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PROCESSUS DYNAMO-METAMORPHIQUES DE BONIFICATION DES GÎTES DE FE-TI.

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UNIVERSITÉ DU QUÉBEC À MONTRÉAL

METAMORPHIC ENRICHMENT PROCESSES IN FE-TI DEPOSITS

THESIS PRESENTED TO
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ERIC HÉBERT

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ABSTRACT

The Pinnacle Formation hosts concentrations of titaniferous heavy minerals near Sutton, Quebec. These metasandstones are included in a volcano-sedimentary sequence of the Oak Hill Group, in the Humber Zone of the Quebec Appalachians. The Sutton paleoplacers underwent two metamorphic events: during Ordovician and Silurian time. Post-depositional enrichment processes transformed iron-rich ilmenite grains into a nearly-pure TiO_2 residual phase. Late metamorphic crystallization of rutile from these porous residual TiO_2 phases occurred during a backthrusting event in Silurian time. A spatial relationship between the distribution of metamorphic rutile and the main backthrusting structure of the area, the Brome Fault, exists and is corroborated by $\delta^{18}O_{water}$ value in equilibrium with metamorphic magnetite.

Metamorphism also induced element transfer and change in fO_2 in the titanium-rich metasediments. A compositional zonality is observed around semimassive concentrations of heavy minerals. Metamorphic fluids leached iron which migrated outward to be incorporated into other oxides and silicates. As a result, titaniferous minerals are completely purged of their iron content and recrystallized as rutile.

New occurrences of titaniferous heavy minerals are described within the subjacent unit of the Pinnacle, i.e. the Call Mill Slate. Such titaniferous concentrations have never been described in the Call Mill. Therefore, the origin of the Call Mill has been re-interpreted using new evidences based on the presence of these Fe-Ti oxides. Our new interpretation suggests that, in the vicinity of Sutton, the Call Mill and its overlying unit, the Pinnacle, have the same source rocks. However, major differences exist between heavy minerals of each unit. The timing of weathering and post-depositional enrichment of the Ti-minerals are the principal cause of these differences. We conclude that the Call Mill was derived from the erosion of a lateritized source rock whereas the Pinnacle was formed from the same, but unweathered, parent rock.

RÉSUMÉ

La Formation de Pinnacle contient des concentrations de minéraux lourds titanifères près de Sutton, Québec. Ces métasédiments font partie d'une séquence volcano-sédimentaire au sein du Groupe de Oak Hill, dans la Zone de Humber des Appalaches québécoises. Les paléoplacers de Sutton ont subi deux événements métamorphiques : à l'Ordovicien et au Silurien. Des processus post-dépositionnels d'enrichissement ont transformé les grains d'ilménite riches en fer en une phase résiduelle se rapprochant d'une composition pure en TiO_2. L'événement Silurien de rétrochevauchement a permis la cristallisation métamorphique du rutile à partir de ces phases titanifères résiduelles. Une relation spatiale existe entre la distribution du rutile métamorphique et la structure régionale de rétrochevauchement, la Faille Brome. Cette relation est aussi corroborée par les valeurs $\delta^{18}O_{eau}$ en équilibre avec la magnetite.

Le métamorphisme a aussi provoqué le transfert d'éléments et un changement de la fugacité d'oxygène dans les métasédiments riches en titane. Une zonalité compositionnelle est observée autour des concentrations semi massives de minéraux lourds. Le fer lessivé par les fluides métamorphiques a ensuite été incorporé dans des silicates et d'autres oxydes. Ainsi, les minéraux titanifères ont été complètement purgés de leur contenu en fer et ont recristallisé en rutile.

De nouvelles concentrations de minéraux lourds titanifères on été trouvées dans l'unité à la base du Pinnacle, c'est-à-dire les phyllades du Call Mill. De telles concentrations titanifères n'ont jamais été décrites au sein du Call Mill. C'est pourquoi l'origine du Call Mill doit être réinterprétée à la lumière de ces minéraux de Fe-Ti. Notre nouvelle interprétation suggère que dans la région de Sutton, les sédiments du Call Mill et du Pinnacle proviennent de la même source. Cependant, des différences majeures au niveau des minéraux lourds distinguent les deux unités. Ces différences s'expliquent principalement par l'intensité et la durée des processus d'enrichissement des minéraux de Fe-Ti. Nous avons conclu que le Call Mill était issu de l'érosion d'une source latéritique, tandis que l'érosion de la partie non affectée par la météorisation a formé les sédiments du Pinnacle.

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Introduction

Metamorphism is known to modify existing ore deposits (Marshall et al., 2000). Mineral changes and/or deformation induced by temperature and pressure elevation can either destroy an ore deposit or contribute to its enrichment (Marshall et al., 2000). Metamorphosed titaniferous paleoplacers occur near the Sutton area, in the Quebec Appalachians. The impact of metamorphism on these titaniferous concentrations has been investigated by the author from 2003 to 2006.

The early field works revealed that residual titanium enrichment occurred. Through all the geological history of these paleoplacers, from the source rock to present, via transport, deposition, reworking, diagenesis, metamorphism, and deformation, enrichment could have occurred. What is exactly the contribution of metamorphism and its timing in the formation of the Sutton titaniferous paleoplacers? Effects of metamorphism on titaniferous deposit are poorly documented, hence the challenge of this project.

First, a detailed mapping and sampling of the titaniferous showings of the region have been done. Then, a preliminary investigation of the timing of enrichment was done from petrographic observations via thin sections. Finally, major elements and isotopical analysis were completed to confirm earlier observations.

This document is subdivided into four chapters. Chapter 1 is a review of literature about enrichment processes which can be involved during the whole formation of a placer. It also indicated that the Sutton metamorphosed paleoplacers are not consistent with any conventional model, thus represent a new type of titaniferous deposit.

Chapter 2 describes the mineralogy of the Fe-Ti oxides present in the Sutton paleoplacers. It focuses on the contribution and timing of metamorphism to the enrichment processes. This chapter has been submitted and accepted for publication in *Economic Geology*.

Chapter 3 focuses on the changes induced by metamorphism and how they affect the chemical composition of titaniferous minerals present in the paleoplacers. The fO_2 and mineral changes during metamorphism are therefore described. The influence of Fe^{2+}-bearing minerals (ilmenite) on metamorphic fluids was also discussed. This paper has been submitted as a short paper in the journal *Mineralium Deposita.*

Chapter 4 describes new occurrences of titaniferous concentrations which were found during field works. These new heavy mineral concentrations occur within another stratigraphical unit, immediately below the formation hosting the paleoplacers. The purpose of this last chapter is to re-interprete the origin of this unit based on these occurrences of Fe-Ti oxides. This manuscript is in preparation for submission.

References:

Marshall, B., Vokes, F.M., Larocque, A.C.L., 2000, Regional metamorphic remobilization: upgrading and formation of ore deposits. In Spry, P.G., Marshall, B., Vokes, F.M. (editors), metamorphosed and metamorphogenic ore deposits, Reviews in Economic Geology, v. 11., p.19-38.

CHAPTER I

Low-grade metamorphic terrains: a potential source rock for rutile

Abstract

Titanium dioxide (TiO_2) is an industrial mineral used as a pigment in paint, paper and plastic. The chloride pigment process actually used by the industry requires a specific mineralogy : enriched ilmenite or rutile. Although ilmenite is usually the predominant oxide in heavy mineral placers, rutile represents the optimal feedstock for the chloride pigment process. However, ilmenite can form huge economic resources when chemical enrichments occur. Therefore, exploration for titanium deposits must focus on chemical processes which could transform uneconomic titanium mineral into chloride pigment process compatible phase. Such chemical enrichment processes include weathering, hydrothermal alteration and metamorphism which could affect either the source rock or directly the placer deposits. High-grade metamorphism—upper amphibolite, granulite and eclogite facies—is the most efficient natural process which transforms titaniferous silicates into oxide. Moreover, such granulite facies rock are usually exposed over several thousands of square kilometers, thus constituting the number one target in titanium exploration in terms of source rock regions. By contrast, low-grade metamorphism has a deleterious effect on titanium mineralogy by incorporating titanium into silicates. Therefore, low-grade metamorphic terrains were systematically rejected as rutile-bearing rocks. Few exceptions have been reported where rutile is preserved in low-grade metamorphic rocks. Such rocks are generally Ca-poor pelites where the preserved rutile probably comes from the erosion of high-grade metamorphosed source rocks. Our recent works revealed that a rutile-generating process could occur on ilmenite-rich sediments during low-grade metamorphism. Such titanium-rich sandstones constituted an intermediate sedimentary host in which enrichment processes occur. The further erosion

of such rocks can locally form unexpected rutile-rich placers. The Sutton region, Quebec Appalachians, hosts such rutile-bearing low-metamorphic rocks. The Sutton titanium deposit is a key example of rutile crystallization during metamorphism. This opens a whole new range of potential source for rutile via an intermediate sedimentary host within low-grade metamorphic terrains.

Introduction

Titanium dioxide (TiO_2) is an industrial mineral used as a pigment in paint, paper and plastic. Actually, placers are the main economic deposits where titanium minerals are concentrated. Although titanium is very abundant in the crust (9th in abundance), a right combination of mineralogy, source rock, chemical and mechanical enrichment processes is required to form economic placer deposits. Therefore, exploration for titanium deposits can be seen in terms of a source rock-erosion-transport-deposition cycle in which chemical and mechanical enrichment processes occur. These enrichment processes are determinant in forming economic placers. This chapter proposes to first review every stage of the cycle and then how chemical and/or mechanical processes contributed to the enrichment of titanium minerals. In the light of this cycle, a new potential source rock for rutile will be described. A key example is the Sutton rutile deposits in the Quebec Appalachians, in which low-grade metamorphism contributed to the beneficiation of deposits during the cycle.

Parent rock

Titanium occurs either into silicates or oxides in a given source rock. Mineralogy is the most important factor in the formation of a titaniferous placer. Oxides are advantageous over silicates in the formation of a placer, because their hardness, density and their relative resistance to chemical alteration make them easier to be preserved and concentrated in sediments (Force, 1991a). Biotite, amphibole and titanite are the most common Ti-bearing silicates, which are generally present in high proportion in rocks. However, these minerals do not distinguish themselves in terms of hardness, chemical stability and density, thus cannot be concentrated as placers. Moreover, no industrial processes have been developed to isolate the TiO_2 from these minerals. By contrast, Ti-oxides, such as rutile and ilmenite, are hard, dense, and resistant, thus can be easily concentrated by sedimentologic processes. Furthermore, these oxides are compatible with actual industrial pigment processes. Only two processes are used by the pigment industry: the sulfate and the chloride processes. The first one has been developed in the 1950s and is used for ilmenite with a relatively low-TiO_2 content (37-54%), such as magmatic ilmenite and hemo-ilmenite. Actually, the sulfate process is less used by the pigment industry due to environmental considerations. Instead, the pigment industry favors the less polluting one, the chloride process. However, this chloride pigment process requires specific mineralogy and a minimum of contaminating elements to be effective: only rutile (>95% TiO_2) and enriched ilmenite (60-70% TiO_2) are compatible (Force, 1991a; Stanaway, 1994). Therefore, the chemical composition of the feedstock has to be taken into account besides the hardness, density and stability of the source rock minerals. High Fe, Mg and other trace elements in magmatic ilmenite make it incompatible with the actual chloride pigment process unless further removal of element occur during the formation of the deposits.

Weathering

At the source rock, different enrichment processes could occur transforming non-economic minerals into a pigment process compatible phase. Deep-weathering conditions affecting the parent rock have usually two beneficial results: a) alter the titanium-bearing minerals into residual titanium oxides, generally anatase, b) destroy or dissolve the gangue minerals, thus residually enrich the source rock in TiO_2. Hartman (1959), Force (1976a), Edou-Minko, (1995) indicated that a saprolitized or lateritized source rock can be enriched in TiO_2 by a factor of two to four. Although this enrichment factor can be very high, again it is the mineralogy that is the most important. During weathering, titanium is found as residual TiO_2-phase, generally porous grains or very fine aggregates of anatase which cannot be transported on a long distance and not be destroyed. For instance, in lateritic or bauxitic profile Ti-bearing silicates are altered into clay and titanium forms fine oxide aggregates generally anatase, a rutile polymorph (Hartman, 1959; Force, 1976a; Force, 1976b; Herz, 1976; Butt, 1985; Narayanaswamy et al., 1987; Force, 1991a). Titaniferous magnetite is also altered into anatase under such conditions. Ilmenite is residually enriched into TiO_2 by leaching of elements such as Fe, Mg, Ca (Grey and Reid, 1975; Dimanche et Bartholomé, 1976; Anand and Gilkes, 1984; Mücke and Chaudhuri, 1991; Schroeder et al., 2002). Rutile is probably the most stable titanium mineral under weathering conditions, unless its Nb content is too high (Force, 1976a). Nevertheless, weathering of ilmenite and rutile has a positive effect by leaching undesirable elements and still preserves the original hardness and density of these minerals. However, weathering alone could not lead to generation of a titanium source rock, unless the rock was previously enriched in rutile or ilmenite.

Hydrothermal processes

The source rock can also be formed or enriched by hydrothermal processes. Alteration zones around porphyry copper usually contain rutile issued from the alteration of ilmenite originally present in the rocks (Czamanske et al., 1981, Force, 1984). Such rutile crystallization from hydrothermalized ilmenite has also been recognized in alteration zones of orogenic gold deposits and around metamorphosed massive sulfides (Nesbitt and Kelly, 1980; Eilu et al., 1999). However, such occurrences of rutile are only present locally on a small-scale area and cannot form a major rutile source rock (Force, 1980).

Metamorphism

Metamorphism can also affect the parent rocks and has either deleterious or beneficial effects on titaniferous minerals. Under low-grade metamorphic conditions, rutile and ilmenite, if present, are destabilized and titanium is incorporated into silicates (Force, 1976a; Goldsmith and Force, 1978). Under specific conditions rutile can be preserved, such as in calcium-poor, aluminium-rich rocks, usually pelite. Again, such occurrence represents small area. By contrast, high-grade metamorphism (granulite and eclogite) transformed Ti-bearing silicates into oxides, either rutile or ilmenite (Force, 1976a; 1980; 1991a; Goldsmith and Force, 1978; Stanaway, 1996; 2005). According to these authors, high-grade metamorphism is the most efficient rutile-generating process. Therefore, granulite facies rocks constituted the optimal source rock for rutile placers.

Moreover, these authors pointed out that such highly metamorphosed rocks usually formed crystalline basement of several square kilometers and provided an extensive source rocks for rutile.

Beneficiation processes affecting the parent rock are limited to chemical changes, such as weathering, hydrothermal alteration and metamorphism, transforming principally the mineralogy. Weathering and hydrothermal processes can participate in the enrichment process, however, the parent rocks must already contain a specific mineralogy, such as rutile or ilmenite, otherwise beneficiation cannot occur. Therefore, no weathering or hydrothermal processes can generate potential source rocks. High-grade metamorphism seems to be the only rutile-generating process which can form large source rocks, regardless of the nature of the parent rocks.

Erosion-transport-deposition

Mechanical enrichment

Without an erosion-transport-deposition cycle, no placer deposits can be formed. Complex sedimentologic processes result in concentration of the valuable minerals from a source rock into the sedimentological record. Mechanical enrichment is predominant over chemical enrichment during transport and reworking. Thus, the density, particle size and hardness of a grain are the most significant properties involved during a placer formation. The harder a mineral is, the better it will be preserved and remains coarse-grained during transport.

Different agents, such as waves, running water and wind are responsible for the mechanical concentration of heavy minerals. Running water is probably the major agent involved in placer formation (Slingerland and Smith, 1986). At this stage, titanium must reside as oxide, either rutile or ilmenite, to be liable to concentration processes, hence the importance of the source rock (Force, 1991a; Stanaway, 1996). Settling, entrainment, differential transport and shearing are the principal mechanisms involved during the formation of a water-laid placer, where particle size and density intervene (Stapor, 1973; Komar and Wang, 1984; Slingerland and Smith, 1986; Stanaway, 1992). Concentration of heavy minerals usually result in a simultaneous combination of these mechanisms. These processes must result in a sorting of heavy minerals from the non-economic minerals to form a placer.

The density is the most important property during settling deposition. Based on this principle, coarse light grains are in equilibrium with finer heavy grains during deposition (Slingerland and Smith, 1986; Force, 1991b). At this point, no enrichment occurs, apart the removal of small light grains and floating particle such as micas and clay.

Entrainment of a grain occurs during reworking of the deposited grain and depends more on the grain size, whatever its density is. According to this principle, on a layer, coarse grains are preferentially removed by transport agents rather than finer ones, due to greater contact area (Slingerland and Smith, 1986; Force, 1991b). Waves, for example, are probably the best natural concentrator of heavy minerals by entrainment, created by wash and back-wash movements on a beach (Force, 1991a). The combination of the settling deposition and entrainment thus results in heavy mineral-rich layers.

The transport sorting by flowing water results in a segregation of coarse particles from finer ones during transport. The large particles move faster than finer ones with increasing velocity of the flowing water. Thus heavy particles can be concentrated by a combination of the above-mentioned hydraulic equivalences (settling and entrainment; Slingerland and Smith, 1986; Force, 1991b).

At the depositional site, heavy minerals can also be concentrated by later mechanical reworking such as shearing, winnowing, shadowing, overpassing, armoring, trapping and hiding (Cheel, 1984; Slingerland and Smith, 1986, Force, 1991b; Stanaway, 1992). For instance, shearing of grains by gravity or fluid forces result in a migration of denser (or larger) particle upward, toward the surface plan (Inman et al., 1966; Komar and Wang, 1984; Slingerland and Smith, 1986). Although concentration of heavy minerals occurs under many environments, the shoreline deposits constitute the great majority of titanium deposits where all the hydraulic processes are efficient to form economic placers.

Chemical enrichment

For many titaniferous placers, chemical enrichment at the depositional site is probably the most important factor for the enrichment of a placer. It is even more significant because ilmenite is usually the most abundant titaniferous oxide present in heavy mineral placers and thus requires further chemical leaching to be compatible with the chloride pigment process. Therefore, the actual deposits must be—or were at a certain time—under sub-tropical to tropical deep-weathering conditions during or after their formation. It is only under such tropical weathering that humic acids can leach efficiently elements from ilmenite, especially iron and magnesium. (Bailey et al., 1956; Karkhanavala, 1959; Lynd, 1960; Welch, 1964; Temple, 1966; Dimanche, 1972; Grey and Reid, 1975; Dimanche and Bartholomé, 1976; Puffer, and Cousminer, 1982; Darby, 1984; Force, 1991; Mücke and Chaudhuri, 1991). A single ilmenite grain containing about 35% TiO_2 can be up-graded to 65%-70% TiO_2 by such chemical leaching. The ilmenite generally altered to leucoxene or anatase via a pseudorutile intermediate stage (Teufer and Temple, 1966; Grey, and Reid, 1975; Dimanche and Bartholomé, 1976; Mücke and Chaudhuri, 1991). Detrital rutile deposits do not require such chemical enrichment to be economic. For instance, the proportion of TiO_2 in some economic

Australian rutile deposits is well-below the crustal average. With a source supplying ilmenite instead of rutile, the geographical or paleogeographical position is a limiting factor in regards to exploration. For instance, large placers of ilmenite occur at Port Leyden (N.Y.), Pointe-Taillon (Qc) and Natashquan (Qc) but are actually non-economic because of their high-latitude position. However, it does not mean that exploration for titaniferous placers should be concentrated under tropical zone. Failing these conditions, other enrichment processes could occur somewhere between the depositional site and the source rock, called intermediate sedimentary hosts by Force (1991a).

Intermediate sedimentary hosts

An intermediate sedimentary host could form a titaniferous deposit in itself or be an intermediate source rock for placer by further reworking. Enrichment processes occurring on such hosts can be considerable. Besides mechanical and chemical enrichment processes already mentioned in previous sections, other transformations can radically change the economic viability of a placer. Diagenesis, hydrothermal alteration and metamorphism can significantly change the mineralogy and thus beneficiate or make possible the further formation of a placer. The Sutton rutile deposit is a key example of such intermediate host where low-grade metamorphic processes changed uneconomic ilmenite into a rutile-bearing potential source rock for local placers.

Example of an enriched intermediate sedimentary host

TiO_2 (rutile and anatase) concentrations are observed in metamorphosed and deformed Cambrian sandstone unit, the Pinnacle Formation, near the town of Sutton, in the Quebec Appalachians (Fig. 1.1). The Pinnacle Formation is part of the Oak Hill Group, between basalts at the base (Tibbit Hill Formation) and sandy dolomitic unit at the top (White Brook; Clark, 1936; Dowling, 1988; Colpron, 1992; Colpron et al., 1994). The whole sequence underwent two major metamorphic events that reached greenschist facies. The first one occur at 469-461 Ma during the Taconian Orogeny. The second one occur during a backthrusting event at 431-411 Ma (Castonguay et al., 2001). Titanium oxide-rich horizons (altered ilmenite, pseudorutile, anatase and rutile) have been recognized over a 20 km^2 area near Sutton. The rutile-hosted stratigraphical unit is cross-cut to the East by a backthrust, the Brome Fault (Colpron, 1992). The original parent rocks for the Sutton heavy mineral concentrations are well-defined: it is the adjacent Grenvillian high-metamorphic terrains and their titaniferous anorthositic complexes that intruded them (Colpron, 1992; Marquis and Kumarapeli, 1993). This Precambrian basement formed one of the major source rocks for titanium oxide placers in the world (Stanaway, 1996). However, the predominant titanium mineral issued from these Precambrian source rock is ilmenite ($FeTiO_3$), a less valuable mineral than rutile. At this point, the only economic placers issued from these rocks are situated in sub-tropical and tropical zones (Florida, Georgia) where deep-weathering conditions can enrich ilmenite. To be economically viable, these ilmenite grains must undergo other chemical beneficiations at the source, at

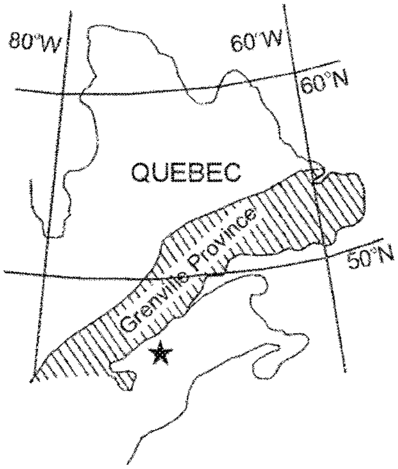

Figure 1.1 Geographical position of the Sutton area (star) and its position relative to the outcropping Grenville Province.

the depositional site or somewhere between the two, such as in an intermediate sedimentary host.

Description

Heavy minerals are concentrated into millimetric to centimetric laminations disseminated in quartzitic sandstones and may be observable in a 5 to 80 meter-thick sequence. Locally, the heavy minerals are present in thin semimassive black beds (up to 60% heavy minerals) reaching only a thickness of 2 to 5 m. Figure 1.2 shows the rutile distribution (% vol.) as either disseminated laminations (triangle) or as semimassive black beds (circle). The rutile is fine-grained (50-200 μm) and forms 1 to 7% of the mineral assemblages in the 5-80 m-thick disseminated laminations and forms 10 to 30% in the 2-5 m-thick semimassive beds. The rutile is present either as euhedral crystals or as detrital ilmenite pseudomorphs.

Enrichment processes

Recent work on Sutton paleoplacers revealed that the rutile is a post-depositional product derived from a two-stage alteration of detrital hemo-ilmenite (Hebert and Gauthier, in press). Figure 1.3 shows the complete evolution of the Sutton paleoplacer mineralogy from the source rock to the metamorphosed sediments. The original hemo-ilmenite has been altered after deposition before and during metamorphism. Pseudorutile and nano-aggregates of anatase were the products resulting from this alteration. In a second part, retrograde metamorphic fluids transformed these nano-aggregates of anatase into coarse-grain rutile, thus beneficiate the original ilmenite in terms of

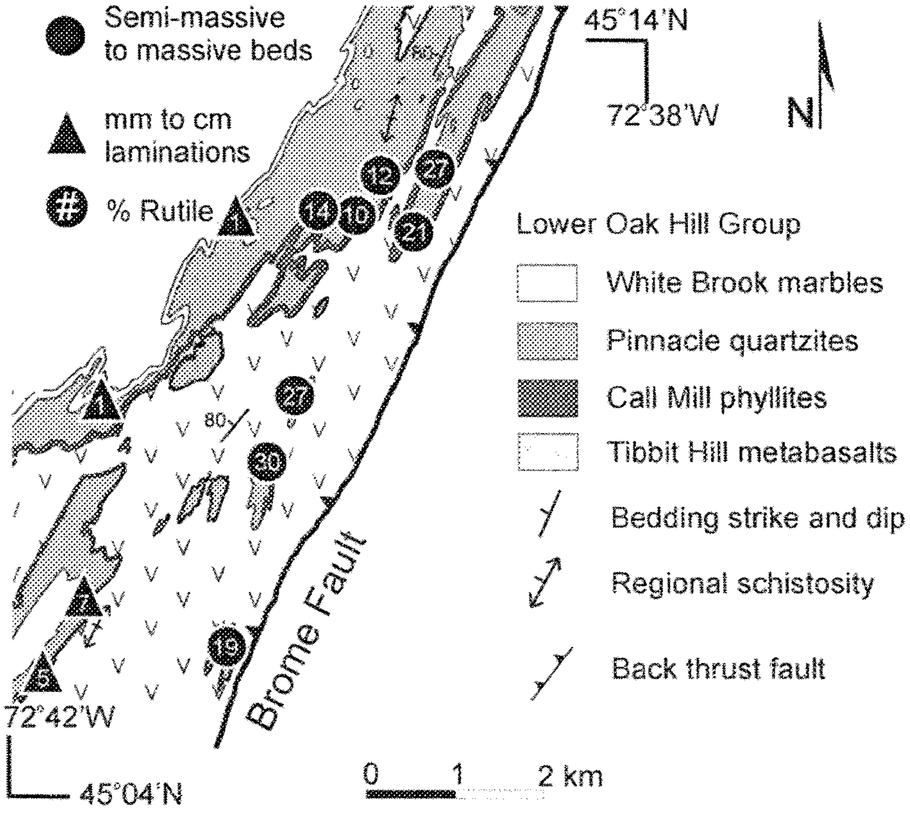

Figure 1.2 Geological map of the Sutton area showing the distribution of semimassive beds (circle) and disseminated laminations of heavy minerals (triangle). Numbers in the circle and triangle represent the % vol. of rutile.

