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The Gulf of Maine Rutile Province--Accumulation of Fine-grained, Authigenic
Titanium Oxide from Sandstone and Shale Source Rocks

by

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Abstract

The Gulf of Maine, an embayment of the New England margin, is floored by shallow, glacially scoured basins that are partly filled with late Pleistocene and Holocene silt and clay containing 0.7 to 1.0 weight percent TiO_2 , chiefly in the form of silt-size rutile. Eleven basins in the gulf together are estimated to contain 479×10^6 metric tons (t) of TiO_2 (to a depth of 10 m) in the U. S. EEZ and 168×10^6 in Canada, based on analyses of surface sediment and of cores 10 to 20 m long. The U. S. annually consumes approximately 1×10^6 t of TiO_2 , of which 73 percent is imported. The inferred amount of fine-grained TiO_2 in the basins is large, and we interpret it to be predominantly rutile; but no attempt has been made yet to mine and beneficiate the fine-grained ore.

The region surrounding the Bay of Fundy in New Brunswick and Nova Scotia are underlain by Carboniferous and Triassic basins that contain extensive red and gray siltstones and sandstones. Northern Maine and northwestern New Brunswick is underlain by Paleozoic sandstones, siltstones, and shales. These sedimentary rocks contain fine-grained rutile crystals, and they have been the major source of the fine-grained sediment in the Gulf of Maine basins during and after the Wisconsinan Glaciation. We conclude that much of the rutile in the Gulf of Maine mud formed authigenically in poorly-cemented Carboniferous and Triassic coarse-grained sedimentary rocks after the dissolution of titanium-rich detrital minerals (ilmenite, ilmenomagnetite). Another major source of rutile is the generally finer-grained Paleozoic sedimentary rocks which contain recycled authigenic rutile that most likely originated in sandstones. Additional Wisconsinan sources of fine-grained, authigenic TiO_2 probably include sedimentary rocks of inferred Triassic age that underlie the Gulf of Maine.

The authigenesis of rutile in coarse sedimentary rocks (especially arkose and graywacke) followed by erosion, segregation, and deposition (and including recycling of fine-grained rutile from shales) can serve as a model for predicting and prospecting for unconsolidated deposits of fine-grained TiO_2 .

Gulf of Maine mud is comparable in TiO_2 content to typical shale. A determination of whether the fine-grained TiO_2 in shales primarily occurs as detrital titanium minerals from metamorphic and igneous sources or as recycled, authigenic titanium oxides from sedimentary sources may assist in interpreting shale provenance and environment of deposition.

Introduction

Rutile (TiO_2) is a major source of titanium dioxide used as a white pigment in the manufacture of paint, paper, rubber, and plastic. It is the preferred mineral for producing titanium metal which is valued for its strength, light weight, and resistance to heat and corrosion in the aerospace and chemical industries. Other minerals that are important sources of TiO_2 are ilmenite (FeTiO_3) and leucoxene, which is diagenetically altered ilmenite enriched in TiO_2 .

The fine-grained sediment of the Gulf of Maine contains 0.7 to 1.0 weight percent TiO_2 and abundant silt-size rutile crystals. The purpose of this report is to describe the rutile and its provenance from Paleozoic, Carboniferous, and Triassic sedimentary rocks in Maine, New Brunswick, and Nova Scotia; to estimate the extent of the deposit and the amount of TiO_2 present; and to propose the geologic setting and processes of this deposit as a model for further exploration for fine-grained titanium resources. Although the deposits in the Gulf of Maine rutile province are rich in TiO_2 , they are unconventional because the size of the rutile crystals (2-12 μ) is smaller than that of the mineral grains ordinarily processed by the titanium mining industry. Beneficiation of the ore described here would require fine-particle processing techniques.

Some terms used here require clarification. We use "authigenic" in reference to fine-grained (silt- and clay-size) minerals that form in situ in sedimentary rocks through diagenetic processes. "Recycled authigenic" refers to minerals (e.g. rutile) that form in a host sedimentary rock and subsequently are transported and deposited elsewhere and, thus, are detrital. They should not be confused with sand-size rutile grains that form in metamorphic and igneous rocks and commonly are referred to in the literature as "detrital".

Methods

Seafloor samples and cores of Quaternary sediment were collected in 1983-1988 from basins and interbasin highs in the Gulf of Maine and from intertidal areas of the Bay of Fundy region. Several seafloor samples from the basins were collected in an earlier study (Hathaway, 1971), as was a core from Stellwagen Basin (Tucholke and Hollister, 1973). The weight percent of silt+clay in all samples from the seafloor and from cores in Stellwagen Basin (core KN 10-1) and in Wilkinson, Murray, and Sharrer Basins (USGS POW 88-1 cores) was re-determined in the present study by weighing the dry sample before and after separation of sand from the silt+clay fraction by wet-sieving. The silt+clay fraction was analyzed by wavelength dispersive X-ray fluorescence (XRF). In all, 139 samples were analyzed from 92 seafloor sites and 64 samples from 4 core sites. The composition of mineral crystals identified as rutile in transmitted light were confirmed by energy dispersive X-ray analysis (EDS) with a scanning electron microscope (SEM).

In addition, sedimentary strata from 27 Paleozoic, Carboniferous, Triassic, and Quaternary localities in Maine, New Brunswick, and Nova Scotia were analyzed for TiO_2 content (43 samples) and inspected for the presence of rutile crystals.

Both the Quaternary sediment and the older sedimentary rocks were chemically leached to concentrate insoluble TiO_2 for identification and

analysis with EDS and SEM. A leaching process developed during this study involved treating the unconsolidated sediments and rock powders (ground to less than 100 microns) with an acetic acid-sodium acetate solution to eliminate carbonates and any adsorbed elements. This was followed by the addition of hydrogen peroxide to eliminate the organic fraction. The remaining sediment was then digested in an aqua regia-hydrofluoric acid solution (French and Adams, 1973) to remove silicates. Between each step the remaining sediment or ground rock material was washed and recovered by centrifugation and decantation. The recovery efficiency of this method was tested using a pure, insoluble rutile standard (whose grain size was equivalent to the sample materials being leached) and found to be 96 percent effective or better. In general, leaching removed 96 to 98 percent of the original sample, and the residue contained mostly TiO_2 and minor to trace amounts of barite, elemental carbon (coal), and insoluble fluorides created as a result of the leaching in hydrofluoric acid.

