UNGAVAITE, Pd$_4$Sb$_3$, A NEW INTERMETALLIC MINERAL SPECIES FROM THE MESAMAX NORTHWEST DEPOSIT, UNGAVA REGION, QUEBEC, CANADA: DESCRIPTION AND GENETIC IMPLICATIONS

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Abstract

Ungavaite, Pd$_4$Sb$_3$, is a new intermetallic mineral species discovered in the Mesamax Northwest deposit, Cape Smith fold belt, Ungava region, northern Quebec. It is associated with monoclinic pyrrhotite, pentlandite, chalcopyrite, galena, sphalerite, cobaltite, a chlorite-group mineral and magnetite. Associated precious-metal minerals include another new mineral species, naldrettite (Pd$_2$Sb), sperrylite, sudburyite, michenerite, Au–Ag alloy, altaite, petzite (Ag$_3$AuTe$_4$) and hessite (Ag$_2$Te). Ungavaite occurs as rare anhedral grains with inclusions of Au–Ag alloy or with attached chalcopyrite and a chlorite-group mineral. Grains of ungavaite vary in size (equivalent circle diameter) from *ca*. 36 to 116 μm, with an average of 73 μm (*n* = 4). Neither cleavage nor fracture was observed. It is distinctly anisotropic, non-pleochroic, has weak bireflectance and does not exhibit discernible internal reflections. Ungavaite appears bright creamy white in association with pentlandite, pyrrhotite, the chlorite-group mineral

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and chalcopyrite. Reflectance values in air (and in oil) for R_1 and R_2 are: 50.2, 50.5 (37.6, 38.0) at 470 nm, 55.6, 55.9 (43.2, 43.5) at 546 nm, 57.9, 58.3 (45.9, 46.3) at 589 nm and 60.2, 60.7 (48.1, 48.5) at 650 nm. The average result of 16 electron-microprobe analyses on one particle is: Pd 54.53, Fe 0.13, Te 0.09, Sb 44.59, Bi 0.42, Hg 0.19, and As 0.20, total 100.15 wt. %, corresponding to empirical formula (based on seven atoms) $Pd_{4.062}(Sb_{2.893}Fe_{0.017}Bi_{0.017}Hg_{0.006}Te_{0.005})_{\Sigma2.938}$, ideally Pd_4Sb_3. The mineral is the Pd-dominant analogue of genkinite. It is tetragonal, crystallizing in one of the possible space-groups $P4_12_12$, $P4_122$, $P4_32_12$, $P4_22_12$, or $P4_222$. Cell dimensions are: a 7.7388 (4), c 24.145(1) Å, with V = 1446.02(1) Å^3 and Z = 8. The calculated density is 7.264(1) g/cm^3. The strongest six lines in the X-ray powder-diffraction pattern [d in Å(I)(hkl)] are: 3.008(90)(008), 2.268(100)(134), 2.147(30)(230), 1.9404(60)(400), 1.2043(30)(22$\underline{1}$8, 452), 1.2002(30)(624). The mineral formed in a narrow (Pd + Sb)-rich zone separating massive and disseminated sulfides. It is likely a product of the hydrothermal remobilization of Pd (and possibly Sb) from the pre-existing massive sulfides. Phase relations suggest that ungavaite developed at a temperature below 400°C, possibly through a solid-state order–disorder transformation.

