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Rutile as a potential indicator mineral for metamorphosed metallic ore deposits

Par

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SUMMARY

Rutile occurs commonly in mineralized zones and alteration haloes of many hydrothermal and metamorphosed ore deposits, and typically has a composition that deviates significantly from pure TiO_2. This project was designed to test the idea that minor elements in rutile may reflect metal associations in ore deposits, and that analyses of rutile derived from such deposits (i.e., in fluvial/glacial sediments) might therefore constitute a new geochemical exploration tool that would indicate a potential for certain styles of mineralization. The project thus addresses several of the major goals of the DIVEX program by diversifying mineral exploration targets in Québec: these include facilitating the search for conventional deposits in (relatively unexplored) metamorphosed terrains, stimulating the search for new styles of mineralization (i.e., those not currently exploited in Québec), and most importantly, in the development of new exploration technology.

Rutile occurs in significant abundance in most metallic ore deposits, and irrespective of metamorphic grade, is most plentiful in sulfide-bearing deposits where high fS_2 and/or fO_2 conditions stabilize rutile at the expense of ilmenite, especially in the presence of minerals such as pyrite and hematite. Rutile is also persistent in weathering environments, and is likely to survive weathering and significant transport by secondary processes. As a common component of heavy mineral sands, rutile is a good candidate for separation by routine magnetic, heavy liquid, and other density methods. For many hydrothermal and magmatic-related deposits, there are reports in the literature of anomalous rutile compositions, characterized by elevated concentrations of ore-related metals; however, until the present study, there have been no broad-based surveys of rutile compositions.

The mineral chemistry of rutile was evaluated and analysed in samples from 26 ore deposits. In Québec, these include the Troilus Au-Cu mine, several Cu-Zn deposits in the Matagami district (Bell-Allard, Norita, Radiore, Garon Lake), the Ansil Cu-Zn mine, the Langlois Zn-Cu mine, the Montauban Au-Cu deposit, the Horne Cu-Au mine, the Lac Bachelor, Siscoe and Geant Dormant Au mines, the East Amphi and Lac Madeleine Au deposits, and the Mines Gaspé Cu deposit. Outside Québec, rocks were analysed from the Lac-des-Iles PGE-Ni-Cu mine, the San Rafael Sn-Cu mine, the Pilok W-Sn deposit, the Olympic Dam Au-Cu-U deposit, the Kidd Creek Zn-Cu-Ag mine, the San Manuel Cu deposit, the Hemlo Au-Mo deposit, the Witwatersrand Au deposit, and the Red Lake, Muruntau and Big Bell Au mines. In general, rutile in volcanogenic massive sulfide Cu-Zn deposits contains Sn (and locally W and/or Cu). Rutile from mesothermal and related gold deposits invariably contains W, and in some of the larger and more important deposits, rutile also contains Sb and/or V. Tungsten-bearing detrital rutile grains in the Witwatersrand deposit suggest that the origin of mineralization was a likely a paleoplacer with a mesothermal gold source. In at least some magmatic-hydrothermal Pd-Ni-Cu deposits, rutile contains Ni and Cu. Rutile associated with granite-related Sn deposits contains strongly elevated concentrations of Sn and W, and granite-pegmatite W-Sn deposits contain rutile with these elements plus Nb and Ta. The Olympic Dam deposit hosts rutile that is enriched in W, Sn and Cu. Rutile associated with porphyry and skarn Cu and Cu-Au deposits tend to contain elevated W, Cu (and sometimes V).

The variability and anomalous nature of compositions noted in this project suggest that rutile has definite potential as an indicator mineral in exploration for a wide variety of metallic ore deposits in metamorphic and other terrains.

1. INTRODUCTION

Rutile is a widely distributed mineral in alteration haloes associated with a variety of hydrothermal and metamorphosed ore deposits, and although poorly studied, anomalous rutile compositions appear to reflect significant metal concentrations in many types of orebodies. On the basis of work on the Hemlo gold deposit (Ontario), Williams-Jones et al. (1998) proposed that anomalous compositions of rutile at this deposit were sufficiently unusual as to serve as potential indicators of mineralization. In fact, it was suggested that such unusual compositions may define "indicator minerals" for Hemlo-style mineralization in the same sense that certain types of pyrope and chromite are used in exploration for diamondiferous kimberlites. The analogy with diamond indicator minerals is not exact, but is nevertheless useful, and can be extended to many types of metallic ore deposits that have relatively high-temperature origins, and those that have been modified by the elevated temperatures and pressures associated with metamorphism.

This project is designed to test the idea that minor and/or trace elements in rutile may reflect metal associations in ore deposits, and that analyses of rutile might therefore constitute a useful new geochemical exploration tool that will *indicate* a potential for certain types of metallic mineralization. The project is thus designed to meet several of the major goals of the DIVEX program by diversifying mineral exploration targets in Québec: these include facilitating the search for conventional deposits in (relatively unexplored) metamorphosed terrains, stimulating the search for new styles of mineralization (i.e., those not currently exploited in Québec), and most importantly, in the development of new exploration technology.

1.1 Objectives

The overall objective of this project was to survey and assess rutile compositions associated with different styles of hydrothermal and/or metamorphosed mineralization. Specifically, our goals have been: 1) to review the literature on metal substitutions in rutile; 2) to develop analytical protocols to analyse minor elements in rutile; and 3) to test the idea that rutile associated with ore deposits has compositions that reflect specific metal associations. Proof of this concept will show that rutile may be useful as an indicator mineral in stream and glacial sediment geochemical surveys, and may provide an important exploration method for a wide variety of metallic ore deposits (e.g., Au, Sb, Pd, Cu, Zn, Mo, Sn, W, Nb, Ta, REE) in metamorphosed and other terrains.

1.2 Background

Most metallic ore deposits are currently exploited in relatively low grade metamorphic zones, leaving large areas of Québec underdeveloped by the mining industry. Exploration in metamorphic terrains affected by elevated pressures and temperatures is hampered by complex geological deformation, and difficulties in the recognition of alteration assemblages. Many so-called indicator minerals have been proposed for geochemical exploration in metamorphosed areas, but most are simply prograde silicate (e.g., kyanite, sillimanite, orthopyroxene, spessartine, anthophyllite, sapphirine, tourmaline, Mn-epidote) or oxide (e.g., corundum, Mg-spinel) minerals that are not compositionally related to the ore metals (cf. Averill, 2002). Previous geochemical use of indicator minerals associated with metamorphosed ore zones has been restricted generally to minerals such as zincian spinel (gahnite) and staurolite, but these are generally practical only in the search for Zn-rich deposits hosted by relatively high grade rocks (cf. Spry and Scott, 1986a,b). Rutile has greater potential utility in that its structure can accommodate substitutions of a wide variety of elements. However, previous attempts to apply rutile as an indicator mineral have been limited to observations specific to particular ore deposit types; for example, Williams and Cesbron (1977) originally suggested that Cu-bearing rutile might be useful in exploration for porphyry copper deposits, and as noted above, Williams-Jones et al. (1998) suggested that W-Sb-V-bearing rutile could be diagnostic of Hemlo-type gold deposits. Other than the initial report from our study (Clark and Williams-Jones, 2003), the only broadly-based implied usage of rutile as an indicator mineral was made by Averill (2002), who observed that “red rutile”, supposedly Cr-bearing, was associated with metamorphosed massive sulfide and magmatic Ni-Cu deposits; however, as will be shown below, this particular suggestion with regard to Cr is not valid.

Rutile in unaltered and barren rocks is usually composed of nearly pure TiO_2. Minor substitutions of Fe, Cr, V, Mg and Mn are common (particularly Fe and to a lesser extent V), but are generally not uniquely diagnostic of particular geological environments. In ore zones, rutile may form from crystallising magmas, from alteration of primary Ti-bearing oxide and silicate minerals, or be present as a constituent in the original unaltered host rocks. Formation of rutile during alteration, and its subsequent preservation, is a product of Ti immobility under many geological conditions, and the overall stability of rutile in most environments. Metamorphism may recrystallize earlier-formed rutile, but rutile is stable to relatively high temperatures and pressures (cf. Zack et al., 2002). In most metamorphic rocks, ilmenite is the stable oxide mineral, but rutile is stable in rocks having low Fe/(Fe+Mg) ratios, and is also favoured in rocks with higher Fe/(Fe+Mg) ratios at increasing pressures (Spear, 1993). Magnesium-rich silicates (e.g., clinochlore) coexist with rutile in reduced assemblages, with rutile+ilmenite in rocks of intermediate fO_2, and with rutile+hematite in oxidized assemblages.

