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Mn-RICH ILMENITE FROM THE SULLIVAN Pb–Zn–Ag DEPOSIT, BRITISH COLUMBIA

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Abstract

Electron-microprobe analyses of 76 ilmenite grains from 13 locations in the footwall, hanging wall, and ore zone of the Sullivan Pb–Zn–Ag deposit, Kimberley, British Columbia, and from regionally developed tourmalinite of the Middle Proterozoic Aldridge Formation show two different modes that reflect two stages of formation. The first stage of ilmenite formation occurred as a result of greenschist-facies regional metamorphism, which also produced the associated Mn-rich garnet. Ilmenite from this stage forms inclusions within garnet and has a relatively low Mn content (<5.5 wt% MnO), owing to the preferential partitioning of Mn into the garnet. A second metamorphic or hydrothermal event resulted in the formation of ilmenite-bearing veinlets (+ chlorite + quartz + sulfides) that cut garnet and associated biotite. This latter type of ilmenite has a higher Mn content (up to 16.7 wt% MnO) that reflects remobilization of Mn within the local environment. Both types of Mn-rich ilmenite are considered to be derived from Mn originally concentrated in pools of dense brine that formed during synsedimentary, submarine-exhalative mineralization.

Keywords: manganese, ilmenite, hydrothermal, metamorphic, Pb–Zn–Ag deposit, Sullivan mine, British Columbia.

Sommaire

Nous avons effectué des analyses à la microsonde électronique de 76 grains d'ilménite provenant de treize endroits dans le gisement à Pb–Zn–Ag de Sullivan, à Kimberley, en Colombie-Britannique (zone minéralisée, roches encaissantes supérieures et inférieures) et d'horizons de tourmalinite de la Formation Aldridge, d'âge protérozoïque, affleurant sur une échelle régionale. Nos résultats mettent en évidence deux différents stades de formation de l'ilménite. Dans le premier, l'ilménite a été formée au cours d'un épisode de métamorphisme régional au faciès schistes verts, épisode responsable aussi de la formation du grenat manganifère associé. Cette génération d'ilménite se trouve inclus dans le grenat, et possède une teneur en Mn relativement faible (<5.5% MnO, en poids), à cause de la répartition préférentielle du Mn dans le grenat. Une seconde génération métamorphique ou bien hydrothermale est responsable de la formation de veinules à ilménite (+ chlorite + quartz + sulfures) qui recoupent le grenat et la biotite associée. L'ilménite dans ce cas est enrichie en Mn (jusqu'à 16.7% MnO), ce qui témoigne de la remobilisation du Mn dans le milieu. Dans les deux cas, il s'agirait de Mn concentré à l'origine dans des nappes de saumures denses formées au cours de minéralisation synsédimentaire par exhalaisons sous-marines.

(Traduit par la Rédaction)

Mots-clés: ilménite, manganèse, hydrothermal, métamorphique, gisement à Pb–Zn–Ag, mine de Sullivan, Colombie-Britannique.

Introduction

An important step necessary for the formation of sedimentary-exhalative ore deposits is the trapping of metal-rich hydrothermal fluids and precipitates in a restricted environment that allows accumulation of sulfide minerals without dispersal or oxidation. Brine pools have been proposed as one such environment (*e.g.*, Goodfellow *et al.* 1993). Such brine pools are envisaged as having been created by the ponding of saline hydrothermal fluids rich in Si, Fe, Mn, and other elements. Brine pools have been inferred in the geological record by the presence of stratiform concentrations of base metals and Mn-rich minerals such as spessartine and manganoan siderite (Spry 1990, Leitch 1992, Slack 1993). We contend that in some geological settings, the presence of Mn-rich ilmenite or of pyrophanite may provide an additional record of a brine-pool environment. Here we report on the occurrence of Mn-rich ilmenite from the sediment-hosted Sullivan Pb–Zn–Ag deposit, and discuss its significance in deciphering the conditions responsible for its formation.

Background Information

In some environments, ilmenite may form solid solutions with geikielite ($MgTiO_3$), pyrophanite ($MnTiO_3$), and ecandrewsite ($ZnTiO_3$). In metamorphosed clastic sedimentary rocks, ilmenite typically appears at (or above) the biotite isograd, having formed from reactions such as: muscovite + ankerite + quartz + chlorite + rutile + pyrite + graphite + siderite = biotite + plagioclase + ilmenite + pyrrhotite + calcite + CO_2 + H_2O + H_2S (Ferry 1984).

Ilmenite with relatively high levels of Mn, extending to pyrophanite (*i.e.*, > 50 mol% $MnTiO_3$), has been reported from several occurrences, *e.g.*, anorthosite from the Stillwater Complex, Montana ($Fe_{0.79-0.96}Mn_{0.03-0.16}TiO_3$, Loferski & Arculus 1993), granite from Fuzhou, China ($Fe_{0.24-0.53}Mn_{0.24-0.59}Zn_{0.01-0.14}TiO_3$, Suwa *et al.* 1987), meta-exhalites from Broken Hill, Australia ($Zn_{0.59}Fe_{0.24}Mn_{0.17}TiO_3$, Birch *et al.* 1988), oxide – sulfate – carbonate ores from the San Valentin Pb–Zn mine, Spain ($Zn_{0.55-0.69}Fe_{0.19-0.30}Mn_{0.10-0.13}TiO_3$, Birch *et al.* 1988), quartz – gahnite – spessartine metasedimentary rocks from Namaqualand, South Africa ($Fe_{0.39-0.78}Mn_{0.10-0.22}Zn_{0.04-0.42}TiO_3$, Whitney *et al.* 1993), and biotite – calcic amphibole – garnet – staurolite metasedimentary rocks from Quetico, Ontario ($Fe_{0.87-0.92}Mn_{0.07-0.12}TiO_3$, Kamineni *et al.* 1991).

