

RARE-EARTH MINERALOGY AND GEOCHEMISTRY OF THE MATTAGAMI LAKE VOLCANOGENIC MASSIVE SULFIDE DEPOSIT, QUEBEC

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ABSTRACT

Allanite, zircon, and other exotic rare-earth minerals, including hellandite, monazite, parisite, synchisite, euxenite, and polycrase, have been found at the Mattagami Lake mine Archean Zn-Cu-Ag-Au volcanogenic massive sulfide (VMS) deposit, Quebec. Zircon in the least-altered rhyolite host-rock is interpreted to be relict, and igneous in origin. Fresh grains of allanite, hellandite, monazite, parisite, and synchisite occur in cross-cutting veins and evidently belong to the late greenschist-facies metamorphism. Metamict grains represent an earlier generation of allanite, and may have crystallized during the hydrothermal alteration associated with the formation of the ore deposit on the seafloor. Euxenite and polycrase replace skeletal ilmenite. Whole-rock analyses and mass-balance calculations reveal that a large proportion of the REE in all rocks of the Mattagami Lake mine resides in these rare-earth minerals, particularly in allanite and zircon, which account largely for the abundances of LREE and HREE, respectively. This illustrates the potential of these minerals for controlling the distribution of REE in VMS deposits. In particular, preferential dissolution and recrystallization of allanite dominate the distribution of the LREE. In contrast, the HREE were relatively immobile, apparently because of the chemical resistance of zircon and (Y,Nb)-oxides.

Keywords: rare-earth minerals, allanite, zircon, hellandite, geochemistry of the rare earths, volcanogenic massive sulfide deposit, Mattagami Lake mine, Quebec.

SOMMAIRE

Nous avons trouvé allanite, zircon, et autres minéraux exotiques enrichis en terres rares, par exemple hellandite, monazite, parisite, synchisite, euxenite et polycrase, dans le gisement archéen de sulfures massifs volcanogéniques à Zn-Cu-Ag-Au de Mattagami Lake, Québec. Le zircon présent dans les rhyolites hôtes les moins altérées serait d'origine ignée. Les cristaux d'allanite, de hellandite, de monazite, de parisite et de synchisite saines se trouvent en veines qui recoupent ces roches, et donc résultent d'une remobilisation sous conditions du faciès schistes verts. Les grains métamictes représenteraient une génération précoce d'allanite, et pourraient avoir cristallisé au cours d'un épisode hydrothermal sur le fond océanique, lors de la formation du gîte. L'euxénite et le polycrase remplacent l'ilménite, squelettique. Les compositions de roches et les résultats de bilans géochimiques révèlent que la plus grande partie des concentrations de terres rares des roches à la mine Mattagami Lake réside dans ces minéraux, et surtout dans l'allanite et le zircon, qui rendent compte des abondances de terres rares légères et lourdes, respectivement. Nos résultats illustrent le potentiel qu'ont ces minéraux pour régir la distribution des terres rares dans les gisements de sulfures massifs volcanogéniques. En particulier, la dissolution préférentielle et la recristallisation de l'allanite exercent le contrôle dominant sur la distribution des terres rares légères. Par contre, les terres rares lourdes démontrent une immobilité relative dans ce milieu, qui serait due à l'insolubilité du zircon et des oxydes à Y et Nb.

(Traduit par la Rédaction)

Mots-clés: minéraux porteurs de terres rares, allanite, zircon, hellandite, géochimie des terres rares, gisement de sulfures massifs volcanogéniques, mine de Mattagami Lake, Québec.

INTRODUCTION

The geochemistry of the rare-earth elements (REE) has been widely applied to models of exploration and genesis for a variety of ore deposits (Kerrick & Fryer 1979, Fleischer 1983, Fryer & Taylor 1987,

Lottermoser 1992, and references therein), and particularly for volcanogenic massive sulfide (VMS) deposits (Graf 1977, Campbell *et al.* 1984, Leshner *et al.* 1986, MacLean 1988, Whitford *et al.* 1988, Barrett *et al.* 1991, Schandl & Gorton 1991, Schandl *et al.* 1991). For example, REE geochemistry is particularly helpful

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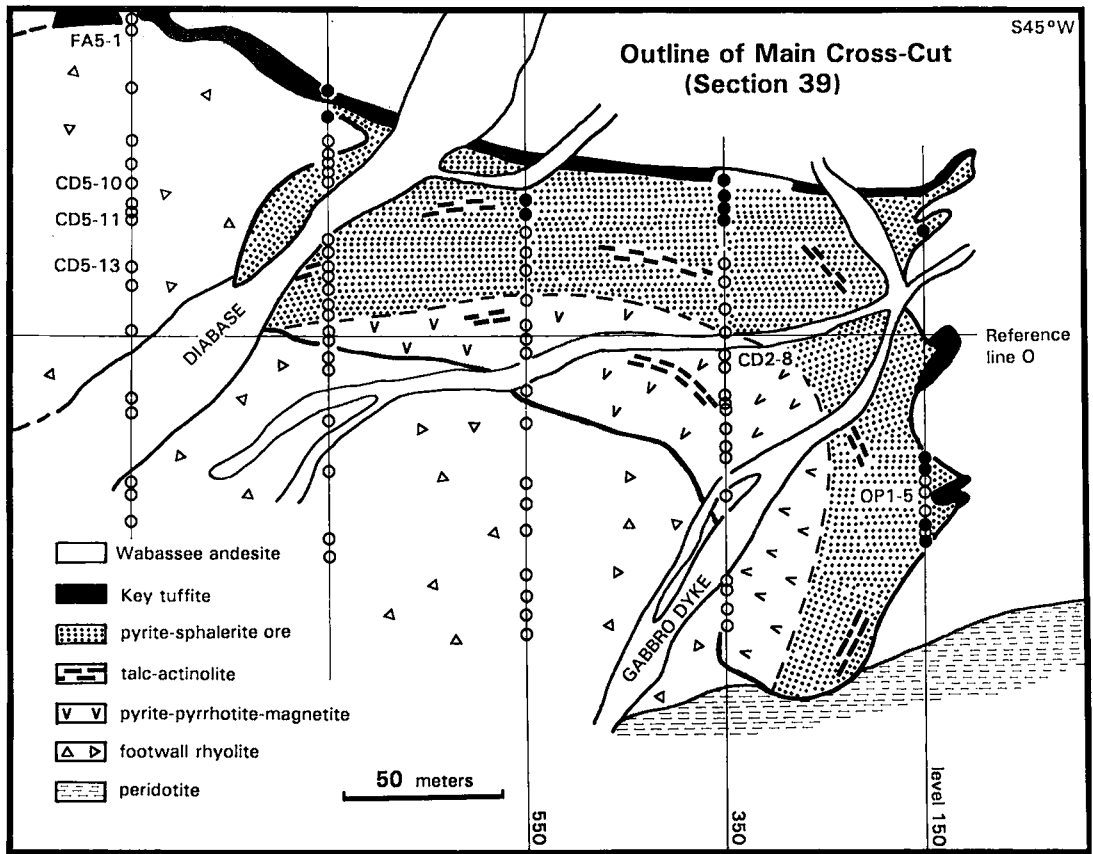


Fig. 1. Geological outline of section 39 of the Mattagami Lake mine orebody, with sample locations (after Costa 1980, Costa *et al.* 1983). Only samples mentioned in the text are indicated; the pyrosulphite-bearing samples of Pan *et al.* (1993a) are represented by solid circles. Sample FR1 (least-altered rhyolite) is located beyond the area shown in Fig. 1.

in the analysis of greenstone-belt stratigraphy to distinguish tholeiitic and calc-alkaline volcanic series (MacLean 1988), and is becoming increasingly important as a direct tool for exploration of VMS deposits (Campbell *et al.* 1984, Leshar *et al.* 1986). Similarly, the characteristics of *REE* distribution in massive sulfide ores and their spatially associated alteration haloes and volcanic host rocks are routinely examined for possible genetic relationships and for constraints on the nature and physicochemical conditions (mixture with seawater, temperature, $f(\text{O}_2)$, pH, *etc.*) of the ore-forming fluids. Alteration pipes below several VMS deposits have provided some of the most convincing examples for *REE* mobility under hydrothermal conditions (*e.g.*, Campbell *et al.* 1984, MacLean 1988, Whitford *et al.* 1988).

