

ALTERATION OF ILMENITE IN THE CRETACEOUS SANDSTONES OF NOVA SCOTIA, SOUTHEASTERN CANADA

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Abstract—Most detrital ilmenite grains in sandstones of the Chaswood Formation are completely altered to pseudorutile, leucoxene and rutile. The textural, chemical and mineralogical changes involved in alteration were tracked using electron microprobe analyses, backscattered electron images, and elemental maps. Ilmenite grains ($Ti/(Ti+Fe) \approx 0.48$) alter patchily to pseudorutile ($Ti/(Ti+Fe) 0.5–0.7$) with volume loss, forming a porous structure and this process continues with the development of leucoxene ($Ti/(Ti+Fe) 0.7–0.9$). Within the pseudorutile and leucoxene, stubby prismatic rutile crystals have been precipitated. Si and Al occur in the altered ilmenite, either (1) inherited from original quartz and muscovite inclusions in the parent crystal or (2) as kaolinite altered from muscovite inclusions or precipitated in the pore space, under pedogenic or early diagenetic conditions. Distribution of alteration phases has been related to facies and diagenetic variations. With increasing amounts of leaching in different types of paleosols, there was increasing alteration of pseudorutile to leucoxene. In light gray mudstones and interbedded sandstones with diagenetic kaolinite that formed beneath the water table from percolating meteoric water, most leucoxene was converted to rutile. Burial diagenesis (to vitrinite reflectance values $>0.4\%$) also promoted the change from leucoxene to rutile. The alteration of ilmenite is an important source of Fe for diagenetic minerals in the Chaswood Formation and correlative offshore deltaic and marine facies of the Scotian basin.

Key Words—Alteration, Diagenesis, Ilmenite, Pseudorutile, Rutile

INTRODUCTION

Setting and purpose of the study

Lower Cretaceous fluvial and deltaic sedimentary rocks were deposited in Nova Scotia and the offshore Scotian basin (Figure 1) under warm humid conditions (Falcon-Lang *et al.*, 2003). Detrital ilmenite was an important component of the sandstones. It is well known from the literature that ilmenite alters during transport and diagenesis with progressive loss of Fe (*e.g.* Teufer and Temple, 1966; Force, 1991; Schroeder *et al.*, 2002, 2004). It alters first to pseudorutile (a mineral with a well defined structure), then to leucoxene (a fine-scale mix of pseudorutile and rutile) and finally to either anatase or rutile. The Fe that is released by this process is available to form such neomorphic or diagenetic minerals as goethite, hematite, pyrite, siderite, sepiolite and chlorite. The paleoenvironment, weathering and diagenesis of the Lower Cretaceous rocks of Nova Scotia are well known and present a range of conditions that can be compared with the observed character of ilmenite alteration products.

The purpose of this work is to use the alteration of the ilmenite in the Lower Cretaceous rocks of Nova Scotia to (1) understand the nature of Cretaceous weathering

and early diagenesis; (2) investigate the chemical changes that ilmenite suffers as alteration proceeds, and in particular what elements are released in the soil and what elements are retained and if the latter elements can be of use in defining provenance; (3) investigate the nature of enrichment in Al and Si of the ilmenite alteration products, which is significant if the sands are mined as a source of titanium; and (4) investigate how much of the alteration of ilmenite grains took place (a) by weathering in the source area, or (b) by *in situ* soil weathering or (c) during burial diagenesis.

GEOLOGICAL SETTING

The Cretaceous sandstones and mudstones on land in Nova Scotia form the Chaswood Formation, up to 200 m thick (Figure 2), which is best preserved in a series of fault-bound basins in central Nova Scotia (Figure 1). The Chaswood Formation consists of a variety of terrestrial facies, principally fluvial sandstone and conglomerate, overbank kaolinitic mudstone with paleosols, and swamps that are now represented by lignite. The upper part of the formation is only loosely consolidated, but the lowest sandstones are well indurated. Ilmenite is the most abundant heavy mineral in the Chaswood Formation sands, making up 40–90% of the heavy mineral fraction and comprising as much as 0.4% of very fine-grained sandstone and progressively smaller proportions of coarser sandstone and conglomerate (Figure 3).

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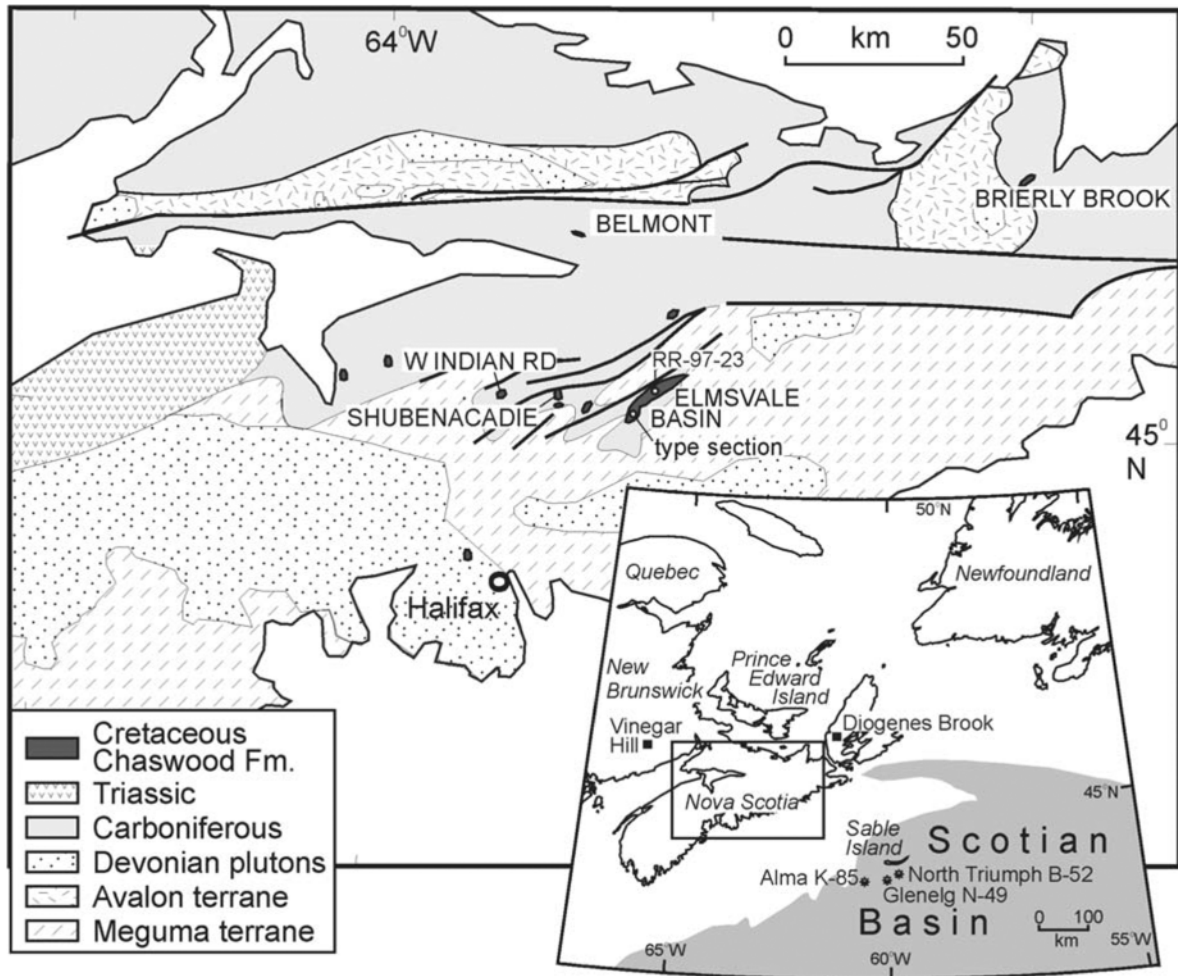


Figure 1. (a) Map of central Nova Scotia showing distribution of the Cretaceous Chaswood Formation and studied locations. (b) Inset of Atlantic Canada showing distribution of the stratigraphically equivalent offshore rocks of the Scotian Basin, locations of wells mentioned in the text, and the Chaswood Formation outliers not shown in Figure 1a.

Stea and Pullan (2001) defined a type section for the Chaswood Formation with three members in boreholes south of Chaswood (Figure 1). These three members can be correlated to borehole RR-97-23, studied in detail by Pe-Piper *et al.* (2005c), and to a series of boreholes at Shubenacadie (Figures 1, 2) (Piper *et al.*, 2005). Farther west, at the West Indian Road pit (WIRP) (Gobeil, 2002), the main sandstone and conglomerate succession is tentatively correlated with the Upper Member at the type section. Moisture content in lignite (Hacquebard, 1984) suggests burial of the Chaswood Formation by ~700 m of Upper Cretaceous and Paleogene strata, now removed by erosion. This interpretation is consistent with apatite fission track (Grist and Zentilli 2003) and vitrinite reflectance data (Hacquebard, 1984; Davies *et al.*, 1984; Stea *et al.*, 1996).

Three styles of Lower Cretaceous soil formation are recognized. (1) In the middle of the Lower Member at borehole RR-97-23 (units M1 and M2, Figure 2) and correlative strata at Shubenacadie, dark gray organic-

rich mudstones predominate, with some lignite and thin sandstones. These rocks contain gley paleosols with early diagenetic pyrite and siderite. (2) Much of the upper part of RR-97-23 consists of Oxisols with pedogenic development of kaolinite and hematite in mudrocks and some hematite staining in interbedded sandstone. In places, hematitic Oxisols are developed in sediment that earlier hosted diagenetic pyrite and siderite. (3) In the thick porous gravelly sandstones at WIRP, goethite is the predominant early diagenetic mineral, forming in Spodosols below intra-formational unconformities. Thick sandstone successions in the Shubenacadie boreholes appear similar.

Previous studies of ilmenite alteration

It is well established in the literature that detrital ilmenite alters readily during fluvial transport and soil formation under warm, humid conditions (Temple, 1966). Ilmenite alters first to pseudorutile, and then either to rutile (*e.g.* Grey and Reid, 1975) or to anatase

