GEOLOGY AND RESOURCES OF TITANIUM

GEOLOGICAL SURVEY PROFESSIONAL PAPER 959–A, B, C, D, E, F ✓

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Titanium Contents and Titanium Partitioning in Rocks

By E. R. FORCE

Metamorphic Source Rocks of Titanium Placer Deposits— A Geochemical Cycle

By E. R. FORCE

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Titanium Minerals in Deposits of Other Minerals

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U.S. DEPARTMENT OF THE INTERIOR
March 3, 1849

UNITED STATES GOVERNMENT PRINTING OFFICE, WASHINGTON : 1976

UNITED STATES DEPARTMENT OF THE INTERIOR

THOMAS S. KLEPPE, ***Secretary***

GEOLOGICAL SURVEY

V. E. McKelvey, ***Director***

Library of Congress Cataloging in Publication Data

Main entry under title:
Geology and resources of titanium.

(Geological Survey Professional Paper ; 959)
CONTENTS: Force, E. R. Titanium contents and titanium partitioning in rocks.—Force, E. R. Metamorphic source rocks of titanium placer deposits, a geochemical cycle.—Blake, M. C., Jr., and Morgan, Benjamin. A. Rutile and sphene in blueschist and related high-pressure-facies rocks.—Herz, Norman. Titanium deposits in anorthosite massifs.—Herz, Norman. Titanium deposits in alkalic igneous rocks.—Force, E. R. Titanium minerals in deposits of other minerals.
Includes bibliographies.

Supt. of Docs. no.: I 19.16:959 A–F
1. Titanium ores—United States. 2. Petrology—United States. I. Series: United States. Geological Survey. Professional Paper ; 959.
QE390.2.T5G46 553′462 75–619269

For sale by the Superintendent of Documents, U.S. Government Printing Office
Washington, D.C. 20402
Stock Number 024-001-02891-3

APPRAISAL OF MINERAL RESOURCES

Continuing appraisal of the mineral resources of the United States is conducted by the U.S. Geological Survey in accordance with the provisions of the Mining and Minerals Policy Act of 1970 (Public Law 91–631, Dec. 31, 1970). Total resources for purposes of these appraisal estimates include currently minable resources (*reserves*) as well as those resources not yet discovered or not presently profitable to mine.

The mining of mineral deposits, once discovered, depends on geologic, economic, and technologic factors; however, identification of many deposits yet to be discovered, owing to incomplete knowledge of their distribution in the Earth's crust, depends greatly on geologic availability and man's ingenuity. Consequently, appraisal of mineral resources results in approximations, subject to constant change as known deposits are depleted, new deposits are found, new extractive technology and uses are developed, and new geologic knowledge and theories indicate new areas favorable for exploration.

This professional paper discusses aspects of the geology of titanium as a framework for appraising resources of this commodity in the light of today's technology, economics, and geologic knowledge.

Other Geological Survey publications relating to the appraisal of resources of specific mineral commodities include the following:

Professional Paper 820—"United States Mineral Resources"

Professional Paper 907—"Geology and Resources of Copper"

Professional Paper 926—"Geology and Resources of Vanadium Deposits"

Professional Paper 933—"Geology and Resources of Fluorine in the United States"

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[Letters designate the chapters]

METRIC-ENGLISH EQUIVALENTS

Metric unit	English equivalent	
	Length	
millimetre (mm)	= 0.03937	inch (in)
metre (m)	= 3.28	feet (ft)
kilometre (km)	= .62	mile (mi)
	Area	
square metre (m^2)	= 10.76	square feet (ft^2)
square kilometre (km^2)	= .386	square mile (mi^2)
hectare (ha)	= 2.47	acres
	Volume	
cubic centimetre (cm^3)	= 0.061	cubic inch (in^3)
litre (l)	= 61.03	cubic inches
cubic metre (m^3)	= 35.31	cubic feet (ft^3)
cubic metre	= .00081	acre-foot (acre-ft)
cubic hectometre (hm^3)	= 810.7	acre-feet
litre	= 2.113	pints (pt)
litre	= 1.06	quarts (qt)
litre	= .26	gallon (gal)
cubic metre	= .00026	million gallons (Mgal or 10^6 gal)
cubic metre	= 6.290	barrels (bbl) (1 bbl=42 gal)
	Weight	
gram (g)	= 0.035	ounce, avoirdupois (oz avdp)
gram	= .0022	pound, avoirdupois (lb avdp)
tonne (t)	= 1.1	tons, short (2,000 lb)
tonne	= .98	ton, long (2,240 lb)
	Specific combinations	
kilogram per square centimetre (kg/cm^2)	= 0.96	atmosphere (atm)
kilogram per square centimetre	= .98	bar (0.9869 atm)
cubic metre per second (m^3/s)	= 35.3	cubic feet per second (ft^3/s)
	Specific combinations—Continued	
litre per second (l/s)	= .0353	cubic foot per second
cubic metre per second per square kilometre [(m^3/s)/km^2]	= 91.47	cubic feet per second per square mile [(ft^3/s)/mi^2]
metre per day (m/d)	= 3.28	feet per day (hydraulic conductivity) (ft/d)
metre per kilometre (m/km)	= 5.28	feet per mile (ft/mi)
kilometre per hour (km/h)	= .9113	foot per second (ft/s)
metre per second (m/s)	= 3.28	feet per second
metre squared per day (m^2/d)	= 10.764	feet squared per day (ft^2/d) (transmissivity)
cubic metre per second (m^3/s)	= 22.826	million gallons per day (Mgal/d)
cubic metre per minute (m^3/min)	= 264.2	gallons per minute (gal/min)
litre per second (l/s)	= 15.85	gallons per minute
litre per second per metre [(l/s)/m]	= 4.83	gallons per minute per foot [(gal/min)/ft]
kilometre per hour (km/h)	= .62	mile per hour (mi/h)
metre per second (m/s)	= 2.237	miles per hour
gram per cubic centimetre (g/cm^3)	= 62.43	pounds per cubic foot (lb/ft^3)
gram per square centimetre (g/cm^2)	= 2.048	pounds per square foot (lb/ft^2)
gram per square centimetre	= .0142	pound per square inch (lb/in^2)
	Temperature	
degree Celsius (°C)	= 1.8	degrees Fahrenheit (°F)
degrees Celsius (temperature)	= [(1.8 × °C) + 32]	degrees Fahrenheit

Titanium Contents and Titanium Partitioning in Rocks

By E. R. FORCE

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TITANIUM CONTENTS AND TITANIUM PARTITIONING IN ROCKS

By E. R. FORCE

ABSTRACT

Basic (but not ultrabasic) and alkalic rocks tend to have the highest TiO_2 contents of igneous rocks. Few igneous, sedimentary, or metamorphic rock types have an average TiO_2 content as much as an order of magnitude different from the crustal average.

In many rocks, common silicate minerals rather than oxides contain most of the TiO_2 in the rock. Because only oxide minerals are economically useful at present, the economic geology of titanium is as much a function of mineralogy as it is of chemistry.

DISTRIBUTION OF TITANIUM AMONG ROCK TYPES

EARTH'S CRUST

The elemental abundance of titanium in the Earth's crust has been estimated to be about 0.45 percent, or 0.75 percent as TiO_2 (Clarke and Washington, 1924; Goldschmidt, 1954; Vinogradov, 1962; Wedepohl, 1967). Lee and Yao (1970) revised these estimates to 0.64 and 1.07 percent, respectively, partitioned as shown in table 1. Titanium is reported in chemical analyses of rocks and minerals as TiO_2; all subsequent discussion refers to TiO_2 rather than elemental titanium.

IGNEOUS ROCKS

Vinogradov (1962) stated that the average TiO_2 content of some igneous rock types is 0.05 percent for ultramafic rocks, 1.5 percent for mafic rocks, 1.3 percent for rocks of intermediate composition, and 0.38 percent for felsic rocks. Nockolds (1954) and Beus (1971) averaged TiO_2 analyses of a large number of samples of each type for a wide variety of igneous rocks; the results are given in table 2.

TABLE 1.—*Average titanium abundance in the Earth's crust from Lee and Yao (1970)*

Crust type	Titanium content (weight percent)		Percent of total crustal volume
	Ti	TiO_2	
Total crust	0.64	1.07	100
Oceanic crust	.81	1.35	37
Continental crust	.53	.88	63
Shields	.55	.92	44
Fold belts	.50	.83	19

Basic and intermediate igneous rocks generally contain more TiO_2 than ultramafic or acidic igneous rocks; for most rock types, alkalic varieties are richer in TiO_2 than the nonalkalic varieties. Variations are subtle, however, and departures of an order of magnitude from average crustal abundance are remarkable (table 2).

Economic concentrations of titanium occur in the igneous rocks anorthosite, norite, and nepheline syenite, although the average TiO_2 content of all three rocks is lower than the average crustal abundance (table 2). Apparently, the average TiO_2 content of the rock and the formation of local concentrations of valuable titanium minerals are quite separate in igneous rocks. Because of the local prominence of titanium minerals in Precambrian gabbro and anorthosite, however, Rose (1969, p. 41) thought that these rocks contain most of the titanium in the crust; the foregoing analyses show this is not the case.

SEDIMENTARY ROCKS

According to Goldschmidt (1954) and Vinogradov (1962), sedimentary rocks contain an average of 0.75 percent TiO_2; this is slightly lower than the average abundance in continental crust (table 1). Considerable variation is found among the average percentages of TiO_2 in different sedimentary rocks (table 3). Shales have the highest average TiO_2 content and limestones the lowest. Of the sandstones, those of low textural and (or) mineralogic maturity have the highest average values; placer concentrations of heavy minerals, however, are normally mature and have a high TiO_2 content.

TABLE 2.—*Average* TiO_2 *content (in weight percent) of some igneous rocks*

Rock type	Nockolds' (1954) value		Beus' (1971) value recalculated	
	TiO_2	Number analyzed	TiO_2	Number analyzed
Ultramafic rocks:				
Dunite	0.20	9	0.07	118
Peridotite	.81	23	.53	196
Alkali peridotite	1.30	12	---	---
Pyroxenite	.53	46	.83	294
Alkali pyroxenite	3.31	21	---	---
Hornblendite	2.86	15	---	---
Kimberlite	1.43	14	2.17	4.21
Basic rocks:				
Tholeiitic basalt	2.03	137	---	---
Olivine tholeiite	1.65	28	---	---
Normal alkali basalt	2.63	96	---	---
Continental basalt	---	---	1.50	445
Geosyncline basalt	---	---	1.67	360
Oceanic basalt	---	---	2.67	148
Gabbro	1.32	160	1.13	762
Norite	.89	39	---	---
Alkali gabbro	2.86	42	---	---
Anorthosite	.32	17	---	---
Intermediate rocks:				
Diorite	1.50	50	1.00	678
Andesite	1.31	49	.83	866
Tholeiitic andesite	2.60	26	---	---
Alkali andesite	2.84	37	---	---
Acidic rocks:				
Tonalite	.62	58	.77	426
Dacite	.64	50	.57	480
Granodiorite	.57	137	.62	523
Rhyodacite	.66	115	---	---
Adamellite	.56	121	---	---
Dellenite	.42	58	---	---
Granite	.37	72	.33	1967
Rhyolite	.22	22	.33	138
Alkalic rocks:				
Syenite	.83	18	.68	426
Trachyte	.66	24	.67	292
Monzonite	1.12	46	---	---
Latite	1.18	42	---	---
Nepheline syenite	.66	80	.50	584
Phonolite	.59	47	.40	245

TABLE 4.—*Average* TiO_2 *content (in weight percent) of some metamorphic rocks*

Rock type	TiO_2	Number analyzed	Reference
Amphibolite	1.37	370	Beus (1971).
Gneiss	.58	410	Do.
Schist	.60	538	Do.
Slate	.80	8	Billings and Wilson (1965).
Greenschist	1.64	13	Hutton (1940).
Quartzite	.23	7	Billings and Wilson (1965), Clarke (1924).
Serpentinite	.015	91	Clarke (1924), Abdullayev and Guseynova (1970).
Glaucophane schist	.78	5	Clarke (1924).
Eclogite	1.27	16	Beus (1971).

METAMORPHIC ROCKS

The range of TiO_2 content of metamorphic rocks appears to reflect the diversity of parent rocks. The data are much less complete for metamorphic rocks (table 4) than for parent materials (tables 2 and 3); a better compilation would be useful when the possible mobility of titanium during metamorphism is considered. Engel and Engel (1958, 1962a) have demonstrated slight decreases in the titanium content of paragneiss and amphibolite with increasing metamorphism.

DISTRIBUTION OF TITANIUM AMONG MINERALS

OXIDES

The polymorphs of TiO_2—rutile, anatase, and brookite—are all fairly common in nature. Rutile is the stable phase (Schuiling and Vink, 1967; Jamieson and Olinger, 1969), this fact helping to explain the presence of rutile in such diverse geologic environments as alteration products (leucoxene) formed at surface temperatures and pressures, various metamorphic rocks, and igneous rocks.

Ilmenite ($FeTiO_3$) is a common accessory mineral in a wide variety of rocks. Analyses of natural ilmen-

TABLE 3.—*Average* TiO_2 *content (in weight percent) of some sedimentary rocks*

Rock type	Pettijohn's (1963) value		Turekian and Wedepohl's (1961) value	Beus' (1971) value recalculated	
	TiO_2	Number analyzed	TiO_2	TiO_2	Number analyzed
Sandstone:	0.25	253	0.25	0.52	211
Orthoquartzite	.2	26	---	---	---
Lithic arenite	.3	20	---	---	---
Graywacke	.6	61	---	---	---
Arkose	.3	32	---	---	---
Siltstone	.59	235	---	---	---
Shale	.65	78	.77	.63	252
Limestone	---	---	.07	.20	364

ites fall on both sides of the theoretical TiO_2 content of 52.5 percent (see Mackey, 1972); variations are due, among other things, to the presence of intergrowths with hematite and magnetite and to solid solution with hematite (low values) or leaching of iron during alteration (high values). Material called ilmenite in the literature on beach-sand mining can contain more than 60 percent TiO_2 as a result of enrichment during weathering and transport. Much of this material actually consists of alteration products pseudomorphous after ilmenite (see Markewicz, 1969; Garnar, 1972).

Leucoxene is a loose term for the end products of this alteration of ilmenite. The titanium is contained in fine-grained aggregates of rutile, brookite, anatase, hematite, and (or) sphene (Bailey and others, 1956; Baker, 1962; Temple, 1966). Leucoxene can form by hydrothermal alteration as well as by weathering (Ross, 1941).

Another oxide of titanium, perovskite ($CaTiO_3$), is a rock-forming mineral in some alkalic rocks and has economic importance. Normally, it has less TiO_2 than its theoretical content of 59 percent because of the presence of rare earths and niobium.

SILICATES

Although many rock-forming silicate minerals contain TiO_2, those most important to the geochemistry of titanium are sphene, biotite, hornblende, and titanaugite.

Sphene ($CaTiSiO_5$) ideally has 41 percent TiO_2 but may contain less (Leonova and Klassova, 1964). It is a common accessory mineral in a large number of igneous and metamorphic rocks.

Biotite and hornblende contain relatively small amounts of titanium, but, because they are usually much more abundant than titanium-rich accessory minerals, they are important carriers of titanium. In common igneous rocks of calc-alkalic compositions, biotite has as much as 5.9 percent TiO_2, and hornblende as much as 2.7 percent TiO_2 (Deer and others, 1962b, 1963a; Al'mukhamedov, 1967; Lyakhovich, 1970). In common metamorphic rocks, biotite contains as much as 5 percent TiO_2, and hornblende as much as 3 percent; in both minerals, TiO_2 increases with metamorphic grade (Force, 1976). The concentration of TiO_2 in hornblende and biotite is largely independent of the TiO_2 content of the rock in both igneous and metamorphic rocks.

In many volcanic and (or) alkalic rocks, titanaugite is a characteristic phase and may contain as much as 9 percent TiO_2 (Deer and others, 1963a).

In alkalic igneous rocks, two more unusual minerals may also contain titanium. Melanitic andradite garnet contains as much as 17.1 percent TiO_2 (Deer and others, 1962a), and kaersutitic amphiboles as much as 10.3 percent TiO_2 (Deer and others, 1963a).

The common rock-forming silicates that do not contain much titanium also require comment preparatory to a discussion of the geochemical partitioning of titanium. The work of Deer and others (1962a, b, c, 1963a, b) was used as a source of this information, as were the following references cited. In general, minerals that lack large amounts of titanium include silica minerals, feldspars, and other framework silicates (Rankama and Sahama, 1950), muscovite, chlorite, and serpentine (Kwak, 1968; Ernst and others, 1970; Lyakhovich, 1970; Abdullayev and Guseynova, 1970), common garnets (Howie, 1955; Engel and Engel, 1960), kyanite-group minerals, olivine, and epidote-group minerals. Orthopyroxene and metamorphic clinopyroxene contain little titanium, although metamorphic clinopyroxene consistently contains more than coexisting orthopyroxene (Eskola, 1952; Howie, 1955).

PARTITIONING OF TITANIUM BETWEEN OXIDES AND SILICATES

For any element that occurs in valuable nonsilicate minerals, the amount of the element available to form these valuable minerals depends on the extent to which host rocks used the element in silicates (Sullivan, 1948). This is applicable to titanium, since all presently mined titanium minerals are oxides. A study of the partitioning of titanium is thus of potential significance to economic geologists.

Following Ramdohr (1940), authors have traditionally said that oxide minerals contain most of the titanium in rocks (cf. Rankama and Sahama, 1950; Rose, 1969). It will be shown in this section that such a situation is a special, though interesting, case.

Several treatises cover the partitioning of titanium between oxides and silicates in a general way. Ramberg (1948, 1952, p. 72–75, 156–161) approaches the subject from the viewpoint of thermal stability of titanium-bearing silicates (as does Force (1976)). Verhoogen (1962) discussed the effect of oxidation on the partitioning. Shcherbina (1971) mentioned the effect of high Mg/Fe ratio in limiting the stability of ilmenite and of high alumina (Al_2O_3) in limiting the stability of sphene and clinopyroxene relative to plagioclase and orthopyroxene. Others have noted that magmatic rocks having a high ratio of orthopyroxene to clinopyroxene are richer in il-

TABLE 5.—*Partitioning of titanium among minerals of igneous rocks*

Rock type (weight percent in parentheses)	Reference	Mineral	TiO_2 in mineral (weight percent)	Mineral in rock (weight percent)	Percent rock TiO_2 in each mineral
1. Olivine pyroxenite (0.085).	Abdullayev and Guseynova (1970).	Diopside	0.134	47.4	74.0
		Enstatite	.073	22.2	20.0
		Olivine	.00	16.3	.0
		Serpentine	.017	11.0	2.4
		Magnetite	.080	3.1	2.4
2. Olivine pyroxenite (0.073).	do	Diopside	.105	42.8	61.6
		Enstatite	.070	32.3	30.1
		Olivine	.00	12.5	.0
		Serpentine	.027	10.9	4.1
		Magnetite	.087	1.5	1.4
3. Peridotite (0.048)	do	Diopside	.102	22.0	47.9
		Enstatite	.080	13.3	22.9
		Olivine	.00	44.4	.0
		Serpentine	.060	18.3	22.9
		Magnetite	.108	2.3	4.2
4. Olivine norite (0.79)	Wager and Mitchell (1951, p. 142).	Hypersthene	.93	28.5	25
		Olivine	----	21.5	----
		Plagioclase	----	48.0	----
5. Picritic diabase (0.59)	Al'mukhamedov (1967).	Pyroxene	.50	23.38	20.34
		Olivine	.07	41.37	5.09
		Biotite	5.86	3.12	30.53
		Plagioclase	.23	19.83	8.47
		Magnetite	3.72	3.86	23.72
		Ilmenite	52.6	.13	11.85
6. Diabase (1.32)	do	Clinopyroxene	.79	36.36	21.96
		Olivine	.19	7.85	.76
		Plagioclase	.13	48.71	4.54
		Magnetite	18.88	1.43	20.54
		Ilmenite	49.56	1.26	47.03
7. Biotite pyroxene-calcite carbonatite.	Samoylov and Razvozzhayeva (1972).	Pyroxene	.64–1.29	----	13–58
		Biotite	1.89–3.49	----	39–72
8. Amphibole-pyroxene-calcite carbonatite.	do	Pyroxene	.64–1.29	----	90
		Amphibole	.62–3.34	----	5–8
9. Ijolitic carbonatite	do	Sphene	----	----	54–90
10. Nepheline syenite	Popolitov, Kovalenko, and Znamensky (1966).	Pyroxene and amphibole	----	----	11–19
		Biotite	----	----	32–42
		Titanomagnetite and ilmenite	----	----	29–41
11. Syenite	do	Pyroxene and amphibole	----	----	16–25
		Biotite	----	----	15–19
		Titanomagnetite and ilmenite	----	----	53–57
12. Syenite (0.57)	Leonova and Klassova (1964).	Biotite	3.45	3.0	18.2
		Pyriboles	.78	13.0	17.8
		Magnetite	4.64	4.5	36.6
13. Granite	Znamensky (1957).	"Silicates"	----	----	69–77
14. Granite (0.20)	Leonova and Klassova (1964).	Biotite	2.06	3.9	40.2
		Sphene	22.42	.3	33.6
		Magnetite	.8	.7	3.0
15. Granite (0.14)	do	Biotite	4.2	2.7	80.7
		Sphene	17.8	.14	17.8
		Magnetite	1.2	.3	2.5

menite (Goldschmidt, 1954, p. 413; Deer and others, 1962c, p. 31).

Relatively few sources, however, give precise figures for the partitioning of titanium because precise figures require chemical and modal analyses of a rock as well as chemical analyses of all titanium-bearing phases in the rock. Such data have seldom been acquired.

Table 5 shows some published information for the partitioning of titanium in igneous rocks. The type of data varies considerably and consists of unsupported statements (No. 13), summaries of partitioning studies of rock suites (Nos. 7–11), and partitioning analyses of individual rocks (the others). Not all rocks listed are common.