Although the rapidly growing body of whole-rock abundances of the *REE* has provided much insight into VMS deposits, very few studies have been accompa-

nied by detailed petrographic descriptions or mineralogical data. In particular, the *REE*-bearing minerals are rarely described (Schandl & Gorton 1991, Schandl *et al.* 1991, Pan & Fleet 1992, 1993). Most ancient VMS deposits have experienced a regional metamorphic or late-stage episode of hydrothermal alteration (or both) after the syngenetic mineralization on the seafloor (Franklin *et al.* 1981, Schandl *et al.* 1990, Large 1992, Pan *et al.* 1993a). Therefore, the petrographic and mineralogical characteristics of all rock types, including ore and gangue, alteration pipes (or haloes), and host volcanic suites, must be well defined in order to permit a meaningful interpretation of the geochemistry of the *REE* in VMS deposits.

In this paper, we report on texture and chemistry of some exotic rare-earth minerals, including allanite, hellandite, monazite, parisite, synchisite, euxenite, and polycrase, as well as zircon, from the Mattagami Lake mine Archean Zn-Cu-Ag-Au massive sulfide deposit

of the Matagami mining district, Quebec. The Mattagami Lake mine is a classic example of an Archean volcanogenic massive sulfide deposit that has been generated by syngenetic processes on the seafloor and subsequently subjected to a regional metamorphism of greenschist-facies grade (Roberts 1975, Roberts & Reardon 1978, Costa 1980, Costa *et al.* 1983, Pan *et al.* 1993a). Detailed observations of texture were made in order to establish the paragenetic sequence of the rare-earth minerals. Their chemical compositions were characterized by electron-microprobe analysis. In addition, whole-rock analyses and mass-balance calculations were performed to assess the potential of these accessory minerals in the control of the distribution of the REE in the Mattagami Lake mine and other VMS deposits that have undergone low-grade metamorphism. Finally, the present study also has an important bearing on the behavior of the REE, Nb, Y, and Zr in alteration pipes or haloes associated with VMS deposits (Campbell *et al.* 1984, MacLean & Kranidiotis 1987, MacLean 1988, Whitford *et al.* 1988, Schandl & Gorton 1991, Schandl *et al.* 1991).

GEOLOGICAL SETTING

The Mattagami Lake mine is the largest of thirteen Archean polymetallic (Zn-Cu-Ag-Au) massive sulfide deposits in the Matagami mining district, north-western Quebec, which lies within the northernmost volcanic center of the Abitibi greenstone belt, Superior Province (Roberts 1975, Roberts & Reardon 1978, Costa 1980, Costa *et al.* 1983, MacLean 1984). The geology of the Matagami mining district and its massive sulfide deposits have been described by a number of investigators (Roberts 1975, Roberts & Reardon 1978, MacGeehan & MacLean 1980, Costa 1980, Costa *et al.* 1983, MacLean 1984, MacLean & Kranidiotis 1987). Most of the orebodies of the Mattagami mining district lie at the top of rhyolites of the Watson Lake Group and are overlain by the Key tuffite, a distinctive unit of intercalated chemical sediments and epiclastic materials of trondhjemitic composition, and the Wabasseé andesite (Fig. 1). Regional metamorphism in the Matagami mining district varies from greenschist to amphibolite facies (Jolly 1978).

The Mattagami Lake mine includes two orebodies of 19 and 2 million tonnes, respectively, with an average of 12.8% Zn, 0.7% Cu, 40 g/t Ag, and 0.6 g/t Au (Costa 1980, Costa *et al.* 1983). The deposit is located on the hinge of a local, second-order anticline of a regional anticline, and is clearly seen to be deformed if its present configuration is outlined relative to the overlying andesite - Key tuffite contact (Roberts 1975). The larger orebody is characterized by a regular vertical zonation in sulfide - oxide - silicate mineral assemblages; this includes, stratigraphically

downward, the Key tuffite, a pyrite - sphalerite unit, and a pyrite - pyrrhotite - magnetite unit (Fig. 1; *cf.* Roberts 1975, Roberts & Reardon 1978, Costa 1980, Costa *et al.* 1983). The footwall to the Mattagami Lake mine is a vitroclastic rhyolite, which constitutes the uppermost volcanic unit of the Watson Lake Group and exhibits varying degrees of alteration. The least altered footwall rocks are characterized by the assemblage K-feldspar, albite-oligoclase, quartz, and biotite, with subsidiary chlorite, epidote, allanite, ilmenite, calcite, zircon, and polycrase, and were classified by Costa *et al.* (1983) as quartz keratophyres. Proximal to the orebody, albite is progressively consumed by chlorite, which preserves perlitic and spherulitic textures and may comprise up to 90% of the rock (Costa 1980, Costa *et al.* 1983); these chlorite-rich rocks are hereafter referred to as chloritite. The upper portions of the chloritite footwall zone also are characterized by numerous, irregularly distributed veins and microveins of sulfides and silicates transecting the chloritite matrix. The veins and microveins are composed of variable amounts of pyrite, pyrrhotite, and sphalerite together with quartz, talc, phlogopite, chlorite, stilpnomelane, rare actinolite (Costa 1980, Costa *et al.* 1983), allanite, and hellandite (see below). Electron-microprobe analyses by

TABLE 1. COMPOSITIONS OF ALLANITE FROM THE MATTAGAMI LAKE MINE

Sample	FR1	CD2-8	CD5-10	CD5-11	CD5-13	OP1-5
Analysis	(2)	(2)	(2)	(3 ^f)	(4 ^f)	(3 ^m) (2)
SiO ₂ (wt. %)	31.16	30.21	30.22	30.55	31.46	31.02 32.11 31.52
TiO ₂	0.05	0.08	0.33	0.44	0.09	0.23 0.06 0.06
Al ₂ O ₃	17.15	12.27	14.48	15.20	18.32	16.44 19.45 18.72
Fe ₂ O ₃ *	4.39	8.00	5.11	3.08	4.12	3.05 2.75 2.45
FeO	9.47	8.95	10.87	11.16	8.55	10.15 8.66 9.00
ZnO	nd	nd	nd	0.00	0.00	0.84 0.00 0.46
MnO	0.55	0.50	0.32	0.33	0.30	0.28 0.28 0.27
MgO	0.42	1.41	0.41	0.01	0.06	0.13 0.02 0.50
CaO	11.01	9.62	9.41	10.16	12.95	10.87 12.56 12.13
Y ₂ O ₃	0.15	0.17	0.20	0.13	0.67	0.25 0.46 0.10
La ₂ O ₃	4.78	4.86	4.26	4.48	3.68	4.36 3.55 5.47
Ce ₂ O ₃	10.23	11.17	10.86	11.15	8.05	9.62 7.69 10.73
Pr ₂ O ₃	1.13	1.73	1.59	1.62	1.23	1.47 1.19 1.02
Nd ₂ O ₃	5.36	6.62	7.07	7.19	5.00	6.46 5.23 3.74
Sm ₂ O ₃	0.96	1.09	1.50	1.51	1.01	1.80 1.36 0.19
Eu ₂ O ₃	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05 <0.05 <0.05
Gd ₂ O ₃	0.56	0.52	0.66	0.91	0.76	1.50 1.32 0.08
Dy ₂ O ₃	0.22	0.19	0.18	0.07	0.06	0.22 0.18 0.05
F	0.24	0.29	0.27	0.18	0.42	0.15 0.42 0.37
Os=F	0.10	0.12	0.11	0.08	0.18	0.06 0.20 0.03
Total	97.73	97.50	97.63	98.09	96.55	98.78 97.15 97.29
structural formulae based on 12.5 oxygen atoms						
Si	2.976	3.000	2.983	2.995	2.956	2.987 2.980
Ti	0.003	0.006	0.024	0.032	0.006	0.017 0.004 0.005
Al	1.930	1.428	1.685	1.756	2.029	1.866 2.132 2.086
Fe ³⁺	0.315	0.596	0.388	0.227	0.291	0.221 0.192 0.174
Fe ²⁺	0.754	0.741	0.896	0.913	0.671	0.816 0.672 0.710
Mg	0.059	0.209	0.047	0.048	0.042	0.040 0.039 0.038
Zn	—	—	—	0.000	0.000	0.050 0.000 0.022
Mn	0.012	0.042	0.034	0.000	0.005	0.019 0.002 0.040
Ca	1.129	1.025	0.996	1.069	1.307	1.123 1.254 1.231
Σ(Y + REE)	0.814	0.951	0.943	0.961	0.713	0.895 0.710 0.748

sample FR1 is a least-altered rhyolite; CD2-8, talc-actinolite rock; CD5-10, CD5-11 and CD5-13, chloritites; OP1-5, massive sulfide ore; (4) indicates an average of 4 analyses; f, fresh (unmetamict) grains; m, metamict grains; wt. %, weight percent; *, Fe₂O₃ content estimated from charge balance; nd, not determined; Eu is invariably below its estimated detection limit of 0.05 wt. % Eu₂O₃; Na, K, Cl, Nb, Ta, W, Th, U, Er, and Yb were also sought for, but were not detected.