Sommaire

La ungavaïte, Pd_4Sb_3, est une nouvelle espèce minérale intermétallique découverte dans le gisement Mesamax Northwest, dans la ceinture orogénique du Cap Smith, région d'Ungava, dans le nord du Québec. Lui sont associés pyrrhotite monoclinique, pentlandite, chalcopyrite, galène, sphalérite, cobaltite, un membre du groupe de la chlorite, et magnétite. Les minéraux suivants porteurs de métaux précieux lui sont aussi associés: naldrettite (Pd_2Sb), aussi une nouvelle espèce minérale, sperrylite, sudburyite, michenerite, alliage Au–Ag, altaïte, petzite (Ag_3AuTe_4) et hessite (Ag_2Te). L'ungavaïte se présente en rares grains xénomorphes avec inclusions d'un alliage Au–Ag ou rattachée à la chalcopyrite et un minéral du groupe de la chlorite. Ces grains varient entre environ 36 to 116 μm (diamètre d'un cercle équivalent), et sont en moyenne 73 μm (n = 4). Nous ne pouvons déceler ni clivage, ni fracture. Le minéral est distinctement anisotrope et non-pléochroïque, fait preuve d'une faible biréflectance, et ne montre aucune réflexion interne discernable. L'ungavaïte est blanc crémeux brillant en association avec la pentlandite, la pyrrhotite, la chlorite, et la chalcopyrite. Les valeurs de réflectance dans l'air (et dans l'huile) pour R_1 et R_2 sont: 50.2, 50.5 (37.6, 38.0) à 470 nm, 55.6, 55.9 (43.2, 43.5) à 546 nm, 57.9, 58.3 (45.9, 46.3) à 589 nm, et 60.2, 60.7 (48.1, 48.5) à 650 nm. Le résultat moyen de seize analyses d'une particule, effectuées avec une microsonde électronique, est: Pd 54.53, Fe 0.13, Te 0.09, Sb 44.59, Bi 0.42, Hg 0.19, et As 0.20, pour un total de 100.15% (poids), ce qui correspond à la formule empirique (fondée sur sept atomes) $Pd_{4.062}(Sb_{2.893}Fe_{0.017}Bi_{0.017}Hg_{0.006}Te_{0.005})_{\Sigma2.938}$ ou, de façon idéale, Pd_4Sb_3. Le minéral serait l'analogue à dominance de Pd de la genkinite. La ungavaïte est tétragonale, et cristallise dans un des groupes d'espace suivants: $P4_12_12$, $P4_122$, $P4_32_12$, $P4_22_12$, ou $P4_222$. Les dimensions de la maille sont: a 7.7388 (4), c 24.145(1) Å, avec V = 1446.02(1) Å^3 et Z = 8. La densité calculée est 7.264(1) g/cm^3. Les six raies les plus intenses du spectre de diffraction (méthode des poudres) [d en Å(I)(hkl)] sont: 3.008(90)(008), 2.268(100)(134), 2.147(30)(230), 1.9404(60)(400), 1.2043(30)(22$\underline{1}$8, 452), et 1.2002(30)(624). On trouve l'ungavaïte dans une étroite zone enrichie en (Pd + Sb) entre les sulfures massifs et les sulfures disséminés. Elle résulterait probablement de la mobilisation hydrothermale du Pd (et possiblement du Sb) aux dépens des sulfures massifs. D'après les relations de phases, l'ungavaïte se serait développée au dessous de 400°C, peut-être au cours d'une réaction de mise en ordre.

(Traduit par la Rédaction)

Introduction

Ungavaite (УНГАВАИТ), ideally Pd_4Sb_3, is a new mineral species discovered in drill-core rejects (MXNW 02–50) from the Mesamax Northwest Ni–Cu–Co–PGE deposit (61°34'25" N and 73°15'36" W), located in the Cape Smith fold belt of the Ungava region, northern Quebec, Canada. The area is known for the many Ni–Cu–PGE showings and deposits contained within it, and currently hosts one operating mine, the Raglan deposit (Falconbridge Ltd.).

As part of an ongoing study to characterize the platinum-group mineral (PGM) assemblage from a (Pd + Sb)-rich zone in the Mesamax Northwest deposit, two previously unknown Pd antimonides have been recognized. The first, naldrettite (Pd_2Sb), recently described by Cabri *et al*. (2005), is by far the dominant Pd antimonide in this zone. In this report, we describe the characteristics and genetic implications of a second new Pd antimonide, ungavaite.

The name recalls the region in which the mineral was discovered. The mineral and mineral name were unanimously approved by the Commission on New Minerals and Mineral Names, IMA (IMA 2004–020). Holotype material is catalogued in the collections of the Natural History Museum, Cromwell Road, London, SW7 5BD, UK (polished section; catalogue number BM 2004, 34) and the Canadian Museum of Nature, Ottawa (polished section; catalogue number CNMMN 84397).