Geological Setting

The Sullivan deposit, located in Kimberley, British Columbia, is a giant sediment-hosted exhalative (sedex-type), conformable Pb–Zn–Ag orebody within clastic metasedimentary rocks of the Middle Proterozoic Aldridge Formation (Hamilton *et al.* 1982). A vent complex associated with the deposit consists of a discordant, sulfide-poor (relative to the orebody) breccia pipe of altered rocks overlain by a lower conformable massive pyrrhotite body and an upper pyrrhotite – sphalerite – galena orebody. The presence of a zone of albite – chlorite – pyrite alteration immediately overlying the deposit suggests continued hydrothermal activity (not necessarily related to sulfide deposition: Turner & Leitch 1992) following burial of seafloor sulfides. The most common alteration assemblages are tourmalinite, chlorite – pyrrhotite, muscovite, and albite – chlorite – pyrite. Tourmalinite is abundant in the footwall of the deposit, where it forms a funnel-shaped pipe; relict tourmalinite (recognized by the local replacement of tourmaline by chlorite) is also present in the hanging wall of the deposit. The minerals in the altered rocks define a metamorphic texture, but their formation is interpreted to be premetamorphic in origin (Hamilton *et al.* 1982). Regional metamorphism after ore formation and associated hydrothermal alteration probably was related to the Middle Proterozoic East Kootenay orogeny. Conditions of metamorphism reached those of middle to upper greenschist facies, with temperatures of up to 400°C and pressure of ~2.0 kbar (McMechan & Price 1982, De Paoli & Pattison 1995).

Petrography

Ilmenite and other Ti-bearing minerals (titanite and rutile) are common accessory phases at Sullivan. Ilmenite displays several modes of occurrence. It may form subhedral to euhedral grains up to 0.1 mm in length, typically associated with chlorite, pyrrhotite, and titanite in the most altered rocks. For example, in sample R–10–30–3, collected from the R–10–30 decline that passes through the base of the pyrrhotite body into the underlying footwall tourmalinite, ilmenite forms randomly oriented acicular prisms in a chlorite matrix containing Mg-rich tourmaline, the latter having formed during the chlorite alteration (Fig. 1). No other Ti-bearing minerals were found in this sample, although abundant titanite-rich altered rocks have been described from this locality (Leitch 1991, Leitch & Turner 1991, Schandl & Gorton 1992).

Ilmenite also occurs as a minor constituent that coexists with garnet, tourmaline, pyrrhotite, quartz, chlorite, and muscovite in tourmalinite, coticules (spessartine – quartz rocks), and sulfide ores from Sullivan, and in regional metasedimentary rocks and tourmalinite. In most of these occurrences, ilmenite is present both in the matrix and as inclusions within spessartine. In some samples, ilmenite occurs in ilmenite – pyrrhotite – quartz veinlets (samples JS–81–72A and JS–92–12C) or ilmenite – chlorite veinlets (sample 397–1) that cut spessartine. In sample JS–92–38A, an ilmenite – calcite vein cuts tourmalinite. Leitch & Turner (1991) described samples in which ilmenite forms a core surrounded by a rim of titanite in sulfide-matrix breccias. In this study, ilmenite also was found as a core rimmed by titanite in stratiform tourmalinite sample JS–92–7D from the Can Am prospect, although without associated sulfides. Relics of ilmenite also have been found in the center of titanite grains within altered gabbro (Leitch & Turner 1991). In addition, minor ilmenite occurs in association with sulfides within veins and as a bedding-parallel replacement in the Sullivan vent complex (Leitch & Turner 1991).

It is likely that ilmenite is paragenetically earlier than other Ti-rich minerals at Sullivan. Leitch (1991) distinguished four paragenetic assemblages in the Sullivan footwall, including early tourmaline – quartz, later pyrrhotite – ilmenite, arsenopyrite – titanite and, finally, chalcopyrite – boulangerite – rutile. Titanite typically is more abundant than either ilmenite or rutile. The occurrence of abundant euhedral titanite together with Mg-rich chlorite locally in the footwall and hanging-wall alteration zones of the Sullivan

