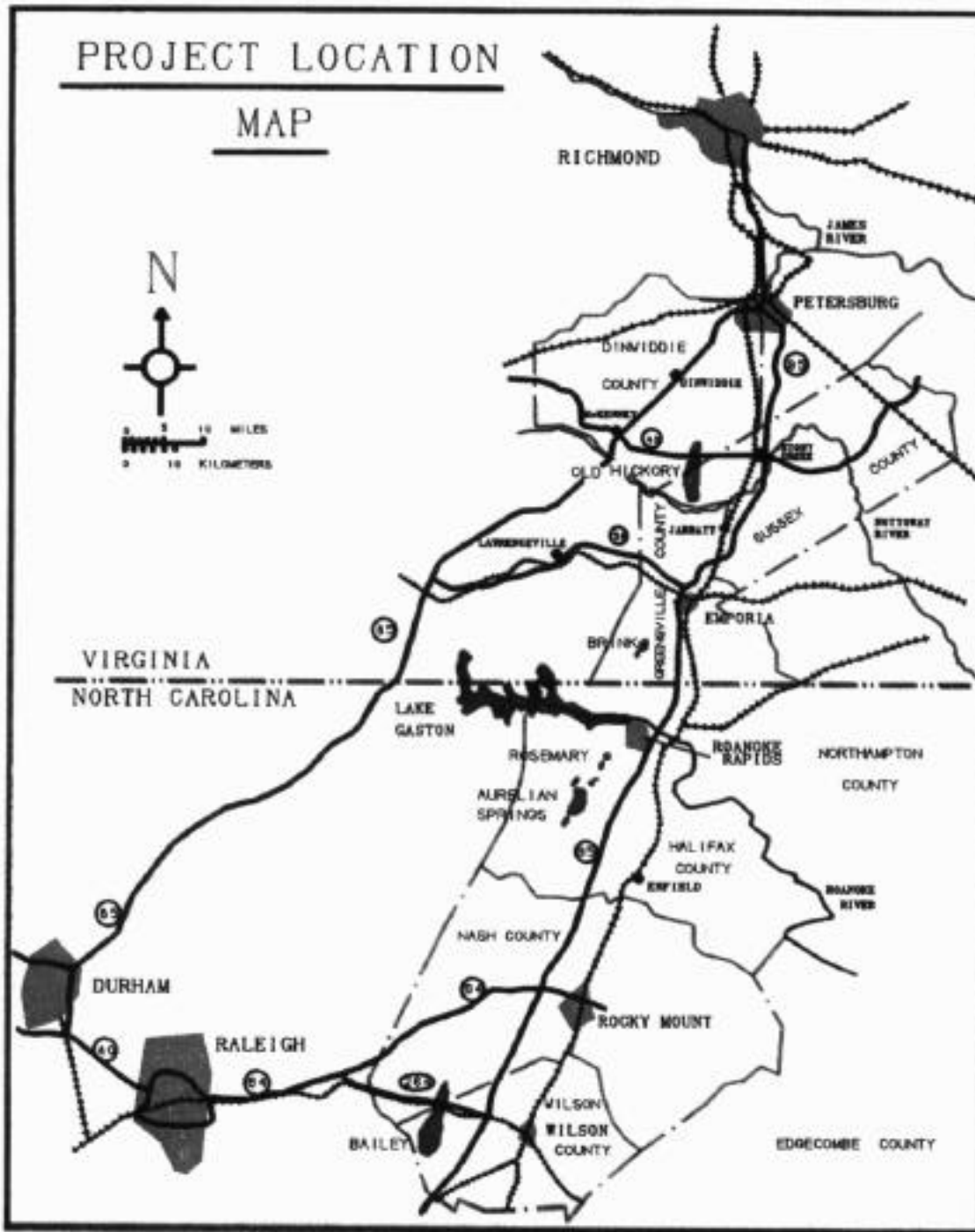
Figure 17 - Map of the Old Hickory Deposit and related deposits along the Fall Zone in Virginia and North Carolina. The Old Hickory and other major deposits including Brink, Aurelian Springs, and Bailey can all be seen extending southward in a line approximately 10 miles west of I-95. Used with the permission of RGC Mineral Sands Limited.

Carpenter and Carpenter (1991) assigned an age of 3.5 to 3.0 million years (Upper Pliocene) to the Old Hickory and its related deposits. This would agree well with the age determinations of Cronin and others (1984) who estimated the age at the base of the Yorktown Formation to be about 4.0 m.y. Sea-level curves by Haq et al. (1987) do in fact show a eustatic sea-level rise of approximately 65 m (210 feet) during this time. In addition, Zimmerman and others (1984) determined that the onset of cyclic glacial-interglacial alterations in the northern hemisphere occurred about 2.4. m.y. ago. The resulting global marine regression would have marked the last possible stage of deposition at the site.

Provenance

Precise determination of the source of the heavy minerals found at the Old Hickory site is probably an impossible task. The extensive mechanical weathering and sorting strongly suggests a multi-cyclic origin, such as reworked Miocene sediments, for much of the material (Carpenter and Carpenter, 1991). In addition, ilmenite, rutile, and zircon all occur in a variety of rock types. Thus source material could have come from multiple sources along the coast and been transported and mixed by longshore currents.

Nevertheless, while a definitive answer remains elusive, several important clues about the likely provenance of sediments can be pieced together. Given its proximity, there is little doubt that the crystalline basement complex of the Piedmont and the Blue Ridge served as the original source for the bulk of the heavy minerals. As noted by Gillson (1959), source rocks need not necessarily be rich in such minerals for a heavy mineral placer deposit to form because of their resistance to weathering and selective concentration during transport and deposition. Obviously, however, the process is favored when such minerals are in fact more abundant than usual in the source rock. Certain Grenville-age basement rocks in the Roseland District of Central Virginia have long been known to be unusually rich in ilmenite and rutile (Watson, 1913; Ross, 1941). These include the Roseland Anorthosite and the nearby Pedlar Charnockite. Concentrations are especially high in the many nelsonite dikes which cross-cut the Roseland Anorthosite and the surrounding country rock. In fact, commercial hard-rock mining operations for rutile took place at Roseland District from

about 1900 to 1949. Saprolite was also mined for titanium at several area localities up until 1971 (Minard et al., 1976; Force and Herz, 1982). This region is drained by several small rivers which in turn empty into the James. Erosion of this material may have been a primary source of heavy mineral bearing sediments at the Old Hickory site.

Using bulk X-ray diffraction (XRD) techniques, Darby (1984) was able to make use of trace element content in ilmenite as a discriminant function to help determine the provenance of Holocene and Pleistocene beach sands. Statistically, of course, variations between individual drainage basins must be greater than natural variation between samples for this type of approach to be successful (Darby and Tsang, 1987). Such a technique also works best for unweathered ilmenites since, as will be shown, the alteration process has a major impact on trace element composition. Nevertheless, Darby (1993) was able to broadly correlate the trace element ranges of ilmenite grains from the Old Hickory with several local rivers including the James.

Taking a different approach, Basu and Molinaroli (1989) argued that the widths and morphologies of exsolution lamellae in ilmenite, while highly variable at the individual level, could on the whole be indicative of the parent-rock assemblage. In general, they reasoned, igneous rocks cool faster than metamorphic ones. Therefore, the hematite exsolution lamellae should be more numerous but smaller, narrower, and more irregular in shape in ilmenite from igneous source rocks. Based on this criteria, the ilmenite found in the Old Hickory Deposit would appear to have an igneous origin. However, staurolite and kyanite, which are also found in small amounts in the heavy mineral assemblage, are both commonly formed as a result of high-grade regional metamorphism of aluminum-rich rocks (Klein and Hurlbut, 1993).

There are two possible explanations, though, for this apparent discrepancy in source lithologies for the different types of heavy minerals found at the Old Hickory. First, the Raleigh Belt Gneiss which underlies part of the deposit contains both staurolite and kyanite which could easily have been incorporated by reworking of older sediments. Also the Roseland Anorthosite pluton and the cross-cutting nelsonite dikes, which likely served as a major source for the ilmenite, were emplaced in pre-Grenville age basement which had

undergone granulite facies metamorphism. Based on the mineral assemblages present and other petrographic evidence, Force and Herz (1982) estimated that peak temperatures and pressures in this gneiss reached 800^0 C and 8 Kb respectively, conditions ideally suited for the formation of staurolite and kyanite.

ANALYTICAL RESULTS

Examination of ilmenite grains in polished section using reflected light microscopy, the scanning electron microscope, and the electron microprobe revealed a wide range of styles and degrees of alteration. This section presents some of the results that were obtained using these techniques. The many images and photographs contained herein are especially helpful in conveying this information. A discussion of the underlying chemistry behind these phenomena is presented in the following section.

As previously indicated, ilmenite makes up the bulk of the heavy minerals present at the Old Hickory Deposit, comprising 60 to 65% of the overall heavy mineral assemblage. The grains are sub-rounded to well-rounded and average about 0.15 mm in size (See Figure 6). The surface of the grains are finely pitted and often embayed. Using reflected light microscopy, a number of interesting textures can be seen. Examples of each of these are given in the following pages. Most readily apparent are the exsolution lamellae resulting from ilmenite-hematite solid solution at high temperatures. What is particularly striking, however, is that in all of the cases where these lamellae are present, the hematite has been fully leached away, leaving behind rows of minute empty pits (See Figure 12). Other common textures include alteration around the rim of grains (See Figures 24 and 25) and along fractures (See Figure 26). Under the microscope, this alteration often appears slightly darker and more granular. Stringers and patches of alteration may cut across grains following zones of weakness (See Figures 27-29). In addition, a small number of grains are somewhat porous in nature as a result of material being removed internally (See Figure 30). Under optical observation of the same samples, though, many of the ilmenite grains appear to have undergone little or no alteration. Analysis by more advanced tools, however revealed varying degrees of alteration in these cases as well (See Figures 31-36).

The use of backscattered electrons (BSE) for imaging, which reveals differences based on average atomic number, paralleled and confirmed the results seen optically. Heavier elements, with their higher density, cause a higher percentage of incident electrons to be backscattered. Because the beam electrons can travel significant distances from the impact

site relative to the beam spot size before escaping as backscattered electrons, however, there is some loss in the ability to resolve fine details (Goldstein, et al., 1992). In addition to sample BSE images, a few trial image maps were also made on the scanning electron microscope. The energy-dispersive spectrometers (EDS) used on this system, however, are far less precise than the wavelength-dispersive spectrometers (WDS) with which the electron microprobe was equipped. Therefore all final results were obtained using the microprobe.

Before element mapping of grains, a series of preliminary traverses were conducted using the electron microprobe across altered areas within selected ilmenite grains to determine the elements present and to gain some insight with regard to how they changed as a result of the alteration process. A number of elements were monitored for, based on possible substitutions known to exist in ilmenite or in related mineral species such as geikielite ($MgTiO_3$) and pyrophanite ($MnTiO_3$). In order of increasing atomic number these elements included Mg, Al, Si, Ti, Cr, Mn, Fe, Co, Ni, As, Zr, Nb, Sn, Sb, and Ta. Not surprisingly, based on a careful review of the traverse results, many of these elements could be removed from the analytical scheme. For example, the elements As, Zr, Nb, Sn, Sb, and Ta, if actually present in the samples at all, were not found in amounts sufficiently distinguishable from the background continuum or "bremsstrahlung" X-ray radiation to permit positive identification. The decision was also made to remove aluminum from the analytical scheme because of the possibility of interference in the results from the presence of aluminum in the polishing compounds used in sample preparation.

This left eight elements including Mg, Si, Ti, Cr, Mn, Fe, Co, and Ni which were present in statistically meaningful amounts (See Table 3). All of these eight also showed definite variations across the grains analyzed. Measurements for Si were highly variable and seemed to correlate much more closely with Al than either Ti or Fe. Three elements Cr, Co, and Ni were all found to be present in amounts < 1% with localized "hot spots." Of these three, Cr had both the highest maximum and highest average concentration. Fortunately from an economic standpoint, none of the trace elements were found in amounts that might otherwise reduce the potential market value of the ore.

Table 3 - Summary results of quantitative analysis of ilmenite grains.

3A)   Cation Concentration (wt. %) - Unaltered Ilmenite

	Average	SD	Maximum	Minimum
Mg	0.03	< 0.01	0.03	0.02
Si	0.02	0.01	0.03	0.01
Ti	31.33	0.07	31.43	31.23
Cr	0.04	0.01	0.05	0.03
Mn	1.88	0.01	1.89	1.86
Fe	34.84	0.22	35.08	34.59
Co	0.08	0.01	0.10	0.07
Ni	0.06	0.01	0.07	0.05

3B)   Cation Concentration (wt. %) - Altered Ilmenite

	Average	SD	Maximum	Minimum
Mg	0.01	< 0.01	0.02	0.01
Si	0.13	0.01	0.14	0.11
Ti	53.58	0.98	54.85	52.39
Cr	0.02	0.01	0.04	0.02
Mn	0.01	0.01	0.02	0.00
Fe	5.44	0.29	5.86	5.03
Co	0.01	< 0.01	0.02	0.01
Ni	< 0.01	< 0.01	0.01	0.00

Note: The above values were taken from traverses done using the electron microprobe at one micron intervals on three different grains of ilmenite that showed signs of alteration. Part A shows typical values found in unaltered regions of the grains. In contrast, Part B shows typical values in regions of the ilmenite grains which had undergone extensive alteration. Note the considerable differences in concentrations of Ti, Mn, and Fe. Also, as might be expected, the altered areas showed more variability in concentration. Measurements taken near to the edges of grains during the traverses were found to be suspect and were discarded.