Occurrence and Associated Minerals

The Cape Smith fold belt, located in the Ungava (Nunavik) region of northern Quebec, is a 370-km-long, east–west-trending belt of lower to middle Proterozoic rocks representing a rifted continental margin and arc–continent collision zone. The belt consists of a klippe of Hudsonian fold-and-thrust rocks that have been thrust over the northern extremity of the Superior Province. The stratigraphy can be divided into three broad lithological groups: a lower sedimentary group, the central Povungnituk Group (shelf sediments and dominantly continental tholeiitic basalts) and the upper Chukotat Group (komatiitic and tholeiitic basalts). Mineralized Cu–Ni–PGE zones with a Ni:Cu ratio around 3:1 occur at the transition between the Povungnituk and Chukotat groups within a series of 1920 Ma peridotitic lenses that are interpreted to represent olivine orthocumulates focused in extrusive komatiitic flows. A series of deposits have been recognized in the area, each occurring as a channel or pod in topographic lows at or near the base of a composite sequence of peridotitic komatiitic basalts. The basalts are variably mineralized, commonly with ~1% fine, disseminated sulfides (principally pyrrhotite and pentlandite), grading into ore-grade areas with >10% disseminated, heavily disseminated or net-textured massive sulfides (pyrrhotite, pentlandite, chalcopyrite, pyrite and traces of magnetite and sphalerite). Chalcopyrite-rich stringers and veinlets, locally present in footwall rocks to the channel ore, are considered to represent remobilized ore.

Mesamax, discovered in the late 1960s, is found on the eastern margin of the Raglan South trend, specifically within the South trend. Generally, sulfide ores in the area display a Ni:Cu ratio of 1:1. The Mesamax Northwest deposit is located in the so-called Mesamax area, which contains the Main and NW grids. Geologically, it consists of a large, internally differentiated gabbronorite dike with a composition corresponding to komatiitic basalt or basaltic komatiite. The dike intruded tholeiitic basalt and silicate-facies iron formation of the Beauparlant Formation (Povungnituk Group), and contains disseminated to massive Cu–Ni–PGE mineralization. The mineralization occurs within a metapyroxenitic zone of the dike, specifically within a depression of the basal portion of the dike. Both the disseminated and the massive portions of the mineralized body have Pd contents varying from 3 to 10 ppm, with the Pt and Cu contents of the massive sulfides being considerably higher than those in the disseminated material. The one- to two-meter contact zone separating the massive and disseminated mineralization typically contains several tens of ppm Pd, about an order of magnitude greater than the mineralization on either side of it. In some samples, concentrations of Pd and Sb can reach 1100 and 1000 ppm, respectively. Without exception, the occurrence of such enriched samples coincides with the first appearance of massive sulfide in the drill cores

(J.E. Mungall, unpubl. data). Palladium mineralization in this Pd-enriched contact zone is clearly dominated by Pd antimonides. There is a notable absence of correlation between Pd and Cu in the Pd-rich samples (both of which are expected to behave incompatibly during crystallization of sulfide magmas), suggesting that such samples have been influenced by postmagmatic processes, rather than those that typify magmatic sulfide fractionation. It appears that both Pd and Sb were removed from the massive sulfides during a late-stage magmatic event (possibly deuteric) or during regional (amphibolite-grade) metamorphism and precipitated on the margin of the massive sulfide body.

Non-magnetic and magnetic heavy-mineral concentrates of sample 196406 (0.563 kg), obtained from drill-hole rejects (MXNW 02–50) were subjected to heavy-mineral separation using a HS–02 Hydroseparator (Rudashevsky $et\ al.$ 2001, 2002, Cabri 2003, 2004). More than 1000 grains of precious-metal-bearing minerals were found in the heavy-mineral concentrates, most being Pd antimonides. Only PGM from the non-magnetic fractions (<45, 45–75, 75–125, 125–180 and 180–350 μm) and one magnetic fraction (75–125 μm) were examined in detail, as this provided a sufficient number of PGM grains to characterize the sample. It should also be noted that those PGM in the magnetic fraction are not attached to magnetite, but had been entrained in the magnetic concentrate.