Sediment bulk density (grams of sediment in a cubic centimeter of wet sample) for the Stellwagen Basin core was calculated using reported values for saturated bulk density and for weight percent of water (Tucholke and Hollister, 1973). Bulk density of the Wilkinson, Murray, and Sharrer Basin core samples and of 14 seafloor samples collected in Wilkinson-Murray Basin in 1987 was determined from the weight of water (not corrected for salinity) and sediment in a known volume of wet sample.

Geologic Setting of the Gulf of Maine

The Gulf of Maine is bounded on the north, west, and east by low glaciated terrain of New England, New Brunswick, and Nova Scotia (Fig. 1). To the south, it is separated from the deep ocean by Georges Bank and Browns Bank, which rise to depths of 60 m and shallower over a wide area. Exchange of shallow water occurs between the gulf and the Atlantic Ocean across the bank areas; flow of deeper water between the gulf and the ocean is restricted to the Northeast Channel, a narrow, 240-m deep passage that separates Georges Bank and Browns Bank.

The gulf is a glacially-eroded depression made of up many large and small basins that are separated by elevated ridges of glacial rubble and resistant bedrock (Fig. 2). Eleven basins considered here vary from 79 to 4646 km^2 in area and from 93 to 377 m in depth. Pleistocene glacial till and moraine deposits of variable thickness overlie Paleozoic and Mesozoic basement rocks and probably range up to 80 to 100 thick based on seismic reflection surveys. Late Pleistocene and Holocene mud overlies the coarse Pleistocene strata and is up to 30 m or more thick in the basins but is very thin or absent between basins (Uchupi, 1965, 1966a,b, 1970; Tagg and Uchupi, 1966; Oldale and Uchupi, 1970; Oldale et al., 1973; Ballard and Uchupi, 1972, 1975; Fader et al., 1977; Austin et al., 1980; Oldale, 1988). Visual observations from submersibles revealed that elevated areas between basins are bare or are covered by a thin veneer of fine sediment on glacial sand and gravel and on bedrock.

The marine environment on the Gulf of Maine seafloor is relatively tranquil. Bottom currents at depths greater than 200 m, observed on 38 submersible dives in basins and on swells, generally did not exceed 0.1 to 0.3 kt (5 to 15 cm/s) in June, July, and August (1983-1985). In northern Jordan Basin, near the Bay of Fundy, currents reached 0.4 kt (20 cm/s) and in central Georges Basin 0.8 kt (40 cm/s). By contrast, on the south and southeast of the gulf, strong tidal and storm currents transport sand and fine sediment

from Georges Bank and Browns Bank into a portion of Georges and Crowell Basins.

Coastal Maine and New Hampshire bound the gulf on the north where the terrain is composed of Paleozoic metamorphic (greenschist to high-grade amphibolite facies) and granitic intrusive rocks (Fig.1). Overlying them in Maine are coarse non-marine and marine Pleistocene glacial debris and the Presumpscot Formation, a clayey marine silt similar to the Quaternary mud in the gulf that was deposited as the Wisconsinan ice front retreated northward (Fig. 2). Isostatic rebound since glacial retreat has raised the depositional area above sea level, and the Presumpscot Formation is present in river valleys to an elevation of approximately 100 m (Stuiver and Borns, 1975; Thompson and Borns, 1985). Minor rivers flow into the gulf from the glacially abraded crystalline and metamorphic terrain of New England, and the relatively small amount of sediment they transport is deposited mainly in coastal estuaries (Meade, 1969, 1971; Folger, 1972; Meade et al., 1975). Northern Maine and northwestern New Brunswick are underlain by weakly metamorphosed Paleozoic sandstones, siltstones, and shales that are pierced by granitic plutons (Potter et al., 1979; Osberg et al., 1985).

The Bay of Fundy, to the northeast of the gulf, is surrounded and underlain by relatively soft Carboniferous and Triassic red and gray siltstones and sandstones in New Brunswick and Nova Scotia (Powers, 1916; Klein, 1962; Belt, 1964, 1965; Swift and Lyall 1968; King and MacLean, 1976; Keppie, 1979; Potter et al., 1979). Vigorous tidal currents flow in and out of the bay, eroding and transporting both coarse- and fine-grained sediment from this friable terrain. Coarse sediment is deposited from bed load in the Bay of Fundy, and fine fractions are carried southward in suspension into the Gulf of Maine (Burbank, 1929; Forgeron, 1962; Miller, 1966; Swift et al., 1973; Munday et al., 1981).

Description and Source of Basin Sediment

Texture and color

Holocene sediment in the Gulf of Maine basins contains up to 99 weight percent silt and clay with minor amounts of very fine (4 phi) sand (Hathaway, 1971; this study). Late Pleistocene and Holocene sediment in the 21.74-m Stellwagen Basin core and in the 10-m Wilkinson, Murray, and Sharrer Basin cores contain 95 to 99 percent silt and clay. Seafloor and subsurface sediment on basin margins and on interbasin highs often contains an appreciable amount of Pleistocene sand and gravel.

In the Bay of Fundy region, intertidal sediment eroded from adjacent Carboniferous and Triassic red beds in St. Mary's Bay and in the Minas Basin is red (2.5YR) and reddish brown (5YR) in color (Munsell Color, 1975). Seafloor sediment varies from red to reddish brown (2.5YR to 5YR) in the Bay of Fundy to dark brown (10YR and 2.5Y) throughout the Gulf of Maine; sediment in the northern and eastern gulf near the Bay of Fundy is slightly more red (10YR 3/3, 4/2, 4/3) than it is to the south in Crowell and Georges Basins (2.5Y 4/2) (Forgeron, 1962; Stanley, 1969; this study). The fine-grained late Pleistocene and Holocene sediment in the Stellwagen Basin core (KN 10-1) in the western gulf is gray to greenish-gray in color (Tucholke and Hollister, 1973). The Wilkinson Basin core (POW 88-1-2) is dark gray (5Y 4/1) from the seafloor to 7 m and dark greenish gray (5GY 4/1) down to 10 m; and the cores from Murray (POW 88-1-8) and Sharrer (POW 88-1-12) Basins show a similar

trend. Some of the other POW 88-1 cores, located on basin margins and on interbasin highs, penetrated fine to coarse, ice-rafted sediment that is red and gray color-banded.

Composition

Sand in surficial sediment throughout the Gulf of Maine is chiefly quartz, feldspar, rock fragments, and heavy minerals (Burbank, 1929; Ross, 1970a,b; Trumbull, 1972). X-ray diffraction analyses showed that in seafloor sediment the major clay minerals are illite/mica, and chlorite, and that only 2 to 3 weight percent CaCO_3 is present (Hathaway, 1971). Marine mud from Wilkinson Basin (USGS rock standard MAG-1) has been analyzed thoroughly for grain size, for sand, clay, and bulk mineralogy, and for chemical and trace element composition (Fabbi and Espos, 1976; Manheim et al., 1976). Fine-grained basin sediment, as observed in transmitted light, is composed mainly of clay minerals, silt-size quartz and feldspar grains, and many small crystals of rutile and hematite as accessory minerals.