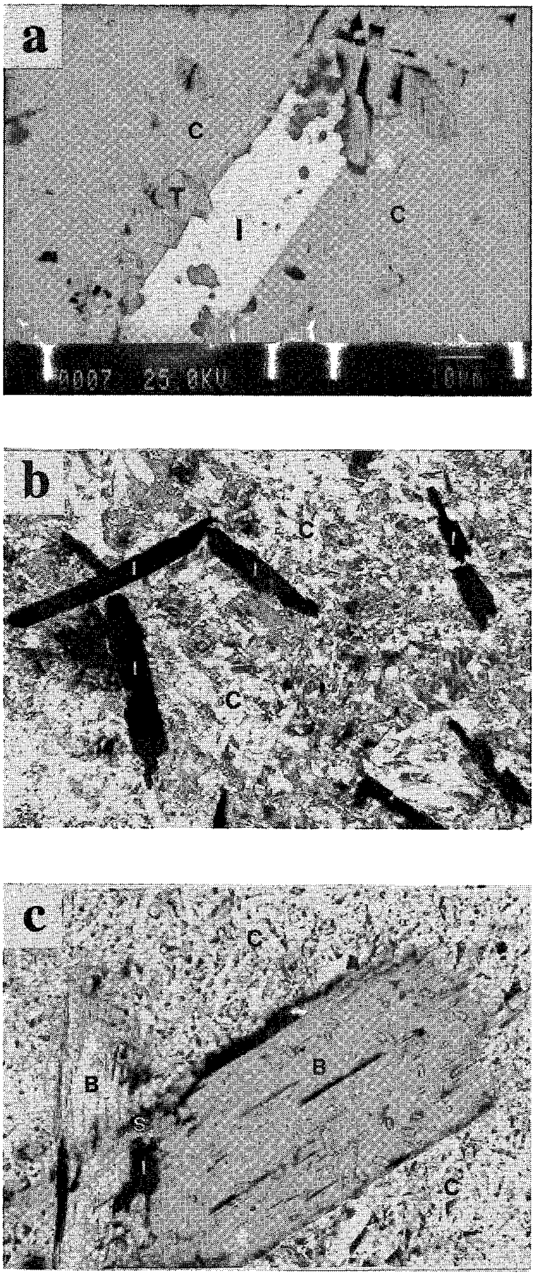

FIG. 1. a) Back-scattered-electron image of ilmenite (I), tourmaline (T), and chlorite (C) in sample R–10–30–3, showing ilmenite replaced by tourmaline. b) Photomicrograph of ilmenite (I) in matrix of chlorite (C) in sample R–10–30–3. Ilmenite is cut and replaced by chlorite and tourmaline (field of view: 3 mm). c) Photomicrograph of biotite (B) flake in chlorite (C) matrix in sample SY2415–1. Ilmenite (I) and sulfides (S) as veinlet-filled fractures in biotite (field of view: 12 mm).

orebody has been interpreted to suggest a mafic volcanic protolith (Leitch & Turner 1991), although widespread alteration by seawater-derived fluids is now considered the more likely origin of the Mg-rich chlorite (C.H.B. Leitch, pers. comm., 1995).

On the basis of these observations, we propose that there were two main stages of ilmenite formation. The first was associated with the crystallization of garnet during regional metamorphism related to the Middle Proterozoic East Kootenay orogeny. This metamorphism occurred after the hydrothermal processes responsible for sulfide mineralization and albite – chlorite – pyrite alteration, and formed the ilmenite inclusions in garnet and the disseminated crystals of ilmenite. The second stage was related to a later metamorphic or hydrothermal event and led to the formation of the ilmenite-bearing veinlets that cut the garnet and biotite. In some cases, the distinction between stage-1 inclusions of ilmenite in garnet and later stage-2 ilmenite in veinlets is unclear on a petrographic basis, as fractures in garnet crystals that contain ilmenite, for example, may have developed either prior to, or coevally with, the ilmenite.

MINERAL CHEMISTRY

Ilmenite was analyzed with a JEOL–8600 electron microprobe at 15 kV accelerating voltage and 15 nA beam current, using the following standards: synthetic $SrTiO_3$ for Ti, Fe_2O_3 for Fe, MnO for Mn, $CaSiO_3$ for Ca, $MgAl_2O_4$ for Al, olivine for Mg, and quartz for Si. Representative average results of analyses are given in Table 1. The standard deviations of the data for individual samples range from 0.4 to 1.2 wt% for FeO and from 0.1 to 0.9 wt% for MnO. These standard deviations are considerably smaller than the differences in FeO and MnO levels measured among the different samples. Ti contents (50.6 to 54.0 wt% TiO_2) are essentially constant at one atom per formula unit. There is only minor Fe^{3+} in the ilmenite; the inferred Fe_2O_3 contents are less than 3.1 wt% (Fe_2O_3 contents were calculated by charge balance). Fe^{2+} and Mn levels are variable, with FeO between 28.1 and 45.7 wt% and MnO between 0.48 and 18.6 wt%. Mg and Ca contents are negligible (<0.26 wt% CaO and <0.83 wt% MgO, respectively). The data conform to a solid solution between the Fe and Mn end-members of the ilmenite group.

Representative compositional data on titanite are shown in Table 2. In contrast to ilmenite, the titanite from Sullivan and regional metasedimentary rocks lacks elevated levels of Mn. The titanite compositions display comparatively large variations in SiO_2, TiO_2, Al_2O_3, FeO, and CaO.

The ilmenite inclusions studied in the garnet are all larger than 5 µm across (generally >10 µm), compared to the electron-microprobe beam size of 1–2 µm; hence the ilmenite data are not significantly affected by

TABLE 1. REPRESENTATIVE RESULTS OF ELECTRON-MICROPROBE ANALYSES OF Mn-RICH ILMENITE FROM SULLIVAN AND IN THE REGIONAL PROSPECTS