The electron microprobe used for the study was equipped with four high-resolution wavelength-dispersive spectrometers. For chemical mapping purposes this meant that only four elements could be analyzed in one pass. As compared to an EDS system, wavelength-dispersive spectrometers offer several advantages such as greater peak separation and higher peak-to-background ratios. Required scanning times, however, are much longer (Goldstein, et al., 1992). Given time and cost constraints involved, the decision was made to limit scans to a maximum of four elements, enabling a greater number of grains to be examined. This was done by eliminating Si, Fe, Co, and Ni from the analytical scheme. While removing iron may at first seem counterintuitive there was a legitimate rationale behind this decision. Aside from oxygen, iron and titanium are the primary constituents of ilmenite, greatly outweighing any of the trace elements. Analysis of the traverses revealed that as expected the iron and titanium concentrations are inversely proportional, tracking one another quite closely at different stages of alteration (See Figure 18). Thus an image map of iron concentration in a given grain would essentially look like a negative of that for titanium. Since there was little to be gained by repetition once this fact had been established, the choice was made to ignore iron in most cases and to analyze instead for titanium, magnesium, manganese, and chromium. The exception to this general rule was made for grains in which hematite exsolution lamellae were, or had been, present.

The following sections describe the different types of ilmenite alteration most commonly observed in sediment from the Old Hickory Deposit. Note that more than one type of alteration texture may be present in a given grain. The use of elemental concentration maps and other images reveals, often rather dramatically, the chemical changes which the grains undergo during this process. As will be seen there are many similarities in the different types of alteration, suggesting that the same fundamental processes are at work. Unless otherwise noted, all grains are from the Old Hickory Deposit and were examined in polished section. For all of the elemental concentration maps, lighter shades are used in the scanned image to represent higher concentrations of the element in question. Some observations related to the analysis of the zircon grains from the deposit are also included at the end.
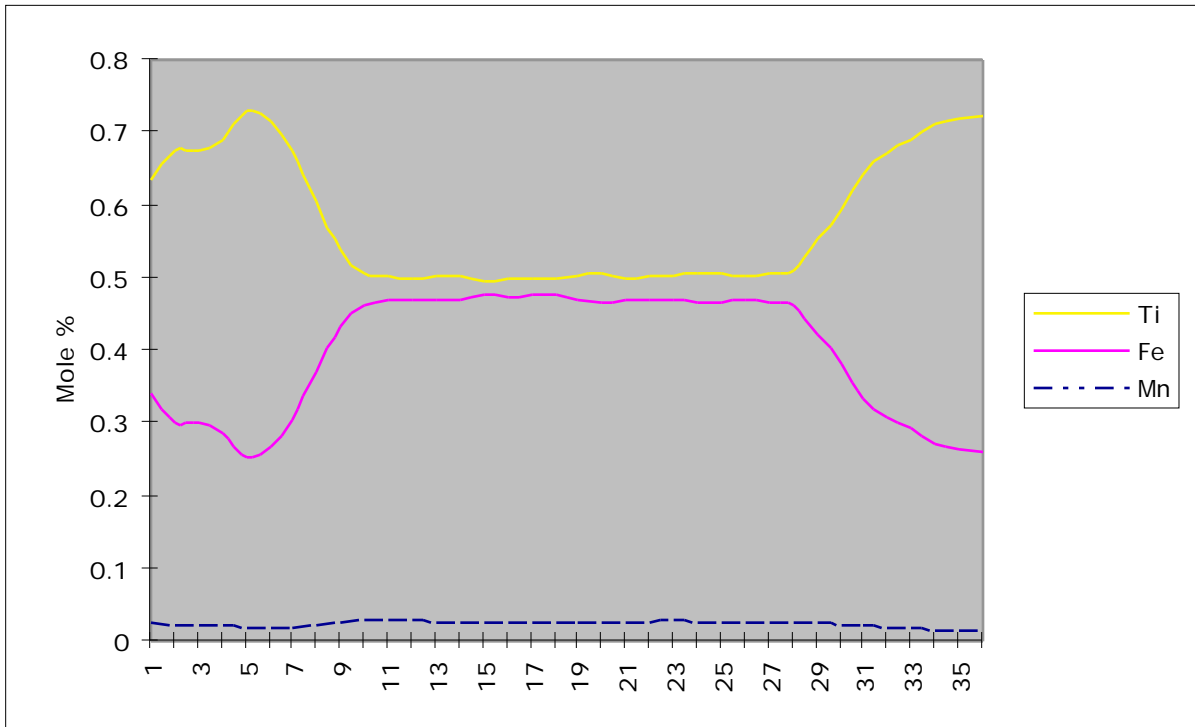
Figure 18 - Results of a traverse of ilmenite grain m2b taken normal to an alteration front showing the variation in cation concentration across the grain. Note that concentrations of Mg and Cr are too low to show up effectively at this scale. The center part of the diagram shows relatively unaltered ilmenite with nearly equal titanium and iron concentrations while the ends are both in altered zones where the ratio can be seen to exceed 2:1. A total of 36 data points, taken at 1 micron step intervals, are shown in the graph above. (Those nearest to the edge were discarded as unreliable.)

Hematite Exsolution Lamellae

Upon examining a polished section of heavy mineral grains from the deposit, one is struck by the many grains of ilmenite which are filled with regular rows of exsolution lamellae. These are the result of hematite exsolving out of the ilmenite structure. As previously discussed the two phases have complete solid solution at high temperatures but unmix upon cooling. In the case of ilmenite grains from the Old Hickory Deposit, however, the hematite has been completely leached out the grains, leaving behind a series of empty pits (See Figures 12 and 19). This is true even inside of the grains, not just at the outer surface where one might expect. The mechanisms by which this may occur are considered in the discussion section which follows. Systematic searching of grains mounts from the Old Hickory failed to reveal any ilmenite grains in which the relict hematite exsolution lamellae had not been leached away. Most of the hematite had also already been removed from ilmenite grains taken from modern beach sediments at Emerald Isle, North Carolina (See Figure 13). For comparison purposes, a similar sample of detrital ilmenite from the sand and gravel of the Citronelle Formation near Lilesville, North Carolina which still had some hematite present as exsolution lamellae in many grains was also examined (See Figures 14 and 20-22).

Variations in iron concentration in these ilmenite grains from Lilesville which still had some hematite exsolution lamellae present were also studied. This was done to determine whether or not iron had been removed from the dominant ilmenite phase at the same time as the hematite was being leached away. Using the SEM, a total of twenty points each were analyzed on two representative grains. Half of these were done in regions where the hematite lamellae were still present, the other half in portions were they were gone. Peak counts were compared to determine the approximate titanium to iron ratio in each region. The results of this investigation showed conclusively that iron was being removed from the ilmenite structure at the same time as the hematite lamellae were being dissolved away. In the portions of the two grains where the hematite lamellae were still present the titanium to iron ratio averaged 1.34 and 1.58 but where they were gone the ratio jumped to 1.96 and 2.01 respectively (See Figure 23).
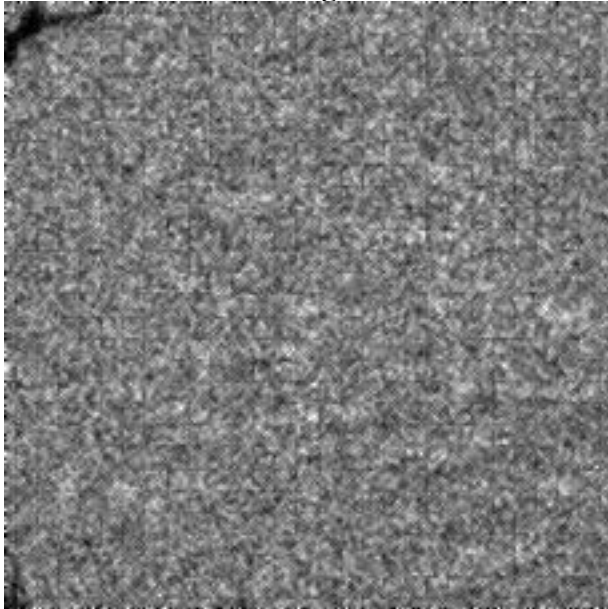
Ti
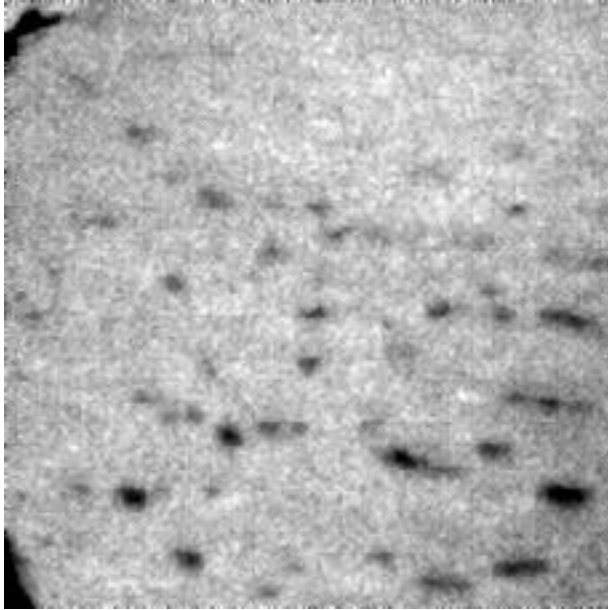
Mn
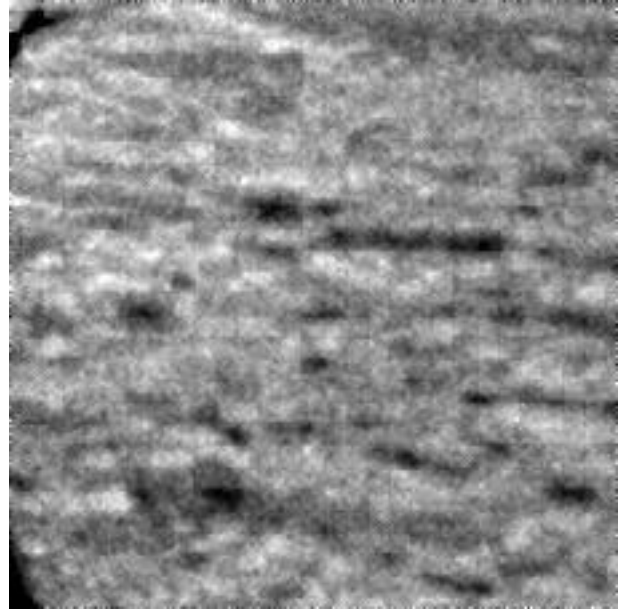
Mg

Figure 19 - Element concentration maps representing a cross-section through a portion of the same ilmenite grain (Sample m2e) from the Old Hickory Deposit shown in the photo in Figure 12. Subparallel rows of empty pits left by the dissolution of hematite exsolution lamellae are clearly evident. (The empty pits show up here as black holes.) All of the original hematite has been removed, as was found to be the case throughout the samples from the Old Hickory Deposit. Field of view is 70 microns.