In metamorphosed alteration zones, rutile generally has a wide stability range, and is the principal Ti oxide that coexists with pyrrhotite and/or pyrite; e.g., $FeTiO_3 + 0.5S_2 = FeS + TiO_2 + 0.5O_2$. In most alteration zones associated with metallic ore deposits, sulfide minerals are common and fS_2 is relatively high compared to the host rocks; under such conditions, formation of rutile is favoured (Fig. 1). Once formed, rutile remains stable due to buffering by sulfidation-oxidation reactions and the lack of available Fe in silicate alteration minerals. In altered rocks, rutile tends to be stable under high fO_2, high fS_2, and low fO_2-high fS_2 conditions, except where reactions involving titanite and CO_2 and/or graphite dominate (e.g., $TiO2 + CaCO_3 + SiO_2 = CaTiSiO_5 + CO_2$). Rutile may alter to titanite, but tends to completely replace rutile only in rocks that have Ca-rich bulk compositions or high values of XCO_2 (cf. Frost et al., 2000). In many altered rocks, titanite may rim or partly replace rutile where retrograde metamorphism

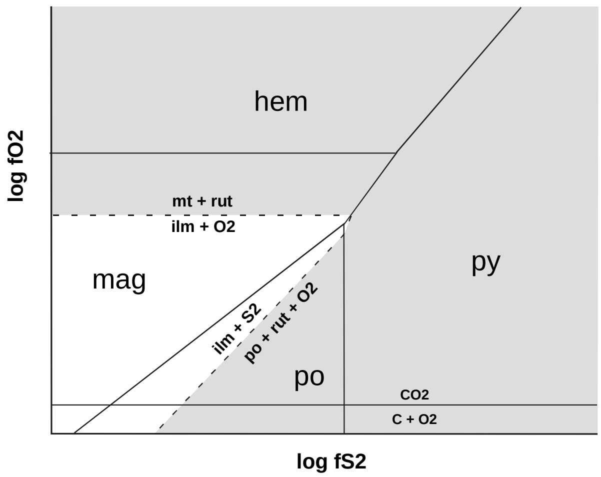

Fig. 1. Schematic log fO_2-log fS_2 diagram for the Fe-Ti-O-S system at lower amphibolite grade conditions. Rutile (grey shading) predominates at both high fO_2 and fS_2, and overlaps with the stability fields for pyrite and hematite, much of the pyrrhotite field, and parts of the magnetite field.

has resulted from more rapid decreases in pressure than temperature.

Although rutile may form and be preserved in many hydrothermal and metamorphic environments, the conditions under which rutile will accept minor element substitutions are not well known, and there have been no systematic studies of rutile compositions in mineralized systems. Nevertheless, there are scattered references to rutile analyses in the literature, and the data clearly indicate that rutile associated with high temperature and/or metamorphosed metallic ore deposits may be characterised by anomalous substitutions of W, Sn, Sb, Cu, Zn, Pb, V, Cr, Nb and Ta. Such unusual compositions not known for rutile in deposits formed at low temperatures, and the lower temperature/pressure limits for significant metal substitution are uncertain. Enrichments of components like Nb and Ta are typically products of advanced degrees of magmatic evolution, and these elements are unlikely to be mobile in most hydrothermal or metamorphic environments (i.e., Nb and Ta concentrations are likely to be inherited from precursor minerals). However, other metals are clearly at least locally mobile under greenschist through granulite grade metamorphic conditions (~350 to 750+ °C); whether rutile can absorb these components under lower grade conditions has not been studied in any detail.

Previous work on rutile from metamorphosed ores has demonstrated distinctive compositions at the Hemlo Au-Mo deposit (avg. 1.1 wt% Sb_2O_3, 0.7 wt% WO_2, 1.4 wt% V_2O_3; Williams-Jones et al., 1998; see also Harris, 1989, and Urban et al., 1992). In addition, analyses from the mesothermal Big Bell (Australia) Au deposit (avg. 1 to 2 wt% Sb_2O_3, 2 to 6 wt% WO_2; Graham and Morris, 1973), and the volcanogenic massive sulfide Geco Cu-Zn deposit (up to 2.9 wt% SnO_2; Peterson, 1986), indicate at least some significant substitutions of ore-related metals in rutile. Although the data for deposits other than Hemlo are very limited, high temperature hydrothermal ore deposits are also known to host rutile with anomalous compositions, and as noted above, rutile is likely to be preserved in many metamorphic environments. In fact, as long as rutile is preserved, anomalous compositions will probably be enhanced by further substitutions during metamorphism and remobilization of ore constituents. Limited data on rutile compositions from hydrothermal and magmatic-related ores and altered zones include porphyry Cu deposits (0.01 to 0.06 wt% Cu; Williams and Cesbron, 1977; Williams and Forrester, 1995), porphyry Cu-Au deposits (median 1.21 wt% V_2O_3, 0.12 wt% WO_3; Scott, 2003); stockwork Mo and Mo-Cu deposits (up to 0.5 wt% Zn, 0.1 wt% Cu, 0.1 wt% Pb, 17 wt% Nb_2O_5, 3 wt% Ta_2O_5; Sotnikov et al., 1979; Xu, 1992), skarn Sn-W and Mo-W deposits (up to 8 wt% WO_3, 2 wt% V_2O_3, 0.4 wt% PbO, 0.02 wt% SnO_2; Baksheev et al., 1994; Kwak, 1983), granite-related Sn and W-Sn deposits (up to 2 wt% SnO_2, 6 wt% WO_3, 26 wt% Nb_2O_5, 7 wt% Ta_2O_5; Scott, 1988; van Gaans et al., 1995), Sb-bearing veins (up to 34 wt% Sb_2O_5; Smith and Perseil, 1997), pegmatite-hosted Ta-Nb deposits (up to 2 wt% Nb_2O_5, 27 wt% Ta_2O_5, 1 wt% SnO_2; Cerny et al., 1998), Mo-bearing aplites (up to 7.2 wt% WO_3, 16.8 wt% Nb_2O_5; Michialidis, 1996), and carbonatite-hosted REE deposits (up to 0.04 wt% SnO_2, 1 wt% WO_3, 6 wt % Nb_2O_5; Scott et al., 1993). Kimberlite-hosted diamond deposits are also known to host unusual rutile compositions, with up to 16 wt% Cr_2O_3; Haggerty, 1991; Sobolev and Yefimova, 2000). Finally, W-bearing rutile has been reported from late stage hydrothermal (possibly even supergene) assemblages in polymetallic-Au deposits (up to 5.3 wt% WO_3; Rice et al., 1998). It is thus clear that hydrothermal and magmatic-related deposits containing commodities such as Au, Sb, Cu, Zn, Mo, Sn, W, Nb, Ta and REE provide an environment favourable for the formation of rutile with anomalous compositions, and that high temperature metamorphic processes augment concentrations of these metals in rutile.

Rutile is a relatively common mineral in many ore deposits, with an average abundance of ~0.05 to 0.5 % by volume in many alteration zones; rutile is thus much more abundant (up to several orders of magnitude) than Au or other rare elements in dispersion haloes from eroding ore deposits, and provides a larger exploration target. In the case of base-metal sulfide deposits, most sulfide minerals degrade during weathering, whereas rutile is much more persistent and is likely to survive significant transport distances. Rutile is a common component of heavy mineral sands, and is thus an excellent candidate for mineral separation from stream and glacial sediments.

2. METHODOLOGY

2.1 Samples

The project was designed so that field work would not be required. We therefore relied on in-house research collections, and loans and donations of polished thin sections (PTS) or raw sample material from other universities and mining/exploration companies, and in addition, cut new PTS from samples in existing collections. Collaborators have included M. Jebrak and M. Gauthier (UQAM), R. Wares (Cygnus), R. Linnen (Waterloo), G. Olivo (Queen's), W. MacLean (McGill), S. Goodman (SRK), R. Penczak (Goldcorp), T. Armstrong (McWatters), and C. Beaudry (Noranda-Falconbridge). In addition, we have been collaborating with V. Bodycomb (DIVEX) and H. de Corta (FPMJ) on a related project from which samples were also supplied for use in this study.

It should be noted that samples were generally selected initially not for any particular geological or mineralogical features, but rather were based primarily on their simple availability. For deposit collections that were extensive, it was considered to be important to have representative samples, but in essence, many samples can be considered to have been randomly selected.

2.2 Analytical work

Samples were examined petrographically by optical microscopy to assess whether they contain rutile, and if so, to evaluate the relative position of rutile in the paragenesis. Rutile grains were then analysed using a Jeol JXA-8900L electron microprobe, operating at 20 kV and 40 nA, with counting times optimized to obtain 3-sigma detection limits on the order of 100 to 400 ppm (as oxide). Considerable effort was made to balance the need to analyse a large suite of elements at conditions adequate to attain reasonable detection limits, with the eventual goal of creating an analytical protocol that would be sufficiently cost-effective for commercial application.

Our approach was to test a large number of elements that have been reported previously to occur in rutile from metallic ore deposits; these are the major/minor elements Si, Ti, Fe, Cr, Mn and Mg, plus trace elements W, Sn, Mo, V, Sb, Cu, Zn, Pb, Nb and Ta. In our initial deposit studies, we found that Mn and Mg in rutile are almost always at or below the lower detection limits, and since these elements are also not normally ore-related, they were omitted from further analyses. Molybdenum was not detected in even relatively Mo-rich deposits, and therefore was not routinely evaluated in most deposits. Similarly, Zn and Pb substitutions in rutile were not detected in any deposits, and were thus omitted in from the analytical routine in the latter part of our study. Arsenic and Ni, which although not known previously to be concentrated in rutile, are candidates for substitution in some ore types (e.g., Au and Ni-Cu-Pd mineralization, respectively), and were evaluated in several deposits. Overall, the most useful elements to characterize rutile in metallic ore deposits were found to be Si, Ti, Fe, Cr, W, Sn, V, Sb, Ni, Cu, Nb and Ta.