TABLE 2. COMPOSITIONS OF OTHER REE-RICH MINERALS FROM THE MATTAGAMI LAKE MINE

Mineral	Hln	Prs	Syn	Mnz	Exn	Ply	Zrn	
Sample	CD5-13	CD5-11	CD5-11	CD5-13	CD5-11	CD5-11	FR1	CD5-13
Analysis	(6)	(2)	(2)	(2)	(3)	(3)	(2)	(2)
SiO ₂ (wt. %)	25.11	0.00	0.00	0.00	4.48	1.05	26.93	26.78
TiO ₂	0.00	0.00	0.00	0.00	2.03	41.95	0.00	0.00
Al ₂ O ₃	4.84	0.00	0.00	0.05	2.21	0.94	1.83	1.69
FeO*	0.80	0.00	0.00	0.04	5.47	2.03	0.77	1.04
MgO	0.64	0.00	0.00	0.00	1.96	0.00	0.00	0.00
MnO	0.00	0.00	0.00	0.03	0.92	0.00	0.00	0.05
ZnO	0.35	0.00	0.00	0.00	0.00	0.00	nd	nd
CaO	15.13	10.14	17.54	0.00	2.39	0.27	1.40	1.38
P ₂ O ₅	nd	0.00	0.00	29.95	0.00	0.00	2.80	3.12
Nb ₂ O ₅	0.00	0.00	0.00	0.00	42.76	9.29	0.24	0.34
WO ₃	0.00	0.00	0.00	0.00	1.88	2.40	0.00	0.09
ZrO ₂	nd	nd	nd	nd	nd	nd	57.82	57.49
HfO ₂	nd	nd	nd	nd	nd	nd	1.67	1.74
ThO ₂	nd	nd	nd	0.76	1.10	0.82	0.31	0.33
UO ₃	nd	nd	nd	0.27	0.32	0.25	0.22	0.18
Y ₂ O ₃	23.12	3.32	1.46	0.95	13.10	15.20	1.89	1.75
La ₂ O ₃	0.00	9.03	8.41	13.42	0.05	0.05	0.00	0.00
Ce ₂ O ₃	0.00	21.85	19.47	31.07	1.42	0.00	0.08	0.00
Pr ₂ O ₃	0.00	3.06	2.72	4.71	0.32	0.00	0.00	0.00
Nd ₂ O ₃	0.12	15.21	13.15	18.40	2.24	0.50	0.15	0.00
Sm ₂ O ₃	0.24	2.95	2.67	3.47	1.98	1.33	0.08	0.10
Eu ₂ O ₃	0.42	0.15	0.12	0.15	1.22	1.78	0.00	0.00
Gd ₂ O ₃	2.58	2.41	2.23	2.02	4.53	8.44	0.21	0.22
Dy ₂ O ₃	4.77	0.46	0.33	0.23	5.69	9.05	0.43	0.44
Er ₂ O ₃	2.64	0.00	0.00	0.00	2.31	2.74	0.57	0.62
Yb ₂ O ₃	1.48	0.00	0.00	0.00	1.31	1.23	1.36	1.32
F	0.00	7.04	5.89	0.00	0.46	0.48	nd	nd
B ₂ O ₃ †	14.48							
H ₂ O†	3.68							
CO ₂ ‡		23.90	27.56					
O=F	0.00	2.96	2.48	0.00	0.19	0.20		
Total	100.43	96.56	99.07	99.81	97.08	98.66	98.81	98.68

see Table 1 for lithologies of samples; Exn represents euxenite; Hln, hellandite; Mnz, monazite; Prs, parisite; Ply, polycrase; Syn, synchisite; Zrn, zircon; wt. %, weight percent; *, total iron content as FeO; nd, not determined; †, B₂O₃ and H₂O contents in hellandite calculated according to the stoichiometry of Mellini & Merlino (1977); ‡, CO₂ contents in parisite and synchisite calculated according to their respective stoichiometries (see text).

Costa *et al.* (1983) revealed that the chlorite in the cross-cutting microveins is more magnesian than its counterpart in the matrix.

The Mattagami Lake mine is a Noranda-type Archean VMS deposit according to the two-fold classification of Morton & Franklin (1987). Although an epigenetic origin involving processes of hydrothermal replacement was proposed by earlier investigators, the polymetallic massive sulfide deposits, including the Mattagami Lake mine, are presently accepted as classic examples of syngenetic massive sulfide bodies, generated by contemporaneous, coupled volcanic, hydrothermal, and sedimentary processes (Roberts 1975, Roberts & Reardon 1978, MacGeehan & MacLean 1980, Costa 1980, Costa *et al.* 1983, 1984, MacLean 1984, MacLean &

Kranidiotis 1987). Based on a detailed study of major and trace-element geochemistry, mineral chemistry, stable isotopes, and fluid inclusions, Costa and coworkers (Costa 1980, Costa *et al.* 1983, 1984) concluded that the Mattagami Lake ore and gangue were precipitated from a brine pool on the seafloor (see also Pan *et al.* 1993a) that was ponded in a seafloor depression at the top of the Watson Lake Group rhyolite. Subsequently, the Mattagami Lake deposit was metamorphosed to a regional greenschist facies (Jolly 1978, Costa *et al.* 1983, Pan *et al.* 1993a). In addition, the bleached nature and the local presence of quartz and plagioclase phenocrysts with extremely irregular margins (corroded? *cf.* MacGeehan & MacLean 1980) in the least-altered rhyolite indicate that seafloor weathering also may have occurred in the area.

ANALYTICAL PROCEDURES

A large number of samples from the Mattagami Lake mine VMS deposit, including many in the Suffel Collection in the Department of Geology at the University of Western Ontario, were at our disposal. Petrographic observations of the present study were based mainly on a suite of samples (Fig. 1) collected by Costa (1980) and Costa *et al.* (1983). Six representative samples (one of massive sulfide ore, one of talc – actinolite rock, three of chloritite, and one of the least-altered rhyolite) were studied in detail by electron-microprobe (EMP) analysis and modal analysis. Characterization of the rare-earth minerals was made by a combination of transmitted- and reflected-light microscopy, X-ray diffraction, back-scattered electron imaging, and quantitative chemical analysis by EMP.

The chemical composition of rare-earth minerals and REE-bearing minerals (*i.e.*, zircon, titanite, and apatite) was determined using a JEOL JXA-8600 Superprobe fitted with four automated wavelength-dispersion spectrometers, at the University of Western Ontario. Analytical procedures were generally similar to those in Pan & Fleet (1990, 1991), but included four separate schedules because of the large number of elements required for comprehensive analyses. One schedule specifically for elements of atomic number less than 26 (Tables 1, 2) was carried out at an accelerating voltage of 15 kV, a beam current of 10 nA, a beam diameter of 2–5 μm , 20 s count, using minerals as standards. The other elements were included in three separate schedules (all containing Si, Al, Fe, and Ca for matrix-correction purposes) at an accelerating voltage of 25 kV, 20 nA beam current, 2–5 μm beam diameter, and 30 s count. Standards included the synthetic glasses of Drake & Weill (1972) for REE (with peak selections and peak-overlap corrections after Roeder 1985) and Y ($L\alpha$), $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ for Nb ($L\alpha$), manganotantalite for Ta ($M\alpha$), pure Th for Th ($M\alpha$), pure U for U ($M\alpha$), scheelite for W ($M\alpha$), and zircon for Hf ($L\alpha$) and Zr ($L\alpha$). Matrix corrections were made on-line using the Tracor Northern ZAF program.

Major elements and Nb, Y, and Zr for three samples of the footwall chloritite were determined by XRF at the University of Western Ontario. Eight samples were selected for REE analyses: four of massive sulfide ores, one of talc – actinolite rock, and three of chloritite. Concentrations of the REE were determined by instrumental neutron activation analysis (INAA) at the University of Western Ontario.