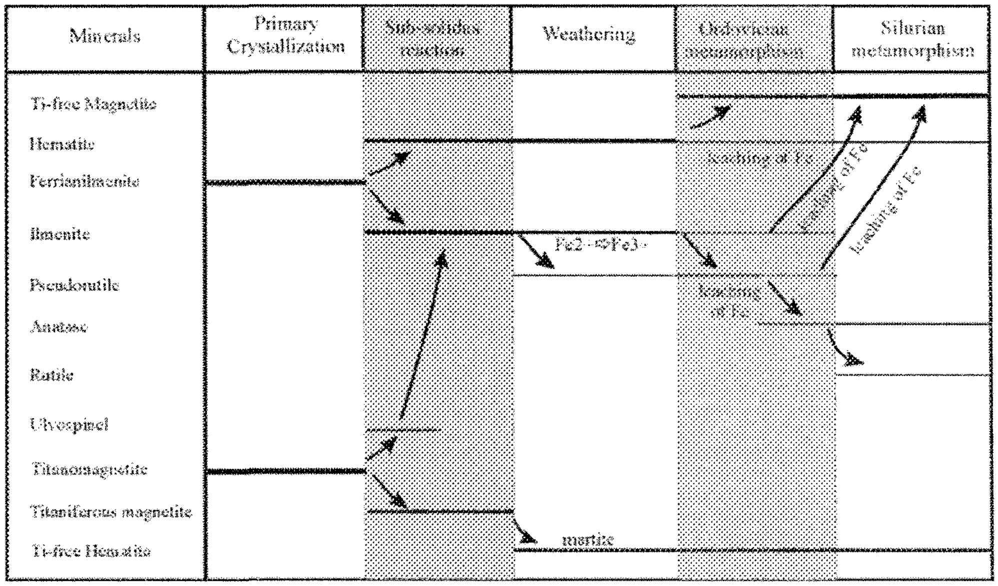

Figure 1.3 Diagram showing the evolution of the Sutton heavy minerals through time.

mineralogy (rutile) and physical properties (no-longer a porous and fragile aggregate). Such low-grade metamorphic transformation of nano-anatase into rutile has never been reported elsewhere in titanium deposits.

Economic applications

Many authors (Grey and Reid, 1975; Dimanche and Bartholomé, 1976; Force, 1991a; Mücke and Chaudhuri, 1991) pointed out the importance of weathering on the Fe-Ti heavy minerals at the depositional site. Weathering processes allow chemical leaching of elements such as iron and magnesium from the titaniferous minerals and thus increase the TiO_2 proportion of the oxide grains. However, chemical alteration of ilmenite grains commonly results in a micro-aggregate of titanium oxides known as leucoxene, which could not survive transport on a long distance and keep its original coarseness (Grey and Reid, 1975; Force, 1991). Unless other processes are involved, pre-depositional weathering of ilmenite, either directly at the source rock or intermediate sedimentary host, has a deleterious effect because it breaks the original properties of ilmenite (i.e. density, hardness) that can facilitate concentration by sedimentologic processes. Under special circumstances, metamorphism affecting such intermediate sedimentary hosts may recrystallize these porous leucoxene grains into single coarse-grained rutile, thus can be preserved and be concentrated in placers. Until now, no metamorphic rutile-generating processes were known to occur under greenschist facies and low-grade metamorphic rocks were therefore systematically rejected as rutile-bearing source rocks. However, our new observations at Sutton open a whole new range of potential sources for rutile via an intermediate sedimentary host within low-metamorphic terrains. Furthermore, placers formed from such intermediate sedimentary hosts did not require further tropical weathering because the enrichment had already occurred. Thus, potential rutile placers could be expected under higher latitude than the actual sub-tropical and tropical exploration targets.

References

Anand, R.R. and Gilkes, R.J., 1984, Weathering of ilmenite in a lateritic pallid zone: Clays and Clay Minerals, v. 32, p. 363-374.

Bailey, S.W., Cameron, E.N., Spedden, H.R. and Weege, R.J., 1956, The alteration of ilmenite in beach sands: Economic Geology, v. 51, p. 263-279.

Butt, C.R.M., 1985; Granite weathering and silcrete formation on the Yilgarn Block, Western Australia: Australian Journal of Earth Sciences, v. 32, p. 415-432.

Castonguay, S., Ruffet, G., Tremblay, A. and Féraud, G., 2001, Tectono-metamorphic evolution of the southern Quebec Appalachians: 40Ar/39Ar evidence for Middle Ordovician crustal thickening and Silurian-Early Devonian exhumation of the internal Humber zone: Geological Society of America Bulletin, v. 113, no 1, p. 144-160.

Cheel, R.J., 1984, Heavy mineral shadows, a new sedimentary structure formed under upper-flow-regime conditions: its directional and hydraulic significance: Journal of Sedimentary Petrology, v. 54, No. 4, p. 1175-1182.

Clark, T.H., 1936, A Lower Cambrian Series from Southern Quebec: Transactions of the Royal Canadian Institute, no 45, v. 21, part I, p. 135-151.

Colpron, M., 1992, Géologie de la région du lac Brome (Estrie): ET- Direction Générale de l'Exploration Géologique et Minérale ET-90-09. 96 pp.

Colpron, M., Faure, S. and Dowling, W., 1994, Géologie de la région de Sutton (Montérégie): Ministère des Ressources Naturelles du Québec, ET 92-05. 85 pp.

Czamanske, G.K., Force, E.R., and Moore, W.J., 1981, Some geologic and potential resources aspects of rutile in porphyry copper deposits: Economic Geology, v. 76, p.2240-2245.

Darby, D.A., 1984, Trace elements in ilmenite: A way to discriminate provenance or age in coastal sands: Geological Society of America Bulletin, v. 95, p. 1208-1218.

Dimanche, F., 1972, Évolution minéralogique de quelques sables titanifères d'Afrique du Sud: Annales Société Géologique de Belgique, t. 95, p. 183-190.

Dimanche, F., and Bartholomé, P., 1976, The alteration of ilmenite in sediments: Minerals Science Engineering, v. 8, p. 187-200.

Dowling, W.M., 1988, Depositional environment of the lower Oak Hill Group, southern Quebec: implications for the late Precambrian breakup of North America in the Quebec reentrant: University of Vermont: Burlington, VT, United States; Master's, 186 pages.

Edou-Minko, A., Colin, F., Trescases, J.J., 1995, Altérabilité des minéraux titanés (ilménite et rutile) et mobilité du titane dans les profils d'altération du secteur d'Ovala (Gabon) : Journal of African Earth Sciences, v. 21 no. 2, p. 313-318.

Eilu, P.K., Mathison, C.I., Groves, D.I., Allardyce, W.J., 1999, Atlas of alteration assemblages, styles and zoning in orogenic lode-gold deposits in a variety of host rock and metamorphic settings: Geology and Geophysics Department (Centre for Strategic Mineral Deposits) & UWA Extension, The University of Western Australia, Publication NO. 30, 40p.

Force, E.R., 1976a, Metamorphic source rocks of titanium placer deposits; a geochemical cycle: U.S. Geological Survey Professional Paper 959-B, 16p.

Force, E.R., 1976b, Titanium minerals in deposits of other minerals: U.S. Geological Survey Professional Paper 959-F, 5p.

Force, E.R., 1980, The provenance of rutile: Journal of Sedimentary Petrology, v. 50, p.485-488.

Force, E.R., 1991a, Geology of titanium-mineral deposits: Geological Society of America, Special Paper 259, 112 pp.

Force, E.R., 1991b, Placer deposits, in: Force, E.R., Eidel, J.J., and Maynard, J.B. (Editors), Sedimentary and diagenetic mineral deposits: a basin analysis approach to exploration: Reviews in economic Geology, v.5, p.131-140.

Force, E.R., Sukirno, D., and van Leeuwen, T., 1984, Exploration for porphyry metal deposits based on rutile distribution; a test in Sumatra: U.S. Geological Survey Bulletin 1558-A, 9p.

Goldsmith, R., and Force, E.R., 1978, Distribution of rutile in metamorphic rocks and implications for placer deposits: Mineralium Deposita, v. 13, p. 329-343.

Grey, I.E. and Reid, A.F., 1975, The structure of pseudorutile and its role in the natural alteration of ilmenite: American Mineralogist, v. 60, p. 898-906.

Hartman, J.A., 1959, The titanium mineralogy of certain bauxites and their parent materials: Economic Geology, v. 54, p. 1380-1405.

Hébert, E., and Gauthier, M., in press, Unconventional rutile deposits in the Quebec Appalachians: Product of hypogene enrichment during low-grade metamorphism: Economic Geology.

Herz, N., 1976; Titanium deposits in alkalic igneous rocks: U.S. Geological Survey Professional Paper, 959-E, 6p.

Inman, D.L., Ewing, G.C., and Corliss, J.B., 1966, Coastal sand dunes of Guerrero Negro, Baja California, Mexico: Geological Society of America Bulletin, v. 77, p.787-802.

Karkhanavala, M.D., 1959, The alteration of ilmenite: Economic Geology, v. 54, p. 1095-1102.

Komar, P.D., and Wang, C., 1984, Processes of selective grain transport and the formation of placers on beaches: Journal of Geology, v. 92, p. 637-655.

Lynd, L.E.,1960, Alteration of ilmenite: Economic Geology, v. 55, p. 1064-1068.

Marquis, R., and Kumarapeli, P.S., 1993, An early Cambrian deltaic model for an Iapetan riftarm drainage system, southeastern Quebec: Canadian Journal of Earth Sciences, v. 30, p. 1254-1261.

Mücke, A., and Chaudhuri, J.N.B., 1991, The continuous alteration of ilmenite through pseudorutile to leucoxene: Ore Geology Reviews, v. 6, p. 25-44.

Narayanaswamy and Ghosh, S.K., 1987, Lateritisation of gabbro-granophyre rock units of the Ezhimala Complex of north Kerala, India: Chemical Geology, v. 60, p. 251-257.

Puffer, J.H., and Cousminer, H. L., 1982, Factors controlling the accumulation of titanium-iron oxide-rich sands in the Cohansey Formation, Lakehurst area, New Jersey: Economic Geology, v. 77, p. 379-391.

Schroeder, P.A., Le Golvan, J.J., and Roden, M.F., 2002, Weathering of ilmenite from granite and chlorite schist in the Georgia Piedmont: American Mineralogist, v. 87, p.1616-1625.

Slingerland, R., and Smith, N.D., 1986, Occurrence and formation of water-laid placers: Annual Reviews on Earth and Planetary Sciences, v.14, p. 113-147.

Stanaway, K.J., 1992, Heavy mineral placers: Mining and Engineering, v. 44, p. 352-358.

Stanaway, K.J., 1994, Overview of titanium dioxide feedstocks: Mining Engineering, p.1367-1370.

Stanaway, K.J., 1996, The Eastern North America Titanium Province-A Review: Lithology and Mineral Resources, v. 31, no. 6, p. 509-517.

Stapor, Jr. F.W., 1973, Heavy mineral concentrating processes and density/shape/size equilibria in the marine and coastal dune sands of the Apalachicola, Florida, region: Journal of Sedimentary Petrology, v. 43, no.2, p. 396-407.

Temple, A. K., 1966, Alteration of ilmenite: Economic Geology, v. 61, p. 695-714.

Teufer, G., and Temple, A.K., 1966, Pseudorutile-a new mineral intermediate between ilmenite and rutile in the natural alteration of ilmenite: Nature (London), 211, p.179-181.

Welch, B.K., 1964, The ilmenite deposits of Geographe Bay: Australasian Institute of Mining and Metallurgy Proceedings, no. 211 p. 25-48.

CHAPTER II

Unconventional Rutile Deposits in the Quebec Appalachians: Product of Hypogene Enrichment during Low-Grade Metamorphism

(In press in Economic Geology)

Abstract

Unconventional rutile deposits occur in heavy mineral paleoplacers of the Pinnacle Formation in the Humber Zone of the Quebec Appalachians. Detrital hemo-ilmenite represents 65% of the heavy mineral assemblage and is the main titanium mineral. Detrital rutile is also present in trace amounts. Post-depositional and metamorphic alteration processes increased the titanium content of the hemo-ilmenite grains by leaching elements, particularly Fe. New minerals created by these processes include pseudorutile, anatase (a TiO_2 polymorph), and neorutile. Early metamorphic magnetite enclosed detrital grains and preserved evidence of premetamorphic weathering or diagenetic processes by isolating the grains from metamorphic fluids, thus preventing further leaching. Detrital grains that were not protected by this magnetite were metamorphically leached to the purer TiO_2 mineral phase of anatase. Grains of anatase locally recrystallized to neorutile during a late orogenic back thrusting event in the Silurian. This is supported by $\delta^{18}O_{water}$ in equilibrium with metamorphic magnetite and by the fact that neorutile is limited to the eastern part of the synformal keel near the back thrust fault and is rarely observed further west, where anatase is predominant. Rutile formed under greenschist metamorphic conditions from primary hemo-ilmenite detrital grains via intermediate pseudorutile and anatase phases. This is the first known report of titanium mineral enrichment occurring under low pressure and temperature metamorphic conditions. Our results could have significant implications for mineral exploration because they demonstrate that paleoplacer source regions are not restricted to eclogite and granulite facies terrains.

Introduction

Previous studies have shown that the optimum source rocks for titaniferous placers are limited to rocks that underwent high pressure and temperature metamorphism, such as eclogite and granulite facies (Goldsmith and Force, 1978; Force, 1991; Stanaway, 1996). Above the sillimanite zone, titanium is released from silicate phases and recrystallized as oxides, particularly rutile. Below the sillimanite zone, titanium preferentially combines with calcium to form titanite, or with uranium to form brannerite. Rutile is only preserved under specific conditions, such as in calcium-poor host rocks (Goldsmith and Force, 1978; Force 1991). The Cambrian metasediments in the Sutton region of the Quebec Appalachians have unusually high concentrations of rutile and anatase for rocks which contain a greenschist mineral assemblage. In this area, the Ti-bearing strata contain more than 20% TiO_2, are 5 to 30 m thick, and crop out over an area of 20 km^2.

Exceptional sedimentary processes and post-depositional weathering were initially invoked to explain the abundance of rutile in these greenschist facies metasediments (Colpron et al., 1994; Gauthier et al., 1994). The present study re-evaluates this hypothesis by examining the role of metamorphism on the Fe-Ti-bearing oxides. We show that greenschist facies metamorphism played a major role in the Ti-enrichment of detrital and paleoweathered hemo-ilmenite grains as a result of recrystallization to coarse neorutile grains. To our knowledge, this is the first report of a rutile-generating process at low pressure and temperature. This finding has implications for recognizing potential source regions for titanium mineral placer deposits.

Supergene enrichment of ilmenite grains by iron leaching is well known in unconsolidated Quaternary and Tertiary placers (Bailey et al., 1956; Karkhanavala, 1959; Lynd, 1960; Welch, 1964; Temple, 1966; Dimanche, 1972; Grey and Reid, 1975; Dimanche and Bartholomé, 1976; Puffer, and Cousminer, 1982; Darby, 1984; Force, 1991; Mücke and Chaudhuri, 1991). However, very few papers describe the enrichment of ilmenite in consolidated placers (Faure, 1978; Coipel and Dimanche, 1981; Morad and Aldahan, 1986) or studies of metamorphosed placers (Muresan, 2002). Although they can represent considerable resources of titanium, such as american Cretaceous shoreline deposits, no specific criteria have been developed to evaluate the effects of metamorphism on titanium oxide-rich metasediments (Force, 1991; 2000; 2001, Stanaway, 2005). The Sutton paleoplacers have a range of metamorphic titanium oxide phases, presenting an ideal case study of the effects of metamorphism on hemo-ilmenite grains.

Geological Setting

The rutile-rich horizons at Sutton are hosted by sedimentary rocks of the Cambrian Lower Oak Hill Group, located in the Humber Zone of the Quebec Appalachians, south of the Precambrian Grenvillian basement (Fig. 2.1). Colpron (1992), and Marquis and Kumarapeli (1993) proposed that the source rocks for the Sutton deposits were the highly deformed and metamorphosed Grenvillian gneisses and the anorthosite suites that intruded them. They proposed that the Iapetan Ottawa River drained these titanium oxide-rich source regions during Cambrian time to form heavy mineral placers in a rift-associated basin that comprises the Oak Hill Group (Marquis and Kumarapeli, 1993). The heavy mineral paleoplacers examined during this study are hosted by the Pinnacle Formation, a 150-m thick sandy unit within the Oak Hill Group (Fig. 2.2; Clark, 1936; Dowling, 1988; Colpron, 1992; Colpron et al., 1994). The Pinnacle Formation is overlain by a dolomitic marble of the White Brook Formation and underlain by the alkaline metavolcanic rocks of the Tibbit Hill Formation. The Call Mill phyllite member, defined by Charbonneau (1980) as a distinct unit within the Pinnacle Formation, is locally present between the Pinnacle metasandstones and the Tibbit Hill metabasalts. The Oak Hill Group was deformed and metamorphosed to a greenschist facies mineral assemblage during the Taconian Orogeny (469-461 Ma) and was subjected to backthrusting in the Silurian (431-411 Ma; Castonguay et al., 2001). In the Sutton region, the Pinnacle Formation is preserved within a 5 x 10 km synformal keel and is bounded to the east by the Brome back thrust fault that trends NNE and dips 30° to the NNW.

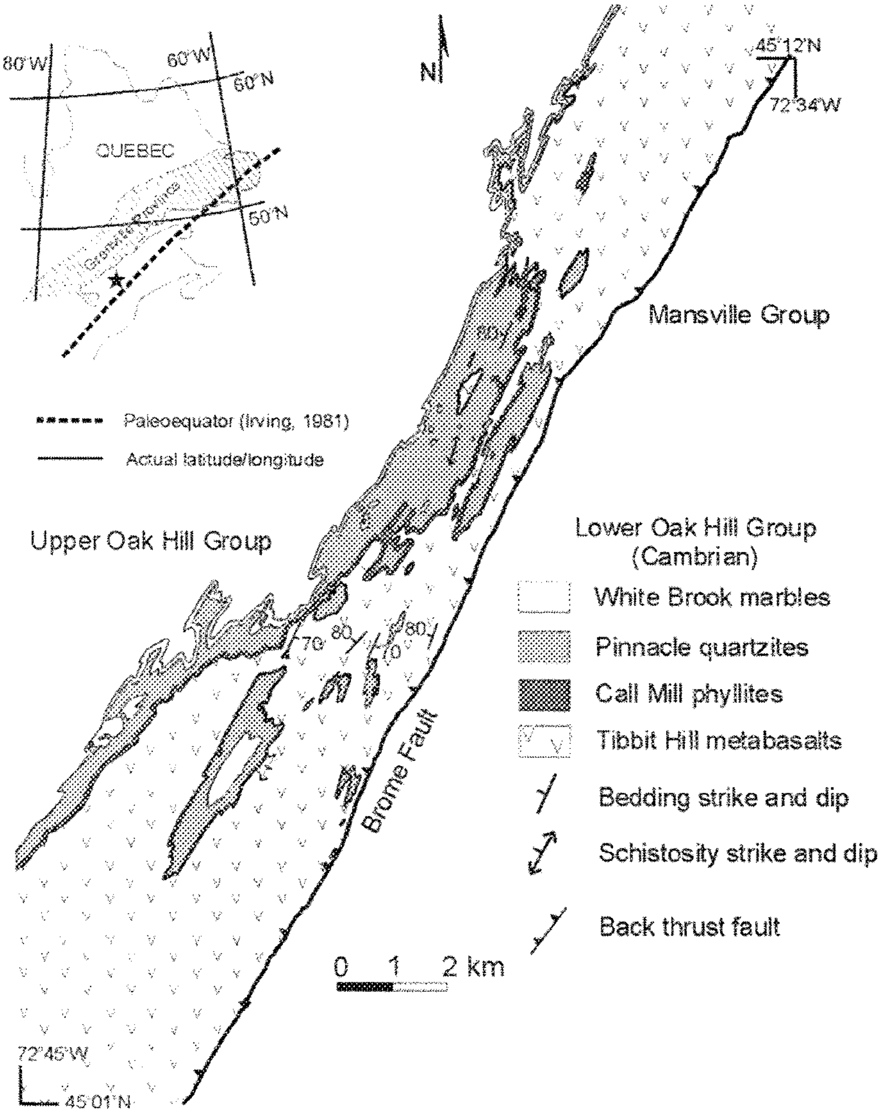

Figure 2.1 Geological map of the Sutton area and its position relative to the Grenville Province (after Colpron, 1992, and Colpron et al., 1994). The inset shows the paleoequator position of the region during Cambrian time (Irving, 1981).

Dowling (1988) subdivided the Pinnacle metasandstones into Lower and Upper units. In the present study, the Pinnacle is instead divided into three units: lower, middle and upper (Fig. 2.2). This new subdivision is based on matrix compositions and the relative abundance of heavy minerals. The lower unit, a medium-grained quartzite with a muscovite-rich matrix, is 3 to 20 m thick near the Brome Fault and thickens westward up to 70 m. The middle unit is a cross-laminated or semimassive, black to dark green, 7 to 80 m-thick sandstone with abundant heavy minerals in a chlorite-rich matrix. The upper unit of the Pinnacle Formation, a cross-laminated muscovitic metawacke with millimeter-scale layers of heavy minerals, is 10 to 55 m thick and is only preserved in the western part of the synformal keel. Dolomite locally comprises 5 to 15% of the rock.

The middle unit is the main focus of this study. The heavy minerals locally comprise up to 60 vol.% of the rock and are concentrated in distinctive millimeter- to centimeter-scale layers that are cross-bedded at the meter scale. Several types of fine-grained (200 to 250 μm) Fe-Ti mineral oxides form the heavy mineral assemblage: anatase (20%), rutile (18%), ilmeno-hematite (hematite with exsolutions of ilmenite; 15%), pseudorutile (12%), hemo-ilmenite (ilmenite with exsolutions of hematite; 5%) and strongly martitized titaniferous magnetite (3%; Fig. 2.3). Titanium-free magnetite is closely associated with the heavy mineral laminations and forms 10% of the assemblage. It is a characteristic of the middle unit and differs from the detrital titaniferous magnetite grains because of its coarser grain sizes (0.5 to 2 mm) and euhedral nature (Fig. 2.4A). Chlorite occurs in pressure shadows around Ti-free magnetite, indicating that magnetite crystallization occurred at the onset of metamorphism during the Taconian Orogeny (Charbonneau, 1981). Zircon is also present and accounts for 10 vol.% of the heavy

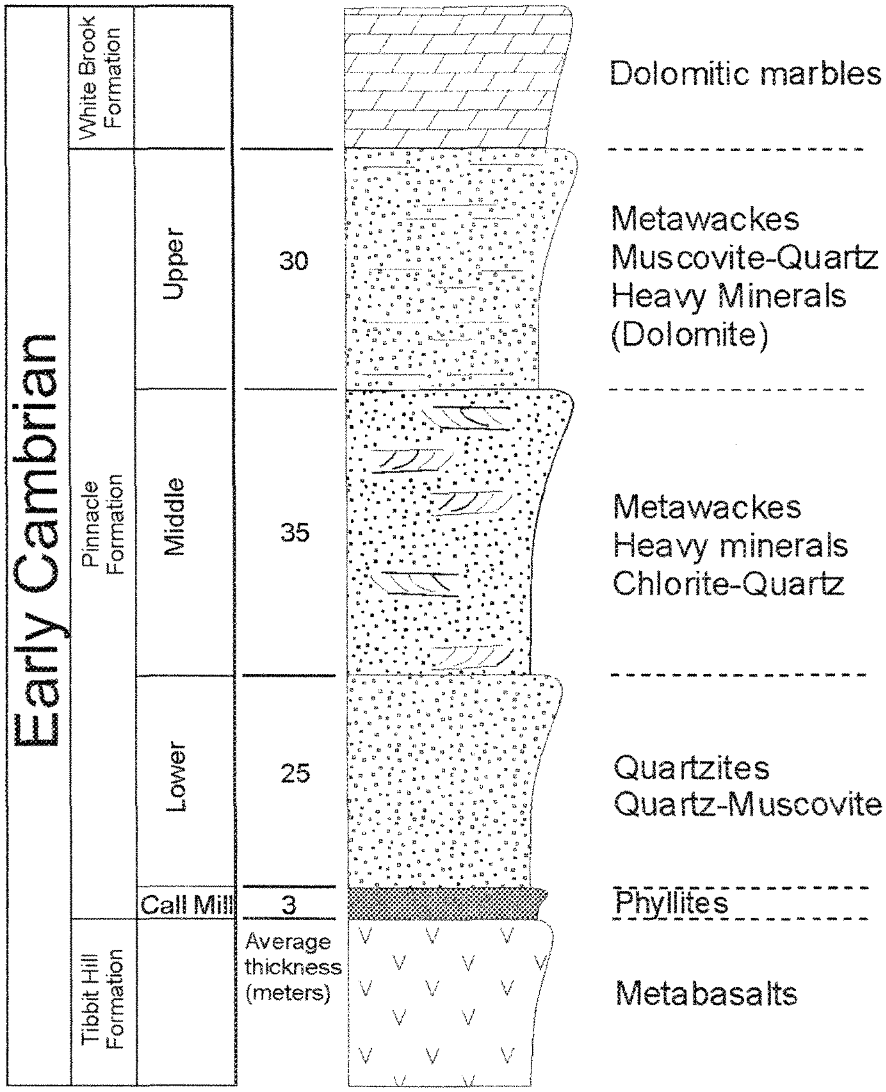

Figure 2.2 Schematic stratigraphic column of the Pinnacle Formation and its four units (modified from Dowling, 1988) showing the heavy mineral concentrations of the middle Pinnacle unit.

Heavy mineral	Heavy mineral fraction % vol observed	Pre-weathered detrital fraction % vol
Rutile	18	Hemo-ilmenite 65
Anatase	20	
Pseudorutile	12	
Hemo-ilmenite	5	
Ti-free Magnetite	10	
Ilmeno-hematite	15	15
Zircon	10	10
Tourmaline	5	5
Titaniferous Magnetite	3	3
Other	2	2

Figure 2.3 Distribution of the heavy minerals in the premetamorphic and metamorphic (italics) assemblages. The central column represents the heavy mineral percentages observed in the samples. The right column represents the interpreted pre-weathered (and premetamorphic) equivalence of some heavy minerals.

mineral fraction. The grains are well preserved, with only a few heavily fractured grains. Detrital tourmaline accounts for about 5% of the heavy mineral fraction. Overgrowths of metamorphic tourmaline surround detrital tourmaline, a process that can also be related to the Taconian Orogeny (Fig. 2.4B; Rickard, 1964). Other heavy minerals occur in minor proportions, notably apatite and detrital rutile.