A total of 794 PGM grains from the heavy-mineral concentrates were analyzed by scanning electron spectrometry (SEM). Results of the SEM study indicate that the majority ($n = 622$) to be the new mineral naldrettite (Pd$_2$Sb), with lesser amounts of sudburyite (PdSb; $n = 67$) and rare grains of ungavaite ($n = 6$). Ungavaite is restricted to the non-magnetic concentrate (naldrettite was the only PGM found in the magnetic concentrate). Other PGM and precious-metal-bearing minerals present (both as inclusions and discrete grains) include, sperrylite (PtAs$_2$), michenerite (PdBiTe), gold–silver alloy ($n = 67$, representing 8.5% of all precious metal minerals) and two particles each of the tellurides petzite (Ag$_3$AuTe$_4$) and hessite (Ag$_2$Te). Naldrettite has an average composition ($n = 19$ for grains from the <45 and 75–125 μm fractions) of (Pd$_{1.996}$Fe$_{0.006}$)$_{\Sigma 2.002}$ (Sb$_{0.982}$As$_{0.014}$S$_{0.002}$)$_{\Sigma 0.998}$. Sudburyite has variable contents of Sb, Te and Bi, with an average ($n = 14$) composition of Pd$_{0.99}$(Sb$_{0.64}$Te$_{0.22}$Bi$_{0.22}$)$_{\Sigma 1.08}$. The Au–Ag alloy is silver-rich (Au$_{1.02}$Ag$_{0.98}$), on the basis of the average result of 10 analyses (energy-dispersion spectrometry). The common base-metal sulfides (BMS) consist of pyrrhotite, pentlandite, chalcopyrite, galena, sphalerite, and cobaltite. Altaite (PbTe) is also noted to occur, generally in conjunction with sudburyite. The pyrrhotite is considered to be monoclinic in symmetry as the empirical formula (based on $n = 7$) corresponds to (Fe$_{6.95}$Ni$_{0.04}$)$_{\Sigma 6.99}$S$_{8.01}$ (Ni content averages 0.4 wt.%, ranging from below detection to 0.6 wt.%). Pentlandite ($n = 7$) has Ni in excess of Fe and the empirical formula

$(Ni_{4.74}Fe_{4.24}Co_{0.35})_{\Sigma 9.33}S_{8.09}$. The average result of three analyses of cobaltite by energy-dispersion spectrometry (EDS) gives $(Co_{0.76}Ni_{0.16}Fe_{0.06})_{\Sigma 0.98}As_{0.95}S_{1.06}$. One analysis of sphalerite by EDS gave 6.8 wt.% Fe. Other associated minerals include a chlorite-group mineral, magnetite, chromite and calcite.

PHYSICAL AND OPTICAL PROPERTIES

In the concentrates, ungavaite occurs as liberated anhedral grains ($n = 3$; Figs. 1A, B, C), one grain with inclusions of Au–Ag alloy (Fig. 1F) and one with attached chalcopyrite and chlorite (Fig. 1D). Grains of ungavaite vary in size (equivalent circle diameter) from *ca.* 36 to 116 μm, with an average of 73 μm ($n = 4$). The mineral is metallic, opaque and dark grey in color. The streak was not determined. Cleavage appears to be absent, and no fracture was observed. A micro-indentation hardness could not be determined owing to the small size of the grains. The mineral appears to be somewhat malleable, as evidenced by its behavior during extraction from the grain mount. A measured density could not be determined owing to the small size of the grains involved. The calculated densities range from 7.257(1) (grain #28) to 7.264(1) g/cm^3 (grain #192, used for both X-ray diffraction and quantitative measurements of reflectance).