Detection limits lower than the 100 to 400 ppm noted above could be attained through higher voltage and/or current conditions during analyses, and/or longer counting times. However, many rocks in the ore and alteration suites contain relatively fine-grained (often <20 μm in diameter) rutile, and therefore energy conditions were limited to avoid fluorescence from adjacent grains. In practice, this would not be a problem for rutile grains derived from heavy mineral concentrates, where grain size could, to a degree, be controlled during the sample preparation process. In the latter case, significantly higher voltages and/or beam currents could be employed to reduce detection limits, although such conditions would entail greater amounts of interference between elements.

Several elements of potential interest (particularly some with higher atomic numbers) are problematic in terms of peak and/or background interferences. For example, common analytical problems include those caused by Ti interference on V, V on Cr, Ta on Si, and Ta on Cu. Peak interferences can be compensated for by choosing secondary emission lines. Unfortunately, secondary peaks are generally of much lower intensity than primary peaks, resulting in significantly higher detection limits. The normal solution is to acquire counts for relatively long periods, but this approach has diminishing returns beyond several minutes counting time. This would also make analytical costs prohibitive since cost factors are important in terms of the ultimate goal of creating an exploration tool. To overcome peak interference problems while maintaining adequate detection limits, we analysed standards of known compositions, and fit equations to correct target element concentrations for any concentration of the interfering element. Background interferences were much more difficult to minimize, and could only be overcome by conducting large numbers of analytical experiments on synthetic rutile of known composition.

Rutile was evaluated and analysed in samples from a total of 26 ore deposits. In Québec, these include the Troilus Au-Cu mine, several Cu-Zn deposits in the Matagami district (Bell-Allard, Norita, Radiore, Garon Lake), the Ansil Cu-Zn mine, the Langlois Zn-Cu mine, the Montauban Au-Cu deposit, the Horne Cu-Au mine, the Lac Bachelor, Siscoe and Geant Dormant Au mines, the East Amphi and Lac Madeleine Au deposits, and the Mines Gaspé Cu deposit. Outside Québec, we analysed material from the Lac-des-Iles PGE-Ni-Cu mine, the San Rafael Sn-Cu mine, the Pilok W-Sn deposit, the Olympic Dam Au-Cu-U deposit, the Kidd Creek Zn-Cu-Ag mine, the San Manuel Cu deposit, the Hemlo Au-Mo mine, the Witwatersrand Au deposit, and the Red Lake, Muruntau and Big Bell Au mines. Petrographic work was also conducted on rocks from the Geco Zn-Cu mine and the Broken Hill Pb-Zn-Ag deposit, but rutile was not present in the limited samples available for study. In the former case, Sn-bearing rutile has been reported previously from the deposit (Peterson, 1986); in the latter case, the samples available were calcite-rich and only titanite was present.

3. RESULTS

Petrographic work indicates that rutile occurs in almost all deposits. Generally, rutile is associated with sulfide-bearing mineralized and alteration zones, and often constitutes the most important or at least a major reservoir of Ti. Most often, rutile partially replaces ilmenite, Ti-magnetite or ferro-magnesian silicates during hydrothermal alteration. Rutile itself may be locally replaced by titanite, or more rarely, by ilmenite. As noted above, Ca-rich rocks (especially those with calcite in altered sedimentary rocks) tend to contain titanite rather than rutile, but in most such deposits, rutile nevertheless occurs in more clastic sublayers. Rutile colour is extremely variable, and although metal substitutions can cause systematic colour changes within a given deposit, such variations are not always apparent between different deposits. It appears that the colour of rutile grains is a product of many factors, including such non-deposit specific variables such as Fe. However, in a general way, there are some common denominators, including the medium to dark brown W-Sb-V-bearing rutile in the Hemlo, Big Bell and Red Lake deposits, and the greenish brown tints that are often associated with Sn-bearing rutile.

Analytical studies of rutile are summarized in Tables 1, 2 and 3. The most common minor elements that substitute into rutile in most environments are Fe, Cr , V, Nb and Ta. Like Ti, the latter two elements are essentially immobile in most non-magmatic metallic ore deposits, and their concentrations in rutile are largely influenced by precursor mineral compositions. Iron, Cr and V concentrations vary considerably in rutile hosted by ore deposits, and their concentrations reflect combination of precursor mineral composition and that of the local mineralized or altered rock environment. Chromium is not specifically indicative of mineralization in any of the studied deposits. With a few notable exceptions (i.e., V in gold-rich deposits), there does not appear to be a relationship between concentrations of these elements and style or grade of mineralization. Minor Si values are also often present in the analyses, but these commonly reflect silicate inclusions in rutile, and/or fluorescence from surrounding silicate minerals.

The main elements that substitute into rutile in most metallic ore deposits are, in decreasing order of importance, W, Sn, Sb, Cu and Ni. There is insufficient data to quantitatively define anomalous concentration values for elements that substitute into rutile, particularly since such backgrounds vary from one deposit (and one host rock) to another. However, in a qualitative sense, the data show that concentrations of metallic elements such as Sn, W, Sb, Cu and Ni can be considered to be anomalous if they exceed the analytical detection limits. Whereas substitutions of these metals are always worthy of note in rutile, V concentrations may or may not be significant depending

Table 1. Rutile compositions in VMS base metal deposits

		Weight Percent																	
	Comments	SiO2	TiO2	WO3	SnO2	Fe2O3	Cr2O3	V2O3	As2O3	MnO	MgO	NiO	CuO	ZnO	PbO	Sb2O5	Nb2O5	Ta2O5	Total
		%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
Ansil (Cu-Zn)	average ore (n=19)	0.14	96.59	0.04	0.46	0.84	0.01	0.25	0.00	--	--	0.00	0.05	0.01	0.00	0.00	1.15	0.01	99.86
	average subore (n=14)	0.24	97.62	0.02	0.03	0.73	0.01	0.23	0.00	--	--	0.00	0.01	0.00	0.00	0.00	0.21	0.00	99.42
Bell-Allard (Zn-Cu)	average ore (n=27)	0.26	97.26	0.02	0.95	0.92	0.01	0.17	--	0.01	0.02	--	0.00	0.00	0.01	0.00	0.08	0.00	99.72
	average subore (n=34)	0.18	98.52	0.00	0.10	0.74	0.00	0.17	--	0.01	0.01	--	0.00	0.00	0.00	0.00	0.04	0.00	99.79
Garon Lake (Cu-Zn)	average ore (n=10)	0.01	98.22	0.03	0.71	0.52	0.11	0.37	--	0.01	0.00	--	0.02	0.00	0.00	0.00	0.21	0.01	100.22
	average subore (n=9)	0.02	98.97	0.00	0.13	0.78	0.00	0.16	--	0.01	0.01	--	0.01	0.00	0.00	0.00	0.09	0.01	100.18
	average wallrock (n=6)	0.11	98.30	0.00	0.00	1.01	0.00	0.13	--	0.01	0.01	--	0.01	0.00	0.01	0.01	0.36	0.02	99.97
Kidd Creek (Zn-Cu-Ag)	average ore (n=23)	0.16	97.60	0.22	0.35	0.39	0.27	0.29	0.00	--	--	0.00	0.01	0.00	0.02	0.00	0.37	0.01	99.70
Langlois (Zn-Cu)	average ore (n=37)	0.08	97.17	0.27	0.49	0.64	0.03	0.24	0.00	--	--	0.00	0.01	0.01	0.00	0.08	0.42	0.02	99.45
	average subore (n=33)	0.09	97.82	0.02	0.19	0.71	0.01	0.27	0.00	--	--	0.00	0.01	0.00	0.00	0.01	0.45	0.01	99.60
	average wallrock (n=64)	0.10	98.22	0.01	0.00	0.61	0.07	0.26	0.00	--	--	0.00	0.01	0.00	0.00	0.00	0.45	0.01	99.74
Norita (Cu-Zn)	average ore (n=10)	0.39	96.77	0.14	0.15	1.84	0.00	0.14	--	0.00	0.01	--	0.02	0.00	0.00	0.00	1.22	0.00	100.81
Radiore (Cu-Zn)	average subore (n=28)	0.11	97.42	0.05	0.17	0.87	0.00	0.15	--	0.00	0.01	--	0.00	0.00	0.01	0.00	1.01	0.02	99.83
	average wallrock (n=23)	0.07	98.53	0.00	0.00	0.93	0.00	0.29	--	0.00	0.01	--	0.01	0.01	0.00	0.00	0.19	0.01	100.05
Modified or controversial VMS deposits (see text):																			
Horne (Cu-Au)	average ore (n=16)	0.16	97.57	0.08	0.11	1.19	0.00	0.16	0.00	--	--	0.00	0.01	0.01	0.00	0.00	0.48	0.00	99.78

Note - Typical lower detection limits at 3SD are 0.01 wt% for SiO2, MnO, MgO, CuO and ZnO; 0.02 wt% for TiO2, SnO2, Fe2O3, Cr2O3, V2O3, Sb2O5, Nb2O5, and NiO;
0.03 wt% for As2O3; and 0.04 wt% for WO3, PbO and Ta2O5. Dashes indicate element not analysed.
Designation "ore" indicates well-mineralized rocks; "subore" indicates weakly mineralized and/or variably altered rocks; "wallrock" indicates no visiible mineralization or alteration.