Ti
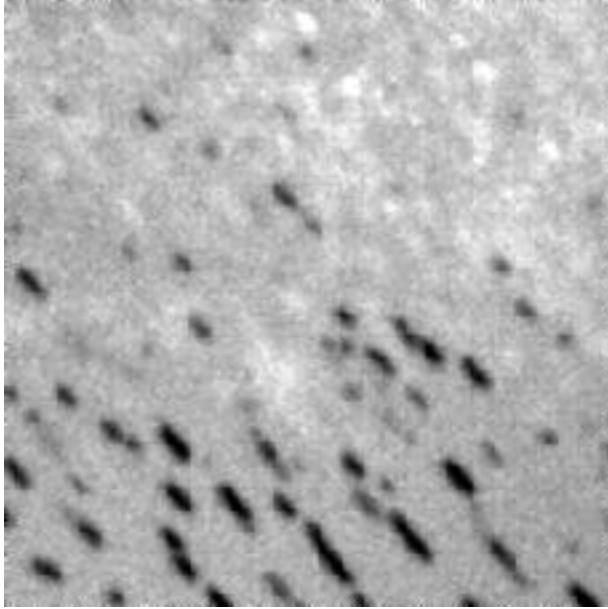
Mn
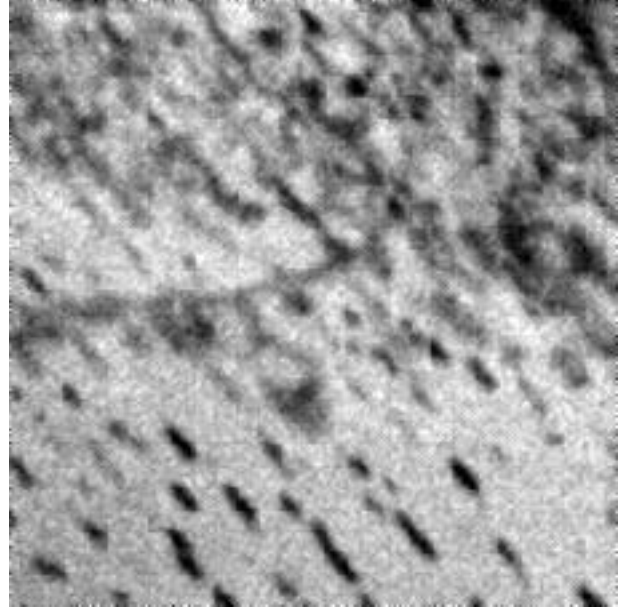
Mg
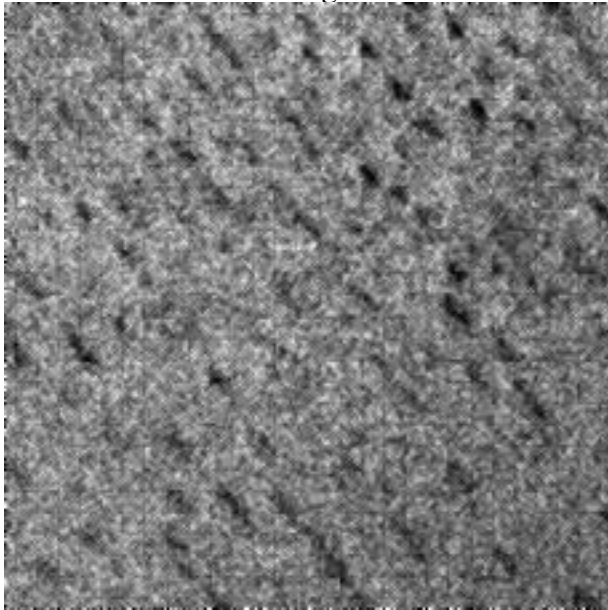
Figure 20 - Element concentration maps of a portion of the ilmenite grain (Sample 1859) from Lilesville, North Carolina shown in Figures 14 and 21. While outer ones have dissolved away leaving empty pits, some of the original hematite exsolution lamellae are still present near the center of the grain. The upper two images show this boundary most clearly. In the top half of the grain, hematite has been leached away leaving the sample enriched in titanium and depleted in Fe and Mn. In the bottom half, though, hematite lamellae are still present. Field of view is 70 microns.
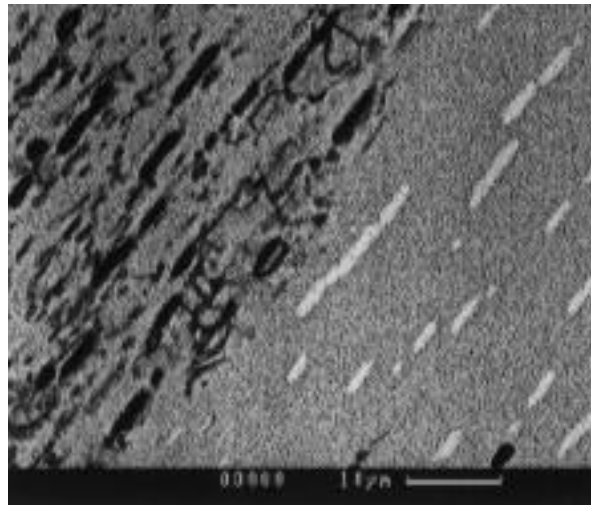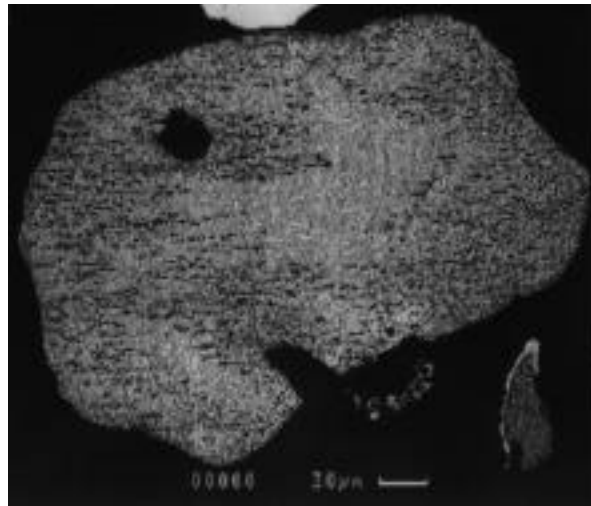
Figure 21 - Backscattered electron images of the same ilmenite grain from Lilesville, North Carolina shown in Figures 14 and 20. The average atomic weight differences between iron and titanium are sufficient that hematite exsolution lamellae (light gray) can easily be seen in the figures above, especially at higher magnification. The elongated black spots in the images are holes and show where hematite has been removed from considerable portions of the grain.
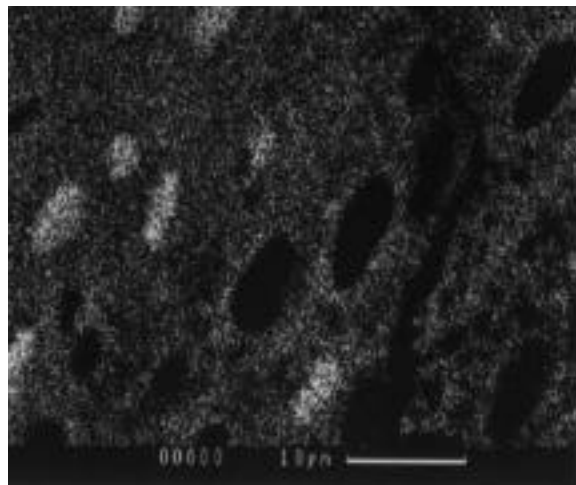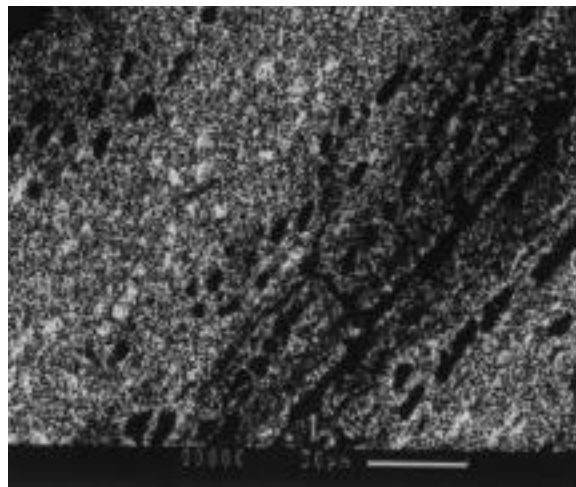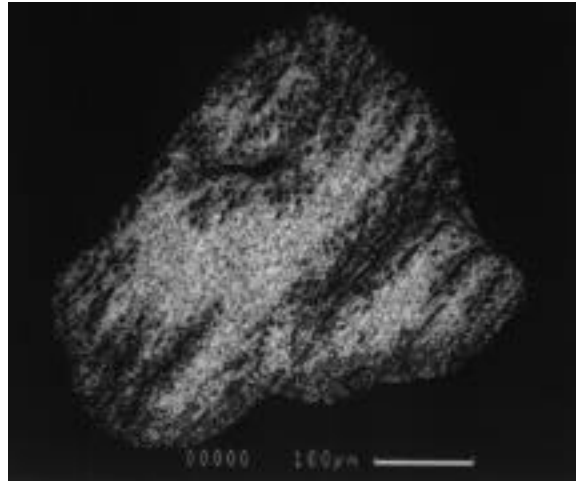
Figure 22 - Backscattered electron images of a second grain of ilmenite from Lilesville, North Carolina showing the full grain and then finer details. The light gray hematite lamellae can still be seen in portions of the grain but many of them have been leached away, especially near the edges.
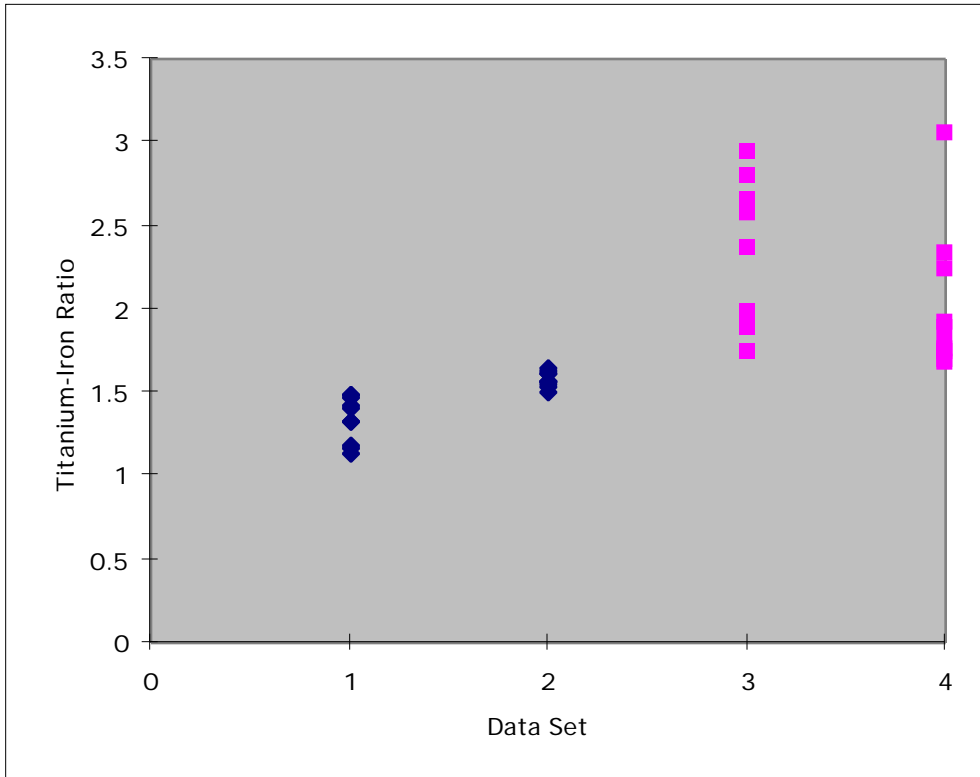
Figure 23 - Variability in titanium-iron ratios in ilmenite grains with only part of the hematite exsolved (See Figures 21 and 22). Data sets 1 and 2 are from areas in the two grains where hematite exsolution lamellae are still present. Data sets 3 and 4 respectively are from portions of the same grains where hematite has been leached away. Note the greater variability and higher titanium-iron ratios in the both data sets 3 and 4, indicating that iron is also being removed from the ilmenite structure while hematite is being leached away.

Surface-Inward Alteration

Besides the high concentration of iron in exsolution lamellae, iron and other elements are also dispersed throughout the grains crystal structure and are also affected by chemical weathering processes. It is not uncommon in many different types of minerals to see a rim of weathered material surrounding a core of relatively unaltered material. Circulating fluids will naturally tend to alter grains from the periphery inward. In the case of ilmenite, however, as the surface becomes enriched in titanium, some passivation (buildup of altered material which slows further alteration) may occur, thereby reducing the rate of reaction. As will be seen in the following section, however, fractures and microcracks in grains are common. This, of course, greatly reduces the potential impact of surface passivation in slowing alteration because circulating fluids can then also get inside of the grains.

Under reflected light, many grains from the Old Hickory Deposit show a darker-colored rim of altered material. Temple (1966) noted that the reflectivity of altered ilmenite tends to initially decrease from that of the original mineral but then to increase as alteration progresses further. The material in the rim tends to be very fine-grained.   In most cases where such rims are found, they encompass only part of the grain (See Figure 24). The boundaries between the core and rim tend to be sharp and are often truncated at the grain edge.