In plane-polarized reflected light, ungavaite appears bright creamy white in association with naldrettite,

pentlandite, pyrrhotite, chalcopyrite and chromite, and shows no discernible internal reflections. The mineral shows weak bireflectance, no pleochroism, and weak anisotropy, with rotation tints that are pale blue-grey to deep blue. Reflectance was measured (n_{oil} 1.515, DIN 58.884 at 20°C) relative to a WTiC standard (Zeiss 314), following the methodology of Stanley *et al.* (2002). The reflectance data and color values for the ungavaite grain that was analyzed (#192) are given in Tables 1 and 2.

CHEMICAL COMPOSITION

After the initial SEM–EDS analyses, chemical analyses (wavelength-dispersion spectrometry) were carried out using a JEOL 8900 electron microprobe, an accelerating voltage of 20 kV, a beam current of 20 nA, a beam diameter of 5 μm, and counting times of 50–100 s. Two grains (#28, #192) were analyzed multiple times, the results being given in Table 3. The empirical formulae (based on seven atoms) for the two grains analyzed are: $Pd_{4.062}(Sb_{2.893}Fe_{0.017}Bi_{0.017}Hg_{0.006}Te_{0.005})_{\Sigma 2.938}$ for grain #192 and $Pd_{4.042}(Sb_{2.889}As_{0.021}Fe_{0.018}Bi_{0.016}Hg_{0.007}Te_{0.006})_{\Sigma 2.957}$ for grain #28. The ideal formula is Pd_4Sb_3. Overall, results of analyses of the two grains are very similar, both in terms of major and minor elements. The complete absence of Pt in the mineral is of note, indicating a strong Pd:Pt fractionation.

X-RAY CRYSTALLOGRAPHY

X-ray powder-diffraction data (XRPD; Table 4) were collected on grain #192 with a Gandolfi camera 114.6 in diameter and Fe-filtered CoKα radiation ($\lambda = 1.7902$ Å). The observed intensities were determined from a scanned XRPD film. Ungavaite is considered to be isostructural with genkinite, $(Pt,Pd)_4Sb_3$ (Cabri *et al.* 1977), based on similarities in their X-ray powder patterns (PDF 29–1033) and chemical compositions. Results of the study of Cabri *et al.* (1977) on genkinite indicate that the crystal structure and space-group

TABLE 1. REFLECTANCE DATA FOR UNGAVAITE

λ nm	R_1 %	R_2 %	$^{im}R_1$ %	$^{im}R_2$ %	λ nm	R_1 %	R_2 %	$^{im}R_1$ %	$^{im}R_2$ %
400	45.0	45.3	32.6	32.9	560	56.4	56.8	44.0	44.4
420	46.4	46.7	33.9	34.2	580	57.4	57.8	45.3	45.7
440	47.8	48.1	35.5	35.9	**589**	**57.9**	**58.3**	**45.9**	**46.3**
460	49.4	49.7	36.9	37.3	600	58.4	58.8	46.4	46.8
470	**50.2**	**50.5**	**37.6**	**38.0**	620	59.2	59.7	47.2	47.7
480	50.9	51.2	38.3	38.7	640	59.8	60.4	47.8	48.2
500	52.4	52.7	39.8	40.2	**650**	**60.2**	**60.7**	**48.1**	**48.5**
520	54.0	54.3	41.3	41.7	660	60.5	61.0	48.4	48.8
540	55.2	55.6	42.9	43.2	680	60.7	61.3	49.0	49.4
546	**55.6**	**55.9**	**43.2**	**43.5**	700	61.6	62.0	49.6	50.1

The COM recommended values are shown in bold.