Table 2. Rutile compositions in mesothermal gold deposits

		Weight Percent																		
	Comments	SiO_2 %	TiO_2 %	WO_3 %	MoO_3 %	SnO_2 %	Fe_2O_3 %	Cr_2O_3 %	V_2O_3 %	As_2O_3 %	MnO %	MgO %	NiO %	CuO %	ZnO %	PbO %	Sb_2O_5 %	Nb_2O_5 %	Ta_2O_5 %	Total %
Big Bell (Au)	average ore (n=26)	0.03	95.33	1.63	--	0.00	0.98	0.06	0.86	0.00	--	--	0.00	0.01	0.00	0.00	1.09	0.05	0.00	100.05
	average subore (n=10)	0.03	98.22	0.07	--	0.02	0.22	0.07	0.41	0.00	--	--	0.00	0.01	0.00	0.00	0.07	0.25	0.02	99.40
E. Amphi (Au)	average ore (n=53)	0.05	98.00	0.14	--	0.01	0.73	0.22	0.32	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.11	0.00	99.62
	average subore (n=19)	0.06	97.86	0.29	--	0.00	0.77	0.21	0.25	0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.01	0.35	0.01	99.83
	average wallrock (n=40)	0.07	98.71	0.06	--	0.01	0.49	0.17	0.25	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.13	0.00	99.93
Geant Dormant (Au)	average ore (n=4)	0.21	98.10	0.09	--	0.02	0.51	0.03	0.22	0.00	--	--	0.00	0.01	--	--	0.00	0.24	0.00	99.42
	average subore (n=21)	0.04	98.27	0.23	--	0.01	0.46	0.29	0.23	0.00	--	--	0.00	0.01	--	--	0.00	0.21	0.00	99.76
Hemlo (Au-Mo)	average ore (n=63)	0.05	96.31	1.03	0.00	0.01	0.18	0.03	1.44	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.77	0.09	0.01	99.69
	average subore (n=65)	0.07	98.40	0.47	--	0.00	0.32	0.01	0.48	--	0.00	0.00	--	0.01	0.00	0.00	0.28	0.09	0.01	99.96
	average wallrock (n=5)	0.19	99.12	0.00	--	0.00	0.22	0.00	0.15	--	0.01	0.00	--	0.01	0.00	0.00	0.00	0.05	0.01	99.76
Lac Bachelor (Au)	average ore (n=41)	0.20	97.67	0.17	--	0.01	0.56	0.14	0.43	0.00	--	--	0.00	0.01	0.00	0.00	0.01	0.17	0.00	99.40
	average subore (n=19)	0.15	98.56	0.03	--	0.00	0.50	0.00	0.27	0.00	--	--	0.00	0.01	0.01	0.00	0.00	0.06	0.00	99.59
Lac Madeleine (Au)	average wallrock (n=11)	0.15	98.53	0.00	--	0.01	0.24	0.25	0.39	0.00	--	--	0.00	0.02	0.01	0.00	0.00	0.04	0.00	99.63
Muruntau (Au)	average subore (n=10)	0.25	98.58	0.01	--	0.00	0.19	0.12	0.49	0.00	--	--	0.00	0.01	--	--	0.01	0.35	0.02	100.05
Red Lake (Au)	average ore (n=18)	0.06	96.87	0.64	--	0.01	0.34	0.48	0.85	0.00	--	--	0.00	0.01	0.01	0.00	0.65	0.04	0.00	99.97
	average subore (n=23)	0.10	96.95	0.77	--	0.00	0.10	0.18	1.16	0.00	--	--	0.00	0.02	0.01	0.00	0.12	0.03	0.00	99.46
Siscoe (Au)	average ore (n=17)	0.11	98.50	0.28	--	0.00	0.47	0.22	0.24	--	0.00	0.00	--	0.01	0.00	0.01	0.00	0.14	0.00	99.97
	average wallrock (n=10)	0.10	99.25	0.00	--	0.00	0.58	0.01	0.34	--	0.00	0.01	--	0.00	0.00	0.00	0.00	0.04	0.01	100.35
Modified or controversial Au deposits (see text):																				
Troilus (Au-Cu)	average ore (n=35)	0.13	98.06	0.63	--	0.00	0.78	0.05	0.19	--	0.02	0.01	--	0.00	0.01	0.00	0.01	0.49	0.02	100.37
	average subore (n=24)	0.07	99.10	0.29	--	0.00	0.28	0.34	0.23	--	0.00	0.00	--	0.01	0.01	0.00	0.11	0.17	0.00	100.57
Montauban (Au-Cu)	average ore (n=34)	0.04	96.92	0.12	--	0.01	0.65	0.05	0.39	--	0.01	0.00	--	0.01	0.00	0.02	0.00	1.55	0.04	99.80
	average - Au rich (n=5)	0.10	95.78	0.36	--	0.00	0.77	0.14	0.40	--	0.00	0.00	--	0.00	0.00	0.00	0.00	1.86	0.03	99.44

Note - Typical lower detection limits at 3SD are 0.01 wt% for SiO_2, MnO, MgO, CuO and ZnO; 0.02 wt% for TiO_2, SnO_2, Fe_2O_3, Cr_2O_3, V_2O_3, Sb_2O_5, Nb_2O_5, and NiO; 0.03 wt% for As_2O_3; and 0.04 wt% for WO_3, PbO and Ta_2O_5. Dashes indicate element not analysed.

Designation "ore" indicates well-mineralized rocks; "subore" indicates weakly mineralized and/or variably altered rocks; "wallrock" indicates no visiible mineralization or alteration.

Table 3. Rutile compositions in miscellaneous metallic ore deposits

		Weight Percent																	
	Comments	SiO2	TiO2	WO3	SnO2	Fe2O3	Cr2O3	V2O3	As2O3	MnO	MgO	NiO	CuO	ZnO	PbO	Sb2O5	Nb2O5	Ta2O5	Total
		%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
Gaspe (Cu)	average dyke rocks (n=33)	0.13	97.74	0.12	0.01	0.60	0.02	0.33	--	0.00	0.01	--	0.00	0.00	0.00	0.00	0.46	0.02	99.44
Lac des Iles (Pd-Ni-Cu)	average ore (n=18)	0.14	98.03	0.03	0.00	0.83	0.08	0.31	0.00	--	--	0.02	0.01	0.00	0.00	0.00	0.01	0.00	99.48
Olympic Dam (Au-Cu-U)	average ore (n=37)	0.10	95.06	0.09	0.05	2.22	0.00	0.20	0.01	--	--	0.00	0.05	0.00	0.00	0.01	1.41	0.05	99.26
	average Cu-U ore (n=27)	0.09	94.37	0.11	0.07	2.75	0.00	0.19	0.01	--	--	0.00	0.07	0.00	0.00	0.01	1.56	0.06	99.28
	average Au ore (n=10)	0.15	96.94	0.03	0.00	0.79	0.01	0.22	0.00	--	--	0.00	0.01	0.00	0.01	0.02	1.00	0.01	99.19
	average subore (n=28)	0.12	95.24	0.13	0.14	2.26	0.01	0.20	0.01	--	--	0.00	0.02	0.00	0.00	0.01	1.43	0.05	99.63
Pilok (W-Sn)	average subore (n=19)	0.05	83.91	0.72	1.72	3.98	0.00	0.18	0.00	--	--	0.00	--	0.00	0.00	0.00	7.15	1.88	99.58
San Manuel (Cu)	average ore (n=29)	0.04	97.52	0.06	0.03	0.97	0.06	0.38	0.00	--	--	0.00	0.03	--	--	0.01	0.41	0.03	99.55
	average subore (n=5)	0.27	96.45	0.02	0.00	1.53	0.01	0.19	0.01	--	--	0.00	0.01	--	--	0.00	0.14	0.00	98.64
San Rafael (Sn-Cu)	average ore (n=21)	0.15	95.05	2.73	0.34	1.31	0.01	0.14	--	0.02	0.00	--	0.00	0.00	0.00	0.00	0.41	0.03	99.99
	average subore (n=38)	0.10	97.44	0.53	0.18	0.65	0.06	0.18	--	0.01	0.00	--	0.00	0.00	0.00	0.00	0.62	0.06	99.79
	avg wk alt granitoid (n=29)	0.12	97.85	0.42	0.16	0.63	0.03	0.22	--	0.00	0.00	--	0.00	0.00	0.00	0.00	0.62	0.04	100.08
Witwatersrand (Au)	avg ore matrix (n=10)	0.25	98.12	0.00	0.01	0.23	0.38	0.24	0.00	--	--	0.00	0.01	--	--	0.00	0.18	0.01	99.43
	avg ore detrital (n=16)	0.12	97.87	0.03	0.01	0.20	0.39	0.29	0.00	--	--	0.00	0.02	--	--	0.00	0.39	0.03	99.37
	average wallrock (n=1)	0.12	99.16	0.00	0.00	0.11	0.25	0.39	0.00	--	--	0.00	0.02	--	--	0.00	0.07	0.00	100.12

Note - Typical lower detection limits at 3SD are 0.01 wt% for SiO2, MnO, MgO, CuO and ZnO; 0.02 wt% for TiO2, SnO2, Fe2O3, Cr2O3, V2O3, Sb2O5, Nb2O5, and NiO; 0.03 wt% for As2O3; and 0.04 wt% for WO3, PbO and Ta2O5. Dashes indicate element not analysed.