PETROGRAPHY AND MINERAL CHEMISTRY

Allanite

Allanite has been found as a trace constituent of variable size in several samples of the least-altered

rhyolite. Within the orebody, it is exceedingly rare in massive sulfide ores, but is locally abundant in the talc–actinolite rock (Fig. 2a). In the footwall chloritite, allanite has been found in all samples examined in this study. Most interestingly, there is a general increase in the modal abundance of allanite toward the orebody, which corresponds to the increase in intensity of chloritization. However, it was not possible to quantify the distribution of allanite, and exceptions to the correlation do exist on a local (*i.e.*, hand-specimen) scale, reflecting an inhomogeneous distribution of this mineral. Moreover, two textural varieties of allanite are readily distinguished in the footwall chloritite; extensively altered (nearly amorphous, metamict) grains are commonly surrounded by fresh (or less metamict) crystals (Figs. 2b, c). Grains of fresh allanite also occur in the cross-cutting veins of quartz, sulfides (Fig. 2d) and silicates, and two textural varieties of allanite in the talc–actinolite rock of the orebody also are locally distinguished. However, this textural distinction is not possible in the massive sulfide ores, where allanite occurs only as single discrete grains with no evidence of metamictization; a replacement texture involving allanite has not been observed either in the least-altered rhyolite.

Compositional zonation is a characteristic feature of allanite in the least-altered rhyolite and is present in a few grains in the talc – actinolite rock, but has not been observed in either of the textural varieties of allanite in the footwall chloritite. As expected, the metamict grains commonly yielded lower EMP oxide totals than the fresh grains (Table 1). The allanite grains in the talc – actinolite rock of the orebody are noticeably richer in Mg and Fe than those in other lithologies (Table 1), indicating control by whole-rock composition of host rocks. Several grains of allanite in direct contact with sphalerite from the orebody and in sample CD5-13 from the chloritite footwall zone contain a minor amount of Zn (up to 0.8 wt.% ZnO; Table 1). Zinc has been reported as a minor element in allanite grains associated with sphalerite by Ovchinnikov & Tzimbaleiko (1948) and by Johan *et al.* (1983). Several silicate minerals (*e.g.*, actinolite, dannemorite, and manganpyrosmalite) from the orebody of the Mattagami Lake mine also contain minor amounts of Zn (Pan *et al.* 1993a). A minor amount of F is present in all grains of allanite from the Mattagami Lake mine (Table 1), but Cl was not detected.

A minor amount of Y is present in all grains of allanite of the Mattagami Lake mine, and the metamict grains appear to have slightly higher values of this element than the fresh ones (Table 1). Surprisingly, Th and U were not detected in allanite by EMP in this study, including in the metamict grains, from which these two elements may have been preferentially leached to form monazite; see Figs. 2b, c; *cf.* Pan & Fleet 1991, Pan *et al.* 1993b). With respect to the

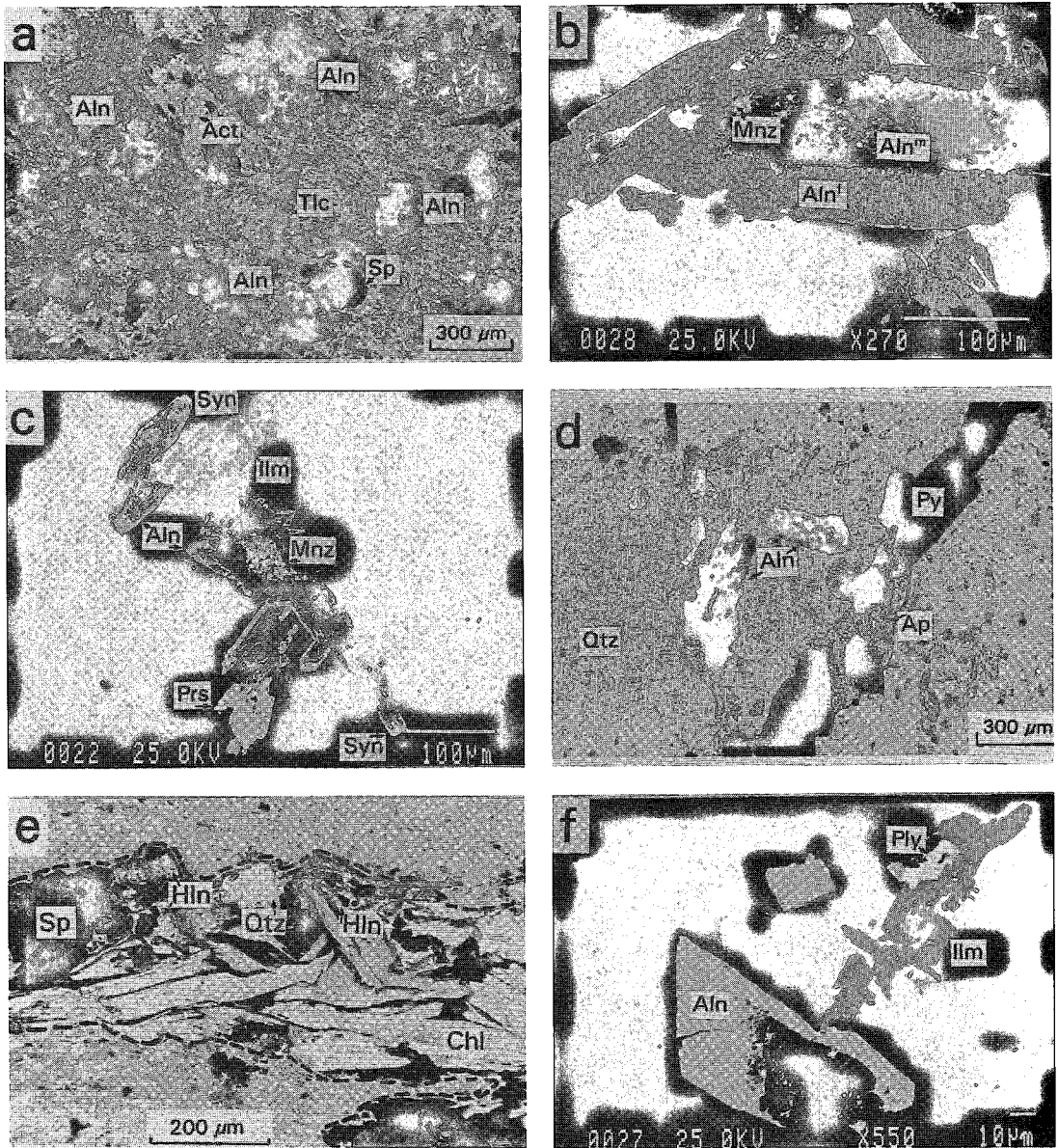


FIG. 2. Photomicrographs (a,d,e) and back-scattered electron images (b,c,f) illustrating rare-earth minerals from the Mattagami Lake mine: a) locally abundant allanite (Aln) in the talc – actinolite (Tlc and Act) rock of the orebody; b) fresh allanite (Aln^f) replacing metamict allanite (Aln^m) in the footwall chloritite, with monazite (Mnz) at their boundary; c) fresh allanite (Aln) replacing metamict allanite; note monazite (Mnz) after metamict allanite, and parisite (Prs) and synchisite (Syn) as small patches (bright) rimming fresh allanite; d) allanite (Aln) and apatite (Ap) in a cross-cutting vein of quartz (Qtz) and pyrite (Py) from the footwall chloritite; e) hellandite in a cross-cutting microvein (highlighted) of quartz (Qtz), sphalerite (Sp), and Mg-rich chlorite (Chl) from the footwall chloritite; f) polycrase (Ply) in intimate intergrowth with ilmenite (Ilm) from the footwall chloritite.

levels of the REE, the metamict grains are noticeably lower in total abundances than the fresh ones. However, the chondrite-normalized REE patterns of

these two textural varieties from a given sample are remarkably parallel to each other (Fig. 3c). Allanite grains in all rock types are characterized by marked