Rutile and anatase constitute a low percentage of the sand-size heavy mineral assemblage found on the margins of Gulf of Maine basins, on interbasin highs, and on the Maine shelf, and none is present on the Fundy beaches of Nova Scotia (Nolan, 1963; Ross, 1970a). By contrast, we have found silt-size rutile to be abundant both in surficial sediment and in underlying strata, as observed in transmitted light and the SEM.

Analyses of surficial sediment from 11 basins by XRF have revealed consistent concentrations of 0.7 to 1.0 weight percent TiO_2 in the silt+clay fraction. Analysis of the 21.74-m core from Stellwagen Basin (Tucholke and Hollister, 1973, core KN 10-1) during the present study showed that the section is 95 to 99 percent silt and clay, that fine-grained rutile is abundant, and that the silt+clay fraction contains 0.7 to 0.9 weight percent TiO_2 , increasing with depth (Table 1). The Wilkinson Basin core (POW 88-1-2) is 99 percent silt+clay and contains 0.7 to 0.8 percent TiO_2 (Table 2). Sediment in other 10-m cores from Murray and Sharrer Basins are similar in texture and TiO_2 content (Table 3).

Results of XRF analyses of 5 samples from Jordan Basin and the Maine shelf show that TiO_2 weight percent in the silt fraction alone (0.77 to 0.86 percent) is higher than it is in the silt+clay fraction (0.50 to 0.69 percent). The clay fraction was analyzed in 2 of these samples, and the TiO_2 content was 0.22 and 0.45 percent. Particle size analysis with the SEM of a silt+clay sample from Georges Basin showed that of 179 rutile crystals measured, 78 percent occur in the 2.5 to 12.5 μ interval.

Water content and bulk density

Water content and bulk density were determined for a suite of 14 seafloor samples collected from Wilkinson-Murray Basin in 1987. Water weight percent in the 1 to 7 cm depth interval averaged 67 and bulk density averaged 0.42 g/cc.

In Stellwagen Basin sediment (cores 33GC5 and KN 10-1), water decreased from 57 weight percent to 38 percent in the 0 to 10 m depth interval, and the bulk density increased from 0.60 to 1.02 g/cc. By contrast, the Wilkinson Basin core (POW 88-1-2) contained more water in the same depth interval; water content decreased from 62 to 54 weight percent and bulk density increased from

0.51 to 0.70 and then decreased to 0.62 g/cc. Bulk density values from the Stellwagen, Wilkinson, and Sharrer Basin cores (Tables 1-3) are used in calculations to estimate the TiO_2 content of the Gulf of Maine basin deposits to a depth of 10 m.

Sediment sources

Reconstructions of late Wisconsinan glacial advance and retreat in the Gulf of Maine by Stuiver and Borns (1975), Hughes et al. (1985), Smith (1985), Dyke and Prest (1987a, b, c), Schnitker (1988), and Oldale (in press) suggest that deposition of the sediment that we have shown to contain fine-grained rutile occurred after 18 ka, the start of ice sheet retreat from the Georges Bank. Sedimentation rates in the Gulf of Maine have slowed since the disappearance of glacial meltwater at about 11 ka. The mouths of all the major rivers in Maine and New Brunswick now are flooded, and most river-borne sediment is deposited in estuaries. The bulk of the fine-grained sediment in the gulf basins is glacially derived and was deposited from suspension. Some of our cores (POW 88-1 series) reveal that this mud deposit overlies coarser-grained strata composed of angular gravel clasts floating in a mud matrix that is typical of ice-rafted sediment.

Several lines of evidence provide information about modern sediment sources. Sediment transport in and out of the Bay of Fundy is by strong tidal currents and by a mean counter-clockwise gyre that flows northeastward along the Nova Scotian shore past the mouths of Minas Basin and Chignecto Bay and turns southwestward along the New Brunswick shore into the Gulf of Maine (Forgeron, 1962; Miller 1966; DeWolfe, 1981). Eastern basins of the gulf, near this sediment source, contain more silt than clay, whereas clay predominates in western basins; and the color of surficial sediment in the gulf decreases in red hue (from 2.5YR to 2.5Y) with increasing distance from continental red bed exposures in Nova Scotia and New Brunswick.

In addition, mineral distribution patterns in surficial sediment (sand fraction) show that an augite-dominated heavy mineral assemblage and high concentrations of dark minerals, and iron-stained quartz and feldspar extend southwestward from the Bay of Fundy far into the Gulf of Maine (Ross, 1970a,b; Trumbull, 1972). The North Mountain Basalt that forms the east coast of the Bay of Fundy is the source of the augite (neither rutile nor anatase are present in beach samples from that coast; Nolan, 1963). In the western Gulf of Maine, surficial sand from Wilkinson-Murray Basin is generally less iron-stained and amphibole dominates the heavy mineral assemblage, suggesting an additional sediment source in New England; and in small, restricted coastal areas of Maine and New Hampshire, distinctive heavy mineral assemblages indicate that sand there was deposited from rivers after the last glacial retreat (Ross, 1970a,b).

Thus, the principal source of modern, fine-grained sediment for the gulf is the relatively soft Carboniferous and Triassic red and gray sedimentary strata of the hydraulically energetic Bay of Fundy region, with a very minor contribution from the small New England rivers that drain a predominantly metamorphic and igneous terrane covered by Wisconsinan glacial debris. The source rocks of the underlying, glacially-derived mud are discussed in a following section.