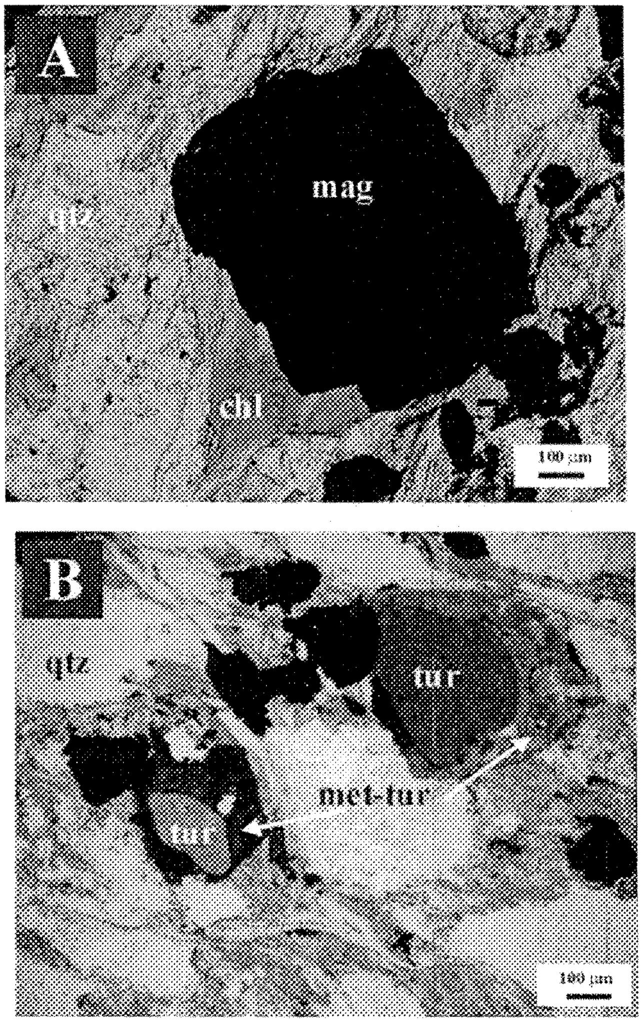

Figure 2.4 Photomicrographs of metamorphic mineral assemblages observed under plane polarized transmitted light. A) Ti-free magnetite, showing chlorite in its pressure shadow. Chl = chlorite, mag = magnetite, qtz = quartz. B) Detrital tourmaline grains with metamorphic overgrowths of tourmaline. Met-tur = metamorphic tourmaline, qtz = quartz, tur = tourmaline.

Mineralogy of Fe-Ti Oxides

The titanium oxide minerals in the Sutton rocks comprise mineral phases that correspond to four different stages of transformation : hemo-ilmenite with a pitted texture (stage 1), pseudorutile (stage 2), nanocrystalline anatase (stage 3), and neorutile (stage 4). A petrographic study of more than 3000 grains was carried out to determine whether the crystallization of rutile occurred during post-depositional weathering or during metamorphism. Pitted hemo-ilmenite from stage 1 exhibit low porosity and relict hematite exsolution patterns (Fig. 2.5A). Grains of stage 2 pseudorutile display a more homogeneous texture with abundant voids that are interpreted to be a product of leaching of iron from of hemo-ilmenite (Fig. 2.5B). Pseudorutile, also known as arizonite, was defined as a distinct mineral by Overholt (1950), Teufer and Temple (1966), Grey and Reid (1975), and Mücke and Chaudhuri (1991). Nanocrystalline anatase from stage 3 consists of nearly pure TiO_2 and is interpreted to be a residual phase. The original hemo-ilmenite exsolution pattern is still recognizable and gives the anatase grains their highly porous mesh-like texture (Fig. 2.5C and D). During stage 4, nanocrystalline anatase was completely recrystallized into coarse-grained rutile, which destroyed any associated voids and porosity (Fig. 2.5E and F). Some grains show features that are intermediate between stage 3 and stage 4, where the nucleation and growth of rutile occurred at the interface between anatase nanoparticules (Fig. 2.6). If all four stages represent different degrees of transformation of original hemo-ilmenite grains, it is possible to infer that the proportion of detrital hemo-ilmenite in the original (pre-consolidation) heavy mineral fraction was 65 vol.% (Fig. 2.3). The compositions of these Fe-Ti oxides were analyzed using a JEOL

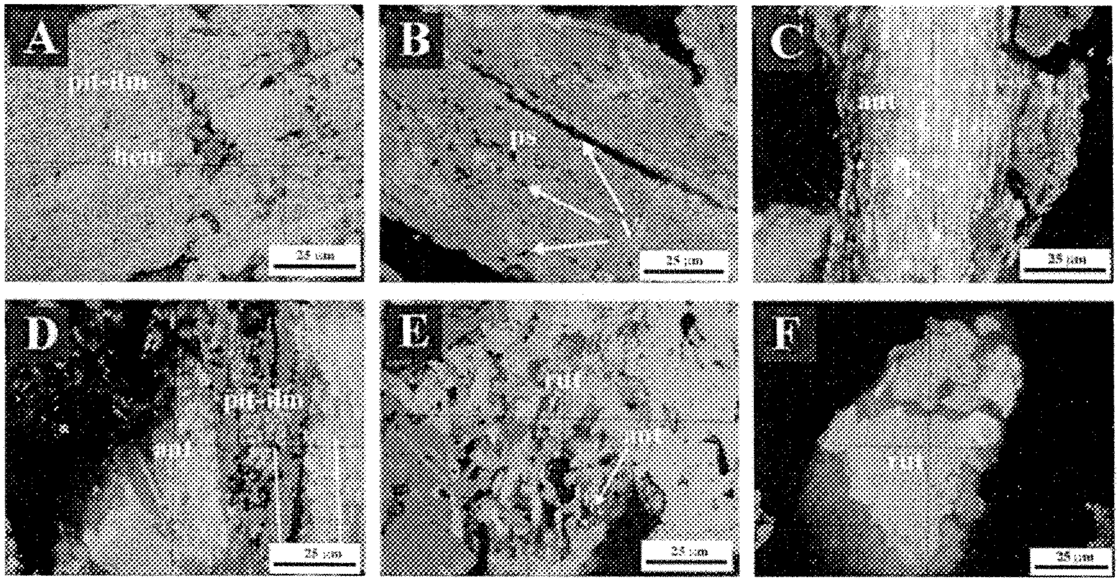

Figure 2.5 Photomicrographs of hemo-ilmenite grains showing features that are interpreted to represent different stages of iron leaching (observed under oil in natural reflected light). A) Stage 1 pitted hemo-ilmenite grain. Note that the hematite lamellae are not affected. Hem = hematite, Pit-ilm = pitted ilmenite. B) Stage 2 pseudorutile grain showing a more homogeneous texture. Voids are preferentially developed along hematite exsolution planes. Ps = pseudorutile, v = void. C) Stage 3 mesh-textured grain of anatase showing well-developed porosity. Ant = anatase. D) Stage 3 partially mesh-textured anatase grain with residual pitted ilmenite showing an exsolution pattern parallel to the nanocrystalline texture of the anatase grain (indicated by white lines). E) Stage 4 neorutile crystals developed from nanocrystalline anatase. Rut = rutile. F) Single grain of Stage 4 coarse-grained neorutile.

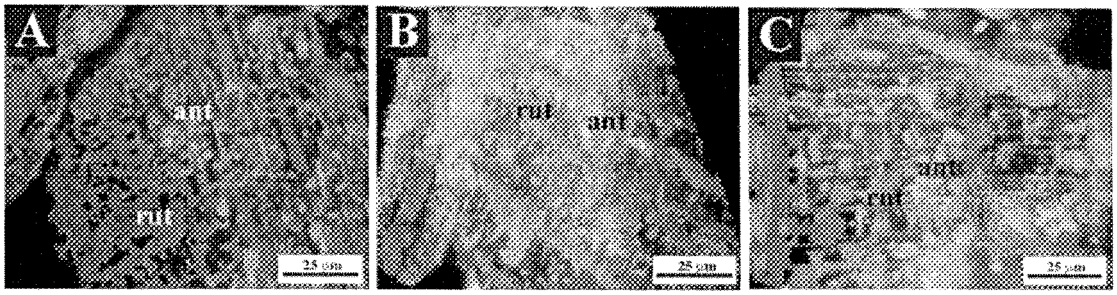

Figure 2.6 Photomicrographs of rutile that nucleated and grew from the nanocrystalline anatase interfaces (observed under oil in natural reflected light). Anatase shows lighter internal reflections than rutile. Rutile has a more homogeneous aspect. Ant = anatase, rut = rutile.

JXA-8900 electron microprobe operated at 15kV, with a specimen current of 20nA and a beam diameter of 10 μm. The range of mineral compositions is interpreted to reflect significant iron leaching, upgrading the proportion of TiO_2 from 37 wt.% up to 99 wt.% (Fig. 2.7).

Some of the leached detrital hemo-ilmenite grains were trapped as inclusions during the crystallization of metamorphic magnetite, which formed widely during the Taconian orogeny (Charbonneau, 1981). During its crystallization, the metamorphic magnetite isolated the trapped grains and preserved them from further leaching by metamorphic fluids (Fig. 2.8A and B). All other Fe-Ti oxide grains appear to have been subjected to iron leaching by metamorphic fluids. This is illustrated by the fact that some partially exposed inclusions in magnetite show a different degree of leaching than the fully enclosed grains (Fig. 2.8C). Preserved exsolutions of hematite in trapped grains show that no metamorphic reaction took place between magnetite and their inclusions. Thus, trapped grains record the degree of titanium enrichment that occurs before the backthrusting-associated metamorphism. Pitted hemo-ilmenite (stage 1), pseudorutile (stage 2) and a minor proportion of anatase (stage 3) were all found as inclusions in the metamorphic magnetite; however, no rutile was found (Fig. 2.9A). About 71% of the free grains comprise either anatase (stage 3) or rutile (stage 4; Fig. 2.9B). The crystallization of rutile must have occurred during the metamorphism associated with the last part of the Taconian orogeny and/or during the back thrusting event during the Silurian, because no other thermal event is recognized in the area.

The distribution of rutile and anatase with respect to the Brome Fault, a backthrust of Silurian age suggests that the crystallization of rutile after anatase was related to this

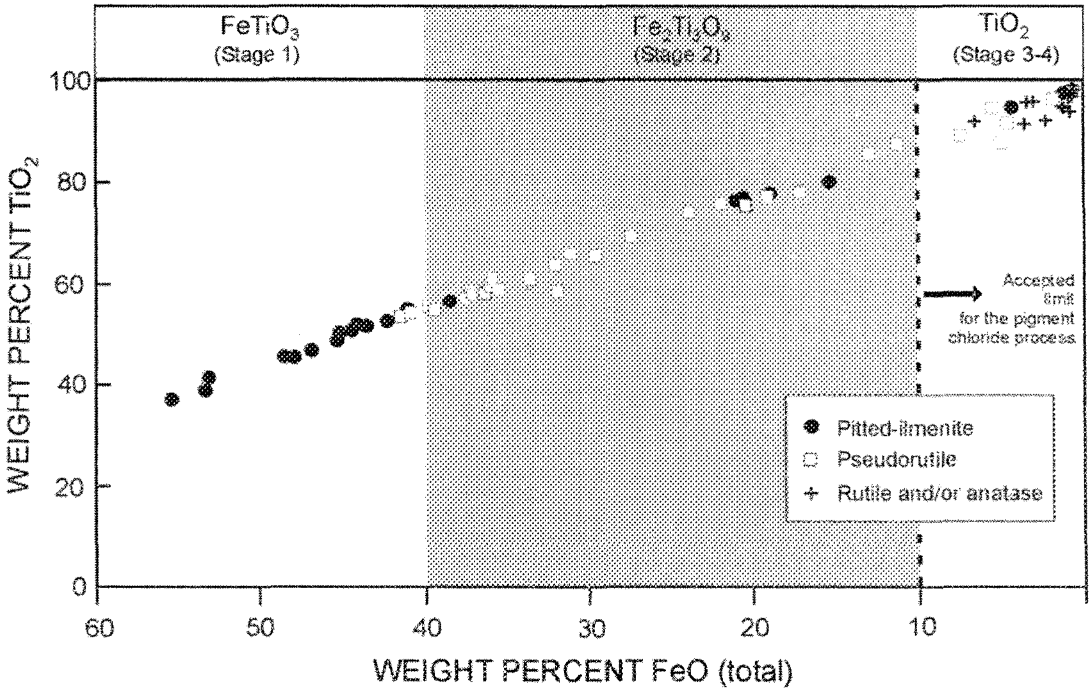

Figure 2.7 Diagram showing the progressive enrichment in TiO_2 of the Fe-Ti oxides (pitted-ilmenite, pseudorutile, anatase/rutile), analyzed using a microprobe (see Appendix A). The accepted limit for iron in titanium oxides is shown by the vertical dash line (10%, according to Stanaway 1994).

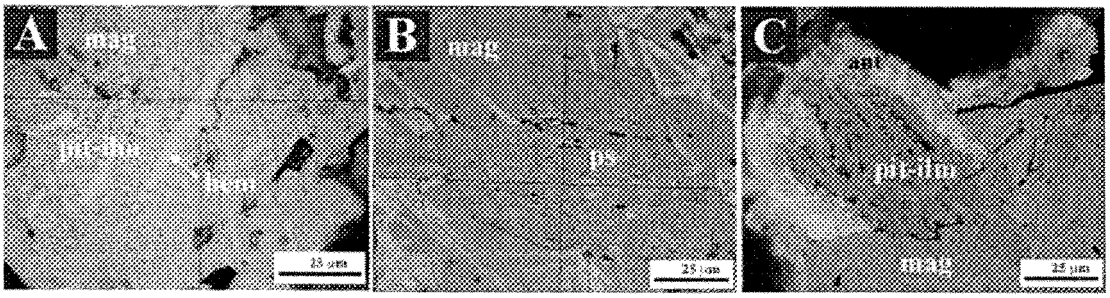

Figure 2.8 Photomicrographs of a hemo-ilmenite grains trapped by metamorphic magnetite (observed under oil in natural reflected light). A) The apparent leaching of the trapped grain is characteristic of pitted hemo-ilmenite of stage 1. Note that the hematite lamellae are not affected, which is typical of this stage of leaching. Hem = hematite, mag = magnetite, pit-ilm = pitted ilmenite. B) Trapped pseudorutile grain corresponding to Stage 2. Ps = pseudorutile. C) Partially trapped grain. The exposed part shows a deeper leaching level and comprises nanocrystalline anatase of Stage 3. The trapped part shows a different leaching level, corresponding to pitted hemo-ilmenite of Stage 1. Note that the exsolution lamellae of hematite are still preserved in the trapped part. Ant = anatase.

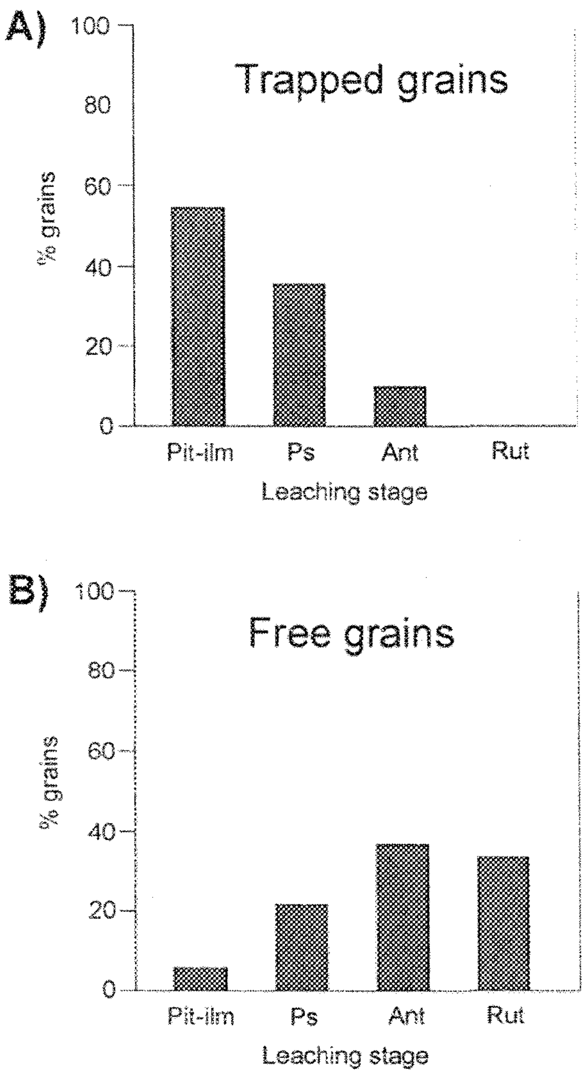

Figure 2.9 Histogram showing the percentage of different Fe-Ti oxide grains according to their stage of alteration (pitted hemo-ilmenite, pseudorutile, anatase and rutile), based on a petrographic study performed on more than 3,000 grains from across the region. A) Grains trapped in magnetite (n=367). B) Free grains (n=2,828). Note that trapped grains are dominantly pitted hemo-ilmenite or pseudorutile, whereas more than 70% of free grains are anatase or rutile.

late-stage fault. Metamorphic neorutile grains are restricted to the eastern part of the synformal keel, near the Brome Fault, whereas the majority of the titanium oxides in the western part are anatase (Fig. 2.10). There is no other mineralogical indication of different metamorphic conditions around the Brome Fault. However, the high density of quartz veins and veinlets near the fault suggests extensive fluid flow during the Silurian back thrust event (A. Tremblay, pers. commun., 2006). Focussing of such fluids by the Brome Fault could have been responsible for the anatase-to-rutile transition, as rutile is most abundant in the vicinity of the Brome Fault.

Figure 2.10 Geographical distribution and relative abundances of rutile and anatase from selected locations (squares). Rutile is dominant near the Brome Fault, but the proportion drops sharply to the west where anatase is more abundant.

Oxygen Isotopes

Oxygen isotope analysis of the metamorphic magnetite was carried out to determine if the paleoplacer deposits could have been affected by fluid flow along the Brome Fault. Samples were taken along cross-sections perpendicular to the Brome Fault to test for any zonation in the isotopic composition of fluids that could explain the rutile/anatase distribution. Twenty-five samples were collected and crushed into a fine powder. Magnetite was isolated and dissolved in a bromine pentafluoride at 600°C. The oxygen produced was fixed to carbon via a carbon rod with a platine catalyzor. The CO_2 was then analyzed by mass spectrometry where $\delta^{18}O$ was compared to the Vienna-Standard Mean Ocean Water (V-SMOW). The isotopic composition of water in equilibrium with the magnetite was calculated using the magnetite-water fractionation factors of Cole et al. (2004) at 300°C and 400°C (cf. Trzcienski and Birkett, 1982; Castonguay and Tremblay, 2003). The calculated $\delta^{18}O$ value of water varies from 9.6‰ to 16.5‰, consistent with metamorphic water (Hoefs, 2004; Fig. 2.11). Contour lines of $\delta^{18}O_{water}$ shown in Figure 2.12 show a strong zonation away from the Brome Fault, confirming that the structure likely acted as a major conduit for late-stage metamorphic fluids.

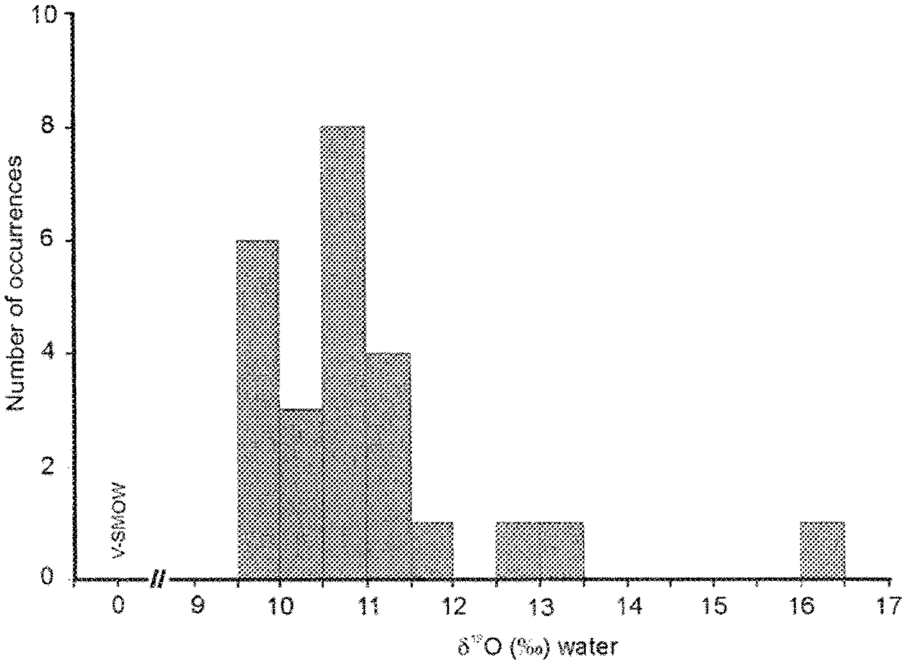

Figure 2.11 Histogram showing calculated $\delta^{18}O$ values of water in equilibrium with metamorphic magnetite.

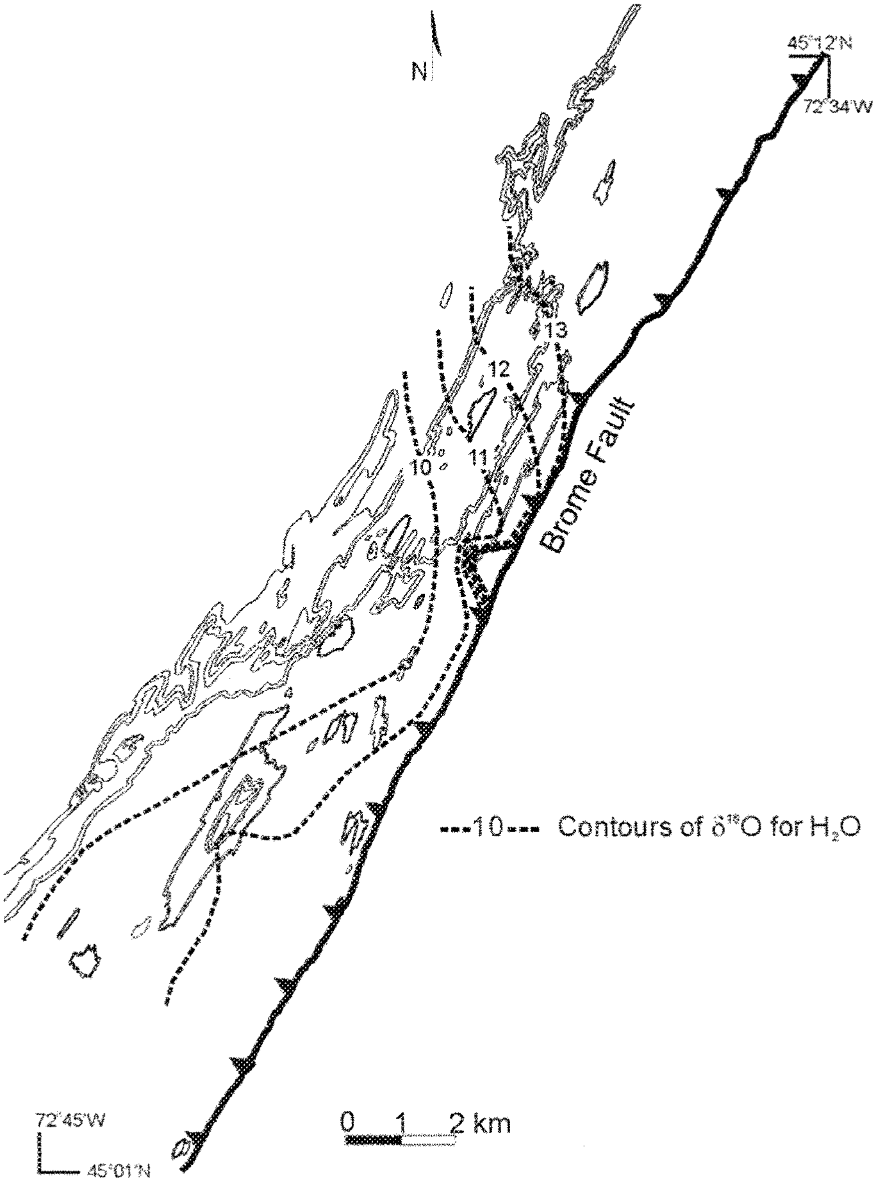

Figure 2.12 Contour lines of calculated $\delta^{18}O$ values of water showing a distribution parallel to the Brome Fault.

Discussion

Petrographic observations of the Sutton paleoplacers suggest that post-depositional weathering leached iron from detrital hemo-ilmenite grains. Complete Fe-leaching resulted in a pure-TiO_2 phase, usually anatase, similar to that observed in tropical weathering conditions in which humic acids contribute to iron leaching (Grey, and Reid, 1975; Dimanche and Bartholomé, 1976; Mücke and Chaudhuri, 1991). Sutton paleoplacers were subjected to such conditions during Cambrian time (Irving, 1981; Fig. 2.1), and post-depositional weathering would be expected to have affected the detrital hemo-ilmenite grains. Hemo-ilmenite grains trapped in metamorphic magnetite reveal that this premetamorphic weathering mainly produced pseudorutile (stage 2) and lesser anatase (stage 3), but not pure TiO_2. Further leaching through the interaction with prograde metamorphic fluids, as demonstrated by the grains that were not encased by magnetite, may account for the local occurrence of anatase. However, such weathering could not explain the locally abundant rutile, which usually occurs at high pressure and temperature (Shannon and Pask, 1964; Goldsmith and Force, 1978; Force 1991). At low pressures and temperatures the anatase to rutile transformation typically only occurs in the presence of cations (e.g. Mo, Cu or Fe) that may catalyze the reaction (Iida and Ozaki, 1961; Heald and Weiss, 1972; Eppler, 1987). However, Gribb and Banfield (1997), Penn and Banfield (1999), Zhang and Banfield (1999) have demonstrated experimentally that rutile can crystallize from nanocrystalline anatase, similar to that found in the Sutton deposits, under hydrothermal conditions. The distribution of rutile suggests that its crystallization was related to fluid flow along the Silurian backthrust fault. To our knowledge this is the first time that a transformation of anatase to rutile has been reported in low pressure and temperature metamorphic rocks. However, it is evident that the nanocrystalline anatase intermediate stage is an important precursor to rutile formation.

Summary and Implications

Consolidated placers in the Pinnacle Formation of Sutton contain hemo-ilmenite grains that have undergone pervasive post-depositional Fe-leaching. Crustal thickening in Middle Ordovician time caused regional metamorphism, which also participated in the leaching history of hemo-ilmenite grains, forming almost pure TiO_2 minerals (anatase). Neorutile did not crystallize until backthrusting of the Brome Fault in the Silurian focussed hydrothermal fluids into the area.