TABLE 2. COLOR VALUES FOR UNGAVAITE

	C illuminant				A illuminant			
	R_1	R_2	$^{im}R_1$	$^{im}R_2$	R_1	R_2	$^{im}R_1$	$^{im}R_2$
X	0.326	0.326	0.332	0.331	0.461	0.461	0.465	0.465
Y	0.332	0.332	0.337	0.337	0.412	0.412	0.413	0.413
Y (%)	56.0	56.4	43.7	44.1	56.8	57.2	44.6	45.0
λ_d	578	578	578	578	587	587	587	587
P_e %	8.5	8.5	11.3	11.2	12	12.2	16.2	16.2

TABLE 3. ELECTRON-MICROPROBE DATA FOR UNGAVAITE

Element	wt.%[1]	range[1]	wt.%[2]	range[2]	standard
As	0.20	0.17 – 0.26	n.d.	n.d.	Pd₃As (synthetic
Fe	0.13	0.05 – 0.31	0.12	0.04 – 0.40	chalcopyrite
Te	0.09	0.03 – 0.14	0.08	0.03 – 0.14	Te
Sb	44.59	43.32 – 44.95	43.95	43.62 – 44.19	NiSb (synthetic)
Bi	0.42	0.34 – 0.48	0.44	0.35 – 0.50	Bi
Hg	0.19	0.09 – 0.35	0.16	0.09 – 0.29	temagamite (synthetic)
Pd	54.53	53.31 – 54.98	53.94	52.76 – 54.64	Pd₃As (synthetic)
Total	100.15	95.97 – 98.49	98.69	97.86 – 99.08	

1. Grain #192, 16 analyses; 2. Grain #28, 15 analyses. In addition, the following elements were sought, but not detected: Se, S, Ag, Zn, Cu, Ni, Co, Pt, Rh and Ru. The ideal formula Pd₄Sb₃ requires Pd 53.82, Sb 46.18, total 100 wt.%.
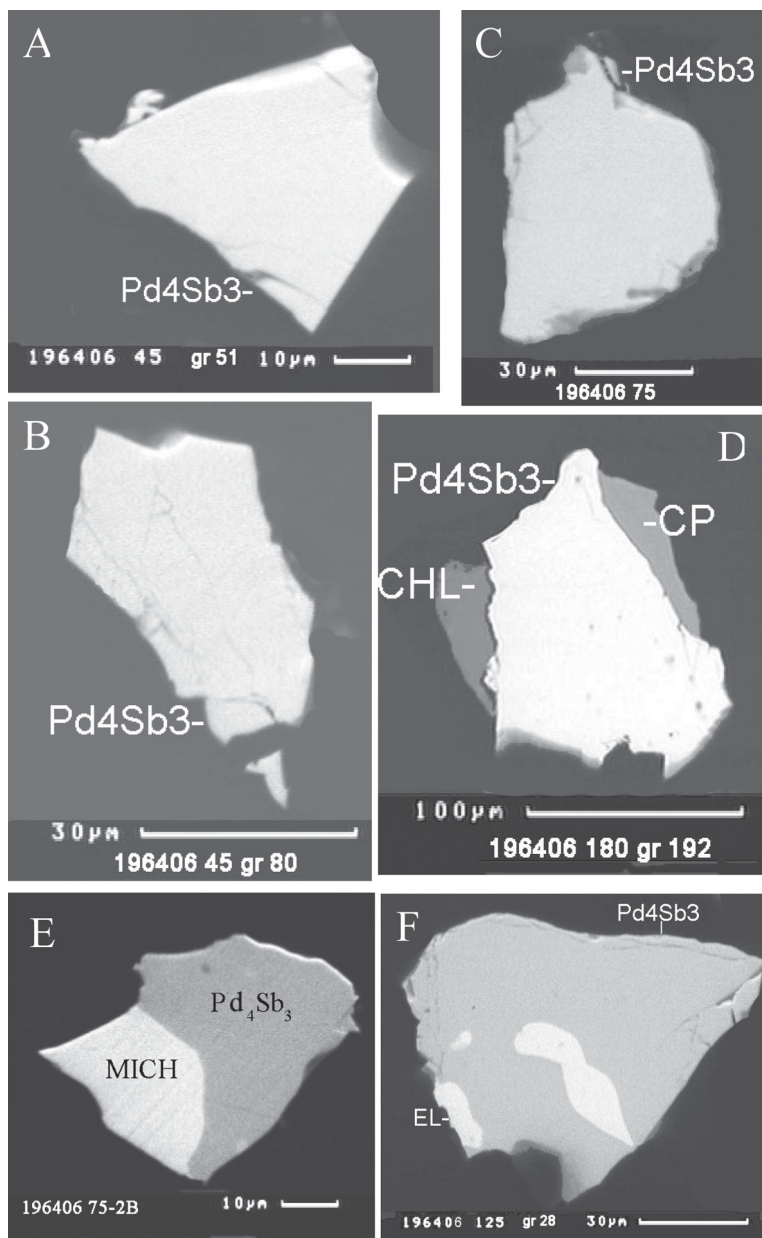
FIG. 1.   Back-scattered electron images of ungavaite. A, B. Monomineralic, liberated grains (<45 μm). C. Monomineralic, liberated grain (45–75 μm). D. Grain #192 with attached chlorite-group mineral (CHL) and chalcopyrite (CP) (180–350 μm). E. Grain with large inclusion of michenerite (MICH) (45–75 μm). F. Grain with droplet-like inclusions of Au–Ag alloy (EL) (75–125 μm).