Table 6 shows the partitioning of titanium among minerals of some high-grade quartzofeldspathic paragneisses of simple mineralogy. Information is selected from Engel and Engel (1958, 1960); the calculations are mine. Titanium oxide not present in the silicate phases probably is in ilmenite (rutile is not present). Table 6 also shows TiO_2 present in hornblende of associated amphibolites (Engel and Engel, 1962a, b); again, the remainder must be in ilmenite.

Table 7 shows the partitioning of titanium in a suite of high-grade gneisses of simple mineralogy from the North Carolina Blue Ridge. Titanium is present virtually only in rutile and biotite in these rocks; this situation is unusual but allows an easy calculation of partitioning without mineral analyses.

Partitioning for some other metamorphic rocks is shown in table 8. For those rock types that are unusual even in the terranes in which they occur (tectonic inclusions and eclogites), representative analyses were selected from those available. The figures

TABLE 6.—*Partitioning of titanium among minerals of high-grade metamorphic rocks from northwestern Adirondacks, New York, calculated from Engel and Engel (1958, 1960, 1962a, b)*

QUARTZOFELDSPATHIC PARAGNEISS

Rock number	TiO_2 (weight percent)	Percent of rock TiO_2 present in mineral (remainder presumably in ilmenite)		
		Biotite	Garnet	Sphene
		Emeryville and West Balmat groups (amphibolite facies)		
Qb 228	0.87	79	0	Absent
Qb 235 M	.67	81	Absent	Do.
Qb 230	.65	83	0	Do.
Qb 231	.66	82	Absent	Do.
Qb 236	.81	86	do	Do.
Qb 3	.62	95	do	Do.
Bgn 27	.70	94	do	Do.
		Russell and Pierrepont groups (intermediate)		
Bgn 14	1.02	89	0	Absent
Bgn 4	.56	82	0	Do.
Bgn 9	.51	77	0	Do.
Bgn 6	.68	88	0	Do.
Bgn 25	.76	98	0	3
		Colton group (granulite facies)		
Bgn 20	0.67	74	0	Absent
Bgn 19	.57	62	1	Do.
Bgn 21	.52	74	1	Do.

AMPHIBOLITE

Rock number	TiO_2 (weight percent)	TiO_2 content of hornblende (weight percent)	Hornblende in rock (weight percent)	Percent rock TiO_2 in hornblende (remainder presumably in ilmenite)
		Emeryville group (amphibolite facies)		
A3	1.20	1.37	73	85
AE317	1.17	1.32	66	75
AE415	2.48	1.32	77	41
AE334	2.11	1.19	76	43
AE337	2.07	1.45	75	53
AE326	2.13	1.27	71	42
AE338	2.04	1.30	68	43
		Colton group (granulite facies)		
A10	1.40	2.49	31	56
A67	.99	2.26	12	28
A104	1.60	2.24	23	32
A105	1.56	2.26	21	31
AC342	1.71	2.61	41	64
AC358	1.74	2.49	58	83
AC348	1.78	2.30	26	34
AC341	1.55	2.71	44	72
AC362	1.74	2.42	24	34

TABLE 7.—*Partitioning of titanium between rutile and biotite in some quartz-garnet-feldspar-biotite-sillimanite-cummingtonite-pyroxene-graphite gneisses from Mason Mountain, Macon County, N.C.*

[Mineral percentage established by 2,000-point counts corrected for specific gravity; rapid-rock analyses by U.S. Geological Survey, samples provided by F. G. Lesure]

Number	TiO_2 (weight percent)	Biotite in rock (weight percent)	Rutile in rock (weight percent)	Percent rock TiO_2 in rutile (remainder mostly biotite)
MM 1	0.84	3.3	0.36	43
MM 4	1.6	18.5	.72	45
MM 8	.96	3.6	.94	98
MM 11	1.0	absent	1.05	100
MM 14	.78	do.	.72	92(?)
MM 17	.73	30.1	.43	59

are inexact; the analyses are not sufficiently accurate for this purpose, and I attempted to correct the modal analyses for specific gravity. As is the situation for igneous rocks, information on most common types of metamorphic rocks cannot be found. Available analyses necessarily are heavily biased toward higher grade assemblages having grains coarse enough to be easily counted.

On the basis of tables 5–8, it can be said that, in general, silicates contain much of the titanium in most rocks. Silicates contain more than 90 percent of the TiO_2 in the ultrabasic rocks listed, about half the TiO_2 in basic volcanics, almost all the TiO_2 in carbonatites, and more than 60 percent of the TiO_2

TABLE 8.—*Partitioning of titanium among minerals of some other metamorphic rocks*

Rock type and number (weight percent TiO_2 in parentheses)	Mineral	TiO_2 in mineral (weight percent)	Mineral in rock (weight percent)	Percent rock TiO_2 in each mineral
Tectonic blocks from California serpentinites (Ernst and others, 1969, 1970)				
Glaucophane schist 50CZ60 (2.17)	Glaucophane	0.22	17	2
	White mica	.27	15	2
	Chlorite	.09	7	0
	Actinolite	.11	21	1
	Garnet	.25	13	1
	Epidote	---	20	--
	Sphene	---	8	Remainder?
	Rutile	---	0.1	
Amphibolite 189B (1.26)	Hornblende	1.07	99	83
	Sphene	---	1	Remainder?
Garnet amphibolite CAT 4 (2.41)	Hornblende	.90	40	15
	Garnet	.34	50	6
	Rutile	---	1	Remainder?
Mafic quartzo-feldspathic schist, oligoclase zone (Mason, 1962)				
Callery-Waiho R. (1.72)	Quartz	---	14	--
	Plagioclase	---	34	--
	Hornblende	1.03	2	1
	Biotite	1.70	22	22
	Almandine	.57	25	8
	Opaque	---	5	Remainder?
Madras charnockites (Howie, 1955; Howie and Subramaniam, 1957)				
Garnet enderbite Ch113 (0.99)	Quartz	---	20	--
	K-feldspar	---	14	--
	Plagioclase	---	32	--
	Garnet	.03	14	0
	Hypersthene	.30	13	4
	Biotite	---	1	0 (probably)
	"Ores"	---	2	Remainder?
Charnockite 4639 (0.56)	Quartz	---	41.8	--
	K-feldspar	.02	28.5	1
	Plagioclase	---	19.5	--
	Hypersthene	.94	7.9	13
	"Ores"	---	2.2	Remainder?
Charnockite 6436 (0.40)	Quartz	---	34.6	--
	K-feldspar	.02	26.5	1
	Plagioclase	.16	31.8	13
	Hypersthene	1.78	4.8	2
	"Ores"	---	2.1	Remainder?
Garnetiferous leptynite 3708 (0.31)	Quartz	---	50.5	--
	K-feldspar	.0	38.7	0
	Garnet	.07	4.5	1
	"Ores"	---	2.1	Remainder?

TABLE 8.—*Partitioning of titanium among minerals of some other metamorphic rocks*—Continued

Rock type and number (weight percent TiO_2 in parentheses)	Mineral	TiO_2 in mineral (weight percent)	Mineral in rock (weight percent)	Percent rock TiO_2 in each mineral
Madras charnockites (Howie, 1955; Howie and Subramaniam, 1957)—Continued				
Intermediate rock 137 (0.77)	Quartz	---	20.7	--
	K-feldspar	---	33.5	--
	Plagioclase	---	36.6	--
	Hornblende	2.06	1.7	4
	Hypersthene	.15	3.4	1
	"Ores"	---	3.6	Remainder?
Intermediate rock 2270 (1.61)	Quartz	---	6.1	--
	K-feldspar	.0	3.8	0
	Plagioclase	.0	52.9	0
	Hornblende	1.85	1.4	2
	Biotite	4.61	7.9	22
	Hypersthene	.15	5.5	1
	Augite	.24	13.7	2
	Magnetite	1.53	4.8	4
	Ilmenite	43.55	2.8	76?
Dioritic charnockite 4642a (1.12)	Plagioclase	.0	45.0	0
	Hornblende	1.72	0.9	0
	Hypersthene	.11	25.2	2
	Augite	.30	24.8	7
	Ilmenite	48.90	2	85
	Magnetite	6.38	2	10
"Norite" 2941 (1.18)	Plagioclase	.05	37.8	2
	Hornblende	.50	9.3	4
	Hypersthene	.65	30.0	16
	Augite	.70	19.4	12
	"Ores"	---	3.2	Remainder?
"Pyroxenite" 3709 (1.32)	Hornblende	1.48	8.7	10
	Hypersthene	.10	56.4	4
	Augite	.68	25.4	13
	Hercynite	1.42	4.2	5
	"Ores"	---	5.1	Remainder?
Other charnockites (Howie, 1958, 1965)				
Mafic charnockite, Sudan 7286 (1.04)	Hornblende	2.10	20	40
	Augite	.38	17	6
	Ferrohypersthene	.18	15	3
Hypersthene diorite, Uganda S347 (1.52)	Hypersthene	---	---	1
	Augite	---	---	3
	Hornblende	---	---	15
	Almandine	---	---	1
	Plagioclase	---	---	0
	Orthoclase	---	---	0
	Magnetite	---	---	1
	Ilmenite	---	---	68
	Biotite	---	---	14
	Quartz	---	---	0
Eclogite (Coleman and others, 1965; Ernst and others, 1969, 1970)				
B102A (0.98)	Garnet	0.26	61	16
	Clinopyroxene	.79	13	10
	Hornblende	.87	18	15
	Rutile	---	1	Remainder?
36NC62 (2.1)	Omphacite	.18	34	3
	Garnet	.54	29	7
	Glaucophane	.31	18	3
	Sphene	---	1.5	Remainder?
	Rutile	---	2.0	
102RGC58 (1.5)	Omphacite	.15	67	7
	Garnet	.38	16	4
	Chlorite	---	10	--
	Sphene	---	2.5	Remainder?
	Rutile	---	.5	

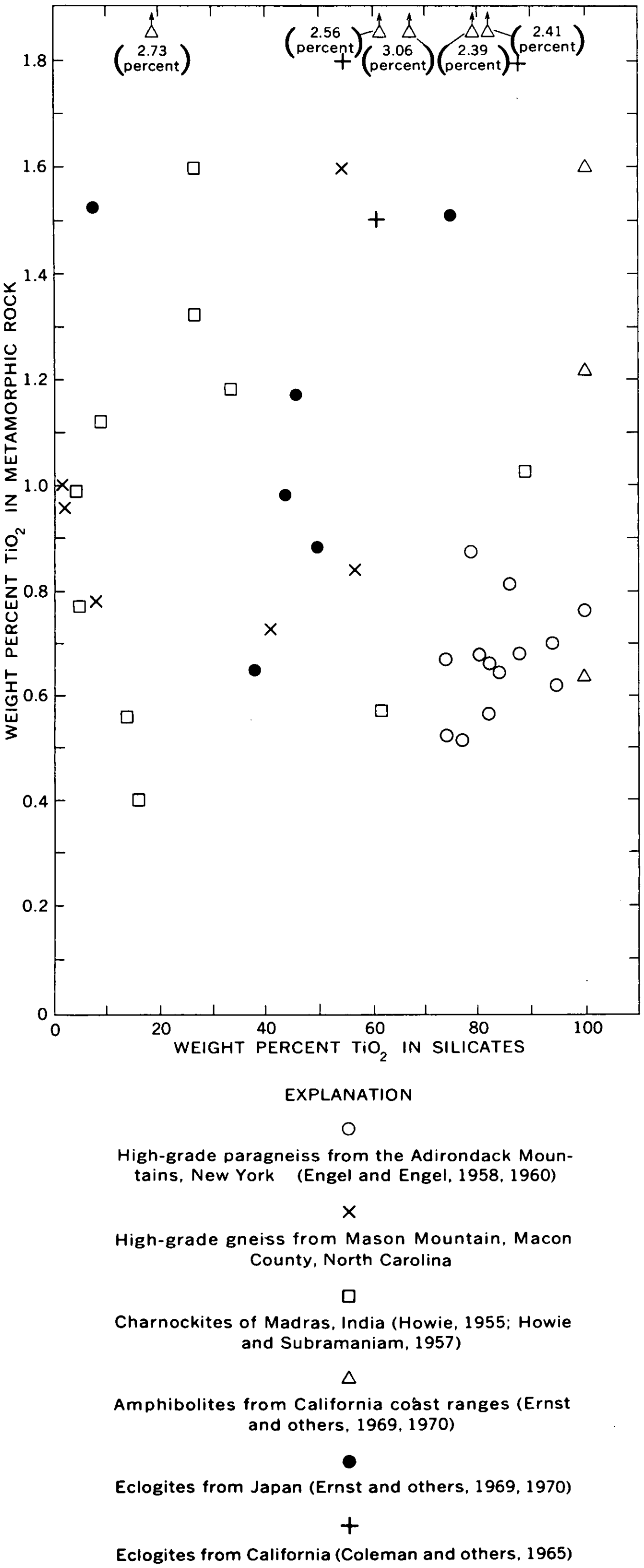

FIGURE 1.—Variation diagram of TiO_2 content and its partitioning in some metamorphic rocks.

in felsic intrusive rocks. In metamorphic rocks, the partitioning varies rather widely; this variation will be discussed by Force (1976).

Figure 1 shows that, for some metamorphic rock suites, the partitioning is quite independent of the TiO_2 content of the rocks involved (some suites partly listed in table 8 are fully represented in fig. 1). The diagram as a whole, and the data for each suite, shows a scattering of points. For two rocks having a given TiO_2 content (and, in fact, most rock types do have TiO_2 contents within the same order of magnitude), the mineralogy of the titanium can be strikingly different. The processes that control the mineralogy are most worthy of attention.

Ore deposits of titanium are all examples of an extreme of partitioning in which the titanium occurs in oxide form. Although some titanium ores are enriched in titanium far beyond the average crustal abundance, others are not, as is shown in table 9. In fact, the rutile sands of eastern Australia now being mined have TiO_2 values well under the average crustal abundance! The value of these low TiO_2 ores is in their mineralogy and ease of beneficiation.

It is misleading to assume that the TiO_2 content of potential titanium resources is an indicator of their value. For example, Thomas and Berryhill (1962) reported high TiO_2 values in Alaskan beach sands; probably very little titanium of economic value is present because the high TiO_2 values occur in nonmagnetic fractions of the sand in which sphene, augite, and hornblende are reported as prominent components and titanium-bearing oxides are sparse or absent. Therefore, it would be wasted effort to prospect here by chemical analysis for TiO_2.

TABLE 9.—*Economic cutoff grades for some titanium ores in the United States*

Location	Host rock	Ore mineral	TiO_2 cutoff grade (percent)
Sanford Lake (Tahawus), N.Y.[1]	Ilmenite rock in anorthosite and norite	Ilmenite and ilmenite-magnetite intergrowths	13.5
Lakehurst, N. J.[2]	Fossil river (?) sand placer	Altered ilmenite	~1.5
Trail Ridge, Fla.[3]	Fossil beach sand placer	Altered ilmenite	~1.5

[1] Gross (1968).
[2] Markewicz (1969).
[3] Pirkle and Yoho (1970).

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Metamorphic Source Rocks of Titanium Placer Deposits— A Geochemical Cycle

By E. R. FORCE

GEOLOGY AND RESOURCES OF TITANIUM

GEOLOGICAL SURVEY PROFESSIONAL PAPER 959-B

U.S. DEPARTMENT OF THE INTERIOR
March 3, 1849

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ABSTRACT

Progressive normal (Barrovian) metamorphism shifts titanium from sphene, biotite, and hornblende in lower metamorphic grade rocks to ilmenite and rutile in rocks of sillimanite and higher metamorphic grade. Ilmenite and rutile, if present in the parent rock, are residually concentrated in its weathered product; when freed, they can form placer concentrates in situations where contamination by other mineral suites is low and when hydraulic energy is great but hydraulic equivalence is not attained.

Many valuable placers are the result of an optimal geochemical cycle of high-grade metamorphism, repeated intense weathering, and short dispersal path. Complicating factors in this model are rock composition and oxygen pressure during metamorphism and intermediate sedimentary hosts during dispersal.

Titanium mineral provinces consist of different weathering and erosion products of the same source terrane. Saprolite and fluvial and beach placer deposits (of any age, if unmetamorphosed) may each form resources in the millions of tons of contained TiO_2.

INTRODUCTION

In this paper, one possible geochemical cycle of titanium is followed from Barrovian metamorphism through weathering into the realm of sedimentation. The purpose is to put the formation of titanium placer deposits into a geologic context that may have predictive value. The cycle starts with the beginning of metamorphism because, although the parent-rock types may vary widely, metamorphism of even the lowest grades usually repartitions the titanium in the rock. Even during slight metamorphism of placer deposits, the mineralogy of titanium is usually reset, an indication that the "cycle" is complete.

LOW-GRADE METAMORPHISM

This section includes discussion of metamorphic grades as high as the kyanite zone, which is substantially higher than common usage of the term "low-grade metamorphism."

The most important carrier of titanium in the lower grade metamorphic rocks is fine-grained sphene; intergrown anatase is also a significant carrier. As prograde reactions produce biotite and hornblende, they become important carriers.

At low metamorphic grades, ilmenite and rutile from precursor rocks are unstable with respect to sphene and anatase, even in rocks rich in TiO_2 such as slightly metamorphosed placer deposits or magmatic segregations of titanium minerals (Harker, 1932, p. 6; Ross, 1941; Goldschmidt, 1954, p. 415; Carroll and others, 1957; Carpenter and others, 1966). In heavy-mineral laminations of sandstone from the Great Smoky Group in the biotite zone of metamorphism, intergrowths of sphene and an unknown opaque mineral form pseudomorphs of titanium oxides.

THE LOWEST GRADES

For those rocks that show zeolite facies and prehnite-pumpellyite facies metamorphism, sphene is present as a metamorphic mineral in many rock types (Coombs and others, 1959, p. 60; Seki, 1961; Turner, 1968, p. 265–266). In some literature (see Hutton, 1940, p. 62; Seki and others, 1971), sphene in these lowest grade rocks is referred to as "leucoxene" because of its occurrence in very fine grained aggregates and dusty coatings.

GREENSCHIST FACIES

Sphene continues as a stable metamorphic phase through the greenschist facies and is present in many rock types (Turner, 1968, p. 271–284). Hutton (1940) described a transition within the chlorite zone; in the low-grade textural subzone, fine-grained "leucoxene" is in skeletal aggregates as pseudomorphs after ilmenite and, together with chlorite, replaces titanaugite, biotite, and matrix. In the higher grade textural subzone, sphene occurs as rounded or spindle-shaped coarse and discrete grains.

Although partitioning of titanium among minerals of low-grade rocks is difficult to study because of the fine grain sizes involved, most of the titanium in rocks of the chlorite zone of the greenschist facies must be in sphene because other minerals that contain titanium are absent, unless relict minerals persist. Anatase may be present as intergrowths with sphene. Magnetite may be present but contains very little titanium in these low-grade rocks (Abdullah and Atherton, 1964). If metamorphism reaches the biotite zone of the greenschist facies, some of the titanium can enter biotite. Brown (1967) showed that chlorite from the chlorite zone averaged 0.1 percent TiO_2, whereas biotite in adjacent rocks of the biotite zone averaged 1.2 percent TiO_2.

LOWER AMPHIBOLITE FACIES

Partitioning of titanium in biotite-bearing rocks of the lower amphibolite facies probably remains unchanged from that of the biotite zone of the greenschist facies. Force (1976a, table 8) shows a partitioning analysis for such a rock; the analysis was calculated from data gathered by Mason (1962). In mafic rocks, hornblende is a carrier of significant amounts of titanium.

RUTILE IN LOWER GRADE METAMORPHIC ROCKS

Rutile can occur in the lower grade rocks—it is common, for example, in slate as an alteration product of clastic biotite (Harker, 1932, p. 46), but it appears to be restricted to pelitic or other aluminous rocks (Hutton, 1940; Zen, 1960; Espenshade and Potter, 1960; Mason, 1962; Albee and others, 1965). In mineral assemblages from which rutile has been described, the CaO content is low, which inhibits the formation of sphene, and (or) the Al_2O_3 content is high (Shcherbina, 1971). In the rutile-bearing rocks investigated by Zen and by Espenshade and Potter, the ratio Al_2O_3:CaO is over 200. In other rocks of lower metamorphic grades, rutile forms by introduction of fluids that cause the breakdown of ilmenite or biotite. The fluids may contain magnesium (Chidester, 1962, p. 69; Southwick, 1968), sulfur (Force, 1976b), or CO_2 (Schuiling and Vink, 1967).

Occurrences of rutile in lower grade terranes may be numerous, but, because they are controlled by local alteration or special rock chemistry, they are not comparable to regional occurrences of rutile in higher grade terranes. Detrital rutile is generally destroyed in the lower grades of metamorphism, except in special circumstances where rutile is stable relative to sphene at a low grade, as it is in an extremely aluminous sediment. Rutile in higher grade rocks is thus generally metamorphic rather than detrital.

HIGHER GRADE METAMORPHISM

Several texts (Rankama and Sahama, 1950, p. 563; Deer and others, 1962b, p. 31; Turner, 1968, p. 325, 329) discuss in a general way the formation at the onset of granulite-facies metamorphism of titanium oxides at the expense of titaniferous silicates. Ramberg (1948, 1952, p. 72–75, 156–161) has covered the topic in more detail than others. Except for Ramberg's (1948) work, discussions of the process in a context of economic geology are few and obscure.

The mechanism for the segregation of titanium into oxides seems clear on a superficial level. The titanium-rich silicates—biotite, hornblende, and sphene—have progressively restricted stability fields at the higher grades of metamorphism and may not be present at all in pyroxene granulites (Howie, 1955; Turner, 1968, p. 329). Silicates that form in their place (hypersthene, diopside, pyrope-almandine garnet, plagioclase, and potash feldspar) contain much smaller amounts of titanium that their precursors; the excess TiO_2 in the rock then forms oxides. Which oxides form is partly a function of oxygen pressure.

TITANIUM OXIDES IN THE SILLIMANITE ZONE

Some authors have said that, in rocks of sillimanite grade, biotite breaks down to sillimanite and other minerals including ilmenite and rutile (Harker, 1932, p. 58; Abdullah and Atherton, 1964; Overstreet and others, 1968, p. 15). This point remains moot, however, because other authors have interpreted the same textural evidence as growth of sillimanite without destruction of biotite (Chinner, 1961; Evans and Guidotti, 1966).