Economic Aspects of Gulf of Maine TiO₂

Amount of TiO₂ in basin deposits

The following criteria are used to estimate the amount of TiO₂ in metric tons in the Gulf of Maine basins (Tables 1-4):

1. Weight percent of silt+clay and its contained TiO₂ to a depth of 10 m are values from cored intervals in Stellwagen (KN 10-1), Wilkinson-Murray (POW 88-1-2), and Sharrer-Howell (POW 88-1-12) Basins. For Rodgers Basin, values are from the core in adjacent Sharrer Basin (POW 88-1-12); and for all other basins values from seafloor samples are used and are held constant to a depth of 10 m.
2. Bulk density of the sediment for Stellwagen Basin is based on data from the upper meter in core 33GC5 (USGS 1988, unpublished), located near core KN 10-1, and from below 1 m in core KN10-1 (Tucholke and Hollister, 1973). Bulk density values are from cored intervals in Wilkinson-Murray (POW 88-1-2) and Sharrer-Howell (POW 88-1-12) Basins. For Rodgers Basin, values are from the Sharrer Basin core (POW 88-1-12); and for all other basins, bulk density is based on data from the Wilkinson Basin core (POW 88-1-2).
3. Size of each basin deposit is the area below the 200-m isobath. Basin area was reduced by 10 percent for the calculations to accommodate thinning of deposits at basin margins. The size of Georges Basin is restricted to the area below 300 m water depth due to the sandy, nonuniform texture of its margins. Stellwagen Basin is shallow, and basin size is the area below 80 m.
4. Volume of each basin deposit is determined to a depth of 10 m. The basins probably contain, on average, 10 m of fine-grained sediment. The amount of TiO₂ was determined for each basin by adding the metric tons of TiO₂ contained in each of 10, 1-m intervals that extend throughout the basin.

The resulting estimates indicate the fine-grained, total TiO₂ content is large, exceeding 479×10^6 t for the U. S. and 168×10^6 t for the Canadian regions of the gulf basins (Table 5). However, the region as a whole probably contains far more TiO₂ than estimated here because the fine-grained sediment is present in variable thickness in non-basin areas, some of the smaller basins are not treated here, and the weight percent TiO₂ probably increases with depth in deposits thicker than 10 m as demonstrated in Stellwagen Basin.

Preliminary results from experimental leaching of the Gulf of Maine mud, coupled with XRF analyses, indicate that at least 77 percent of the TiO₂ in the silt+clay fraction is in the form of insoluble TiO₂. Further leaching experiments are in progress.

TiO₂ resources: U. S., and worldwide

A recent compilation of titanium resources in the world's major deposits and districts (Towner et al., 1988) shows that world rutile resources are 74.1×10^6 t (contained TiO₂) of which 6.7×10^6 t are in the U. S. (Table 5). Ilmenite (including leucoxene and perovskite) resources are greater, 1604.6×10^6 t (contained TiO₂), of which 57.6×10^6 t are in the U. S. During 1988, the U. S. consumed approximately 0.34×10^6 t of TiO₂ as rutile and synthetic rutile, of which 68 percent was imported; and approximately 0.68×10^6 t of TiO₂ as ilmenite, titanium slag, and leucoxene, of which 76 percent was

imported (Lynd, 1989a,b). In all, the U. S. consumed approximately 1×10^6 t of TiO_2 , of which 73 percent was imported.

The ore grade and amount of TiO_2 in the Gulf of Maine basins have been evaluated only on the basis of analyses of surficial samples and several cores. No attempt has been made to mine and beneficiate this unconventional, fine-grained rutile.

Beneficiation of TiO_2 Ore

In the present economic climate and using conventional mining and milling methods, the exploitation of an unconsolidated rutile deposit requires that the mineral grains be coarser than 20 μ , and that the deposit must contain at least 0.09 percent TiO_2 and more than 100,000 t of TiO_2 (Force and Lynd, 1984; Fantel et al., 1986). Although the inferred amount of TiO_2 in the Gulf of Maine is more than 600×10^6 t, and the sediment contains 0.7 to 1.0 weight percent TiO_2 , the small size of the rutile crystals (2-12 μ) poses a problem for beneficiation of the ore. Rutile crystals in the gulf deposits are too small to be concentrated using conventional gravity, magnetic, and electrostatic techniques. However, many other methods have been developed to concentrate fine (10 to <100 μ) and ultrafine (<10 μ) particles (Somasundaran, ed., 1980).

For example, the kaolin clay industry uses fine-particle processing techniques to selectively remove a fine-grained TiO_2 impurity to improve color and brightness of their product which is used as a white pigment and as a paper coating and filler (Sennett and Young, 1979). The TiO_2 is present in kaolinite deposits as rutile crystals ranging in size from 5 to 30 μ (most are >10 μ) and as anatase crystals ranging in size from 1.5 to 20 μ (most are <5 μ). Rutile and large anatase crystals are removed by washing, screening, and centrifugation, and the remaining anatase generally makes up 1.5 weight percent of the washed kaolin. The typical grain size of this wet-processed kaolin product is less than 5 μ , with 92 percent less than 2 μ . Anatase crystals less than 5 μ in size are removed by flotation, flocculation, and high-intensity magnetic separation processes. Anatase is concentrated to approximately 15 percent in the tailings, and by reprocessing it can reach 60 to 80 percent (Paul Sennett, personal communication 1987). At present, the anatase is discarded.

Origin and Provenance of Fine-grained TiO_2

The silt-size rutile in the Gulf of Maine mud is associated with fine-grained hematite, iron-stained quartz and feldspar, and clay minerals, all of which probably were transported together in suspension. We hypothesize that the detrital, fine-grained rutile in surface and subsurface Quaternary sediment in the gulf is predominantly authigenic in origin, and that it formed after the dissolution primarily of ilmeno-magnetite and ilmenite in sedimentary source rocks.

Authigenesis of Fine-grained TiO_2

The authigenesis of titanium oxides in red and gray sedimentary rocks of widely varying ages is well-documented (Sun and Allen, 1957; Dimanche and Bartholome, 1976; Hubert and Reed, 1978; Reynolds and Goldhaber, 1978a,b; Ixer et al., 1979; Turner, 1980; Morad and Aldahan, 1982, 1986; Morad, 1983, 1986). Authigenic titanium oxides of silt and clay size are formed in both oxidizing

and reducing environments by the alteration of detrital sand-size iron-titanium oxides such as ilmenite and ilmeno-magnetite as well as biotite and, to some extent, hornblende and pyroxenes. In an oxidizing environment, iron in detrital minerals is liberated to form hematite giving red beds their color. In a reducing environment, iron is incorporated into pyrite, marcasite, and chlorite, imparting a gray color to the rocks.

Dissolution and alteration or replacement of detrital iron-titanium mineral grains produces fine-grained rutile, anatase, brookite, and leucoxene. Reynolds and Goldhaber (1978a) linked an increase in the TiO_2 content of the silt and clay fraction in a mineralized tuff deposit to the formation of authigenic TiO_2 by the alteration of iron-titanium oxides. Morad (1983) reported that titanium oxide minerals, mostly authigenic, constitute up to 3.5 percent of the total rock in arkoses and feldspathic sandstones of the Visingsö Group of Sweden.