Analysis with the electron microprobe revealed that altered areas were enriched in titanium due to the removal of iron. Trace elements including Mn, Mg, and Cr all tended to follow iron out of the ilmenite structure during alteration as can be seen in rather dramatically in Figure 25. The alteration fronts for these elements are virtually identical within the cross-section of the grain shown.
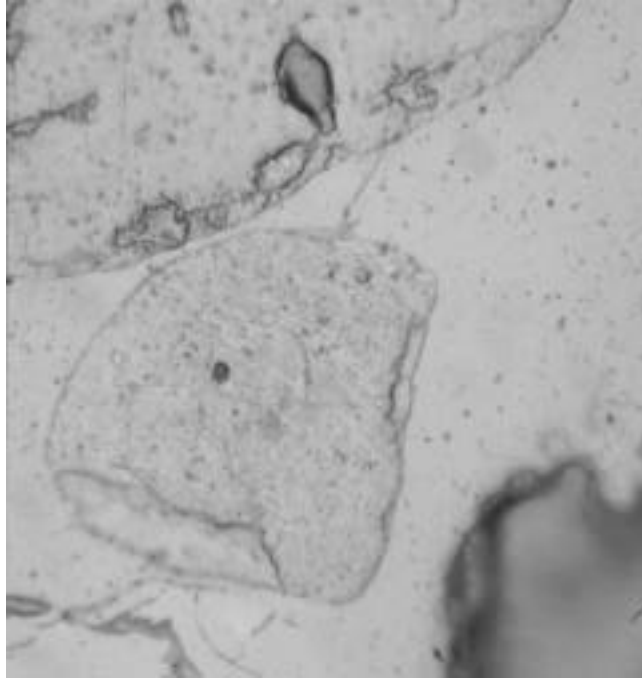
Figure 24 - Photomicrograph of an ilmenite grain (lower-left of center) from the Old Hickory deposit. As is common, alteration rims encompass only a part of the grain, suggesting that they may have been abraded off during transport. Field of view equals 0.6 mm.
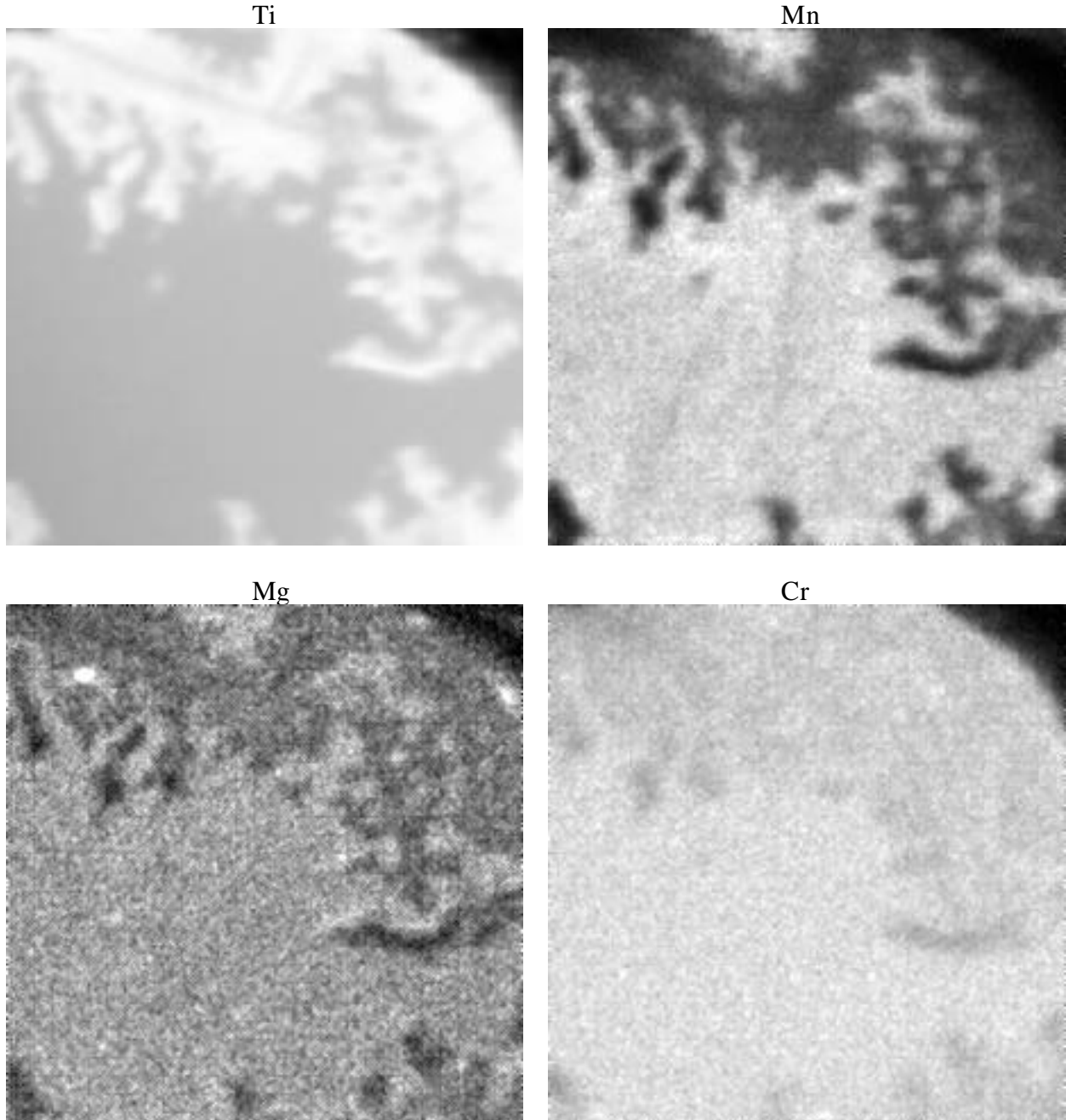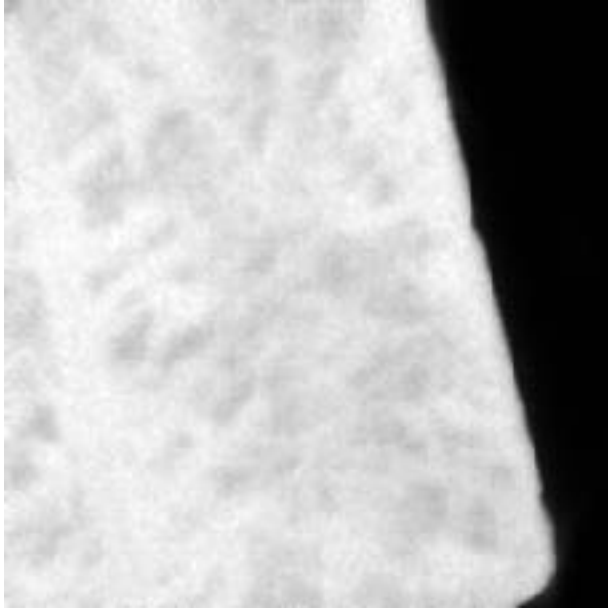
Figure 25 - Element concentration maps across ilmenite grain (sample m4b) which shows alteration proceeding from the outer boundaries of the grain (top and right) inward. All three trace elements show clear similarity with regard to concentration changes, indicating that they are being leached away at the same time as iron. Among, the grains analyzed, this example most clearly shows the trend for Cr migration. Field of view is 77 microns.

Fractures and Internal Alteration

As with core and rim textures, alteration along fractures and other zones of weakness within grains is a very common phenomena. Ilmenite has a hardness of 6.0 - 6.5 which helps to make it resistant to mechanical weathering but it is not uncommon to see internal fractures in many of the detrital ilmenite grains found at the Old Hickory Deposit. Such fractures allow circulating fluids to penetrate deep inside of grains, greatly increasing the effective surface area on which alteration can then occur. This fact is especially important as experiments by Barton and McConnel (1979) proved that the rate of dissolution of ilmenite in an acidic solution was controlled by the rates of chemical processes on the mineral surface and not by the rate of transport in solution.

Complex branching patterns of alteration may be seen running through some grains forming networks or channels. These may sometimes be seen to follow the crystallographic orientation of the ilmenite grain but often no clear pattern is present. Removal of iron during alteration leads to a volume reduction which in turn opens up additional microcracks. The result is dendritic patterns of alteration branching off from larger fractures. As multiple radiating alteration fronts within the grain intersect and merge, the grain may take on a patchy appearance. The following series of figures (26 - 29) show different stages in this process. In all of the cases removal of iron results in enrichment of titanium. Mn tends to follow iron out of the ilmenite while Mg does so to a lesser extent. Cr, shown only in Figures 27 and 28 tends to follow the same trend in these cases although it can often be difficult to see.
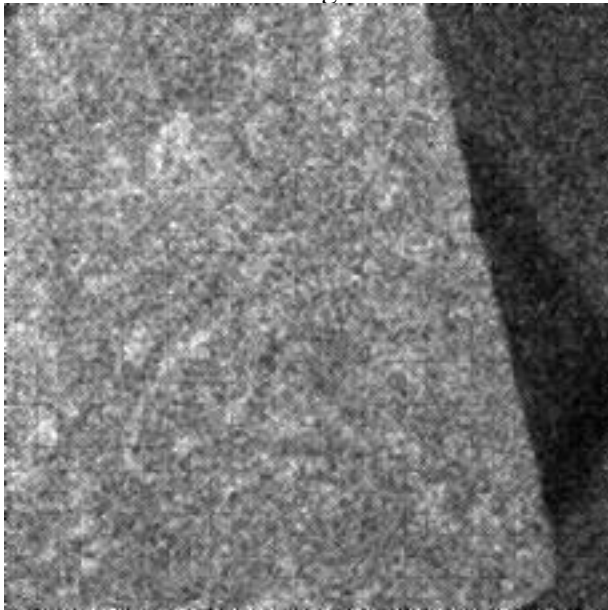
Ti