Designation "ore" indicates well-mineralized rocks; "subore" indicates weakly mineralized and/or variably altered rocks; "wallrock" indicates no visiible mineralization or alteration.

on background V values; in some deposits, it can be demonstrated clearly that V has been added to the rocks during alteration associated with mineralization.. In general, these metal substitutions are dependent on the availability of such elements in the deposits (and temperature of either deposit formation or metamorphism), but if present, substitutions occur to a degree that is measurable in routine electron microprobe analyses. We have chosen to summarize the most significant substitutions in rutile on a series of ternary cation diagrams, with the apices Ti, 100(Fe+Cr+V), and 1000(x), where x is the element or combination of elements of major interest. The factors 100 and 1000 serve to expand the spread of data, and better illustrate substitutions; however, note that these factors also introduce distortion when projected onto the ternary surface. Pure TiO_2 would of course plot at the Ti apex; most natural rutile from unaltered rocks plots along or near the Ti-(Fe+Cr+V) axis, with rutile from more mafic rocks plotting somewhat closer to the (Fe+Cr+V) apex, and rutile from more felsic rocks plotting closer to the Ti apex. The choice of cation plots also alleviates problems associated with the choice of valences for elements such as W, V and Sb, which in the historic literature have been variably reported, but are now thought to be dominated by W^{6+}, V^{3+} and Sb^{5+}, respectively (cf. Smith and Perseil, 1997, Rice et al., 1998

3.1 VMS base metal deposits

As shown in Table 1, rutile associated with volcanogenic massive sulfide (VMS) Cu-Zn±Pb±Ag±Au mineralization is invariably anomalous in Sn, and occasionally anomalous in Cu, W or Sb. Iron and V concentrations are low (generally ≤1 wt% Fe_2O_3, <0.4 wt%V_2O_3), and Cr concentrations are at or below the lower detection limit (<0.02 wt% Cr_2O_3). The data for deposits for which there is a variety of ore grade, weakly mineralized, altered, and unaltered wallrock samples indicate that Sn concentrations are highest in well-mineralized rocks, lower but still anomalous in subore/altered rocks, and below the detection limit (0.02 wt% SnO_2) in unaltered wallrocks.

One of the more extensive sample suites was obtained from the Langlois Zn-Cu mine in the Quévillon region, which is also in the area of interest of the DIVEX rutile pilot project. Langlois rocks are moderately to strongly deformed, and rutile in the ore zones varies from light brown to dark greenish brown, whereas wallrock rutile tends to have light yellowish brown to medium brown colouration. Ore zone rutile has strongly elevated Sn concentrations (Fig. 2), lower but still significant W concentrations, and sporadically high Sb concentrations. A total of 76 % of all rutile grains contain anomalous levels of Sn in the ore zones, and 74 % of grains do so in both ore and subore/altered rocks. Similarly, in ore zone rocks, 60 % of rutile grains contain W, and 24 % contain Sb at levels above the detection limit.

The Matagami area (Québec) hosts several volcanogenic massive sulfide deposits, which have been metamorphosed to upper greenschist grades; rutile compositions were evaluated in the Bell-Allard Zn-Cu deposit, and the Garon Lake, Norita and Radiore Cu-Zn deposits. Analyses for Bell-Allard show that rutile in mineralized rocks contains strongly elevated concentrations of Sn throughout most of the Key Tuffite horizon (79 % of rutile from ore grade samples, and 66 % of rutile from all samples). Similarly, at Garon Lake, rutile contains equally elevated concentrations of Sn, and, based on limited samples, there appears to be a correlation between base metal grades and the Sn content of rutile. A total of 95 % of all grains from mineralized samples contained anomalous Sn, and 100 % of those from ore grade material. At Radiore, the sample suite did not include well-mineralized samples, but subore grade material was available. Rutile from these rocks contains strongly elevated Sn concentrations, and 100 % of all such grains were above the lower detection limit for Sn; rutile from the wallrock contains virtually no Sn. Rutile in some of the more Cu-rich rocks also contains anomalous W, but results for this element are less consistent than those for Sn. Analyses of a limited number of rutile grains from massive sulfides at Norita indicate that there are moderately elevated concentrations of Sn, and that in addition some grains contain detectable W and Cu (90, 40 and 70 % of grains were above the detection limit, respectively).

Ore zone rocks at the Ansil Cu-Zn mine contain rutile that averages 0.46 wt% SnO_2, compared to 0.03 wt% SnO_2 in altered rocks surrounding the deposit. Unaltered wallrock samples were not available for study. Fully 100 % of ore zone rutile is anomalous in Sn, along with 74 % of rutile grains for Cu, and 26 %

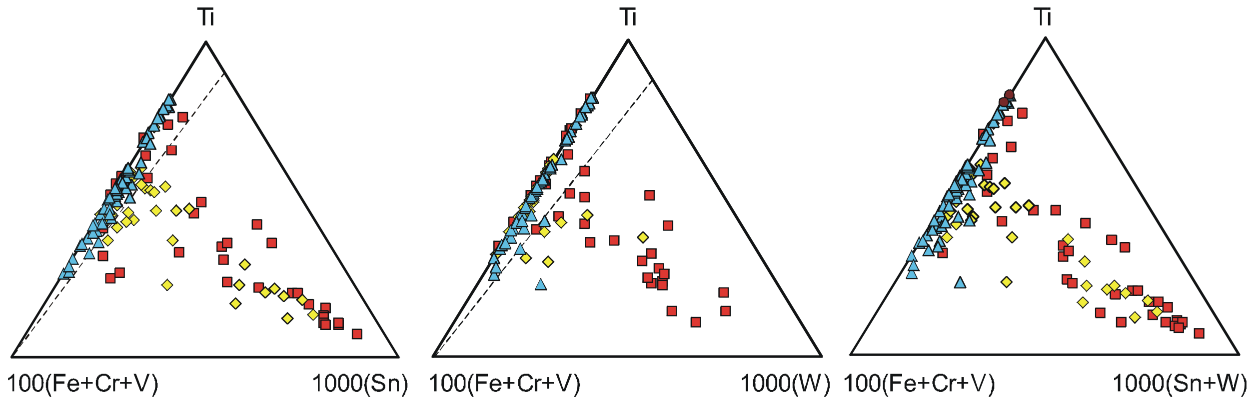

Fig. 2. Rutile compositions for the Langlois Zn-Cu deposit, Québec, showing strongly elevated concentrations of Sn in ore (red squares) and subore (yellow diamonds) zones, compared to unaltered wallrock (blue triangles). Concentrations of W are more erratic but also high, and the combination of Sn+W shows that most rutile grains are anomalous compared to background. The dashed lines represents projections of the 0.02 and 0.04 wt% detection limits for SnO_2 and WO_3, respectively.

for W. In combined terms, 73 % of all rutile grains from ore and altered rocks are anomalous in Sn.

The Horne Cu-Au (Québec) and Kidd Creek Zn-Cu-Ag (Ontario) massive sulfide deposits are hosted by relatively low grade metamorphic rocks, and initially it was thought that rutile in lower greenschist grade rocks would not be associated with significant metal substitutions. In fact, rutile in both deposits contains elevated concentrations of Sn, and lesser, more erratic W and Cu. At Horne, rutile contains detectable Sn in 44 % of grains in the ore zone, and 31 % of grains contain W, but the dataset is relatively limited due to the small number of available samples. The W content of Horne rutile is perhaps not surprising considering the Au enrichment of the deposit, which is likely to have been either superimposed or at least augmented by post-VMS (possibly mesothermal) hydrothermal activity. Kidd Creek ore zone rocks often contain minor cassiterite and stannite, and rutile has strongly elevated concentrations of Sn. Rutile grains in some well-mineralized rocks (particularly those that are Ag-rich?) also have moderately elevated W contents. When Sn and W are combined, almost all ore zone rutile appears to be anomalous. Quantitative wallrock rutile compositions could not be obtained from Kidd Creek samples due to extremely fine (<20 μm) grain sizes and abundant silicate inclusions, but semi-quantitative data indicates that Sn and W concentrations in such grains are below the lower detection limits.