Origin of Coarse-grained Rutile

A study by Force (1980) has shown that detrital, coarse-grained (sand-size) rutile found in sedimentary rocks is derived principally from high-grade metamorphic terranes that occupy large geographic areas; and that felsic and mafic igneous rocks contain little or no rutile (except for alkalic rocks). Force described a metamorphic geochemical cycle in which: a. coarse-grained, detrital rutile in sedimentary rocks does not survive metamorphism above the chlorite zone of the greenschist facies (this would also apply to fine-grained, authigenic TiO_2); b. titanium in rocks above the chlorite zone through the staurolite zone (low-rank amphibolite facies) chiefly occurs in silicate minerals (sphene, biotite, hornblende); c. these silicates, in turn, become unstable in medium- and high-rank amphibolite facies (kyanite and sillimanite zones) where titanium is recrystallized into coarse-grained rutile. In the Gulf of Maine seafloor sediment, sand-size rutile is an insignificant constituent of the heavy mineral fraction (Ross, 1970a,b).

Morphology of Fine-grained TiO_2 Crystals

The diagenetic alteration of Fe-Ti oxides produces a variety of fine-grained, authigenic TiO_2 products, as identified and illustrated by Dimanche and Bartholome (1976), Reynolds and Goldhaber (1978a,b), and Morad and AlDahan (1986). Authigenic TiO_2 takes the following forms: crystallographically-oriented TiO_2 lamellae (trellis structure) pseudomorphic after ilmenite lamellae in ilmenomagnetite grains; euhedral TiO_2 crystals that precipitate on detrital grain surfaces or as linings and fillings of pore spaces; overgrowths of TiO_2 crystals on altered grain surfaces; and host grains altered to micro- and cryptocrystalline TiO_2 . The Gulf of Maine mud and sedimentary source rocks described here contain similar fine-grained TiO_2 crystals, although some morphological types are more common than others (Fig. 3).

Individual rutile prisms are the most prevalent fine-grained TiO_2 particles found (Fig. 3A-C). Many are short, but others are elongate with well-formed prism faces and terminations. In addition, twinned crystals and clusters of prisms are present (Fig. 3D,G,H). A second major morphological type is composed of interlocking elements of TiO_2 , commonly called a trellis structure (Fig. 3E,F,I). Crystallographically-oriented ilmenite exsolution lamellae contained in a magnetite host (ilmenomagnetite) have been altered to TiO_2 and the magnetite removed. The interlocking elements of the trellis structure take two forms; one is well-formed prisms (Fig. 3E,I), and the other is

irregularly-shaped laths (Fig. 3F). Trellis structures that have fallen apart may be the principal source of the many elongate rutile particles observed in the samples.

A third type of fine-grained TiO_2 is grains of ilmenite that have been altered to TiO_2 , generally as masses of very small crystals (Fig. 3G,H). These grains may disaggregate to produce the smallest rutile prisms (compare Fig. 3A and G). Some of the ilmenite grains contain hematite exsolution lamellae that have been removed, leaving voids and a distinctive fabric in a cryptocrystalline mass of TiO_2 (Fig. 3J,K). A fourth morphological type is irregular, broken fragments from coarse (sand-size) rutile crystals that probably are not authigenic but that originated in metamorphic and igneous rocks (Fig. 3L).

Source Rocks of Gulf of Maine TiO_2

Studies of the Nova Scotian Triassic red beds in the St. Mary's Bay and in the Minas Basin regions (Fig. 1) have noted little sand-size rutile but an appreciable amount (2 to 2.4 percent) of opaque heavy minerals, primarily hematite, ilmenite, and magnetite (Mertz, 1980; Hyde, 1981; Perkins, 1981; Forlenza, 1982). A search with the SEM of 22 rock chips from 11 Carboniferous and Triassic localities in Nova Scotia and New Brunswick has revealed fine-grained rutile and anatase crystals and cryptocrystalline TiO_2 in pore spaces.

Insoluble TiO_2 crystals can be concentrated effectively by acid-leaching of host rocks. A total of 40 samples from potential source areas (24 localities) in Maine, New Brunswick, and Nova Scotia were leached and the residues examined (Fig. 1). The rocks are Paleozoic, Carboniferous, and Triassic in age and range in lithology from sandstone to shale. Most samples contain fine-grained TiO_2 crystals similar to those described above from the Gulf of Maine basin mud deposits. Elongate rutile prisms are dominant overall, but they vary in abundance with cryptocrystalline TiO_2 and broken fragments of larger crystals. Three samples from the clayey silt Presumpscot Formation (Pleistocene) of coastal Maine (Fig. 2) contain 0.83 to 0.85 weight percent TiO_2 and abundant silt- and clay-size rutile crystals. Several samples from the 4 sites in the Paleozoic metamorphic terrane in Maine (Fig. 1) contain rutile crystals that appear to be of metamorphic origin.

Modern sediment from widely separated intertidal areas near Carboniferous and Triassic exposures in the Bay of Fundy region (St Mary Bay, Minas Basin, Chignecto Bay; Fig. 1) contain abundant silt- and clay-size rutile crystals; and XRF analysis of 8 samples showed they contain 0.7 to 1.0 weight percent TiO_2 . In addition, suspended matter filtered from water collected in Jordan Basin at the seafloor, at intermediate depths, and at the sea surface contains silt-size rutile crystals, indicating that today fine-grained TiO_2 is being transported in suspension from Bay of Fundy source rocks.

Our observations have shown that fine-grained rutile is present in the water column and in the seafloor and subsurface sediment of the Gulf of Maine, in intertidal silt and clay near Carboniferous and Triassic exposures around the Bay of Fundy, and in the Paleozoic, Carboniferous, and Triassic rocks of Nova Scotia, New Brunswick, and northern Maine. The rutile crystals exhibit a variety of morphologic types that are distinctive and that appear to be found predictably in the silt+clay size fraction of sedimentary rocks and modern sediments.

It is probable that fine-grained TiO_2 crystals in the Gulf of Maine sediment have an authigenic origin in sedimentary rocks and have been recycled from the following sources (Fig. 1): a. Ordovician, Silurian, and Devonian sandstones, siltstones, and shales in northern Maine and northwestern New Brunswick (Potter et al., 1979; Osberg et al., 1985); b. Carboniferous and Triassic red and gray sandstones and siltstones exposed in New Brunswick and Nova Scotia and underlying the Bay of Fundy (Keppie, 1979; King and MacLean, 1976; Potter et al., 1979); c. sedimentary strata of probable Triassic age that lie buried beneath Pleistocene sediment in the Gulf of Maine (Austin et al., 1980, Fig. 6).