Mn
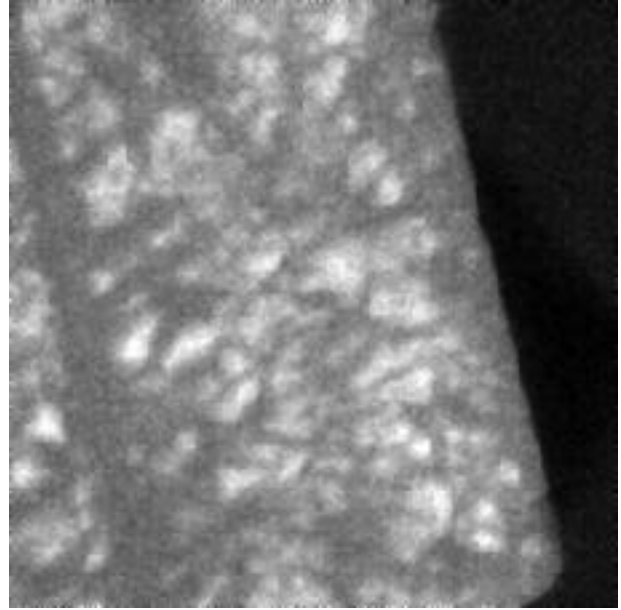
Mg

Figure 26 - Element concentration maps of sample m4h showing criss-crossing bands of alteration within ilmenite forming a complex network. The wide band of titanium-enriched material at the left follows a large fracture running through the grain while the multiple narrow bands reflect alteration along microcracks. Field of view is 70 microns.
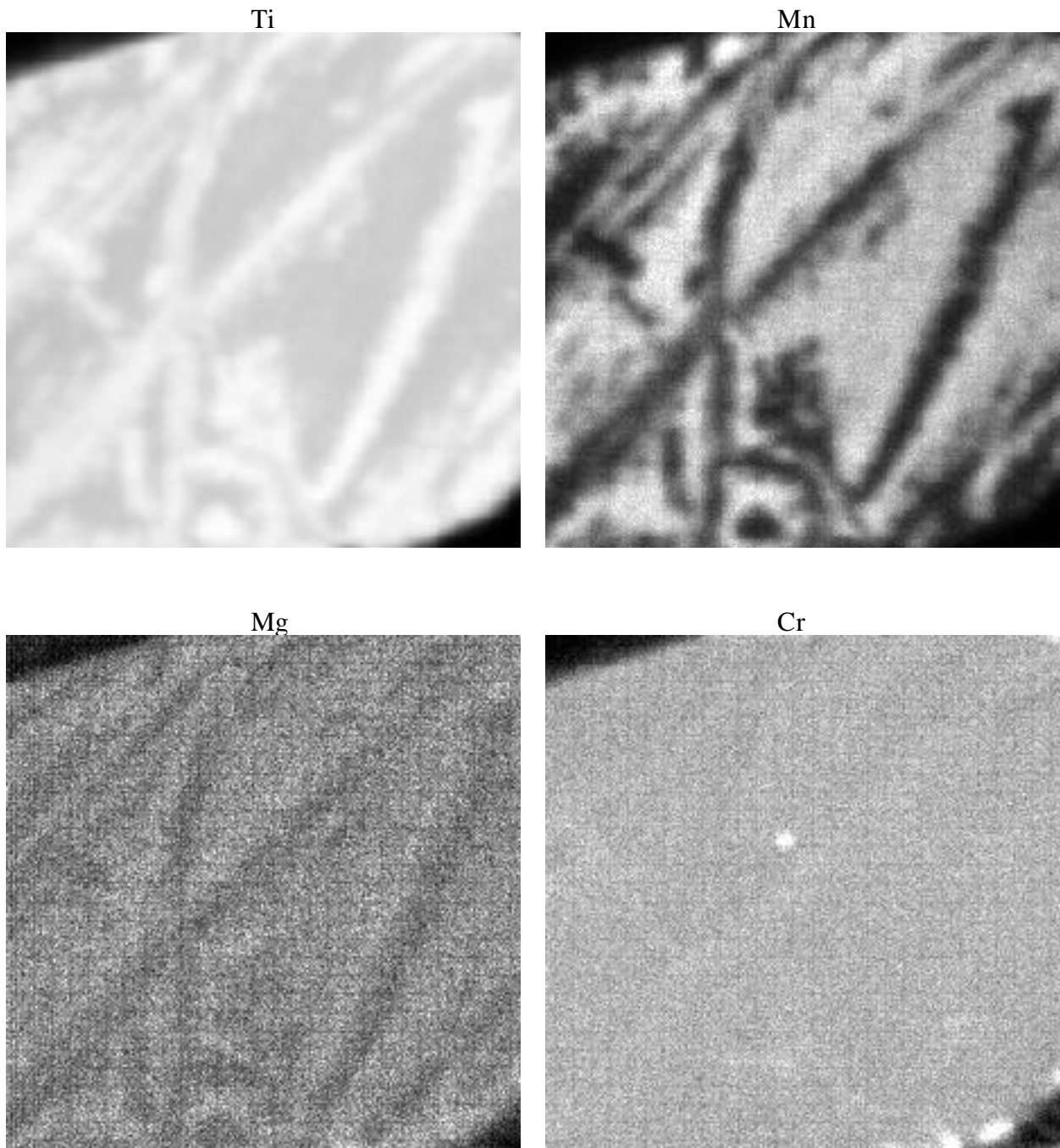
Figure 27 - Element concentration maps of sample m2c1 showing linear alteration features extending through ilmenite grain along microcracks. Alteration has also started to proceed into adjacent regions of the grain alongside these initial points of weakness. Field of view is 77 microns.
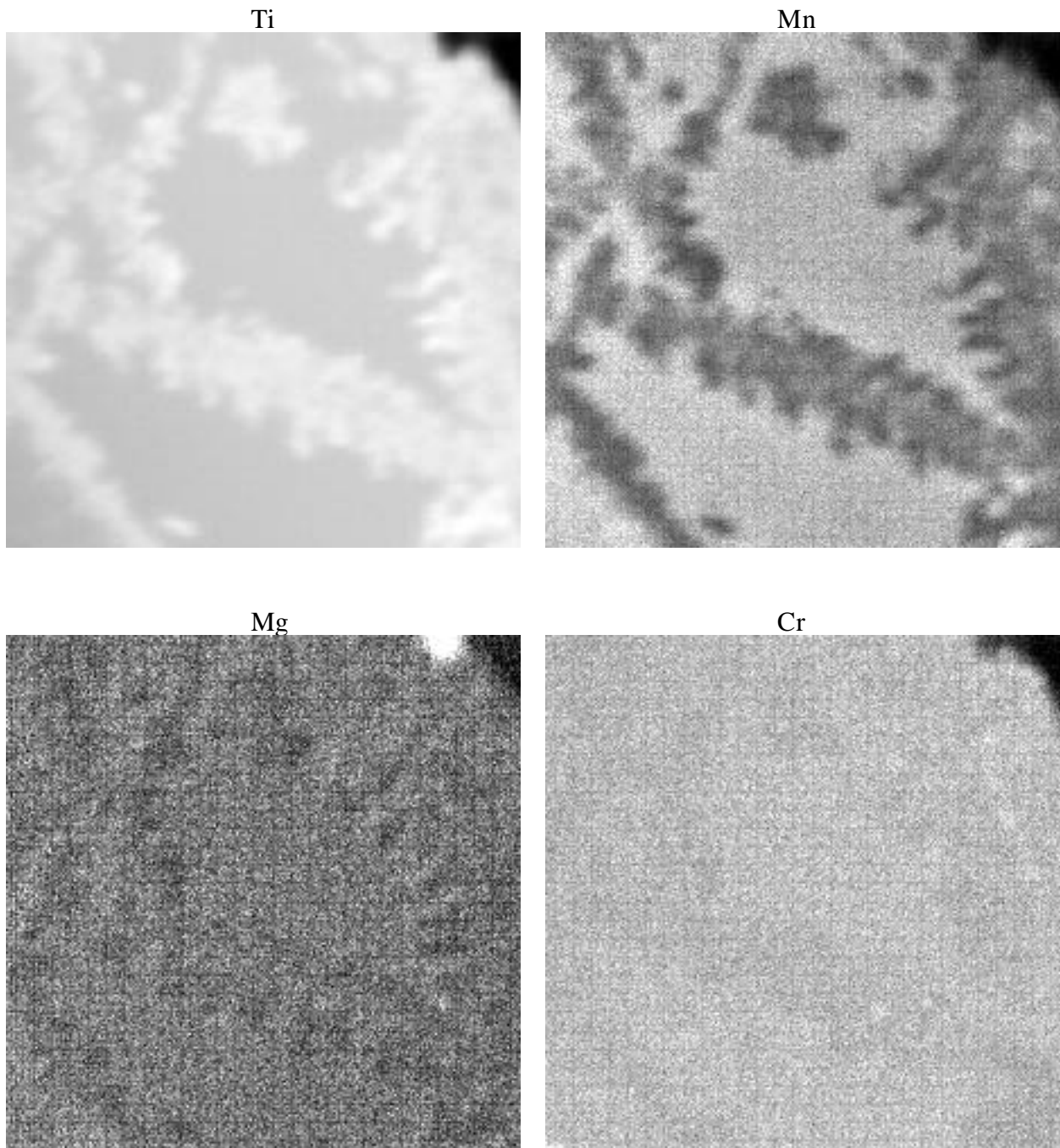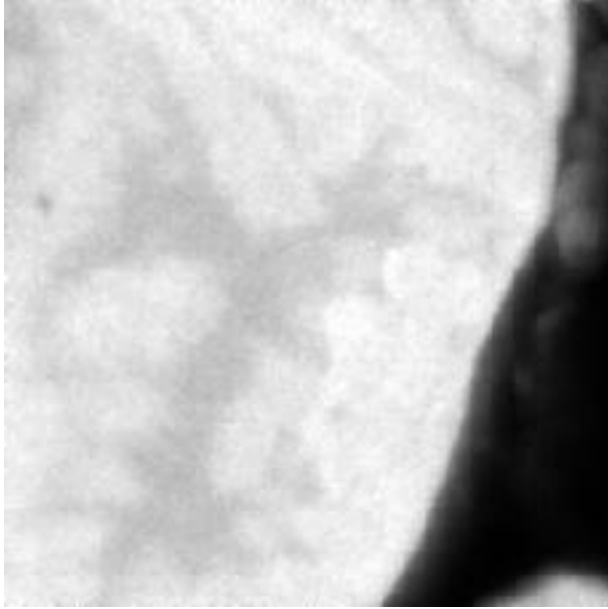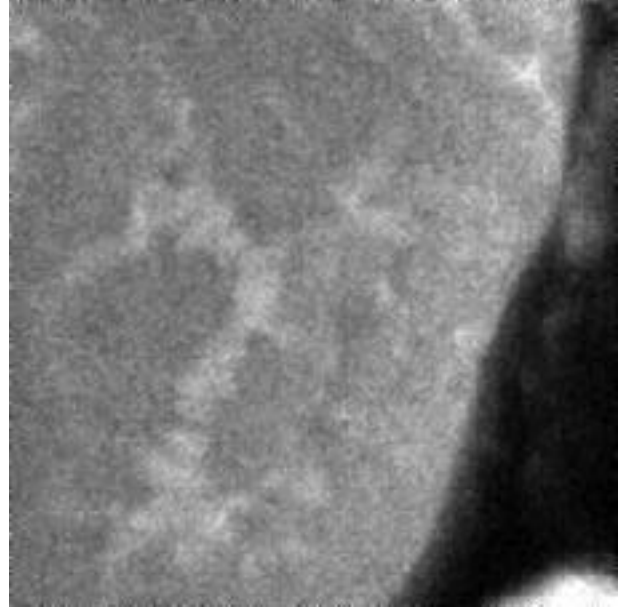
Figure 28 - Element concentration maps of sample m5e which are similar to the preceding example but alteration is slightly more advanced. Delicate dendritic branching patterns, resembling some fractals, can be seen extending outward from originally linear alteration features. This is a result of microcracks caused by volume reduction as iron is removed. Field of view is 77 microns.

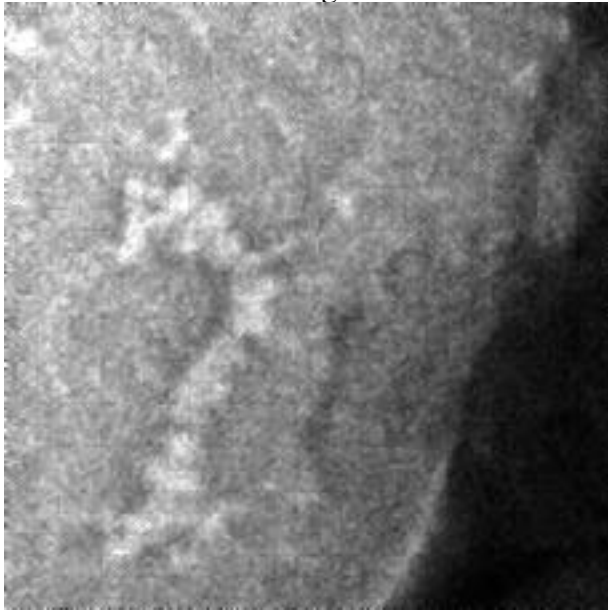Ti   Mn

Mg

Figure 29 -Element concentration maps of sample m2g showing linear alteration features with irregular edges coalescing together, leaving only a narrow band of less altered material. Field of view is 70 microns.

Porous Grains

Isovolumetric alteration results in greater space within the crystal structure as iron and trace elements are removed. The density of both rutile (4.18 - 4.25) and anatase (3.9) are much less than that of ilmenite (4.7). Of course, the removal of hematite from those grains with exsolution lamellae present also opens up extra space. All of this increased internal space can manifest itself as dissolution voids within grains, giving them a very mottled, "porous" type of appearance. Figure 30 shows a photomicrograph under reflected light of such a grain. An attempt to map one such grain was made but is not included here due to the highly variable and hence unreliable nature of the results when such extensive porosity is present.
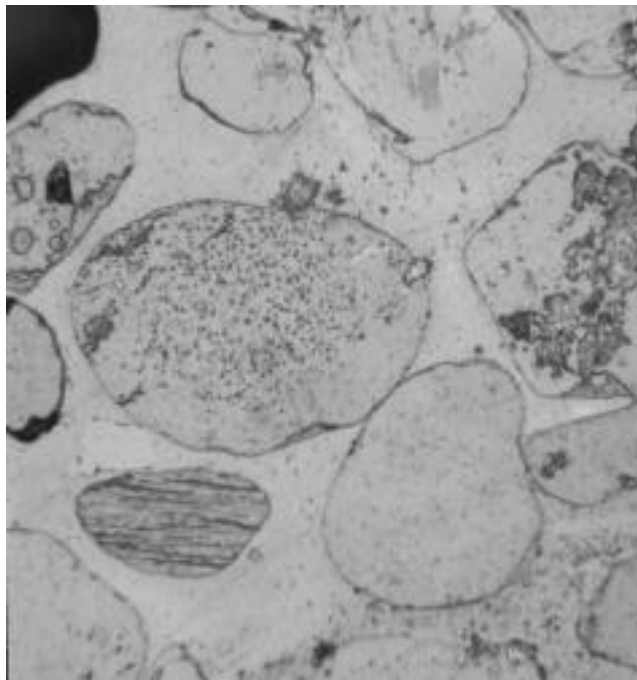
Figure 30 - Photomicrograph of ilmenite from the Old Hickory Deposit showing the porous nature of some grains after alteration. Field of view equals 0.6 mm.

Leucoxene and Rutile

Taken to completion, the alteration product of ilmenite will be nearly pure TiO_2 in the form of microcrystalline rutile $\pm$ anatase. Such secondary grains are easy to distinguish, however, from primary grains of rutile. Leucoxene is a finely crystalline aggregate, giving it a patchy appearance throughout (See Figure 7). Under crossed polars, it will often show bright internal reflections, resembling a dirty snowball in appearance. In contrast, rutile grains from the site are much more clear and uniform, with reddish-brown internal reflections. Rutile may also exhibit twinning although this was rarely observed (See Figure 8).

"Unaltered" Grains

Under optical observation using reflected light, a substantial portion of the ilmenite grains appear essentially homogenous throughout, which would seem to suggest that they are unaltered. Detailed examination under the electron microprobe, however, reveals that in actuality this is often not the case. In fact, as revealed by mapping, early stages of alteration were already evident in many of these grains. Figures 32, 34, and 36 are element concentration maps showing this alteration. Optical photomicrographs of these same grains (Figures 31, 33, and 35 respectively) are included for comparison. While reflected light microscopy in general is an effective tool for observing alteration in ilmenite, these results show that more subtle changes may be missed. Trace elements can be subject to much greater percentage changes in concentration than Fe or Ti. While Mg shows little apparent change in these examples, Mn appears to be ideal for monitoring for incipient alteration in ilmenite grains.
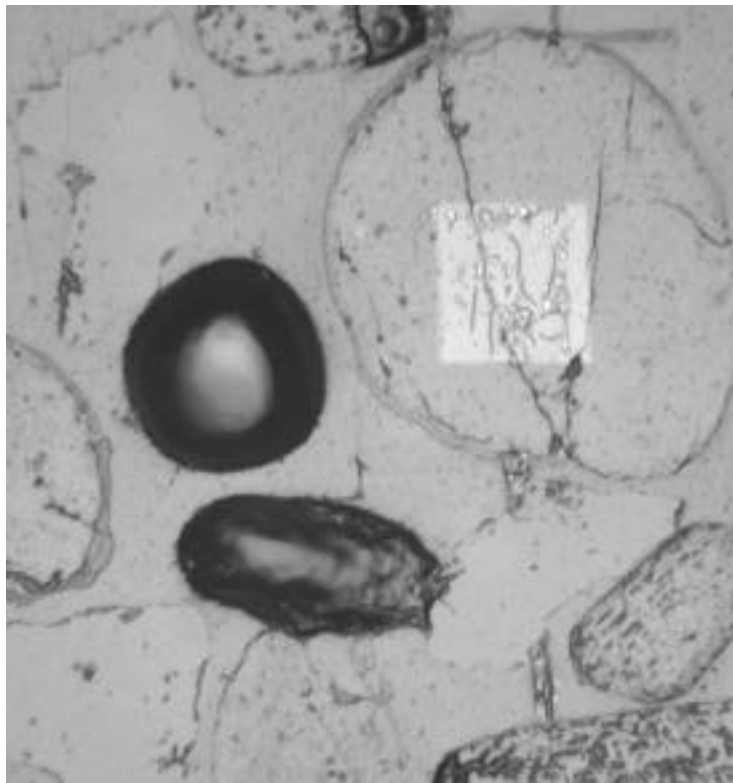
Figure 31 - Photomicrograph of an ilmenite grain from the Old Hickory Deposit which appeared unaltered optically in spite of the large fractures seen running through the grain. Field of view equals 0.6 mm. The following figure shows the elemental concentration maps for this same grain as determined in the square area shown above.