Compositional data for rutile associated with VMS base metal deposits is summarized in Figure 3, which clearly illustrates that rutile in ore zone rocks typically contains strongly elevated concentrations of Sn. Weakly mineralized and variably altered rocks also host rutile with significant Sn, but to a lesser degree than the ore zones. Wallrock rutile contains only traces of Sn, usually less than 0.02 wt% SnO_2, and generally below the lower detection limit. Approximately 82 % of rutile grains from well-mineralized rocks are anomalous in Sn, as are 76 % of combined ore and subore/alteration zone rutile. In addition, rutile in VMS deposits is often enriched in W, and occasionally also in Cu or Sb, which together with Sn serve to discriminate most rutile compositions.

3.2 Mesothermal gold deposits

Rutile associated with mesothermal gold deposits invariably contains elevated concentrations of W, and occasionally anomalous Sb or V (Table 2). Iron values are low (usually ≤1 wt% Fe_2O_3), and Cr varies considerably depending on host rock bulk compositions. However, there is no direct correlation between Cr in rutile and gold mineralization. Vanadium is enriched in rutile only in a small but important subset of mesothermal rocks, and averages ≤0.5 wt% V_2O_3 in most gold deposits. The data for deposits for which there is a variety of ore grade, weakly mineralized, altered, and unaltered wallrock samples indicate that W concentrations are highest in well-mineralized rocks, lower but still anomalous in subore/altered rocks, and below the detection limit (0.04 wt% WO_3) in most wallrocks.

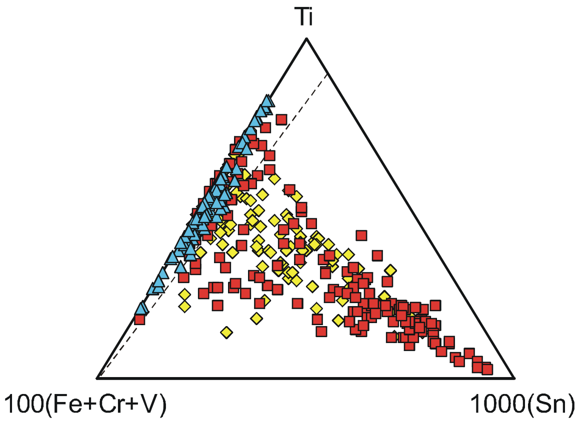

Fig. 3. Summary of Sn concentrations in rutile from variably metamorphosed Canadian (mainly from Québec) VMS base metal deposits, indicating that most ore zone (red squares) and subore/alteration zone (yellow diamonds) rutile contains strongly elevated values of Sn, compared to unaltered wallrock rutile (blue triangles). The dashed line represents a projection of the 0.02 wt% detection limit for SnO_2.

The deposit for which we have the most extensive dataset is Hemlo, Ontario, which is one of the largest gold deposits currently exploited in Canada. As noted earlier, the idea of rutile as a potential indicator mineral was stimulated by the observation that rutile at the Hemlo Au-Mo deposit contains strongly elevated concentrations of W, Sb and V (each up to several wt% as oxide). Figure 4 illustrates these substitutions, as well as the fact the rutile grains that contain the most W and Sb also tend to be associated with higher grade ore. However, there is considerable overlap of gold grades with W and Sb concentrations due to post-ore remobilization events. Hemlo rutile is also distinctive in that it has elevated V concentrations, and in fact is one of only a few deposits (the others are Big Bell and possibly Red Lake) where V enrichment is significant. As shown in Figure 4, virtually all ore zone rutile contains anomalous W and Sb (98 and 100 % of analysed grains, respectively). When W and Sb are combined, all rutile associated with bulk rock values of >3 g/t Au is very strongly anomalous compared to rutile from least altered wallrocks. It is also noteworthy that rutile is only stable in the ore and alteration zones of the deposit; ilmenite is the stable Ti-oxide mineral in the surrounding upper amphibolite grade host rocks, which limits the availability of wallrock rutile for analyses.

The Red Lake Au deposit in Ontario has received considerable attention from explorationists recently, due to the high grade nature of its ore. Like Hemlo, the deposit is hosted by strongly metamorphosed rocks (upper greenschist to amphibolite facies), and it appears that Red Lake is remarkably similar in terms of rutile composition; both deposits contain strongly elevated concentrations of W and Sb (and probably V). Red Lake rutile from well-mineralized rocks averages 0.64 wt% WO_3 and 0.65 wt% Sb_2O_5, and 100 % of all rutile grains in both ore and subore rocks are anomalous in W and Sb. Vanadium also appears to be elevated in Red Lake rutile, but enrichments cannot be quantified as unaltered wallrock samples have not been analysed. Another Au deposit hosted by amphibolite grade rocks is Big Bell (Australia), which also contains rutile with high concentrations (up to several wt% as oxide) of W, Sb and V. Again, 100 % of rutile grains from the ore zones contain anomalous W and Sb, and 70 % of subore rocks are anomalous in W.

Abitibi-type mesothermal gold deposits in relatively low grade metamorphic rocks usually contain rutile, and in some cases, rutile is quite abundant in mineralized zones adjacent to and as inclusions within veins, as well as the surrounding unaltered wallrock. One example is the Siscoe Au deposit (Québec), where the C-vein is associated with rutile that exhibits moderately to strongly elevated concentrations of W. Rutile in unaltered wallrock contains no detectable W, and 65 % of grains from ore grade material are anomalous. Similarly, at the East Amphi Au deposit (Québec), rutile contains moderately but erratically elevated concentrations of W. Rutile from weakly mineralized talc-chlorite schist adjacent to the deposit contains negligible W, and again, this element in rutile from the unaltered wallrock is below the detection limit. Fifty-eight percent of rutile grains from ore grade material contain significant tungsten. North of these deposits, the Géant Dormant Au mine contains rutile with an average of 0.09 wt% WO_3 in ore zone rocks, and 0.23 wt% WO_3 in subore/altered rocks. The greater concentrations of W in subore rocks is likely a simple function of the limited dataset for well-mineralized samples, although only 50 % of ore zone rutile and 42 % of subore rutile in anomalous in W. In most deposits hosted by lower grade metamorphic rocks, rutile compositions are more erratic than those in higher (i.e., amphibolite and above) grade rocks. As indicated by the distribution of W (compare Hemlo to Abitibi area deposits), metamorphism tends to homogenize metal substitution in rutile.

The Quévillon area hosts the Lac Bachelor and Lac

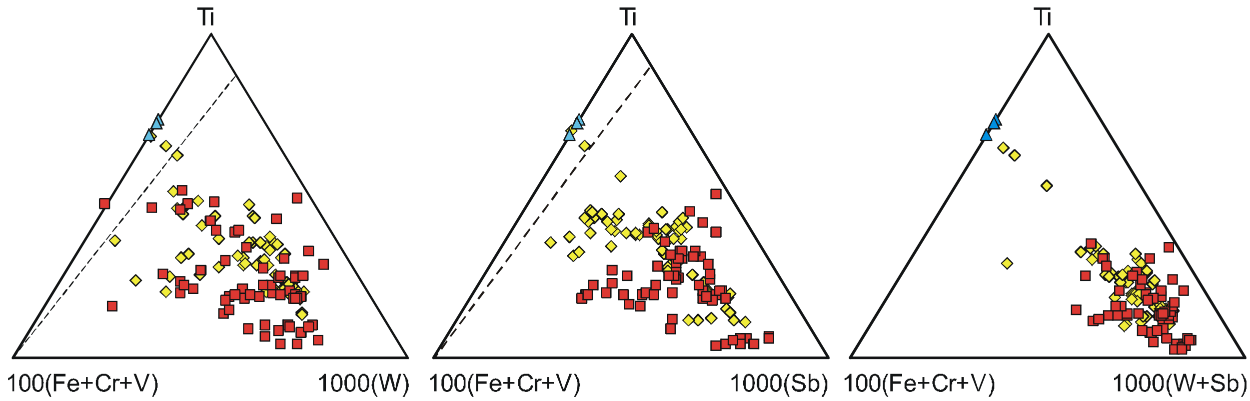

Fig. 4. Rutile compositions for the Hemlo Au-Mo deposit, Ontario, showing strongly elevated concentrations of W and Sb. Red squares are ore zone samples (>3 g/t Au), yellow diamonds are weakly mineralized (<3 g/t Au) and/or altered samples, and blue diamonds are least altered wallrock samples. The dashed lines represent projections of the 0.04 wt% WO_3 and 0.02 wt% Sb_2O_5 detection limits, respectively. Hemlo rutile is also enriched in V, which causes scatter toward the (Fe+Cr+V) apex. The combination of W and Sb provides clear discrimination of all rutile grains from the ore and alteration zones.