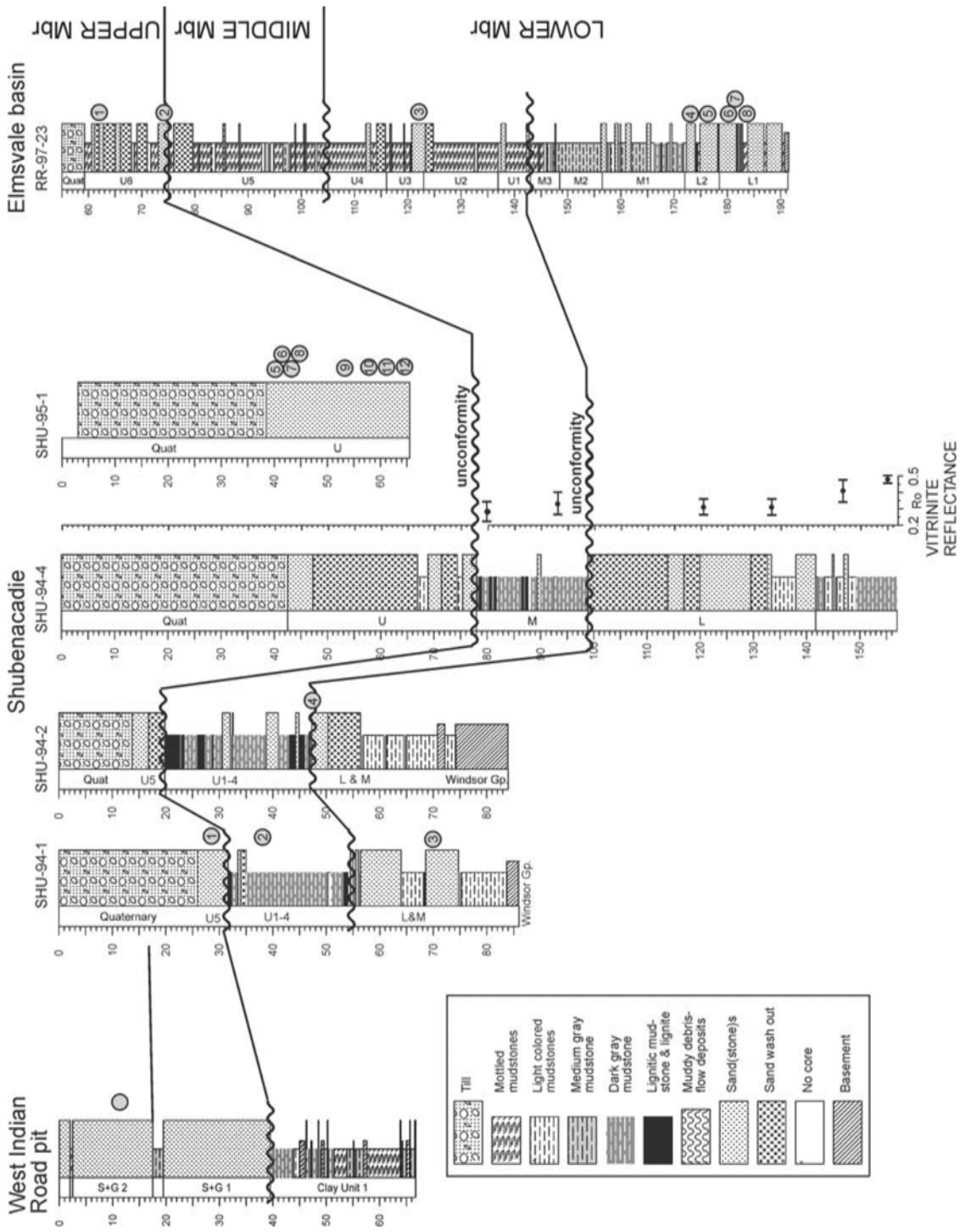


Figure 2. Stratigraphic sections of the Chaswood Formation, showing the locations of samples, lithologies, local stratigraphic units (U, M, L, U6, S+G2 etc.), regional stratigraphic correlation into Upper, Middle and Lower members. Vitritine reflectance in borehole SHUB-94-4 based on Stea *et al.* (1996).

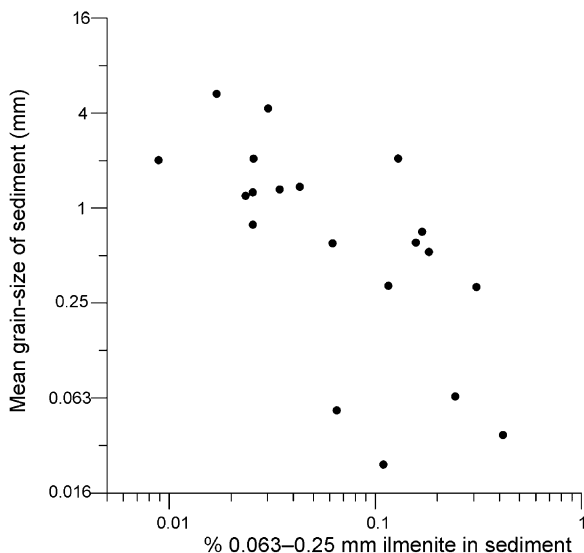


Figure 3. Variation in ilmenite abundance with grain-size in sandstones and mudstones from boreholes in the Chaswood Formation at Shubenacadie (based on data in Pe-Piper *et al.* 2004).

(*e.g.* Anand and Gilkes, 1984). The term leucoxene is applied to a mixture of disordered pseudorutile and rutile. Teufer and Temple (1966) and Grey and Reid (1975) found that microcrystalline rutile in altered ilmenite grains developed as oriented aggregates by epitaxial growth upon the close-packed anion layers of ilmenite. According to Grey and Reid (1975), rutile in altered ilmenite grains is present in a triply twinned arrangement and probably resulted from dissolution followed by epitaxial precipitation of TiO_2 . In contrast, Anand and Gilkes (1984) and Schroeder and Shiflet (2000) found anatase, not rutile, to be developed from the alteration of ilmenite.

MATERIALS AND METHODS

This study is based on detailed examination of the alteration patterns of the ilmenite that occurs in the sands and sandstones of borehole RR-97-23 in the central Elmsvale basin, three boreholes at Shubenacadie to the NW of the Elmsvale basin, and in the WIRP farther to the west (Figure 1). The setting of the samples used in this study is detailed in Table 1. Samples were disaggregated and sieved to separate the 63–250 μm fraction and polished thin-sections were prepared from heavy mineral separates (using tetrabromoethane) for petrographic observations. Those polished thin sections with the most informative textures were examined by electron microprobe. In addition, sandstone samples were examined from conventional core from the offshore wells Alma K-85, North Triumph B-52 and Glenelg N-49 (Figure 1) and polished thin-sections were made. Sandstones were also examined from outliers of Chaswood Formation at Brierly Brook,

Diogenes Brook and Belmont in northern Nova Scotia and Vinegar Hill in southern New Brunswick (Figure 1).

Minerals were analyzed with a JEOL-733 electron microprobe having four wavelength spectrometers and a Tracor Northern 145 eV energy-dispersion detector. The beam was operated at 15 kV and 20 nA, with a beam diameter of 1–10 μm . Data were reduced using a Tracor Northern ZAF matrix-correction program. Mineral morphology was characterized using backscattered electron images (BEI). Elemental maps were made of selected grains using the wavelength dispersive spectrometer, with a beam diameter of <1 μm and 80–90 ms counting time per 1–2 μm pixel size. The geochemical diagrams used in this paper are based on ~300 spot analyses. Geochemical data are publicly available in a series of Open File reports (Pe-Piper *et al.* 2004, 2005a, 2005b).

MAJOR ELEMENT CHEMISTRY OF ILMENITE ALTERATION PRODUCTS

Partially altered ilmenite grains from the Chaswood Formation show an increase in TiO_2 and a corresponding decrease in Fe compared with unaltered ilmenite. We use the ratio $\text{Ti}/(\text{Ti}+\text{Fe})$ to name the mineral phases in the altered grains, based on Frost *et al.* (1983), with ilmenite <0.5; pseudorutile 0.5–0.7; leucoxene 0.7–0.9; and rutile >0.9 (Figure 4). The ‘pseudorutile’ so defined consists of a microcrystalline mix of the minerals ilmenite and disordered pseudorutile, whereas ‘leucoxene’ is a mix of disordered pseudorutile and rutile. The individual phases in these microcrystalline mixtures are too small to analyze separately by electron microprobe. The distinction of rutile from anatase is based: (1) on the mode of occurrence of the TiO_2 minerals as observed in back-scattered electron imagery (BEI) and (2) X-ray diffraction (XRD) analysis of bulk rock samples of both sandstone and mudstone (Pe-Piper *et al.*, 2005c). The latter identifications have indicated the presence of rutile, but only rarely, and with a lower level of confidence, the presence of anatase.

Representative analyses of all mineral phases, with their atomic formulae, found in the altered ilmenite grains of this study are given in Table 2. The atomic formula of pseudorutile was calculated on the basis of 9 oxygen atoms and of rutile on the basis of 2 oxygen atoms, assuming all of the Fe is present as Fe^{3+} . The atomic formulae of analyses giving compositions between rutile and pseudorutile were calculated as if they were pseudorutile. Representative chemical analyses of other minerals associated with altered ilmenite grains are given in Table 3.

Samples from all stratigraphic levels of the RR-97-23 borehole (Figure 4, Table 1) consist principally of pseudorutile with $\text{Ti}/(\text{Ti}+\text{Fe})$ values of 0.5–0.7. A small number of analyses have $\text{Ti}/(\text{Ti}+\text{Fe})$ between 0.7 and 0.95 (leucoxene) and a larger number are almost

pure rutile. Samples from the Shubenacadie boreholes show a greater abundance of ilmenite and also of leucoxene. In contrast, most samples from the WIRP have Ti/(Ti+Fe) values between 0.65 and 0.9 (leucoxene) (Figure 4). In offshore wells, ilmenite, pseudorutile and leucoxene grains are infrequent, but rutile apparently derived from alteration of ilmenite is common.

TEXTURES OF ALTERED ILMENITE

The alteration products of the ilmenite, in most cases, are interpreted to have retained the overall shape of the parent ilmenite. Backscattered electron images (Figures 5–7) show a wide range of textures, some of which may be inherited from the original ilmenite and others that are interpreted as entirely or principally diagenetic. Elemental maps of selected grains (Figures 8–12) also reveal textural changes, as the Ti/(Ti+Fe) ratio changes with progressive alteration.

The simplest grains are those that appear to have altered from homogeneous ilmenite grains, such as Figure 6a and the small grain in Figure 6e. Some

ilmenite grains have large numbers of unoriented rounded inclusions of quartz (Figures 5c,d; 7a,b) and in some cases other minerals such as tourmaline (Figure 5a), suggesting that they may be derived from granite.

The alteration of uniform ilmenite grains is characterized by dark, dusty areas, probably due to the creation of pores as the development of pseudorutile begins (Figure 6a). Commonly, annular voids develop around rounded quartz inclusions (Figures 5c,d), some of which appear filled with clay minerals (Figure 9d). In some samples, low reflectivity areas in BEI (corresponding to dusty areas in transmitted light) are very elongate (Figures 5b,c). Pseudorutile and leucoxene alteration may occur in zones (*e.g.* Figure 5a), in which the variation in Fe, Mn and Ti is quite patchy (Figure 8a,b). Other grains have more homogeneous development of pseudorutile-leucoxene (central part of Figure 5d), allowing better quality electron microprobe analyses and more uniform distribution of Ti, Fe and Mn, as shown in the central part of the grain in Figure 10. In other grains, irregularity in the distribution of Ti, Fe and

Table 1. Summary of sample locations and abundance of alteration phases of ilmenite.

Location or borehole	Depth (m) (or field sample number)	Sample number	Soil-forming or diagenetic environment*	Number of grains analyzed	Number of ilmenite grains	Number of pseudo-rutile grains	Number of leucoxene grains	Number of rutile grains	% rutile
SHUB 94-1	29.0	1	?3	6	0	1	2	3	50.0
	38.1	2	1	8	2	4	2	0	0.0
	73.2	3	4	6	0	1	1	4	66.7
SHUB 94-2	47.2	4	?2	8	0	5	1	2	25.0
SHUB 95-1	34.4	5	?2	4	4	0	0	0	0.0
	40.0–40.9	6	?2	30	7	7	16	0	0.0
	44.0–44.4	7	?3	10	4	2	1	3	30.0
	45.4	8	?3	8	5	1	2	0	0.0
	55.3	9	?3	3	1	2	0	0	0.0
	58.9	10	?3	9	0	8	1	0	0.0
	61.9	11	?3	17	0	6	10	1	5.9
	64.9	12	?3	7	0	1	4	2	28.6
RR-97-23	62.4	1	2	23	0	19	2	2	8.7
	74.0	2	2	29	0	23	1	5	17.2
	123.0	3	2	26	1	18	3	4	15.4
	173.9	4	1	5	0	5	0	0	0.0
	177.3	5	2	15	0	10	1	4	26.7
	180.5	6	2	18	0	10	3	5	27.8
	181.1	7	2	30	0	19	2	9	30.0
	184.6	8	2	5	0	0	0	5	100.0
WIRP	S50-3.5		3	15	0	4	7	4	26.7
	S50-4.0		3	9	0	3	4	2	22.2
	S56-3.0		3	14	0	1	6	7	50.0
	S56-3.5		3	16	0	3	11	2	12.5
	S70-3.0		3	27	0	2	17	8	29.6
	S70-3.5		3	21	0	3	12	6	28.6

* 1 = poorly-drained organic-rich soil; 2 = mudstone with Oxisol; 3 = thick porous gravelly sands; 4 = kaolinite diagenesis below the water table by percolating meteoric water. ? indicates uncertainty because of poor recovery of sample from boreholes.