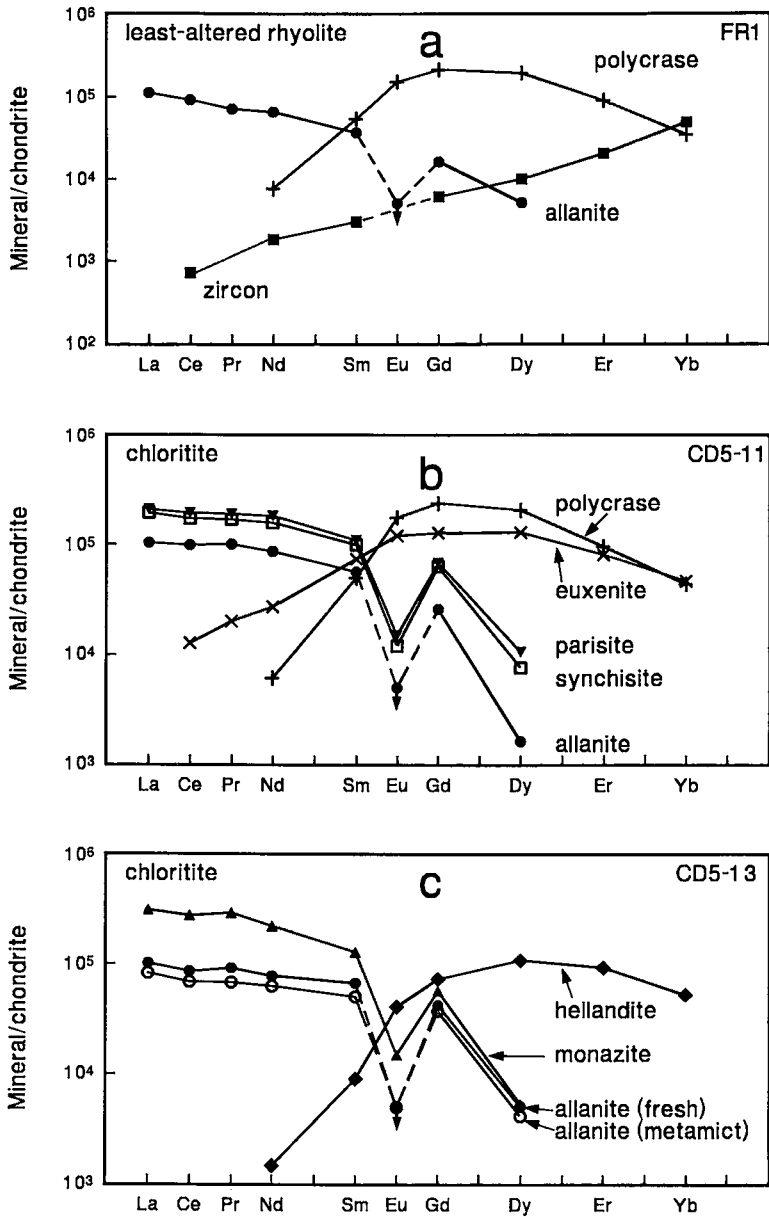


FIG. 3. Chondrite-normalized REE patterns of a) allanite, zircon, and polycrase in sample FR1; b) allanite, euxenite, parisite, polycrase, and synchisite in sample CD5-11; c) metamict allanite, fresh allanite, hellandite, and monazite in sample CD5-13. The negative Eu anomaly in allanite is indicated by its Eu abundances below the estimated detection-limit of 0.05 wt.% Eu_2O_3 (circles with down-pointing arrows). For clarity, monazite and zircon in sample CD5-11, and euxenite, polycrase, and zircon in sample CD5-13, are not shown. Chondritic values are those of Taylor & McLennan (1985).

enrichments of LREE over HREE (Fig. 3), and their degree of LREE/HREE fractionation varies from one sample to another. Europium is invariably undetectable in all cases, indicating pronounced negative Eu anomalies (Fig. 3).

Hellandite

Hellandite is a rare (Ca,Y,REE) borosilicate mineral, first reported in a granite pegmatite near Kragerø, Norway (Brøgger 1903; cf. Hogarth *et al.* 1972,

Mellini & Merlino 1977). To date, only four other occurrences have been described and, again, all are hosted by granite (Predazzo, Italy; Emiliani & Gandolfi 1965) and pegmatites (Wakefield, Quebec, Hogarth *et al.* 1972; Quyang, China, Ma *et al.* 1986; Tahra, Japan, Miyawaki *et al.* 1987). A crystal-structure determination by Mellini & Merlino (1977) established that hellandite has a silicoborate chain structure and a formula of $[\text{Ca}_{5.5}(\text{Y}, \text{REE})_{5.0} \square_{1.5}](\text{Al}, \text{Fe})_2(\text{OH})_4[\text{Si}_8\text{B}_8\text{O}_{40}(\text{OH})_4]$ for the Italian material.

Hellandite at the Mattagami Lake mine was found by petrographic investigation, and subsequently confirmed by EMP analysis and X-ray diffraction. Hellandite occurs as a major constituent within the cross-cutting microveins of quartz, sphalerite, chlorite (Fig. 2e), and phlogopite in sample CD5-13 from the chloritite footwall zone. It is the only B-bearing mineral in the Mattagami Lake mine; tourmaline, regarded as a common B-bearing mineral in massive sulfide deposits elsewhere [Slack & Coad (1989) and references therein], has not been observed.

The hellandite of the Mattagami Lake mine occurs as stubby prismatic grains (generally less than 100 μm in maximum dimension), with {100} polysynthetic twinning (see also Hogarth *et al.* 1972), and commonly in intimate intergrowth with sphalerite (Fig. 2e). X-ray single-crystal precession photographs are consistent with a space group $P2_1/a$ (*cf.* Hogarth *et al.* 1972, Mellini & Merlino 1977). X-ray powder diffraction (Gandolfi camera, $\text{CrK}\alpha$ radiation) yielded sharply defined diffraction lines and gave a 18.88(2), b 4.70(1), c 10.27(3) \AA , β 111.6(3) $^\circ$, in agreement with values in the literature (Hogarth *et al.* 1972).

At the Mattagami Lake mine, the hellandite contains a significant Al content and only minor amounts of Fe and Mn (Table 2). It is characterized by a marked enrichment in the middle REE (particularly Gd and Dy) over other REE, and thus exhibits a concave-downward chondrite-normalized REE pattern devoid of a Eu-anomaly (Fig. 3c).

Monazite, parisite, and synchisite

Monazite $[(\text{REE})\text{PO}_4]$ is present as small grains (less than 30 μm in diameter) along fractures and grain boundaries of metamict allanite (Figs. 2b, c) in samples CD5-11 and CD5-13. The monazite contains minor amounts of Y, Th, and U (Table 2), and is characterized by high LREE/HREE fractionation and a pronounced negative Eu-anomaly (Fig. 3c).

Parisite $[\text{Ca}(\text{REE})_2(\text{CO}_3)_3\text{F}_2]$ and synchisite $[\text{Ca}(\text{REE})(\text{CO}_3)_2\text{F}]$ are present as small grains (less than 30 μm in diameter) along the fractures of metamict allanite and also as small patches (less than 10 μm wide) rimming grains of fresh allanite (Fig. 2c) in sample CD5-11. Parisite and synchisite both contain significant contents of Y (Table 3) and have nearly parallel chondrite-normalized REE patterns;

TABLE 3. WHOLE-ROCK CONTENTS OF REE AND OTHER SELECTED ELEMENTS FROM THE MATTAGAMI LAKE MINE

Sample	CD2-8	CD5-10	CD5-11	CD5-13	FA5-1	FR1
La (ppm)	11	28	25	86	nd	55 ^a
Ce	30	86	83	248	nd	137
Nd	21	59	55	175	nd	97
Sm	5.1	16	14	43	nd	26
Eu	2.6	3.0	2.1	5.3	nd	5
Tb	0.62	3.2	3.3	9.8	nd	6
Yb	1.8	19	17	37	nd	14
Lu	0.18	3.0	2.8	5.5	nd	nd
La _N /Yb _N	4.40	1.01	0.96	1.59		2.65
log(Eu _N /Eu _N *)	0.63	-0.50	-0.79	-1.09		-0.60
Al ₂ O ₃ (wt. %)	nd	9.53 ^b	8.88	7.29	10.47	10.83
TiO ₂	nd	0.24	0.23	0.19	0.22	0.27
Zr (ppm)	nd	408	416	402	533	477
Y	nd	177	113	100	149	169
Nb	nd	17	22	18	28	49

see Table 1 for lithologies of samples; FA5-1 is a chloritite; ppm, parts per million; wt. %, weight percent; nd, not determined; a and b, data from Costa (1980) and Costa *et al.* (1983).

both minerals are characterized by marked enrichments in LREE over HREE and pronounced negative Eu-anomalies (Fig. 3b).