The Carboniferous and Triassic continental red and gray sandstones and siltstones in the Bay of Fundy region are an obvious source of authigenic TiO_2 . However, the provenance of fine-grained TiO_2 from Maine is more complex. The weakly metamorphosed (zeolite facies) Ordovician, Silurian, and Devonian sedimentary rocks of northern Maine (analyzed in this study) and northwestern New Brunswick are potential major sources for authigenic TiO_2 that formed in situ or that has been recycled from other sources. By contrast, southern Maine is an unlikely source for fine-grained rutile. The metamorphic (above chlorite zone) and igneous rocks there should not contain appreciable amounts of rutile, and crystals from high-grade metamorphic rocks would be coarser-grained (Force, 1980) than those present in Gulf of Maine mud. Moreover, there is little rutile in the Gulf of Maine sand fraction (Ross, 1970a,b). But, as mentioned above, some samples from the northern part of the metamorphosed region contain TiO_2 crystals that may be of metamorphic origin. We have not analyzed samples from the southern part of that region yet. At present, the relative importance of high-grade metamorphic rocks as producers of fine-grained rutile is unknown. The morphology of such crystals (anhedral, showing evidence of intergrowth with other crystals) may be distinctive enough to set them apart from those of authigenic origin in sedimentary rocks.

Chemical weathering at the earth's surface of igneous and metamorphic rocks that contain iron-titanium oxides (ilmenomagnetite, ilmenite) and titaniferous silicates (biotite, amphibole, pyroxenes, sphene) also produces authigenic, fine-grained TiO_2 commonly as anatase (Loughnan, 1969). Soils that formed from the igneous and metamorphic rocks that were exposed in southern Maine after glacial retreat possibly are a minor source of fine-grained TiO_2 .

Further Implications

TiO_2 in Shales

Previous studies of the composition of terrigenous sedimentary rocks have shown that the TiO_2 content generally is higher in shales than in sandstones (Clarke, 1924; Middleton, 1960; Pettijohn, 1963; Force 1976; Schultz et al., 1976; Correns, 1978). These analyses show that shales and slates contain 0.42 to 1.13 weight percent TiO_2 , whereas most sandstones contain a maximum of about 0.50 percent (with the exception of graywackes which can contain up to 1.0 percent). Paleozoic siltstones and shales (19 samples) from northern Maine examined in this study contain 0.5 to 1.3 weight percent TiO_2 , with a mean of 0.9. All but three samples from Maine contain fine-grained TiO_2 . Carboniferous and Triassic arkosic siltstones and sandstones (21 samples) from New Brunswick and Nova Scotia contain 0.1 to 1.0 weight percent TiO_2 with a mean of 0.7; all samples contain fine-grained TiO_2 .

The minerals containing titanium in sandstones are chiefly: a. sand-size detrital minerals of varied provenance such as ilmenite, ilmeno-magnetite, biotite, hornblende, pyroxenes, rutile, and sphene; b. fine-grained authigenic TiO_2 (rutile and polymorphs; leucoxene). In addition, minor amounts of titanium presumably are present in clay lattices and as silt-size detrital, titaniferous minerals. In shale, it is unclear whether the titanium resides primarily: a. in detrital, silt-size fragments of the non-authigenic minerals listed above; b. or in detrital, naturally fine-grained, authigenic titanium oxides that have been sorted and concentrated during transport in suspension to the depositional area. Additionally, diagenesis of detrital titanium-bearing minerals and/or invasion by mineralizing solutions during consolidation of mud into shale, conceivably, could produce authigenic titanium oxides in situ. We hypothesize that the TiO_2 in sandstones is attributable both to detrital titaniferous oxides and silicates and to authigenic rutile, whereas the TiO_2 in shales is attributable mostly to recycled, authigenic rutile from sandstone sources.

Analyses reported in the literature show that composite samples of various fine-grained sediment types contain the following amounts of TiO_2 : Mississippi delta silt (235 samples), 0.59 weight percent; marine red clay (51 samples), 0.98 percent; marine green and blue mud (52 samples), 1.27 percent (Clarke, 1924). The mean value of TiO_2 in oceanic sediment from all oceans (25 samples, carbonate-free) is 0.90 percent (Chester and Aston, 1976); and in sediment from the central Atlantic Ocean (178 samples, carbonate-free) it is 0.71 percent (Correns, 1978). Most of the TiO_2 in oceanic sediment is terrigenous in origin, although locally it is derived from volcanic sources (Chester and Aston, 1976). Hirst (1962) reported that 12 clay samples from shelf depths in the Gulf of Paria contain from 0.6 to 0.9 weight percent TiO_2 , and he implied that the titanium is in the form of fine-grained oxides that were weathered and transported along with the clay fraction through the Orinoco River drainage system. If the sediment in the Gulf of Maine basins were to be buried and altered to a shale, it would contain 0.7 to 1.0 weight percent TiO_2 , mostly as detrital, fine-grained rutile of authigenic origin.

By determining the nature of titanium-bearing minerals in shales (and in other sedimentary rocks), it might be possible to answer questions about their provenance and environment of deposition. Titanium oxide grains of authigenic origin tend to be silt-size or smaller and to possess the characteristic shapes described above, whereas detrital rutile grains of metamorphic and igneous origin generally are larger and are anhedral or irregular in shape. Are shales high in TiO_2 because of the presence chiefly of fine-grained rutile or of other titaniferous minerals? Is the rutile in shales mostly of authigenic origin, recycled from other sedimentary rocks? Do the relative amounts and kinds of rutile particles (or their absence) in a shale shed light on its provenance; and can they be utilized as indicators to set limits on the metamorphic grade of sedimentary rocks? If shales contain an appreciable amount of TiO_2 , are they also potential source rocks of fine-grained rutile?

Predicting the Occurrence of Fine-grained TiO_2

Rutile and its polymorphs are stable minerals, and their stability ensures that authigenic TiO_2 crystals will be passed through multiple sedimentary cycles involving both coarse and fine clastic rocks and that many of them eventually will be concentrated in fine-grained deposits.

The geologic processes and settings outlined here might serve as a useful model for predicting and prospecting for unconsolidated deposits of fine-grained rutile. For instance, metamorphic and igneous rocks would be sources both of coarse-grained, non-authigenic rutile and of Fe-Ti oxides and silicates. Following erosion, rutile (coarse grains and fine crystal fragments) and Fe-Ti minerals are deposited in a "sandstone" environment. There, the Fe-Ti minerals are diagenetically altered to produce fine-grained, authigenic TiO_2 . Erosion of the sandstone, followed by segregation of fine particles concentrates the authigenic rutile and the fine fragments of non-authigenic rutile in a "shale" environment. Further erosion and deposition (recycling) of shales coupled with TiO_2 authigenesis in sandstones leads to greater concentrations of fine-grained TiO_2 in younger shales.