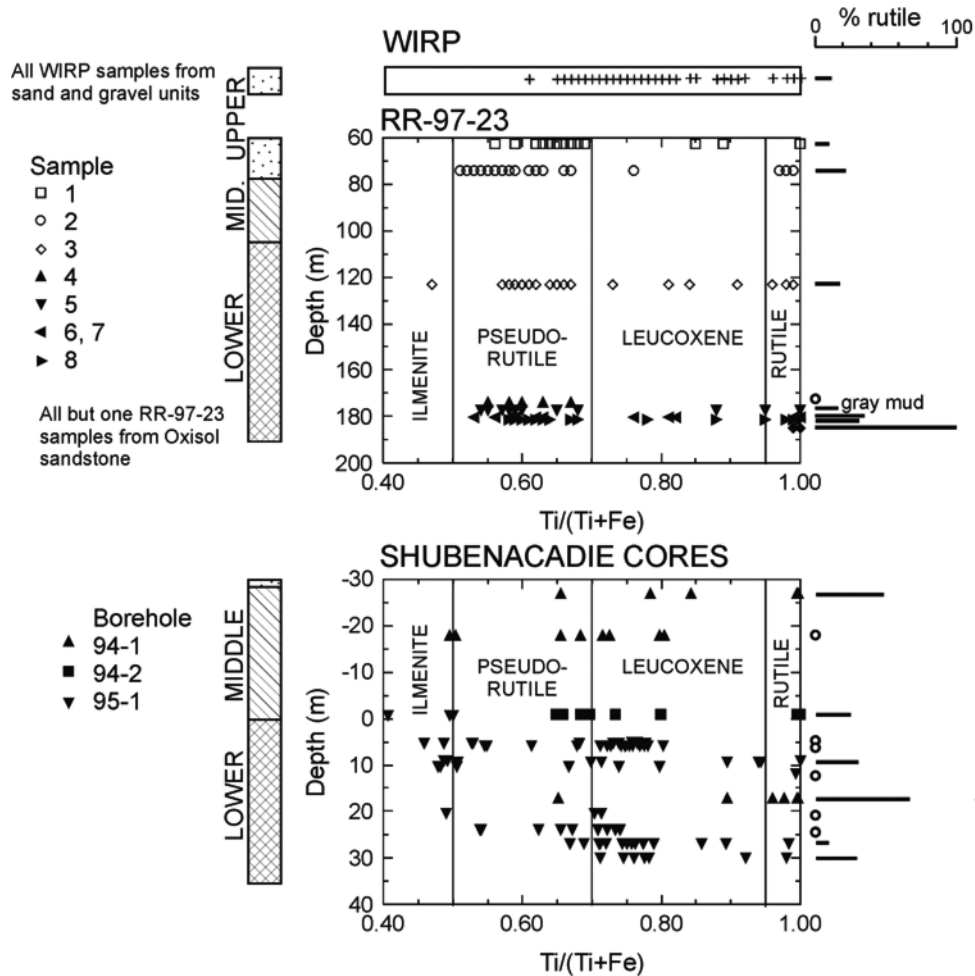


Figure 4. Variation with stratigraphic level of $Ti/(Ti+Fe)$ atomic ratio (alteration of ilmenite) and the abundance of rutile.

Mn is on the scale of μm -sized crystallites (Figure 11a–c).

Some grains show textures of rutile that resemble the textures developed during high-temperature oxidation of ilmenite exsolved from titanomagnetite with cubic symmetry, including the trellis-type structure (nomenclature of Haggerty, 1976) shown by rutile in Figures 6d, 5e and the margins of 7b. Similar epitaxial rutile crystallites are present in places in the grain in Figure 5d. The short spindles of rutile in Figure 5f also resemble an ilmenite exsolution texture. The rutile plates illustrated in Figure 5c resemble the sandwich style of ilmenite exsolution, principally along one set of $\{111\}$ planes. In this grain, the low reflectivity (dark) linear zones orthogonal to the rutile plates have Fe, Ti and Mn content (Figure 9) similar to that of the higher reflectivity (lighter) rutile plates, but in transmitted light appear dusty. Blocky euhedral crystals with octahedral terminations pseudomorphed by rutile (Figure 5f) resemble the composite style of ilmenite exsolution from titanomagnetite. In contrast, textures such as wispy lenses of rutile

particularly along $\{0001\}$ planes (Figures 5b, 6b and 7d) are characteristic of high-temperature oxidation of homogenous ilmenite with rhombic symmetry (Haggerty, 1976).

Not all rutile crystallites in altered ilmenite grains show epitaxial behavior. Stubby rutile crystallites in Figures 6c and 7c appear to lack a systematic orientation. Rutile is also found as discrete domains at the rim of a leucoxene grain (Figure 5b), with dusty streaks visible in transmitted light (low reflectivity in BEI) continuing from the leucoxene to the rutile domains.

Detrital rutile is very different from rutile derived from ilmenite alteration, consisting of transparent brownish to reddish translucent grains, in contrast to the dusty opaque appearance of rutile derived from alteration of ilmenite. The detrital rutile in Figure 6e was deeply corroded along certain crystallographic planes, with the pore space filled with silica cement. In addition, rare corroded quartz grains are found with muscovite and kaolinite inclusions and rutile overgrowths (Figure 7f).

Table 2. Electron microprobe chemical analyses (wt.% oxides) of selected altered ilmenite grains illustrated in Figures 5–7.

Grain type Locality Analysis Figure	Pseudorutile							Leucoxene							Rutile								
	RR-97-23			WIRP				WIRP							RR-97-23								
	1 7d	2 7d	3 7e	4 6b	5 6e	6 6c	7 5a	7 5a	8 5d	8 5c	9 5c	9 5c	10 5c	11 5b	11 5b	12 5b	13 5a	14 5a	15 5d	16 5c	17 5c	18 5f	19 6e
SiO ₂	0.00	0.01	0.00	0.50	0.41	0.37	0.40	0.41	0.41	0.56	0.60	0.60	0.62	0.62	0.37	1.24	0.85	2.03	1.59	0.43	0.42	0.42	0.48
TiO ₂	51.05	48.30	55.27	57.32	63.03	60.07	60.86	64.56	63.88	63.88	66.82	66.82	66.32	67.83	67.83	69.89	77.51	93.86	96.32	96.72	97.73	95.23	95.23
Al ₂ O ₃	0.02	0.00	0.05	0.47	0.32	0.28	0.38	0.33	0.46	0.46	0.61	0.61	0.82	0.45	1.60	2.10	1.43	0.62	0.29	0.29	0.29	0.30	0.30
Cr ₂ O ₃	0.17	0.15	0.16	0.26	0.25	0.23	0.22	0.22	0.22	0.21	0.22	0.22	0.25	0.20	0.20	0.31	0.20	0.28	0.28	0.28	0.19	0.27	0.27
FeO _T	40.37	33.82	36.28	36.51	34.56	32.33	35.38	30.51	29.85	29.85	22.87	23.28	23.28	22.79	17.81	11.94	1.46	0.89	0.86	0.86	0.90	0.51	0.51
MnO	7.88	11.21	2.87	1.81	1.15	4.36	2.74	3.59	3.67	3.67	5.11	2.99	2.99	4.38	4.38	1.22	0.28	0.22	0.27	0.23	0.23	0.21	0.21
MgO	0.04	0.03	0.02	0.22	0.32	0.18	0.19	0.19	0.18	0.18	0.20	0.20	0.26	0.13	0.22	0.19	0.17	0.17	0.17	0.15	0.15	0.16	0.16
CaO	0.00	0.01	0.01	0.20	0.18	0.20	0.16	0.19	0.18	0.18	0.20	0.20	0.20	0.33	0.26	0.32	0.17	0.16	0.15	0.15	0.17	0.16	0.16
Na ₂ O	0.00	0.00	0.00	0.16	0.14	0.16	0.13	0.15	0.14	0.14	0.21	0.17	0.17	0.07	0.15	0.16	0.12	0.14	0.14	0.14	0.12	0.13	0.13
K ₂ O	0.00	0.00	0.02	0.14	0.14	0.13	0.14	0.13	0.14	0.14	0.14	0.12	0.12	0.13	0.31	0.11	0.46	0.12	0.12	0.12	0.12	0.14	0.14
Total	99.53	93.53	94.68	97.59	100.50	98.31	100.60	100.28	99.27	96.98	96.98	95.03	95.03	95.20	96.11	94.71	100.18	100.51	99.41	100.32	97.59	97.59	97.59
No of oxygens	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	2	2	2	2	2	2	2
Si	0.000	0.000	0.000	0.033	0.026	0.024	0.026	0.026	0.036	0.036	0.039	0.041	0.041	0.025	0.081	0.055	0.027	0.021	0.006	0.006	0.006	0.007	0.007
Ti	2.940	2.955	3.219	2.843	3.010	2.971	2.929	3.104	3.099	3.304	3.304	3.317	3.387	3.435	3.768	3.768	0.935	0.957	0.976	0.976	0.977	0.978	0.978
Al	0.003	0.000	0.006	0.037	0.024	0.022	0.029	0.025	0.035	0.035	0.047	0.064	0.064	0.035	0.123	0.160	0.022	0.010	0.005	0.005	0.005	0.005	0.005
Fe ³⁺	2.327	2.070	2.114	2.014	1.836	1.778	1.893	1.631	1.611	1.611	1.258	1.295	1.266	1.266	0.973	0.645	0.016	0.010	0.010	0.007	0.007	0.006	0.006
Cr	0.009	0.009	0.009	0.014	0.013	0.012	0.011	0.011	0.011	0.011	0.011	0.013	0.013	0.010	0.013	0.016	0.002	0.003	0.003	0.002	0.002	0.003	0.003
Mn	0.510	0.771	0.189	0.101	0.062	0.243	0.149	0.194	0.201	0.285	0.285	0.168	0.168	0.163	0.242	0.067	0.003	0.002	0.003	0.003	0.003	0.002	0.002
Mg	0.006	0.003	0.003	0.022	0.030	0.018	0.018	0.018	0.017	0.020	0.020	0.026	0.026	0.013	0.021	0.018	0.003	0.003	0.003	0.003	0.003	0.003	0.003
Ca	0.000	0.000	0.000	0.014	0.012	0.014	0.011	0.013	0.012	0.014	0.014	0.014	0.014	0.023	0.018	0.022	0.002	0.002	0.002	0.002	0.002	0.002	0.002
Na	0.000	0.000	0.000	0.020	0.017	0.020	0.016	0.019	0.018	0.027	0.027	0.022	0.009	0.019	0.020	0.003	0.003	0.004	0.004	0.004	0.003	0.003	0.003
K	0.000	0.000	0.003	0.012	0.011	0.011	0.011	0.011	0.011	0.012	0.012	0.010	0.010	0.011	0.026	0.009	0.008	0.002	0.002	0.002	0.002	0.002	0.002
Ti/(Ti+Fe)	0.53	0.56	0.58	0.59	0.62	0.63	0.61	0.66	0.66	0.72	0.72	0.72	0.73	0.78	0.85	0.98	0.99	0.99	0.99	0.99	0.99	0.99	0.99

Table 3. Electron microprobe analyses (wt.%) of minerals associated with altered ilmenite grains.

Mineral Analysis Figure Occurrence	Muscovite				Kaolinite	
	A 5f	B 7f	C 7a	D 6e	E 6d	F 7e
	inc	cont	inc	inc	cont	inc
SiO ₂	45.57	45.19	46.12	46.85	46.51	46.73
TiO ₂	1.72	0.82	1.17	0.88	0.44	0.88
Al ₂ O ₃	34.89	37.11	36.58	35.96	36.89	37.08
Cr ₂ O ₃	0.21	0.18	0.17	0.10	0.12	0.10
FeO _T	2.52	0.93	1.38	0.85	1.19	0.41
MnO	0.17	0.16	0.22	b.d.	0.15	0.02
MgO	0.67	0.34	0.55	0.25	0.19	0.06
CaO	0.18	0.12	0.12	b.d.	0.18	0.13
Na ₂ O	0.78	1.45	0.98	1.35	0.10	0.02
K ₂ O	9.75	8.90	9.46	8.85	0.11	0.08
Total	96.46	95.20	96.75	95.09	85.88	85.51

inc: inclusion in altered ilmenite

cont: in contact with altered ilmenite grain

b.d.: below detection limit

OTHER MINERALS PRESENT WITHIN THE ALTERED ILMENITE

Unaltered ilmenite grains may contain inclusions of quartz, muscovite and tourmaline. The quartz and tourmaline inclusions seem to persist without any change throughout the alteration processes. Muscovite inclusions usually give chemical analyses with good totals when the ilmenite grains are partially altered to pseudorutile (Tables 2 and 3). However, in grains with a high proportion of rutile and leucoxene, the chemical analyses have low totals, which may indicate the hydration of some muscovite to illite. Some muscovite inclusions seem to have altered to kaolinite (*e.g.* Figure 7e).