Reports of quartzofeldspathic gneisses and schists containing both sillimanite and rutile are too numerous to list. In many such rocks, sphene becomes unstable with respect to rutile at a slightly higher grade than that at which sillimanite appears but, apparently, before the onset of granulite facies. Figure 1 shows the distribution of rutile in metamorphic rocks in parts of the Blue Ridge and Great Smoky Mountains of North Carolina. Rutile is primarily restricted to the sillimanite zone and is most common in or near sillimanite-orthoclase- or hypersthene-zone rocks. Rutile in the kyanite zone was found only in pelitic rocks; none was found in staurolite and lower zones. The fact that isograds and rutile dis-

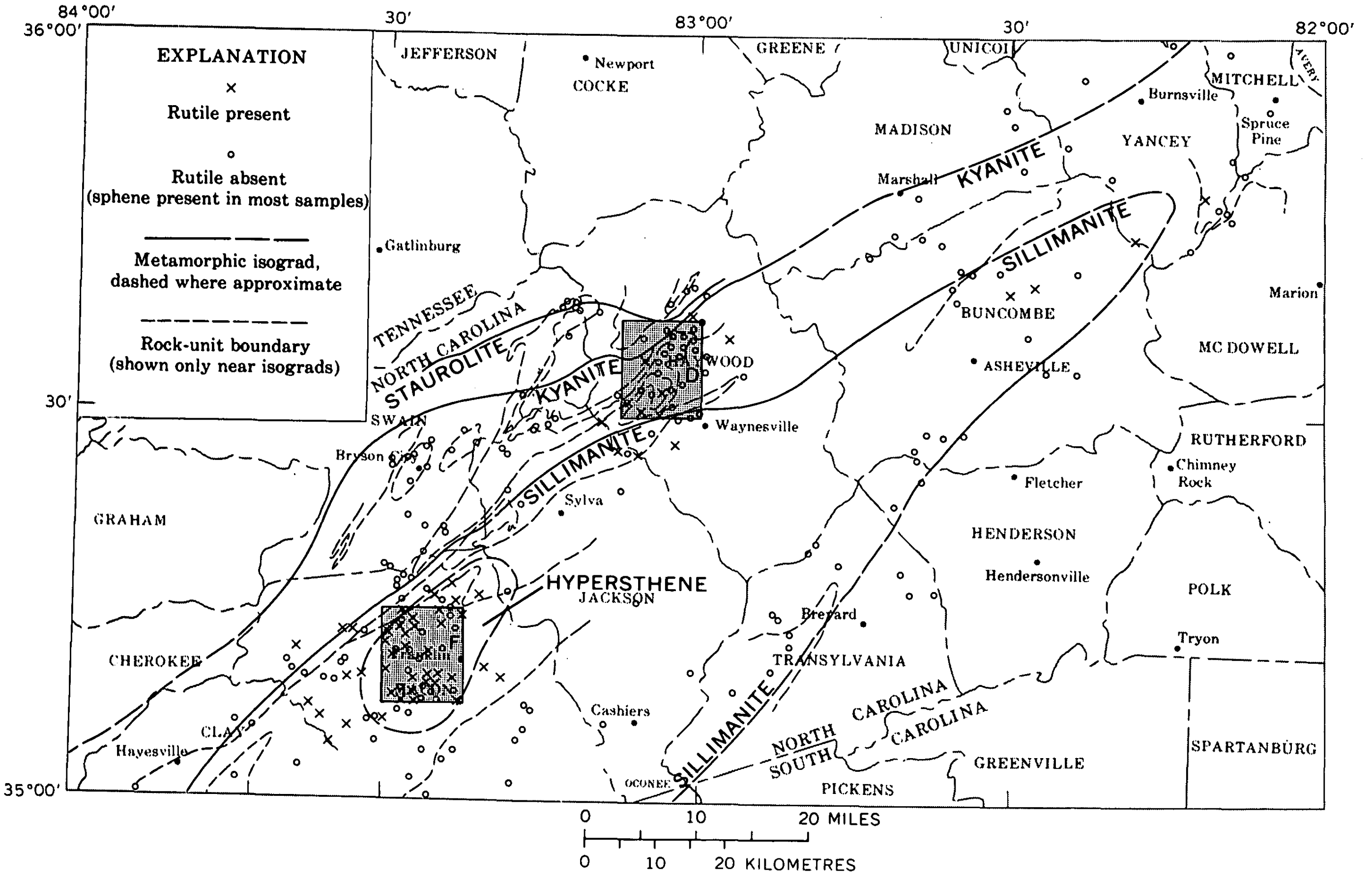

FIGURE 1.—Rutile in the Blue Ridge–Great Smoky part of the Knoxville 2-degree quadrangle (Hadley and Nelson, 1971). All rock-unit boundaries and zoned isograds except hypersthene after Hadley and Nelson. Rutile distribution and hypersthene isograd (boundary of granulite facies) based on study of about 500 thin sections obtained from Richard Goldsmith, F. G. Lesure, J. B. Hadley, and A. E. Nelson (U.S. Geological Survey). Hypersthene is roughly coextensive with sillimanite-orthoclase pairs. Information from Franklin (F) and Dellwood (D) 7½-min quadrangles (shaded areas) is summarized.

tribution together cross numerous lithologic boundaries in the sillimanite zone implies limits to the influence of stratigraphic or compositional control of rutile appearance. In the area shown, many rocks have either sphene or rutile, but rocks having both are rare. A few rocks in zones lower in grade than sillimanite-orthoclase have rutile rimmed by sphene or ilmenite, but sphene probably is not in equilibrium with rutile even in these rocks. Biotite is present in both sphene- and rutile-bearing rocks.

Overstreet and others (1968, pl. 2) also observed that rutile distribution directly correlates with sillimanite distribution from the Piedmont province in North Carolina and South Carolina. Sphene is present in rocks of all grades locally present, but rutile is common only within the sillimanite zone (Overstreet and Griffitts, 1955, p. 561).

TITANIUM OXIDES IN THE GRANULITE FACIES

Rutile and ilmenite are apparently stable phases in metamorphic facies lower than granulite, but they are much more common in granulite-facies rocks. In that facies, the stability fields of the titanium-rich silicates—sphene, hornblende, and biotite—are greatly restricted. Magnetite may also decrease. The disappearance of each mineral will be discussed in turn.

Sphene.—Many authors have mentioned the disappearance of sphene in the granulite facies (cf. Howie, 1955). Cooray (1962) found that rutile takes the place of sphene in leucocratic granulites. The most thorough treatment is given by Ramberg (1952, p. 72–75), who discussed reactions in which rutile and ilmenite form by the breakdown of sphene. In some lime-rich rocks, however, sphene remains a stable phase in the granulite facies (Ramberg, 1952, p. 160; Deer and others, 1962a, p. 75).

Turner (1968, p. 325) has stated that the disappearance of sphene in amphibolites is a useful indication of granulite facies. Engel and Engel (1962a, p. 53–57) found that the disappearance of sphene in amphibolite coincides roughly with the appearance of metamorphic clinopyroxene and precedes the appearance of orthopyroxene. The titanium thus liberated from sphene apparently is incorporated in ilmenite, which shows an increase in average abundance from 2 percent in the lower grade rocks to 3.5 percent in the granulite facies. The difference is attributable to reactions involving hornblende and magnetite as well as sphene.

Hornblende.—By definition, hornblende is stable with orthopyroxene in the hornblende granulite subfacies (lower grade than pyroxene granulite subfacies (Turner, 1968)). Hornblende contains as much as 3.9 percent TiO_2 in granulite-facies rocks (Ramberg, 1948, table 1; Eskola, 1952, p. 133; Howie, 1955, table 6), whereas in lower grade rocks hornblende contains less TiO_2 (Engel and Engel, 1962b; Bushlyakov, 1970). The increase of TiO_2 in hornblende is more than compensated for by the decrease in the amount of hornblende (Force, 1976a, table 6), and the TiO_2 present as hornblende decreases as metamorphic grade increases. In the pyroxene granulite subfacies, the silicates that replace hornblende as stable phases contain little TiO_2, and the TiO_2 from hornblende forms oxides (Force, 1976a, table 8). In mafic rocks, ilmenite is the most common mineral to form, but rutile is present in mafic granulites near Franklin in Macon County, N.C., and presumably elsewhere. In more silicic hypersthene gneisses, rutile is a more common metamorphic mineral (fig. 2*A*).

Biotite.—Biotite is also stable in the lower subfacies of the granulite facies; in quartzofeldspathic gneisses it may be the major mafic mineral (cf. Engel and Engel, 1958). Biotite in granulite-facies rocks has a TiO_2 content as great as 6 percent (Ramberg, 1948, table 2; Kretz, 1959; Engel and Engel, 1960, table 13). Although the titanium content of biotite increases with metamorphic grade (Engel and Engel, 1960; Kwak, 1968; Zakrutkin and Grigorenko, 1968; Bushlyakov, 1970), the total amount of TiO_2 present in biotite (as in hornblende) decreases as the amount of biotite decreases (Force, 1976a, table 6). Garnet, sillimanite, pyroxene, quartz, and feldspar that take the place of biotite are low in TiO_2, and the excess TiO_2 forms oxides (rutile in fig. 2*B*).

Magnetite.—Metamorphic grade is one of the two factors that control the amount of magnetite in a metamorphic rock; the other is oxygen pressure. As metamorphic grade increases, the amount of magnetite decreases and the amount of TiO_2 present in the magnetite increases (Overstreet and Griffitts, 1955, p. 561; Buddington and others, 1963; Abdullah and Atherton, 1964). The overall effect is to decrease the TiO_2 present in magnetite in granulite-

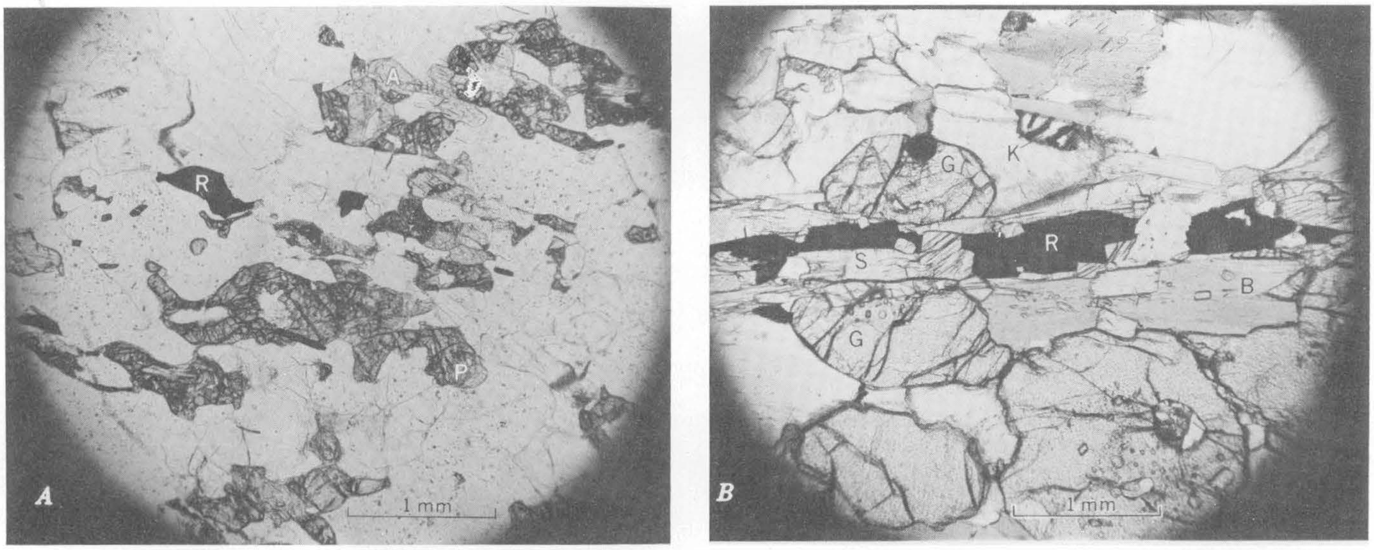

FIGURE 2.—Photomicrographs of rutile in high-grade metamorphic rocks from the Franklin area of Macon County, N.C. *A*, Rutile (R) with pyroxene (P), pale amphibole (A), quartz, and two feldspars in gneiss of intermediate composition. Plane-polarized light, 250×. *B*, Rutile (R) with sillimanite (S), garnet (G), biotite (B), and perthitic potash feldspar (K) in sillimanite gneiss. Plane-polarized light, 250×.

facies rocks (calculations from Buddington and others, 1963, table 2). Under ideal conditions, the progress of reactions reducing magnetite (and increasing ilmenite) might be mapped by using textures on aeromagnetic maps.

High oxygen pressure also has the effect of decreasing the amount of magnetite and increasing the amounts of hematite, ilmenite, rutile, or intergrowths of these minerals (Buddington and others, 1963; Lindsley, 1962).

Sphene, hornblende, and biotite may disappear altogether, and the abundance of magnetite may decrease in rocks of pyroxene granulite subfacies, in which no silicates contain appreciable amounts of TiO_2, and the rock's titanium is mostly in ilmenite and (or) rutile. Where eclogites are associated with granulites (Coleman and others, 1965), the characteristic high rutile content of eclogite makes it an end member along with pyroxene granulite (Goldschmidt, 1954; Turner, 1968; cf. Force, 1976a, table 8).

WEATHERING

The behavior of titanium and titanium-bearing minerals during weathering is not understood in detail. It seems clear, however, that titania as a chemical entity is residually enriched and that grains of rutile and "ilmenite" are residually enriched. Ilmenite begins its alteration to "leucoxene" during weathering.

CHEMICAL BEHAVIOR DURING WEATHERING

The ratio of ionic charge to ionic radius of titanium is such that during weathering it forms insoluble compounds (Mason, 1966, p. 163) that remain in the weathered rock. A classical study by Goldich (1938) showed TiO_2 enriched over granitic gneiss parent rock by a factor of 4 in a residual clay (constant weight calculation). Studies in temperate and tropical zones show residual enrichment of TiO_2 in weathered felsic and mafic rock (Goldich, 1938; Jackson and Sherman, 1953; Wells, 1960; Short, 1961; Dennen and Anderson, 1962; Loughnan, 1969, p. 90, 112; Parker, 1970). In Hawaii, Sherman (1952) observed soils over basalt that contain 25 percent TiO_2, present mostly as concretions; only under extraordinarily reducing conditions is TiO_2 leached from these soils. In bauxites, enrichment of TiO_2 over parent rocks by factors of 2 to 4 is characteristic (Patterson, 1967, table 4; Valeton, 1972, table 32).

The chemical enrichment of titanium during weathering is reflected mineralogically by two processes: (1) Titanium-bearing silicates and titaniferous magnetite alter to clays, iron oxides, and fine-grained dispersed titanium oxides and (2) titanium oxides resist weathering.

WEATHERING OF TITANIFEROUS SILICATES

Titanium-bearing silicates, with the exception of some occurrences of sphene (cf. Overstreet and others, 1963), break down during weathering. Goldschmidt (1954, p. 419–420) recorded that sagenitic rutile is a product of weathering of biotite and that other fine rutile needles are a product of weathering of other silicate minerals. In bauxite, TiO_2 occurs mostly in grains finer than 325 mesh (40μ), which form by weathering of titaniferous silicates (Hartman, 1959, p. 1380). Anatase is the most common alteration product containing titanium in both tropical (Valeton, 1972, p. 32, 186) and temperate soils (McLaughlin, 1955).

WEATHERING OF TITANIUM OXIDES

Ilmenite is a relatively stable mineral in the weathering process (Jackson and Sherman, 1953, p. 232–235; Loughnan, 1969, p. 25). In Liberia, West Africa, rocks that contain both ilmenite and magnetite weather to saprolite that contains ilmenite but not magnetite (cf. White, 1972, p. 86). Gullies cut in saprolite are floored with ilmenite and quartz grains. In Cleveland County, N.C., Overstreet and others (1963) found ilmenite to be a common constituent and magnetite a rare constituent of saprolite over many types of metamorphic rock; Goldich (1938) recorded an enrichment of ilmenite and impoverishment of magnetite in soil over a Minnesota gneiss. Ilmenite is also a residual mineral in high-alumina saprolite over basalt (Roedder, 1956; Hosterman, 1969, p. 35; Patterson, 1971, p. 26). In other bauxites over a variety of parent rocks, ilmenite grains are present, though commonly altered (Hartman, 1959).

"Ilmenite" as mined in placer deposits commonly contains much more TiO_2 than the chemical formula for ilmenite allows and actually consists partly of fine-grained TiO_2 minerals, which form as alteration products (Force, 1976a). Some studies show that in situ weathering of parent rock can produce "ilmenite" that consists partly of fine-grained anatase and rutile alteration products (Hartman, 1959 (bauxite); Carroll and others, 1957, p. 180; Houston and Murphy, 1962, p. 31 (weathered sandstone);

Rumble, 1973 (weathered schist)). Jackson and Sherman (1953, p. 289–290) show that "leucoxene," the TiO_2-rich end product of this alteration process, can form if weathering is intense. Cannon (1950, p. 209) noted that some alteration of ilmenite grains to material richer in TiO_2 takes place during alluvial transport. Leucoxene can also be the result of post-depositional weathering of an unconsolidated placer deposit above the water table (Pirkle and Yoho, 1970).

Rutile is considered by some (summarized by Pettijohn, 1957, p. 502–508) to be among the minerals most resistant to weathering. It is a constituent of saprolite in Cleveland County, N.C. (Overstreet and others, 1963), and Virginia (Fish, 1962). In Macon County, N.C., gullies cut in gneiss saprolite are floored with grains of quartz, garnet, and rutile. Unlike ilmenite grains, rutile grains normally do not form other alteration products; microcrystalline rutile itself is an alteration product formed in the weathering zone, so metamorphic (or igneous) rutile is generally already stable there. Where weathering is intense, rutile high in niobium and iron may be unstable and recrystallize to aggregates of fine anatase.

ECONOMIC SIGNIFICANCE OF WEATHERING

Probably TiO_2 is enriched by all normal weathering processes over all rocks, and the amount of enrichment is proportional to the intensity of weathering. Where the parent rocks contain TiO_2 in potentially useful form—that is, oxides coarser than silt size, as in the high-grade metamorphic rocks previously described—the friable weathering product is enriched in these minerals, which may even be leached of undesirable elements. Saprolite deposits of titanium are potential ores in some areas (Fish, 1962; Herz, 1976), and, because so little attention has been directed toward saprolite, the discovery of more titanium resources in saprolite is likely.

FORMATION OF PLACER DEPOSITS

The formation of placer deposits is a complicated topic approached here only in the context of the geochemical cycle of titanium.

Udden (1914) observed that heavy minerals are finer than the light minerals with which they occur in clastic deposits; Rubey (1933) noted that small heavy minerals and large light minerals have equal settling velocities in water. Since then, most discussions of placer deposits have been approached from the viewpoint of Rittenhouse's (1943) concept of hydraulic equivalence (cf. Baker, 1962; Briggs, 1965, p. 940–941; Tourtelot, 1968). Simply stated, hydraulic equivalence prevails when minerals of the same settling velocity are found together.

More detailed sedimentologic studies, discussed herein, show that, in general, hydraulic equivalence does not prevail in natural deposits and that hydraulic factors other than settling velocity enter in. Certainly, complications are involved in the formation of rich placer concentrates; any single hydraulic mechanism can, at best, explain only the observed size relations of heavy minerals to light minerals but not the concentration of heavy minerals relative to light minerals that characterizes a rich placer. The complications may be hydraulic, such as local erosion or wind ablation, or partially hydraulic, such as natural heavy-media separations or lack of constant relative availability of mineral sizes.

STREAM PLACERS

The first possible site of placer concentration is in upstream deposits near the mineral source. Stream deposits of this type are most important for minerals having specific gravity greater than 7, such as gold and cassiterite (Emery and Noakes, 1968). Locally, they offer possibilities for significant concentrations of the titanium minerals rutile and ilmenite (Herz and others, 1970) and other heavy minerals having specific gravity around 5, such as monazite (Overstreet and others, 1968). Upstream placer deposits are closely tied to particular source rocks, and the small drainage basin limits dilution by barren debris to a minimum. In the small drainage basins, however, hydraulic sorting is generally poor. The volume of placer deposits may be small because of either bedrock stream beds or narrow valleys or both. In Sierra Leone, an exceptional rutile deposit, probably a weathered upstream placer, is of both large volume and high grade (Spencer and Williams, 1967).

Farther downstream, dilution by sediment poor in valuable minerals is more severe (see summary of this and related processes by Pettijohn (1957, p. 556–573)). Hydraulic sorting, however, is commonly more effective downstream than in upstream areas and may locally have produced placer concentrations (cf. McGowen and Groat, 1971). Van Andel (1950) showed that deposition patterns of heavy minerals in rivers are not always in accord with predictions from hydraulic equivalency; sorting by size but not density is prevalent, and concentration of a given mineral occurs because it is supplied to the stream in a size that is locally concentrated

(Briggs, 1965; White and Williams, 1967). Experimental and theoretical work (Grigg and Rathbun, 1969; Brady and Jobson, 1973) has shown that erosional ("reentrainment") processes, which produce residual enrichments of fine-grained particles independent of density, are a factor in producing alluvial concentrations (cf. Hjulström, 1939).

BEACH PLACERS

Most important placer concentrations of ilmenite and rutile are modern or fossil beach deposits. Dunes associated with beach placers may also contain concentrations of titanium minerals. In the beach deposits, titanium minerals are concentrated along with other heavy minerals in lenses of black sand.

Concentrations of heavy minerals can be observed to form in the upper swash zone during storms; differential erosion of larger light-mineral grains leaves behind a residue of heavy minerals (Cannon, 1950, p. 206; Whitworth, 1956; Gillson, 1959, p. 425). Overstreet (1972) stated that a natural jigging action of the sand on the beach by normal wave energy improves the concentrate by subjecting the rising light minerals to erosion. Differential removal of large light grains by wind may also improve the concentrate.