Both unconsolidated placers and magmatic ilmenite deposits account for more than 90% of current titanium world production (Force, 1991; TZ Minerals International, 2005). These conventional deposits are being depleted at a rapid rate due to rising global demand. The closing or opening of one or two deposits could radically change the supply-and-demand situation (TZ Minerals International, 2005; Heap, 2005). At the present time, only unconsolidated deposits provide economic resources of placer rutile. Leached hemo-ilmenite in the form of pseudorutile or anatase also occurs in these deposits as the product of iron leaching by humic acids. This type of deposit is limited to tropical and subtropical regions. This paper demonstrates that rutile may also occur in greenschist facies metamorphic rocks as a neoformed metamorphic mineral. New sources of rutile can thus be developed in low pressure and temperature metamorphic terrains. In the Sutton environment, metamorphic fluids driven by backthrust faulting are interpreted to have caused hypogene enrichment when weathered hemo-ilmenite grains recrystallized to neorutile.

Acknowledgements

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References

Bailey, S.W., Cameron, E.N., Spedden, H.R. and Weege, R.J., 1956, The alteration of ilmenite in beach sands: Economic Geology, v. 51, p. 263-279.

Castonguay, S., and Tremblay, A., 2003, Tectonic evolution and significance of Silurian-Early Devonian hinterland-directed deformation in the internal Humber zone of the southern Quebec Appalachians: Canadian Journal of Earth Sciences, v. 40, no 2, p. 255-268.

Castonguay, S., Ruffet, G., Tremblay, A. and Féraud, G., 2001, Tectono-metamorphic evolution of the southern Quebec Appalachians: 40Ar/39Ar evidence for Middle Ordovician crustal thickening and Silurian-Early Devonian exhumation of the internal Humber zone: Geological Society of America Bulletin, v. 113, no 1, p. 144-160.

Charbonneau, J.M., 1980, Région de Sutton (W): Ministère de l'Énergie et des Ressources du Québec, DPV-681, 89 pp.

Charbonneau, J.M., 1981, Analyse structurale et relations déformation-métamorphisme, Groupe d'Oak Hill, région du mont Sainte-Marguerite, Appalaches du Québec: Canadian Journal of Earth Sciences, v. 18, p. 1051-1064.

Clark, T.H., 1936, A Lower Cambrian Series from Southern Quebec: Transactions of the Royal Canadian Institute, no 45, v. 21, part I, p. 135-151.

Coipel, J. and Dimanche, F., 1981, Évolution diagénétique des oxydes de fer, chrome et titane: Bulletin de Minéralogie v. 104, p. 64-69.

Cole, D.R., Horita J., Eniamin, V., Polyakov, V.B., Valley, J.W., Spicuzza, M.J., Coffey, D.W., (2004) An experimental and theoretical determination of oxygen isotope fractionation in the system magnetite-H_2O from 300 to 800°C: Geochimica et Cosmochimica Acta, v. 68, p. 3569-3585.

Colpron, M., 1992, Géologie de la région du lac Brome (Estrie): ET- Direction Générale de l'Exploration Géologique et Minérale ET-90-09. 96 pp.

Colpron, M., Faure, S. and Dowling, W., 1994, Géologie de la région de Sutton (Montérégie): Ministère des Ressources Naturelles du Québec, ET 92-05. 85 pp.

Darby, D.A., 1984, Trace elements in ilmenite: A way to discriminate provenance or age in coastal sands: Geological Society of America Bulletin, v. 95, p. 1208-1218.

Dimanche, F., 1972, Évolution minéralogique de quelques sables titanifères d'Afrique du Sud: Annales Société Géologique de Belgique, t. 95, p. 183-190.

Dimanche, F., and Bartholomé, P., 1976, The alteration of ilmenite in sediments: Minerals Science Engineering, v. 8, p. 187-200.

Dowling, W.M., 1988, Depositional environment of the lower Oak Hill Group, southern Quebec: implications for the late Precambrian breakup of North America in the Quebec reentrant: University of Vermont: Burlington, VT, United States; Master's, 186 pages.

Eppler, R.A., 1987, Effect of antimony oxide on the anatase-rutile transformation in titanium dioxide: Journal of The American Ceramic Society, v. 70, no 4, p. C-64-C-66.

Faure, P.-P., 1978, Les grès à rutile et zircon du massif armoricain: PhD thesis, École National Supérieure des Mines de Paris, 305 pp.

Force, E.R., 1991, Geology of titanium-mineral deposits: Geological Society of America, Special Paper 259, 112 pp.

Force, E.R., 2000, Titanium mineral resources of the Western U.S.–an update: Open-File Report 00-442, 37 pp.

Force, E.R., Butler, R.F., Reynolds, R.L., Houston, R.S., 2001, Magnetic ilmenite-hematite detritus in Mesozoic-Tertiary placer and sandstone-hosted uranium deposits of the Rocky Mountains: Economic Geology, v. 96, p. 1445-1453.

Gauthier, M., Chartrand, F., Trottier, J., 1994, Metallogenic epochs and metallogenic provinces of the Estrie-Beauce region, Southern Quebec Appalachians: Economic Geology, v. 89, issue 6, p.1322-1360.

Goldsmith, R., and Force, E.R., 1978, Distribution of rutile in metamorphic rocks and implications for placer deposits: Mineralium Deposita, v. 13, p. 329-343.

Grey, I.E. and Reid, A.F., 1975, The structure of pseudorutile and its role in the natural alteration of ilmenite: American Mineralogist, v. 60, p. 898-906.

Gribb, A.A. and Banfield, J.F., 1997, Particle size effects on transformation kinetics and phase stability in nanocrystalline TiO_2: American Mineralogist, v. 82, p. 717-728.

Heald, E.F., and Weiss, C.W., 1972, Kinetics and mechanism of the anatase/rutile transformation, as catalyzed by ferric oxide and reducing conditions: American Mineralogist v. 57, p. 10-23.

Heap, A., 2005, Booming demand for titanium products: Mining Journal, London, September 30, p.18-21.

Hoefs, J., 2004, Stable Isotope Geochemistry, 5th, Revised and Updated Edition, Springer, 244 pp.

Iida, Y., and Ozaki, S., 1961, Grain growth and phase transformation of titanium oxide during calcination: Journal of The American Ceramic Society, v. 44, no 3, p. 120-127.

Irving, E., 1981, Phanerozoic continental drift: Physics of the Earth and Planetary Interiors, v. 24, Issues 2-3, p.197-204.

Karkhanavala, M.D., 1959, The alteration of ilmenite: Economic Geology, v. 54, p. 1095-1102.

Lynd, L.E.,1960, Alteration of ilmenite: Economic Geology, v.55, p. 1064-1068.

Marquis, R., and Kumarapeli, P.S., 1993, An early Cambrian deltaic model for an Iapetan riftarm drainage system, southeastern Quebec: Canadian Journal of Earth Sciences, v. 30, p. 1254-1261.

Morad, S., and Aldahan, A. A., 1986, Alteration of detrital Fe-Ti oxides in sedimentary rocks: Geological Society of America Bulletin, v. 97, p. 567-578.

Mücke, A., and Chaudhuri, J.N.B., 1991, The continuous alteration of ilmenite through pseudorutile to leucoxene: Ore Geology Reviews, v. 6, p. 25-44.

Muresan, M., 2002, Traces d'une paléoprovince sédimentaire de minéraux lourds (principalement titanifères) dans la pile épimétamorphique du Groupe Tulghes-Ordovicien Inférieur (Carpates Orientales): Revue Roumaine de Géologie, v. 46, p. 81-94.

Overholt, J.L., 1950, The nature of "Arizonite": American Mineralogist, v. 35, p. 117-119.

Penn, R.L., and Banfield, J.F., 1999, Formation of rutile nuclei at anatase {112} twin interfaces and the phase transformation mechanism in nanocrystalline titania: American Mineralogist, v. 84, p. 871-876.

Puffer, J.H., and Cousminer, H. L., 1982, Factors controlling the accumulation of titanium-iron oxide-rich sands in the Cohansey Formation, Lakehurst area, New Jersey: Economic Geology, v. 77, p. 379-391.

Rickard, M.J., 1964, Metamorphic tourmaline overgrowths in the Oak Hill series of Southern Quebec: Canadian Mineralogist, v. 8, p. 86-91.

Shannon, R.D., and Pask, J.A., 1964, Topotaxy in the anatase-rutile transformation: American Mineralogist, v. 49, p. 1707-1717.

Stanaway, K.J., 1994, Overview of titanium dioxide feedstocks: Mining Engineering, p.1367-1370.

Stanaway, K.J., 1996, The Eastern North America Titanium Province-A Review: Lithology and Mineral Resources, v. 31, no. 6, p. 509-517.

Stanaway, K.J., 2005, Four world titanium mining provinces: Heavy minerals 2005, Society for Mining, Metallurgy, and Exploration, p. 47-59.

Temple, A. K., 1966, Alteration of ilmenite: Economic Geology, v. 61, p. 695-714.

Teufer, G., and Temple, A.K., 1966, Pseudorutile-a new mineral intermediate between ilmenite and rutile in the natural alteration of ilmenite: Nature (London), 211, p.179-181.

Trzcienski, W., and Birkett, T.C., 1982, Compositional variations of pumpellyite along the western margin of the Quebec Appalachians: Canadian Mineralogist, v. 20, p. 203-209.

TZ Minerals International, 2005, Outlook for titanium feedstocks to 2006: Mining Journal, London, April 1, p. 16-17.

Welch, B.K., 1964, The ilmenite deposits of Geographe Bay: Australasian Institute of Mining and Metallurgy Proceedings, no. 211 p. 25-48.

Zhang, H., and Banfield, J.F., (1999), New kinetic model for the nanocrystalline anatase-to-rutile transformation revealing rate dependence on number of particles: American Mineralogist, v. 84. Issue 4, p. 528-534.

CHAPTER III

Iron migration and f_{O2} variation around metamorphosed titaniferous paleoplacers in the Sutton area, Southeastern Quebec

Abstract

A metamorphic zonation is observed around semimassive Fe-Ti oxide-rich paleoplacer beds of Cambrian age in the southeastern Quebec Appalachians. Migration of elements from the oxide zone into the surrounding sandstone host rocks during regional metamorphism created a distinctive mineralogical assemblage that can be used as an exploration tool for finding high-grade titanium deposits or buried oxide zones. The alteration of detrital ilmenite to pseudorutile was responsible for this mineral zonation. Iron leached during the breakdown of the ilmenite was both recrystallized as an oxide phase and incorporated into silicate minerals in the alteration halos. The oxidation of ferrous iron to ferric iron in the ilmenite during the transformation lowered f_{O2} values within and around the titaniferous oxide zones. The ilmenite-rich zone thus acted as an oxygen trap. During the ilmenite–pseudorutile reaction, approximately two thirds of ilmenite's iron was bound into the pseudorutile structure, while the remainder migrated outward as ferrous iron. The resulting low f_{O2} conditions allowed further leaching of iron from pseudorutile to form anatase—a purer titanium oxide mineral. The pseudorutile-anatase transformation liberated oxygen and the reaction thus buffered redox conditions in the system.

Introduction

Many researchers have studied the interactions between massive sulfide orebodies and their host rocks during regional metamorphism (e.g., Ducktown deposits of Tennessee, USA; Nesbitt and Kelly, 1980). In many of these cases, variations in f_{O2} and f_{S2} create multi-meter alteration halos which zoned the orebody surrounding rocks. Consequently, mineral changes have been used to develop exploration tools that can identify hidden massive sulfide deposits. Few studies, however, have examined the interactions that occur between oxide-rich horizons and their host rocks during regional metamorphism (Southwick, 1968). Metamorphic halos around semimassive titanium oxide-rich beds in the Sutton region of southern Quebec provide a suitable candidate for investigating such interactions. This paper evaluates f_{O2} changes and iron transfer between Ti-rich oxide zones and host rocks during metamorphism of the Sutton paleoplacers as well as their effect on mineralogy. Changes in f_{O2} conditions affected the stability of specific minerals in the host rocks, a feature that can be exploited as an exploration tool. Another purpose of this study is to demonstrate that the alteration of ilmenite to pseudorutile produces reducing conditions that enhance the beneficiation of Fe-Ti-oxides.

Geological Setting

The Sutton region is located in the Humber zone of the Quebec Appalachians (Fig. 3.1). Rocks of the study area consist of volcano-sedimentary strata of the Cambrian Oak Hill Group. The basal sequence comprises alkaline basaltic lavas of the Tibbit Hill Formation, which are overlain by a 150-m-thick metasandstone unit of terrigenous origin known as the Pinnacle Formation (Clark, 1936; Dowling, 1988; Colpron, 1992; Colpron et al., 1994). A 1- to 5-m-thick phyllite locally present at the base of the Pinnacle Formation is designated the Call Mill Member (Charbonneau, 1980). The dolomitic White Brook Formation stratigraphically overlies the Pinnacle Formation. Strata of the Oak Hill Group record a rifting episode during the break up of the Laurentian craton and the initial opening of the Iapetus Ocean. The lower 3 to 40 m of the Pinnacle Formation are characterized by titanium-rich heavy mineral paleoplacers that form black centimeter-scale laminations to semimassive beds. Although the Pinnacle Formation is extensive, having been mapped for hundred kilometers in all directions beyond the study area, the distribution of heavy mineral beds is restricted to a 5-km wide by 7-km long synclinal keel in the vicinity of Sutton Village. Colpron (1992), Marquis and Kumarapeli (1993) proposed that Pinnacle sandstones are pro-delta deposits that formed at the mouth of the Iapetan Ottawa River, which drained the adjacent Grenville Province during Cambrian time. Anorthosite complexes in the Precambrian basement are the proposed sources for the ilmenite in the Sutton paleoplacers (Colpron, 1992).

According to Colpron (1992) and Colpron et al. (1994), at least three deformational events—D1, D2, and D3—affected the deposits. Large WNW-trending recumbent folds associated with D1 deformation developed during the first part of the

Taconian Orogeny in Ordovician time. D2 and D3 produced a NNE-trending schistosity that reflects a Silurian backthrusting event. Backthrust faults of D2–D3 age include the Brome Fault, which cuts the eastern part of the Oak Hill Group in that area (Fig. 3.1). Our recent work reveals that this back thrust was a main conduit for fluids that helped enrich the titanium grade of the deposits (Hebert and Gauthier, in press).

Prograde regional metamorphism reached greenschist facies and was accompanied by D1 deformation during the Taconian orogeny from 469-461 Ma (Castonguay et al., 2001). The rocks were also affected by retrograde metamorphism during the D2–D3 back thrusting event from 431-419 Ma (Colpron, 1994; Castonguay et al., 2001).

Geology of the oxide zone

Oxide zones, as defined in this paper, are those portions of the Pinnacle Formation in which heavy minerals are concentrated into black centimeter-scale laminations or semimassive fine-grained beds. The thickness of these heavy mineral-rich units varies from a few meters in the case of the semimassive concentrations, to 30 m for the laminations. The detrital heavy mineral fraction typically accounts for 60% of these rocks by volume and consists of approximately 25% neorutile+anatase, 20% pseudorutile, 20% pitted ilmenite with hematite exsolutions, 15% hematite with ilmenite exsolutions, 10% zircon, 5% titaniferous magnetite, and 3% tourmaline. Neorutile, anatase, and pseudorutile are derived from the metamorphic alteration of ilmenite (Hebert and

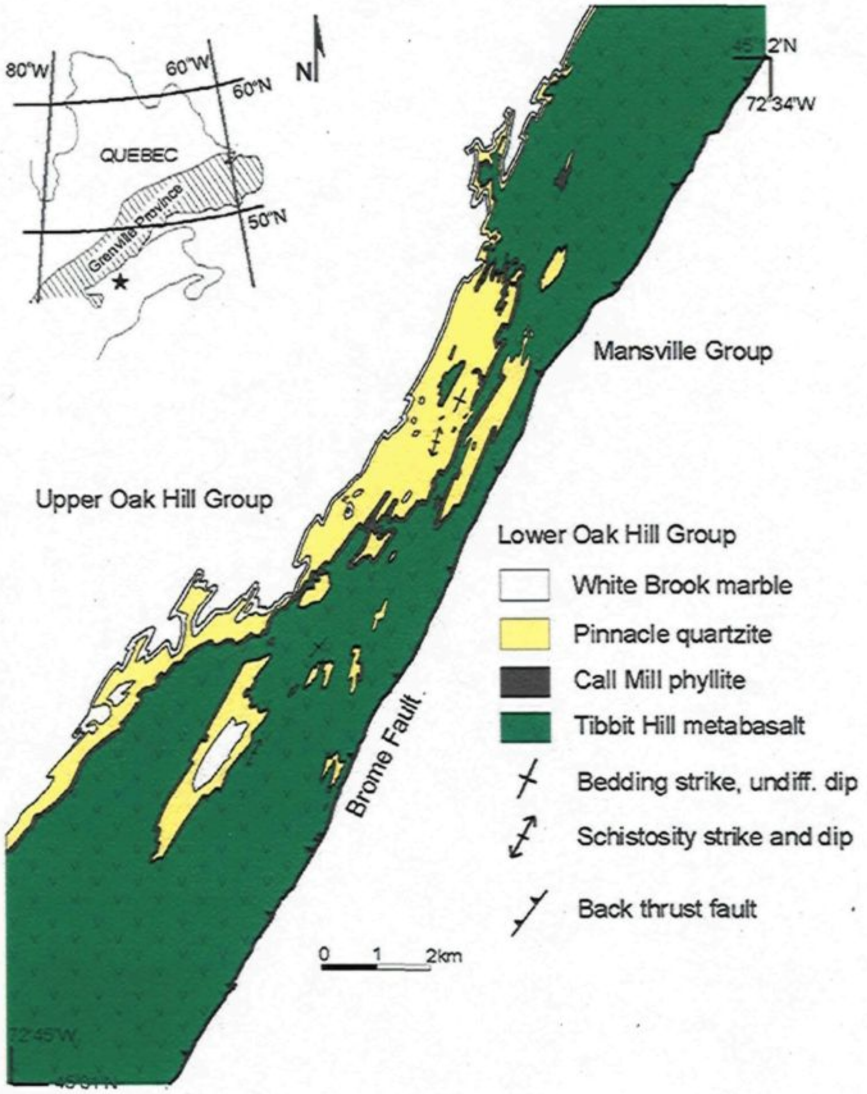

Figure 3.1. Geological map of the Sutton area and its position relative to the Grenville Province (after Colpron, 1992, and Colpron et al., 1994).

Gauthier, in press). The proportion of ilmenite in the original detrital heavy mineral fraction was thus 65%, with the remainder consisting of ilmeno-hematite, zircon, titaniferous magnetite, and tourmaline. Metamorphic euhedral crystals of Ti-free magnetite are present and account for up to 20% of the rock. The matrix consists almost exclusively of chlorite and accounts for approximately 20% of the rock. Thus, an assemblage of neorutile, Ti-free magnetite and chlorite constitutes the characteristic metamorphic assemblage in the titanium-rich semimassive beds (Fig. 3.2E).

Geology of the country rocks

Medium-grained quartzites of the Pinnacle Formation are the country rocks of the paleoplacer deposits. The matrix (5 to 15 vol%) consists mainly of muscovite (Fig. 3.2A). Metamorphic Ti-free hematite (2%) is present as fine-grained flaky crystals oriented parallel to the regional schistosity, and also occurs around detrital grains of ilmenite. No concentration of detrital heavy minerals is observed in the country rocks.

Metamorphic zonation

A metamorphic zonation of oxide and silicate minerals occurs around the semimassive titanium-rich beds of the oxide zone. Three zones—A (distal) to C (proximal)—have been distinguished based on the appearance or disappearance of minerals in the country rocks (Fig. 3.3). Each zone ranges from 1 to 15 m in thickness around the oxide zone, with the most distal zone (A) observed as far as 45 m away.

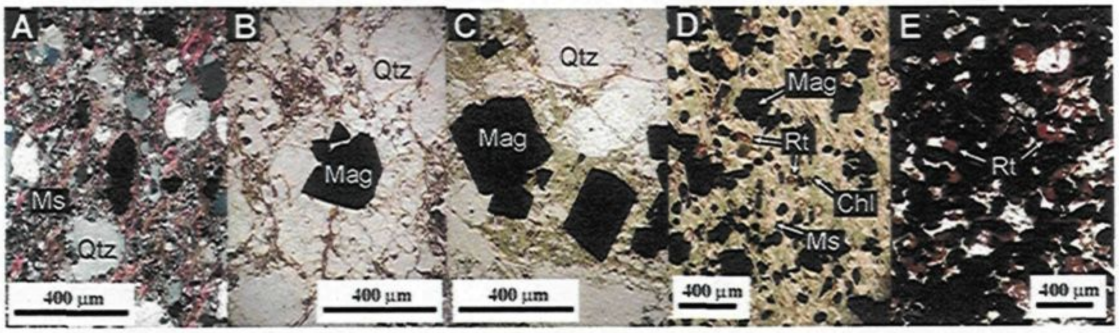

Figure 3.2. Photomicrographs of the different zones observed under plane polarized transmitted light, except "A" under cross polarized light. A) Country rock; B) Zone A; C) Zone B; D) Zone C; E) Oxide zone. Qtz = quartz, Ms = muscovite, Mag = magnetite, Chl = chlorite, Rt = rutile.

Zone A has roughly the same overall composition as the adjacent country rocks; i.e., quartzite with a muscovite-rich matrix (Fig. 3.2B). The presence of millimeter-scale laminations mainly composed of detrital ilmenite is the only notable sedimentary difference compared to the country rocks, where heavy minerals are disseminated and uncommon. The metamorphic assemblage is characterized by the disappearance of hematite and the appearance of discrete magnetite (about 1%) as Ti-free euhedral crystals 1 to 2 mm in diameter.

The intermediate zone, Zone B, contains more millimeter-scale heavy mineral laminations than Zone A, but is otherwise similar with respect to primary features. Chlorite appears in the matrix (Fig. 3.2C), and is preferentially concentrated around fine laminations of heavy minerals. Chlorite and muscovite occur in roughly equal proportions. Metamorphic magnetite accounts for up to 5% of the rock.

In Zone C, adjacent to the ore zone, the following differences in primary depositional features are observed: quartz is less abundant, the matrix reaches 25 to 30% of the rock, and centimeter-scale heavy mineral laminations appear. In this zone, magnetite is also very abundant (up to 10%) as disseminated millimeter-scale octahedra. The matrix is chloritic; muscovite is minor (Fig. 3.2D). Anatase and rutile occur as secondary minerals derived from intense alteration of detrital ilmenite via an intermediate stage involving pseudorutile, as observed in the oxide zone (Hebert and Gauthier, in press).

Analytical results

Chlorite was analyzed for major elements using a JEOL JXA-8900 electron microprobe operated at the following analytical conditions: accelerating voltage of 15kV, specimen current of 20nA, and beam diameter of 5μm. Compositional variations are observed in chlorite from Zone B, where it first appears, to the oxide zone, where chlorite is most abundant. The total iron content of chlorite in the semimassive beds of the oxide zone is about 32 wt% FeO, which progressively decreases away from the oxide zone to a low of 18-20 wt% FeO in Zone B (Fig. 3.3). Higher proportions of magnesium compensate for the lower amounts of iron in chlorite from zones B and C. Magnetite follows the same iron zonation trend, being more abundant in the oxide zone (almost 20 vol%) and decreasing outward in the host rocks to only 1 vol% in Zone A.

Detrital tourmaline grains in the oxide zone exhibit distinct metamorphic overgrowths (Rickard, 1964). The dark blue color of the overgrowths suggests that they are Fe-rich compared to the yellow detrital cores (Fig. 3.4A), which is confirmed by X-ray mapping of a tourmaline grain. (Fig. 3.4B).

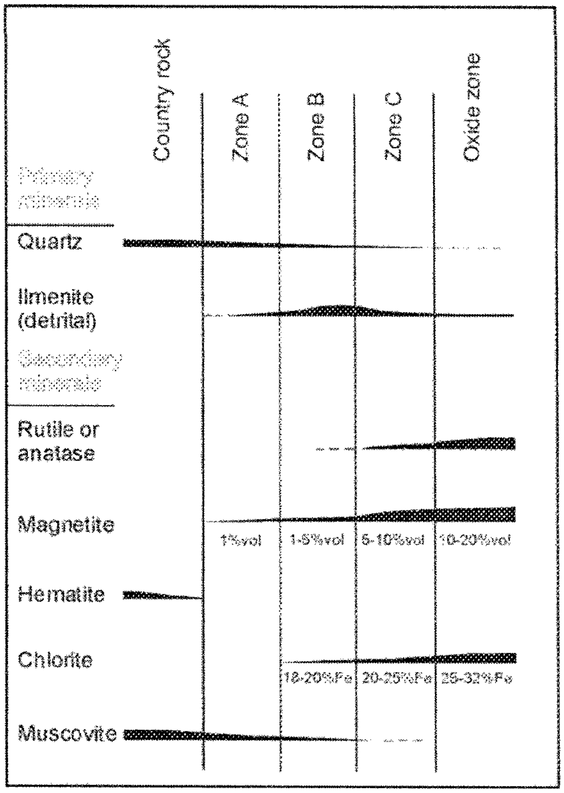

Figure 3.3 Diagram showing the mineralogical variations according to the different zones. The proportion of magnetite is indicated as percentage of volume. The weight percent of iron is indicated for chlorite. (20 samples)

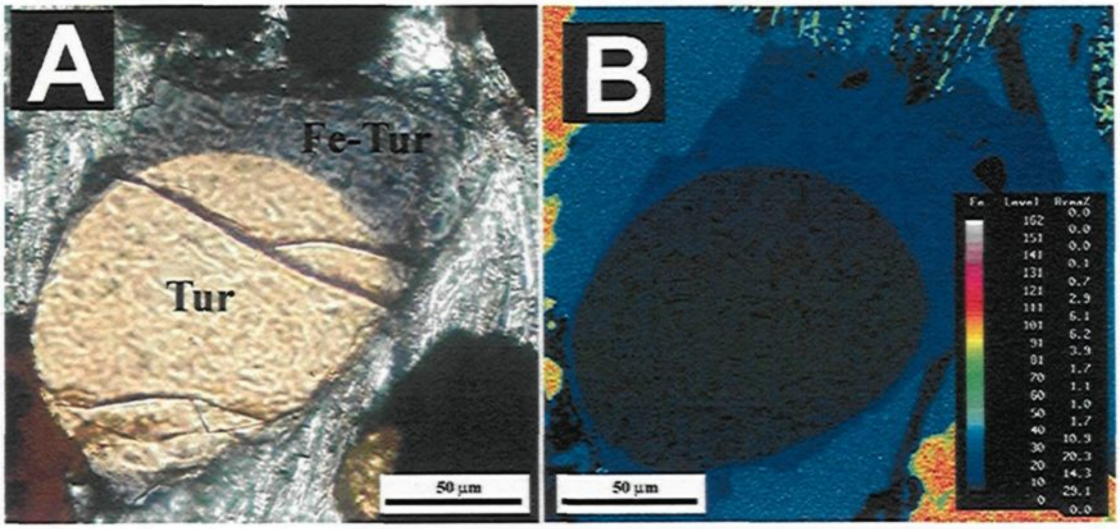

Figure 3.4 A) Photomicrograph of a detrital tourmaline grain with a metamorphic overgrowth of iron-rich tourmaline observed under plane polarized transmitted light. Tur: tourmaline; Fe-Tur: ferriferous tourmaline overgrowth. B) Iron mapping of a tourmaline grain using a JEOL JXA-8900 microprobe, accelerating voltage of 15kV, specimen current of 20nA. The scale for iron content is showing in the right inset.