(wt%)	1	2	3	4	5	6	7	8	9	10
TiO_2	51.96	51.76	51.88	51.88	51.91	51.43	52.28	51.33	53.17	51.55
SiO_2	0.05	0.48	0.02	0.33	0.32	0.14	0.17	0.05	0.02	0.11
Al_2O_3	0.03	0.13	0.00	0.16	0.08	0.07	0.07	0.01	0.00	0.03
Fe_2O_3	0.70	0.15	0.39	0.14	0.31	0.42	0.00	1.98	0.00	0.71
FeO	39.85	38.01	31.41	31.22	29.45	30.76	39.86	40.31	32.30	36.64
MnO	6.56	8.47	14.62	15.35	16.66	15.04	6.49	5.74	12.86	9.17
MgO	0.04	0.00	0.04	0.12	0.02	0.04	0.04	0.01	0.11	0.02
CaO	0.09	0.42	0.15	0.03	0.09	0.01	0.08	0.07	0.02	0.18
Total	99.27	99.42	98.53	99.24	98.84	97.92	99.00	99.50	98.48	98.40
Numbers of ions on the basis of 6 oxygens and 4 cations										
Ti	1.985	1.969	1.994	1.977	1.988	1.990	2.002	1.960	2.048	1.986
Si	0.003	0.024	0.001	0.016	0.016	0.007	0.009	0.002	0.001	0.005
Al	0.002	0.008	0.000	0.009	0.005	0.004	0.004	0.000	0.000	0.002
Fe^{3+}	0.027	0.006	0.015	0.006	0.012	0.016	0.000	0.075	0.000	0.027
Fe^{2+}	1.693	1.608	1.343	1.322	1.254	1.323	1.697	1.711	1.383	1.570
Mn	0.282	0.363	0.633	0.659	0.719	0.655	0.280	0.247	0.558	0.398
Mg	0.003	0.000	0.003	0.009	0.001	0.003	0.003	0.001	0.008	0.001
Ca	0.005	0.023	0.008	0.002	0.005	0.001	0.005	0.004	0.001	0.010
$FeTiO_3$	85.59	81.58	67.84	66.45	63.52	66.78	85.70	87.35	70.96	79.73
$MnTiO_3$	14.26	18.42	32.01	33.10	36.41	33.06	14.14	12.61	28.63	20.21
$MgTiO_3$	0.15	0.00	0.14	0.45	0.07	0.16	0.17	0.04	0.41	0.05

Sample descriptions: 1. inclusions of ilmenite in garnet from garnet-rich tourmalinite from Sullivan footwall, sample DS-77-81; 2. anhedral ilmenite grain in tourmaline-quartz-biotite-chlorite matrix in sample DS-77-81; 3. disseminated euhedral ilmenite in chlorite matrix from Sullivan footwall, sample R-10-30-3; 4. euhedral ilmenite grains in veinlet in garnet from Sullivan footwall coticule rock (JS-81-72A); 5. inclusions/veinlet of ilmenite in garnet from Sullivan footwall coticule rock (JS-92-12C); 6. anhedral ilmenite disseminated in biotite matrix from sample JS-92-12C; 7. inclusion of ilmenite in garnet from sample JS-92-12C; 8. ilmenite inclusions in garnet from Sullivan bedded Pb-Zn-Ag ore (JS-91-8F); 9. ilmenite-sphalerite veinlet in biotite fracture in biotite-chlorite rock (SY2415-1) from Sullivan ore zone; 10. ilmenite-chlorite veinlet in garnet from Sullivan hangingwall garnet-chlorite rock (397-1).

contributions from the surrounding garnet.

The Mn content of the ilmenite from the Sullivan mine area and that for regional samples are presented separately in Figure 2. Among the samples from the mine area, there is a group of Mn-rich ilmenite compositions centered around a concentration of ~16 wt% and a range of 12.0 to 18.6 wt% MnO. The rest of the ilmenite data display an irregular distribution, but all have less than 9.5 wt% MnO, including values as low as 0.6 wt%. All examples of high-Mn ilmenite (except those in sample R–10–30–3) occur in small veinlets cutting other minerals (garnet or biotite), as disseminated grains, or in uncertain settings (veinlets or inclusions). In contrast, all of the ilmenite inclusions within garnet have less than 8.5 wt% MnO. None of the ilmenite grains in samples from regional prospects outside the immediate Sullivan mine area has MnO contents greater than 6.5 wt%, regardless of setting.

The highest Mn content (up to 18.6 wt% MnO) established in this study was found in ilmenite from sample JS–92–12C, a coticule rock from Sullivan. Ilmenite from another coticule rock (sample JS–81–72A) also has high Mn contents (15.3 to 15.5 wt% MnO, Table 1). These two samples also contain the highest whole-rock Mn concentrations (9.6 and 8.1 wt% MnO, respectively) of any rocks analyzed from Sullivan (J.F. Slack, unpubl. data), most of which is contained in spessartine-rich garnet. However, high-Mn ilmenite has also been found in Sullivan samples that lack garnet. Sample R–10–30–3, a footwall chlorite-rich rock, contains ilmenite with 13.9 to 16.2% MnO. In sample SY2415–1, a biotite – chlorite-altered rock from the ore zone, ilmenite contains between 12.0 and 13.7% MnO. These samples of ilmenite all contain high levels of Mn regardless of their associated mineral assemblage, *i.e.*, with or without coexisting spessartine-rich garnet.