Features of a Gulf of Maine model would include: a. coarse-grained sedimentary source rocks (especially arkose and graywacke) that originally contained an appreciable amount of detrital iron-titanium oxides and/or titaniferous silicates; b. past intrastratal solution of Fe-Ti minerals and formation of authigenic titanium oxides; c. fine-grained sedimentary source rocks (shale) that contain recycled, authigenic titanium oxides from sandstone sources; d. past chemical weathering of igneous and metamorphic source rocks that contain iron-titanium oxides and titaniferous silicates and the formation of authigenic titanium oxides in soils; e. a sedimentary environment that incorporates vigorous erosion of source rocks, geographic segregation of bedload and suspended sediment, and a quiet depositional area that receives fine-grained sediment predominantly from the source areas described above.

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TABLE 1. Stellwagen Basin Total Fine-grained TiO₂ Content

Depth interval	Bulk density	Silt+clay	TiO ₂ in silt+clay	Contained TiO ₂ , 10 ⁶ metric tons		
				Unit deposit ^{>}	Basin deposit ^{>>}	Cumulative basin deposit
m	g/cc	wt pct	wt pct			
0-1	0.60	97	0.74	0.430	0.843	0.843
1-2	0.67	98	0.73	0.479	0.939	1.782
2-3	0.69	98	0.73	0.494	0.968	2.750
3-4	0.74	98	0.72	0.522	1.023	3.773
4-5	0.76	98	0.74	0.551	1.080	4.853
5-6	0.76	98	0.77	0.573	1.123	5.976
6-7	0.87	98	0.78	0.665	1.303	7.279
7-8	0.94	97	0.80	0.729	1.429	8.708
8-9	1.00	96	0.82	0.787	1.543	10.251
9-10	1.02	96	0.84	0.822	1.611	11.862
10-11	1.02	98	0.84	0.840	1.646	13.508
11-12	1.03	98	0.84	0.848	1.662	15.170
12-13	1.04	97	0.85	0.857	1.680	16.850
13-14	0.85	98	0.86	0.716	1.403	18.253
14-15	0.83	99	0.87	0.715	1.401	19.654
15-16	0.92	99	0.89	0.811	1.590	21.244
16-17	1.02	99	0.92	0.929	1.821	23.065
17-18	1.16	99	0.93	1.068	2.093	25.158
18-19	1.19	99	0.92	1.084	2.125	27.283
19-20	1.19	99	0.94	1.107	2.170	29.453
20-21	1.19	98	0.94	1.096	2.148	31.601
21-21.5	1.23	95	0.91	0.532 ^{<}	1.043 ^{<}	32.644

Note: Calculations based on analysis of core KN 10-1 (Fig. 2).

Core KN 10-1 sampled for texture and TiO₂ at 53 cm and at 94 cm and thereafter at 1-m intervals to bottom of core. Silt+clay and TiO₂ weight percent values picked at midpoints of 1-m intervals from curves of plotted values (this study).

Bulk density calculated from saturated bulk density and water content values determined at approximately 1-m intervals:

a. 0-1 m interval is value at 0.5 m from core 33GC5 located near KN 10-1 site (USGS unpublished); b. below 0-1 m interval, values are midpoints of 1-m intervals from curve-plots for core KN 10-1 in Stellwagen Basin (Tucholke and Hollister, 1973).

[>] Contained TiO₂ (10⁶ metric tons) calculated for unit deposit: (A g/cc)(B/100)(C/100)(10¹⁴ cc)(mt/10⁶ g)(1/10⁶).

A=bulk density (=g sediment in cc of wet sample); B=wt pct silt+clay; C=wt pct TiO₂ in silt+clay; 10¹⁴ cc=volume of unit deposit, 100 km² x 1 m; mt=10⁶ g.

^{>>} Basin area = 196 km²; TiO₂ in basin deposit = 1.96 x unit deposit.

[<] Values for deposit 0.5 m thick.

TABLE 2. Wilkinson-Murray Basin Total Fine-grained TiO₂ Content

Depth interval	Bulk density	Silt+ clay	TiO ₂ in silt+ clay	Contained TiO ₂ , 10 ⁶ metric tons		
				Unit deposit ^{>}	Basin deposit ^{>>}	Cumulative basin deposit
m	g/cc	wt pct	wt pct			
0-1	0.51	99	0.77	0.389	17.867	17.867
1-2	0.54	99	0.76	0.406	18.648	36.515
2-3	0.57	99	0.74	0.418	19.199	55.714
3-4	0.61	99	0.74	0.448	20.577	76.291
4-5	0.65	99	0.75	0.483	22.184	98.475
5-6	0.70	99	0.75	0.520	23.884	122.359
6-7	0.69	99	0.75	0.512	23.516	145.875
7-8	0.68	99	0.77	0.518	23.792	169.667
8-9	0.67	99	0.79	0.524	24.067	193.734
9-10	0.62	99	0.78	0.479	22.000	215.734

Note: Calculations based on analysis of core POW 88-1-2 (Fig. 2). Core POW 88-1-2 sampled for texture and TiO₂ at 20, 82, 100, and 132 cm and thereafter at each meter to bottom of core. Silt+clay and TiO₂ weight percent values picked at midpoints of 1-m intervals from curves of plotted values.

Bulk density (calculated from weight of water and sediment in a known volume of wet sample) determined at 20, 82, and 132 cm and thereafter at each meter to bottom of core; values are midpoints of 1-m intervals from curve-plots of core data.

[>] Contained TiO₂ (10⁶ metric tons) calculated for unit deposit, 100 km² x 1 m (see Table 1 note).

^{>>} Basin area = 4593 km²; TiO₂ in basin deposit = 45.93 x unit deposit.