Euxenite and polycrase

Electron-microprobe analyses (Table 2) established that some extremely small (less than 20 μm in diameter) opaque grains in intimate intergrowth with ilmenite (Fig. 2f) in samples CD5-11 and CD5-13 are (Y,REE) Nb-Ti oxides with a general formula of AB_2O_6 . Rare-earth, AB_2O_6 -type Nb-Ti oxides include a number of mineral species (aeschnite, euxenite, polycrase, *etc.* *cf.* Ewing 1976, Černý & Ercit 1989). Both Nb- and Ti-dominant varieties have been analyzed in these two samples, although the latter (Ti-dominant) is relatively more common than the former. Both oxides have Y as the most abundant cation in the A site and, therefore, may be classified as euxenite and polycrase, respectively, according to the nomenclature of Ewing (1976). An X-ray powder-diffraction study of these oxides was unsuccessful owing to their small size. They probably are metamict and pervasively altered as well (*cf.* Ewing 1976, Černý & Ercit 1989). Several grains of polycrase also have been found in intimate intergrowth with ilmenite in a sample of the least-altered rhyolite (FR1).

The euxenite contains significant amounts of Al, Fe, Si and Ca, all of which are generally low in abundance in the polycrase (Table 2). Both minerals are characterized by high concentrations of the middle REE, and thus exhibit concave-downward chondrite-normalized REE patterns (Fig. 3b). However, the euxenite is considerably lower in absolute contents of Y and REE than the polycrase (Table 2). In addition, a

minor amount of W has been detected in both minerals (Table 2), and scheelite also occurs as a trace phase in their chloritite host-rocks. Thorium and U contents have also been detected but are surprisingly low in both euxenite and polycrase of the Mattagami Lake mine (Table 2; *cf.* Ewing 1976). The polycrase in the least-altered rhyolite has a similar, concave-downward chondrite-normalized REE pattern to those of the footwall chloritite (Fig. 3a).

Zircon, titanite, and apatite

Zircon is a common but minor or trace constituent in all samples of the least-altered rhyolite and the footwall chloritite. All grains of zircon are compositionally similar and contain significant amounts of Hf (up to 2 wt.% HfO_2), Y (2 wt.% Y_2O_3), and REE (3 wt.% $\Sigma\text{REE}_2\text{O}_3$, mainly the HREE; Table 2, Fig. 3a), and minor Th and U contents (less than 0.5 wt.% of their respective oxides).

Titanite and apatite are present in trace amounts in all rock types of the Mattagami Lake mine. A minor amount of Y (up to 0.65 wt.% Y_2O_3) has been detected in titanite. However, rare-earth elements were

not detected in either mineral by EMP analysis, even where they are in close association with allanite.

WHOLE-ROCK GEOCHEMISTRY

The whole-rock geochemistry (major- and selected trace-elements) of the massive sulfide orebody, footwall chloritite, and host volcanic rocks at the Mattagami Lake mine has been studied in detail by Costa and coworkers (Costa 1980, Costa *et al.* 1983). These authors recognized that the least-altered rhyolites and the footwall chloritite are all characterized by high concentrations of Zr, Y and Nb, and by constant ratios of Al_2O_3 to TiO_2 (Fig. 4a), Zr (Fig. 4b), Hf and Sc, which they attributed to a single parental rock of uniform initial composition. An inspection of the data in Table 2 of Costa *et al.* (1983) reveals that there is also a linear correlation between Y and Al_2O_3 (Fig. 4c), but no apparent correlation between Nb and Al_2O_3 (Fig. 4d). We attribute the latter to analytical problems for Nb in the study of Costa *et al.* (1983) based on the following three observations. Firstly, the mineralogical data of the present study indicate that Nb is immobile in the footwall chloritite (see below).

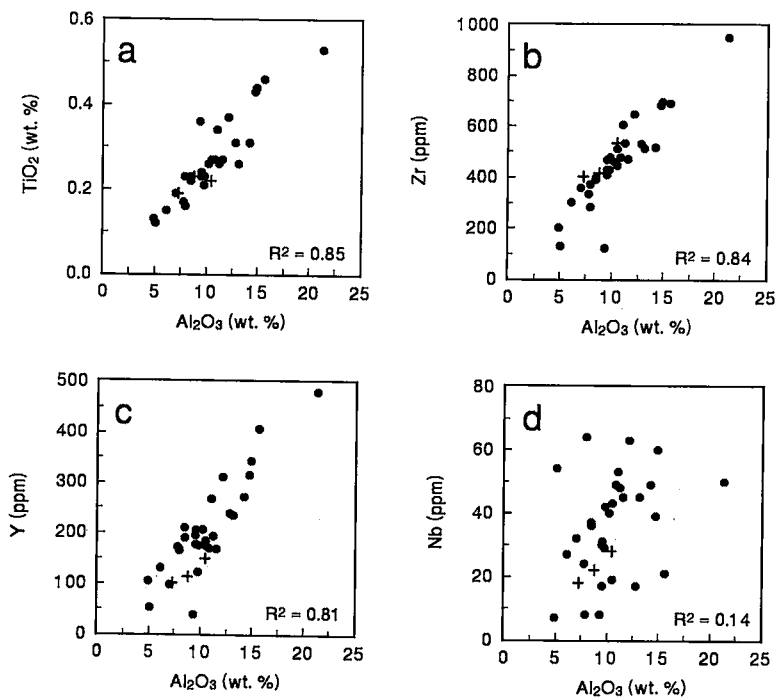


FIG. 4. Plots of TiO_2 , Nb, Y and Zr versus Al_2O_3 in the host rhyolite and the footwall chloritite of the Mattagami Lake mine. Solid circles represent data from Costa (1980) and Costa *et al.* (1983); crosses, data of this study. R^2 , squared correlation-coefficient.

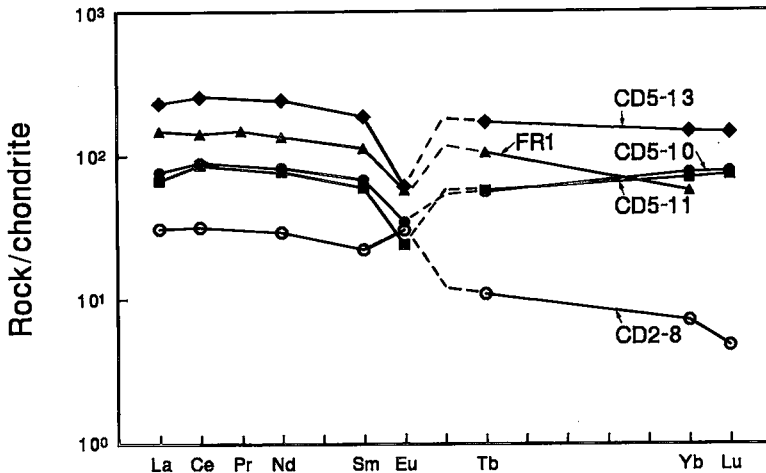


FIG. 5. Chondrite-normalized *REE* patterns of whole-rock samples of the Mattagami Lake mine. FR1 is the least-altered rhyolite of Costa (1980) and Costa *et al.* (1983); CD2-8 is a talc – actinolite rock; CD5-10, CD5-11, and CD5-13 are all chloritites. Chondritic values are those of Taylor & McLennan (1985).

Secondly, there appears to be a correlation between Nb and Al_2O_3 among the present three samples (Fig. 4d). Thirdly, MacLean & Kranidiotis (1987) have documented a linear correlation between Nb and Al_2O_3 in chloritites at the Phelps Dodge deposit in the Mattagami mining district.

The *REE* abundances in all four samples of the massive sulfide ores are near or below the limits of detection by INAA (results not presented here; see also Barrett *et al.* 1991). The talc – actinolite rock (CD2-8) from the orebody contains measurable contents of the *REE* (Table 3), giving a *LREE*-enriched chondrite-normalized pattern ($\text{La}_N/\text{Yb}_N = 4.40$), with a positive Eu anomaly [Fig. 5; $\log(\text{Eu}_N/\text{Eu}_N^*) = 0.63$]. Three samples of the footwall chloritite contain elevated concentrations of the *REE* (Table 3). Their chondrite-normalized patterns are characteristically flat ($0.96 < \text{La}_N/\text{Yb}_N < 1.59$) and exhibit a moderate negative Eu anomaly [$\log(\text{Eu}_N/\text{Eu}_N^*)$ ranging from -0.50 to -1.09], which appears to increase in magnitude with the increase in total *REE* contents (Fig. 5). Costa (1980) and Costa *et al.* (1983) presented chondrite-normalized *REE* patterns of two samples of the least-altered rhyolite (FR1 and FR2), both of which are generally flat, with a pronounced negative Eu anomaly (Fig. 5; see also Figure 5 of Costa *et al.* 1983). Therefore, the host rhyolites of the Mattagami Lake mine, which also are characterized by low Zr/Y ratios, high abundances of high-field-strength (HFS) elements, and low abundances of Sc and Sr (Costa 1980, Costa *et al.* 1983, Leshner *et al.* 1986), belong to the FIIIb subgroup of Archean felsic metavolcanic rocks, according to the classification of Leshner *et al.* (1986).