Diagenetic kaolinite and illite have been identified within the pores of bulk sandstone samples using XRD and BEI (Pe-Piper *et al.* 2005c). Kaolinite occurs in altered ilmenite grains as a replacement of muscovite inclusions, filling the porosity created during the conversion of ilmenite to pseudorutile, and as overgrowths on altered ilmenite grains, either as isolated plates (Figure 5d) or as a continuous microcrystalline rim (as shown by the rims in Figures 11 and 12 with high Si and Al but no K).

CHEMICAL VARIATION IN ALTERED ILMENITE

Examination of electron microprobe analyses of different alteration minerals shows some general trends of trace-element variation. The range of Cr₂O₃ and CaO contents of pseudorutile and rutile are similar in electron microprobe analyses (Figure 13) and elemental maps (not illustrated) confirm that these elements are retained in rutile. Pseudorutile contains greater abundances of MnO and MgO (Figure 13a,b) than rutile, and elemental

maps show the loss of these elements with the development of more Ti-rich phases (Figures 8, 9). However, the abundance of these elements may be diagnostic of the source of ilmenite (Basu and Molinaroli, 1989, 1991; Schroeder *et al.* 2002). Mg-rich ilmenite is typical of mafic igneous rocks (*e.g.* analysis 5 from the small grain in Figure 6e). Mn-rich ilmenite tends to be abundant in some peraluminous granite and metapelite, and is thus characteristic of ilmenite with abundant unoriented quartz inclusions (*e.g.* analyses with >4% MnO in spot 13, Figure 5a and spot 10 in Figure 5c). The grain in Figure 7d contains ~7% MnO (see also Figure 11c). Low-Mn ilmenite is known from both mafic igneous and metamorphic rocks (*e.g.* the low-Mn grain with weakly oriented quartz and muscovite inclusions in Figures 7c and 12).

In making electron microprobe analyses, we attempted to analyze 1–10 µm spots of apparently homogeneous mineral. The analyzed SiO₂ and Al₂O₃ contents are likely principally as tiny inclusions rather than part of the mineral structure. Most electron microprobe analyses of pseudorutile show lower SiO₂ and Al₂O₃ contents (Figure 14a) than do rutile analyses, although a few analyses show high and scattered K₂O (>0.1%), Al₂O₃ and SiO₂ (generally <1%), presumably from larger inclusions. At Ti/(Ti+Fe) values of <0.65, most analyses cluster at <0.1% SiO₂ and Al₂O₃, but at Ti/(Ti+Fe) values of <0.65–0.70 there is a linear increase in both the mean and the minimum Al₂O₃ and SiO₂ contents (Figure 14a). Leucoxene and rutile from the Upper Member at WIRP and RR-97-23 tend to have high SiO₂ (>0.4%), Al₂O₃ (>0.3%) and K₂O compared with samples elsewhere. However, elemental maps clearly show that Al, Si and K are absent from rutile (Figures 9, 10, 11). Any Si is found in inclusions of quartz, muscovite and kaolinite (produced from muscovite) (Figure 12) and in kaolinite plates that have grown diagenetically in pores (Figures 11 and 12). Likewise, K is found in inclusions of muscovite and in pore-filling diagenetic illite and Al is present in muscovite and kaolinite inclusions and pore-filling kaolinite and illite.

DISCUSSION

The origin of the textures in altered ilmenite

The observed textures in altered ilmenite grains may have two principal origins. Some textures are inherited from the igneous or metamorphic protolith whereas others have developed through weathering and diagenesis. Inclusions of quartz and associated minerals (*e.g.* Figures 5a, 7c,e) are clearly inherited from a granite or metamorphic protolith, although the development of kaolinite and illite is probably the result of diagenetic alteration of feldspar and muscovite precursors. The great abundance of grains with well developed rutile crystals (Figure 4), compared with the scarcity of rutile

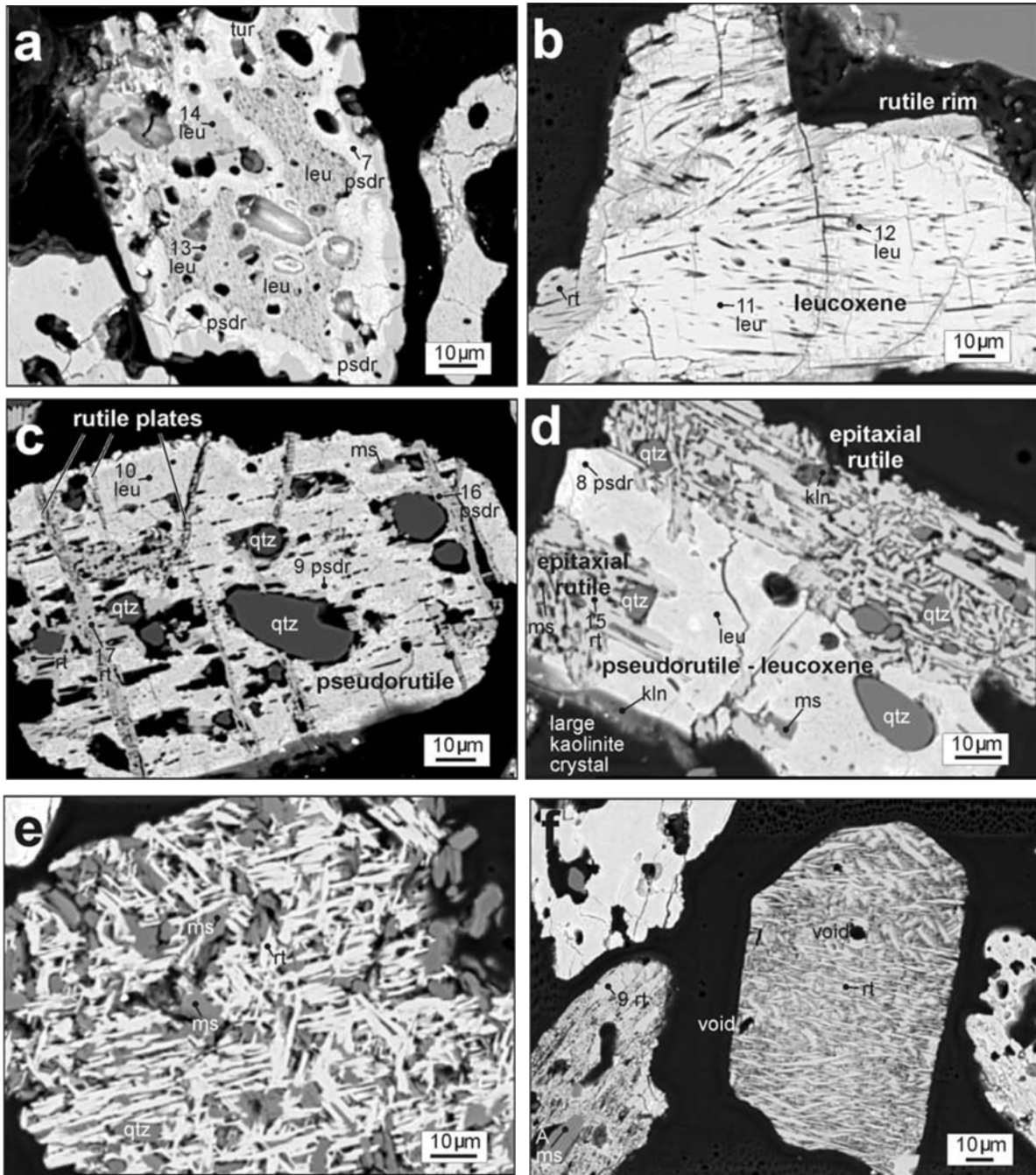


Figure 5. BSE images of altered ilmenite grains from WIRP. Pseudorutile (psdr) and leucoxene (leu) are distinguished chemically (Figure 4), as is rutile (rt) which may include other TiO_2 polymorphs. Other minerals, using the abbreviations of Kretz (1983) include: kln = kaolinite; ms = muscovite (including hydromuscovite-illite); qtz = quartz; tur = tourmaline. Dots indicate electron microprobe analyses: numbers refer to selected chemical analyses in Table 2 and letters to analyses of other phases in Table 3. (a) Zoned grain of altered ilmenite (S56-3.0) made up mostly of pseudorutile and leucoxene. The darkness of the various zones is due to variations in pseudorutile content. Chemical variation is shown in Figure 8. (b) Leucoxene with rutile overgrowths (S56-3.0). (c) Prominent rutile plates within a pseudorutile grain (S70-3.5). Note the voids in the structure, particularly around quartz inclusions. Chemical variation is shown in Figure 9. (d) Epitaxial growth of rutile prisms on pseudorutile and leucoxene (S70-3.5). Chemical variation is shown in Figure 10. (e) Ilmenite grain completely replaced by rutile needles and prisms (S70-3.5). (f) Ilmenite grain completely replaced by rutile with rare voids (S56-3.0).

in ilmenite from potential source areas in the Appalachian basement to the north, argues that much

of the rutile is of pedogenic or diagenetic origin. We use the term rutile because bulk XRD analysis shows only

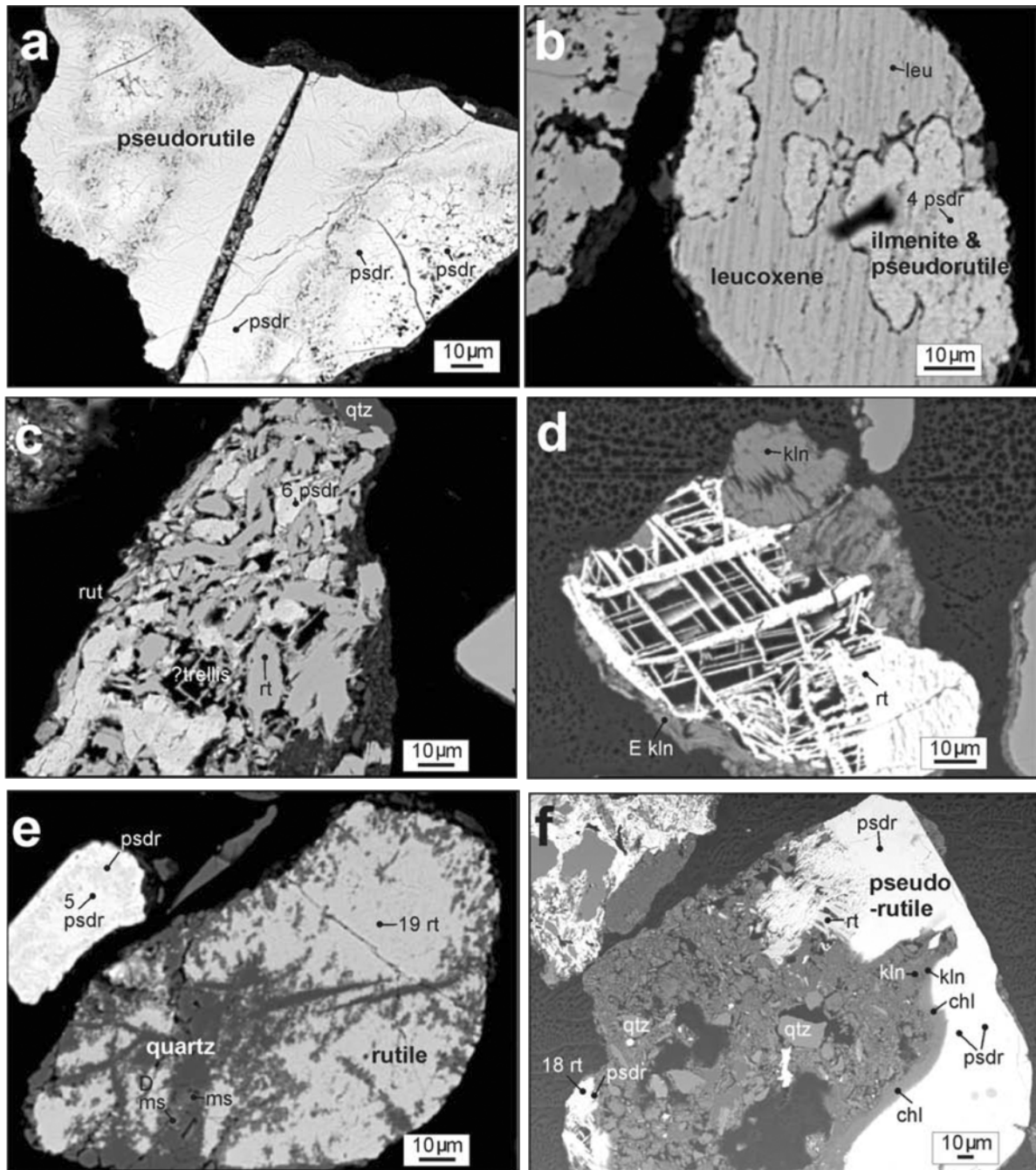


Figure 6. BSE images of altered ilmenite grains from the upper part of borehole RR-97-23. For abbreviations, see the caption for Figure 5. (a) Ilmenite altered to pseudorutile (sample 1). (b) Ilmenite altered to leucoxene (sample 2). (c) Ilmenite grain replaced by pseudorutile and rutile, with some rutile showing open trellis structure with large voids (sample 2). (d) Rutile with open trellis structure with large voids (sample 2). (e) Detrital rutile showing corrosion and silicification (sample 2). The small grain on the left is altered ilmenite. (f) Ilmenite overgrowths on an original igneous crystal, probably feldspar with quartz inclusions, that has been converted mainly to kaolinite, with a chlorite rim at the contact with ilmenite (sample 3).

the presence of the rutile polymorph of titania, but other polymorphs could be present in individual grains.