Madeleine Au mines. Rutile from Lac Bachelor ore zones contains an average 0.17 wt% WO_3, and that from adjacent alteration zones 0.03 wt% WO_3. Wallrock samples were not available from Lac Bachelor, but at the Lac Madeleine deposit, wallrock rutile contains no detectable W. A total of 73 % of rutile grains from Lac Bachelor contain rutile with W values above the detection limit, as do 32 % of rutile in subore samples.

A limited number of analyses were conducted on rutile from the Muruntau (Uzbekistan), a major gold deposit hosted by upper greenschist to amphibolite grade rocks. Unfortunately, only subore samples were available, and the rutile contains W values that are near or below the lower detection limit. However, since scheelite is a common mineral in the deposit, it is likely that a more representative suite of mineralized samples would yield rutile that is anomalous in W, consistent with other mesothermal Au deposits.

The Troilus Au-Cu deposit in Québec is hosted by lower amphibolite grade metamorphic rocks, and is variably classified as either porphyry or mesothermal mineralization. Rutile occurs throughout the deposit in mineralized and altered sulfide-rich zones. In ore grade rocks, rutile contains strongly elevated concentrations of W, and weaker concentrations of Sb. However, rutile in altered but only weakly mineralized rocks contains moderately to strongly elevated concentrations of Sb, as well as fairly consistently elevated W. The combination of W and Sb at Troilus allows discrimination of both ore and subore grade rutile, except for a few grains that are near the detection limit for both W and Sb. In the latter case, such rutile is hosted by brecciated and sheared rocks, and is characterized by lower Fe concentrations than the anomalous grains. In the ore zones, 96 % of rutile grains contain detectable W, and in subore rocks, 69 % of grains contain W above the detection limit (80 % of all grains from mineralized or altered rocks in the deposit). Similarly, 41 % of all rutile grains from ore and subore rocks in the deposit contain detectable Sb. The presence of Sb and W in rutile supports a mesothermal origin for mineralization (at least for gold), as Sb is not known to occur in rutile hosted by Au-porphyry systems.

Metamorphic rocks in the area of the Montauban Au-Cu deposit (Québec) attained upper amphibolite to granulite facies grades. Rutile in the ore zones has moderately elevated concentrations of W, and particularly high Au grades are associated with enhanced W concentrations. Seventy-three percent of rutile grains in ore grade samples contain detectable W. Montauban is thought to be a VMS-type deposit that was either gold-rich or had a gold event superimposed upon it. The W-rich rutile compositions support a mesothermal origin for at least the gold mineralization, and the lack of Sn is problematic for a VMS origin for the base metal sulfides.

Compositional data for rutile associated with mesothermal gold deposits is summarized in Figure 5,

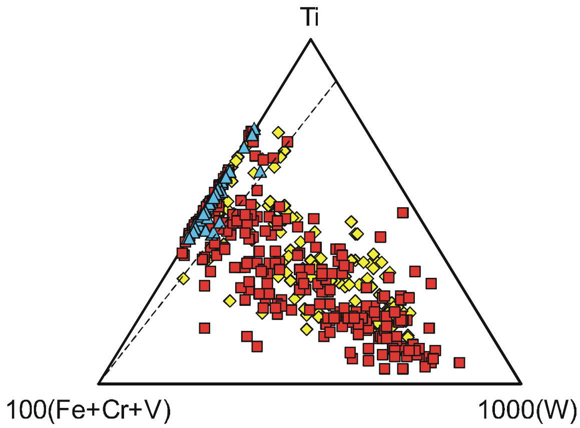

Fig. 5. Summary of W concentrations in rutile from variably metamorphosed worldwide (mainly from Canada and specifically Québec) mesothermal gold deposits, indicating that most ore zone (red squares) and subore/alteration zone (yellow diamonds) rutile contains strongly elevated values of W, compared to unaltered wallrock rutile (blue triangles). The dashed line represents a projection of the 0.04 wt% detection limit for WO_3.

and clearly indicates that rutile in ore zone rocks is typified by strongly elevated concentrations of W. Weakly mineralized and variably altered rocks also host rutile with significant W, but to a lesser degree than the ore zones. Wallrock rutile contains only traces of W, usually less than 0.04 wt% WO_3, and generally below the lower detection limit. Approximately 79 % of rutile grains from well-mineralized rocks are anomalous in W, as are 79 % of combined ore and subore/alteration zone rutile. In addition, rutile in mesothermal gold deposits is sometimes enriched in Sb, and occasionally in V, and the addition of these elements to W allow discrimination of the vast majority of rutile compositions.

3.3 Other metallic ore deposits

In addition to the VMS base metal and mesothermal Au deposits that are common exploration targets in metamorphosed terrains, there are numerous other types of mineralization that are currently not exploited in Québec. Table 3 lists data for such deposits, and indicates that rutile from a wide variety of metallic ore deposits is anomalous in elements that include Sn, W, Ni, Cu, Nb and Ta. Iron, V and Cr concentrations are quite variable; Fe in rutile is highest (~4 wt% Fe_2O_3) in granite-pegmatite-hosted deposits, and Cr is generally very low (near detection limits), except in Witwatersrand rutile. Vanadium concentrations are also low (≤0.4 wt% V_2O_3), but appear to be anomalous in rutile from some porphyry-related systems. The data for deposits for which there is a full suite of ore grade, weakly mineralized, altered, and unaltered wallrock samples indicate that anomalous metal substitutions are highest in well-mineralized rocks, and lower but still anomalous in subore/altered rocks. Rutile in some rock types, particularly granitoids, appears to be associated with fairly extensive anomalies, even in rocks that exhibit only weak alteration.

The Mines Gaspé Cu deposit is no longer in operation, but this type of skarn-, manto- and porphyry mineralization associated with felsic dykes and intrusions remains an important exploration target in Québec. The skarn and manto zones do not contain rutile, as high *a*Ca in the altered carbonate sediments stabilize titanite at the expense of rutile. However, the dyke rocks contain relatively abundant rutile, often within millimeters of the dyke-skarn contacts. Rutile in the dykes is only sporadically anomalous, with 13 % of grains containing detectable W (avg. 0.12 wt% WO_3 due to a few high outliers, but most grains below the detection limit). There are also a few grains with minor, anomalous concentrations of Sn and Cu. The Mines Gaspé data is disappointing in terms of the potential use of rutile as an indicator mineral for this type of deposit, but it is notable that the dataset does not include rutile from Porphyry Mountain, which is the intrusive center of the deposit area, and which hosts large tonnage but low grade porphyry Cu mineralization.

Rutile associated with the San Manuel porphyry Cu deposit in Arizona contains relatively low but significant concentrations of W, Sn, Cu and V in ore zone rocks, averaging 0.06 wt% WO_3, 0.03 wt% SnO_2, and 0.03 wt% CuO, respectively. Tungsten values are erratic, and only 24 % of all rutile grains in ore and subore/altered rocks are anomalous; however, Sn and Cu concentrations are more uniform, with anomalous values in 53 % and 68 % of grains, respectively. Fresh granitic wallrocks were not available for analyses, so it is difficult to evaluate V in rutile, but rutile in well-mineralized rocks contain twice as much V as that in subore rocks. Based on a limited dataset, there are no major differences in rutile compositions in potassic versus propylitic alteration assemblages, although rutile in potassic rocks tends to contain more Cu and V.

The San Rafael Sn-Cu deposit (Peru) represents a hydrothermal, granite-related type of mineralization that is not known to occur in Québec, but one that is nevertheless very important economically. Rutile in this type of deposit is quite abundant, and analyses indicate that compositions are also significantly anomalous. Figure 6 illustrates strongly elevated concentrations of W and Sn in rutile. In ore zone rocks, W is uniformly anomalous (100 % of grains). Tin, although enriched in rutile, has much more erratic concentrations than W, with 84 % of grains above the detection limit. Rutile in strongly altered (mainly chloritic) rocks that contain only minor bulk Sn contain generally elevated concentrations of both W and Sn. Rutile associated with weakly altered (mainly sericitic) granitoid rocks is also significantly enriched in Sn, and to a lesser extent W. The combination of W and Sn in rutile allows clear discrimination of rutile from both ore and altered zones, including that from weakly altered but "fertile" granitoid rocks. Rutile associated with fertile Sn granitoids can be distinguished, on a first approximation, from Sn-bearing VMS rutile by higher average Ta concentrations in the former, and generally lower W:Sn ratios in the latter.

The Pilok deposit (Thailand) is an example of granite and granite-pegmatite-hosted W-Sn mineralization. Rutile from Pilok contains elevated concentrations of W and Sn (0.72 wt% WO_3, 1.72 SnO_2), and extreme enrichments of Nb and Ta (7.15 wt% Nb_2O_5, 1.88 wt% Ta_2O_5). Only subore rocks were available for analyses, but a total of 94 % of all rutile grains were anomalous in W, and 100 % of grains contained detectable Sn.