Storm-generated beach concentrates may be dispersed between storms, unless they are deposited beyond normal high tide (Whitworth, 1956). Deposits may be preserved from erosion by wind transport into the dune system beyond the beach (Cannon, 1950, p. 207). Neiheisel (1958) and Gillson (1959, p. 425) noticed that the heavy-mineral fraction of dune sands is poor in the heaviest minerals and that the highest dunes contain the least amount of heavy minerals. Apparently, wind cannot concentrate heavy minerals as efficiently as waves, but it can carry most of a concentrate formed on the beach well above high tide. Where modern beach placers are mined, the deposit is renewed to some extent by storm waves (Whitworth, 1956; Gillson, 1959, p. 428; Overstreet, 1972).

The grain size of a mineral in beach deposits is generally in inverse proportion to its density. Rutile, however, is commonly of finer grain size than its density would predict, probably because rutile is fine grained in original source rocks (Gillson, 1959, p. 423). Some detailed studies have shown that light and heavy minerals are generally not hydraulically equivalent in beach deposits, and the difference has been ascribed to the lack of constant relative availability of minerals of all sizes (McMaster, 1954, p. 197, 211) or to the effects of preferential wave erosion of coarser light grains that stick up out of the bed (McIntyre, 1959, p. 294–296; Hand, 1967, p. 516).

Hand (1967) found that the heaviest minerals departed the most from hydraulic equivalency with the light minerals. Martens (1935) found that the heavy-mineral suites of lean natural concentrates are poor in the heaviest minerals, whereas those of the richest concentrates consist almost entirely of the heaviest minerals. The combination of both lines of evidence suggests that rich concentrates are the result of significant departures from hydraulic equivalence.

PRELITHIFICATION DIAGENESIS OF PLACERS

During early diagenesis of placer deposits, unstable heavy minerals may disappear or become skeletal in shape (Hutton, 1959; Neiheisel, 1962) and thus enrich a placer concentrate in the more stable titanium minerals. Ilmenite may be leached of iron and other elements (Dryden and Dryden, 1946; Temple, 1966) or even complete its alteration to "leucoxene" if it is above the water table (Pirkle and Yoho, 1970), but ilmenite and rutile are resistant to complete destruction by intrastratal solution (Pettijohn, 1957, p. 502–520).

INFLUENCE OF SOURCE ROCK ON PLACER DEPOSITS

The mineralogy of placer deposits is inherited from source rocks, with modifications by the weathering process. Formation of a heavy-mineral concentrate is apparently the result of several hydraulic and some nonhydraulic factors, one of which, the relative abundance of different sizes of each mineral, is largely inherited from source rocks. Although the formation of placer deposits can be studied from a hydrodynamic viewpoint, the influence of source rocks is certainly strong enough to warrant a search for optimal conditions where mineralogy and grain size of the source rock are favorable and dilution by other debris is low.

Formation of placer concentrates of ilmenite and rutile raises the TiO_2 content of the deposit far beyond its average value in sandstone. The converse, however, is not true; anomalous TiO_2 values in heavy-mineral concentrates need not reflect the presence of ilmenite and rutile but may be caused by fine magnetite-ilmenite intergrowths (Talati, 1971), titaniferous magnetite (Wright, 1964), or sphene (Thomas and Berryhill, 1962), all of which locally form heavy-mineral concentrations. In unusually immature deposits, a high TiO_2 content may even reflect the abundance of titanaugite and hornblende (Thomas and Berryhill, 1962).

APPLICATION OF THE SOURCE-ROCK MODEL TO TITANIUM MINERAL PROVINCES

Where processes of metamorphism, weathering, and sedimentation are optimal, provinces of titanium deposits can occur. In these provinces, titanium deposits are likely to be of several types, including saprolites, modern or fossil fluvial placers, and modern or fossil marine placers (table 1). Any type may contain millions of tons of TiO_2, as in saprolite near Roseland, Va.; river deposits at Sherbro, Sierra Leone; modern beach deposits of India; or fossil beach deposits at Trail Ridge, Fla. (values from Klemic and others, 1973). The most valuable deposits may consist of titanium minerals that have passed through many of these stages without substantial dilution, such as, for example, a weathered fossil beach deposit, material for which was derived from weathered older sedimentary rocks, which were, in turn, derived from a deeply weathered acidic granulite-facies terrane. Relations between source rocks and placer deposits can be studied in some detail where intermediate host rocks are not important or where ancient dispersal patterns are known.

WESTERN COAST OF AUSTRALIA

For ilmenite and rutile beach placer deposits on the western coast of Australia, an almost direct connection can be made between placers and source rocks. The rivers drain limited areas along the coast; the interior is poorly drained. Placer deposits are thus near their possible source rocks, and dilution by other debris is low.

Beach placer deposits of ilmenite at Capel and Bunbury (fig. 3) occur in a suite, which also contains zircon, garnet, sillimanite, and pyroxene similar to detritus from the Cape Naturaliste area and gneisses to the east (Carroll, 1939). Granulite-facies metamorphic rocks are common in both areas, and laterite cover is widespread (Lowry and others, 1967; Wilson, 1964, 1969). Nearby Tertiary and Permian sedimentary rocks also have probably contributed debris to the placer deposits but have a relatively impoverished heavy-mineral suite (Carroll, 1939); they could not have been the predominant source.

A recently discovered rutile-ilmenite placer deposit at Eneabba, western Australia (fig. 3), is an immature Tertiary beach deposit formed by the reworking of a fossil alluvial fan (Baxter, 1972). The immediate source rocks for the fan and beach deposit are continental Mesozoic sandstones. The Mesozoic rocks and the placer deposit are lateritized. The ultimate source rocks are gneisses that are locally of granulite facies and predominantly of acidic composition (Wilson, 1964, 1969).

Whitworth (1956) mentioned a beach placer rutile deposit near Albany (fig. 3) that apparently is not being worked. Nearby streams drain small areas in which granulite-facies gneisses are prominent (Wilson, 1964, 1969).

EASTERN COAST OF AUSTRALIA

The beach deposits of rutile on the eastern coast of Australia, at present the world's most important rutile reserve, only very weakly support a case connecting placer to source rock; despite some careful work, the full transportation history of this rutile is not known. Streams draining Permian and Mesozoic sandstones are the immediate source of the rutile (Whitworth, 1956; Connah, 1961), but the mineral assemblage in the placer deposits is unlike that in

TABLE 1.—*Provenance and types of deposits in some* TiO_2 *provinces*

[X, titanium resource; ?, not documented but likely; (2), two sedimentary cycles; P, present; --, not known]

	High-grade metamorphic bedrock	Intensely weathered bedrock	Old sedimentary host rock	Weathered old sedimentary host rock	Modern stream placer	Modern marine placer
Capel and Bunbury, western coast of Australia.	P	P	P	?	?	X
Eneabba, western coast of Australia	P	?	(2), P	X	--	--
Eastern coast of Australia	?	?	P	?	?	X
Southern India and Ceylon	P	P	X	X	?	X
Sherbro, Sierra Leone	P	X, ?	X	X	--	--
Man, Ivory Coast	P	P	--	--	X	--
Roseland, Va.	X	X	X	--	X	--
Franklin, N.C.	P	P	X	P	X	--
Lakehurst, N.J.	P	--	(2), P, X	X	--	--
Trail Ridge, Florida-Georgia	P	P	(2), P, X	X	--	--

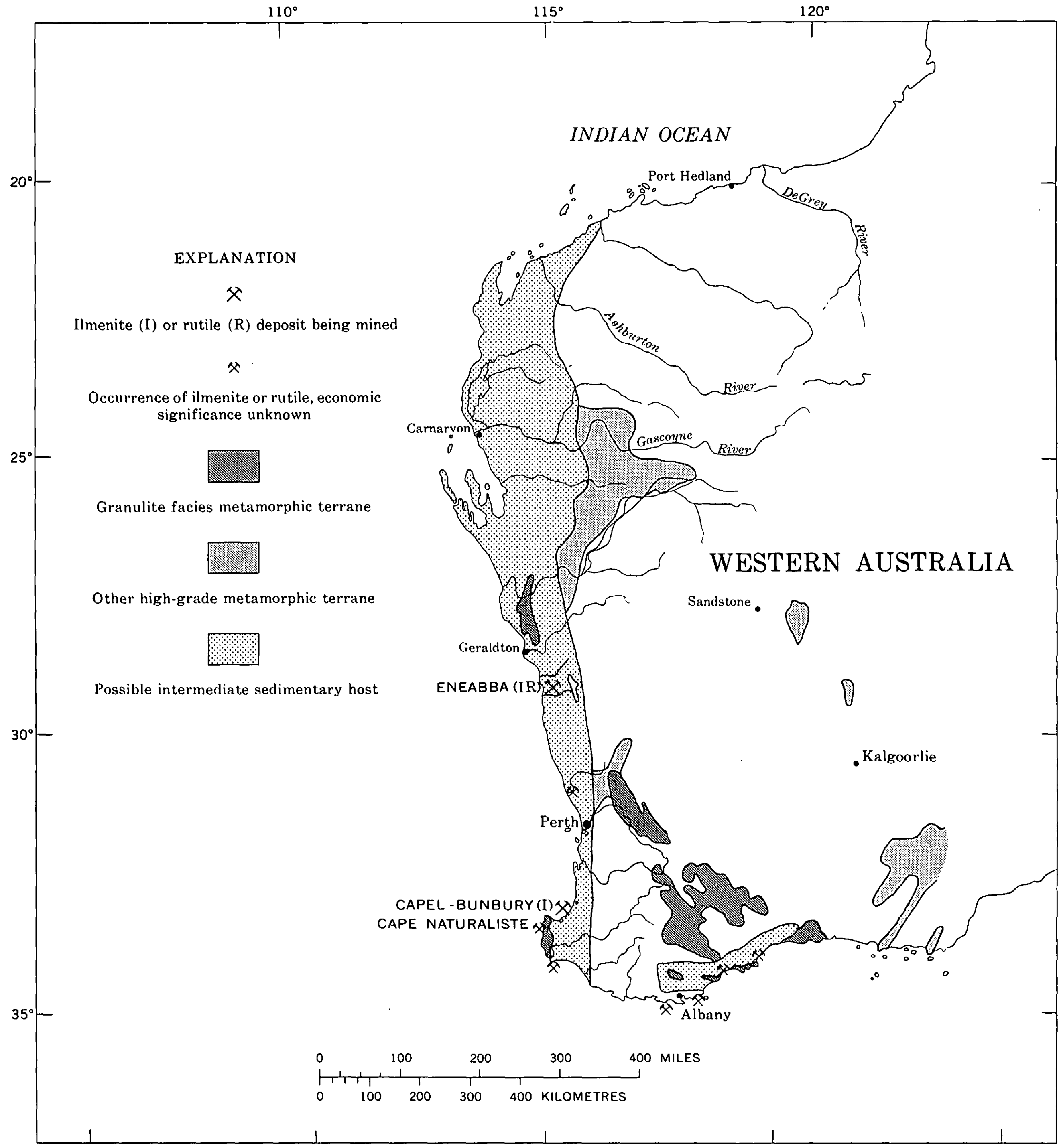

FIGURE 3.—Relationship of beach placer titanium deposits, modern drainage, possible intermediate sedimentary hosts, and granulite-facies metamorphic terrane along the western coast of Australia. Metamorphism is from the *Geologic Map of Western Australia* (Horwitz, 1966) and Wilson (1969). Titanium deposits are from *Regional Divisions and Reported Mineral Occurrences in Western Australia* (Western Australia Department of Mines, 1968) and Baxter (1972).

any local primary rocks (Whitworth, 1956). Overstreet (1967, p. 84–91) found, on the basis of monazite composition, that rocks of higher metamorphic grade than any locally present must have formed the source. Mesozoic drainage patterns (Brown and others, 1968) were such that the assemblage may have been derived from far in the interior where several large areas of granulite-facies rocks are present (Wilson, 1964, 1969). Most of these hypothetical source areas are at present poorly drained, but nearby desert sand contains rutile (Layton, 1966). A better picture of possible source rocks could be given if the distribution of sillimanite-bearing rocks were known, since reactions at sillimanite grade are known in other areas to produce rutile, as reactions at granulite grade do.

SOUTHERN INDIA AND CEYLON

India has long been an important producer of high-TiO_2 ilmenite. Figure 4 shows the locations of the mining operations, all of which are on modern beaches. Rutile and monazite are coproducts; garnet, sillimanite, and hypersthene are also common; magnetite is present but in small amounts (Jacob, 1956).

The deposits are localized by headlands and, in most places, can be linked to specific streams (Jacob, 1956). The immediate sources of the ilmenite are young but weathered coastal plain sands (Jacob, 1956; Gillson, 1959; Overstreet, 1972, p. 48–57) and thick laterite deposits (Gillson, 1959); these have the same heavy-mineral assemblage as the beach placers (Menon, 1966; Rajamanickam, 1968). The ultimate source is deeply weathered crystalline rock of the interior, of which granulite-charnockite terrane forms a prominent part. The most important sources of ilmenite, rutile, and monazite are apparently leptynites (quartz-garnet-feldspar gneisses) and charnockites (Jacob, 1956; Menon, 1966). The distribution of placer deposits matches fairly well the small drainages having headwaters in granulite terrane (fig. 4); the fit in sillimanite-bearing rocks might be better.

Relatively modern geomorphic evolution of the drainage has been important in controlling precise deposit locations in India (Gillson, 1959, fig. 2, p. 429). Unknown geomorphic changes are likely to have had great effect on the dispersal of titanium minerals into older intermediate sedimentary host rocks. Fine tuning of relations between source rocks and placers is probably not worthwhile.

It might be thought that ilmenitic placers could be derived from the Deccan traps, but heavy-mineral concentrates on the coast near the traps consist partly of titaniferous magnetite and titanaugite (Talati, 1971). The previously discussed placers mined in southern India are deficient in these two minerals (Jacob, 1956).

Placer deposits of ilmenite, rutile, and monazite are also important in Ceylon. The major deposit is at Pulmoddai, on the eastern coast. Metamorphic rocks of the pyroxene granulite facies are so prevalent in Ceylon that relating them to the location of placer deposits becomes trivial. Cooray (1962, table 1, p. 263) found that leptynites and khondalites common within the granulite facies contain rutile, whereas other gneisses at lower grades contain sphene. Overstreet (1972) stated that the location of modern placers is controlled to a significant degree by an intermediate Pleistocene host, which is itself an important ilmenite resource.

WESTERN AFRICA

The literature on western African metamorphic belts and titanium deposits is insufficient to make a definitive association between them. Some information from Sierra Leone and the Ivory Coast is suggestive.

Sherbro, in Sierra Leone, is a large rutile deposit, probably formed as an alluvial placer in a small drainage area. Some saprolite may be present in the deposit also. The deposit itself has been lateritized. Besides rutile, the sands contain zircon, ilmenite, monazite, sillimanite, and kyanite (Spencer and Williams, 1967). Local source rocks are the Kasila belt of gneisses in the granulite facies (Andrews-Jones, 1966, p. 22–23). Rutile in alluvial concentrates is closely associated with granulite terrane throughout the belt (Junner, 1929).

In the Ivory Coast, alluvial placer deposits of rutile near Danane are found in a restricted drainage and are reportedly derived from rutile-bearing leptynites (Bagarre, 1964). In the whole district, the occurrence of alluvial rutile is closely associated with the granulite-charnockite province of Man.

EASTERN AFRICA

Bloomfield (1958) noted that, in the granulite-facies terrane (Morel, 1961) of Malawi, rutile occurs in biotite-free varieties of acidic garnet-pyroxene gneiss and in associated migmatite and garnet pegmatite. Colluvium of the adjacent Shire River plain contains rutile, ilmenite, and garnet; resource information has apparently not been published.

EASTERN UNITED STATES

Deposits of ilmenite in the coastal plains of New Jersey and Florida-Georgia are the most important placer deposits of titanium minerals in the United States. Alluvial deposits, probably of less impor-

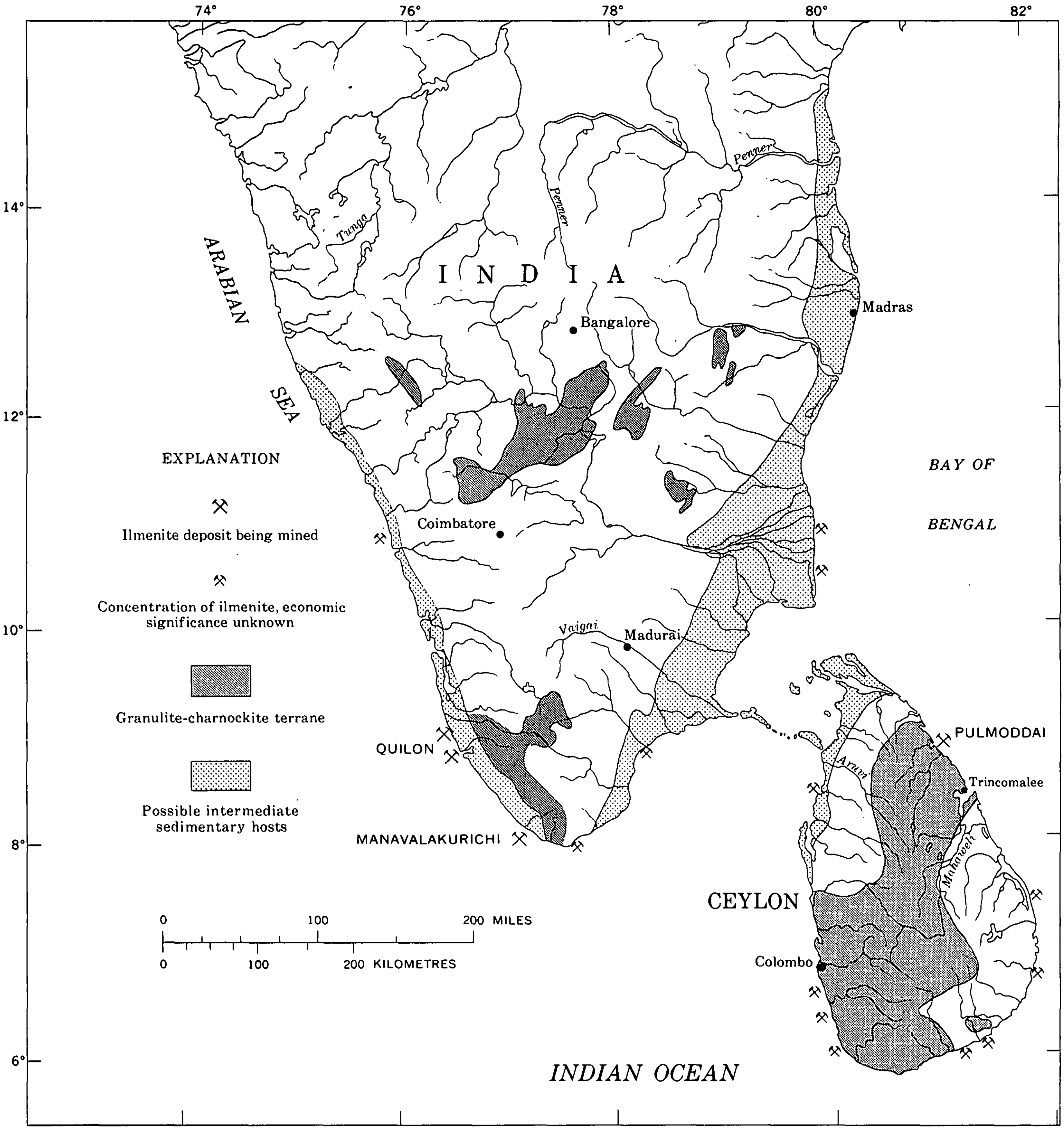

FIGURE 4.—Relationship of beach placer titanium deposits, modern drainage, possible intermediate sedimentary hosts, and granulite-facies metamorphic terrane in southern India and Ceylon. Metamorphism and sedimentary rocks are from the India Geological Survey (1963), Narayanaswami and Mahadevan (1964), and Cooray (1968). Titanium deposits are from Jacob (1956) and the U.N. Economic Commission for Asia and the Far East (1963).

tance, in the Blue Ridge province will be discussed first, however, since the association between deposits and source rocks is simpler.

In the Blue Ridge province near Roseland, Va., a Precambrian alkalic anorthosite body is intruded into gneisses that locally are in the granulite facies

(Herz, 1968). Anorthosite and adjacent gneiss contain rutile; anorthosite, dike rocks, and gneiss contain ilmenite. This area was formerly an important titanium mining district (Ross, 1941). Much of the titanium resource of the area is in saprolite over anorthosite, dike rocks, and gneiss (Fish, 1962). A Cambrian sandstone nearby contains a fossil placer of ilmenite and subordinate rutile (Bloomer and de Witt, 1941). Modern placer deposits of ilmenite and rutile are forming in streams draining anorthosite and gneiss (Herz and others, 1970). Ilmenite placers are also forming in streams draining gneiss alone.

Near Franklin, in Macon County, N.C., also in the Blue Ridge province, some gneisses of upper amphibolite facies (sillimanite grade) and most gneisses of granulite facies contain rutile (fig. 1). Saprolite over these gneisses is residually enriched in rutile and ilmenite, and alluvium from natural washing of saprolite in small gullies consists primarily of quartz, garnet, rutile, and ilmenite. Larger streams draining the area carry the heavy minerals garnet, ilmenite, kyanite-sillimanite, zircon, and monazite in average order of abundance. Five short channel samples of sandy alluvium from the Little Tennessee River and six samples from the river's larger tributaries in this area average about 0.25 percent rutile and about 1.0 percent ilmenite. Large-volume deposits of this material have not been discovered; placer and residual accumulations of rutile have been mined at nearby Shooting Creek. Precambrian (?) sandstones to the north and east locally contain detrital concentrations of titanium minerals (Carpenter and others, 1966), pseudomorphous after rutile and ilmenite.