Nevertheless, rutile in a few grains may be inherited either directly from an igneous protolith or from exsolution of ilmenite within a titanomagnetite host.

Grains with a very open trellis structure of rutile, such as in Figure 6d, presumably developed from a titanomagnetite precursor, in which ilmenite exsolution had occurred. The residual magnetite oxidized to hematite or goethite or was reduced to pyrite and was removed

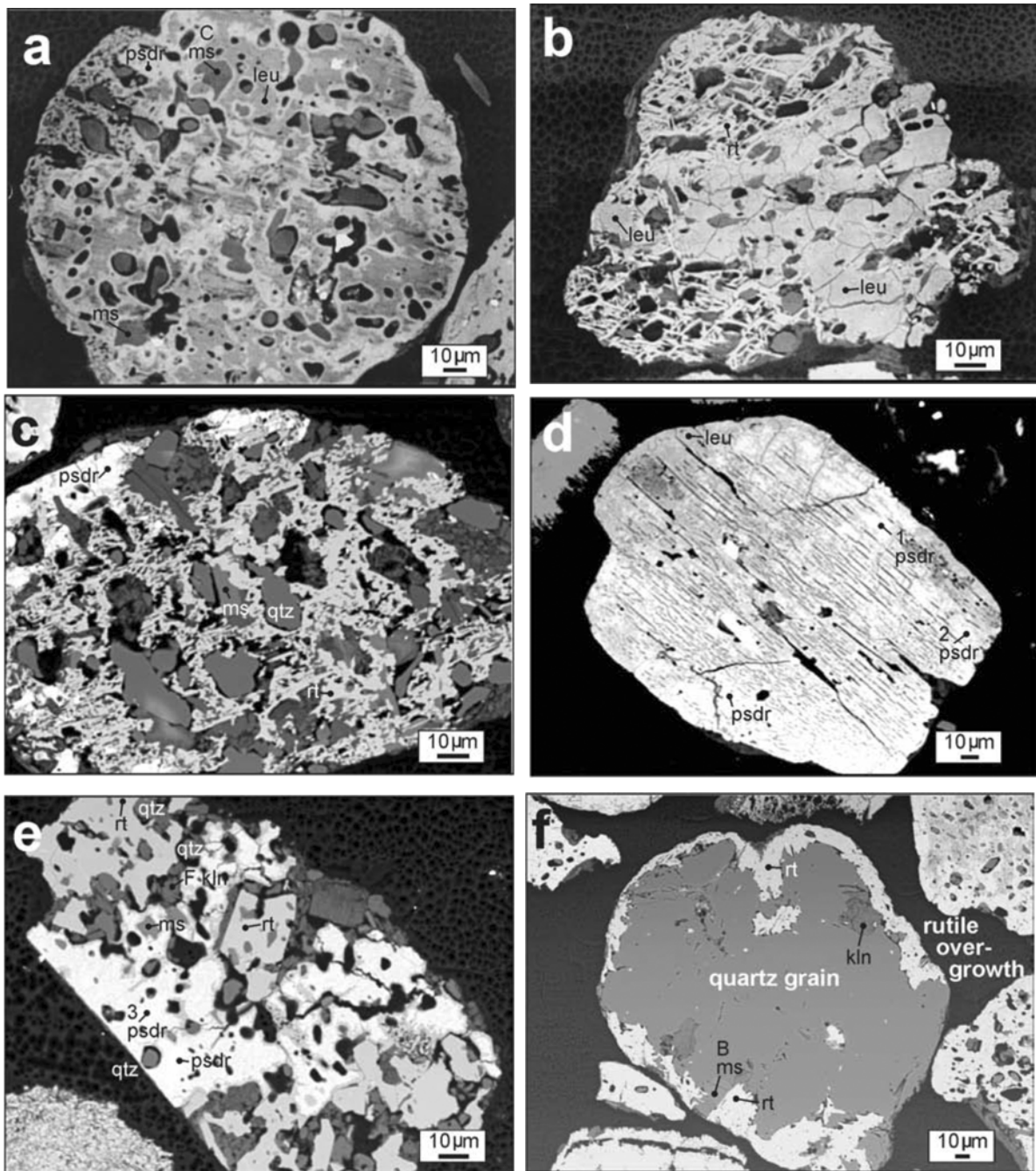


Figure 7. BSE images of altered ilmenite grains from the lower part of borehole RR-97-23. For abbreviations, see the caption for Figure 5. (a) Ilmenite grain altered to pseudorutile and leucoxene (sample 5). (b) Epitaxial growth of rutile on pseudorutile (sample 5). (c) Ilmenite grain almost completely altered to rutile (sample 5). Chemical variation is shown in Figure 12. (d) Ilmenite grain altered to pseudorutile (sample 6). Chemical variation shown in Figure 11. (e) Epitaxial growth of rutile on ilmenite and pseudorutile (sample 6). (f) Quartz grain with muscovite and kaolinite inclusions and rutile overgrowth (sample 7).

during weathering and/or diagenesis: it is difficult to imagine the rutile trellis being transported unbroken with other sand grains. Textural relationships show only that diagenetic growth of kaolinite took place at the margin of the grain. The presence of a similar trellis structure in the interior of Figure 6c suggests a similar

origin, but in this case the protolith grain consisted of titanomagnetite overgrown by ilmenite, with the pseudorutile demonstrating the original presence of ilmenite.

The rutile plates in pseudorutile in Figure 5c may have exsolved within the protolith. Where adjacent to quartz inclusions, little or no void is formed, suggesting

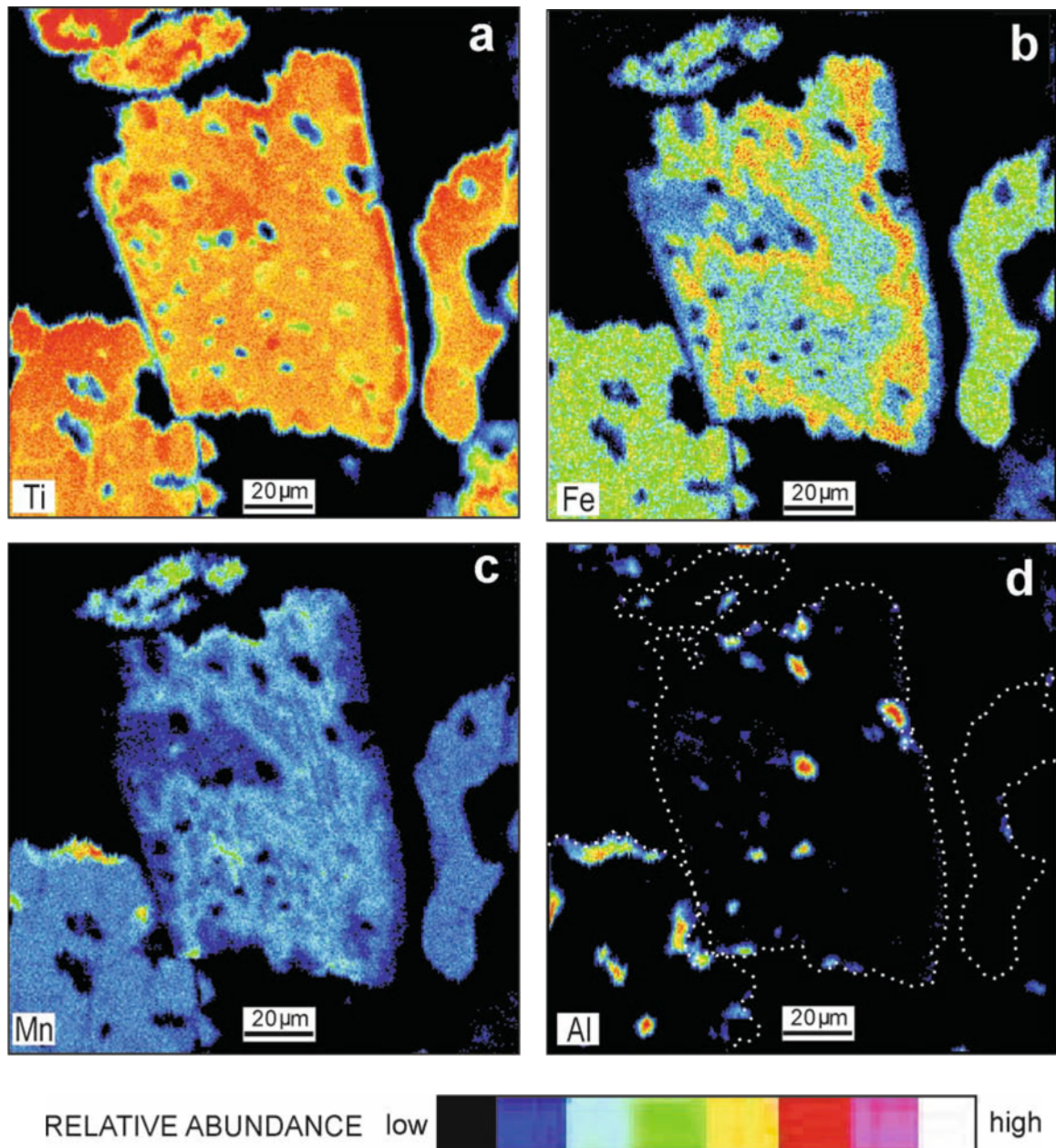


Figure 8. Electron microprobe elemental map of the altered ilmenite grain of Figure 5a (sample: S56-3.0). Note: the different zones of pseudorutile (Fe), the rutile spots (reddish areas in Ti), the distribution of Al as isolated patches (Al) and the retention of Mn in pseudorutile (Mn).

that the rutile did not form *via* a pseudorutile precursor. Likewise, the finely crystalline rutile rim in Figure 5b is also a texture that is probably inherited from an igneous protolith. The texture of the rutile is unlike that argued below to be of diagenetic origin and titania rims of pseudobrookite are known from igneous ilmenites (*e.g.* Haggerty, 1976). Which titania polymorph is represented by the “rutile” in this sample is unknown. In other grains, subtle variations in chemistry of pseudorutile and leucoxene may parallel original zoning in an ilmenite crystal (Figures 5a and 8).