Discussion

Iron migration

Oxygen fugacity variations in the Sutton deposits and iron migration at the meter scale were responsible for the observed mineralogical changes. Changes in the composition of chlorite and in the abundance of magnetite reveal that iron migrated from the oxide zone toward the host rock (Fig. 3.3). Iron-rich metamorphic overgrowths on detrital tourmaline grains also reflect the availability of iron during metamorphism (Fig. 3.4).

The leaching of hematite exsolutions in ilmenite grains was the main source of iron. Formation of pseudorutile during the alteration of ilmenite also released iron according to the following reaction:

$$3\ Fe^{(2+)}TiO_3 + 2H^+ + \frac{1}{2}\ O_2 = Fe_2{}^{(3+)}Ti_3O_9 + Fe^{2+} + H_2O \qquad (1)$$

where the liberated ferrous iron is incorporated into chlorite or magnetite (Grey and Reid, 1975; Dimanche and Bartholomé, 1976; Morad and Aldahan, 1986; Mücke and Chaudhuri, 1991). Although the alteration of about one third of the ilmenite grains pre-dates metamorphism (Hebert and Gauthier, in press), any iron released by that process was probably still present in the rocks as cement and thus remained available during metamorphic processes (Force, 1991, 2000). The destabilization of ferromagnesian silicate minerals in the Sutton sandstones also provided iron along with a considerable amount of magnesium (Dowling, 1988).

According to Desborough (1963), Morad and Aldahan (1987), iron leached from Fe-Ti oxides can be mobilized and form pyrite where sulfur is present, or can be incorporated into chlorite and oxides if sulfur is absent. In some Fe-Ti-rich sandstones, it has also been demonstrated that chlorite formed directly from feldspar or muscovite by the addition of Fe and Mg released from ilmenite and ferromagnesian silicates (Desborough, 1963; Morad and Aldahan, 1987). The enrichment of iron in chlorite and the greater abundance of metamorphic magnetite near the oxide zone reflect the metamorphic transfer of iron from Fe-Ti oxides into silicates and iron oxides.

Variations in f_{O2}

The predominance of magnetite in the Fe-Ti oxide-rich beds at Sutton indicates that the rocks were metamorphosed under reducing conditions (Eugster, 1959; Thompson, 1972; Spear, 1993). In contrast, surrounding rocks are characterized by an oxidizing environment as shown by the presence of metamorphic hematite. The reducing environment is thus restricted to the semimassive beds and their metamorphic halos. Some minerals, such as graphite, are known to change redox conditions by consuming oxygen (Miyashiro, 1964), yet graphite is not present in the Pinnacle Formation, nor are there any horizons rich in organic matter that could explain such a spatially limited reducing environment. Therefore, the f_{O2} variations observed from the oxide zone to the host rocks must be caused by another mineral. Studies have demonstrated that Fe^{2+}-bearing minerals like ilmenite can produce reducing conditions during oxidation of their ferrous iron if they are present in sufficient quantity (Ohmoto and Goldhaber, 1997; Force et al., 2001), and that the alteration of ilmenite to pseudorutile consumes oxygen

(Grey and Reid, 1975; Frost, 1991). It has also been demonstrated that low f_{O2} values are required for iron removal from pseudorutile (Gruner, 1959; Adams et al., 1974; Grey and Reid, 1975; Dimanche and Bartholomé, 1976; Frost, 1991). The fact that reducing conditions are restricted to the Sutton oxide zones and their metamorphic halos suggests that ilmenite was sufficiently abundant to act as an oxygen trap and create reducing conditions in the metamorphic fluids (see Equation 1). Liberated ferrous iron migrated outward, forming a reducing halo in the surrounding rocks. This is also seen in sediment-hosted uranium deposits where ilmenite in reducing environments is strongly altered and leached, but ilmenite in uranium-free oxidized rocks remains unaltered (Adams et al., 1974; Reynolds and Goldhaber, 1978a, b; Spirakis, 1996). Any changes in f_{O2} conditions in the Pinnacle sandstones, however, would have been rapidly buffered by the subsequent alteration of pseudorutile to anatase, which liberates oxygen.

Metamorphic oxidation of ilmenite thus created reducing conditions around the semimassive titanium-rich beds, as revealed by the presence of metamorphic magnetite instead of hematite. The reducing conditions caused further alteration of Fe-Ti oxide grains to locally produce fine-grained anatase from the breakdown of ilmenite. Anatase is only present in the oxide zone and its adjacent alteration zone (Zone C). The presence of rutile is explained by the subsequent crystallization of anatase, which appears to have only occurred in the eastern part of the study area near the Brome Fault where fault-driven metamorphic fluids catalyzed the reaction (Hebert and Gauthier, in press).

Conclusions

The Cambrian Pinnacle sandstones were metamorphosed under oxidizing conditions as demonstrated by the abundance of accessory metamorphic hematite. In contrast, reducing occurred where ilmenite-rich beds are present. The ilmenite-rich beds acted as oxygen traps when oxygen was consumed during the metamorphic transformation of ilmenite to pseudorutile. Breakdown of ilmenite released approximately one third of its iron content in the form of ferrous iron that migrated into the host rocks to create a characteristic mineral assemblage: Fe-rich chlorite, magnetite, and Fe-rich tourmaline. This assemblage can be used as an exploration tool for finding high-grade titanium deposits or buried oxide zones. The remainder of the iron was conserved in the pseudorutile structure, until continued metamorphic alteration under the prevailing reducing conditions leached it quantitatively and left a nearly pure, residual TiO_2 phase. It is thus evident that decreasing f_{O2} during metamorphism is a determining step in the natural beneficiation of Fe-Ti oxides.

Acknowledgements

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References

Adams SS, Curtis HS, Hafen PL (1974) Alteration of detrital magnetite-ilmenite in continental sandstones of the Morrison Formation, New Mexico. In: Formation of uranium deposits. Vienna, International Atomic Energy Agency Proceedings Series ST1/PUB/374, pp.219-253.

Castonguay S, Ruffet G, Tremblay A, Féraud G (2001) Tectonometamorphic evolution of the southern Quebec Appalachians: 40Ar/39Ar evidence for Middle Ordovician crustal thickening and Silurian-Early Devonian exhumation of the internal Humber zone. Geological Society of America Bulletin 113: 144-160.

Charbonneau JM (1980) Région de Sutton (W). Ministère de l'Énergie et des Ressources du Québec, DPV-681, 89 pp.

Clark TH (1936) A Lower Cambrian Series from Southern Quebec. Transactions of the Royal Canadian Institute, no 45, v. 21, part I, p. 135-151

Colpron M (1992) Géologie de la région du lac Brome (Estrie): ET- Direction Générale de l'Exploration Géologique et Minérale ET-90-09. 96 pp.

Colpron M, Faure S, Dowling W (1994) Géologie de la région de Sutton (Montérégie): Ministère des Ressources Naturelles du Québec, ET 92-05. 85 pp.

Desborough GA (1963), Mobilization of iron by alteration of magnetite-ulvöspinel in basic rocks in Missouri. Econ Geol: 58, 332-346.

Dimanche F, Bartholomé P (1976) The alteration of ilmenite in sediments. Minerals Science Engineering: 8, 187-200.

Dowling WM (1988) Depositional environment of the lower Oak Hill Group, southern Quebec: implications for the late Precambrian breakup of North America in the Quebec reentrant : University of Vermont : Burlington, VT, United States; Master's, 186 pp.

Eugster HP (1959) Reduction and oxidation in metamorphism: Abelson, P.H. (ed.) Researches in geochemistry, p. 397-426.

Frost BR (1991) Stability of oxide minerals in metamorphic rocks. Reviews in mineralogy: 25, 468-487.

Force ER (2000) Titanium mineral resources of the Western U.S., an update; with a section on Ione Basin, California by Force, E.R. and Creely, S.: U.S. Geological Survey Open-File Report 00-442, 43pp.

Force ER (1991) Geology of titanium-mineral deposits. Geological Society of America, Special Paper 259, 112 pp.

Force ER, Butler RF, Reynolds RL, Houston RS (2001) Magnetic ilmenite-hematite detritus in Mesozoic-Tertiary placer and sandstone-hosted uranium deposits of the Rocky Mountains. Econ Geol: 96, 1445-1453.

Grey IE, Reid AF (1975) The structure of pseudorutile and its role in the natural alteration of ilmenite. Am Min: 60, 898-906.

Gruner JW (1959) The decomposition of ilmenite. Econ Geol: 54, 1315-1316.

Hébert, E., and Gauthier, M., in press, Unconventional rutile deposits in the Quebec Appalachians: Product of hypogene enrichment during low-grade metamorphism: Economic Geology.

Marquis R, Kumarapeli PS (1993) An early Cambrian deltaic model for an Iapetan riftarm drainage system, southeastern Quebec. Can J of Earth Sci: 30, 1254-1261.

Miyashiro A, (1964) Oxidation and reduction in the Earth's crust with special reference to the role of graphite. Geochim Cosmochim Acta: 28, 717-720.

Morad S, Aldahan AA (1986) Alteration of detrital Fe-Ti oxides in sedimentary rocks. Geol Soc Am Bull: 97, 567-578.

Morad S, Aldahan AA (1987) Diagenetic chloritization of feldspars in sandstones. Sedim Geol: 51, 155-164.

Mücke A, Chaudhuri JNB (1991) The continuous alteration of ilmenite through pseudorutile to leucoxene. Ore Geol Reviews: 6, 25-44.

Nesbitt BE, Kelly WC (1980) Metamorphic zonation of sulfides, oxides, and graphite in and around the orebodies at Ducktown, Tennessee. Econ Geol: 75, 1010-1021.

Ohmoto H, Goldhaber MB (1997) Sulfur and Carbon isotopes. In: Barnes, H.L. (Editors), Geochemistry of hydrothermal ore deposits, pp. 517-607.

Reynolds RL, Goldhaber MB (1978a) Iron-titanium oxide minerals and associated alteration phases in some uranium-bearing sandstones. U.S. Geological Survey Journal of research: 6, no.6, 707-714.

Reynolds RL, Goldhaber MB (1978b) Origin of a South Texas roll-type uranium deposit; part I, Alteration of iron-titanium oxide minerals. Econ Geol: 73, 1677-1689.

Rickard MJ (1964) Metamorphic tourmaline overgrowths in the Oak Hill series of Southern Quebec. Can Mineralogist: 8, 86-91.

Southwick DL (1968) Mineralogy of rutile –and apatite-bearing ultramafic chlorite rock, Harford County, Maryland. U.S. Geological Survey Professional Paper 600-C, 38-44.

Spear FS (1993) Metamorphic phase equilibria and pressure-temperature-time paths. Mineralogical Soc Am (ed.) 799 p.

Spirakis CS (1996) The roles of organic matter in the formation of uranium deposits in sedimentary rocks. Ore Geol Reviews: 11, 53-69.

Thompson JB Jr (1972) Oxides and sulfides in regional metamorphism of pelitic schists. 24th International Geological Congress- Section10, 27-35.

CHAPTER IV

Origin of the Call Mill Slate, Oak Hill Group: New insights based on Fe-Ti oxides

Introduction and previous works

The studied area is part of the Quebec Appalachians, in the Humber Zone, within a Cambrian volcano-sedimentary sequence, the Lower Oak Hill Group, near the town of Sutton (Fig. 4.1). The first stratigraphic studies were done by Clark (1931; 1934; 1936). He described alkaline volcanites at the base that he defined as the Tibbit Hill Formation. This Formation is overlied by a thin argillic unit, the Call Mill Slate and a thick sandy unit, the Pinnacle Formation. Locally, concentrations of heavy minerals formed titaniferous paleoplacer deposits within the Call Mill and the Pinnacle. Colpron (1992), and Marquis and Kumarapeli (1993) proposed that the source rocks for these placers were the anorthositic complexes of the Grenville Province. With the White Brook dolomite at the summit, this whole stratigraphic sequence represents a complete volcano-sedimentary cycle associated with the development of a rift during the opening of the Iapetus ocean (Fig. 4.2). The whole sequence has been deformed and metamorphosed to greenschist facies during the Taconian orogeny in Ordovician time (469-461 Ma) and during a Silurian backthrusting event (431-419 Ma; Castonguay, 2001).

Clark (1934) defined the Call Mill Slate as the inferior Member of the Pinnacle Formation. Later, Eakins (1964) considered the Call Mill Slate as a distinct unit and defined it as the Call Mill Formation. Charbonneau (1980) insisted on the thinness of the Call Mill and defined it as a Member being an integral part of the Pinnacle Formation. However, more recent workers still consider the Call Mill Slate as a distinct Formation from the terrigenous sediments of the Pinnacle (Dowling, 1988; Marquis

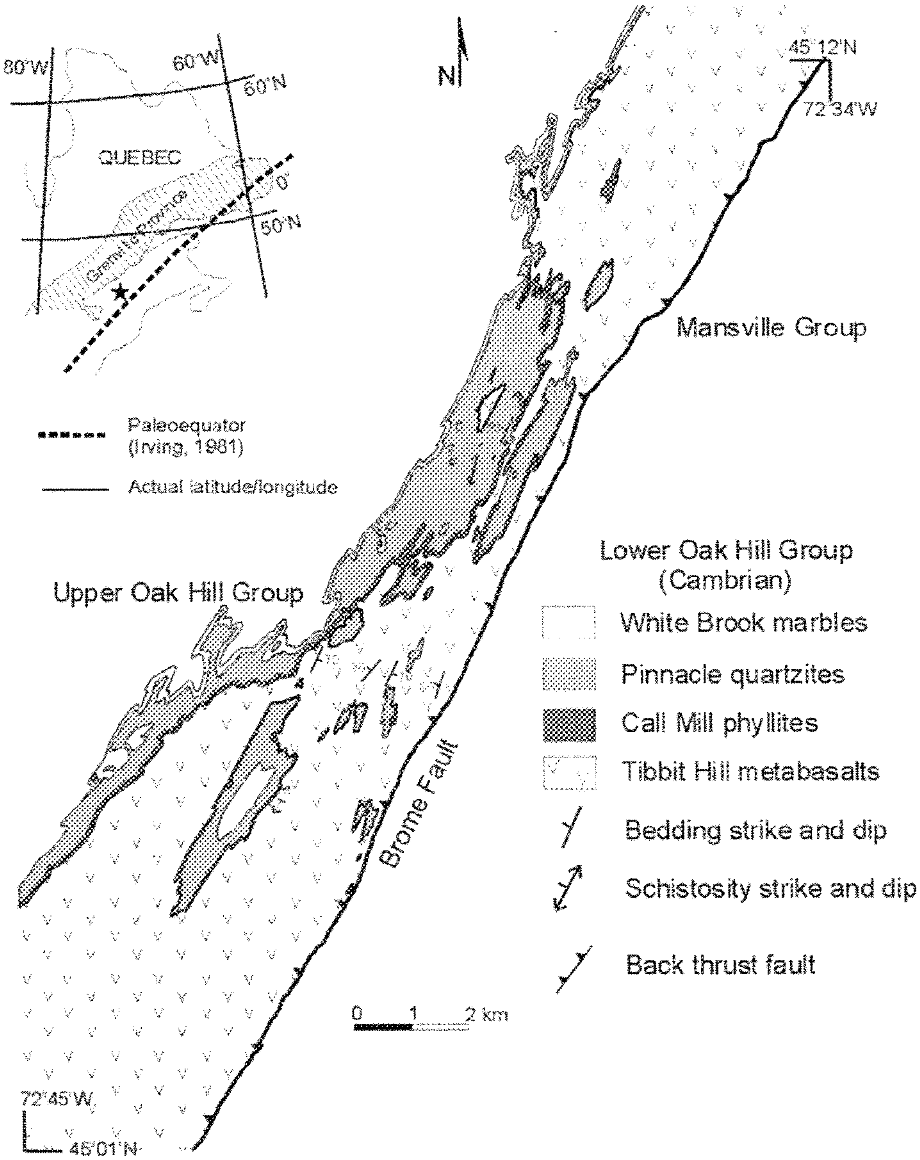

Figure 4.1 Geological map of the Sutton area and its position relative to the Grenville Province (after Colpron, 1992, and Colpron et al., 1994). The inset shows the paleoequator position of the region during Cambrian time (Irving, 1981).

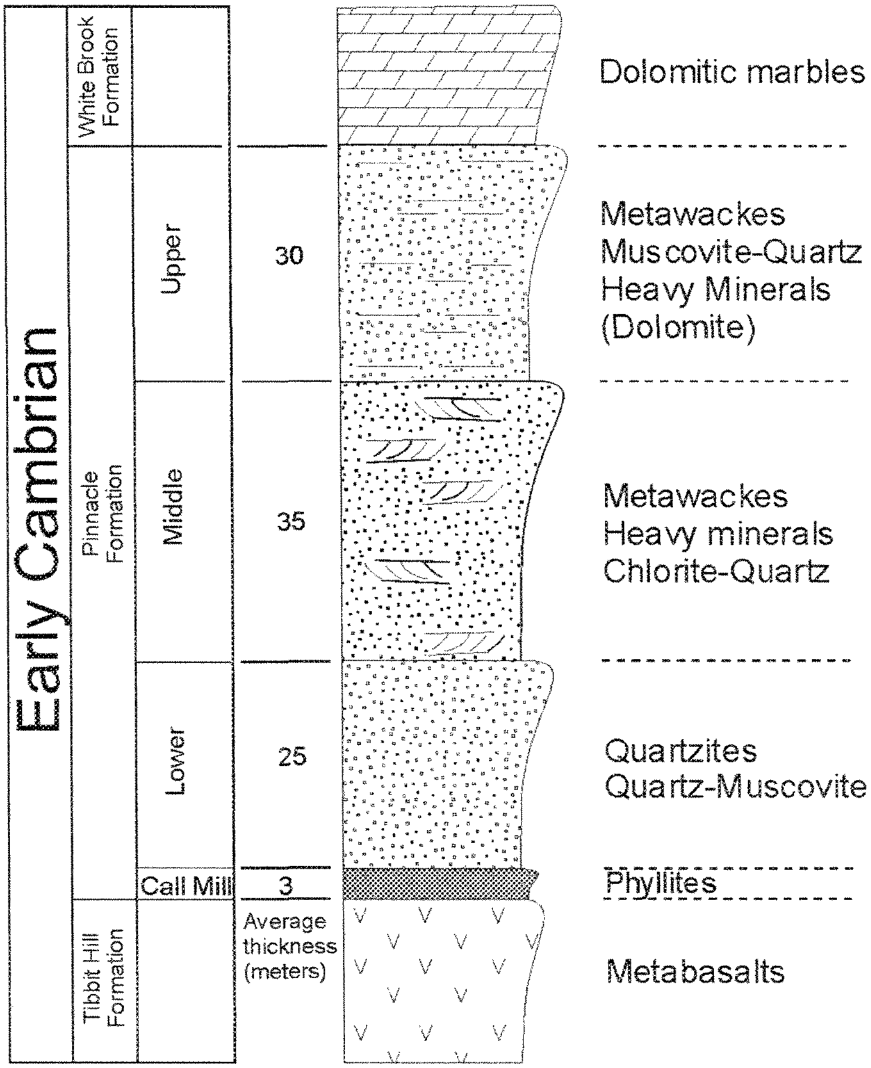

Figure 4.2 Schematic stratigraphic column of the Pinnacle Formation and its four units (modified from Dowling, 1988) showing the heavy mineral concentrations of the middle Pinnacle unit.

1991). Dowling (1988) pointed out that the Call Mill thickness is constant and continuous over several kilometers. He proposed that the underneath unit, the Tibbit Hill, may have formed a relatively flat relief, caused by erosion. Thus, these volcanic rocks were, during Cambrian time, exposed to subaerial weathered. The occurrence of conglomerates with chloritoid pebbles present within the Call Mill testify of the Tibbit Hill volcanic rocks erosion (Marquis, 1991). Marquis (1991) proposed that these chloritoid pebbles may come from the erosion of lateritized volcanic rocks, justifying the classification of the Call Mill as Formation. Moreover, he also stated that the Call Mill Slate was composed exclusively of volcanitic materials derived from the erosion of the Tibbit Hill.

According to Dowling (1988), Colpron et al. (1994), and Gauthier et al. (1994), the titaniferous heavy mineral concentrations are exclusively associated to the Pinnacle sandstones. However, our field works revealed that titaniferous heavy mineral concentrations also occur in the Call Mill Slate (Colpron, 1992). Therefore, the Call Mill origin and its relationship with the Pinnacle Formation must be re-examined, hence the purpose of this paper. Although several differences exist between these two units, the Call Mill Slate and the Pinnacle sandstones have the same source rocks, the difference residing in the pre-depositional weathering history of each unit.

Description of the Call Mill

The Call Mill Slate is a 1 to 5-m thick phyllite continuously distributed over several kilometers (Fig. 4.3). Muscovite is the main mineral observed with fine-grained detrital quartz (50-150μm). Hematite is also very abundant (up to 30%), developed as fine-flaked crystals parallel to bedding, giving the Call Mill its shiny purple color (Fig. 4.4).

Locally, a heavy mineral thin bed, generally single, is observed in the Call Mill Slate, usually at the top and in sharp contact with the surrounding argillic sediments. This 10 to 60 cm-thick bed is continuous only on a meter-scale, but is very massive and contains up to 95% of detrital heavy minerals (Fig. 4.5). Coarseness varies from 100 to 175 μm of well-rounded and spherical grains. Ilmeno-hematite (hematite with small exsolutions of ilmenite) are the main detrital fraction component (45%; Fig. 4.6A). Fine, well-rounded, elongated grains of pseudorutile, an alteration product of hemo-ilmenite (ilmenite with small exsolutions of hematite) constitute 35% of the detrital fraction. Zircon is well preserved and accounts for 10% of the detrital fraction. Tourmaline and titaniferous magnetite constitute the rest of the detrital fraction. Ti-free hematite is also present in this facies, as fine flakes between detrital grains (Fig. 4.6B). Metamorphic overgrowths of hematite also surround detrital Fe-Ti oxide grains, clearly distinguishable from the ilmeno-hematite by the absence of ilmenite exsolutions (Fig. 4.6C). A characteristic feature of the heavy mineral beds is that detrital pseudorutile grains are dissociated into hematite and rutile. In some grains, rutile is observed in the

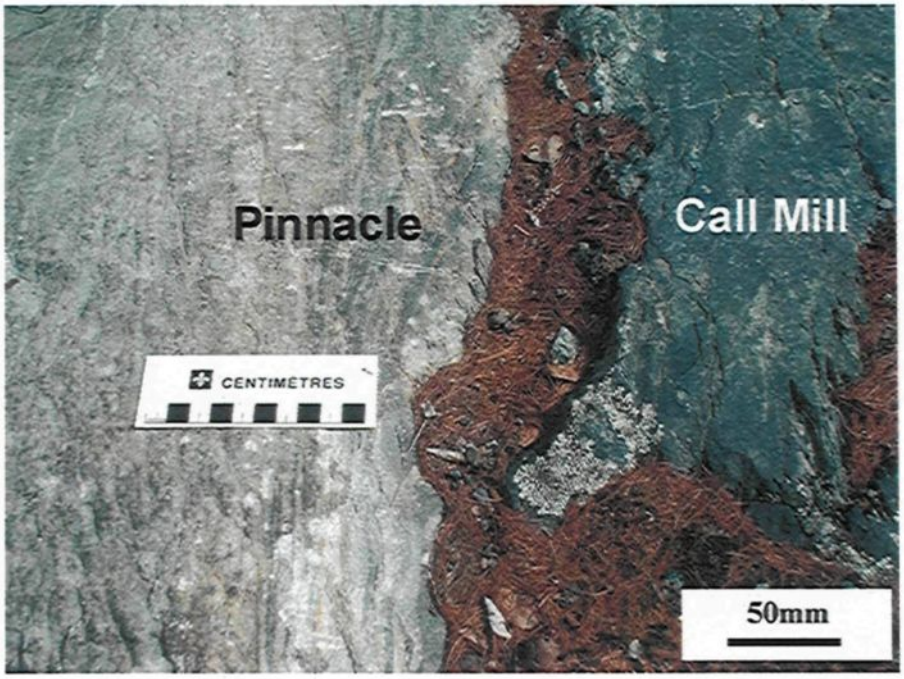

Figure 4.3 Photograph of an outcrop showing the Call Mill phyllite in contact with the Pinnacle sandstones.

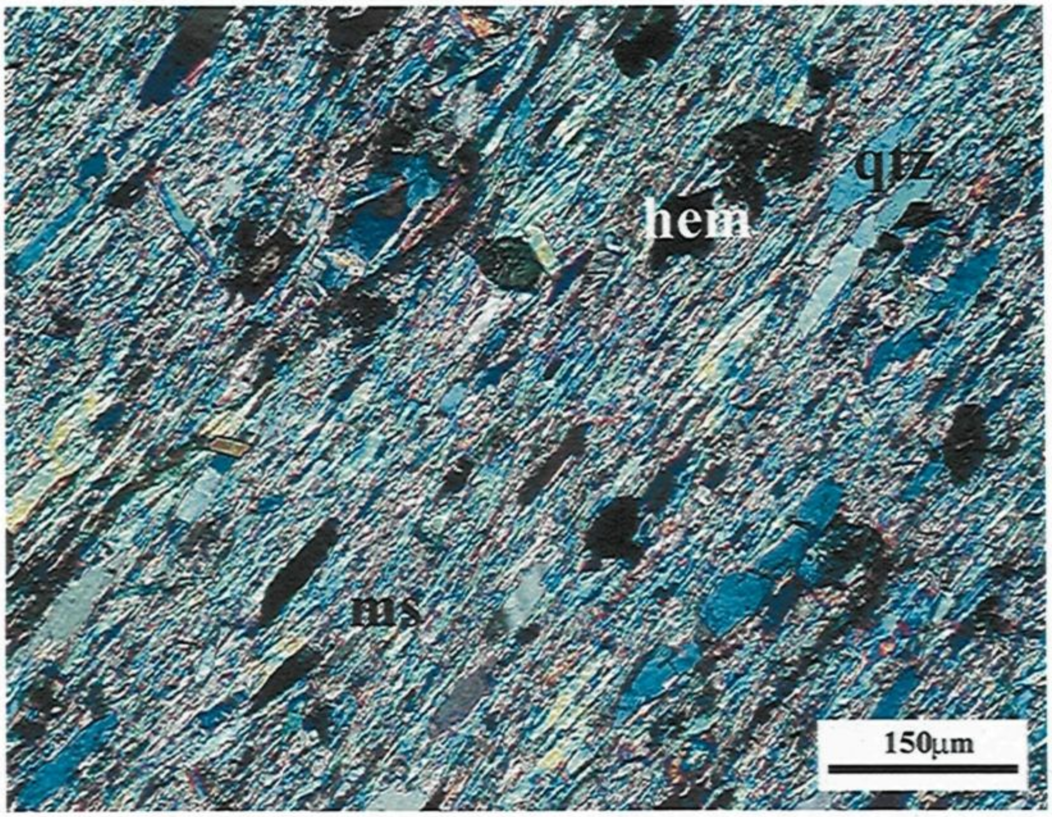

Figure 4.4 Photomicrographs of metamorphic mineral assemblages of the Call Mill Slate observed under plane polarized transmitted light. Hem = hematite, ms = muscovite, qtz = quartz.