TABLE 3. Sediment Texture, Weight Percent TiO₂, and Bulk Density in Murray and Sharrer Basins

Depth interval m	Core no.	Bulk density g/cc		Silt+ clay wt pct		TiO ₂ in silt + clay wt pct	
		8	12	8	12	8	12
0-1		0.51	0.52	99	99	0.76	0.75
1-2		0.59	0.57	99	99	0.75	0.75
2-3		0.61	0.62	99	99	0.76	0.77
3-4		0.61	0.64	99	99	0.75	0.78
4-5		0.66	0.64	99	99	0.74	0.78
5-6		0.68	0.66	99	99	0.75	0.81
6-7		0.73	0.73	99	99	0.75	0.81
7-8		0.75	0.77	99	99	0.74	0.80
8-9		0.76	0.78	99	99	0.76	0.80
9-10		0.76	0.78	99	99	0.79	0.81

Note: Cores are POW 88-1-8 and POW 88-1-12 located in Murray and Sharrer Basins, respectively (Fig. 2). Values are midpoints of 1-m intervals from curve-plots of data analyzed at 1-m intervals.

TABLE 4. Gulf of Maine Basins Total Fine-grained TiO₂ Content

Basin	Silt+ clay	TiO ₂ in silt+ clay	U. S. (Canada)	Contained TiO ₂ , 10 ⁶ metric tons >>		
				Area ² km ²	U. S. (Canada) Deposit thickness	U. S. (Canada)
	wt pct	wt pct		1 m	5 m	10 m
Wilkinson-Murray	99	0.74-0.79 ^{<}	4593	17.9	-	215.7
Jordan	99	0.74	3071	11.5	(5.9)	140.3
Crowell	63	0.83	-	-	(3.6)	-
Sharrer-Howell	99	0.75-0.81 ^{<}	751	2.9	-	39.6
Rodgers	99	0.75-0.81 ^{<}	551	2.1	-	28.9
Georges	73	0.88	93	0.3	(4.3)	3.7
Lindenkohl	98	0.78	400	1.6	-	19.1
Stellwagen	96-98 ^{<}	0.73-0.84 ^{<}	196	0.8	-	11.9
Truxton	99	0.80	214	0.9	-	10.6
Ammen	99	0.80	107	0.4	-	5.4
Davis	99	0.81	79	0.3	-	3.8
			Total	38.7	(13.8)	479.0
					217.7	(77.6)
						(168.4)

> Basin area boundary is 200 m isobath except for Stellwagen Basin (80 m) and for Georges Basin (300 m).
 >> See text for criteria used to estimate fine-grained TiO₂ content in basins.
 < Values vary with depth in cores: Wilkinson-Murray (core POW 88-1-2); Sharrer-Howell and Rodgers (core POW 88-1-12); Stellwagen (core KN 10-1).

TABLE 5. Gulf of Maine Total Fine-grained TiO₂ Content Compared with United States and World Identified Titanium Resources

Wt pct TiO ₂ =	Contained TiO ₂ , 10 ⁶ metric tons			
	Rut (95)	Ilmen + Leucox + Perov (54) (67) (59)	Ana (95)	
Identified titanium resources ^{<} (coarse-grained minerals)				
World - - - - -	74.1	1604.4	145.4	
United States - - - - -	6.7	57.6	-	
Gulf of Maine TiO ₂ content (fine-grained TiO ₂)				
U.S. basins	217.7 ^{>} 479.0 ^{>>}	-	-	
Canadian basins	77.6 ^{>} 168.4 ^{>>}	-	-	

[<] Based on data in Towner et al., 1988.
[>] Basin deposit 5 m thick.
^{>>} Basin deposit 10 m thick.

FIG. 1. Geologic map showing source areas in Maine, New Brunswick, Nova Scotia, and the Gulf of Maine for Quaternary sediment deposited in the Gulf of Maine during Wisconsinan glacial advance and retreat. Sedimentary and metamorphic rocks, and intertidal sediment from St. Mary Bay, Minas Basin, and Chignecto Bay, were analyzed for TiO_2 content by XRF, and subsequently leached and inspected in the SEM for TiO_2 crystals. SMB, St. Mary Bay; MB, Minas Basin; CB, Chignecto Bay; PEI, Prince Edward Island. Geology from Keppie (1979), Potter et al. (1979), Austin et al. (1980), and Osberg et al. (1985).

FIG. 2. Map of Gulf of Maine showing locations of major basins and sample and core sites. Depositional area of Presumpscot Formation (Pleistocene) in coastal Maine is shaded (Thompson and Borns, 1985). Core KN 10-1 (Tucholke and Hollister, 1973) is 21 m long; POW 88-1 cores are up to 10 m long. Most seafloor grab samples were collected by submersible; some dots represent multiple samples collected within several hundred meters of each other.

FIG. 3. SEM photomicrographs of fine-grained TiO_2 particles representative of those found in Gulf of Maine Quaternary mud and in source rocks of Maine, New Brunswick, and Nova Scotia. A. Rutile prisms and crystal fragments; Gulf of Maine seafloor mud (Quaternary; Wilkinson Basin); sample leached to concentrate fine-grained TiO_2 . B. Titanium X-ray map of particles shown in 3A. C. Rutile prisms and crystal fragments; Madrid Formation, sandstone (Devonian; Maine); leached sample. D. Cluster of rutile crystals; Gulf of Maine seafloor mud (Quaternary; Wilkinson Basin). E. Lattice of rutile prisms (trellis structure); probably formed by replacement of crystallographically-oriented ilmenite lamellae in magnetite host (ilmenomagnetite); Gulf of Maine seafloor mud (Quaternary; Georges Basin). F. Lattice of rutile prisms and laths (trellis structure); probably formed as did grain in 3E; Wolfville Formation, sandstone (Triassic; Nova Scotia). G. Cluster of TiO_2 crystals resulting from alteration of Fe-Ti grain; Wolfville Formation, sandstone (Triassic; Nova Scotia). H. Cluster of rutile crystals resulting from alteration of Fe-Ti grain; Cumberland Group, sandstone (Carboniferous; Nova Scotia). I. Lattice of rutile prisms; probably a trellis structure formed by replacement of crystallographically-oriented ilmenite lamellae in magnetite host (ilmenomagnetite); Blomidon Formation, sandstone (Triassic; Nova Scotia). J. Grain of ilmenite (dark) containing hematite exsolution lamellae (light); Allard Lake iron-titanium deposit (Proterozoic; Quebec), not in Gulf of Maine source area; example of an unaltered sand-size Fe-Ti grain that can occur in sedimentary rocks. K. Grain of cryptocrystalline TiO_2 ; probably formed by replacement of ilmenite host; voids probably represent hematite exsolution lamellae that have been removed during diagenesis (compare with 3J); Gulf of Maine seafloor mud (Quaternary; Wilkinson Basin). L. Fragment of TiO_2 crystal; probably part of a larger, non-authigenic rutile crystal, possibly of metamorphic or igneous origin; Gulf of Maine seafloor mud (Quaternary; Wilkinson Basin).