The ilmenite grains, which vary from being euhedral to anhedral, generally are associated with pyrrhotite, sphalerite, quartz, and chlorite, suggesting a hydrothermal origin. Sample R–10–30–3 is exceptional in that the ilmenite forms discrete euhedral to subhedral acicular prisms randomly scattered in a chlorite-dominant matrix. From the mineral assemblage and textural relations (Fig. 1), it is possible that the ilmenite in this sample predates the formation of Mg-rich

TABLE 1-continued

(wt%)	11	12	13	14	15	16	17	18	19	20
TiO_2	50.98	52.32	52.38	51.84	52.97	53.88	52.92	51.88	52.40	53.31
SiO_2	0.22	0.17	0.02	0.05	0.09	0.03	0.34	0.07	0.06	0.01
Al_2O_3	0.08	0.12	0.00	0.03	0.07	0.00	0.15	0.03	0.00	0.00
Fe_2O_3	1.16	0.00	0.00	0.92	0.00	0.00	0.00	0.57	0.00	0.00
FeO	44.46	45.36	43.78	40.58	38.39	40.47	42.42	40.96	43.48	45.78
MnO	1.18	0.94	2.23	5.49	6.45	5.29	2.94	4.67	2.47	0.65
MgO	0.14	0.10	0.04	0.17	0.19	0.06	0.03	0.11	0.06	0.00
CaO	0.18	0.09	0.11	0.19	0.21	0.31	0.03	0.18	0.16	0.23
Total	98.41	99.10	98.57	99.27	98.36	100.03	98.82	98.47	98.64	99.98
Numbers of ions on the basis of 6 oxygens and 4 cations										
Ti	1.964	2.002	2.018	1.979	2.041	2.045	2.032	1.998	2.016	2.017
Si	0.011	0.009	0.001	0.003	0.004	0.001	0.017	0.003	0.003	0.000
Al	0.005	0.007	0.000	0.002	0.004	0.000	0.009	0.002	0.000	0.000
Fe^{3+}	0.045	0.000	0.000	0.035	0.000	0.000	0.000	0.022	0.000	0.000
Fe^{2+}	1.904	1.929	1.875	1.723	1.645	1.707	1.811	1.754	1.860	1.926
Mn	0.051	0.041	0.097	0.236	0.280	0.226	0.127	0.202	0.107	0.028
Mg	0.010	0.007	0.003	0.013	0.015	0.004	0.003	0.008	0.004	0.000
Ca	0.010	0.005	0.006	0.010	0.012	0.017	0.001	0.010	0.009	0.013
$FeTiO_3$	96.87	97.57	94.94	87.36	84.81	88.12	93.32	89.25	94.35	98.57
$MnTiO_3$	2.60	2.05	4.90	11.98	14.44	11.66	6.55	10.32	5.43	1.42
$MgTiO_3$	0.53	0.37	0.17	0.66	0.75	0.22	0.13	0.43	0.23	0.01

Sample descriptions: 11. ilmenite inclusions in garnet from sample 397-1; 12. ilmenite inclusions in garnet from Sullivan hangingwall chlorite-garnet rock (397-2); 13. anhedral ilmenite from chlorite-biotite matrix in sample 397-2; 14. ilmenite inclusions in garnet from tourmalinite at the Mount Mahon prospect, sample JS-92-23A; 15. veinlet of ilmenite in garnet from sample JS-92-23A; 16. anhedral ilmenite in tourmaline-quartz-chlorite-biotite matrix in sample JS-92-23A; 17. anhedral ilmenite in tourmaline-quartz-chlorite matrix in tourmalinite from Can Am prospect, sample JS-92-7D; 18. ilmenite inclusions in garnet from sample JS-92-7D; 19. anhedral ilmenite in tourmaline-quartz matrix in tourmalinite from Neg prospect, sample JS-92-22A (garnet absent); 20. euhedral ilmenite grains in ilmenite-calcite veinlet in tourmalinite from Vulcan prospect, sample JS-92-38A.

tourmaline and chlorite, which are considered to be products of late hydrothermal metasomatism related to subjacent gabbro intrusion at depth (Leitch 1992, Jiang *et al.* 1995). Leitch & Turner (1991) also suggested that ilmenite occurrences within veins in sulfides and bedding-parallel replacements at Sullivan are hydrothermal in origin. However, a post-hydrothermal metamorphic origin cannot be precluded for the ilmenite in sample R–10–30–3.

Discussion

Ilmenite-bearing veinlets cut spessartine-rich garnet in samples JS–92–12C and JS–81–72A and infill fractures in biotite in sample SY2415–1 (Fig. 1c), indicating that formation of this generation of ilmenite postdates that of the spessartine-rich garnet and biotite. A similar vein-type occurrence of ilmenite is present in sample 397–1, but it has a lower Mn content (Table 1). In this sample, taken from a garnet – chlorite-altered rock, an ilmenite – chlorite veinlet cuts the garnet. The ilmenite contains 8.7–9.4 wt% MnO, whereas the chlorite in the veinlet is rich in Fe (35–36% FeO) and poor in Mg (6–7% MgO), similar to the chlorite dispersed in the rock (~34% FeO and 8–9% MgO) (Jiang *et al.*, unpubl. data). The garnet in this sample also has low Mn contents (3.4–13.6 wt% MnO) compared to the garnet in samples JS–92–12C (17.9–27.6 wt% MnO) and JS–81–72A (15.4–25.0 wt% MnO). These data suggest that the levels of Mn in the ilmenite reflect local redistribution of Mn rather than mobilization on a deposit-wide scale.