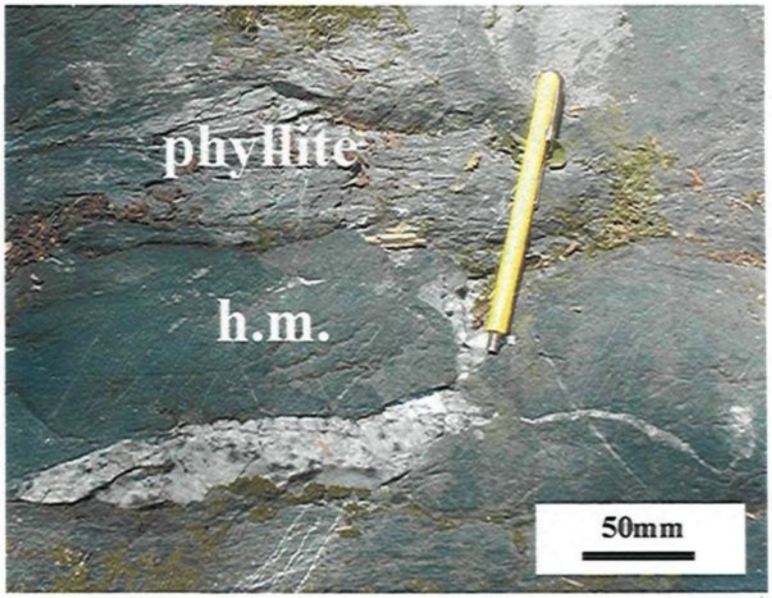

Figure 4.5 Photograph of an outcrop showing a heavy mineral bed (h.m.) within the Call Mill phyllite.

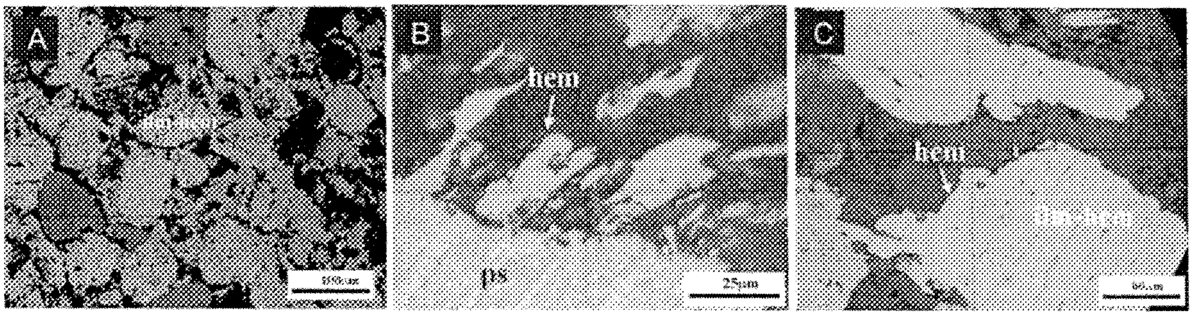

Figure 4.6 Photomicrographs of the Call Mill heavy mineral beds observed in natural reflected light. A) Ilmeno-hematite constitutes the main detrital fraction. Ilm-hem = ilmeno-hematite. B) Fine-flakes of Ti-free hematite (under oil). Hem = hematite, Ps = pseudorutile. C) Ti-free hematite surrounding a detrital grain. Note the absence of ilmenite exsolutions.

middle of the grains, coated by the hematite, leaving the pseudorutile margins unaffected (Fig. 4.7A). In contact with other grains, the pseudorutile is partially recrystallized into rutile (Fig. 4.7B). Compaction and pressure-dissolution seem to explain the rutile crystallization rather than element transfer between the two Fe-Ti grains, because the same phenomenon occurs even when a silicate is in contact with pseudorutile (Fig. 4.7C).

The Call Mill locally contains fine laminations of nanograins of anatase (Fig. 4.7D). These horizons are generally devoid of fine-flaked hematite. Conglomerates of chloritoid schist well-rounded pebbles also occur locally within the muscovite-rich and fine-quartz slates (Fig. 4.8).

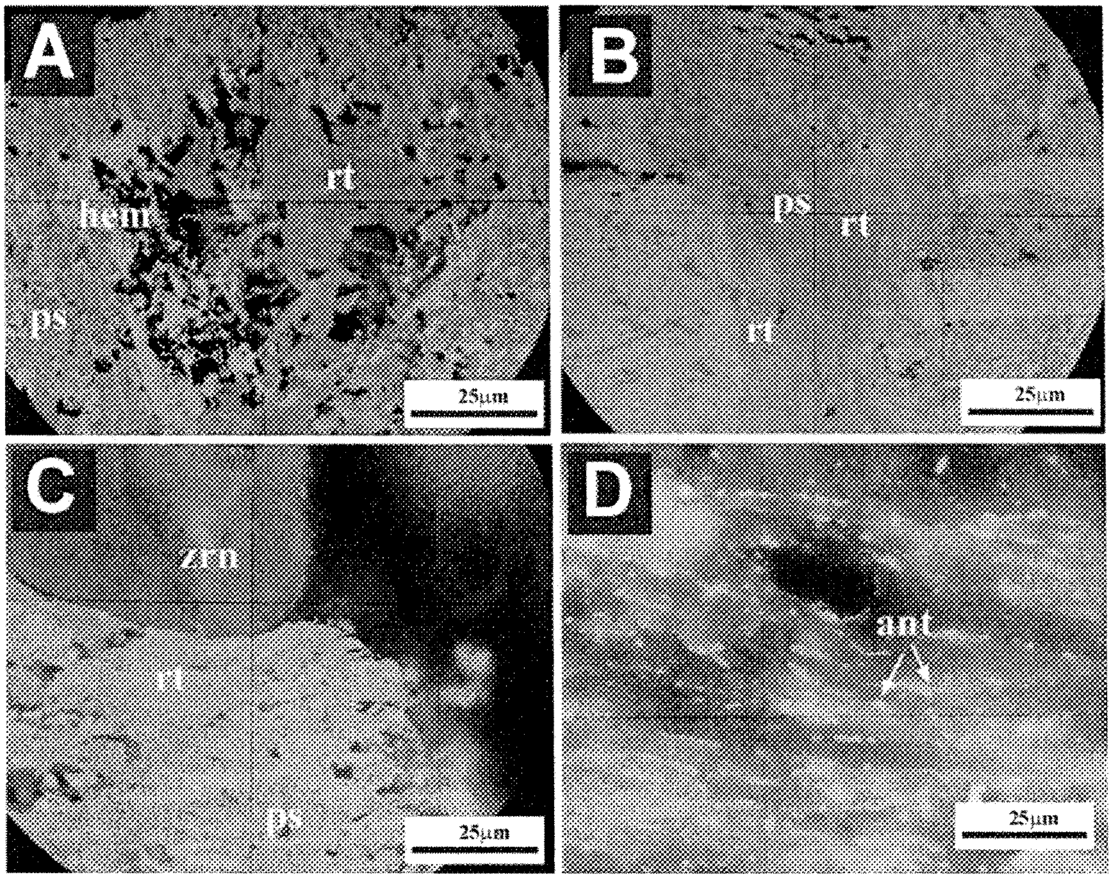

Figure 4.7 Photomicrographs of a Fe-Ti oxide grains observed under oil in natural reflected light. A) A pseudorutile grain dissociated into rutile and hematite. Note that the dissociation occurs in the middle of the grain, leaving the margin undissociated. Hem = hematite, Ps = pseudorutile, Rt = rutile. B) A pseudorutile grain transformed into rutile at the contact with other grains. C) A pseudorutile grain transformed into rutile at the contact with a silicate. Zrn = zircon. D) Horizons of nanograins of anatase. Ant = anatase.

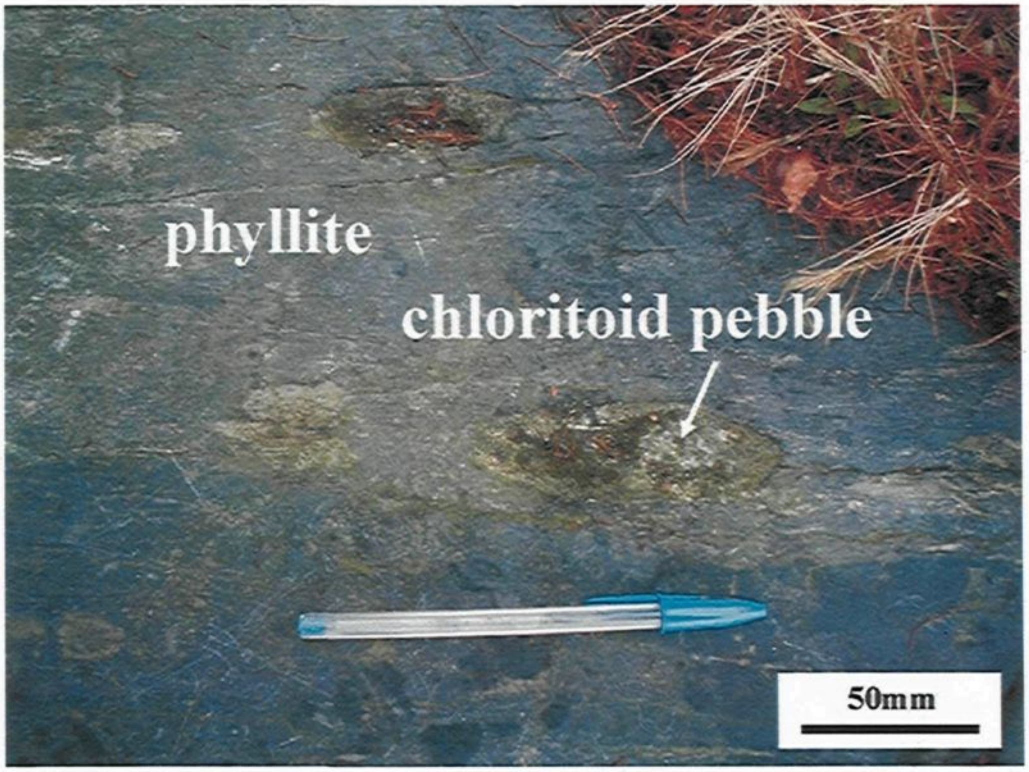

Figure 4.8 Photograph of an outcrop showing a conglomeratic horizon with chloritoid pebbles.

Pinnacle Description

Pinnacle sandstones lie stratigraphically above the Call Mill. In the Sutton area, at the base, the Pinnacle sandstones are composed of a quartz-muscovite-hematite assemblage, followed by chloritic sandstones in the middle, with occurrences of centimetric to semimassive black beds of heavy minerals. The upper part of the Pinnacle is composed of muscovite-hematite-(dolomitic) wackes with millimetric cross-bedded laminations of heavy-minerals. Altogether, these facies form the 150-m thick unit of the Pinnacle. The semimassive black beds are constituted of almost 60% of fine-grained detrital heavy minerals within a chloritic matrix with metamorphic Ti-free magnetite and detrital quartz (Fig. 4.9). The heavy mineral detrital fraction is composed essentially of hemo-ilmenite grains (65%), which have been altered totally or partially into rutile, through a pseudorutile and anatase intermediate stage by both pre-consolidation weathering and metamorphic processes (Fig. 4.10; Hebert and Gauthier, in press). Ilmeno-hematite constitutes 15% of the detrital fraction with fewer amounts of zircon (10%), titaniferous magnetite (5%), tourmaline and apatite (3%).

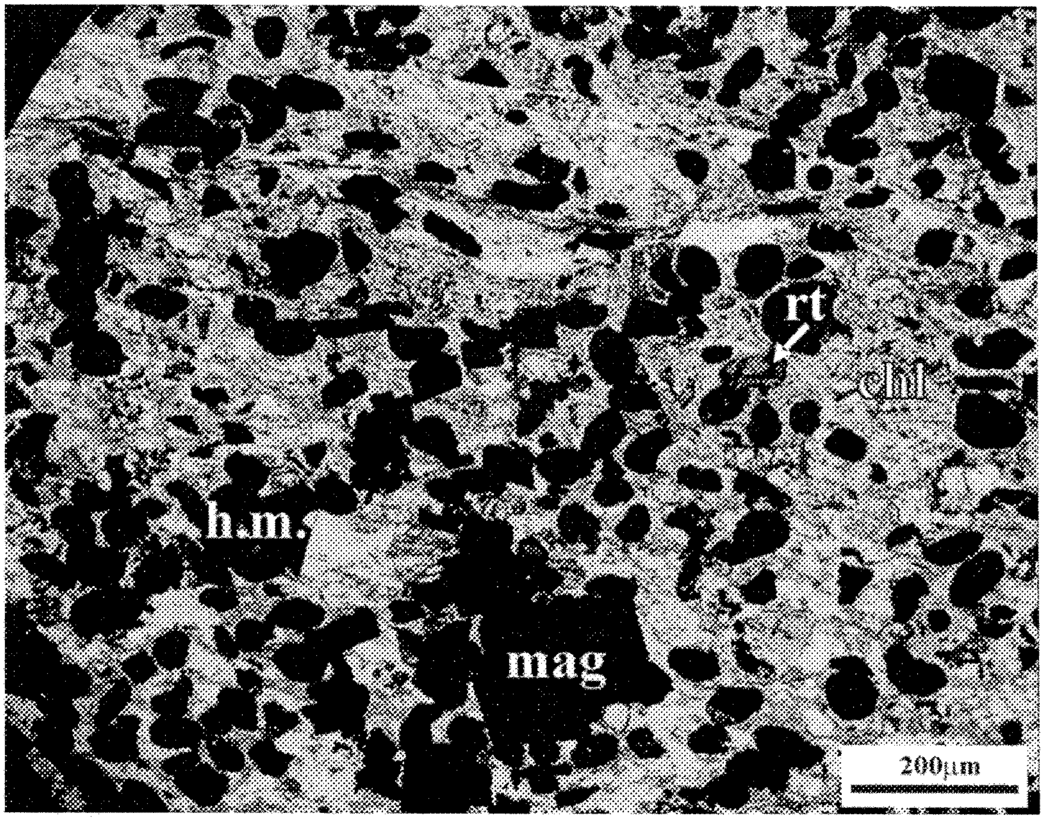

Figure 4.9 Photomicrographs of metamorphic mineral assemblages of the Pinnacle sandstones observed under plane polarized transmitted light. Chl = chlorite, H.m. = heavy minerals, Mag = magnetite, Rt = rutile.

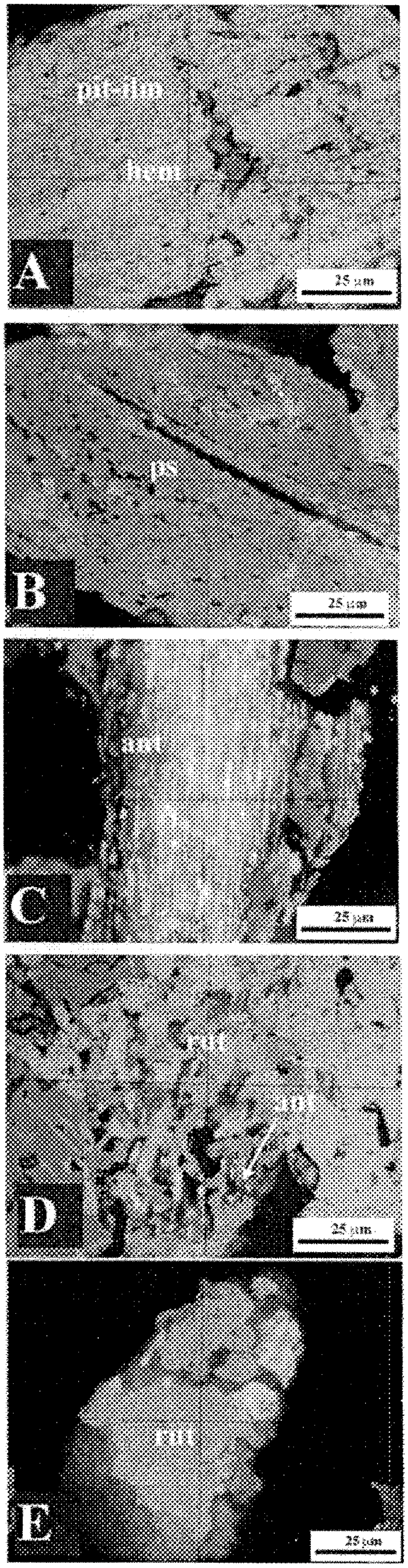

Figure 4.10 Photomicrographs of hemo-ilmenite grains showing features that are interpreted to represent different stages of iron leaching (observed under oil in natural reflected light). A) a pitted hemo-ilmenite grain. Note that the hematite lamellae are not affected. Hem = hematite, Pit-ilm = pitted ilmenite. B) a pseudorutile grain showing a more homogeneous texture. Voids are preferentially developed along hematite exsolution planes. Ps = pseudorutile, C) a mesh-textured grain of anatase showing well-developed porosity. Ant = anatase. D) a neorutile crystals developed from nanocrystalline anatase. Rt = rutile. E) Single grain of Stage 4 coarse-grained neorutile.

Fe-Ti minerals

Concentrations of Fe-Ti oxides occur both within the Call Mill Slate and the Pinnacle sandstones. Although these Fe-Ti oxides seem to come from the same source area, major differences exist between these two units (Fig. 4.11). The principal differences lie in the relative proportion of heavy mineral phases, the sedimentologic and metamorphic aspect.

Ilmeno-hematite/hemo-ilmenite

The Call Mill heavy mineral beds systematically contain a high proportion of ilmeno-hematite, which is about 45%. These ilmeno-hematite are well-rounded and have a spherical shape (Fig. 4.12A). Ilmeno-hematite in the Pinnacle heavy mineral beds does not exceed 15%, whereas hemo-ilmenite represents 65% of the heavy mineral assemblage. Hemo-ilmenite in both unit are systematically elongated and well-rounded (Fig. 4.12B).

Massive aspect

Call Mill heavy mineral beds are thin (10 to 60 cm) with sharp contacts with the surrounding slates and are characterized by their extremely massive aspect (up to 95%; Fig. 4.13A). In these beds, the detrital grains are fine (100μm), whereas the Pinnacle heavy minerals are coarser (200-250μm), systematically less massive (max 60%) and the contact with the surrounding quartzite are less defined (Fig. 4.13B).

Call Mill	Pinnacle
Ilmeno-hematite > hemo-ilmenite	Hemo-ilmenite > ilmeno-hematite
Thin massive beds (95% H.M.)	Thick semi-massive beds (60% H.M.)
Phyllite-hosted	Sandstone-hosted
Muscovite-hematite	Chlorite-magnetite
Detrital micro-anatase horizons	Mesh-texture anatase grains
Rutile => dissociation of pseudorutile	Crystallization after anatase

Figure 4.11 Diagram showing the major differences between the Call Mill Slate and the Pinnacle sandstones.

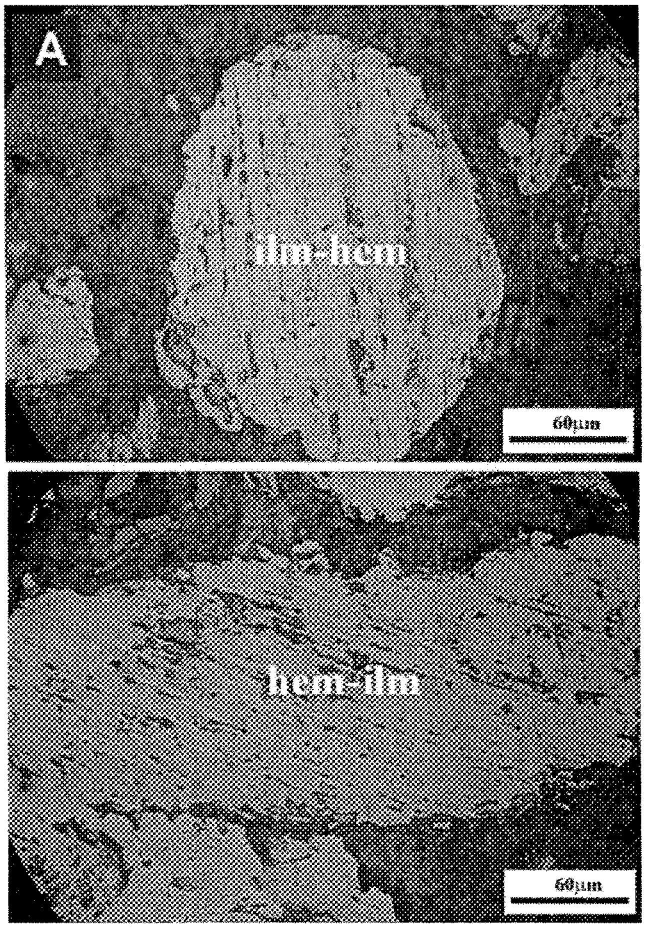

Figure 4.12 Photomicrographs of Fe-Ti oxides observed in natural reflected light. A) Ilmeno-hematite grain of the Call Mill. Note the spherical shape. Ilm-hem = ilmeno-hematite. B) An elongated grain of hemo-ilmenite from the Pinnacle sandstones. Hem-ilm = hemo-ilmenite.

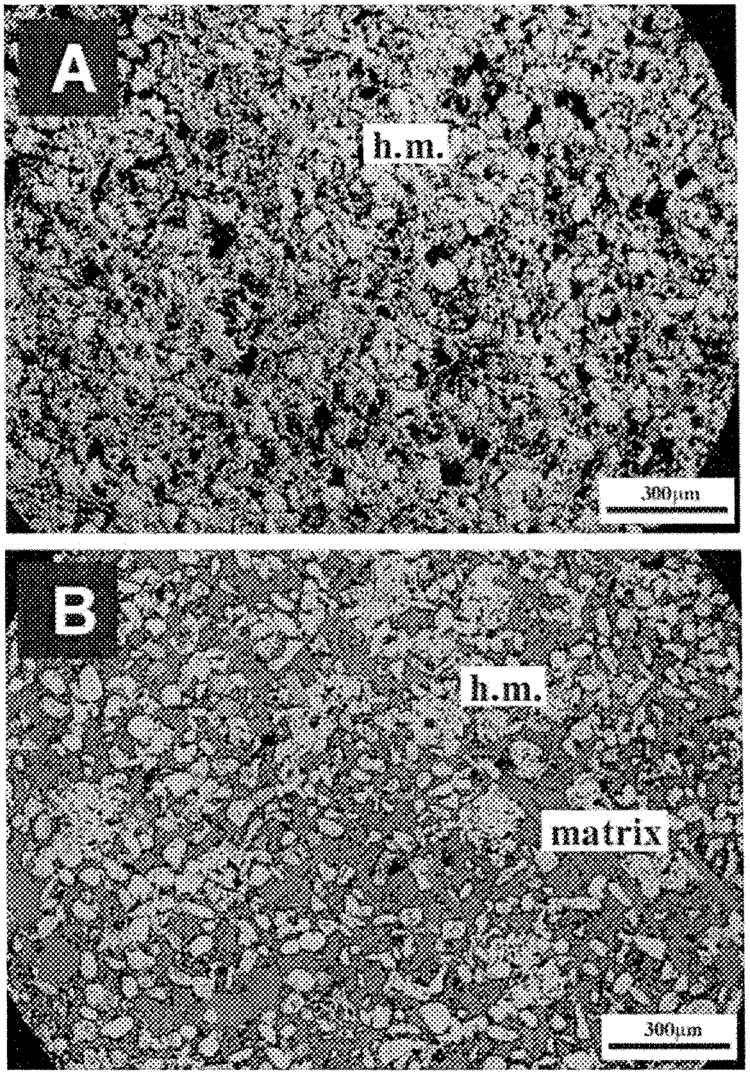

Figure 4.13 Photomicrographs of heavy minerals observed in natural reflected light. A) Call Mill massive heavy mineral concentration. B) Pinnacle semimassive heavy mineral concentration. The matrix of chlorite is dark gray.

Metamorphic minerals

The characteristic metamorphic minerals associated with the heavy mineral beds are magnetite, hematite, chlorite and muscovite. Although exceptions exist, hematite and muscovite are closely associated with the Call Mill, whereas the occurrence of magnetite and chlorite are systematically associated with the Pinnacle heavy mineral semimassive beds.

Pseudorutile

The grains of pseudorutile in the Call Mill heavy mineral beds are usually dissociated into rutile and hematite (Fig. 4.7A). Therefore, iron is not leached out of the grain. By contrast, the iron of the Pinnacle pseudorutile is leached out, leaving a porous residual TiO_2 grain (Fig. 4.10C).

Ti-enrichment

During the formation of a heavy mineral placer, the titaniferous oxides can be enriched either before (i.e. at the source), during or after deposition. Many criteria have been developed to discriminate the timing of each enrichment (Force, 1991). Both Call Mill and Pinnacle detrital Fe-Ti oxides show a residual enrichment, as demonstrated by the progressive leaching of iron (Fig. 4.14; see also Chapter 2 for enrichment processes).

Pre-depositional weathering

The Call Mill Fe-Ti oxides show some pre-depositional weathering features. Coarse grains of leucoxene are observed among finer grains of ilmenite; this reflects a pre-depositional weathering (Fig. 4.15; Wilcox, 1971; Force, 1991). The Call Mill Slate contains a greater proportion of ilmeno-hematite (45%) than hemo-ilmenite (35%) compared with the 15% of ilmeno-hematite present in all the other heavy mineral concentrations of the Pinnacle sandstones. The abundance of ilmeno-hematite may reflect deep pre-depositional weathering because the thick exsolution of hematite (or ilmeno-hemanite) are more resistant to weathering than ilmenite (or hemo-ilmenite) which is usually leached in lateritic or saprolitic environment (Overstreet et al., 1963; Herz, 1976; Force, 1991). The ilmenite is usually transformed into a porous residual aggregate of TiO_2 (leucoxene). Such fragile aggregate could hardly survives transport. These destroyed grains may remain or deposit among argillic particles, or mud such as the nano-grains of anatase found in the Call Mill Slate (Fig. 4.7D; Valentine and Commeau, 1990).