"Ilmenite" deposits in young coastal plain formations near Lakehurst, N.J., were discovered by Markewicz (1969), who used a source-rock and dispersal-path model. A major hypothetical source rock is gneiss, much of it in granulite facies, of the New Jersey highlands, and the hypothetical dispersal path is an ancestral Delaware River. The deposition-

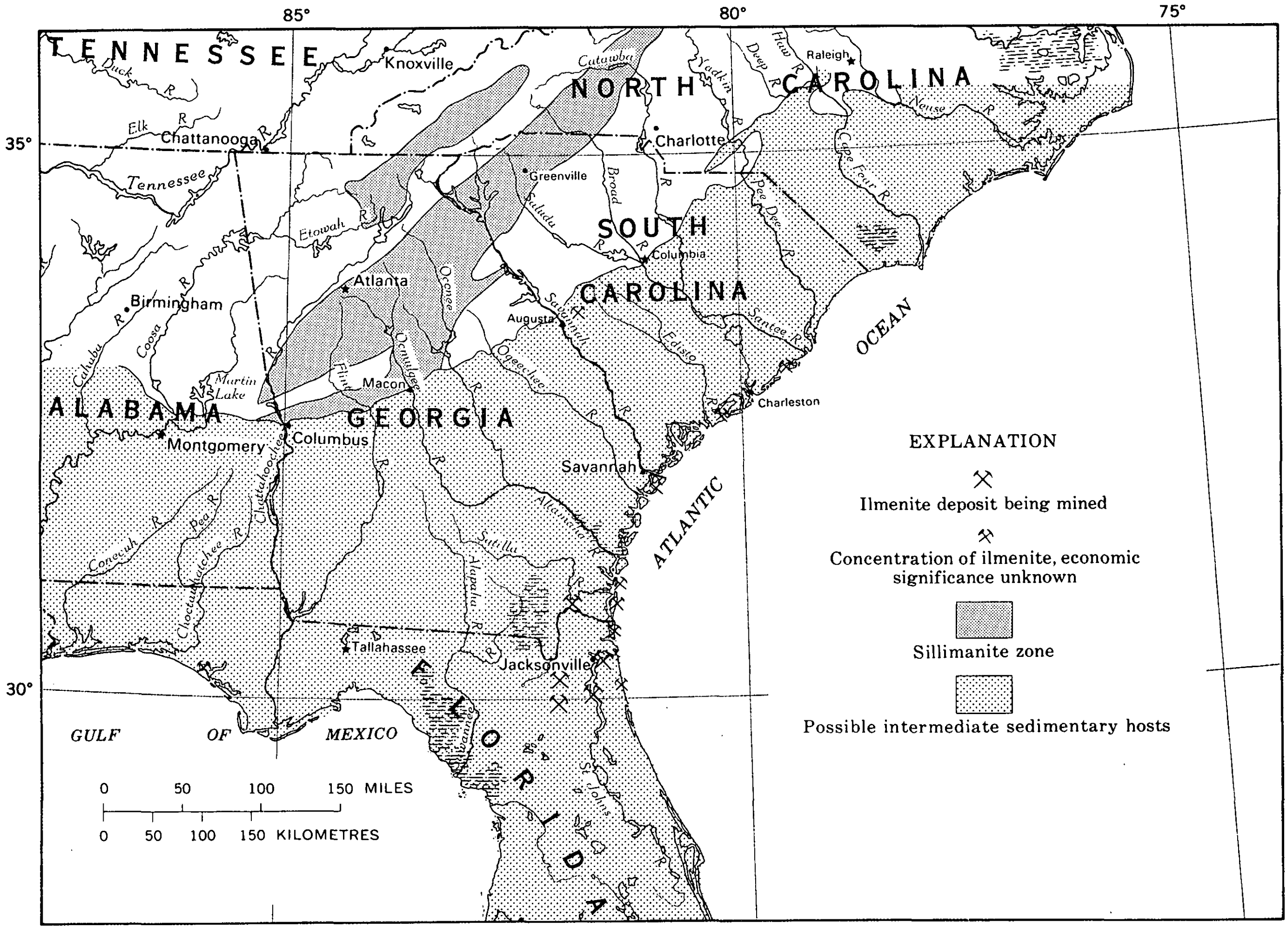

FIGURE 5.—Relationship of fossil and modern placer titanium deposits, possible intermediate sedimentary hosts, and metamorphic terrane in the southeastern United States. Metamorphism is from Morgan (1972).

al environment of the main formation in which "ilmenite" was finally deposited is in dispute; it may have been a beach. "Ilmenite" here was formed by weathering and is actually a black, slightly magnetic aggregate of fine rutile and iron oxides much higher in TiO_2 than is true ilmenite (Markewicz, 1969).

"Ilmenite" deposits of Trail Ridge, in Florida and Georgia, are in a Pleistocene beach deposit probably formed as a spit connected to an eroding headland of older coastal plain deposits (Pirkle and Yoho, 1970). "Ilmenite" is a weathered aggregate containing fine-grained rutile (Garnar, 1972) and occurs with rutile and zircon. There were probably two main sources of titanium minerals (fig. 5); one is the previously discussed high-grade metamorphic terrane in the Blue Ridge of North Carolina, and the other is a high-grade metamorphic terrane in the Piedmont province of North and South Carolina (Overstreet and others, 1968). Their relative contribution as sources is uncertain. A history of the Trail Ridge deposits would probably record transportation and deposition in intermediate host rocks.

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Rutile and Sphene in Blueschist and Related High-Pressure-Facies Rocks

By M. C. BLAKE, JR., and BENJAMIN A. MORGAN

GEOLOGY AND RESOURCES OF TITANIUM

GEOLOGICAL SURVEY PROFESSIONAL PAPER 959-C

U.S. DEPARTMENT OF THE INTERIOR
March 3, 1849

CONTENTS

ILLUSTRATION

RUTILE AND SPHENE IN BLUESCHIST AND RELATED HIGH-PRESSURE-FACIES ROCKS

By M. C. BLAKE, JR., and BENJAMIN A. MORGAN

ABSTRACT

Sphene and rutile are characteristic accessory minerals of blueschist-facies metamorphic rocks. Only sphene, however, is present in lower grade blueschist assemblages. In many areas of the world, these blueschists pass into, or are in fault contact with, higher grade glaucophane schists, rutile-bearing amphibolites, and eclogites. The origin of the rutile may be related to a prograde metamorphic reaction that alters sphene to rutile, but few data are available to support this hypothesis. It seems more probable that the rutile crystallized directly from ilmenite or titanium-rich clinopyroxene and magnetite in basalts and gabbros during the conversion of these rocks to amphibolites and eclogites containing omphacite, amphibole, and garnet. Regardless of its origin, rutile in the higher grade blueschists is a potential titanium resource and is currently being mined from eclogite and glaucophane-ecologite rocks in the Soviet Union, where resources of contained TiO_2 could range as high as millions of tons.

INTRODUCTION

Low-grade metamorphic rocks of the blueschist facies, characterized by minerals such as glaucophane, jadeitic pyroxene, aragonite, and sphene, have been described from many parts of the world (Irwin and Coleman, 1972). According to most workers, blueschist-facies rocks formed under conditions of relatively high pressure and low temperature (5 to 7 kbar and 150° to 300°C) and are most likely the products of subduction in island arcs and active continental margins (Coleman, 1972). Detailed petrologic studies in a number of areas, including California (Coleman and Lee, 1963; Blake and others, 1967; Ernst and others, 1970), Japan (Hashimoto and others, 1970; Ernst and others, 1970), New Caledonia (Brothers, 1970; Brothers and Blake, 1973), Venezuela (Morgan, 1969, 1970), and the Alps (van der Plas, 1959; Bearth, 1959, 1966; Ernst, 1971, 1973), have demonstrated that, with increasing metamorphism, these rocks locally pass into amphibolites, eclogites, or glaucophane eclogites containing garnet, blue-green hornblende, epidote, omphacite, and rutile in addition to glaucophane. Oxygen isotope studies suggest that the higher grade rocks formed at temperatures on the order of 400° to 550°C and at pressures of 9 to 10 kbar (Taylor and Coleman, 1968). Belts containing these higher grade amphibolites and eclogites usually lie closer to the inferred subduction zones than the lower grade blueschists do, and the sense of the metamorphic progression is believed to mark the direction of lithospheric underthrusting (Ernst, 1971).

Although this division into two high-pressure mineral facies appears to be reasonably well established, differentiation in specific geographic areas is difficult. Problems include: (1) Differences in mineral assemblages related to host-rock chemistry (for example, epidote is known to occur in low-grade blueschists containing abundant ferric iron as well as in higher grade rocks), (2) faulting of the higher grade rocks such that they occur as either isolated fault blocks or tectonic inclusions in lower grade blueschists, and (3) retrogression of many higher grade blueschists to low-grade mineral assemblages.

No documentation of a prograde reaction converting sphene to rutile was found in this review of detailed studies on the petrography of blueschists. In fact, only the retrograde sequence has been described from many areas; rutile in high-grade blueschist rocks is rimmed and partially replaced by sphene. If the sphene-rutile transition is to represent a potentially valuable isograd, the reaction must be defined. The present data strongly suggest that rutile does not form at the expense of sphene in blueschist-facies metamorphic terranes.

DESCRIPTION OF INDIVIDUAL LOCALITIES

WESTERN CALIFORNIA

The presence of rutile and sphene in metamorphic rocks of the Franciscan assemblage has long been known (Taliaferro, 1943, p. 170; Bailey and others, 1964, p. 97). Borg (1956) pointed out the association of sphene with glaucophane and lawsonite schists and of rutile with eclogites in part of northern California. Coleman and Lee (1963) subdivided similar rocks into three metamorphic types in part on the basis of the presence of sphene versus rutile. They showed that rutile-bearing high-grade schists and eclogites are metabasalts occurring as tectonic inclusions ("knockers") in less metamorphosed Franciscan rocks; subsequent studies have verified this conclusion over large areas of the Coast Ranges (Bailey and others, 1964; Ernst and others, 1970).

In a very detailed study, Lee and others (1966) described one of these "knockers," a glaucophane schist, from the Cazadero area and showed that the primary metamorphic mineral assemblage, which consists of glaucophane, actinolite, epidote, garnet, and rutile, was more or less replaced by retrograde pumpellyite, chlorite, and sphene. Modal analyses of four parts of this rock showed sphene ranging from 6.1 to 8.1 volume percent, whereas rutile made up only 0.1 to 0.3 percent (fig. 1*A*). Coleman and Lee (1963, p. 286) suggested the following retrograde reactions: (1) Pumpellyite + lawsonite + sphene $\leftrightharpoons$ epidote + rutile + water + quartz and (2) lawsonite + sphene $\leftrightharpoons$ epidote + rutile + water + quartz. Both reactions suggest that the rutile-bearing assemblages would be favored by higher pressures and (or) higher temperatures; this inference is supported by the previously mentioned isotopic studies. Chemical analyses of the rutile- and sphene-bearing metabasalts, as well as of unmetamorphosed basalts from the Franciscan assemblage, indicate that these rocks are all very similar and suggest that the metamorphism was essentially isochemical.

Undoubtedly, the most extensive area of rutile-bearing "high-grade" metamorphic rocks in the California Coast Ranges is found on Catalina Island, where Bailey (1941) mapped an area of about 10 km^2 of gneisses containing albite, hornblende, diopside, rutile, and rare kyanite and structurally overlying lower grade lawsonite- and sphene-bearing schists along a low-angle fault. Detailed mineralogical and chemical studies of coexisting phases from a few of these rocks were described by Ernst and others (1970); the titanium-bearing phases, however, were not included in their study.

Rutile-bearing metamorphic rocks also occur in the Sierra Nevada foothills in central California. In this area, tectonic blocks of garnet amphibolite and rare eclogite are found along serpentinite-marked fault zones. Neither lawsonite nor glaucophane has been reported from these rocks, but recent work by Morgan (1973) suggested that, in many respects, these rocks are similar both chemically and mineralogically to high-grade amphibolite "knockers" in the Franciscan assemblage to the west. The higher grade assemblage studied by Morgan consists of garnet-amphibole-albite-rutile that is being retrograded to epidote, chlorite, ilmenite, and sphene. Rutile in these rocks occurs as scattered grains as large as 0.5 mm and is either retrograded to sphene or to ilmenite and minor sphene (fig. 1*B*).

NEW CALEDONIA

A remarkably continuous metamorphic terrane is present in the northwestern part of New Caledonia (Espirat, 1963; Coleman, 1967; Lillie and Brothers, 1970). Here one can walk from unmetamorphosed Eocene cherts and siliceous shales to Cretaceous phyllites with lawsonite-glaucophane-sphene and on to schists and gneisses containing several mappable metamorphic isograds including garnet, epidote, and blue-green hornblende within a radius of 15 km. The rocks strike northwest and dip to the southwest; their structural thickness is on the order of 20,000 m (Lillie, 1970). The highest grade part of this sequence crops out along the northwestern coast between Balade and Touho, a distance of about 100 km. Locally, these rocks consist of extremely coarse grained schists and gneisses with individual crystals of glaucophane, blue-green hornblende, epidote, omphacite, albite, phengite, and garnet locally as large as 2.5 cm. Rutile is found as 1- to 2-mm grains in glaucophane-rich metabasalt and amphibolite (fig. 1*C*) and in veins cutting these rocks. At least some of these coarse-grained rocks are found in serpentinite-rich mélange zones and may not be conformable with the enclosing schists. The detailed mineralogy and chemistry of these rocks and included phases were being studied in 1973 by Phillipa Black at Auckland University in New Zealand.

SANBAGAWA BELT, JAPAN

Numerous detailed studies have been carried out on the metamorphic rocks of the Sanbagawa belt of Japan, which extends along the Pacific Ocean side of the Japanese islands for more than 1,000 km. The width of the belt is 20 to 50 km. The highest grade rocks are to the north and west, and metamorphic grade decreases south and east into upper Paleozoic and Mesozoic sedimentary rocks (Miyashiro, 1972; Seki and others, 1964; Ernst and others, 1970). In Sikoku, where numerous detailed studies have been

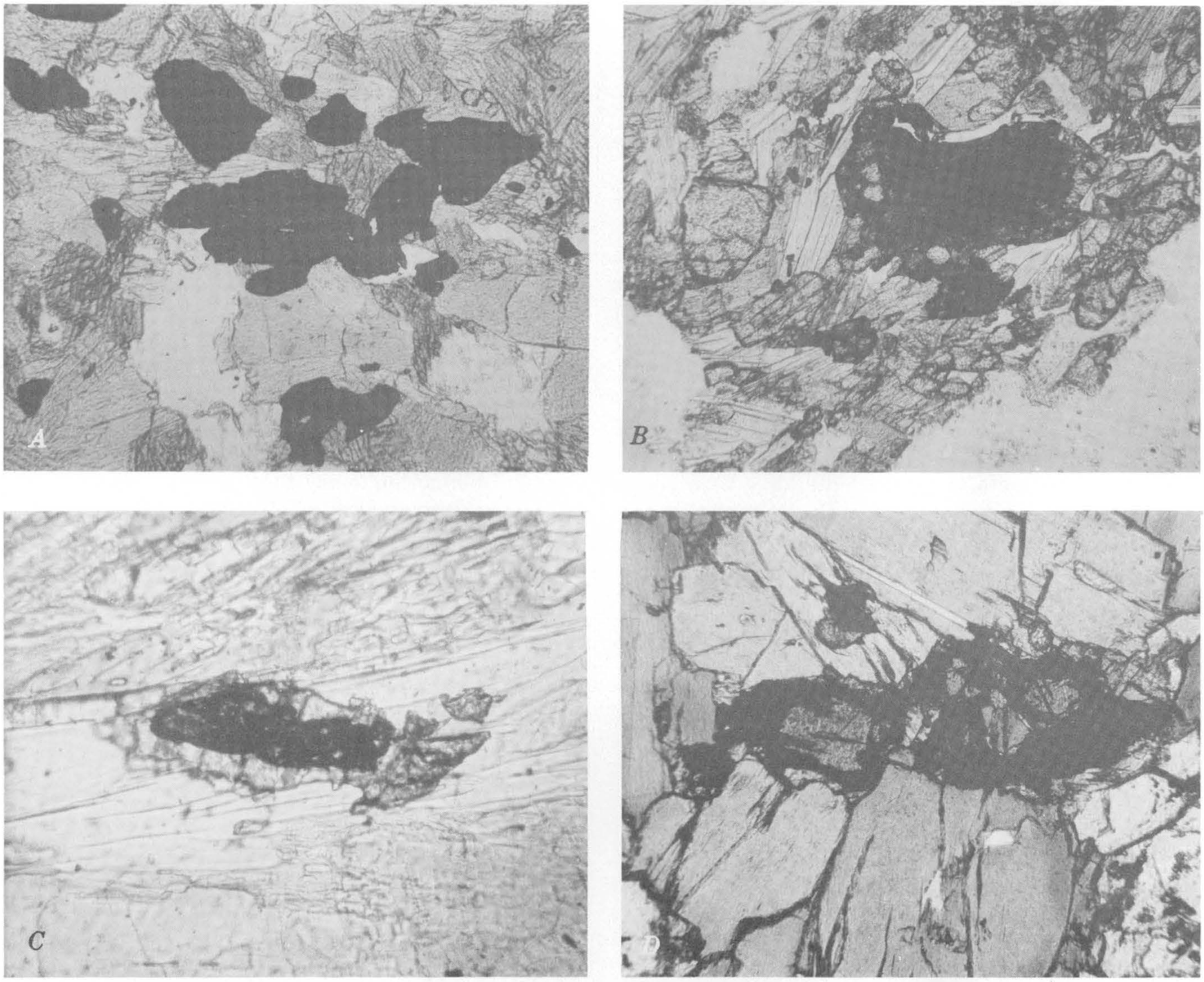

FIGURE 1.—Photomicrographs of rutile-sphene relations in high-pressure metamorphic rocks. *A*, Garnet-glaucophane amphibolite (sample 50CZ60) from Cazadero, Calif.; plane-polarized light showing cluster of rutile grains mantled by sphene. Other minerals include garnet, phengite, and glaucophane. Field of view is 1.4 mm. *B*, Garnet amphibolite (sample 2126) from Chinese Camp 7½-min quadrangle, western Sierra Nevada, California; plane-polarized light showing two grains of rutile mantled by ilmenite, which in turn is mantled by minor sphene. Large gray grains are amphibole. Field of view is 1.4 mm. *C*, Glaucophane amphibolite (sample 9677) from New Caledonia; plane-polarized light showing a group of dark rutile crystals with no mantling by sphene. Other minerals are phengite and glaucophane. Field of view is 1.4 mm. *D*, Eclogite-amphibolite (sample 1115) from Puerto Cabello, Venezuela (Morgan, 1970); plane-polarized light showing grain of rutile completely mantled by sphene. Other minerals include paragonite and amphibole. Field of view is 0.35 mm.

made (Hide, 1961; Iwasaki, 1963; Suzuki, 1964; Ernst and others, 1970), three metamorphic mineral zones have been mapped. In zone I, mafic schists contain epidote, chlorite, actinolite, albite, sphene, and minor glaucophane. Farther north in zone II, the mafic rocks are characterized by coarser grain size and the assemblage of epidote, chlorite, calcic amphibole (actinolite grading northward into blue-green hornblende), sphene, white mica, garnet, and sodic amphibole. Within zone III, the mafic rocks contain abundant porphyroblasts of albite plus blue-green hornblende, with epidote, chlorite, garnet, rutile, and sphene; rutile also has been reported from siliceous rocks of this zone (Ernst and others, 1970). Elsewhere in Sikoku, rutile-bearing eclogites represent an even higher grade of metamorphism (Banno, 1964, 1966), but these rocks seem to be tectonic slices similar to those described from California.

CENTRAL ALPS

The metamorphic zonation in the central Alps is not developed in a simple, roughly continuous succession but represents a series of complex nappes, metamorphosed and emplaced over a long period of time (Ernst, 1971, 1973). In the north, the Pennine, Sesia-Lanzo, and Helvetic nappes collectively form a relatively high pressure metamorphic terrane, which is structurally overlain to the south and east by the Austroalpine nappes (and southern Alps) representing a relatively high temperature metamorphic terrane. The tectonic contact between these two contrasting terranes has been named the Alpine Suture (Ernst, 1973). Within the high-pressure terrane, three metamorphic events have been recognized, which began during the Cretaceous and continued into the Oligocene: (1) Early Alpine blueschist-type facies, (2) a later greenschist-type facies, and (3) a late Alpine higher temperature event ranging from greenschist to amphibolite facies. During the early Alpine event, a progressive metamorphic sequence was formed with zeolite- and prehnite-pumpellyite-facies rocks grading southward through a zone composed of both greenschists and blueschists into an albite-amphibolite facies containing eclogite. The southernmost rocks contain rutile and grade northward into sphene-bearing lawsonite blueschists and laterally into greenschists (Bearth, 1962, 1966; Chatterjee, 1971). The details of this transition, however, are not given.

SOVIET UNION

Rutile-bearing eclogite and garnet-glaucophane schists are found in the southern Ural Mountains of the Soviet Union (Chesnokov, 1960). The rocks occur as scattered blocks or slabs as long as 1 km and as thick as 150 to 200 m surrounded by quartz-muscovite schists, graphite-mica schists, and garnet-glaucophane-muscovite-quartz schists. According to Chesnokov, the rocks probably represent isolated metamorphosed gabbro bodies in a metasedimentary terrane.

The amount of rutile in the eclogite and garnet-glaucophane schists ordinarily does not exceed 1 or 2 percent, but locally higher values exist, and TiO_2 content is as high as 5.3 percent, presumably all as rutile. Size analyses show that the rutile crystals generally fall between 0.1 and 0.2 mm. Four potential orebodies are mentioned and described by Chesnokov, and, according to N. L. Dobretsov (oral commun., 1973), at least one of these deposits is currently being mined.

VENEZUELA

Eclogite, eclogite-amphibolite, garnet-amphibolite, and garnet-glaucophane schist are found in northern Venezuela in a broad belt extending along the coast west from Caracas for nearly 200 km (Dengo, 1950; Morgan, 1969, 1970). The eclogites and related rocks occur as irregular lenses in rocks of the epidote-amphibolite facies. This terrane is structurally overlain to the south by thrust sheets of greenschist- and lower grade blueschist-facies rocks (Shagam, 1960; Piburn, 1968). Although field relations are complicated by extensive thrust faulting, the regional metamorphism can be attributed to former subduction zones that presumably lay north of the present coastline (Bell, 1972).