Sample 397–1 also contains irregularly shaped ilmenite grains with low Mn contents (0.5–2.2 wt% MnO) that occur as inclusions within spessartine-rich garnet. The MnO content of the included ilmenite grains varies according to their position in the garnet. Those grains nearest the core of the garnet have higher Mn contents than those near the rim, mimicking the Mn-zoning of garnet in this sample. This pattern is seen in other garnet-bearing rocks, such as sample 397–2, a chlorite – garnet rock from the hanging wall at Sullivan, sample JS–92–23A, garnet-bearing tourmalinite from the Mount Mahon prospect, and sample JS–92–7D, garnet-bearing tourmalinite from the Can Am prospect. Low-Mn ilmenite (6.5 wt% MnO) also

TABLE 2. REPRESENTATIVE RESULTS OF ELECTRON-MICROPROBE ANALYSES OF TITANITE FROM SULLIVAN AND IN THE REGIONAL PROSPECTS

(wt%)	1	2	3	4	5	6	7	8	9	10
SiO_2	31.29	32.59	30.46	30.75	30.21	30.54	30.50	25.78	31.90	30.63
TiO_2	30.97	23.78	36.23	37.75	37.02	36.68	37.39	38.84	37.56	37.22
Al_2O_3	7.32	13.12	2.63	1.47	1.67	2.52	2.38	2.60	2.23	2.41
FeO	3.54	2.47	0.24	0.59	0.80	0.84	0.43	5.12	0.29	0.70
MgO	1.96	0.40	0.00	0.01	0.02	0.02	0.00	0.13	0.02	0.00
MnO	0.00	0.00	0.11	0.15	0.20	0.13	0.06	0.65	0.14	0.13
CaO	25.00	27.57	29.09	28.42	28.38	28.79	28.91	24.56	28.20	28.50
Na_2O	0.13	0.12	0.08	0.09	0.09	0.06	0.02	0.15	0.18	0.07
K_2O	0.45	0.00	0.00	0.03	0.00	0.00	0.05	0.02	0.08	0.04
F	0.72	1.35	0.00	0.32	0.00	1.21	0.02	1.27	0.00	0.49
Cl	0.01	0.02	0.01	0.00	0.00	0.00	0.00	0.01	0.06	0.01
Total	101.38	101.41	98.84	99.56	98.38	100.78	99.75	99.13	100.66	100.21

Sample descriptions: 1. JS-92-27AA of Sullivan footwall tourmalinite, titanite replaced tourmaline; 2. DS-77-81 of Sullivan footwall garnet-rich tourmalinite, titanite occurs as anhedral grain in tourmaline-quartz-biotite-chlorite matrix; 3. SY2415-1 of biotite-chlorite rock from Sullivan ore zone, titanite as veinlet in biotite fracture; 4-5. JS-93-48 of North Star garnet-rich tourmalinite, titanite coexists with biotite in tourmaline-quartz-biotite-chlorite matrix; 6. Nstar-2 of North Star tourmalinite, titanite as inclusion within chlorite; 7-9. JS-92-23A of Mount Mahon tourmalinite, titanite altered ilmenite (7), titanite-quartz veinlet (8), titanite-K feldspar veinlet (9); 10. JS-92-7D of Can Am tourmalinite, titanite as anhedral grain in tourmaline-quartz-chlorite matrix.

occurs as inclusions in garnet from sample JS–92–12C, although the majority of the ilmenite in this sample has high Mn contents (13.2–18.6 wt% MnO).

The different levels of concentrations of Mn in ilmenite are interpreted to reflect their different stages of formation. Inclusions of low-Mn ilmenite in the garnet are considered to have formed synchronously with the garnet, with the lower Mn contents being due to participation of ilmenite in the garnet-forming reaction, in which Mn is preferentially incorporated into the garnet structure (*e.g.*, Kamineni *et al.* 1991). Some of the low-Mn ilmenite in the matrix of these rocks (*e.g.*, samples 397–2, JS–92–23A, and JS–92–7D) also may have crystallized during garnet-forming reactions, or they may reflect low levels of Mn in the protolith.

The Mn content of ilmenite in the matrix of the samples is generally higher than that of ilmenite included in garnet (*e.g.*, samples DS–77–81 and 397–2) (Table 1). Owing to the absence of garnet in the matrix of these samples, there was less competition for Mn available for incorporation in the ilmenite. In sample JS–92–7D, garnet-bearing tourmalinite from the Can Am prospect, the ilmenite inclusions within the garnet have slightly higher Mn contents than ilmenite in the matrix. The relatively high Mn-contents of the ilmenite inclusions may be due to the very low modal abundance of garnet in this sample (~5 vol.%), which localized the high-Mn environment around the garnet.

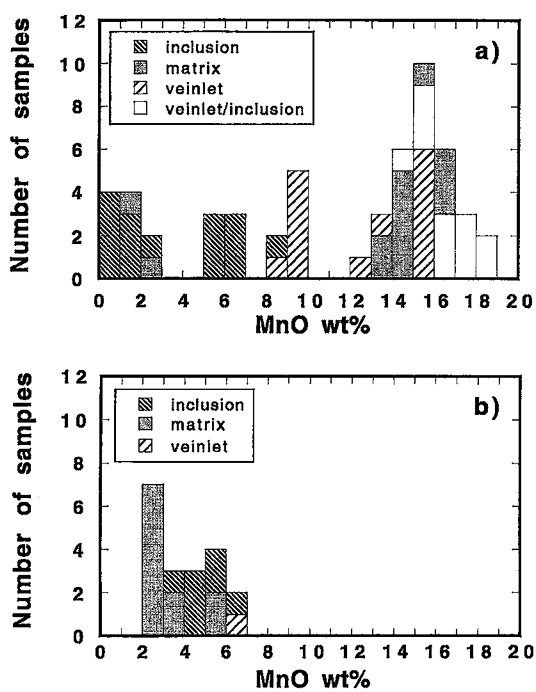

FIG. 2. Histogram of MnO concentrations of individual ilmenite grains. a) Sullivan mine area, b) regional prospects.