Ti
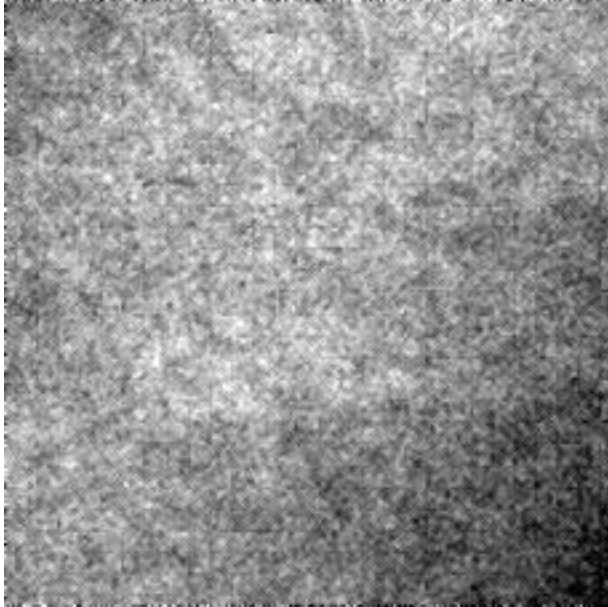
Mn
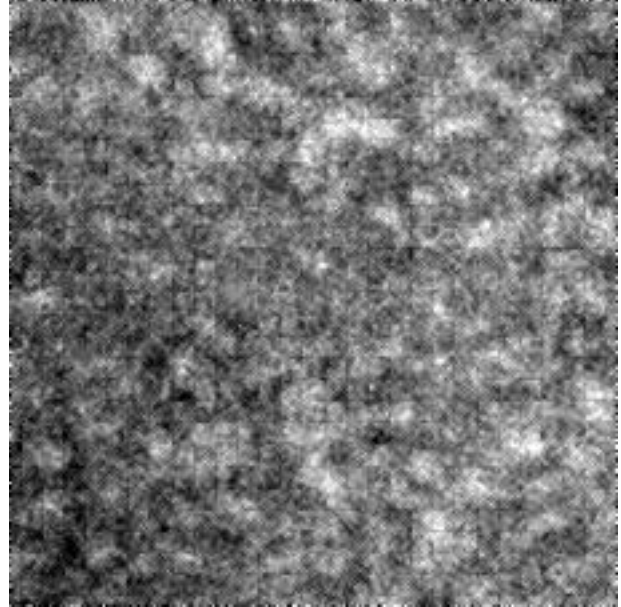
Mg
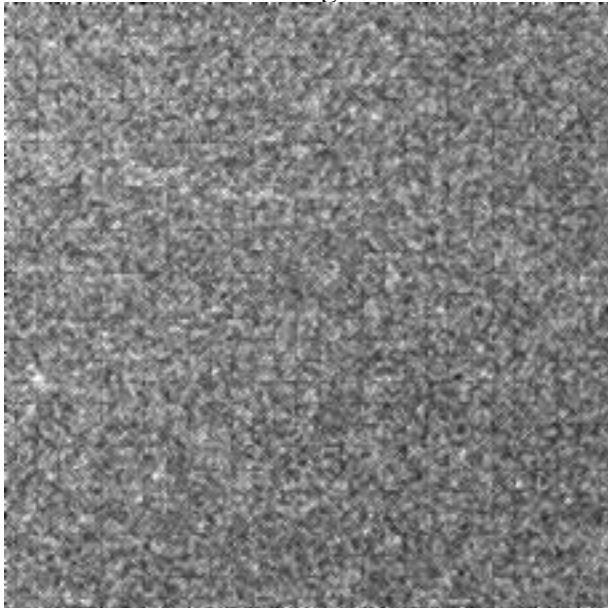
Figure 32 - Element concentration maps of sample m3e showing a very early stage of alteration in ilmenite grain which appeared optically homogenous (See Figure 30). Some slight enrichment in titanium can already be seen. Note, however, that the fractures evident optically do not show up as altered areas in this case . This indicates that the fractures were formed more recently than in some of the preceding examples. Field of view is 70 microns.
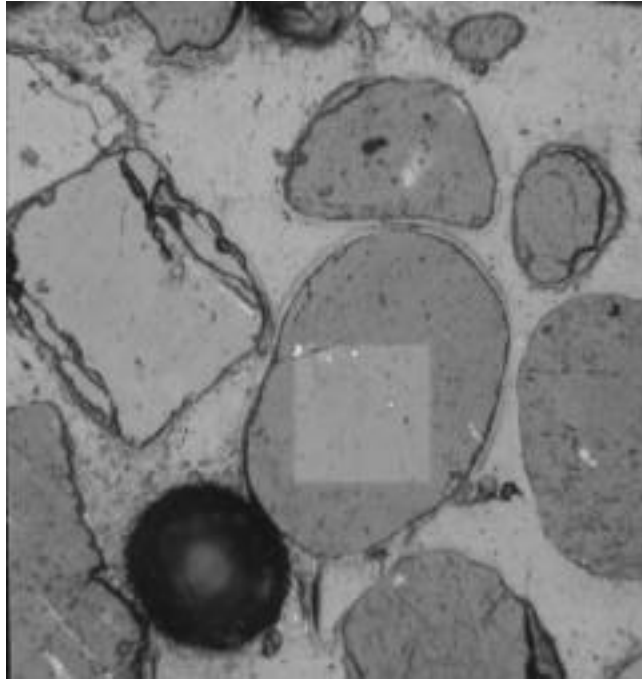
Figure 33 - Photomicrograph of a second ilmenite grain from the Old Hickory Deposit which appeared unaltered under optical observation. The following figure shows the element concentration maps for the same grain. Field of view equals 0.6 mm.

Ti
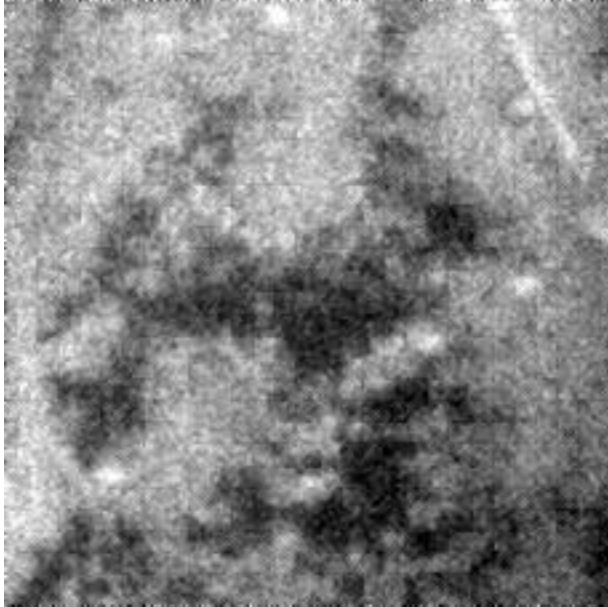
Mn
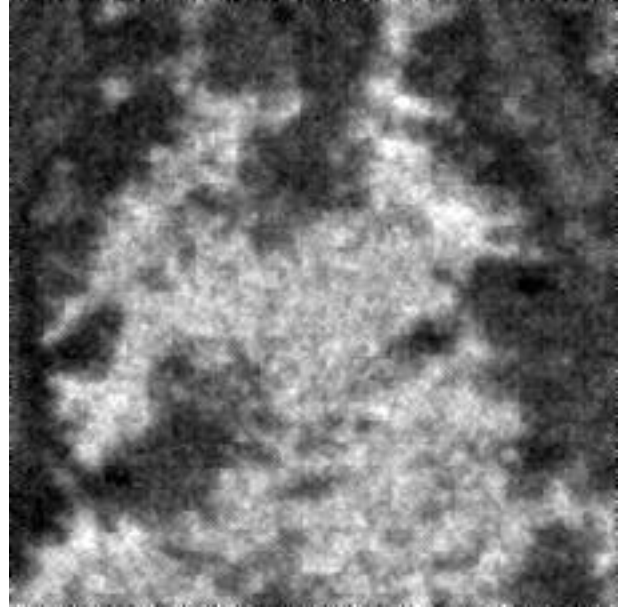
Mg
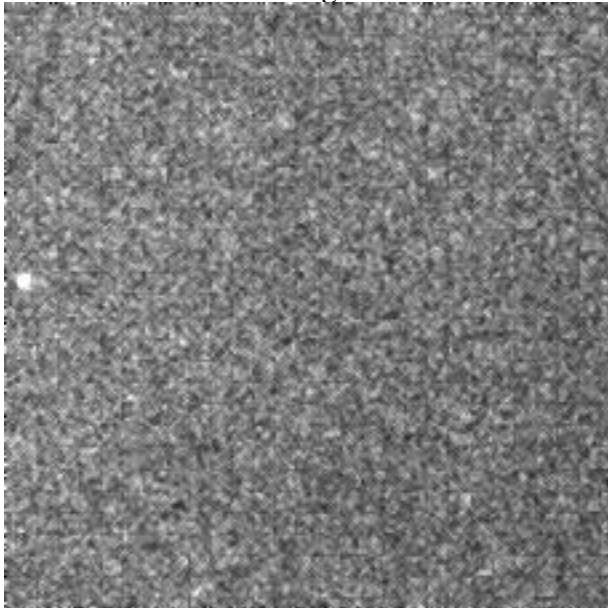
Figure 34 - Element concentration maps of sample m2f. While this grain appeared uniform optically as shown in Figure 33, alteration proceeding from the periphery inward along converging fronts is clearly evident with regard to the Ti and Mn concentration gradients. Field of view is 70 microns.
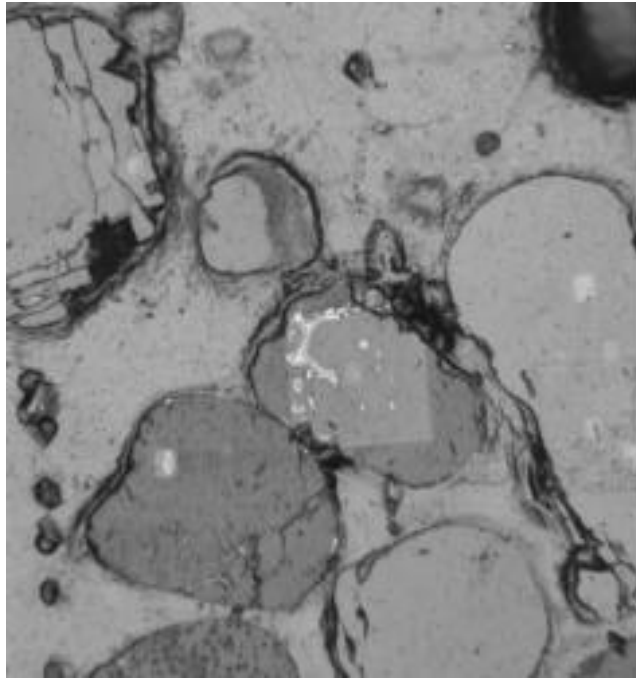
Figure 35 - Photomicrograph of a third ilmenite grain from the Old Hickory Deposit which appeared unaltered under optical observation. Again as shown in the element concentration maps in the next figure, the extent of actual alteration only becomes evident using more advanced analytical techniques. Field of view equals 0.6 mm.

Ti
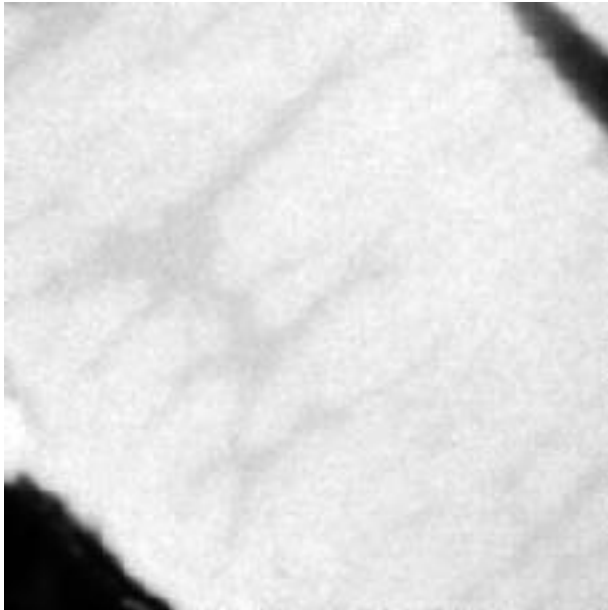
Mn
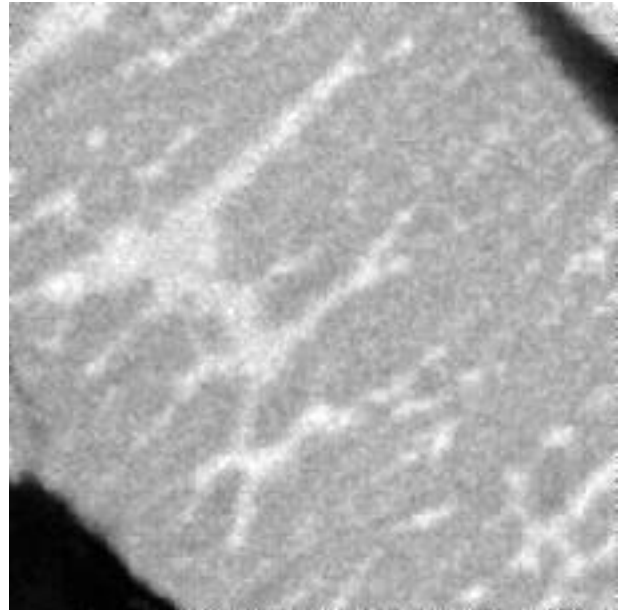
Mg
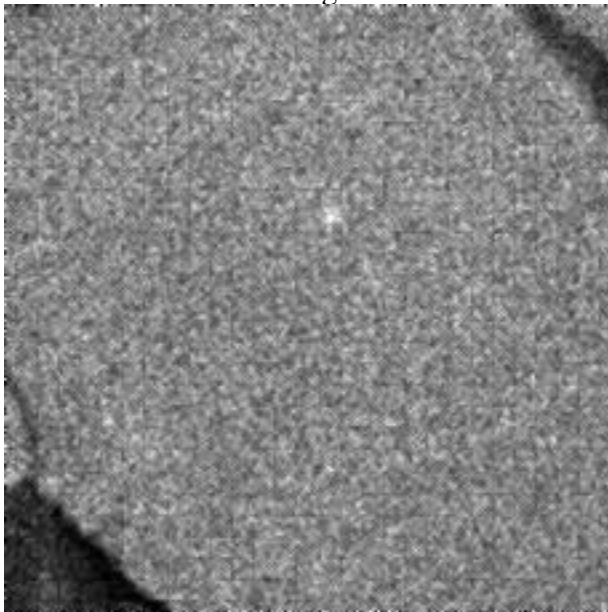
Figure 36 - Element concentration maps of sample m2h, another ilmenite grain which appeared unaltered under optical observation (See Figure 35). As shown here, however, by the microprobe images only a small irregular core of unaltered material is actually left. Field of view is 70 microns.