Within the lower grade blueschist rocks, rutile is absent and sphene is rare. Rutile as small (less than 0.5 mm) round grains, however, is a common accessory mineral in the eclogites and related high-grade rocks. Rutile grains are rimmed by sphene in those eclogites that are boudins in marble. This alteration may be related to the reaction rutile + quartz + calcite $\rightarrow$ sphene + CO_2 (fig. 1*D*). According to Morgan (1970), the conditions of metamorphism for the eclogites and associated rocks include temperatures of about 525°C and pressures of about 7 kbar.

DISCUSSION

Rutile-bearing eclogites, amphibolites, and garnet-glaucophane schists occur in the areas just described as (1) tectonic inclusions in lower grade sphene-bearing blueschists (California) and (2) thrust sheets overlying lower grade rocks (central Alps) and in (3) relatively coherent metamorphic terranes (New Caledonia, Venezuela, and Japan), where rutile is presumably replaced by sphene at a lower grade, although the details of this transition are not known. In nearly every area, there is petrographic evidence for retrograde metamorphism of rutile to sphene, but nowhere has the progression from sphene to rutile been documented. Because sphene is stable in Barrovian metamorphic terranes well into the sillimanite zone, it might appear that the formation of rutile is related to unusual chemistry of the host rocks. As Force (1976) pointed out, however, rutile is found in low-grade metamorphic rocks low in CaO; in the blueschists, nearly all of the rocks are metamorphosed basalts high in CaO. A more convincing hypothesis is that the rutile is derived from titanium-rich minerals such as ilmenite, magnetite, and clinopyroxene in the original basalt. During metamorphism, titaniferous augite and plagioclase are converted to omphacitic pyroxene, amphibole, and garnet, the titanium being left to form rutile. Examples of the conversion of titanium-bearing clinopyroxene to omphacite and rutile in the central Alps have been documented by Miller (1970) and by Chinner and Dixon (1973). During subsequent retrograde metamorphism, the breakdown of omphacite and other minerals releases calcium, which reacts with the rutile to form rims of sphene. This hypothesis certainly fits the observed field and petrographic data for tectonic slices from California, but it remains to be seen whether rutile is derived directly from primary minerals in more coherent terranes where gradational cases might be observed.

RESOURCE POTENTIAL

The large grain size and abundance of rutile in many eclogites and related high-pressure rocks warrant its classification as a titanium resource. As was mentioned earlier, rutile is currently being mined from these kinds of rocks in the Urals, and similar potential orebodies may exist in New Caledonia, on Catalina Island (California), and in northern Venezuela. In all of these areas, the mineral potential is greatly enhanced by the possibility of shoreline placer deposits of rutile.

The magnitude of rutile resources in deposits of high-pressure rocks has not been published, but the figures cited above for grade and size of low-grade resources in eclogitic tectonic blocks of the Urals imply millions of tons of contained rutile.

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Titanium Deposits in Anorthosite Massifs

By NORMAN HERZ

GEOLOGY AND RESOURCES OF TITANIUM

GEOLOGICAL SURVEY PROFESSIONAL PAPER 959-D

U.S. DEPARTMENT OF THE INTERIOR
March 3, 1849

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TITANIUM DEPOSITS IN ANORTHOSITE MASSIFS

By Norman Herz

ABSTRACT

Anorthosite massifs are economically important sources of titanium minerals. The most valuable titanium deposits occur in andesine anorthosite massifs rather than in labradorite anorthosite massifs or stratiform anorthosites and are of two types: (1) Ilmenite bodies associated with gabbro in the border zones of nonalkalic andesine anorthosite massifs and (2) rutile and ilmenite disseminated along the borders of alkalic andesine anorthosite massifs. Deposits of titanium minerals in anorthosite commonly contain millions of tons contained TiO_2.

INTRODUCTION

The term anorthosite has been applied to all igneous rocks that are composed almost entirely of plagioclase of calcic to intermediate composition, though different processes can form a rock that conforms to this definition. Anorthosites occur both as massifs and in stratiform complexes, the latter developing by gravity stratification in ultramafic and mafic complexes. These stratiform complexes, generally Precambrian but occasionally as young as Tertiary, are characterized by rhythmic layering, show many cumulate features, do not develop giant megacrysts, and have a plagioclase composition in the bytownite-anorthite range. Associated rocks are olivine- and pyroxene-rich ultramafics, generally layered and gravity stratified and occurring with chromitite and sulfides.

Nearly all the important igneous deposits of titanium minerals, however, are associated with massif-type anorthosites and their related rocks. The largest ilmenite deposit in the United States occurs in the Adirondack anorthosite of New York, and the largest rutile deposit in the Roseland anorthosite of Virginia. The largest ilmenite deposit in Canada is the Lac Tio deposit in the Allard Lake anorthosite of Quebec. Large rutile deposits are associated with the Pluma Hidalgo anorthosite of Oaxaca, Mexico, and the St. Urbain anorthosite of Quebec, Canada. Large ilmenite deposits occur in anorthosite at Egersund-Sogndal, Norway, and in the Ukraine, U.S.S.R. Noritic gabbro, an end member of common anorthositic assemblages, contains ilmenite deposits, such as those at Otanmäki, Finland. Deposits in granulite-facies wall-rock gneisses may be closely related to those in adjacent anorthosite, as they are at Roseland.

Some massif anorthosites, such as those in Nain and Michigamau, Labrador, show gravity layering, but, in most complexes, gravity layering is generally poorly developed or absent. Ages determined to date on all massif anorthosites are Precambrian, about 1,300±200 m.y. (Herz, 1969). These rocks crystallized under slow cooling conditions in the upper mantle or lower crust; the resulting megacrysts are commonly tens of centimeters in length. The feldspars are andesine, in places antiperthitic, or labradorite; pyroxenes are the most common accessory minerals, but olivine may be present, as it is in the Laramie anorthosite of Wyoming. Some of the minerals show kink banding, and plagioclase twin lamellae may be bent or broken.

The name applied to a rock of the anorthosite suite depends on the amounts of mafic minerals present. The name anorthosite is reserved for rocks containing 90 percent plagioclase or more; gabbroic, noritic, or troctolitic anorthosites have 10 to 22.5 percent mafic minerals; anorthositic gabbro, norite, or troctolite have 22.5 to 35 percent mafic minerals (Isachsen, 1968, p. 435).

According to the terminology of Buddington and others (1963), titanium-bearing oxides in anorthosites can include ilmenite, rutile, ilmeno-magnetite (ilmenite as fine intergrowths in magnetite), ilmeno-hematite (ilmenite as fine intergrowths in hematite), hemo-ilmenite (hematite as fine intergrowths in ilmenite), titano-magnetite (titanium present in magnetite structure), and ulvospinel (Fe_2TiO_4). Titaniferous magnetite is a generic term that does not specify presence or type of phases other than magnetite.

The titanium-rich minerals crystallize late in the magmatic history of anorthositic complexes. The behavior of titanium during the crystallization of any magma is controlled by several factors, including the initial abundance of titanium in the magma, the chemical activities of silicon, aluminum, and iron, the partial pressure of oxygen, the formation of titanium-rich immiscible melts, and the temperature of crystallization (Verhoogen, 1962). In a normally crystallizing tholeiitic magma having sufficiently high oxygen fugacity, titanium and iron will form oxides early in the magmatic history. These oxide minerals may segregate out and accumulate by gravity settling because of their high specific gravity. Another possible factor in the formation of titanium oxide minerals is the formation of an immiscible liquid that has the composition of iron and titanium oxides plus phosphate within a predominantly silicate liquid magma chamber (Philpotts, 1967). The formation of some ilmenite- and titaniferous magnetite-apatite orebodies has been ascribed to this phenomenon.

The early crystallization history of anorthositic plutons is a much debated topic (Yoder, 1968; Green, 1969), but it is generally agreed that the rocks rich in iron-titanium oxide and mafic minerals are emplaced later than the anorthosites themselves (Isachsen, 1968). If the later rocks have crystallized from a magma, it must be one enriched in iron and titanium either by processes of differentiation or by formation of an immiscible liquid.

TYPES OF ANORTHOSITE MASSIFS

Anorthosite massifs can be divided into two distinct types based on their plagioclase and oxide compositions (Anderson and Morin, 1968). At St. Urbain, Quebec, one type can be seen intruding the other, but this relationship is exceptional; any one massif generally consists of only one type. The two types recognized are (1) labradorite anorthosite massifs characterized by plagioclase of An_{68-45} composition and either titano-magnetite or its oxidized equivalent, magnetite+ilmenite, and (2) andesine anorthosite massifs containing plagioclase An_{48-25}, hemo-ilmenite, and En:An ratios (En content of orthopyroxene and An content of plagioclase) greater than one. The latter is generally called "Adirondack type" (Buddington, 1931) and is associated with the world's principal ilmenite deposits. An unusual type of andesine anorthosite massif, found in Roseland, Pluma Hidalgo, and St. Urbain, contains feldspar megacrysts that are strongly antiperthitic and has a K_2O content of 3 to 4 percent, which is about double the normal amount. This type has been called "alkalic anorthosite" (Herz, 1968) and has associated deposits of rutile as well as ilmenite.

Some typical labradorite anorthosite massifs include the Michigamau of Labrador (Emslie, 1970) and the Duluth Gabbro Complex of Minnesota (Taylor, 1964); andesine anorthosites include massifs of the Adirondack Mountains in New York (Buddington, 1931), Allard Lake in Quebec (Hargraves, 1962), and Roseland, Va. (Herz, 1968). These massifs will be discussed below as typical examples of the two types of anorthosite massifs.

LABRADORITE ANORTHOSITE MASSIFS

The Michigamau anorthosite pluton occurs in west-central Labrador and covers an area of 65×40 km (Emslie, 1970). The main rock units, in order of crystallization, are a border zone of olivine gabbro, which is fine grained at the contact and probably chilled, a thick series of layered leucotroctolite, a considerable thickness of anorthosite that grades upward into leucogabbro and gabbro, and ferrous iron-rich rocks. Structures and textures indicative of crystal accumulation are developed in leucotroctolite, anorthosite, and leucogabbro. The ferrous iron-rich rocks range from mafic diorite through granodiorite to syenite and locally transgress the anorthosite. The compositions of the mafic minerals indicate a fractionation trend toward enrichment in iron. Concentrations of ilmenite and vanadium-bearing magnetite are in the gabbroic border zone in pods and layers forming a subzone 300 m wide and several kilometers long. They are clearly a product of the trend toward iron enrichment that became pronounced after the crystallization of the main mass of the anorthosite.

The Duluth Gabbro Complex (Taylor, 1964) underlies more than 2,500 km^2, is about 15,000 m thick, and consists, in large part, of anorthosite and anorthositic gabbro. The oldest part of the complex is a coarse-grained anorthositic gabbro that intrudes Keweenawan flows and makes up the upper part of the complex. It contains 75 to 90 percent calcic labradorite and generally abundant titanaugite, olivine, and fine magnetite-ilmenite intergrowths. The anorthositic gabbro was intruded by basaltic magma of a second period of magmatic activity, which formed layered rocks consisting chiefly of troctolite, olivine gabbro, feldspathic gabbro, and syenogabbro. These rocks are 4,500 m thick and show local rhythmic layering, fluxion structure, and gravity stratification. The entire series is cut by bodies of ferrogranodiorite and granophyre and late dikes of basalt and aplite. The iron-titanium oxide minerals are most abundant near the top of the series, in olivine metagabbro where distinct layers of "iron ores" are seen and in magnetite syenogabbro where magnetite averages 12 percent by volume. The oxide minerals are apparently a product of the trend of iron-titanium enrichment during the course of differentiation and fractionation, as at Michigamau.

Both the Michigamau and the Duluth complexes contain fairly large bodies that are high in TiO_2, but no economic titanium deposits have been found in them despite intensive search. The fine-grained intergrowths of magnetite and ilmenite rather than discrete ilmenite grains (Grout, 1950; Grout and others, 1959) render the deposits an economically unimportant source of titanium at present.

ANDESINE ANORTHOSITE MASSIFS

The andesine anorthosites are the most widespread massifs and contain the largest known titanium deposits (Isachsen, 1968). They generally occur as intrusives in granulite or upper amphibolite metamorphic terranes and are, in turn, intruded by a suite of charnockitic rocks, which are characterized by perthitic feldspars and orthopyroxene rather than by two feldspars and hydrous mafic minerals. The anorthositic and charnockitic rocks may be interlayered, as they are in the Lake Placid area of the Adirondack Mountains (Crosby, 1968), or they may be gradational from anorthosite through noritic anorthosite, norite, and mangerite to charnockite, as they are in the Snowy Mountain Dome of the Adirondack Mountains (DeWaard and Romey, 1968). In many places, the charnockite suite only borders the anorthosite, and the exact relations are not too clear.

ADIRONDACK MOUNTAINS, NEW YORK

The Marcy Massif is the main anorthosite pluton in the Adirondack Mountains (Buddington, 1931) and consists predominantly of andesine anorthosite. Plagioclase averages An_{45} in composition and occurs as megacrysts and groundmass, both of which show evidence of cataclasis. Gabbroic or noritic anorthosite, in which are found the ilmenite-magnetite orebodies, forms a border facies against mangerite-charnockite, which surrounds the anorthosite massif for about three-quarters of its perimeter. Anorthosite grades into and is cut by gabbro or norite and then by ilmenite-magnetite-rich gabbro and pyroxenite. Although the initial composition of the material that produced the anorthosite series is unknown, xenoliths and crosscutting relations show that the trend of the later mafic rocks was towards enrichment in iron and titanium and the eventual production of ilmenite-magnetite orebodies.

The ilmenite deposits of the Sanford Lake (Tahawus) mining district in the Adirondack Mountains have produced more titanium ore than any anorthosite deposit in the world. Through 1964, 33,500,000 tons of ore had been produced from the South Extension area of Sanford Lake alone (Gross, 1968).

Anorthosite of the Sanford Lake mining district grades into gabbroic anorthosite, and this, in turn, grades into anorthositic gabbro containing varying percentages of mafic minerals (Gross, 1968). The TiO_2 content of anorthosite at the mine is 0 to 5.4 percent, that of gabbro is 5.5 to 9.4 percent, and that of the ores is 13.5 percent or more. Two types of orebodies are described: (1) "Anorthositic ore" associated with anorthosite is found as irregular massive lenses that show no flow structures, are coarse grained, and have sharp contacts with the anorthosite, and (2) "gabbroic ore" occurs as oxide-enriched layers within gabbro. These are fine to medium grained and have a well-defined flow structure similar to that of the gabbro. The thickness of individual layers ranges from a few millimeters to several meters. Contacts are sharp or gradational with gabbro. The anorthositic type forms a football orebody, and the gabbroic type a hanging wall separated by varying amounts of anorthosite and gabbro. The anorthositic ore and gabbroic ore are chemically different; the anorthositic ore has an $Fe:TiO_2$ ratio of 2:1 or greater, whereas the ratio in gabbroic ore is invariably less than 2:1.

Discrete grains of ilmenite are present as well as exsolution intergrowths of ilmenite and magnetite containing as much as 35 percent $FeTiO_3$ molecule and of ulvospinel and magnetite.

Although there is no agreement on the origin of these ores, Gross (1968) stated that they were originally formed by magmatic processes and reworked during later metamorphic events.

ALLARD LAKE, QUEBEC, CANADA

The largest operating ilmenite mine in Canada is in the Allard Lake anorthosite massif on the northern shore of the St. Lawrence River, about 800 km northeast of Quebec City (Hargraves, 1962). The massif is andesine anorthosite surrounded by mangerites; a mafic zone is in the contact area. Three main rock types are exposed in the northeastern border area of the massif:

1. Coarse-grained massive anorthosite, generally more than 95 percent calcic andesine, which shows considerable cataclasis. Plagioclase matrix grains 3 to 6 mm long and megacrysts 2 to 35 cm long have about the same composition (An_{40-52}). Bronzite is irregularly distributed in the anorthosite as poikilitic crystals enclosing plagioclase or as alined aggregates that transgress primary foliation in the anorthosite.
2. Medium-grained oxide-rich norite consisting of protoclastically deformed plagioclase (An_{40-45}), pyroxenes with hypersthene>augite, apatite (8–10 percent), and two oxides with hemo-ilmenite>magnetite (20–54 percent). This rock occurs in sheets as much as 6 km long by 1 km thick that intrude the anorthosite. The oxide minerals are interpreted by Hargraves as the product of an immiscible melt in the silicate liquid.
3. Pyroxene syenite gneiss that borders the anorthosite massif. The contact zone is characterized by conformable gneissosity and enrichment in mafic minerals.

The ilmenite orebody at Lac Tio in the Allard Lake district occurs as a large sheet or lens of hemo-ilmenite located a few kilometers inside the margin of the anorthosite (Lister, 1966). The anorthosite near the deposit is coarse grained, unfoliated, and composed of andesine (An_{40-44}) containing less than 2 percent pyroxenes and ilmeno-hematite. The ore sheet is made up of massive hemo-ilmenite capped by layered hemo-ilmenite and anorthosite. The lower part of the sheet is over 90 m thick and contains blocks of anorthosite as large as 4.5 m in diameter. The upper part of the orebody is less than 60 m thick and consists of alternating layers of pure ilmeno-hematite and anorthosite containing disseminated hemo-ilmenite; individual layers vary from a few centimeters to a few meters thick.

Typical high-grade ore (table 1) consists of hemo-ilmenite with about 3 percent iron spinel, 0.5 percent pyrite, and a few feldspar remnants. The hemo-ilmenite consists of ilmenite with 20 to 22 percent titanium-bearing hematite disks exsolved in (0001) (Bergeron, 1972).

The immiscible liquid said to have formed the deposit must have had the general composition of the orebody, and later hydrothermal replacement was minor (Lister, 1966, p. 285). The ore magma was injected into a dilation zone that formed within a shear zone in hot anorthosite. In the upper part, the ore sheet developed as the liquid invaded closely spaced shear planes and permeated fractures in crushed anorthosite to form the layered and disseminated deposit.

TABLE 1.—*Analysis of Lac Tio ilmenite ore (from Bergeron, 1972)*

	Weight (percent)
TiO_2	34.3
FeO	27.5
Fe_2O_3	25.2
SiO_2	4.3
Al_2O_3	3.5
CaO	.9
MgO	3.1
Cr_2O_3	.10
V_2O_5	.27
MnO	.16
S	.3
Na_2O and K_2O	.35
P_2O_5	.015

ROSELAND, VIRGINIA

The Roseland alkalic andesine-anorthosite massif is about 15 km long in a northeasterly direction and 4 km wide (Herz, 1968). It occurs in country rock that had been metamorphosed to the pyroxene-granulite facies but later partly retrograded to greenschist facies during a Paleozoic metamorphism. Charnockite, noritic anorthosite, norite, and pyroxene-rich rocks are found largely in the border zone but are also scattered irregularly throughout the anorthosite massif. The anorthosite itself consists of large bluish-gray megacrysts, as long as 20 cm, of andesine antiperthite, $Or_{25}Ab_{51}An_{23.5}Celsian_{0.5}$, and lighter colored granulated zones containing andesine-oligoclase and microcline. Pyroxenes, blue quartz (generally rutilated), clinozoisite, and muscovite are common accessory minerals. This anorthosite and its associated ores are remarkably similar to those in Pluma Hidalgo (Paulson, 1964; T. P. Thayer, written commun., 1973).

Ilmenite and rutile occur in the border area of the alkalic anorthosite massif. Hemo-ilmenite is found disseminated in the contact rocks of the anorthosite, including mafic border phases and possible contact-metamorphosed granulites. Ilmenite also occurs together with apatite in nelsonite dikes, which range as large as 600 m in length by 60 m in width (Watson and Taber, 1913). These dikes form the richest ilmenite deposits in the area and are always found outside the anorthosite body in charnockites and granulites of the border zone. The dikes appear to be later than either the anorthosite or the border rocks but were also deformed together with these rocks in later metamorphic events (Herz, 1968). The dikes approximate a possible eutectic composition in an iron-titanium oxide and phosphate system (Philpotts, 1967) and may represent the later emplacement of an immiscible liquid, which formed in the silicate magma that produced the bordering rocks.

Rutile occurs as disseminated deposits within the anorthosite and other rocks in the contact zone. Much of it is present where anorthosite is interlayered with granulite or is enriched in mafic dikes that cut both rocks. Some rutile appears to have been introduced in fractured zones, and the anorthosite is invariably saussuritized where rutile is abundant. In these zones, rutile grains range from 0.2 mm to 4 cm across and form deposits of an estimated grade of about 5 percent (D. N. Hillhouse, written commun., 1960). Rutile formed in the anorthosite appears to have an unusually large amount of TiO_2 (99.43 percent) (see also Ross, 1941), which is higher than any shown by Deer and others (1962, p. 36), whose TiO_2 values in rutile range from 45.79 to 98.96 percent, and higher than samples from Magnet Cove, Ark., Trail Ridge, Fla., and Shooting Creek, N.C. (table 2).

Saprolite resources over anorthosite, nelsonite, and adjacent rocks near Roseland were estimated by Fish (1962) as 20 million tons of ilmenite and rutile.

PROSPECTING FOR TITANIUM DEPOSITS IN ANORTHOSITE

Prospecting for titanium deposits in anorthosite should take into account the fact that different types of anorthosites have different types of titanium occurrences. Titanium minerals are associated with all types of anorthosites, but, as of yet, economic mineral deposits have been found only in andesine anorthosite massifs, not in labradorite anorthosite massifs or in stratiform anorthosites. The economic massifs form batholithic plutons that appear to be concordant to country rock in Precambrian terranes. Andesine, both as deformed megacrysts as large as 2 m in diameter and as granulated groundmass, comprises more than 90 percent of the rock. Andesine anorthosite massifs are associated with noritic gabbros, other igneous rocks of the charnockite suite, and metamorphic rocks of the pyroxene granulite facies. Gravity measurements over these anorthosite massifs show a substantial negative Bouguer anomaly. Magnetic patterns are featureless. Departures from these norms, however, may occur in border areas. Radiometric absolute ages of the massifs and country rocks are about 1,300 ± 200 m.y.