The presence of Mn-rich ilmenite has been noted in other sulfide ores. In the Kamienica Range, southwest Poland, Mn-rich ilmenite occurs in the metamorphosed wallrock of a cassiterite – sulfide deposit. Here, the Mn content of the ilmenite is commonly greater than in coexisting garnet, which suggests a lack of equilibrium between the two minerals (Cook & Dudek 1994). Ilmenite in the Broken Hill district, Australia, occurs as a metamorphic mineral (Plimer 1990), with the Mn level of the ilmenite controlled by the availability and concentration of Mn in the protolith. This local control over Mn contents of ilmenite during metamorphism was also shown by Whitney *et al.* (1993) in a study of ilmenite – ecandrewsite coexisting in a kyanite-bearing schist from the Black Mountains, Death Valley, California. In this occurrence, the ilmenite has very low Mn owing to low Mn contents in the whole rocks (0.11 to 0.37 %), and the fact that the garnet in the schist is almandine-rich (~87 mol%) with less than 1.1 wt% MnO.

The existence of an enrichment in manganese at Sullivan is well established (Barnett 1982, Hamilton *et al.* 1982, Leitch 1992, Slack 1993). Carbonate minerals intergrown with the sulfide deposits are manganiferous, with Mn contents ranging up to 2 mol% $MnCO_3$ in massive pyrrhotite, 3–10 mol% in the transition zone, 7–13 mol% in the bedded ores, and up to 35 mol% in manganoan siderite from the southeastern fringe zone (Leitch 1992). Garnet in the Sullivan and North Star deposits is generally Mn-rich, containing from 45 to 79% of the spessartine end-member (Leitch 1992). In addition, Leitch (1992) found that other minerals at Sullivan, such as tremolite, diopside, chlorite, and biotite, have anomalously high Mn contents. An ilmenite grain in a regional clastic metasedimentary rock from the Aldridge Formation (which hosts the Sullivan deposit) also was found to have slightly high (7 wt%) MnO content (Leitch 1992). The elevated Mn levels locally in the shallow footwall and peripheral to the Sullivan deposit are considered to be an indication of submarine Mn-rich exhalations (Leitch 1992, Slack 1993). Slack (1993) further suggested that stratiform tourmalinite that contains in excess of 10% fine-grained, spessartine-rich garnet is the product of Fe–Mn–B precipitation in a pool of dense brine. The bedded Pb–Zn–Ag ores, which locally contain spessartine-rich garnet in abundant disseminations and locally in thin (<1 cm) laminations, are also believed to have formed in a brine-pool environment (Leitch 1992, Goodfellow *et al.* 1993).

The Ti in the ilmenite and in other Ti-rich minerals at Sullivan seems most likely derived from the local clastic sediments prior to alteration and mineralization. Shaw *et al.* (1993) reported elevated TiO_2 contents from hydrothermal rocks at Sullivan, for example, albitite that contains 0.7% TiO_2, and chlorite – pyrite and chlorite – pyrrhotite rocks that contain 1% TiO_2, compared to average unaltered metasedimentary rocks of the Aldridge Formation (0.55% TiO_2). More recent analyses suggest that the Ti was residually enriched through leaching of alkalis or other elements (Leitch & Lentz 1994). The breakdown of the original Ti-bearing minerals (*e.g.*, detrital rutile, ilmenite and biotite) during hydrothermal alteration and later regional metamorphism probably provided the Ti necessary for formation of the ilmenite and other Ti-rich minerals in the Sullivan deposit.

The association of Mn-rich ilmenite with economic Pb–Zn–Ag mineralization at Sullivan, and the fact that ilmenite, like other Ti-rich minerals, is very refractory during weathering, mean that it may be possible to use the presence of Mn-rich ilmenite in rocks, soils, and stream sediments as a prospecting guide.

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REFERENCES

BARNETT, R.L. (1982): Manganese variation in garnet, Lower B Band Triplet and 3259 XCE, Sullivan mine. Unpubl. Rep., Cominco Ltd.

BIRCH, W.D., BURKE, E.A.J., WALL, V.J. & ETHERIDGE, M.A. (1988): Ecandrewsite, the zinc analogue of ilmenite, from Little Broken Hill, New South Wales, Australia, and the San Valentin mine, Sierra de Cartegena, Spain. *Mineral. Mag.* **52**, 237-240.

COOK, N.J. & DUDEK, K. (1994): Mineral chemistry and metamorphism of garnet – chlorite – mica schists associated with cassiterite – sulphide-mineralisation from the Kamienica Range, Izera Mountains, S.W. Poland. *Chem. Erde* **54**, 1-32.

DE PAOLI, G.R. & PATTISON, D.R.M. (1995): Metamorphic temperature – pressure conditions of the Sullivan orebody, Kimberley, B.C. *Geol. Assoc. Can. – Mineral. Assoc. Can., Program Abstr.* **20**, A-79.

FERRY, J.M. (1984): A biotite isograd in south-central Maine, U.S.A.: mineral reactions, fluid transfer, and heat transfer. *J. Petrol.* **25**, 871-893.