Zircons

Zircon is the other major heavy mineral of economic present at the Old Hickory Site. Grains are often elongate and tend to have better preserved crystal faces than is the case with the detrital ilmenite found at the site. Nevertheless, a high degree of mechanical weathering is still evident (See Figure 5 and 9). Examination of zircon grains under ultraviolet light revealed considerable fluorescence under short-wavelength light but very little under long-wavelength light. Zircons from the Old Hickory Deposit also exhibit a blue-white cathodoluminesce under the SEM. This phenomena is caused by the emission of energy in the form of visible light when the sample is subjected to electron bombardment and is facilitated by the presence of certain impurities or "activators" in the mineral lattice (Mange and Heinz, 1993).

An irregular reddish coating of iron is often present on the surface of the zircon grains. To determine whether this iron was only a surface coating or was incorporated into the zircon itself, several loose grains mounted on double-sided tape were compared using the electron microprobe with those in polished sections. The sample grains in the polished sections represent random cross-sections through grains at a variety of levels that would reveal the presence of any iron internally within the zircons. A spectral scan showed that iron was present only among the loose, unpolished ones indicating that it was in fact present only on the surface. Interestingly, however, the scans did also reveal the presence of trace amounts of hafnium in both sets of zircon grains.

DISCUSSION

In order to accurately interpret the analytical results for ilmenite grains in various stages of alteration, it is necessary to have a solid understanding of the mineral chemistry involved. Of particular importance are the solubilities of titanium and iron within ilmenite under different conditions. These are critical to determining which of several possible alteration mechanisms was responsible for producing the textures observed. Much of what has been established in the literature in this regard has to do with the interest of the minerals industry in upgrading ilmenite to increase its titanium concentration (Imahashi and Tkamatsu, 1976; Sinha, 1979). The strong acids and high temperatures often used in these processes, however, differ markedly from natural weathering environments.

Experiments by White and others (1994) found that the rate of ferrous iron dissolution from ilmenite was constant for short periods but decreased systematically over a period of 120 days. They hypothesized that the decreasing reaction rates could be well accounted for by a shrinking core model for diffusion of iron out of the structure. As the grain surfaces become enriched in insoluble titanium, transport through these outer product layers becomes rate limiting with time (White et al., 1994). In actuality, many ilmenite grains have internal fractures which behave similarly to the exterior of the grains during the dissolution of iron and other elements. These internal fractures can negate much of the passivation effect as clearly demonstrated by many of the previous image maps. Fractures and microcracking due to volume reduction as iron is removed keep exposing fresh surface area and let circulating fluids reach deep inside the grain.

Grey and Reid (1975) developed a model expanded upon by Dimanche and Bartholome (1976) and Frost and others (1986) which argued that the alteration of ilmenite takes place in two distinct stages. The first of these is an electrochemical corrosion process operating in a groundwater environment. Ilmenite-hematite solid solutions are p-type semiconductors that exhibit decreasing resistivity as the percentage of hematite increases (Ishikawa, 1958). During this first stage of the Grey and Reid model the oxygen layers are left intact while iron is oxidized and diffuses out of the ilmenite structure resulting in the formation of the mineral pseudorutile according to the reaction:

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$$3 \; Fe^{2+}TiO_3 + 2H^+ + 1/2 \; O_2 \; --> \; Fe_2^{3+}Ti_3O_9 + Fe^{2+} + H_2O \quad (1)$$
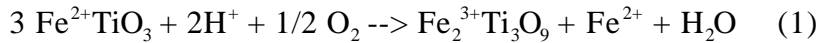
A full one-third of the iron initially present in ilmenite can be removed in this way while the remaining two-thirds is oxidized from the ferrous to the ferric state. Pseudorutile has not been reported in nature other than as an alteration product of ilmenite. Attempts to synthesize it have proven unsuccessful. According to Dimanche and Bartholome (1976) pseudorutile forms only as a metastable phase because the first step in the alteration process is kinetically easier than the second.

In the second stage of this alteration model Grey and Reid (1975) proposed that pseudorutile itself is then altered via an incongruent leaching mechanism, with both iron and oxygen being removed according to the reaction:

$$Fe_2^{3+}Ti_3O_9 + 4H^+ \; --> \; 3TiO_2 + 2Fe^{2+} + 2H_2O + 1/2 \; O \quad (2)$$
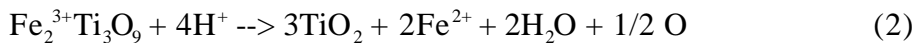
In this stage the iron-titanite dissolves under mildly reducing acidic conditions. The iron stays in solution while the titanium reprecipitates back on the original grain as a colloidal hydrated oxide that crystallizes as rutile or anatase (Frost et. al., 1983). With regard to beach sand deposits of ilmenite, Grey and Reid (1975) noted that the second stage appears to take place near the surface only, where organic acids capable of dissolving the pseudorutile are present.

While widely accepted in the literature, the Grey and Reid model appears to have certain weaknesses. Chief among them is that the two reactions require different environments to proceed, the first an oxidizing one and the second a reducing one. The second stage of the model is particularly problematic with its reliance on reducing conditions in near surface conditions. Also, because of the model's requirement for two sets of distinctly different conditions for alteration, one would expect to see some grains which had completed only the first stage. Such grains would have reached a "plateau" in the alteration process at the composition of pseudorutile (Ti:Fe ratio of 3:2). As previously shown by the grain traverses

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(Figure 18), however, the titanium-iron ratio changes smoothly across the sample and drops well below the 3:2 ratio in highly altered areas.

Mucke and Chaudhuri (1991) argue that the alteration of ilmenite to leucoxene is actually a continuous process. In their model, oxidation and leaching alter ilmenite to pseudorutile. Beyond that, continuing alteration occurs via leaching and hydrolization, as further oxidation is unable to occur. They proposed the following series of reactions, all of which could occur in an oxidizing, acidic environment.

$$6 \; Fe^{2+}TiO_3 + 3H_2O + 1.5 \; O_2 \; \text{-->} \; 2 \; Fe_2^{3+}Ti_3O_9 + 2 \; Fe(OH)_3 \; (3)$$

$$Fe_2^{3+}Ti_3O_9 + 3H_2O \; \text{-->} \; Fe^{3+}Ti_3O_6(OH)_3 + Fe(OH)_3 \qquad (4)$$

$$Fe^{3+}Ti_3O_6(OH)_3 \; \text{-->} \; 3TiO_2 + Fe(OH)_3 \qquad (5)$$
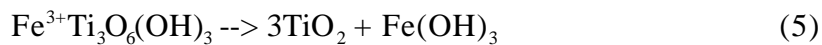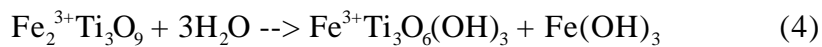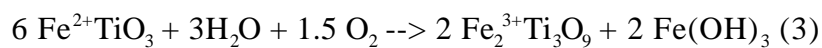
While correct in a theoretical sense, there is some question, however, as to whether these reactions are actually those which take place under real world conditions. The fact that hematite, where present as high-temperature exsolution lamellae, has been preferentially leached out of the ilmenite grains places some very important constraints upon weathering conditions. Hematite is quite stable under oxidizing conditions at moderate pH (See Figure 37). In fact, its solubility is extremely low, so much so that it is lower than even rutile by several orders of magnitude (See Figure 38). Under oxidizing conditions, it would take a strongly acidic solution to dissolve hematite in appreciable amounts. However, under reducing conditions, even a pH as high as 6 to 7 is sufficiently low for aqueous ferrous iron to become the stable phase. Complexing with organic acids under such reducing conditions would further enhance the solubility of iron (Drever and Vance, 1994). White and others (1994) gave possible alteration mechanisms for ilmenite under both oxic and anoxic conditions. That for oxic conditions is the same as Equation 1 listed above from the Grey and Reid model. The one for anoxic conditions, adopted here as the most likely cause of the alteration of ilmenite at the Old Hickory Deposit is as follows:

$$Fe^{2+}TiO_3 + 2H^+ \; \text{-->} \; Fe^{2+} \; (aq) + TiO_2 + H_2O \qquad (6)$$
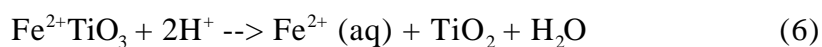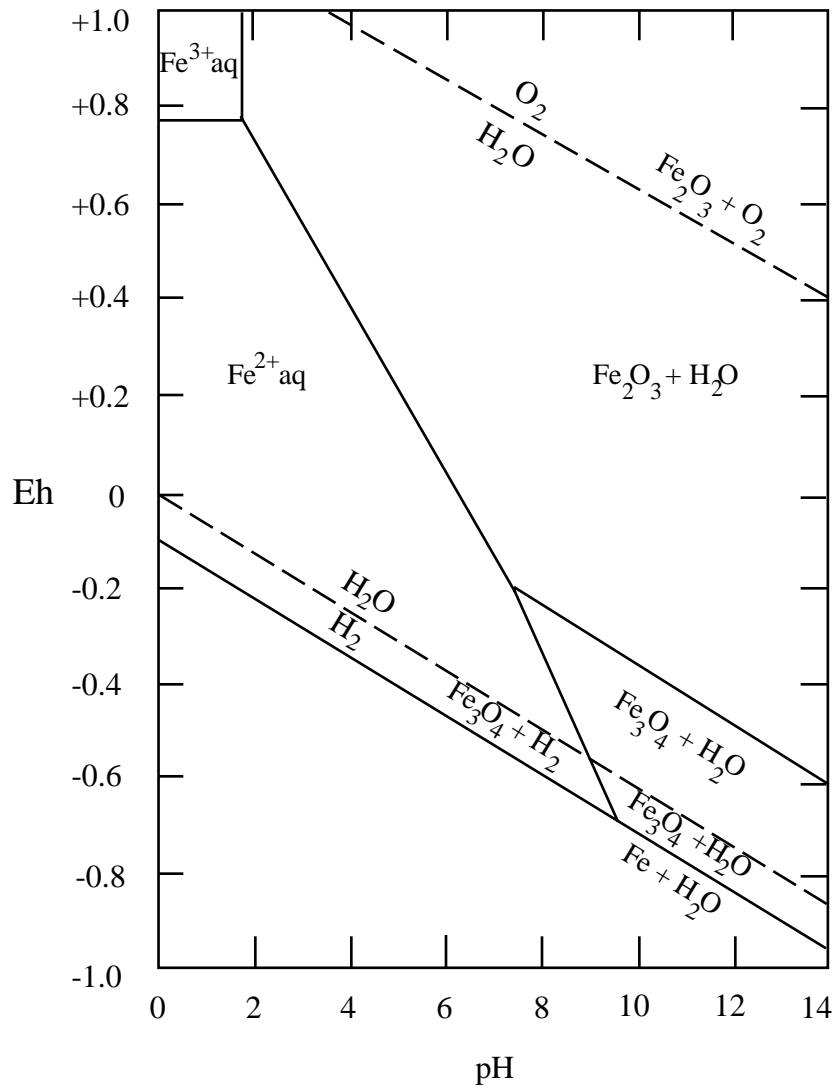
Figure 37 - Eh-ph diagram for iron showing stability fields of hematite, magnetite, and aqeous species in water. Modified after Garrels and Christ, 1965.
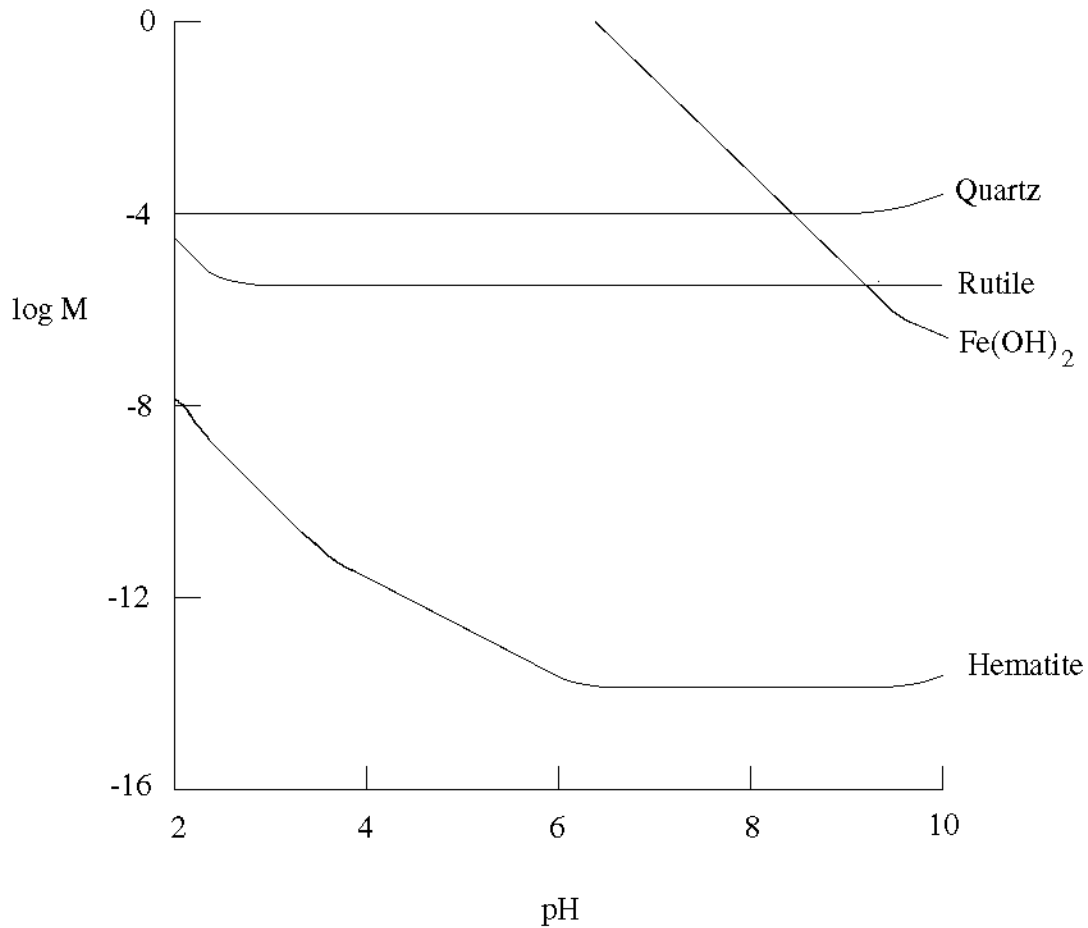
Figure 38 - Solubility diagram (molal) for quartz, rutile, hematite, and Fe(OH)$_2$ under oxidizing conditions. As shown the solubility of hematite is much lower than any of the others throughout the range of naturally occurring pH values. Based on data from Baes and Mesmer, 1976 and Cornell and Schwertmann, 1996.