Once an andesine anorthosite massif has been located, titanium deposits can be found by considering that:

1. Ore deposits occur in peripheral areas of the massif, especially bordering mafic differentiates, and in adjacent country rock.
2. Ilmenite is associated with magnetite and apatite in gabbroic rocks. If plagioclase megacrysts are antiperthitic, rutile may be present as disseminations in anorthosite and country rock or in mafic veins and segregations.
3. Gravity and magnetic features may be anomalously high over iron-titanium ore deposits and associated mafic rocks, in contrast to the rest of the anorthosite (Rose, 1969, p. 30–40).
4. Detrital heavy minerals from small streams can serve as a guide to the distribution of ilmenite and rutile (Herz and others, 1970).

Prospecting by chemical analysis alone is deceptive, since anorthosites themselves generally have very little TiO_2, and, in many of the bordering mafic rocks, TiO_2 is present in unusable mafic silicate min-

TABLE 2.—*Analyses of selected rutile samples (weight percent)*

[Analysts: A, A. C. Vlisidis; B–D, John Marinenko, U.S. Geological Survey, Reston, Va. ND, not detected]

Sample	A Anorthosite (Roseland, Va.)	B Phonolite (Magnet Cove, Ark.)	C Detrital mixture (Trail Ridge, Fla.)	D Garnet schist (Shooting Creek, N.C.)
TiO_2	99.43	93.9	98.3	86.1
FeO	.55	(1)	(1)	12.1
Fe_2O_3	ND	1.2	.2	.9
P_2O_5	ND	.1	<.1	<.1
V_2O_3	(2)	.9	.4	.4
Nb_2O_5	(2)	3.8	.4	.3
H_2O	ND	.2	.2	ND

[1] All Fe reported as Fe_2O_3.

[2] Results of semiquantitative analysis in parts per million: Si=150, Al=100, Mg=20, Ca=15, B=30, Ba=3, Cr=200, Mo=15, Nb=200, V=500, Zr=300. Analysts: W. B. Crandell and Helen Worthing, U.S. Geological Survey, Reston, Va.

erals. Mineralogic studies are necessary to establish the mode of occurrence of titanium and the type of anorthosite.

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Titanium Deposits in Alkalic Igneous Rocks

By NORMAN HERZ

GEOLOGY AND RESOURCES OF TITANIUM

GEOLOGICAL SURVEY PROFESSIONAL PAPER 959-E

U.S. DEPARTMENT OF THE INTERIOR
March 3, 1849

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By NORMAN HERZ

ABSTRACT

Many types of alkalic rocks are enriched in TiO_2 relative to the average content of the crust. Silicate minerals in alkalic rocks may have high TiO_2 content, but the oxides ilmenite, rutile, brookite, and perovskite are characteristic primary phases. These oxides tend to be higher in niobium than the same minerals from other rock suites.

At Tapira, Brazil, titanium minerals in a carbonatite complex comprise tens of millions of tons contained TiO_2. Anatase (as "leucoxene") is present in laterite lying over parent rocks containing perovskite, ilmenite, and rutile. At Magnet Cove, Ark., and the Kola Peninsula in the U.S.S.R., production of titanium minerals is, at best, economically marginal.

INTRODUCTION

In many alkalic rocks, titanium is enriched several times beyond the normal concentration in igneous rocks (the normal being about 0.7 to 1.0 percent TiO_2). Nockolds (1954) listed the following average TiO_2 contents of alkalic rock types, in percent:

Alkali pyroxenite	3.31
Nepheline monzonite	2.49
Essexite	2.81
Ijolite	1.41
Average subsilicic igneous rock (721 analyses).	1.9

Several silicate minerals characteristic of alkalic rocks are high in TiO_2. Except for sphene, melanite garnets from alkalic rocks contain the highest amount of TiO_2 found in silicate minerals; melanite from ijolite in Iron Hill, Colo., has 5.08 percent TiO_2; elsewhere, melanite contains as much as 17 percent (Deer and others, 1962, p. 91). Kaersutite, an amphibole containing 5 to 10 percent TiO_2, and titanaugite, a pyroxene containing 3 to 6 percent TiO_2, are common in, but not restricted to, alkalic rocks.

The principal titanium minerals found in alkalic rocks, ilmenite, titano-magnetite, sphene, perovskite, rutile, anatase, and brookite, commonly contain significant amounts of niobium (Nb) and rare earths (Fleischer and others, 1952). Typical alkalic rocks and deposits are shown in table 1.

Most titanium-oxide minerals form late in the crystallization history of alkalic complexes. Chemical activities of silicon, aluminum, and iron and the partial pressure of oxygen are especially important in determining whether titanium will enter silicate minerals or form independent oxides. Some dikes consisting of iron-titanium oxides and apatite in alkalic rocks have been ascribed to the formation of immiscible melts having the composition of iron and titanium oxides plus phosphate within a predominately silicate liquid magma chamber (Philpotts, 1967). On the basis of extrapolation of experimental data, Philpotts deduced that liquids of magnetite-ilmenite-apatite composition can form immiscible melts in silicate magmas that are enriched in sodium,

TABLE 1.—*Titanium deposits associated with alkalic complexes (modified from Routhier, 1963, p. 958–959)*

Type	Locality	Titanium mineralogy	Related minerals
Nepheline syenite pegmatites.	Iveland-Evje region, south Norway; Kola Peninsula, U.S.S.R.; Ilmen Mountains (Urals), U.S.S.R.	Nb-rutile, euxenite, and other Y-rich titanates.	
Intermediate and basic alkalic rocks.	Khibiny, Kola Peninsula, U.S.S.R.; Oka, Quebec, Canada; Jacupiranga, São Paulo, Brazil; Tapira, Minas Gerais, Brazil.	In ijolite and pyroxenites, titanomagnetite and ilmenite; in "silexocarbonatites," sphene and perovskite with secondary anatase.	Apatite.
Rutile veins in carbonatite	Magnet Cove. Ark.	Nb-rutile with secondary brookite and "leucoxene."	Albite.

have a dioritic composition, and are undergoing strong differentiation. Some titanium orebodies found in alkalic rocks of the Kola Peninsula and Brazil may have formed by such a process.

DESCRIPTION OF INDIVIDUAL LOCALITIES

Titanium production of any significance has been attempted only in deposits in alkalic rocks at Magnet Cove, Ark.; the Kola Peninsula in the U.S.S.R.; and Tapira, Minas Gerais, Brazil.

Potential domestic resources of titanium include occurrences at Iron Hill, Colo. (Larsen, 1942), and Lemhi County in Idaho (Anderson, 1960). Perovskite and ilmenite have been described in mafic alkalic rocks and carbonatite from Iron Hill. Niobium-rich ilmenite (as much as 1 percent Nb) and ilmeno-rutile (niobium-bearing rutile, Nb as much as 13 percent) are found in Lemhi County in a rock type that appears to be a carbonatite.

MAGNET COVE, ARKANSAS

The alkalic complex of Magnet Cove, Ark., consists of a variety of feldspathoid-rich rocks that have intruded sediments of Paleozoic age (Erickson and Blade, 1963). The complex has been dated as early Late Cretaceous (95±5 m.y.) (Zartman and others, 1965), as have some alkalic rocks in Brazil.

The intrusion is essentially a ring-dike complex (fig. 1) that has metamorphosed the country rock as far as 800 m. The core of the ring dike consists of ijolite and carbonatite. The ijolite is a feldspar-free rock, which averages 2.20 percent TiO_2 and is composed of nepheline, sodium-rich pyroxene, titanium-garnet, biotite, sphene, and magnetite; the carbonatite is a coarse-grained calcite rock containing accessory sodium-rich perovskite and zirconium-rich garnet. The intermediate ring is composed of trachyte and phonolite, which average 1.8 percent TiO_2 and contain feldspar, feldspathoids, aegirine, diopside, and sphene. The outer ring consists of sphene-bearing nepheline syenite, garnet pseudoleucite syenite, and jacupirangite. Smaller dikes of alkalic rocks are abundant, both within and outside the complex, as are veins of various types. Quartz-brookite-rutile veins are most common in recrystallized novaculite on the eastern edge of the complex, and feldspar-carbonate, feldspar, quartz-feldspar, and fluorite veins containing rutile occur within the complex. Titanium deposits include the Magnet Cove rutile deposit, the Christy brookite deposit, the Hardy-Walsh brookite deposit, and the Mo-Ti brookite-molybdenite deposit. Of these, the only titanium deposit of any economic significance is the Magnet Cove deposit, which produced 5,000 tons of rutile concentrates from 1932 through 1944 (Erickson and Blade, 1963, p. 89). No production of brookite has been reported from any of the other deposits.

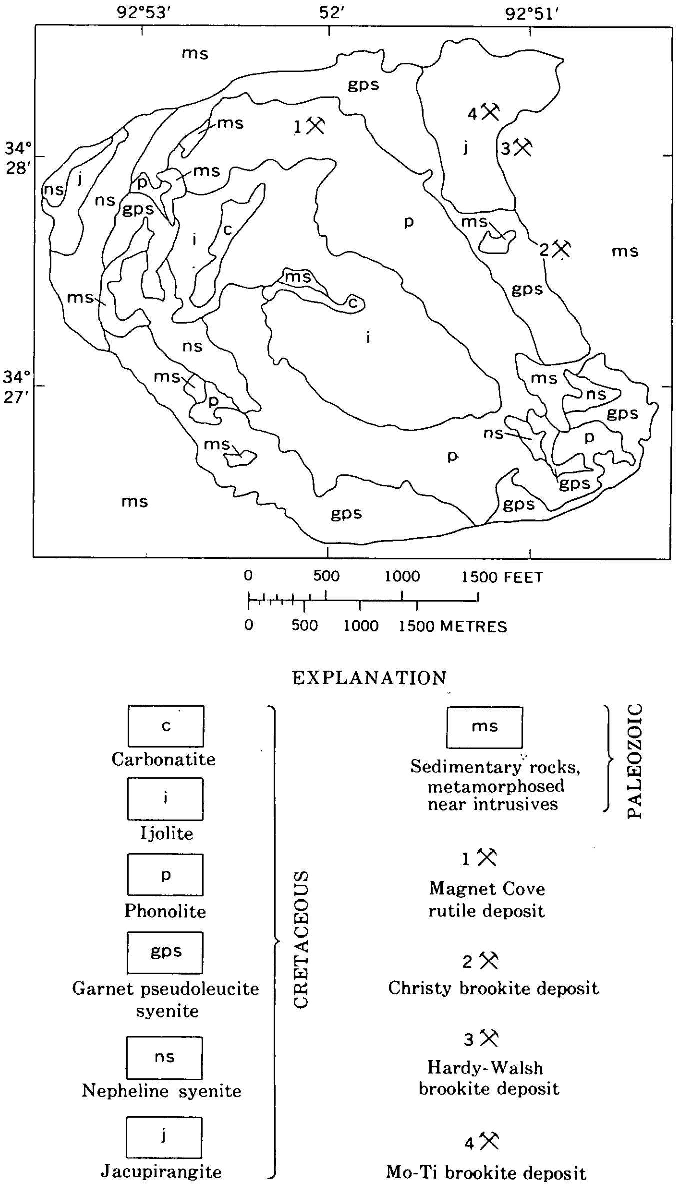

FIGURE 1.—Geologic map of the Magnet Cove area of Arkansas (after Erickson and Blade, 1963).

The Magnet Cove rutile deposit consists largely of phonolite that has been intruded, brecciated, and hydrothermally altered by a number of veins of different types. Rutile is contained in feldspar-carbonate-rutile veins and vein masses that range from several inches to tens of feet in thickness. About 15 to 20 percent of the TiO_2 in the veins is present as "leucoxene" (Fryklund and Holbrook, 1950). The average grade of the deposit is 3 percent rutile. Most of the exposed material has been weathered to a clay-rich, highly friable material; information from drill cores shows that weathering has penetrated to a depth of at least 45 m.

The estimated reserves of rutile-bearing material at Magnet Cove are 7.75 million tons containing approximately 100,000 tons of rutile concentrate containing 95 percent TiO_2 (E. C. Toewe and others, written commun., 1971). Before the deposit can be economically exploited, however, two serious problems must be solved: (1) The best present beneficiation techniques result in a recovery of less than 60 percent of the contained rutile, and (2) the rutile averages 2.2 percent Nb, 1.8 percent Fe, and 0.6 percent V (Herz, 1976, table 2; Erickson and Blade, 1963, p. 80–81)—a composition that cannot be used for welding rod coatings or for the chloride process of pigment and metal manufacturing.

KOLA PENINSULA, U.S.S.R.

Important titanium deposits are found in alkalic rocks of the extreme northwestern part of the Soviet Union, in the Kola Peninsula and in the Karelian Autonomous S.S.R. Specific information on grade and tonnages is not available, although general descriptions of the geology of the mining areas do exist (Malyshev, 1957, p. 204–207; Vlasov and others, 1966; Yudin and Zak, 1971). The area is part of the Precambrian Baltic Shield and consists largely of Archean gneisses, granites, migmatites, and granulites and Proterozoic metasedimentary and volcanic formations, gabbro-anorthosites, basalts, granites, and alkalic gabbros and granites. These are overlain by upper Precambrian and Lower Cambrian platform sediments. Paleozoic alkalic rocks, including ultrabasic-alkalic rocks 340 to 590 m.y. old and nepheline syenites about 290 m.y. old, intrude the Archean and Proterozoic rocks (fig. 2).

The ultrabasic-alkaline group of plutons consists of an earlier phase of olivinite, pyroxenite, and nepheline pyroxenite and a later group of ijolite and related rocks. The earlier ultrabasic rocks include large stocklike bodies of late magmatic perovskite-titanomagnetite ores that are enriched in rare elements (Yudin and Zak, 1971). In the largest deposit, Afrikanda, a pipelike orebody can be traced to a depth of more than 400 m. These ores are characterized by high amounts of TiO_2 (8.5–18.0 percent) and total iron (11–18 percent). The rocks of this phase are generally high in major elements Ca, Mg, Na, Fe, and Ti and in minor elements P, C, Sr, and

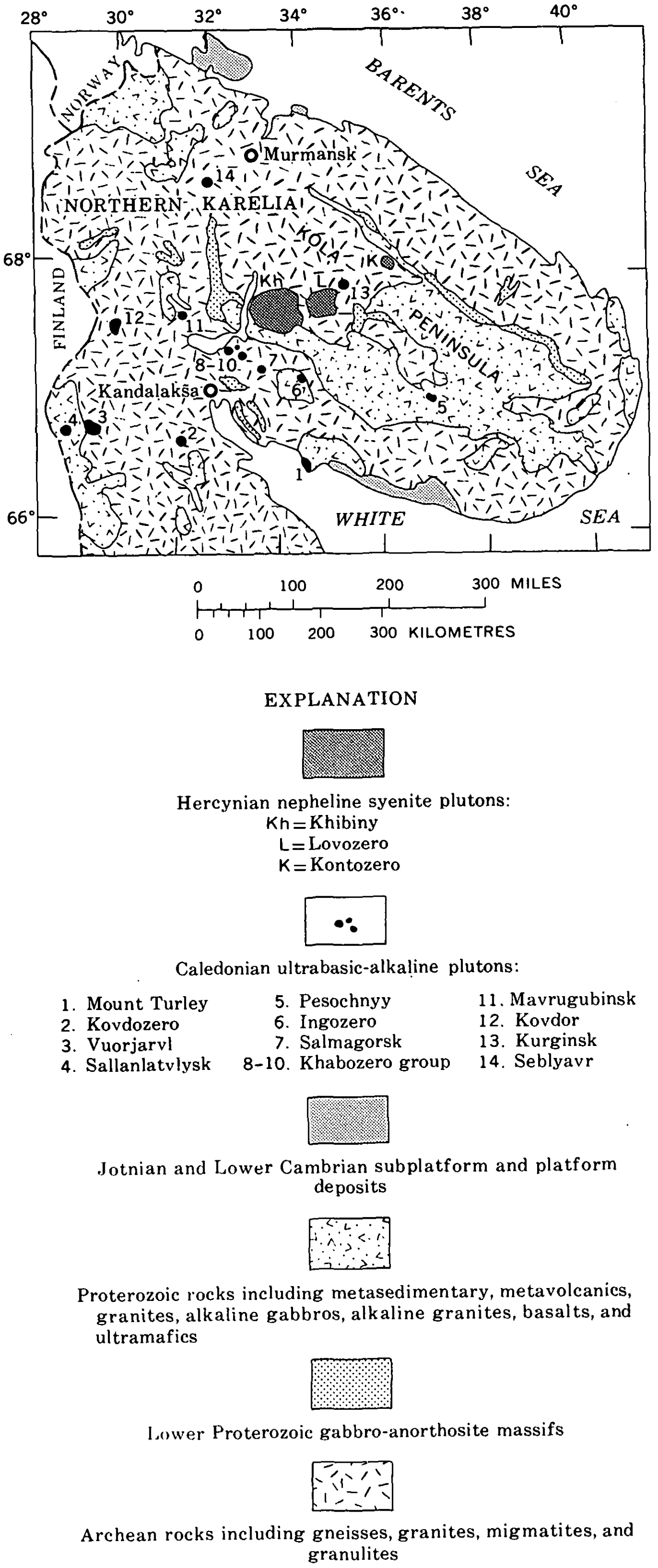

FIGURE 2.—Generalized geologic map of the Kola Peninsula and northern Karelia in the U.S.S.R. (after Yudin and Zak, 1971).

Ba; they are deficient in Si and Al. Younger alkalic plutons caused a contact metasomatism-metamorphism of some of the perovskite-titanomagnetite bodies that locally produced high-quality magnetite ores.

The younger (Hercynian) group of alkalic intrusives consists of nepheline syenite and forms larger bodies than the earlier ultrabasic-alkalic rocks; the Lovozero and Khibiny massifs are typical (fig. 2). The Khibiny is over 800 km² and is made up of seven distinct phases, which are listed in order of decreasing age (Turner and Verhoogen, 1960, p. 393):

1. Syenites and nepheline syenites that have fenitized adjacent Archean gneisses.
2. Coarse aegirine-nepheline syenite injected as a peripheral ring dike.
3. Trachytoid aegirine-nepheline syenite forming an imperfect ring within the peripheral ring dike.
4. Poikilitic micaceous nepheline syenite forming an imperfect ring and consisting of alkali feldspar, nepheline, mica, aegirine, and astrophyllite.
5. A massive cone sheet of nepheline-rich ijolite.
6. Foyaite (feldspathic rock) making up the central core of the massif.
7. Dikes of leucocratic and melanocratic alkalic rocks.

The massif is characterized by concentrations of Na, K, Al, P, F, Ti, Zr, Nb, Sr, and rare earths, especially the Ce group, and is deficient in Si, Mg, Cr, V, Co, and Ni. Segregations of ore minerals have formed in the complex as distinct rock types, including one body that is 2.4 km long and 160 m thick and composed of 45 to 65 percent apatite, nepheline, aegirine, sphene, and titanomagnetite. Zones that are enriched in sphene are 5 to 30 m thick and have an average TiO_2 content of 8 to 11 percent. Apatite and nepheline are presently mined in large quantities, and Yudin and Zak (1971, p. 871) suggested that large amounts of titanomagnetite concentrate having 13.5 percent TiO_2, 0.65 percent V_2O_5, and 42 percent total Fe are available from the tailings, as is sphene concentrate having 26 percent TiO_2.

The nearby Lovozero massif is similar to the Khibiny massif in age and overall geology but is different in titanium mineralogy. Niobium-rich perovskite (loparite) at this locality is an ore mineral of niobium and is in nepheline-rich syenite and trachytoid nepheline syenite (Vlasov and others, 1966; Parker and Adams, 1973).

TAPIRA, MINAS GERAIS, BRAZIL

Belts of alkalic rocks and widespread tholeiitic basalt are found in the southern part of Brazil (Herz, 1966). The basalt plateau of the Paraná basin, which is the largest of its kind, covers (122–133 m.y.) and the other Late Cretaceousness of 1,530 m. The peak of activity responsible for this volcanism occurred about 125 m.y. ago; the span of activity was 119 to 147 m.y. (Amaral and others, 1966). The alkalic volcanism intruded the crystalline Precambrian basement of the Brazilian Shield around the margin of the basalt, mostly to the east of it (fig. 3). Ages obtained by Amaral and others (1967) on alkalic plutons suggest two distinct episodes of volcanism, one Early Cretaceous (122–133 m.y.) and the other Late Cretaceous-early Tertiary (51–82 m.y.). Most of the volcanism, however, coincides with the younger age, and no genetic relationship is immediately evident between the alkalic rocks and the tholeiitic basalt flows.

The Brazilian alkalic rocks are mineralogically highly variable but can be grouped into four general types: (1) Nonfeldspathic rocks, including ijolites and jacupirangites, which consist largely of pyroxenes and nepheline, and titaniferous magnetite, apatite, and sphene, which are locally abundant, as they are at Jacupiranga; (2) feldspathic rocks, including nepheline syenites, tinguaites, and phonolites that consist largely of alkali feldspars, nepheline, and sodium-rich pyroxenes and sphene, apatite, and rare earth minerals that are locally abundant, as they are at Poços de Caldas; (3) carbonatites composed dominantly of carbonate minerals (calcite and dolomite), with the accessory minerals apatite, pyrochlore, perovskite, rutile, and ilmenite (examples include Jacupiranga, Araxá, and Tapira); and (4) feldspathic rocks (fenites) formed locally in place around many alkalic complexes by alkali metasomatism of country rock.