The development of rutile in most grains is interpreted as being of diagenetic origin. Direct evidence that rutile may be of diagenetic origin is provided by a corroded detrital quartz grain that is overgrown by rutile (Figure 7f). Although the patterns of rutile crystals in Figures 5e and 5f at first sight resemble ilmenite to rutile exsolution textures in titanomagnetite (as illustrated by Haggerty, 1976, his figures 1, 4 and 5), the proportion of rutile in these grains is greater than expected for a titanomagnetite precursor (and thus differs from grains such as in Figure 6d, where a titanomagnetite protolith

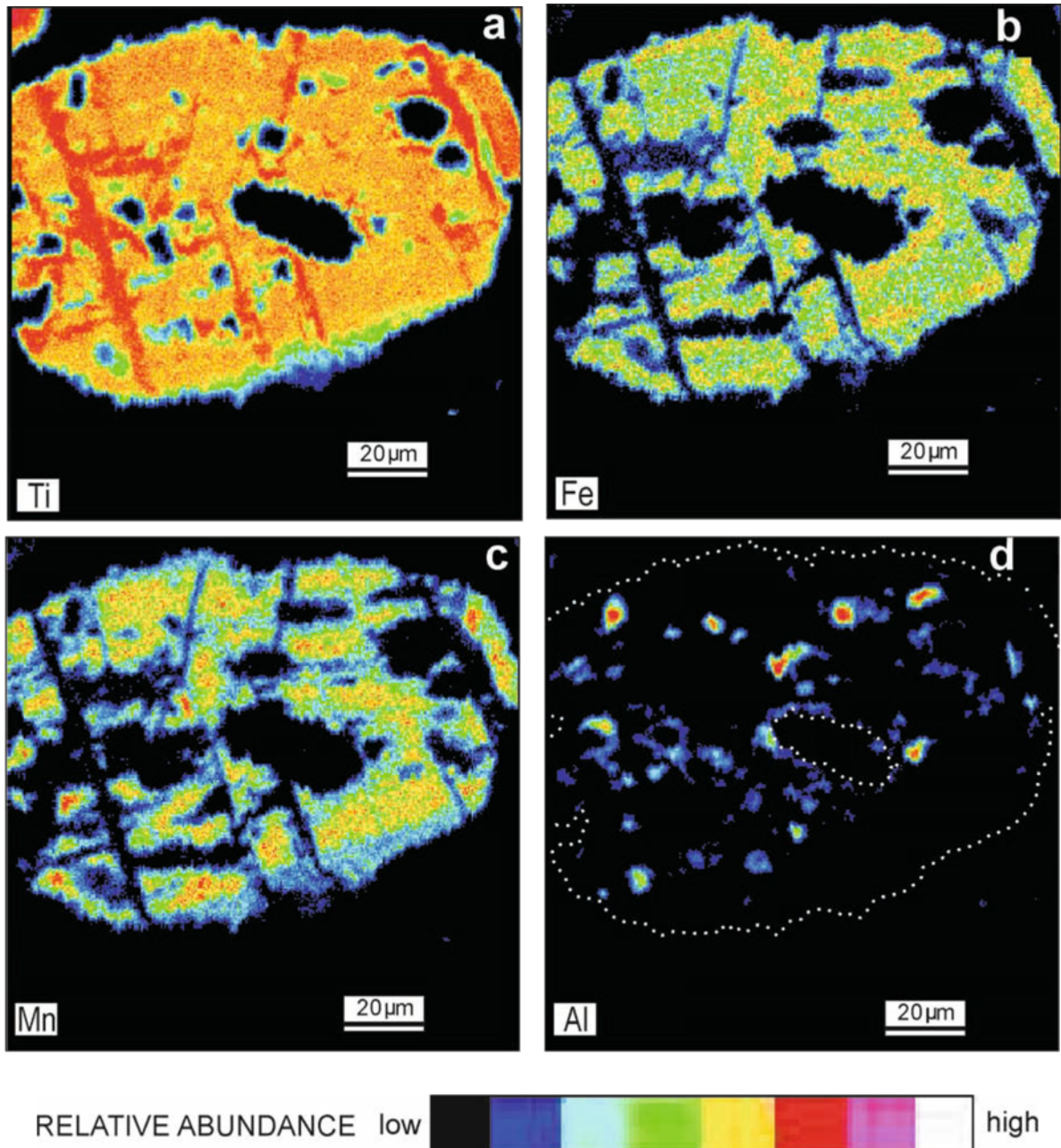


Figure 9. Electron microprobe elemental map of the altered ilmenite grain of Figure 5c (sample: S70-3.5). Note: the epitaxial growth of rutile (Fe, Ti), the distribution of Al as isolated patches and the retention of Mn in pseudorutile but not in rutile (Mn, Ti).

appears likely). Furthermore, in Figure 7c, a similar pattern of rutile does not continue into pseudorutile at the margin of the grain. A similar effect is seen in Figure 5d, where there are epitaxial rutile crystals at the margin of the grain, in places seemingly replacing pseudorutile-leucoxene of rather patchy chemical composition (Figure 10a). To the best of our knowledge, such textural relationships have not been reported from high-temperature oxidation of ilmenite. The epitaxial growth of these rutile crystals at 120° in Figures 5d,e and 7c is consistent with structural control from original

rhombohedral ilmenite. Less regular crystals are seen in Figures 6c,f and 7e.

Observations in this study illustrate and confirm the structural relationships between parent ilmenite, pseudorutile and rutile described by Teufer and Temple (1966) and Grey and Reid (1975), involving the metal atom arrangements within the hexagonal close-packed anion layers for ilmenite, pseudorutile and triply twinned rutile. Most of our data are consistent with the following two chemical reactions suggested by Grey and Reid (1975) as describing the alteration of ilmenite:

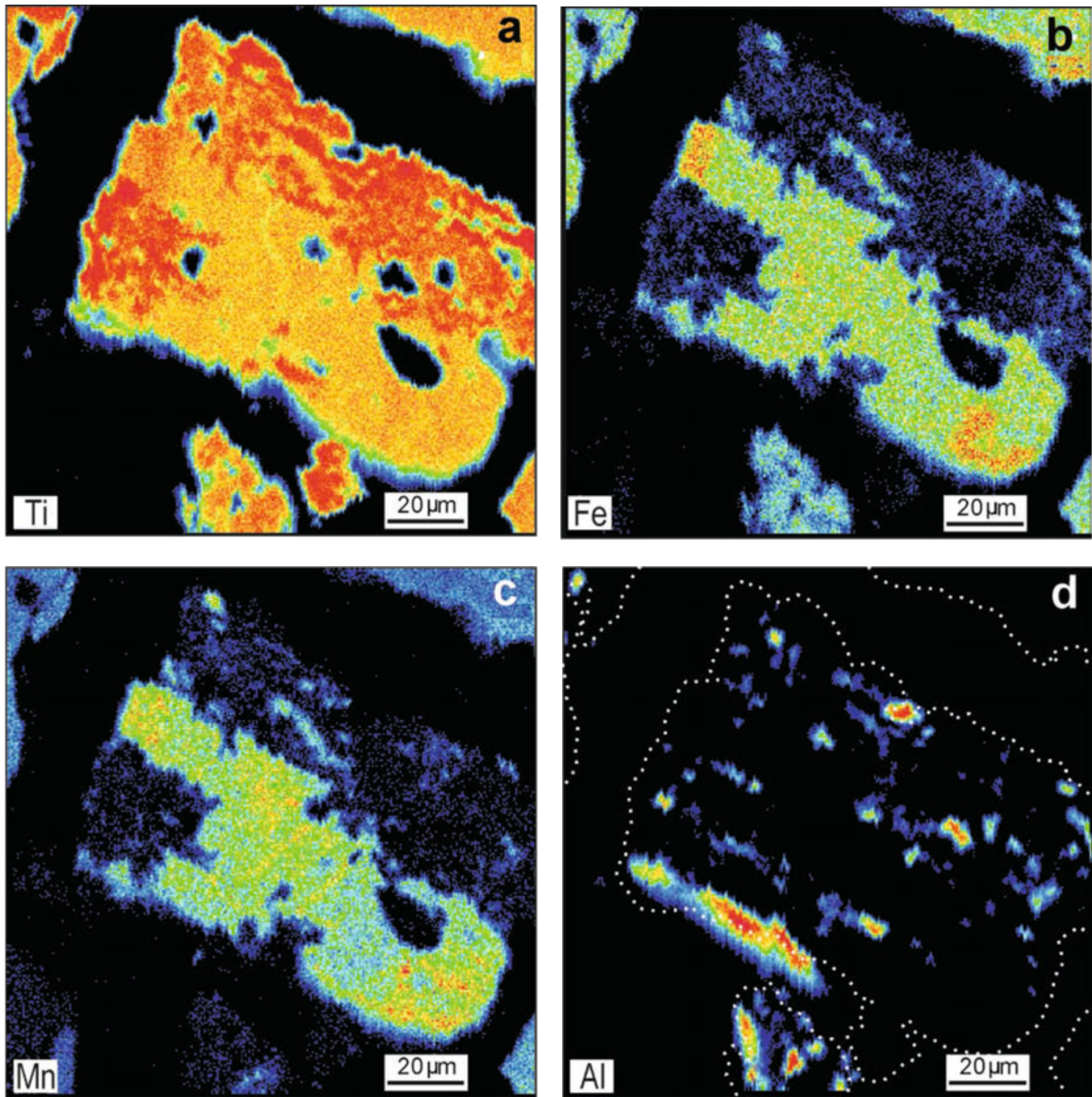
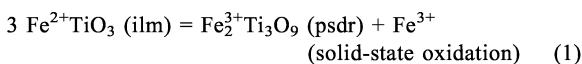
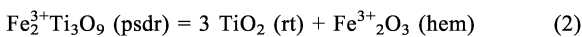


Figure 10. Electron microprobe elemental map of the altered ilmenite grain of Figure 5d (sample S70-3.5). Note the epitaxial growth of rutile on pseudorutile (Fe, Ti) and the distribution of Mn and Al.



and



The same authors have also suggested that the reaction 1 may occur topotactically by the diffusion of Fe through an essentially oxygen structure, whereas reaction 2 must involve dissolution and reprecipitation.

The well documented epitaxial growth of rutile on pseudorutile in our samples (Figures 5d, 6c) is evidence of dissolution and reprecipitation of rutile. The conversion of ilmenite to pseudorutile results in a volume reduction of ~6% (Grey and Reid, 1975), which would produce considerable elastic stress in the oxygen structure at the coherent interface between segments of ilmenite and pseudorutile.

No hematite or any other Fe-oxide/hydroxide grains, has been identified in the studied altered ilmenite grains,