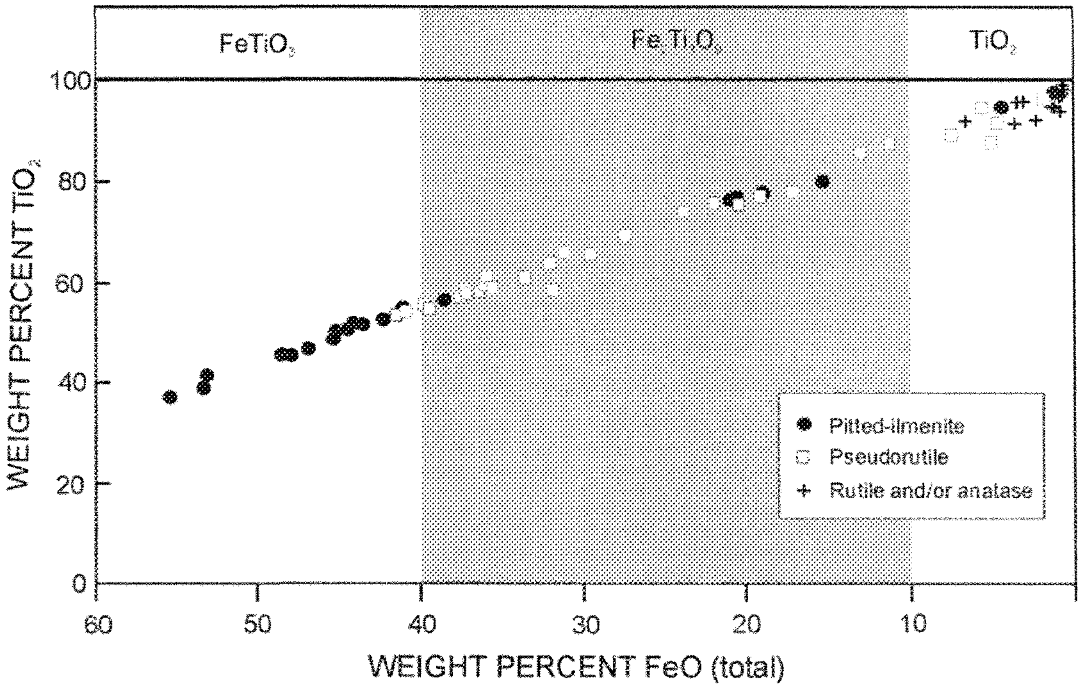

Figure 4.14 Diagram showing the progressive enrichment in TiO$_2$ of the principal Fe-Ti oxides (pitted-ilmenite, pseudorutile, anatase/rutile) of Sutton (Call Mill and Pinnacle).

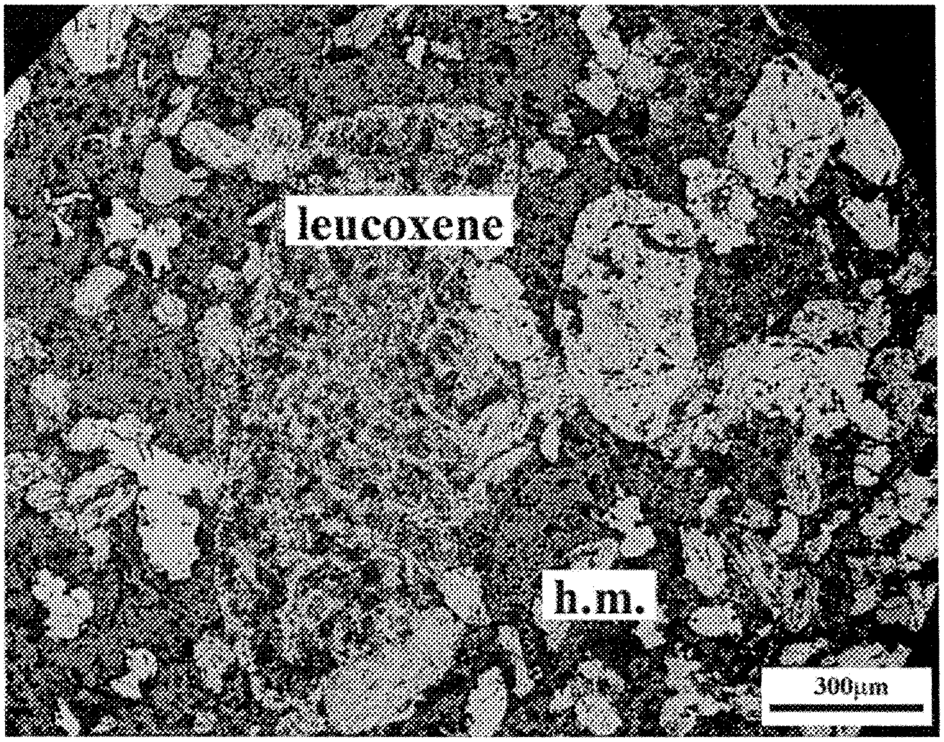

Figure 4.15 Photomicrographs of a Call Mill heavy mineral bed observed in natural reflected light. A coarse leucoxene grain among finer heavy mineral grains. H.M. = heavy minerals.

Depositional environment

Enrichments of heavy minerals occurring at the depositional site are induced principally by mechanical processes during transport and sedimentation. Different agents, such as waves, running water and wind can concentrate heavy minerals at a depositional site. For instance, the Call Mill heavy mineral beds show some depositional enrichment features. They are well-sorted, thin, single, very massive (95% h.m.), continuous on a few meters and generally in sharp contact at the top of argillic sediments (Fig. 4.5). The position of heavy mineral beds at the top of a sequence is a typical sedimentary feature derived from a flash flood event (Lucchitta and Suneran, 1981). However, such concentrations of heavy minerals reaching 95% is rarely observed in nature (K.J. Stanaway, pers. commun., 2006). Nevertheless, according to Lucchitta and Suneson (1981), the accumulation of heavy minerals depend on the availibility of a source in the surrounding rocks. In the Sutton case, the source rocks are the ilmenite-rich Grenvillian terrains. Moreover, the source rocks were probably already residually enriched by the destruction of light minerals during lateritization, thus could easily explain the very high concentration of heavy minerals. This flash-flood concentration implies that during the time of deposition, the Call Mill Slate was under arid or desertic environment (Lucchitta and Suneson, 1981), which is consistant with the previous interpretation (Marquis and Kumarapeli, 1993). By contrast, the Pinnacle semimassive beds are in gradual contact with the surrounding rocks, which are composed of sandstones.

Post-depositional enrichment

After deposition, the Call Mill underwent diagenesis and two metamorphic episodes, both reaching the greenschist metamorphic facies in which the Fe-Ti oxides could have been residually enriched in TiO_2 (Colpron, 1992; Colpron et al, 1994; Castonguay, 2001). The presence of hematite between the grains suggest that iron derived from the leaching of Fe-Ti grains reprecipitated firstly as hydroxides and then metamorphosed to hematite (Force, 1991, Clout, 2005). Thus, this implies that the Call Mill heavy minerals have also been weathered after deposition (Force, 1991).

Discussion

Based on the mineralogy, we proposed that, in the Sutton region, the Call Mill Slate and the Pinnacle sandstones have the same source rock, i.e. a magmatic ilmenite-rich source. However, great differences exist between these two units, such as the sedimentologic aspect and the proportion of heavy minerals. These dichotomies must be taken in account when interpreting the origin of the Call Mill. Although the Call Mill and Pinnacle have the same source rock, the major differences lie in the different weathering history at the source. The paleolatitude of the region during the time of deposition also has to be considered in such interpretation. The Sutton region was near equatorial latitude during Cambrian time, thus deep-weathering would have been active (Fig. 4.1; Irving, 1981).

According to textural and mineralogical evidences, we propose that the Call Mill Slate is formed from the erosion of a lateritic or deep-weathered profile affecting the Fe-Ti anorthositic source rocks, whereas the Pinnacle is the result of the erosion of deeper unweathering profile (Fig. 4.16). The main evidence lies on the Fe-Ti oxides themselves. The presence of detrital micro-grained anatase horizons in the Call Mill Slate suggest a deep-weathered source rock, as observed in unconsolidated titaniferous placers, but also in lateritized and bauxitized igneous rocks (Overstreet et al., 1963; Herz, 1976; Force, 1991). These porous grains can only be preserved when formed at the depositional site, otherwise transport would destroy their fragile structure and isolate the micro-crystals of anatase (Grey and Reid, 1975; Force, 1991). Thus, the presence of fine

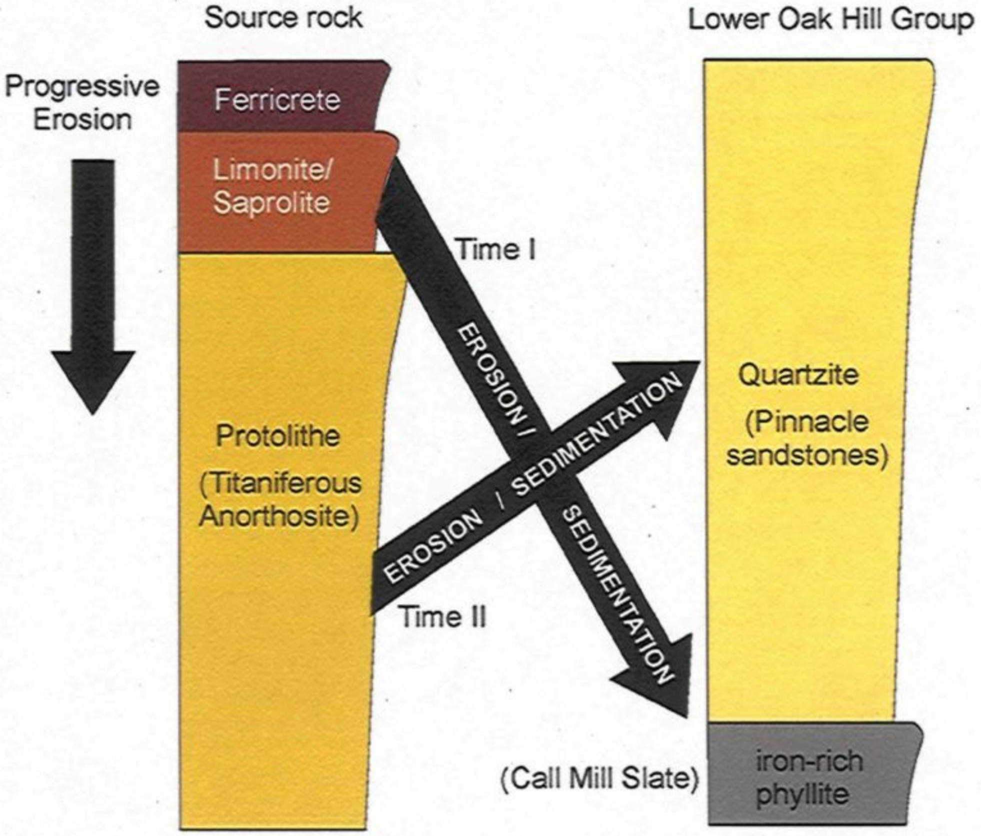

Figure 4.16 Schematic of an hypothetical weathered source rock of the Lower Oak Hill Group (for the Call Mill and the Pinnacle).

laminations of micro-crystalline anatase in the Call Mill Slate implicates that the source rocks must have been deeply weathered.

A second evidence is the high ilmeno-hematite/hemo-ilmenite ratio in the Call Mill massive beds. Under lateritic or deep-weathering conditions, hematite (or ilmeno-hematite) is more stable than ilmenite (or hemo-ilmenite), because ilmenite is altered partially as pseudorutile or completely into a pure TiO_2 phase, such as an aggregate of anatase (Overstreet et al., 1963; Herz, 1976; Force, 1991). Thus, the alteration of hemo-ilmenite, which is proved to occur by the presence of detrital anatase horizons, lead to a residual increasing in the ilmeno-hematite proportion of the source rocks. This implicates that the Fe-Ti oxide detrital grains were already at an advanced stage of alteration when they were deposited in the Call Mill massive beds. Moreover, other light minerals were also chemically destroyed under lateritic conditions, thus increasing the general proportion of detrital heavy minerals in placers (here, up to 95%; Force, 1991). The presence of coarse grains of leucoxene (which have survived transport) in hydraulic equivalence with finer ilmenite grains is observed only in the Call Mill and thus testify a pre-depositional weathering.

The hematite-rich content in the Call Mill Slate also suggests an erosion of a deep-weathered source rock. The fine-flaked texture of hematite observed is simply the metamorphic re-crystallization of an iron-rich mud (Clout and Simonson, 2005). We suggest that the source of this iron is the erosion of iron-rich horizons of the lateritic profile.

Another argument is the stratigraphical position of the Call Mill Slate. It is the first sedimentary unit and is relatively thin, and the main terrigenous unit –the Pinnacle– lies immediately above it. Therefore, the Pinnacle sandstones represent the erosion product of the hypogen non-altered anorthositic source rocks. The absence of detrital anatase micro-grains and the high hemo-ilmenite content of the Pinnacle semimassive beds suggest that the original hemo-ilmenite of the source rock was preserved. The relative abundance of light minerals in the semimassive beds also corroborate the preservation of less stable mineral of the source rocks.

Interpretation and conclusion

We interprete that the Sutton paleoplacer source rock, the Grenville high-metamorphosed terrains, were lateritized. When eroded during Cambrian time, the lateritized part formed the Fe-rich horizon of the Call Mill. While the source region was affected by lateritic conditions, the environment of deposition of the Call Mill is however interpreted to be more desertic (arid conditions), as the heavy mineral flash flood deposits suggest (Lucchitta and Suneson, 1981). Dowling (1988) interpreted the Call Mill to be a lacustral deposit in an unturbulent environment. The abundance of micas and fine-grained quartz point out toward this interpretation. However, the presence of conglomerate and massive heavy mineral beds suggests a dynamic environment instead of an unturbulent lake. These high energy level sediments, such as the well-sorted, massive heavy mineral beds in sharp contact with the matrix-rich slates with angular quartz grains is inconsistent with the previous interpretation of the Call Mill origin. Our observations give new elements regarding the Call Mill origin; however, to reconsider the actual stratigraphy, if it should be describe as a Formation or a Member of the Pinnacle Formation, is premature because the above-mentionned observations are limited to the Sutton area. A more regional field work has to be done before taking any decision.

The timing of enrichment of the Fe-Ti oxides is crucial in regard to economic viability of the titaniferous minerals. In the Call Mill, pre-depositional weathering prevented ilmenite to be leached from its iron content by post-depositional enrichment. Iron cement coated some grains and preserved them from further leaching as shown by the abundance of hematite overgrowths (Force, 1991). Moreover, the Call Mill heavy mineral beds being derived from a weathered source rock, the ilmenite was already oxidized (i.e., transformed into a ferric state, the pseudorutile) and thus could be leached from its iron content by further metamorphic process which required reduced condition (Grey and Reid, 1975). By contrast, ilmenite from the Pinnacle sandstone which are interpreted to be deposit from a unweathered source rock, could undergo further enrichment due to the potential of trapping oxygen (See Chapter 3). In this case, reducing conditions were provided by ferrous-bearing mineral such as unweathered ilmenite, which are abundant in the Pinnacle sandstones.

References

Castonguay, S., Ruffet, G., Tremblay, A. and Féraud, G., 2001, Tectono-metamorphic evolution of the southern Quebec Appalachians: 40Ar/39Ar evidence for Middle Ordovician crustal thickening and Silurian-Early Devonian exhumation of the internal Humber zone: Geological Society of America Bulletin, v. 113, no 1, p. 144-160.

Charbonneau, J.M., 1980, Région de Sutton (W): Ministère de l'Énergie et des Ressources du Québec, DPV-681, 89 pp.

Clark, T.H., 1931, Lowest Cambrian of southern Quebec. Geological Society of America Bulletin, abstract, v. 17, p. 497-522.

Clark, T.H., 1934, Structure and Stratigraphy of Southern Quebec. Geological Society of America Bulletin, v. 45, p. 1-20.

Clark, T.H., 1936, A Lower Cambrian Series from Southern Quebec: Transactions of the Royal Canadian Institute, no 45, v. 21, part I, p. 135-151.

Clout, J.M.F. and Simonson, B.M., 2005, Precambrian iron formations and iron formation-hosted iron ore deposits: Economic Geology 100th Anniversary Volume, p. 643-679.

Colpron, M., 1992, Géologie de la région du lac Brome (Estrie): ET- Direction Générale de l'Exploration Géologique et Minérale ET-90-09. 96 pp.

Colpron, M., Faure, S. and Dowling, W., 1994, Géologie de la région de Sutton (Montérégie): Ministère des Ressources Naturelles du Québec, ET 92-05. 85 pp.

Dowling, W.M., 1988, Depositional environment of the lower Oak Hill Group, southern Quebec: implications for the late Precambrian breakup of North America in the Quebec reentrant: University of Vermont: Burlington, VT, United States; Master's, 186 pages.

Eakins, P.R., 1964, Région de Sutton, Québec. Commission géologique du Canada, Étude 63-34, 3 p.

Force, E.R., 1991, Geology of titanium-mineral deposits: Geological Society of America, Special Paper 259, 112 pp.

Gauthier, M., Chartrand, F., Trottier, J., 1994, Metallogenic epochs and metallogenic provinces of the Estrie-Beauce region, Southern Quebec Appalachians: Economic Geology, v. 89, issue 6, p.1322-1360.

Grey, I.E. and Reid, A.F., 1975, The structure of pseudorutile and its role in the natural alteration of ilmenite: American Mineralogist, v. 60, p. 898-906.

Hébert, E., and Gauthier, M., in press, Unconventional rutile deposits in the Quebec Appalachians: Product of hypogene enrichment during low-grade metamorphism: Economic Geology.

Herz, N., 1976, Titanium deposits in alkalic igneous rocks: U.S. Geological Survey Professional Paper 959-E. 6 p.

Irving, E., 1981, Phanerozoic continental drift: Physics of the Earth and Planetary Interiors, v. 24, Issues 2-3, p.197-204.

Lucchitta, I., and Suneson, N., 1981, Flash flood in Arizona—Observations and their application to the identification of flash-flood deposits in the geologic record: Geology, v. 9, p. 414-418.

Marquis, R., 1991, Géologie de l'anticlinorium des monts Sutton (région de Richmond) : Ministère de l'Énergie et des Ressources, Québec, ET 89-02, 86 p.

Marquis, R., and Kumarapeli, P.S., 1993, An early Cambrian deltaic model for an Iapetan riftarm drainage system, southeastern Quebec: Canadian Journal of Earth Sciences, v. 30, p. 1254-1261.

Overstreet, W.C., Yates, R.G., Griffitts, W.R., 1963, Heavy minerals in the saprolite of the crystalline rocks in the Shelby Quadrangle, North Carolina: U.S. Geological Survey Bulletin, 1162-F, 31 p.

Valentine, P.C., and Commeau, J.A., 1990, Fine-grained rutile in the Gulf of Maine—Diagenetic origin, source rocks and sedimentary environment of deposition, Economic Geology, v. 85, p. 862-876.

Wilcox, J.T., 1971, Preliminary investigation of heavy minerals in the McNairy sand of west Tennessee: Tennessee Division of Geology Report of Investigation 31, 11p.

General Discussion and Conclusion

The titaniferous heavy mineral concentrations of the Sutton metamorphosed paleoplacers underwent several mineral transformations (alterations), which included weathering, diagenesis and metamorphism. New mineral phases, induced by such transformations, were formed; their nature, abundance, and distribution depending on the timing of each transformation process.

In the first part of this study, the different Fe-Ti minerals of the Pinnacle semimassive beds were discussed. A petrographical study demonstrated that post-depositional and metamorphic iron leaching from hemo-ilmenite transformed the grains into a nearly-pure TiO_2 residual phase. Further metamorphism allowed these porous TiO_2 grains to recrystallize as coarse-grained rutile.

It has been demonstrated that reducing conditions during metamorphism were necessary to allow iron leaching. Such reducing conditions, marked by the presence of metamorphic magnetite, were only observed in the Pinnacle semimassive heavy mineral beds. The presence of unweathered hemo-ilmenite grains (i.e. with ferrous iron) in sufficient quantity was essential to induce reducing conditions during metamorphism. Oxidized metamorphic fluids circulating within these rich Fe^{2+}-bearing mineral horizons, which acted as an oxygen trap, were reduced by oxygen consumption during the transformation of ilmenite (Fe^{2+}) into pseudorutile (Fe^{3+}) according to:

$$3\,Fe^{(2+)}TiO_3 + 2H^+ + \frac{1}{2}O_2 = Fe_2^{(3+)}Ti_3O_9 + Fe^{2+} + H_2O$$

Such mineral transformation provides reducing conditions that are necessary to further leaching of the newly formed mineral, i.e. pseudorutile. The leached iron is incorporated into other oxides and silicates, leaving a nearly pure TiO_2 mineral completely purged of its iron.

Iron leaching of Fe-Ti oxides was not observed in the Call Mill massive heavy mineral beds. Our study showed that the Call Mill heavy mineral source rock underwent pervasive weathering. As a result, only weathered ilmenite (or pseudorutile) were present during the time of deposition. When metamorphosed, these Fe-Ti concentrations did not have the capacity of reducing the oxidized metamorphic fluids, as the Pinnacle semimassive ilmenite-rich beds did. The main reason was because the Call Mill heavy minerals were majoritary Fe3+ bearing minerals, typical of a deeply weathered source rock. Therefore, the Call Mill underwent metamorphim under oxidized conditions. As a result, no iron leaching could have occurred during further metamorphism. Such oxidized metamorphic conditions created a completely different mineral paragenesis for Fe-Ti oxides. Instead of finding nearly-pure TiO_2 minerals, due to iron leaching, the Call Mill contains titaniferous oxides intermixed with ferriferous oxides. Pseudorutile dissociated into rutile and hematite, resulting from an oxidizing metamorphism, are therefore only observed in the Call Mill heavy mineral beds.

In conclusion the timing of the weathering is crucial, because it determines if the iron would be leached out of the mineral phase or would remain as two mineral phases intermixed within a single grain, thus affecting the economic viability of the placer.

APPENDIX A
Analysis of Fe-Ti oxides (1)

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1. Grains of Fe-Ti oxides were selected on polished thin sections and analyzed using a JEOL- JXA-8900 electron microprobe operated at 15kV, with a specimen current of 20nA and a beam diameter of 10 μm

APPENDIX A. Analysis of Fe-Ti oxides (wt %)

	Pitted-ilmenite								
Sample # Oxide	30C	30C	30C	30C	30C	30C	30C	30C	30E
SiO_2	0,15	0,21	0,06	0,10	0,15	0,31	0,06	0,08	0,08
TiO_2	45,35	45,49	50,63	48,89	45,84	37,18	52,36	51,44	41,33
Al_2O_3	0,89	0,87	0,35	0,32	0,35	0,40	0,18	0,19	0,50
FeO^1	48,48	47,91	44,42	45,32	48,40	55,42	42,24	44,03	53,11
MnO	0,00	0,00	0,00	0,00	0,03	0,00	0,00	0,00	0,00
MgO	0,01	0,08	0,00	0,02	0,02	0,05	0,01	0,02	0,02
CaO	0,01	0,03	0,03	0,00	0,00	0,03	0,01	0,02	0,00
P_2O_5	0,01	0,00	0,00	0,00	0,02	0,00	0,01	0,00	0,01
V_2O_3	0,11	0,09	0,09	0,13	0,09	0,13	0,16	0,16	0,21
Cr_2O_3	0,08	0,03	0,04	0,02	0,04	0,00	0,00	0,00	0,02
Nb_2O_5	0,00	0,00	0,00	0,09	0,05	0,00	0,00	0,03	0,01
ThO_2	0,00	0,00	0,03	0,00	0,02	0,00	0,00	0,13	0,00
UO_2	0,03	0,02	0,03	0,00	0,02	0,00	0,00	0,00	0,09
Total	95,11	94,70	95,68	94,88	95,02	93,51	95,02	96,11	95,37

[1] Total Fe reported as FeO

APPENDIX A. Analysis of Fe-Ti oxides (wt %)

	Pitted-ilmenite								
Sample # Oxide	30E	30E	30E	30E	30E	30E	30E	30E	30E
SiO_2	0,04	0,13	0,12	0,08	0,13	2,42	0,08	0,12	0,07
TiO_2	50,28	94,70	98,29	97,13	76,97	79,96	77,42	56,48	76,37
Al_2O_3	0,59	0,46	0,09	0,08	0,37	0,48	0,41	0,24	0,13
FeO[1]	45,08	4,30	0,65	1,28	20,57	15,22	18,90	38,43	20,85
MnO	0,00	0,00	0,01	0,01	0,02	0,02	0,01	0,00	0,01
MgO	0,00	0,00	0,01	0,00	0,03	0,12	0,00	0,01	0,01
CaO	0,03	0,04	0,04	0,03	0,03	0,01	0,00	0,01	0,02
P_2O_5	0,01	0,00	0,01	0,00	0,00	0,00	0,01	0,00	0,01
V_2O_3	0,11	0,13	0,10	0,18	0,17	0,21	0,21	0,20	0,10
Cr_2O_3	0,03	0,02	0,04	0,05	0,07	0,04	0,06	0,06	0,03
Nb_2O_5	0,11	0,09	0,17	0,62	0,03	0,15	0,04	0,10	0,15
ThO_2	0,04	0,00	0,01	0,00	0,00	0,00	0,03	0,03	0,00
UO_2	0,00	0,00	0,01	0,02	0,00	0,04	0,08	0,06	0,01
Total	96,33	99,85	99,55	99,46	98,40	98,68	97,23	95,74	97,76

[1] Total Fe reported as FeO

APPENDIX A. Analysis of Fe-Ti oxides (wt %)

	Pitted-ilmenite			
Sample # Oxide	30E	30E	30E	30E
SiO_2	0,35	0,61	0,05	0,41
TiO_2	46,74	38,99	54,76	51,40
Al_2O_3	0,43	0,68	0,01	0,09
FeO^1	46,84	53,33	40,94	43,48
MnO	0,05	0,01	0,01	0,00
MgO	0,12	0,42	0,00	0,00
CaO	0,01	0,02	0,00	0,02
P_2O_5	0,00	0,00	0,01	0,00
V_2O_3	0,21	0,23	0,12	0,18
Cr_2O_3	0,05	0,03	0,00	0,07
Nb_2O_5	0,00	0,00	0,02	0,10
ThO_2	0,00	0,07	0,00	0,05
UO_2	0,00	0,01	0,01	0,02
Total	94,80	94,40	95,93	95,81

[1] Total Fe reported as FeO

APPENDIX A. Analysis of Fe-Ti oxides (wt %)