GOODFELLOW, W.G., LYDON, J.W. & TURNER, R.J.W. (1993): Geology and genesis of stratiform sediment-hosted (SEDEX) zinc – lead – silver sulphide deposits. *In* Mineral Deposit Modeling (R.V. Kirkham, W.D. Sinclair, R.I. Thorpe & J.M. Duke, eds.). *Geol. Assoc. Can., Spec. Pap.* **40**, 201-251.

HAMILTON, J.M., BISHOP, D.T., MORRIS, H.C. & OWENS, O.E. (1982): Geology of the Sullivan orebody, Kimberley, B.C., Canada. *In* Precambrian Sulphide Deposits (R.W. Hutchinson, C.D. Spence & J.M. Franklin, eds.). *Geol. Assoc. Can., Spec. Pap.* **25**, 597-665.

JIANG, SHAO-YONG, PALMER, M.R. & SLACK, J.F. (1995): Chemical and boron isotopic composition of tourmaline from the sediment-hosted Sullivan Zn–Pb–Ag deposit, British Columbia. *Geol. Assoc. Can. – Mineral. Assoc. Can., Program Abstr.* **20**, A-49.

KAMINENI, D.C., STONE, D. & JOHNSTON, P.J. (1991): Metamorphism and mineral chemistry of Quetico sedimentary rocks near Atikokan, Ontario, Canada. *Neues Jahrb. Mineral., Abh.* **162**, 311-337.

LEITCH, C.H.B. (1991): Preliminary fluid inclusion and petrographic studies of parts of the Sullivan stratiform sediment-hosted Zn–Pb deposit, southeastern British Columbia. *Geol. Surv. Can., Pap.* **91-1A**, 91-101.

________ (1992): Mineral chemistry of selected silicates, carbonates and sulphides in the Sullivan and North Star stratiform Zn–Pb deposits, British Columbia, and in district-scale altered and unaltered sediments. *Geol. Surv. Can., Pap.* **92-1E**, 83-93.

________ & LENTZ, D.R. (1994): The Gresens approach to mass balance constraints of alteration systems: methods, pitfalls, examples. *In* Alteration and Alteration Processes Associated with Ore-Forming Systems (D.R. Lentz, ed.). *Geol. Assoc. Can., Short Course Notes* **11**, 161-192.

________ & TURNER, R.J.W. (1991): The vent complex of the Sullivan stratiform sediment-hosted Zn–Pb deposit, British Columbia: preliminary petrographic and fluid inclusion studies. *Geol. Surv. Can., Pap.* **91-1E**, 33-44.

LOFERSKI, P.J. & ARCULUS, R.J. (1993): Multiphase inclusions in plagioclase from anorthosites in the Stillwater Complex, Montana: implications for the origin of the anorthosites. *Contrib. Mineral. Petrol.* **114**, 63-78.

MCMECHAN, M.E. & PRICE, R.A. (1982): Superimposed low grade metamorphism in the Mount Fisher area, southeastern British Columbia: implications for the East Kootenay orogeny. *Can. J. Earth Sci.* **19**, 476-489.

PLIMER, I.R. (1990): The ilmenite – ecandrewsite solid solution series, Broken Hill, Australia. *Neues Jahrb. Mineral., Monatsh.*, 529-536.

SCHANDL, E.S. & GORTON, M.P. (1992): Rare-earth element geochemistry of selected samples from the Sullivan Pb–Zn sedex deposit: the role of allanite in mobilizing rare-earth elements in the chlorite-rich footwall(82G/12). *British Columbia Dep. Mines, Energy and Petroleum Resources, Geol. Fieldwork 1991, Pap.* **1992-1**, 273-279.

SHAW, D.R., HODGSON, C.J., LEITCH, C.H.B. & TURNER, R.J.W. (1993): Geochemistry of albite – chlorite – pyrite and chlorite – pyrrhotite alteration, Sullivan Zn–Pb deposit, British Columbia. *Geol. Surv. Can., Pap.* **93-1A**, 109-118.

SLACK, J.F. (1993): Models for tourmalinite formation in the Middle Proterozoic Belt and Purcell Supergroups (Rocky Mountains) and their exploration significance. *Geol. Surv. Can., Pap.* **93-1E**, 33-40.

SPRY, P.G. (1990): Geochemistry and origin of coticules (spessartine – quartz rocks) associated with metamorphosed massive sulfide deposits. *In* Regional Metamorphism of Ore Deposits and Genetic Implications (P.G. Spry & L.T. Bryndzia, eds.). VSP Publishers, Utrecht, The Netherlands (49-75).

SUWA, K., ENAMI, M., HIRAIWA, I. & YANG, T. (1987): Zn–Mn ilmenite in the Kuiqi granite from Fuzhou, Fujian Province, east China. *Mineral. Petrol.* **36**, 111-120.

TURNER, R.J.W. & LEITCH, C.H.B. (1992): Relationship of albitic and chloritic alteration to gabbro dykes and sills at the Sullivan deposit and nearby area, southeastern British Columbia. *Geol. Surv. Can., Pap.* **92-1E**, 95-105.

WHITNEY, D.L., HIRSCHMANN, M. & MILLER, M.G. (1993): Zincian ilmenite – ecandrewsite from a pelitic schist, Death Valley, California, and the paragenesis of (Zn,Fe)TiO_3 solid solution in metamorphic rocks. *Can. Mineral.* **31**, 425-436.

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