DISCUSSION AND CONCLUSIONS

Significance of rare-earth minerals

The importance of the rare-earth minerals and zircon to the *REE* abundances in their respective host-rocks can be assessed from mass-balance calculations based on comparison of the *REE* concentrations (Tables 1, 2) and modal data of these minerals with their respective whole-rock compositions (Table 4). We emphasize that several uncertainties exist in these calculations, even if the analytical uncertainties in the measurement of *REE* contents are considered to be minimal. For example, the inhomogeneous distribution of these minerals makes representative sampling for both whole-rock and modal analyses difficult, if not impossible. In particular, modal abundances are imprecise because of unfavorable statistics (*i.e.*, there are only a few grains of each of these minerals for more than 10,000 points counted for each sample, and 50,000 points for sample CD5-13). In addition, the compositional heterogeneity of allanite makes accurate estimation of the average *REE* contents in this mineral difficult. However, with the exception of La in CD5-11, the results of all five samples are similar (Table 4) and therefore considered to be representative.

Many studies of granite and rhyolite indicate that trace or minor amounts of rare-earth minerals, such as allanite and monazite, and other accessory minerals (*e.g.*, zircon, titanite and apatite) commonly control the characteristics of the *REE* during magmatic differentiation (*e.g.*, Michael 1988, Stix & Gorton 1990, and

TABLE 4. PROPORTION (%) OF WHOLE-ROCK REE, Zr, Y AND Nb IN ALLANITE, ZIRCON AND POLYCRASE, AS DETERMINED FROM MASS-BALANCE CALCULATION

Sample	CD2-8	CD5-10	CD5-11	CD5-13	FR1
	allanite				
Modal abundance*	0.02	0.07	0.09	0.248	0.10
La	72	90	125	96	74
Ce	63	75	89	74	64
Nd	54	72	86	71	47
Sm	37	58	71	78	32
	zircon				
Modal abundance*		0.09	0.09	0.090	0.08
Yb		57	67	29	68
Zr		95	93	97	72
Y			12	14	7
	polycrase				
Modal abundance*			0.03	0.048	0.02
Yb			19	14	15
Y			32	57	14
Nb			91	84	27

see Table 1 for lithologies of samples; *, modal abundances (%) of allanite, zircon, and polycrase in each sample are based on 10,000 points over two thin sections, except for sample CD5-13 on 50,000 points over 10 thin sections.

references therein). Table 4 shows that a large proportion of the *LREE* in the least-altered rhyolite of the Mattagami Lake mine resides in allanite, whereas the majority of the *HREE* (as monitored by Yb) is hosted by polycrase and zircon. However, the *REE* characteristics of the host rhyolite of the Mattagami Lake mine VMS deposit may not be controlled by the crystallization of accessory minerals during volcanism, because the rare-earth minerals in the least-altered rhyolite (e.g., polycrase) probably postdated the primary magmatic crystallization (see below). Stix & Gorton (1990) reported significant variations of Zr and *LREE* contents in rhyolites, related to the crystallization of zircon and a *LREE*-rich phase(s) which, in turn, may be controlled by iron and volatile contents of the magma.

Table 4 also shows that allanite contains a large portion of the *LREE* in the footwall chloritite and the talc – actinolite rock of the orebody. Similarly, a significant proportion of the *HREE*, Zr, Nb, and Y in the footwall chloritite is hosted by polycrase and zircon (Table 4). Therefore, any preferential dissolution (or resistance to dissolution), crystallization, and recrystallization of these minerals during the seafloor hydrothermal alteration and the subsequent regional metamorphism (see below) would profoundly modify the *REE* characteristics of these rocks.

The significance of these rare-earth minerals, particularly allanite, and zircon as major carriers of *REE* is not confined to the Mattagami Lake mine. Present observations extend this conclusion to many other well-known Canadian VMS camps (e.g., Kidd Creek, Manitouwadge, and Sturgeon Lake, Ontario; Noranda, Quebec; Snow Lake, Manitoba; see also Pan & Fleet 1993). It is noteworthy that allanite is by far the most abundant rare-earth mineral in all of the above camps, although monazite and xenotime have been reported recently by Schandl *et al.* (1991) to be more abundant than allanite in three Ontario VMS deposits (i.e., Kidd Creek, Geco at Manitouwadge, and Winston Lake). We note that allanite, particularly in the form of metamict grains, can be easily overlooked or misidentified in VMS and other ore deposits. Indeed, rare-earth minerals (mainly allanite and, to a lesser extent, monazite) have recently been found to be largely responsible for the local concentration and remobilization of the *REE* in precious-metal deposits (e.g., Hemlo gold deposit, Ontario; Pan & Fleet 1990, 1991) and in the Thompson nickel sulfide deposit of Manitoba, mineralized in platinum-group minerals and gold (Chen *et al.* 1993, Pan & Fleet 1993).

Paragenesis of the rare-earth minerals

It is well known that seafloor weathering, with its oxidizing conditions, would result in separation of the less soluble Ce^{4+} from the trivalent *REE*, consequently leading to a significant Ce anomaly visible in chondrite-normalized *REE* patterns (Graf 1977, Elderfield & Greaves 1981, MacLean 1988). Cerium anomalies are not present in any samples examined in the present study (Fig. 5), and the small ones in the least-altered rhyolites in Figure 5 of Costa *et al.* (1983) are probably attributable to minor analytical errors for Pr (Fig. 5). Therefore, seafloor weathering does not appear to have had a significant effect on the *REE* systematics of the Mattagami Lake deposit.

It has been demonstrated by Costa (1980) and Costa *et al.* (1983) that the Mattagami Lake mine VMS deposit was formed by syngenetic ore-forming processes during hydrothermal alteration on the seafloor; subsequently, it was metamorphosed to a regional greenschist facies (Pan *et al.* 1993a). However, distinction of the effects of these two events within the orebody and the footwall chloritite of the Mattagami Lake mine has proven to be difficult, because of similarity in the mineral assemblages (Pan *et al.* 1993a). Indeed, the very existence of a low- or very-low-grade prograde metamorphism in many VMS deposits, including that at the Mattagami Lake mine, was commonly ignored in many previous studies of these deposits (cf. Slack & Coad 1989). Recently, Schandl *et al.* (1990, 1991) suggested that much of the present sericite – chloritite alteration at Kidd Creek postdated the syngenetic mineralization by

50 to 100 million years. Pan *et al.* (1993a) suggested that the pyrosmalite-series minerals and some other silicates (*e.g.*, phlogopite and the Mg-rich chlorite in the cross-cutting veins of the footwall chloritite; see also Slack & Coad 1989) of the Mattagami Lake mine formed during the greenschist-facies regional metamorphism.

Zircon is a common accessory mineral in almost all rhyolites (*e.g.*, Stix & Gorton 1990). Zircon grains in metamorphosed felsic volcanic rocks from the Abitibi greenstone belt, including those in volcanic rocks associated with the Kidd Creek orebody (Nunes & Pyke 1981), commonly yield U/Pb ages consistent with the age of the felsic volcanism (Corfu *et al.* 1989). Therefore, the zircon in the least-altered rhyolite of the Mattagami Lake mine is interpreted to be a relict, igneous phase. Similarly, the zircon grains in the footwall chloritite, of similar chemical composition to those in the least-altered rhyolite, also are most likely relict, and igneous in origin.

The fresh grains of allanite replacing the metamict ones (*e.g.*, Figs. 2b, c) in the footwall chloritite and the talc – actinolite rocks of the orebody must have crystallized later in the paragenetic sequence, and probably during the greenschist-facies regional metamorphism. This is supported by the local presence of grains of fresh allanite in the cross-cutting veins and microveins of quartz (Fig. 2d), phlogopite, and Mg-rich chlorite. Similarly, monazite, parisite, and synchisite, all in close association with fresh grains of allanite (and replacing metamict allanite) most likely crystallized during the regional metamorphism. This is consistent with the recent studies by Schandl & Gorton (1991) and Schandl *et al.* (1990, 1991). These authors obtained U–Pb ages from monazite, allanite, and rutile in three Ontario VMS deposits (Kidd Creek, Geco, and Winston Lake) that were much younger than their respective volcanic host-rocks. The hellandite of the Mattagami Lake mine, which is restricted to the cross-cutting microveins, also is interpreted to be part of the greenschist-facies regional metamorphic assemblage and, therefore, represents a new type of occurrence for this rare mineral (see above).