	Pseudorutile								
Sample # Oxide	30C	30C	30C	30C	30C	30C	30C	30C	30C
SiO_2	0,17	0,09	0,13	0,06	1,04	0,14	0,12	0,08	0,01
TiO_2	57,74	54,06	57,24	65,46	58,58	58,88	58,14	58,46	87,64
Al_2O_3	0,59	0,37	0,53	0,63	3,14	0,34	0,73	0,39	0,03
FeO^1	37,17	40,82	37,48	29,47	31,80	35,52	36,34	36,65	11,06
MnO	0,02	0,00	0,03	0,01	0,00	0,00	0,01	0,01	0,01
MgO	0,00	0,00	0,00	0,00	0,01	0,00	0,01	0,01	0,02
CaO	0,02	0,01	0,04	0,04	0,03	0,03	0,01	0,02	0,01
P_2O_5	0,00	0,00	0,01	0,00	0,00	0,01	0,03	0,00	0,01
V_2O_3	0,12	0,16	0,11	0,05	0,16	0,12	0,13	0,09	0,11
Cr_2O_3	0,02	0,00	0,02	0,00	0,02	0,01	0,04	0,06	0,02
Nb_2O_5	0,03	0,00	0,42	0,06	0,02	0,00	0,04	0,04	0,61
ThO_2	0,00	0,02	0,00	0,00	0,00	0,02	0,05	0,08	0,04
UO_2	0,00	0,00	0,00	0,00	0,00	0,02	0,08	0,03	0,00
Total	95,88	95,53	96,00	95,78	94,80	95,08	95,72	95,91	99,57

^{1}Total Fe reported as FeO

APPENDIX A. Analysis of Fe-Ti oxides (wt %)

	Pseudorutile								
Sample #	30C	30E	30E	30E	30E	30E	30E	30E	30E
Oxide									
SiO_2	3,22	1,12	0,16	0,54	0,00	1,12	0,09	0,04	0,31
TiO_2	87,76	89,16	59,47	75,40	73,73	77,92	69,05	63,73	77,21
Al_2O_3	1,32	0,60	0,28	0,45	0,10	0,95	0,12	0,20	0,89
FeO[1]	4,88	7,37	35,97	20,37	23,81	17,05	27,35	32,09	18,97
MnO	0,00	0,01	0,01	0,01	0,00	0,00	0,00	0,02	0,00
MgO	0,08	0,24	0,02	0,12	0,00	0,64	0,04	0,00	0,19
CaO	0,06	0,01	0,00	0,05	0,01	0,01	0,01	0,02	0,02
P_2O_5	0,00	0,01	0,02	0,00	0,03	0,01	0,02	0,02	0,00
V_2O_3	0,12	0,13	0,18	0,23	0,18	0,17	0,13	0,18	0,19
Cr_2O_3	0,00	0,03	0,03	0,00	0,01	0,07	0,03	0,03	0,01
Nb_2O_5	0,18	0,10	0,02	0,13	0,36	0,24	0,05	0,12	0,08
ThO_2	0,00	0,05	0,04	0,00	0,05	0,00	0,00	0,00	0,01
UO_2	0,00	0,00	0,05	0,07	0,00	0,00	0,03	0,00	0,00
Total	97,61	98,83	96,25	97,37	98,28	98,18	96,92	96,43	97,87

[1] *Total Fe reported as FeO*

APPENDIX A. Analysis of Fe-Ti oxides (wt %)

	Pseudorutile								
Sample # Oxide	30E	30E	30E	30E	30E	30E	30E	30E	30E
SiO_2	0,07	0,23	0,09	0,06	0,10	0,06	0,93	0,53	0,04
TiO_2	53,56	54,93	85,50	65,72	58,35	61,16	91,59	96,21	94,68
Al_2O_3	0,26	0,55	0,01	0,17	0,14	0,07	0,93	0,21	0,02
FeO[1]	41,40	39,33	12,98	31,14	37,23	35,84	4,65	1,70	5,54
MnO	0,00	0,01	0,00	0,01	0,00	0,04	0,00	0,00	0,00
MgO	0,02	0,13	0,01	0,02	0,01	0,01	0,05	0,08	0,00
CaO	0,01	0,03	0,02	0,02	0,01	0,02	0,06	0,04	0,00
P_2O_5	0,03	0,02	0,02	0,03	0,00	0,03	0,03	0,01	0,01
V_2O_3	0,21	0,22	0,24	0,24	0,18	0,17	0,03	0,14	0,21
Cr_2O_3	0,01	0,05	0,01	0,04	0,07	0,00	0,02	0,04	0,04
Nb_2O_5	0,00	0,00	0,16	0,01	0,03	0,00	0,14	0,16	0,00
ThO_2	0,09	0,01	0,00	0,02	0,00	0,00	0,13	0,00	0,00
UO_2	0,03	0,03	0,04	0,00	0,04	0,03	0,08	0,05	0,00
Total	95,67	95,55	99,07	97,46	96,17	97,42	98,64	99,17	100,54

[1] Total Fe reported as FeO

APPENDIX A. Analysis of Fe-Ti oxides (wt %)

	Pseudorutile			
Sample # Oxide	30C	30C	30E	30E
SiO_2	0,03	0,07	0,07	0,64
TiO_2	75,93	58,62	55,59	60,76
Al_2O_3	0,07	0,32	0,24	0,29
FeO[1]	21,89	36,95	39,69	33,63
MnO	0,00	0,03	0,00	0,01
MgO	0,00	0,01	0,03	0,00
CaO	0,00	0,00	0,01	0,01
P_2O_5	0,00	0,02	0,00	0,00
V_2O_3	0,14	0,09	0,20	0,17
Cr_2O_3	0,00	0,03	0,07	0,16
Nb_2O_5	0,54	0,08	0,06	0,00
ThO_2	0,00	0,06	0,01	0,00
UO_2	0,05	0,03	0,02	0,00
Total	98,66	96,31	95,98	95,67

[1] Total Fe reported as FeO

APPENDIX A. Analysis of Fe-Ti oxides (wt %)

	Anatase-rutile								
Sample #	30E	30E	30E	30E	30E	30E	30E	30E	30E
Oxide									
SiO_2	2,79	0,63	0,11	0,55	0,04	0,13	1,57	0,10	0,06
TiO_2	91,72	97,00	97,62	97,63	99,16	97,94	94,93	99,48	92,35
Al_2O_3	0,43	0,13	0,18	0,15	0,06	0,10	0,31	0,06	0,27
FeO[1]	3,48	1,45	1,02	0,77	0,66	0,81	1,37	0,70	6,48
MnO	0,00	0,00	0,00	0,00	0,01	0,00	0,03	0,01	0,00
MgO	0,12	0,00	0,00	0,01	0,01	0,00	0,11	0,01	0,00
CaO	0,01	0,02	0,03	0,01	0,03	0,09	0,03	0,05	0,03
P_2O_5	0,00	0,00	0,00	0,02	0,01	0,00	0,00	0,00	0,00
V_2O_3	0,20	0,16	0,17	0,21	0,24	0,23	0,13	0,13	0,20
Cr_2O_3	0,00	0,01	0,00	0,02	0,01	0,01	0,01	0,01	0,03
Nb_2O_5	0,18	0,13	0,11	0,08	0,18	0,09	0,83	0,14	0,02
ThO_2	0,05	0,07	0,00	0,08	0,00	0,05	0,00	0,01	0,01
UO_2	0,00	0,06	0,02	0,00	0,01	0,00	0,00	0,05	0,01
Total	98,97	99,67	99,25	99,53	100,41	99,44	99,33	100,75	99,44

[1] Total Fe reported as FeO

APPENDIX A. Analysis of Fe-Ti oxides (wt %)

	Anatase-rutile								
Sample # Oxide	30E	30E	30E	30E	30E	30E	30E	30E	30E
SiO_2	0,13	0,16	0,04	0,01	0,03	2,86	2,14	3,89	0,35
TiO_2	98,30	98,45	97,60	99,07	98,04	95,31	94,67	94,43	97,40
Al_2O_3	0,13	0,03	0,10	0,03	0,06	0,20	0,41	0,12	0,17
FeO^1	0,82	0,67	0,73	0,60	0,83	1,08	1,19	0,72	0,87
MnO	0,00	0,04	0,00	0,00	0,00	0,03	0,00	0,01	0,00
MgO	0,08	0,00	0,02	0,00	0,01	0,08	0,24	0,01	0,03
CaO	0,03	0,03	0,10	0,02	0,03	0,01	0,03	0,03	0,11
P_2O_5	0,00	0,01	0,00	0,00	0,00	0,02	0,01	0,00	0,00
V_2O_3	0,18	0,13	0,20	0,17	0,18	0,15	0,23	0,20	0,22
Cr_2O_3	0,02	0,04	0,00	0,09	0,06	0,00	0,02	0,04	0,00
Nb_2O_5	0,16	0,18	0,07	0,02	0,57	0,10	0,09	0,43	0,05
ThO_2	0,00	0,11	0,00	0,07	0,02	0,00	0,14	0,00	0,00
UO_2	0,02	0,01	0,07	0,00	0,00	0,00	0,04	0,00	0,00
Total	99,85	99,86	98,92	100,08	99,83	99,84	99,18	99,87	99,19

[1] Total Fe reported as FeO

APPENDIX A. Analysis of Fe-Ti oxides (wt %)

				Anatase-Rutile				
Sample # Oxide	30E	30E	30E	30E	30E	30E	30E	30E
SiO_2	0,07	0,02	0,12	0,32	4,19	0,19	0,02	0,06
TiO_2	98,22	98,44	98,15	95,96	92,40	98,15	95,77	98,10
Al_2O_3	0,20	0,04	0,08	0,29	0,10	0,12	0,00	0,04
FeO^1	0,60	0,75	0,85	2,95	2,24	0,80	3,35	0,56
MnO	0,00	0,00	0,01	0,01	0,02	0,00	0,00	0,00
MgO	0,00	0,01	0,00	0,13	0,01	0,00	0,01	0,00
CaO	0,09	0,03	0,10	0,04	0,03	0,09	0,02	0,07
P_2O_5	0,00	0,00	0,00	0,01	0,00	0,01	0,00	0,00
V_2O_3	0,21	0,04	0,12	0,18	0,22	0,22	0,24	0,25
Cr_2O_3	0,00	0,03	0,02	0,01	0,00	0,01	0,03	0,03
Nb_2O_5	0,02	0,29	0,12	0,06	0,13	0,21	0,00	0,09
ThO_2	0,09	0,00	0,00	0,08	0,12	0,00	0,05	0,07
UO_2	0,01	0,04	0,00	0,03	0,01	0,07	0,01	0,08
Total	99,51	99,68	99,55	100,04	99,47	99,87	99,50	99,36

[1] Total Fe reported as FeO

APPENDIX B
Analysis of chlorite (1)

1. Flakes of chlorite were selected on polished thin sections and analyzed using a JEOL- JXA-8900 electron microprobe operated at 15kV, with a specimen current of 20nA and a beam diameter of 10 μm All the samples come from a typical section, outcrop # 30 (see localization map).

APPENDIX B. Analysis of chlorite (wt %)

				Chlorite - Zone B						
SiO_2	24,95	25,96	26,54	25,99	26,09	27,24	26,10	26,37	26,79	26,23
TiO_2	0,17	0,19	0,00	0,07	0,48	0,52	0,04	0,05	0,02	0,07
Al_2O_3	19,98	19,94	19,53	19,56	19,73	20,32	20,24	20,41	19,83	20,12
FeO[1]	19,89	19,88	20,81	19,99	20,27	20,35	20,85	21,12	19,31	18,79
MnO	0,21	0,19	0,22	0,22	0,20	0,18	0,25	0,21	0,40	0,37
MgO	18,19	18,38	19,43	18,99	18,09	17,03	18,77	18,52	19,61	20,46
CaO	0,00	0,00	0,01	0,04	0,00	0,04	0,01	0,01	0,03	0,00
Na_2O	0,01	0,01	0,04	0,10	0,00	0,05	0,03	0,05	0,00	0,00
K_2O	0,04	0,01	0,00	0,06	0,03	0,82	0,06	0,05	0,03	0,00
Total	83,44	84,55	86,58	85,02	84,88	86,53	86,34	86,78	86,00	86,05

[1] Total Fe reported as FeO

APPENDIX B. Analysis of chlorite (wt %)

			Chlorite - Zone C						
SiO_2	25,24	25,33	29,98	24,91	25,88	24,88	28,36	25,13	25,21
TiO_2	0,04	0,05	0,36	0,06	0,06	0,15	0,22	0,30	0,07
Al_2O_3	21,24	21,06	20,39	21,70	21,68	21,37	22,77	21,02	21,30
FeO^1	23,90	24,57	22,94	24,02	23,54	25,25	22,15	23,40	24,33
MnO	0,48	0,44	0,43	0,47	0,46	0,53	0,42	0,25	0,22
MgO	15,59	15,67	15,03	15,82	15,27	15,21	12,38	15,89	16,10
CaO	0,01	0,01	0,01	0,00	0,00	0,00	0,01	0,00	0,01
Na_2O	0,01	0,04	0,01	0,00	0,00	0,00	0,09	0,01	0,01
K_2O	0,02	0,04	0,01	0,02	0,50	0,02	1,93	0,01	0,00
Total	86,53	87,19	89,15	87,00	87,40	87,40	88,33	86,02	87,25

[1] Total Fe reported as FeO

APPENDIX B. Analysis of chlorite (wt %)

			Chlorite - Zone C						
SiO_2	25,52	25,66	25,70	24,74	24,71	25,83	24,59	25,11	24,92
TiO_2	0,06	0,03	0,01	0,12	0,12	0,28	0,19	0,19	0,08
Al_2O_3	21,14	20,90	20,61	21,29	21,22	20,45	20,94	20,90	20,59
FeO^1	23,39	24,04	24,71	23,43	23,64	24,63	24,17	24,22	24,83
MnO	0,25	0,20	0,22	0,30	0,31	0,29	0,43	0,37	0,37
MgO	16,75	16,55	16,29	16,25	16,15	16,02	16,05	16,06	15,56
CaO	0,00	0,01	0,01	0,00	0,00	0,00	0,01	0,02	0,02
Na_2O	0,01	0,00	0,00	0,01	0,00	0,00	0,00	0,03	0,00
K_2O	0,00	0,02	0,00	0,01	0,00	0,01	0,00	0,04	0,00
Total	87,13	87,41	87,55	86,15	86,14	87,49	86,39	86,93	86,37

[1] Total Fe reported as FeO

APPENDIX B. Analysis of chlorite (wt %)

	Chlorite - Zone C					
SiO_2	25,60	24,33	25,80	24,65	24,02	24,26
TiO_2	0,33	0,03	0,12	0,10	0,09	0,11
Al_2O_3	20,34	21,37	19,80	21,93	22,10	21,75
FeO[1]	24,14	26,95	24,48	25,65	26,29	25,15
MnO	0,68	0,72	0,70	0,73	0,74	0,72
MgO	15,65	14,25	15,76	14,66	13,93	14,71
CaO	0,03	0,03	0,04	0,04	0,01	0,07
Na_2O	0,00	0,03	0,02	0,00	0,03	0,02
K_2O	0,00	0,01	0,02	0,00	0,01	0,00
Total	86,77	87,73	86,74	87,76	87,21	86,78

[1] Total Fe reported as FeO

APPENDIX B. Analysis of chlorite (wt %)

			Chlorite - Oxide Zone						
SiO_2	23,50	22,44	23,67	23,21	23,65	23,30	23,20	22,17	22,95
TiO_2	0,11	0,11	0,03	0,03	0,07	0,04	0,06	0,22	0,20
Al_2O_3	22,39	21,79	21,89	21,99	21,87	22,24	22,13	21,58	22,09
FeO[1]	31,39	32,21	28,90	29,25	31,50	32,15	32,18	32,69	29,93
MnO	0,31	0,34	0,30	0,29	0,31	0,27	0,31	0,33	0,32
MgO	9,92	9,60	9,85	9,99	10,63	9,88	10,07	9,21	10,34
CaO	0,03	0,04	0,01	0,01	0,00	0,00	0,02	0,07	0,03
Na_2O	0,03	0,02	0,03	0,04	0,01	0,02	0,04	0,05	0,05
K_2O	0,03	0,03	0,00	0,02	0,00	0,02	0,01	0,03	0,01
Total	87,71	86,58	84,68	84,83	88,04	87,92	88,03	86,35	85,92

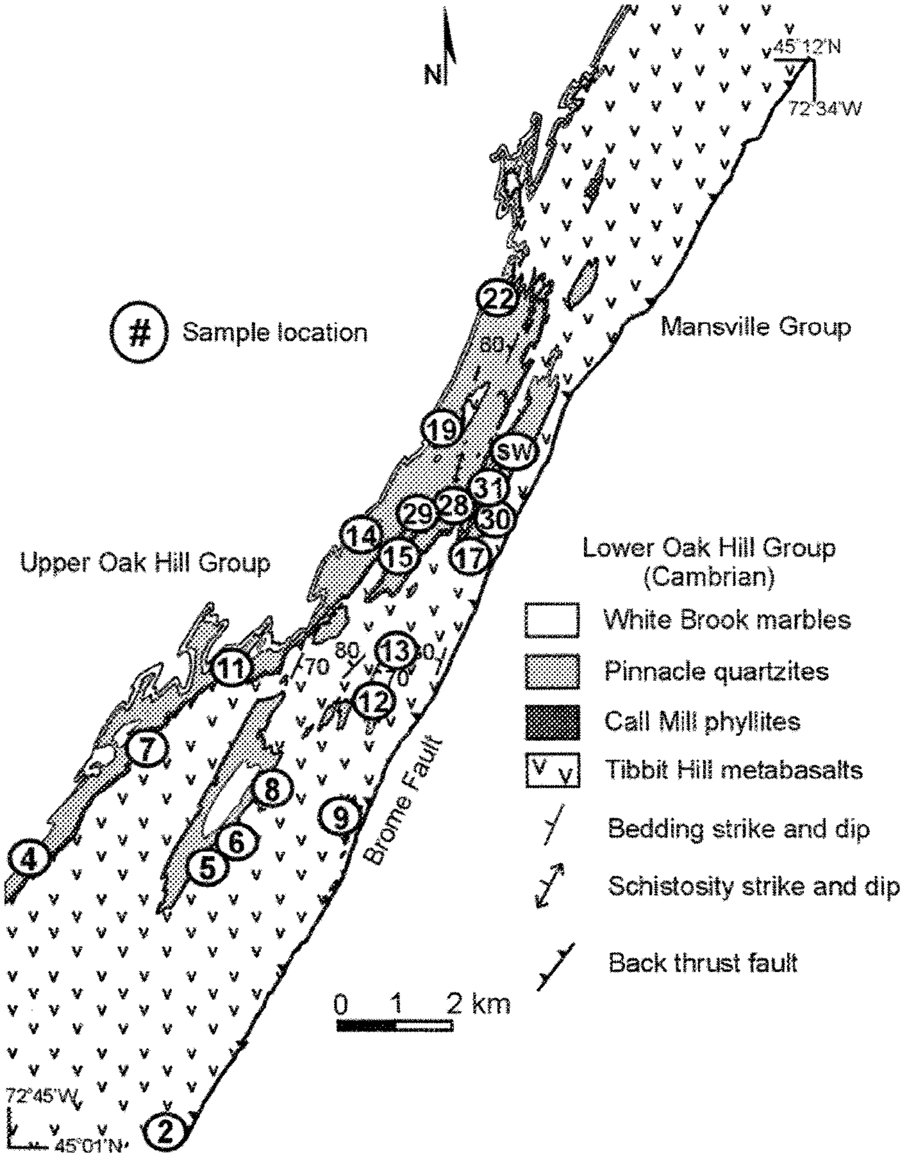
[1] Total Fe reported as FeO

APPENDIX B. Analysis of chlorite (wt %)

			Chlorite - Oxide Zone						
SiO_2	22,86	22,33	23,03	22,90	22,54	24,67	24,62	24,12	24,27
TiO_2	0,21	0,18	0,13	0,14	0,16	0,24	0,11	0,10	0,06
Al_2O_3	22,21	21,44	21,56	22,68	22,70	20,70	22,02	21,60	21,84
FeO^1	30,83	30,42	30,23	30,95	31,66	25,61	25,99	26,18	26,06
MnO	0,28	0,26	0,26	0,33	0,32	0,72	0,68	0,75	0,77
MgO	9,78	9,31	10,07	10,34	9,90	14,46	13,63	14,16	14,16
CaO	0,00	0,01	0,01	0,00	0,00	0,02	0,03	0,01	0,01
Na_2O	0,02	0,02	0,00	0,00	0,01	0,01	0,02	0,02	0,03
K_2O	0,01	0,01	0,02	0,00	0,02	0,08	0,04	0,01	0,03
Total	86,18	83,98	85,30	87,34	87,32	86,49	87,13	86,94	87,21

[1] Total Fe reported as FeO

APPENDIX C
Map of Outcrop position


N
45°12'N
72°34'W
Sample location
Mansville Group
Upper Oak Hill Group
Lower Oak Hill Group
(Cambrian)
White Brook marbles
Pinnacle quartzites
Call Mill phyllites
Tibbit Hill metabasalts
Bedding strike and dip
Schistosity strike and dip
Back thrust fault
Brome Fault
0 1 2 km
72°45'W
45°01'N
22
19
SW
31
29
28
30
14
15
17
13
12
11
7
8
9
6
5
4
2
80
70
80
70

APPENDIX D
Sample Names and Location

APPENDIX D. Sample names and location

# Sample	Eastern (UTM Nad 83)	Northern (UTM Nad 83)
2A	680092	4987732
2B	680165	4987726
2C	680160	4987725
2E	680106	4987594
2F	680100	4987593
2H	680128	4987621
4A	677750	4992914
4B	677672	4992909
4C	677649	4992933
4D	677691	4992958
4E	677638	4992980
4G	677485	4992830
4H	677468	4992858
5A	680531	4993053
5E	680516	4993065
5F	680482	4993078
5I	680498	4992929
6A	680874	4993376
6B	680879	4993386
6D	680878	4993391
6F	680870	4993392
6H	680870	4993391
6J	680854	4993390
6L	680805	4993388
6M	680802	4993390
6M1	680855	4993462
6M2	680757	4993364
6M3	680703	4993367
6N	680811	4993401
6P	680791	4993424
6R	680718	4993372
6T	680723	4993329
7A	679221	4995101
7B	679292	4995123
7C	679159	4995177
7D	679160	4995178

APPENDIX D. Sample names and location

# Sample	Eastern (UTM Nad 83)	Northern (UTM Nad 83)
8A	681510	4994237
8B	681508	4994238
8C	681503	4994241
8E	681500	4994242
8I	681441	4994217
8M	681415	4994230
8Q	681386	4994193
8S	681334	4994204
8T	681326	4994199
8AB	681483	4994311
8AD	681479	4994312
8AE	681471	4994315
8AF2	681449	4994264
8AG	681450	4994265
8AH	681451	4994266
9A	683003	4993783
9B	683004	4993782
9C	683005	4993782
9D	683006	4993783
9E	683010	4993782
9F	683012	4993783
9G	683018	4993789
9H	683031	4993783
9I	683050	4993785
9J	683052	4993786
11A	681340	4996907
11B	681342	4996905
11C	681386	4996858
11D	681444	4996841
11E	681546	4996715
11F	681589	4996728
12B	683445	4996147
12C	683444	4996146
12D	683443	4996145
12E	683442	4996145
12G	683438	4996143

APPENDIX D. Sample names and location

# Sample	Eastern (UTM Nad 83)	Northern (UTM Nad 83)
13A	683797	4996868
13B	683826	4996891
13C	683819	4996897
13D	683816	4996898
13E2	683814	4996899
13F	683811	4996899
13G	683809	4996899
13H	683801	4996927
14A	683078	4999281
14C	683075	4999265
14D	683071	4999240
14E	683070	4999239
14F	683067	4999233
14G	683066	4999231
14H	683070	4999208
15A	683731	4998972
15B	683729	4998973
15C	683722	4998976
15D	683718	4998978
17A	684805	4998873
17B	684949	4999015
17D	684955	4999017
17F	684976	4999023
17G	684980	4999019
17H	684983	4999018
17J	684989	4999029
17K	684943	4998955
19A	684403	5001182
19B	684419	5001188
19C	684433	5001238
19D	684475	5001231
19E	684495	5001209
19F	684486	5001204
19G	684492	5001195
19H	684517	5001219
19I	684554	5001205

APPENDIX D. Sample names and location

# Sample	Eastern (UTM Nad 83)	Northern (UTM Nad 83)
19J	684587	5001234
19K	684607	5001216
19L	684633	5001190
19M	684670	5001217
19N	684681	5001202
19O	684693	5001189
19P	684765	5001181
22B1	685355	5003668
22B2	685356	5003667
22C	685357	5003663
22D	685369	5003663
22E	685380	5003646
22F	685401	5003641
22G	685416	5003632
22H	685441	5003613
28A	683748	4999302
28B	683771	4999322
28C	683861	4999252
28D	683919	4999212
28E	683966	4999188
28F	683964	4999179
28G	684003	4999194
28H	683818	4999210
28I	683983	4999342
28J	684009	4999265
28K	684083	4999270
28L2	684166	4999292
28L3	684170	4999295
28M	684243	4999334
28P	684321	4999248
28Q1	684376	4999240
28Q2	684377	4999239
28S	684436	4999224
28S1	684452	4999234
28T	684458	4999239

APPENDIX D. Sample names and location

# Sample	Eastern (UTM Nad 83)	Northern (UTM Nad 83)
29A	683633	4998995
29B	683633	4999061
29C	683798	4998986
29D	683840	4998980
29E	683853	4998933
29F	683891	4998930
29G	683920	4998803
30A	684523	4999356
30B	684522	4999357
30C	684521	4999357
30D	684519	4999359
30E	684516	4999360
31A	684522	4999609
31B	684541	4999606
31C	684737	4999613
31D	684766	4999618
31E	684783	4999626
31F	684834	4999612
31G	684962	4999648
31H	685131	4999640
31I	685181	4999705
31J	685202	4999693
31K	685225	4999666
31L	685268	4999644
31M	685119	4999548
31N	685056	4999512
32A	685132	4999521
SW-A	685472	5000688
SW-C	685477	5000690
SW-C1	685479	5000695
SW-D1	685443	5000854
SW-F	685832	5001083
SW-H	685832	5001089

APPENDIX E
Oxygen Isotope Results

APPENDIX E. Oxygen Isotope Results

Sample	$\delta^{18}O_{smow}$ Magnetite	$\delta^{18}O_{smow}$ Water
4D	1,9	9,9
5G	2,9	10,9
6M	3,2	11,2
7B	1,6	9,6
8N	2,3	10,3
9D1	3,5	11,5
11F	3,2	11,2
12F	2,8	10,8
17G	8,5	16,5
19F	2,9	10,9
22C	4,8	12,8
25F	5,4	13,4
28B	2,6	10,6
28F	1,9	9,9
30E	2,7	10,7
31M	2,8	10,8
32A	2,4	10,4
SW-G	3,8	11,8

Calibration	**NBS-28**	**K1 (St. inter.)**
x=	9,69	18,78
s=	0,09	0,11
n=	13	21