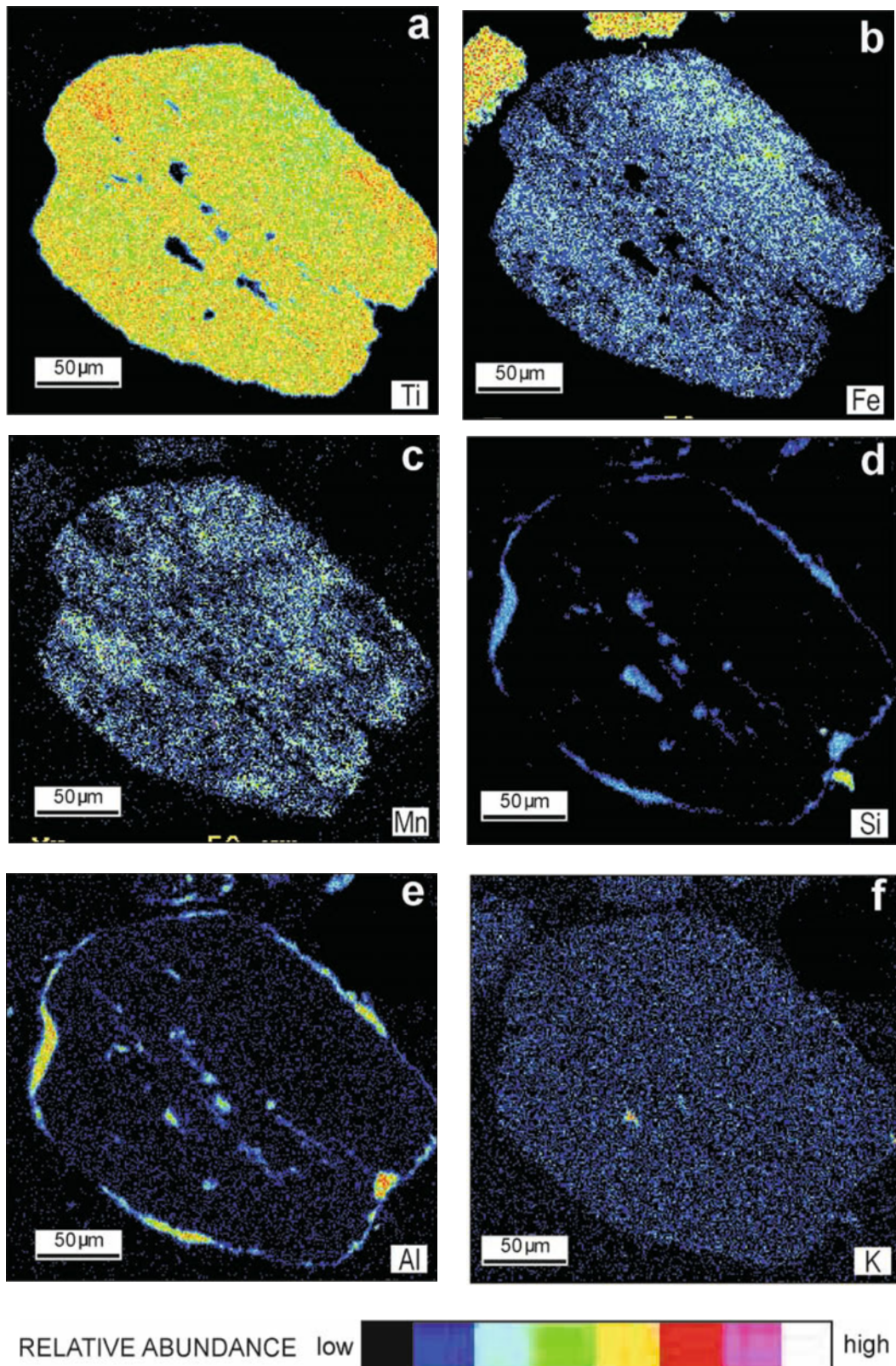


Figure 11. Electron microprobe elemental map of the altered ilmenite grain of Figure 7d (sample 6 of RR-97-23). Note the early stage of ilmenite alteration (Fe, Ti), the kaolinite overgrowths and inclusions (Si, Al, K) and the retention of Mn by the pseudorutile.

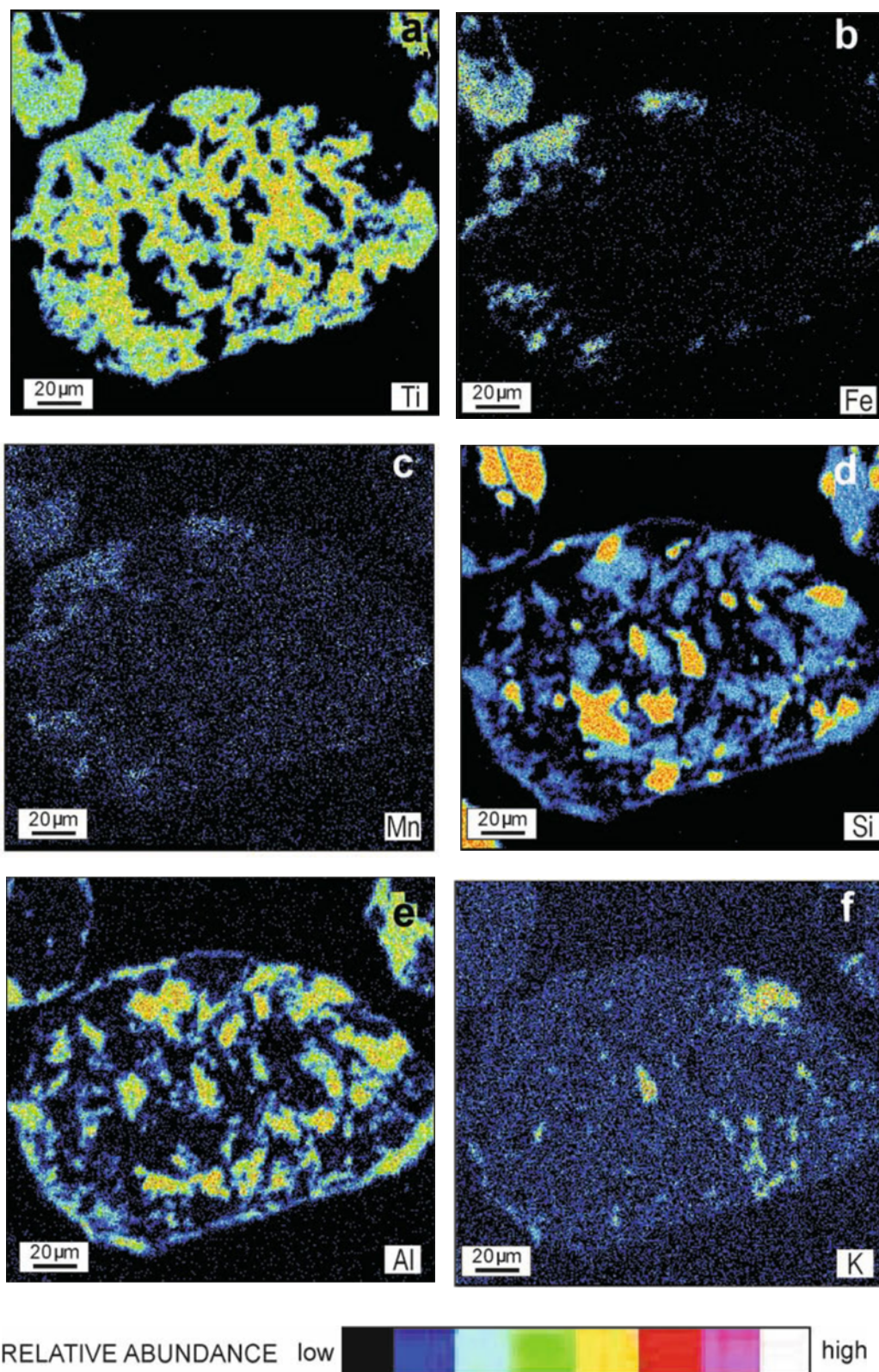


Figure 12. Electron microprobe elemental map of an altered ilmenite grain (sample 5 of RR-97-23). Note the well advanced alteration of ilmenite (Fe, Ti), the several quartz inclusions (Si, Al), some muscovite inclusions (K, Al), several kaolinite patches (Si, Al, K) and the complete removal of Mn.

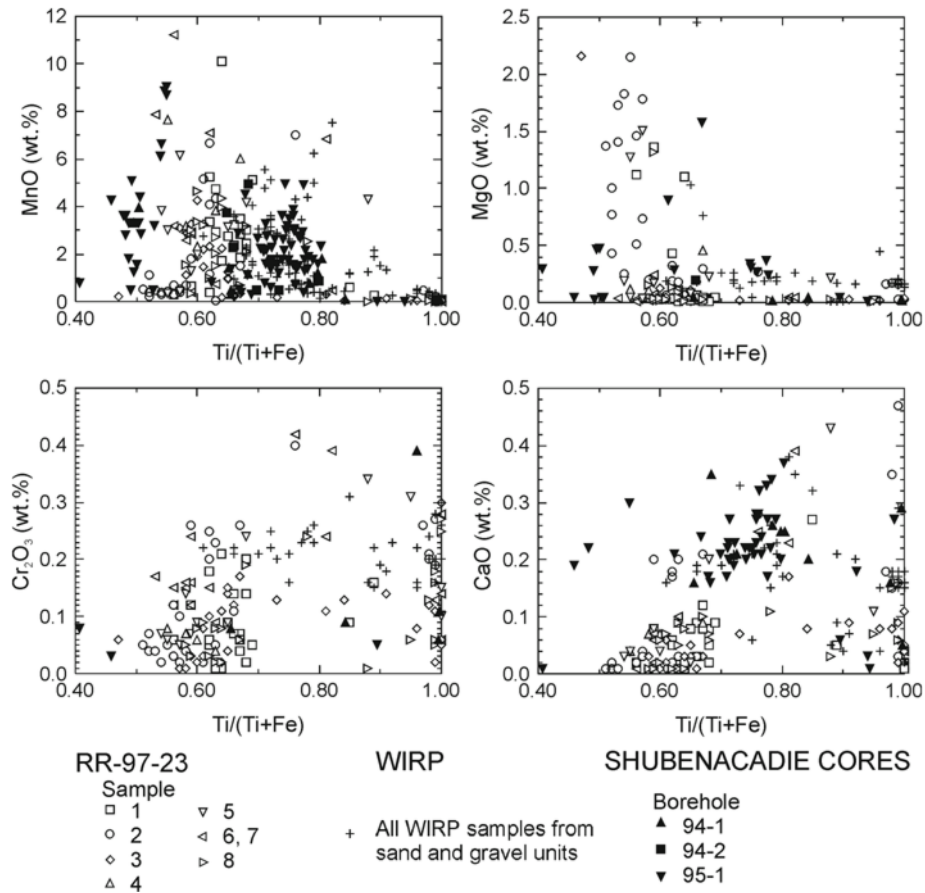


Figure 13. Variation of MnO, MgO, Cr₂O₃ and CaO with the Ti/(Ti+Fe) atomic ratio in altered ilmenite grains.

indicating that during the alteration of the ilmenite grains, hematite did not remain within the altered grains and most of the Fe was leached. Hematite is present in all the samples in which the altered ilmenite is found, but commonly in abundance not commensurate with the amount inferred to be lost from ilmenite, again implying that Fe was leached. Some of this leached Fe accumulated in hematite-rich Bt horizons in paleosols. The

presence of an Fe-rich chlorite rim on altered ilmenite (Figure 6f) also indicates the availability of Fe.

The elemental maps (Figures 8–12) and plots of variation in MnO with Ti/(Ti+Fe) (Figure 13) suggest that some Mn was lost during the alteration of ilmenite to pseudobrookite and the rest was lost during the subsequent alteration to rutile. Magnesium shows a similar behavior (Figure 13). Both Mg and Mn substitute

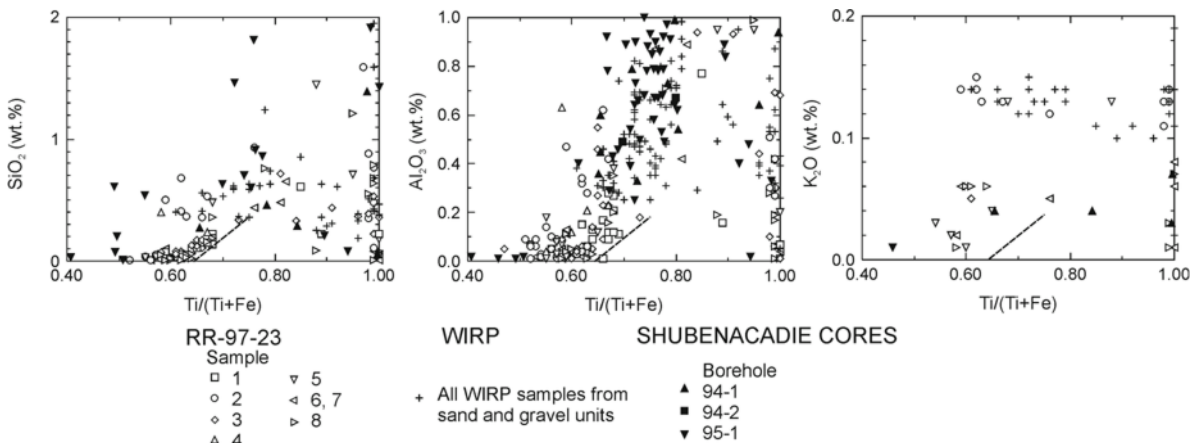


Figure 14. Variation of SiO₂, Al₂O₃ and K₂O with the Ti/(Ti+Fe) atomic ratio in altered ilmenite grains.

for Fe in ilmenite and pseudorutile, but not for Ti in rutile. In contrast, the Cr and Ca distributions do not seem to change with the alteration of ilmenite to pseudorutile and then to rutile (Figure 13).