The Tapira complex was discovered in 1955 during a reconnaissance study for manganese (Alves, 1960). Alves noted strong similarities between that complex and the one just to the north at Araxá. Both are primarily carbonatites and have "explosive" intrusive characteristics such as extensive ultramylonite and breccia zones in the area of contact with Proterozoic sericite schists and quartz-sericite schists. The intrusion itself is in the form of a complex of concentric rings about 6 km in diameter. Weathering of all the rocks of the complex has been intense, so few rock types can be identified with certainty. Among those that can be identified are bos-

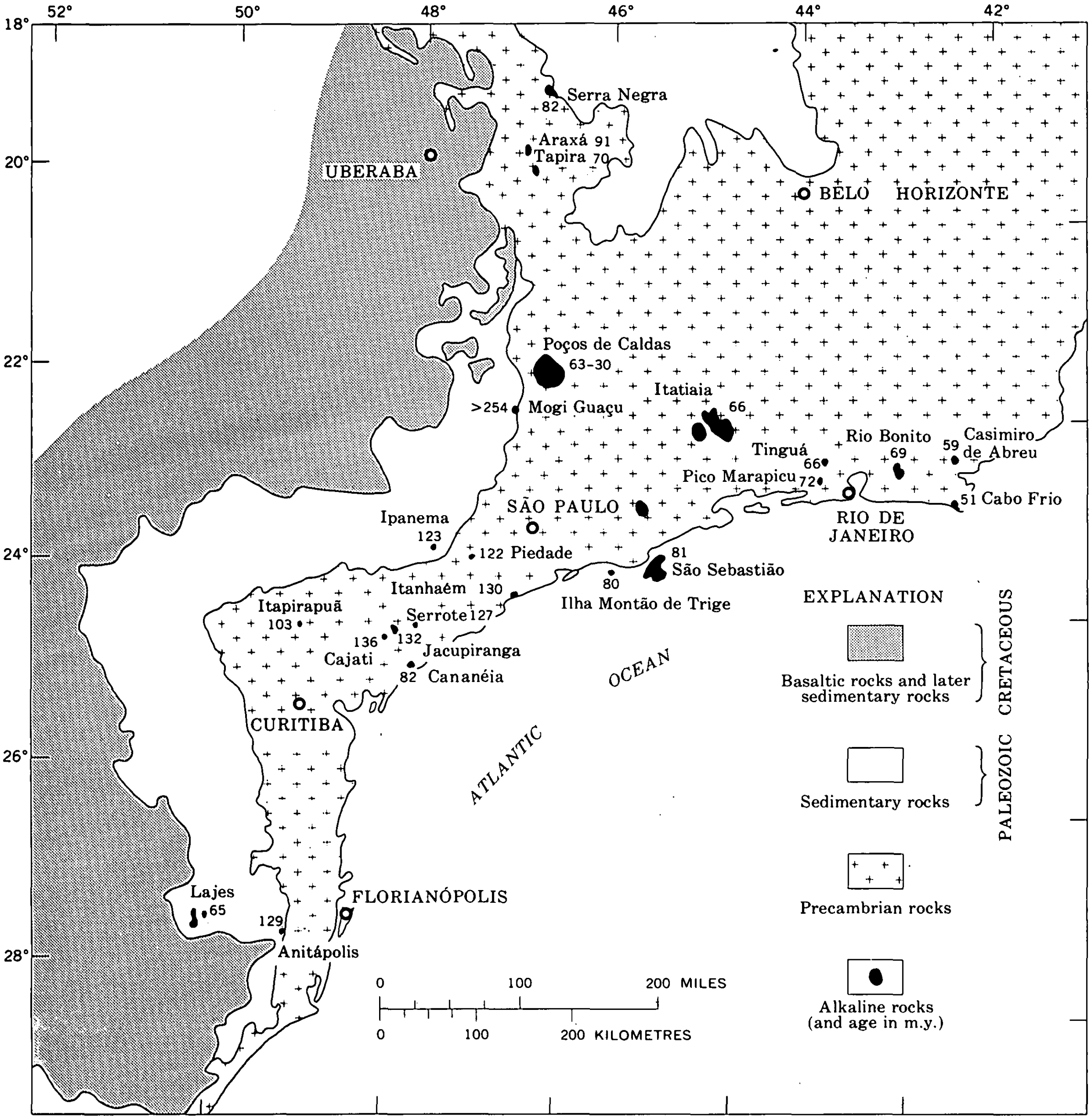

FIGURE 3.—Location and ages of alkalic rocks from southern Brazil (after Amaral and others, 1967).

tonite, which forms part of a ring in the southern part of the complex; volcanic breccia, which forms much of a ring to the southwest; and carbonatite, which is abundant throughout the central part of the complex. Large masses of other types occur, including an apatite rock of abundant perovskite and subordinate sphene and magnetite, which forms parts of two rings, an inner one, 2,000 m long and as high as 300 m on the western side, and another similar one on the eastern side.

The Brazilian Ministry of Mines and Energy (Companhia de Pesquisa de Recursas Minerais, 1972) has extensively explored the area and estimated that it contains almost 132 million tons of ore reserves (measured, indicated, and inferred) averaging 21.6 percent TiO_2. The greatest concentration of titanium minerals at Tapira is in an area about 3×4 km on which a lateritic cover about 100 m thick has formed. The primary titanium minerals of this deposit are perovskite, ilmenite, magnetite, and, rarely, rutile, but the bulk of the reserves are anatase and "leucoxene," the weathering products of the primary minerals. At least 60 percent of the total TiO_2 measured in laterite samples is present as anatase.

Perovskite occurs in veins and disseminations in the country rock; it and its weathered products form as much as 5 percent of the laterite. Magnetite and ilmenite also occur in veins and in the alkalic country rock; they and their weathered products comprise from 20 to 70 percent of some laterite.

The Tapira deposit formed mainly as a result of two processes: (1) Development of a titanium-rich segregation in the carbonatite plug, presumably as an immiscible liquid in the melt, and (2) tropical weathering, which enriched the tenor of titanium in the protore minerals at the expense of calcium and iron and perhaps also niobium. Fresh rutile from Tapira has 0.5 percent Nb_2O_5 as well as 3.5 to 6.8 percent Fe (Alves, 1960, p. 16), which renders fresh rutile from Tapira as economically handicapped as rutile from Magnet Cove, Ark. The composition of fresh perovskite is not known but is likely to be high in niobium also.

OUTLOOK

Titanium is enriched in many alkalic rocks. In many alkalic complexes, however, much of the titanium is in silicates, especially garnet and clinopyroxene; in others, where titanium forms primary minerals like perovskite and rutile, the accessory elements niobium and iron have made the minerals unusable for chloride-process manufacturing of pigment and titanium metal. Titanium at present can be considered a resource in alkalic rocks in two circumstances: (1) Where tropical weathering has produced an economic titanium product by leaching out the undesirable elements, as it has in Tapira and elsewhere in Brazil, and (2) where titanium can be obtained as a byproduct, as it can in mining for niobium and for phosphate, rare earths, and aluminum in the Kola Peninsula.

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Titanium Minerals in Deposits Of Other Minerals

By E. R. FORCE

GEOLOGY AND RESOURCES OF TITANIUM

GEOLOGICAL SURVEY PROFESSIONAL PAPER 959-F

U.S. DEPARTMENT OF THE INTERIOR
March 3, 1849

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TITANIUM MINERALS IN DEPOSITS OF OTHER MINERALS

By E. R. Force

ABSTRACT

Titanium minerals in quantities equivalent to a significant percentage of present world production are moved but not recovered from mines of other minerals. Resources of this type amount to millions of tons of contained TiO_2. Some possible sources of byproduct titanium are (1) ilmenite and minor rutile detrital concentrations in deposits of tin, monazite, gold, platinum, uranium, and sand and gravel, (2) leucoxenitized ilmenite and, locally, rutile in some bauxites, (3) rutile in porphyry copper and related deposits, (4) rutile in kyanite deposits, (5) perovskite and other titanium minerals in deposits of niobium, apatite, and nepheline in nepheline syenites, (6) rutile in alkalic anorthosite deposits of feldspar, and (7) titanium minerals in marine phosphorite.

MAGNITUDE OF POTENTIAL BYPRODUCT RECOVERY

The recovery of titanium minerals as byproducts of other minerals is of interest because limited resources are best conserved by recovery of byproducts and because competing land use and environmental considerations limit new mining of known resources. The appraisal here is intended to include only those situations in which the major product is being mined or has recently been mined; thus, considerations of the major-product economics are eliminated.

Information is available for only a small minority of specific deposits of the general types discussed. Therefore, these specific deposits are just examples. Even so, if all the ilmenite were recovered from these deposits, the present world production of ilmenite could be increased by 20 percent or more (table 1). The percentage for rutile recovery is poorly defined but is probably far greater than 7 percent; the values are limited partly by lack of major-product production figures for deposits in the U.S.S.R. and partly by lack of grade information in several other cases. Some mining operations are already contributing, as byproducts, at least 5 percent of present world titanium production; in still others, titanium minerals are major coproducts.

SAND AND GRAVEL MINING OPERATIONS

Ilmenite and rutile are common minor minerals in a great many fluvial and marine sands and in sandstones. If some other mineral could be mined from these sands and sandstones, ilmenite and (or) rutile could also be recovered; the cost of byproduct recovery, however, is not evaluated herein.

Scant information is available about the presence of titanium minerals or the feasibility of their recovery for certain types of large sand-mining operations, particularly gold and platinum placers and uranium mines in sandstone. Types of deposits for which more information is available are described below.

Tin placers and their "amang" byproducts.—In Malaya, and to a lesser extent in Thailand, alluvial placer deposits mined primarily for cassiterite (tin) are also the source of byproduct ilmenite and other minerals, which are collectively called "amang." All the recovered minerals are apparently derived from granitic stocks.

The ilmenite concentrate from amang is low in chromium and contains about 53 percent TiO_2; thus, it is good raw material for the manufacture of pigment (Industrial Minerals, 1972). As a result of byproduct recovery alone, Malaya currently ranks fifth in the world among ilmenite producers (Noe, 1973). Production of ilmenite from amang could increase about 30 percent if recovery were increased in Thailand and Indonesia, if it is assumed that ilmenite contents are similar throughout the province (from values given by Noe (1973) and in Industrial Minerals (1972)). Hypothetical resources of ilmenite are on the order of 20 million tons (from figures

TABLE 1.—*Estimated resources and potential yearly production of titanium minerals from some deposits of other minerals*
[H, hypothetical; I, identified; R, reserves]

Type	Deposit	Country	Mineral	Estimated resource (10^6 tons)	Potential yearly production (10^3 tons)	Recovered?
Tin placers	-----	Malaya, Thailand, Indonesia.	Ilmenite	15 (H)	240	Mostly.
		Nigeria	do	.2 (H)	1	No?
Multiproduct placers.	Valley County, Idaho.	United States	Low TiO_2 ilmenite	1 (I)	30	When mined.
Sand and gravel	-----	Southeastern United States.	High TiO_2 ilmenite	-----	186	No.
			Rutile	-----	17	No.
Bauxite	-----	-----	High TiO_2 ilmenite	-----	100	No.
	Madras and Orissa	India	Rutile	.06 (R)	---	No.
Porphyry copper	Bagdad, Ariz	United States	do	-----	3	No.
Kyanite	Quartzites	do	do	.4 (I)	2	No?
Anorthosite	Montpelier, Va	do	do	-----	2	Heavy tailings.
Marine phosphorite.	Aurora, N.C	do	Ilmenite	-----	10	No.
	Bone Valley Formation, Fla.	do	High TiO_2 ilmenite	-----	10	No.
			Rutile	-----	1	No.

given by Sainsbury and Reed (1973) and Noe (1973)).

Alluvial cassiterite deposits of Nigeria also contain ilmenite and rare rutile; ilmenite recovery could amount to roughly one-third to one-sixth of the cassiterite production (Mackay and others, 1949). Here, the titanium minerals and the cassiterite apparently have different source rocks, and some lean cassiterite resources have abundant ilmenite and rutile (Raeburn, 1926).

Multiproduct placers of Idaho.—Alluvial placers in and near Valley County in Idaho have been intermittently worked for monazite, euxenite, columbite, tantalite, zircon, ilmenite, and garnet. The deposits are in immature gravel derived from granitic rocks of the Idaho batholith; some of the minerals are localized around specific sources. The placers contain more than 1 million tons of ilmenite (Savage, 1961, 1964), but the average grade is too low to justify mining for ilmenite alone. The "ilmenite" averages 45 percent TiO_2 and has not been used for pigment (Storch and Holt, 1963).

Sand and gravel pits in southeastern United States.—Davis and Sullivan (1971) showed that ilmenite, rutile, and other heavy minerals could be recovered from sand and gravel mined mostly from Cretaceous sandstone and modern alluvium in the southeastern United States. Total heavy minerals average 1 to 2 percent; ilmenite is the most abundant heavy mineral. The TiO_2 contents of ilmenite varied from 51 to 68 percent.

The southeastern States produce only 2 percent of the Nation's sand and gravel. The potential production of ilmenite and rutile from sand and gravel pits in other areas of the United States is unknown; the southeast, however, is probably the most favorable area because the intense weathering there produces high TiO_2 ilmenite. Sand and gravel operations in some tropical countries would likewise be promising sources of titanium minerals.

TITANIUM MINERALS IN BAUXITE

The chemical enrichment of TiO_2 and the residual enrichment of ilmenite and rutile during weathering are particularly evident in bauxitization, and many authors have discussed the possibility of recovering titanium minerals as well as alumina from bauxite (Calhoun, 1950; Patterson, 1967; Stamper, 1970, p. 449). According to Hartman (1959), titanium in bauxite commonly occurs both as grains of ilmenite greatly enriched in TiO_2 ("leucoxene") and as TiO_2 polymorphs finer than 40 μ. The fine-grained material is difficult to separate, and perhaps separation would require chemical means. Some Hawaiian bauxites (Sherman, 1952; Patterson, 1971) and some red mud waste from Indian bauxites (Patterson, 1967, p. 7) contain more than 20 percent TiO_2.

Grains of ilmenite or of "leucoxene" consisting of anatase and rutile are present in most bauxites, and, in bauxite over parent rocks containing significant amounts of ilmenite (such as volcanic rock, sandstone, schist, and syenite), the grains commonly comprise more than 0.5 percent of the bauxite (Hartman, 1959). Such bauxites amount to about one-third of the total bauxite production (from data given by Patterson (1967) and Kurtz (1973, table 16)). It seems plausible that 100,000 tons of ilmenite and "leucoxene" are being discarded each year from these bauxites.

Bauxite in Madras and Orissa States in India (Roy Chowdhury, 1955, p. 210–211) is derived from weathering of leptynite (quartz-garnet-feldspar gneiss) and khondalite (quartz-sillimanite-garnet-graphite gneiss). These rocks probably contain rutile, as do similar rocks nearby; if so, rutile is probably present in the bauxite. On the basis of bauxite reserve estimates (Patterson, 1967, p. 10a) and the assumption that fresh rock contains 0.5 percent rutile, the maximum amount of rutile present is about 60,000 tons. Rutile may also be present in bauxite over gneiss in Guinea in West Africa.

RUTILE IN PORPHYRY COPPER AND RELATED DEPOSITS

Rutile is a common product of hydrothermal alteration in the porphyry copper deposits of the southwestern United States (Creasey, 1966; Schwartz, 1966). At Bagdad, Ariz., it is present in copper ore (Anderson and others, 1955). This rutile contains about 2 percent Nb. Creasey (1966) found that, in propylitic zones of alteration, rutile is present only as "leucoxene," whereas single grains of rutile are present in the argillic zones. Thin sections collected by R. G. Schmidt and D. P. Cox (U.S. Geological Survey) from San Manuel and Ajo porphyry copper deposits show that grains of rutile coarser than 20 μ are limited to the zone of potash feldspar; in this zone, these grains are as coarse as 0.3 mm. Sphene is present with or in place of rutile in several specimens containing carbonate from Ajo; in two such specimens, the weight percent of rutile was 0.08 and 0.10.

Some other types of porphyry and related deposits also contain rutile. A quartz dioritic porphyry copper deposit in Puerto Rico contains rutile (Cox and others, 1973, fig. 4). Rutile, high in niobium, is present in the Climax, Colo., molybdenum porphyry deposit (Wallace and others, 1968, p. 626) and the Urad, Colo., tungsten molybdenum porphyry deposit (P. K. Theobald, oral commun., 1974). Rutile is being produced (A. L. Clark, oral commun., 1973), along with copper, apatite, vermiculite, baddeleyite, monazite, Ti-magnetite, and pyrite, from a mafic alkalic deposit at Palabora, South Africa (South African Mining and Engineering Journal, 1970).

Possibly two reactions are responsible for rutile in hydrothermally altered porphyries. The first involves the introduction of sulfur. Kullerud and Yoder (1963) found that mafic minerals, such as biotite and hornblende, break down in the presence of sulfur to form pyrite, magnetite, and stripped silicates. Although Kullerud and Yoder did not observe titanium minerals among the reaction products, a balanced equation having biotite or hornblende among the reactants would imply their presence. In porphyry copper deposits, high-TiO_2 magmatic biotite breaks down to low-TiO_2 hydrothermal biotite (Moore and Czamanske, 1973), and magmatic titaniferous magnetite breaks down to stoichiometric hydrothermal magnetite (Hamil and Nackowski, 1971). Since sulfides are present, the similarity to Kullerud and Yoder's reactions is apparent; the liberated TiO_2 apparently forms rutile. Probably rutile and copper ore minerals are to some extent products of the same reaction. Rutile in altered mafic intrusives associated with replacement sulfide copper deposits at the Haile mine (Pardee and Park, 1948, p. 112; TiO_2 polymorph is actually anatase, Norman Herz, written commun., 1970) and at the Fontana mine in the southeastern United States also indicates the importance of sulfur in reactions producing rutile.

The second reaction involves the introduction of CO_2. Schuiling and Vink (1967) found that equilibrium between rutile, sphene, and carbonate is a function of CO_2 pressure; high CO_2 pressure pushes the reaction toward rutile and carbonate. At Ajo, the coexistence of all three phases implies unusually high CO_2 pressure.

RUTILE IN KYANITE DEPOSITS

Espenshade and Potter (1960) reported the presence of rutile in kyanite quartzites of the southeastern United States. The rutile content averaged about 0.5 percent in the quartzites analyzed. Identified resources are on the order of 400,000 tons of rutile (from figures given by Espenshade and Potter (1960) and Espenshade (1973)).

Rutile is present in the important kyanite deposits of northern India, but the grade has not been reported (Varley, 1965). Rutile of grades locally as high as 3 percent is commonly present in other deposits of alumino-silicate minerals (Varley, 1965; Espenshade, 1973).

TITANIUM MINERALS IN NEPHELINE SYENITES

Alkalic rocks of the Kola Peninsula are mined for a variety of commodities by means of techniques not common outside the U.S.S.R. Herz (1976b) discusses a situation in which titanium minerals could be a byproduct of mining nepheline (aluminum) and apatite (phosphate and rare earth) from nepheline syenite at the Khibiny massif and of mining Nb-perovskite (niobium) from nepheline syenite at the Lovozero massif.

RUTILE IN ANORTHOSITIC FELDSPAR DEPOSITS

Antiperthitic andesine feldspar is mined from alkalic anorthosite in two areas of Piedmont Virginia. One is the Roseland district, a formerly important source of rutile (Herz, 1976a). Figures for the amount of rutile in the feldspar ore are not available, but, since the areas of the best feldspar and the most rutile are not coextensive, the amount is probably small. The other area is near Montpelier. Rutile was formerly mined here also, from the same pits in which feldspar is now mined. The rutile is coarse grained and occurs as rods in intensely lineated anorthosite. Rutile, sphene, apatite, and ilmenite are presently accumulating in a "heavy tailings" pond.

TITANIUM MINERALS IN MARINE PHOSPHORITE

Ilmenite, rutile, and other valuable heavy minerals are present in the waste products from phosphate mining in Florida (Stow, 1968). These minerals are present as clastic grains in phosphate pebble conglomerate of the Bone Valley Formation, where they compose, on the average, 0.23 percent of the conglomerate (Pirkle and others, 1967). The TiO_2 content of ilmenite is more than 60 percent (Stow, 1968), probably because of weathering alteration. Lamont and others (1972) found recovery of the heavy minerals to be limited by their fine grain size.

Lewis (1974; written commun., 1975) found that phosphate at Aurora, N.C., contains about 0.1 percent ilmenite and that tailings from the flotation plant contain 2.5 percent ilmenite. The TiO_2 content of the ilmenite is 52 percent. A channel sample taken by F. W. Whitmore (U.S. Geological Survey) across about 9 m of Pleistocene(?) silty sand overburden at the mine contains about 0.4 percent fine-grained ilmenite (overburden is not included in table 1).

TITANIUM MINERALS WITH VANADIUM, PLATINUM, AND CHROMIUM IN STRATIFORM MAFIC IGNEOUS ROCKS

Titanium minerals occur within the Bushveld complex of South Africa in some of the world's most important reserves of vanadium, platinum, and chromium.

Vanadium ore occurs as magnetite in plugs and cumulative layers in the upper part of the complex. The ore contains ilmenite as discrete cumulate grains and both ilmenite and ulvospinel as intergrowths in magnetite (Willemse, 1969). The coarser ilmenite comprises from 1 to 10 percent of the ore (Molyneux, 1970). An average of 1 percent would imply about 2 million tons of ilmenite in the ore reserves.

Platinum ore occurs in the Merensky Reef, downsection in the complex. Platinum is present as many compounds in pyroxenite. Other platinoids, gold, nickel, and copper are byproducts. Ilmenite and rutile are present as accessory minerals; a maximum amount of about 2 percent (Cousins, 1969) is set by TiO_2 content.

Cumulate chromite forms chromitite in the lower part of the complex. Rutile is present in some seams as interstitial crystals, but a maximum of 0.4 to 0.7 percent is set by TiO_2 content (Cameron and Emerson, 1959). Because the chromite is smelted in bulk form, rutile cannot presently be recovered.

Similar possibilities of titanium mineral recovery probably exist in other complexes. The chromite deposits of Fiskenaesset, Greenland, contain rutile (Ghisler and Windley, 1967). In some deposits of ilmenite in mafic igneous rocks, vanadium is a byproduct, as it is at Otanmaki, Finland; in other similar rocks, titanium could possibly be the byproduct.

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