The remaining of rare-earth minerals in the Mattagami Lake mine are of uncertain origin. The distinction between the metamict and fresh grains of allanite (Figs. 2b, c) is certainly compositional (*i.e.*, higher U and Th in the former), because the metamict grains are not significantly older relative to the time required for metamictization (*cf.* Pan *et al.* 1993b). The apparent replacement relationship of the metamict grains of allanite by fresh ones does indicate that the former may have crystallized during an earlier paragenetic sequence, such as the seafloor hydrothermal alteration responsible for the base-metal mineralization and chloritization. This is supported by the apparent (but presently not quantified) increase in modal abundance of this mineral in the footwall

chloritite, accompanying the increase in intensity of chloritization toward the orebody.

Euxenite and polycrase in the least-altered rhyolite and the footwall chloritite are associated exclusively with skeletal ilmenite and therefore might be relict, and igneous in origin. However, their small grain-size and irregular shape argue against this interpretation. We suggest that they originated by replacement, and that their specific location was controlled by the proximity of a favorable host, with one oxide replacing another. Thus, these rare-earth minerals would have formed during the initial devitrification and recrystallization of the rhyolite groundmass, that is, in a late-magmatic phase, or at the time of the seafloor alteration, or in the subsequent diagenesis. Alternatively, euxenite and polycrase may have formed during the low-grade metamorphism, representing a final recrystallization of the Y, Nb and HREE oxides. In any event, euxenite and polycrase represent only a very local remobilization of REE, and we believe that the mobility of middle and HREE in the least-altered rhyolite and the footwall chloritite was constrained by their close association with chemically resistant phases and components (*i.e.*, zircon and Y,Nb-oxides). It is noteworthy that euxenite and polycrase in granitic pegmatites are found in assemblages attributed to metasomatic replacement rather than in those of primary magmatic crystallization (Černý & Ercit 1989, Hanson *et al.* 1992). Also, allanite in the least-altered rhyolite most likely formed during low-grade metamorphism.

Comments on REE mobility

There is little doubt that REE are mobile during the extensive hydrothermal alteration that occurred within and around many VMS deposits (Campbell *et al.* 1984, MacLean 1988, Whitford *et al.* 1988, Schandl & Gorton 1991, Schandl *et al.* 1991, among others). REE mobility in the footwall chloritite of the Mattagami Lake mine is demonstrated by not only a wide range of total REE abundances (Table 3), but also varying inter-REE ratios (*e.g.*, La_N/Yb_N ; Table 3), particularly compared to the least-altered rhyolite (Fig. 5). In addition, the apparent general increase in the modal abundance of allanite in the footwall chloritite toward the orebody also indicates REE mobility. Recent studies by Schandl and coworkers (Schandl & Gorton 1991, Schandl *et al.* 1991) suggest that mobilization of the REE in the alteration haloes around VMS deposits postdated the syngenetic ore-forming processes, contradicting earlier studies (*e.g.*, Campbell *et al.* 1984, MacLean 1988, Whitford *et al.* 1988), which linked the alteration assemblages (and consequently the REE remobilization) to the hydrothermal alteration on the seafloor responsible for the syngenetic ore-forming processes. The present study shows that the seafloor hydrothermal alteration

and the subsequent, greenschist-facies regional metamorphism have both contributed to the REE characteristics of the rocks at the Mattagami Lake mine VMS deposit. Much of the observed deposit-scale remobilization of the REE probably occurred during the seafloor hydrothermal alteration. The remobilization of the REE during the low-grade regional metamorphism at the Mattagami Lake mine was very likely localized in scale (see also Pan & Fleet 1990, 1991, 1993). The low-grade regional metamorphism, the last event to cause recrystallization, was more significant in defining the present mineralogy of the REE.

Many studies (e.g., Campbell *et al.* 1984, MacLean 1988, Whitford *et al.* 1988, Schandl *et al.* 1991) have documented that LREE are relatively more mobile than HREE in alteration pipes or haloes associated with VMS deposits. For example, Campbell *et al.* (1984) observed that at Kidd Creek, the LREE were preferentially leached from a stringer copper zone and deposited in an overlying chloritized rhyolite. Schandl *et al.* (1991) noted extensive depletion in the LREE in the sericite schist at the Geco mine, Manitouwadge. The present study shows that the observed remobilization of the LREE at the Mattagami Lake mine was probably largely related to a preferential dissolution in the host rhyolite and reprecipitation as allanite in the chloritite proximal to the orebody. Both of these processes may be temperature-dependent. MacLean (1988) suggested that significant depletions in the LREE are typical of chloritites that have experienced relatively high-temperature leaching, whereas LREE additions simply reflect precipitation of LREE-enriched minerals from the fluid at lower temperatures.

In contrast to the LREE, the HREE in the alteration pipes below VMS deposits are commonly found to be immobile or less mobile (Campbell *et al.* 1984, MacLean 1988, Whitford *et al.* 1988). This appears to be in contradiction with the results of hydrothermal experiments and thermodynamic calculations (e.g., Cantrell & Byrne 1987, Wood 1990), which demonstrated that there is an increased stability of REE complexes (e.g., carbonate, fluoride, *etc.*) with increase in atomic number. The present study shows that most of the HREE in the rhyolite of the Mattagami Lake mine reside in a refractory phase (zircon) and two other phases of uncertain origin (polycrase and euxenite).

In addition, it has been suggested that many high-field-strength (HFS) elements, such as Zr, Hf, and Nb, were highly immobile in the alteration pipes below several VMS deposits (Campbell *et al.* 1984, MacLean & Kranidiotis 1987, MacLean 1988, Whitford *et al.* 1988). This is supported in the Mattagami Lake mine by the linear correlations of these elements (except for Nb, see discussion above) with Al_2O_3 (Fig. 4; *cf.* Costa 1980, Costa *et al.* 1983). The present study indicates that the resistance of zircon and Y,Nb-oxides may have contributed greatly

to the immobility of HFS elements and the HREE in the chloritite of the Mattagami Lake mine. Yttrium, on the other hand, is considered to be immobile by MacLean (1988) and Whitford *et al.* (1988), but mobile by Campbell *et al.* (1984). The linear correlation between Y and Al_2O_3 in the chloritite (Fig. 4c) indicates that Y was probably immobile during the seafloor hydrothermal alteration at the Mattagami Lake mine. However, the occurrence of hellandite in cross-cutting microveins indicates mobility of this element during the low-grade regional metamorphism. It is noteworthy the remobilization of Y during the low-grade metamorphism also is extremely localized in scale (*i.e.*, microveins) and is not evident, even in the whole-rock data (Fig. 4c).

An increase in the magnitude of the negative Eu anomaly in the footwall chloritite with increasing LREE/HREE fractionation and total REE abundances also has been documented in several VMS deposits (Whitford *et al.* 1988). This is commonly attributed to a preferential partitioning of this element to the hydrothermal fluid as Eu^{2+} , and therefore is an indicator for low $f(O_2)$ conditions (MacLean 1988, Whitford *et al.* 1988, and references therein). The lack of data for Eu in allanite and zircon in the present study (Tables 1, 2) prevents a direct evaluation of the relative importance of the seafloor hydrothermal alteration and the low-grade regional metamorphism to the negative Eu anomaly in the footwall chloritite of the Mattagami Lake mine. It is assumed, however, that the Eu remobilization occurred mainly during the seafloor hydrothermal alteration and was consistent with the low $f(O_2)$ conditions that produced the pyrite + pyrrhotite \pm magnetite assemblages during ore formation (see also MacLean 1988). A positive Eu anomaly in the talc - actinolite rock of the orebody (Fig. 5) is common to many VMS deposits and modern vent-sites (Whitford *et al.* 1988, Barrett *et al.* 1991, and references therein). This is also attributed to a preferential remobilization of Eu (as Eu^{2+}) from the footwall (Whitford *et al.* 1988), because it is complementary to the increased negative Eu anomaly within the footwall chloritite.

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