Olympic Dam-type deposits constitute large tonnage Au-Cu-U targets. Rutile from granitic rocks hosting the namesake Olympic Dam (Australia) deposit contains moderately elevated concentrations of W, Sn and Cu, with some additional enrichment of Ta and Nb. Average concentrations for rutile in ore zone rocks are 0.09 wt% WO_3, 0.05 wt% SnO_2, and 0.05 wt% CuO, and 52 %, 89 % and 70% of all grains are anomalous in these elements respectively. Fully 84 % of all rutile grains in ore and subore/altered rocks are anomalous in Sn, and surprisingly, both Sn and W are slightly more enriched in the surrounding altered rocks than in the ore zones. Rutile in gold-rich zones contain W but no detectable Sn or Cu, and are also characterized by slightly elevated concentrations of Sb. Rutile in copper-rich zones contains more Sn and W than that in gold-rich ore.

The Lac des Iles PGE-Ni-Cu deposit (Ontario) is characterized by gabbro-related mineralization that has undergone hydrothermal remobilization and enrichment of Pd. The deposit appears to contain relatively minor rutile, which is associated primarily with the most sulfide-rich parts of the mineralized breccias. Rutile from ore grade rocks contains erratic, slightly to moderately elevated concentrations of Ni and Cu, which nevertheless is potentially significant in terms of exploration. Copper values (50 % of grains contain detectable Cu) are fairly low but more homogenous than those for Ni; nickel values spike to 0.10 wt % NiO in some grains (22 % of grains contain detectable Ni), and this is the first known report of Ni substitution in rutile. The predominance of ilmenite and lack of rutile in weakly altered rocks makes it difficult to evaluate background Ni and Cu values. It is possible for example, that rutile-bearing non-mineralized gabbro may in some areas also be anomalous with respect to Ni and Cu, but further work is necessary to assess this aspect.

The world's most important gold deposit is undoubtedly the Witwatersrand in South Africa. Although it is unlikely that a similar size of deposit could be found in Québec, rutile geochemistry nevertheless can shed some light on the genesis and the exploration potential for this type of mineralization. Rutile occurs as both subround detrital clasts, and as subhedral matrix grains formed during deformation and alteration/recrystallization of the host conglomerate. Matrix rutile is intergrown locally with sericitic alteration, gold and arsenopyrite, but analyses indicate that there are no detectable metal substitutions of consequence in this rutile. By contrast, some grains of detrital rutile contain up to 0.19 wt% WO_3 (avg. 0.03 wt% WO_3), which strongly suggests a paleoplacer origin for gold in this controversial deposit.

4. FUTURE WORK

Although the current rutile study has been completed, and we have demonstrated the potential utility of rutile as an indicator mineral, further work will be required to evaluate the practicality of this new exploration method. A much larger database of rutile compositions will be needed in order to develop a classification scheme that could be used as a framework for the evaluation of anomalous rutile from various metallogenic associations. The latter could be accomplished via a statistical approach using probabilities based on a

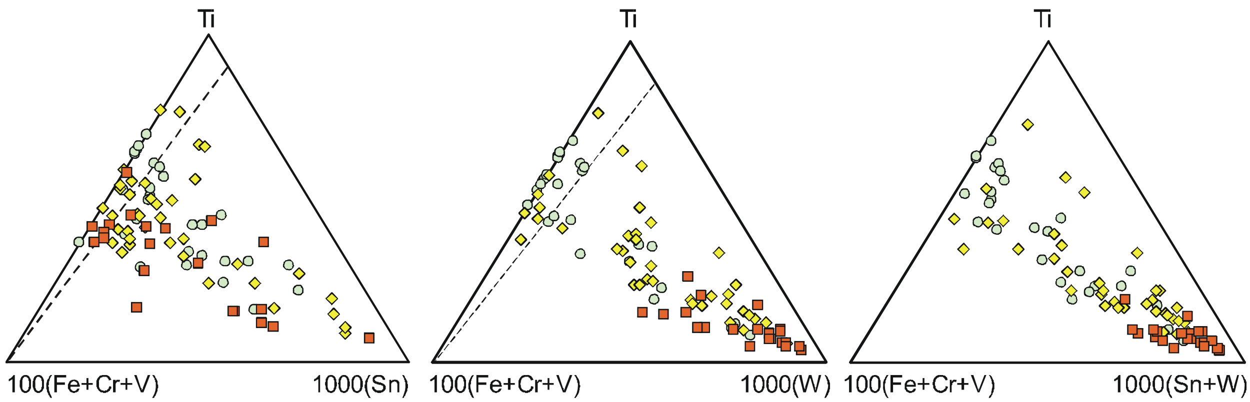

Fig. 6. Rutile compositions for the San Rafael Sn deposit, Peru, showing very strongly elevated concentrations of W and Sn. Red squares indicate ore zone rocks, yellow diamonds indicate weakly mineralized but strongly altered granitoid samples, and green circles represent weakly altered granitoid material. The dashed lines represent projections of the 0.04 wt% WO_3 and 0.02 wt% SnO_2 detection limits, respectively. The combination of W and Sn provides excellent discrimination of rutile from both ore and subore/altered zones, including that from weakly altered but "fertile" granitoid.

database of rutile compositions in various types of metallic ore deposits, as well as a better understanding of background compositions in unmineralized rocks. This will enable explorationists to efficiently screen rutile compositions for anomalies associated with specific target types. For example, there are presently areas of overlap between rutile compositions that could be distinguished by certain combinations of elements and/or elemental ratios. Similarly, we need to develop better ways of discriminating between low-level anomalies in rutile compositions in weakly altered granitoid rocks, and those directly associated with economic mineralization.

The practical application of rutile indicator geochemistry will depend in part of the refinement of rutile separation and grain-picking methods from glacial/fluvial sediments. This is an aspect which has not been addressed in the rutile project, but will be evaluated in a preliminary sense by DIVEX's pilot study of rutile in Quévillon area esker and basal tills. The pilot study so far has demonstrated that rutile grains anomalous in W occur in esker tills down-ice from known Au deposits, and that grains anomalous in Sn occur down-ice from Zn-Cu deposits. However, further work will be needed to better evaluate dispersion patterns around major ore deposits.

There is presently only a limited understanding of the conditions under which rutile will accept metal substitutions. Empirically, temperature is the most important factor, but the interplay between adsorptive and diffusive processes, and nature of coupled substitutions remain poorly constrained. Experiments will be required to evaluate and model such processes.

5. CONCLUSIONS

Rutile occurs in significant abundance in most metallic ore deposits, and irrespective of metamorphic grade, is most plentiful in sulfide-bearing deposits where high fS_2 and/or fO_2 conditions stabilize rutile at the expense of ilmenite in the presence of minerals such as pyrite and hematite (and often pyrrhotite). In metallic ore deposits in medium and high grade metamorphic terrains, rutile contains relatively homogenous concentrations of metals, but lower grade greenschist-hosted deposits also contain rutile with anomalous albeit more erratic metal concentrations. Rutile is common in most alteration zones, often ranging from 0.05 to 0.5 vol%, and is thus several orders of magnitude more abundant than economic metals such as Au. Calcium-rich lithologies such as skarns and other rocks that have been affected by high aCa or XCO_2 fluids tend not to contain rutile, but associated clastic or igneous rocks do host rutile. Rutile is also persistent in weathering environments (fluvial, glacial, desert, lateritic, etc.), and is likely to survive significant transport by secondary processes. As a common component of heavy mineral sands, rutile is a good candidate for separation by routine magnetic, heavy liquid, and other density methods.

Rutile has clearly anomalous compositions and metal associations, and distinctive substitutions in different ore deposit types. In many deposits, rutile contains detectable concentrations of metallic elements such as W, Sb and Sn; V, Cu and Ni are also present in rutile in some deposits. By contrast, rutile in unaltered wallrocks of these deposits is characterized by ore-related metal concentrations that are at or below lower detection limits. Although many deposits have well-defined and diagnostic rutile compositions, there are also some compositional overlaps between deposit types. Element combinations and ratios can be used to distinguish qualitatively between rutile compositions for most ore deposit types, but refinement of a statistical methodology will require a broader database.

In general, rutile in volcanogenic massive sulfide Cu-Zn deposits contains Sn (and locally W and/or Cu). Rutile from mesothermal and related gold deposits invariably contains W, and in some of the larger and more important deposits rutile also contains Sb and/or V. Tungsten-bearing detrital rutile grains in the Witwatersrand deposit suggest that the origin of the mineralization was a likely as a paleoplacer with a mesothermal gold source. In at least some magmatic-hydrothermal Pd-Ni-Cu deposits, rutile contains Ni and Cu. Rutile associated with granite-related Sn deposits contains strongly elevated concentrations of Sn and W, and granite-pegmatite W-Sn deposits contain rutile with these elements plus Nb and Ta. The Olympic Dam Au-Cu-U deposit hosts rutile that is enriched in W, Sn and Cu. Rutile associated with porphyry and skarn Cu and Cu-Au deposits tend to contain elevated W, Cu (and sometimes V).

The variability and anomalous nature of compositions noted in this project suggest that rutile has definite potential as an indicator mineral in exploration for a wide variety of metallic ore deposits in metamorphic and other terrains.

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