Lynd (1960b) found that sulfuric acid and humic acids were the most effective in altering ilmenite at ambient temperatures. Sulfur is released by volcanic activity and has contributed to the weak acidity of rainwater long before pollution associated with industrialization. Humic acids refer to a collection of organic acids resulting from the decomposition of vegetation. Thus both of these leaching agents would be present in near surface zones and no doubt contribute to weathering. However, it is open to question whether these factors alone can account for the high degree of alteration evident in some grains due to the reasons already discussed. Because of this, Austin (1960) argued that most of the alteration of ilmenites observed in marine placers actually took place not on the beach face but before that while sediments were buried episodically, but cumulatively for long periods, during their journey seaward. He noted that swamps or lagoons, in particular, would provide conditions favorable for alteration. This model could also explain the significant differences in the degree of weathering between grains and is similar to the one advanced here.

Bass Becking and others (1960) reported the Eh and pH values of water as measured in a wide range of different geologic environments. They found that these different environments each had characteristic pH values and redox potentials which plotted in a narrow field on an Eh-pH diagram (See Figure 39). The implications of these findings should be obvious in that it then becomes a simple matter to estimate typical Eh and pH values which might be encountered in a given environment. It can readily be seen, for example, that both stream waters and oceanic waters are in the oxidizing part of the diagram and that their pH values therefore are too high for effective dissolution of hematite. Water-logged soils such as might be encountered along floodplains or other low-lying areas are a much better candidate. In addition, even sediments in stream beds can become reducing at a depth of several inches, due to the decay of organic matter (Dr. J. D. Rimstidt, personal communication). In any of these types of water-logged soils the pores are filled with water, greatly limiting the amount of O_2 available. Without molecular oxygen to serve as a terminal electron acceptor, electrons produced by biological respiration processes are transferred to other compounds (Vepraskas and Sprecher, 1997). Under these reducing conditions, Fe^{2+} in solution would become stable. Repeated cycles of burial and exhumation of sediments along streams and riverbanks during transport would thus keep
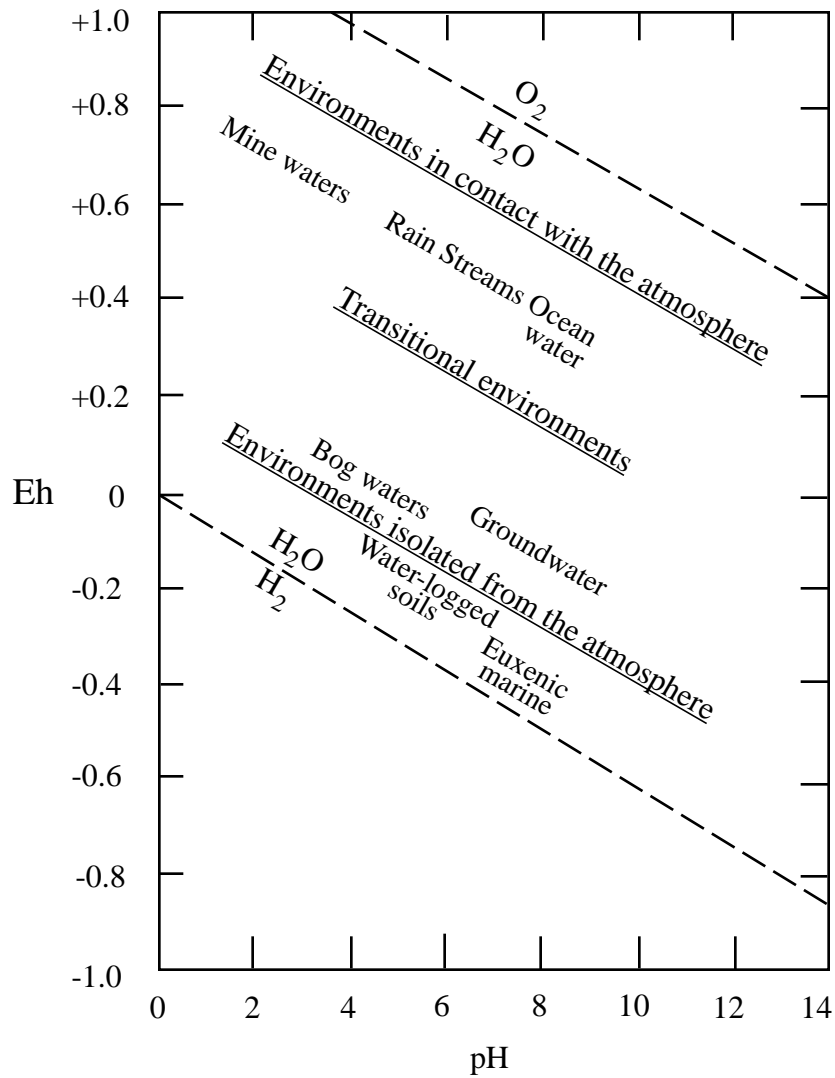
Figure 39 - Approximate Eh and pH of natural waters in different environments. After Bass Becking and others, 1960.

ilmenite grains under conditions well suited to the removal of iron for considerable lengths of time.

During crystallization the substitution of other cations in the ilmenite structure is controlled by several factors including the temperature of crystallization, oxygen fugacity, the amount of suitable cations available, and the size, charge, and electronegativity of those cations relative to iron and titanium (Lister, 1966). During alteration a consistent pattern is seen with regard to changes in concentration of the dominant trace elements Mn, Mg, and Cr. In every case where a change could be observed, all three of these elements tended to parallel the effects found for iron and be leached out of the ilmenite as alteration progresses. From an economic standpoint, this outcome is fortuitous because it helps to further enrich the grains in titanium. The mobilization of these elements likely indicates that they occupy similar structural sites in ilmenite as does iron (Morad and Aldahan, 1986). The alteration fronts for Mg and Mn appear to parallel those of iron quite closely, while those for Cr do so to a lesser degree. The ionic radii of Mg^{2+} and Cr^{3+} are both near to that of ferrous iron, with the Mn^{2+} ion being slightly larger. What controls the course of alteration within grains? Etch test conducted by Lynd (1960b) showed that the degree of etching was clearly dependent on crystallographic orientation. Cleavage planes also may serve as a zone of weakness along which alteration may be concentrated. In the samples analyzed here, however, alteration features generally did not show any clear preferential orientation. Structural discontinuities and other points of weakness can also provide a starting point for alteration. Then, as some iron is removed from these sites, further and deeper oxidation can occur (Temple, 1966). These factors would help to explain the complex branching patterns of alteration seen within grains.

Force (1991) noted the importance of climate in the weathering process. In a comparison of Quaternary shoreline sediments, the most advanced ilmenite alteration was found to occur between 35^0 N and 35^0 S. (Note that the Old Hickory Deposit now lies about two degrees north of this belt.) This is not surprising considering that most chemical weathering reactions proceed faster in more tropical environments. Based on palynological evidence it has been shown that during the Miocene, the middle Atlantic Coastal Plain had a climate which was warmer than at present (Groot, 1991). This contributed to extensive weathering

and mass wasting, resulting in the discharge of large volumes of sediment along the Atlantic passive margin (Poag, 1994). This pulse of sediment provided much of the necessary source materials which could then reworked to form the Old Hickory Deposit.

As Force (1991) points out, it can be difficult to separate changes due to weathering of detrital ilmenite grains which occurred prior to deposition from changes which they experienced together afterwards. Heterogeneity in weathering textures is a very important clue, however, The considerable variations in the degree of weathering between grains at the Old Hickory Deposit strongly suggest that much of it took place prior to deposition at the site. Hugo and Cornell (1991) adopted such a multi-stage model in their study of ilmenite alteration in Holocene dunes in South Africa. It is unlikely that extensively altered grains and unaltered ones would be found together, they point out, unless there was some alteration prior to deposition because otherwise such findings would imply striking differences in the rate of alteration between individual grains. On the other hand, they continue, such features as altered margins are unlikely to survive extensive transportation and reworking, and thus are often indicative of in-situ alteration.

The high degree of roundness of heavy mineral grains found at the Old Hickory site indicates a high-energy depositional environment as well as reworking of previously deposited material. The fact that altered rims on ilmenite grains, where present, commonly only encompass part of the grain and are often truncated at the grain boundary reflect mechanical weathering and abrasion occurring after an initial phase of alteration. This fact coupled with wide variations in the degree of alteration between grains suggests that much of the chemical weathering observed had taken place before final deposition. At the same time, the iron coatings on the surface of the zircon grains and the iron-rich soil found at the site point to abundant iron in the sediments there. One source of this could have been minor continuing post-depositional weathering of ilmenite with the attendant release of iron into the surrounding environment.

CONCLUSIONS

The Old Hickory is one of the largest of titanium-bearing heavy mineral placer deposits discovered in recent years. As such it provides a useful analog for better understanding not only the other related deposits which extend southward along the Fall Zone but also deposits of this type in general. This study sought to examine the nature of alteration on detrital ilmenite grains.

The Old Hickory Deposit lies along the Fall Zone in Cenozoic Coastal Plain sediments. The three major titanium ore minerals, ilmenite, leucoxene, and rutile make up over 70% of the heavy mineral assemblage. A precise determination of the provenance of the Old Hickory Deposit is probably not possible because of the degree of weathering and the fact that grains no doubt represent a mix of sources. A dominant source area, however, would be sediment from the James River which originated in the Roseland District in Central, VA.

Removal of iron from ilmenite during weathering and alteration results in the progressive enrichment of titanium within individual grains. The detailed microscopic examination and elemental mapping of typical ilmenite grains revealed that:

(1) Titanium enrichment, primarily through removal of iron, is widespread among ilmenite grains.

(2) Alteration generally proceeds from the outside of the grains inward and along fractures or other zones of weakness (See Figures 24-29). A variety of textures can arise from this process. Reaction kinetics are slow and multiple stages of alteration may be observed in the same grain.

(3) Hematite lamellae, often found in primary ilmenite, and resulting from initial high-temperature exsolution, are characteristically leached out of placer ilmenite. This process proceeds from the periphery of grains inward (See Figures 11-14 and 19-22).

(4) As the hematite lamellae are removed, iron is also leached from the ilmenite structure (See Figure 23).

(5) Trace elements Mg, Cr, and Mn all tended to be removed at the same time as the iron in the alteration process. (See Table 3) Upgrading of the ore via natural alteration has played an important role in making it economically viable to mine. Trace element concentrations in the ilmenite grains are sufficiently low that they should pose no problem for processing.

(6) Even grains which appear homogenous under optical observation may in fact be undergoing early stages of alteration (See Figures 31-36).

(7) Evidence of mechanical weathering of altered grains and the great variation in the degree of alteration between grains suggests that much of the alteration of ilmenite took place prior to deposition.

(8) Episodic burial under reducing conditions in water-logged soils would provide the ideal environment for such alteration to occur.

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VITA

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