The elemental maps also indicate that Al is absent in ilmenite, pseudorutile and rutile, occurring only in discrete patches which are either muscovite/kaolinite inclusions within the original ilmenite grain or kaolinite precipitated within the pores produced during the alteration of the ilmenite grains. Frost *et al.* (1983) suggested that during the later stages of ilmenite alteration, where rutile precipitates, both Al and Si are extracted and co-precipitated with, or adsorbed on, rutile. Our data do not support this suggestion. Anand and Gilkes (1984) suggested that the altered grain simply acted as a continuation of the porous soil matrix and was pervaded by soil solution from which pedogenic clay crystallized. In this study, Al precipitated as kaolinite in discrete patches and plates in the pores created during the conversion of ilmenite to pseudorutile or as replacement of muscovite inclusions, probably under burial diagenetic conditions, and thus the distribution of Al in rutile differs from that in the anatase of Anand and Gilkes (1975, their Figure 11). The Si in our samples is restricted to the quartz inclusions of the original ilmenite grains.

Relationship to the diagenetic environment

The studied samples come from at least three different soil-forming environments: (1) gley paleosols represented by dark gray organic-rich mudstones, with early diagenetic pyrite and siderite, that formed in poorly drained conditions; (2) mudstones with Oxisols with strong development of kaolinite and hematite; (3) thick, porous, gravelly sandstones with limonite and goethite that formed in Spodosols. In addition, a fourth early diagenetic environment is recognized, (4) where dark gray clays have been oxidized and altered to light gray kaolinitic clays beneath the water table, by percolating meteoric water (Pe-Piper *et al.*, 2005c).

Only two samples (Table 1) come from environment 1. Clays from this environment are interpreted to sample fluvial detritus, with little pedogenic modification (Pe-Piper *et al.*, 2005c). From sample 4 in borehole RR-97-23, only five grains have been analyzed, but all are pseudorutile (mean $Ti/(Ti+Fe) = 0.60$), with no leucoxene or rutile. From sample 2 in borehole SHUB-94-1, two ilmenite, five pseudorutile and one leucoxene grains have been analyzed (mean $Ti/(Ti+Fe)$ of pseudorutile–leucoxene = 0.60). The likely interpretation of the pseudorutile in these samples is that it altered from ilmenite either through weathering in the source area, or during fluvial transport.

In borehole RR-97-23, all samples except sample 4 have experienced weathering environment 2. Ilmenite is virtually absent, and the ratio of rutile to pseudorutile increases down-hole. Little leucoxene is present; pseudorutile predominates at all depths.

Samples from the WIRP are the best example of weathering environment 3. They have an exceptionally high proportion of leucoxene and considerable amounts of rutile, but ilmenite appears to be absent. In borehole SHUB-95-1 (Table 1), samples 5–8 also appear to have experienced weathering environment 3. Ilmenite is present in the upper part of the section, but disappears deeper in the section. In the two deepest samples, rutile and leucoxene predominate.

At least one sample comes from environment 4, sample 3 in SHUB-94-1 (Table 1). Of only six grains, four are rutile and one is leucoxene, suggesting that leaching by meteoric water below the water table effectively promotes alteration to rutile.

In both boreholes SHUB-95-1 and RR-97-23, the down-hole increase in rutile parallels an increase in the degree of lithification of sandstones. Nearby borehole SHU-94-4 (Stea *et al.*, 1996) shows a rapid increase in vitrinite reflectance, from $R_o = 0.3\%$ near the top of the borehole to $R_o \approx 0.45\%$ at 150 m depth (Figure 2), values that are confirmed by spot analyses from other boreholes in the region (Hacquebard, 1984; Davies *et al.*, 1984). We therefore suggest that the greater development of rutile at depth in these boreholes is probably related to burial diagenesis under higher-temperature conditions. A similar process may occur in marine sediments buried to several km depth and sampled in offshore wells, where ilmenite, pseudorutile and leucoxene grains are uncommon, but rutile is common.

Thus the distribution of the different Fe-Ti oxides suggests that the Chaswood Formation rivers supplied predominantly pseudorutile with lesser ilmenite. Leaching by meteoric water to give Spodosols in highly permeable sandstones and conglomerates (environment 3) resulted in alteration to leucoxene and lesser rutile. In less permeable mudrock successions, Oxisol formation led to alteration of ilmenite to pseudorutile in thin sandstone beds (environment 2). This alteration is similar to that inferred for soils in the source areas for the river system. Under conditions of prolonged leaching by meteoric water below the water table (environment 4), alteration resulted in a high proportion of rutile together with the diagenetic development of kaolinite in pore space. Burial diagenesis is inferred to produce rutile, but not leucoxene, and results in crystallization of illite in pore space.

After formulation of the above interpretations, additional samples were analyzed from outliers of the Chaswood Formation (Pe-Piper *et al.* 2005b). At Belmont and Diogenes Brook (Figure 1), where environment 3 predominates, the relative abundance of leucoxene and pseudorutile is similar to that in environment 3 at Shubenacadie, but rutile is less common. At Brierly Brook, where environment 1 predominates, pseudorutile is more abundant, as in sample 4 from environment 1 at RR-97-23.

In some previous studies, randomly oriented microcrystals of anatase were found to be the final alteration

product of ilmenite (e.g. Anand and Gilkes, 1984; their figure 10). Anand and Gilkes (1984) concluded that the anatase structure is much less compact than that of rutile, so that anatase developed in lateritic weathering environments where leaching is extreme, whereas rutile develops in the absence of strong leaching, e.g. in beach sands. The rutile found in this study developed under conditions of considerable leaching (forming Spodosols and Oxisols), although less extreme than is normally associated with lateritic weathering. Indeed, there is sparse evidence for arid conditions at times, perhaps seasonally, in the Chaswood Formation. Corroded detrital rutile with silica cement (Figure 6e) and corroded quartz rimmed with rutile (Figure 7f) are features that develop in silcretes under conditions of net water loss.

Comparison has been made by Stea and Pullan (2001) between the kaolins of the Chaswood Formation and those of the Eocene Huber Formation of Georgia. In contrast to the abundant rutile found in the Chaswood Formation, Schroeder and Schiflet (2000) found that sub- μm -sized anatase was the dominant diagenetic Ti mineral in the kaolins of the estuarine to marine Huber Formation, with only minor rutile present. Schroeder *et al.* (2004) argued that anatase formed as a precipitate following the complete dissolution of pseudorutile. Diagenetic alteration to kaolinite by groundwater recharge is much more advanced in the Huber Formation than in the Chaswood Formation, with the development of well crystallized kaolinite.

A general geological model for variability in ilmenite alteration

Based on the conclusions of this study and on other studies in the literature, we propose a general geological model to account for observed variability in ilmenite alteration products (Figure 15). Rivers transport principally sand-sized ilmenite and pseudorutile, as inferred from environment 1 of the Chaswood Formation and the absence of rutile in the Huber Formation. The volume reduction and resulting elastic stress in the conversion of ilmenite to pseudorutile is likely to favor comminution of pseudorutile grains, thereby leading to a concentration of Ti in the silt fraction (1.0–1.5% TiO_2 in dark gray mudstones of the Chaswood Formation, compared with 0.8–1.0% TiO_2 in average shales). The delicate porous textured leucoxene grains are also unlikely to survive fluvial transport. Comminuted pseudorutile may be a source of labile Fe for early diagenesis of marine sediments in the Sable basin, where early diagenetic Fe-rich minerals are abundant (Drummond, 1992). These marine sediments are also unusually rich in TiO_2 (G. Pe-Piper, unpublished data).

Extreme leaching of ilmenite, either in lateritic soils (Anand and Gilkes, 1984) or with prolonged groundwater recharge (Huber Formation: Schroeder and Schiflet, 2000) produces anatase. Less extreme leaching, both in soils and by groundwater recharge, results in the progressive change from ilmenite to pseudorutile, followed by dissolution and reprecipitation of rutile to

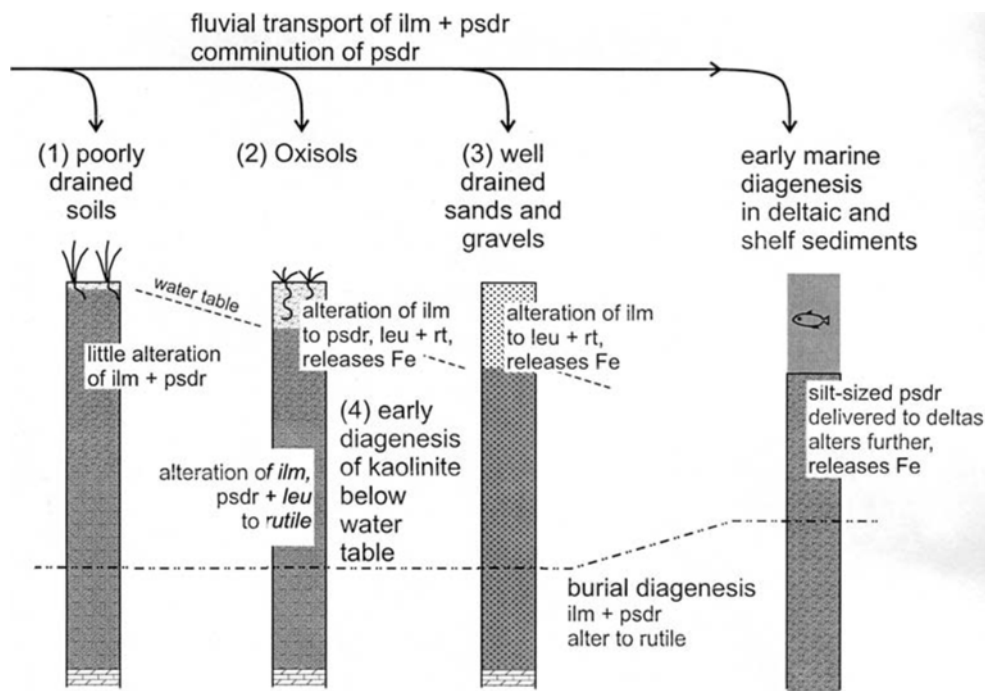


Figure 15. Geological model for environmental controls on the mineralogical products of the alteration of ilmenite.

give microcrystalline 'leucoxene' and the well-developed rutile crystals documented in this study. Under elevated temperature conditions during burial diagenesis, growth of rutile crystals is more rapid and microcrystalline 'leucoxene' is lacking, as shown by the base of the Chaswood Formation and the offshore wells.

Economic implications

Minerals of the ilmenite to rutile series are common in the Chaswood Formation and in glacial tills derived therefrom. They are concentrated in placer deposits in the modern Shubenacadie River which drains a large area underlain by the Chaswood Formation. There has been commercial interest in Ti minerals both as placer deposits and as by-products of silica sand extraction from the Chaswood Formation. The relationship between rutile formation and various types of weathering in the Chaswood Formation provides a genetic model that can be applied to exploration for Ti minerals within the formation. The Al and Si in the altered ilmenite grains occur as discrete minerals (muscovite, kaolinite) and not as substitutes in the pseudorutile and rutile structure, making these impurities easier to remove.

CONCLUSIONS

(1) The textures of altered ilmenite grains in the Lower Cretaceous sandstones studied are in part inherited from textures in the ilmenite protolith and in part result from alteration during weathering and diagenesis. These different origins can be distinguished on the basis of optical appearance, morphology and chemistry of the mineral components.

(2) Alteration of sand-sized grains of ilmenite to pseudorutile to leucoxene and finally to rutile takes place with progressively greater efficiency in four early diagenetic environments in the fluvial Chaswood Formation: (a) organic-rich muddy swamps; (b) Oxisols in muddy sediments; (c) thick porous gravelly sands; and (d) zones of groundwater recharge below the water table. Burial diagenesis (to vitrinite reflectance values >0.4%) resulted in rapid recrystallization of leucoxene to rutile.

(3) The alteration of ilmenite releases Fe, Mn and Mg, but Cr and Ca appear to be retained or reprecipitated in Ti-rich alteration products, suggesting that these two elements can be used as provenance indicators. Al and Si are not co-precipitated in the rutile structure, but are present in original inclusions in the ilmenite grains and in diagenetic clays that formed in porosity created by the ilmenite to pseudorutile to rutile.

(4) Stresses related to volume change from ilmenite to pseudorutile to rutile cause fractures, so that altered ilmenite grains will comminute in fluvial transport and thus concentrate in the silt fraction. Alteration of ilmenite provides a source of labile Fe, present in

pedogenic and early diagenetic siderite, pyrite, goethite and hematite in the Chaswood Formation. Silt-sized pseudorutile may be the source of Fe for the abundant early diagenetic Fe-rich minerals in the Scotian basin.

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