TABLE 4. POWDER X-RAY-DIFFRACTION DATA FOR UNGAVAITE

Ungavaite d_{obs} (Å)	d_{calc} (Å)	hkl	I_{meas}	Genkinite** d_{obs} (Å)	hkl	I_{meas}
1.2912	1.2898	600	5			
1.2852	1.2849*	5110	5	1.285	1510	5
1.2788	1.2797	535	1			
1.2633	1.2649*	3411	10	1.265	3411	40
1.2492	1.2507	2118	20			
	1.2483	1511				
1.2465	1.2449*	614	20	1.244	164	30
				1.215	358	10
1.2043	1.2044	2218	30	1.202	0020	20
	1.2026	452				
1.2002	1.1992	624	30	1.191	0416	10
1.1860	1.1851*	454	10	1.185	454	10
1.1731	1.1723	618	10			
1.1705	1.1694*	5212	15	1.169	2512	20
1.1527	1.1536	630	10			
	1.1532	627				
	1.1524	0220				
	1.1523	631				
	1.1519	3414				
1.1382	1.1393	1514	5	1.140	363	20
	1.1376	6010				
	1.1375	2318				
	1.1373	0121				
1.1280	1.1278*	3119	1	1.129	3119	10
1.1129	1.1133*	629	1	1.113	629	5
1.0926	1.0934	0320	10	1.089	552	5
	1.0933	551				
	1.0915	6210				
	1.0913	1418				
1.0832	1.0844	553	5			
	1.0827	3120				
1.0752	1.0761	1122	5			
	1.0753	6112				
1.0652	1.0660	706	15			
1.0608	1.0598*	639	1	1.059	639	5
1.0505	1.0502	0321	5			
1.0497	1.0496	1613	5			
1.0409	1.0409	6310				
	1.0407	5216	5			
1.0194	1.0186	2222	5			
1.0114	1.0112	648	5	1.012	0223	40B
1.0008	1.0014	1322	15	1.002	278	10
	1.0008	3612				
0.9978	0.9981	6115	10			
	0.9979	6214				
	0.9976	1024				
0.9687	0.9689	7012	20			
0.9663	0.9660	2124	15	0.964	082	5
	0.9665	4515				
0.9638	0.9641	4611	5			
0.9414	0.9414	568	5	0.948	184	30
0.9394	0.9399	7212	1	0.941	086	10
0.9340			10			
0.9320			5	0.9312	4419	5
0.9221	0.9221	7311	30	0.9290	4613	30
	0.9220	1026				
0.9204	0.9204*	4517	15	0.9205	4517	30
				0.9132	286	5
0.9098	0.9100	809	20	0.9089	662	40
	0.9098	3323				
	0.9094	662				
0.9062	0.9070	7312	5	0.9062	663	20
	0.9062	663				
	0.9058	830				
0.9041	0.9040	2618	5	0.9041	2618	50B
0.9038	0.9038	819	20	0.9025	382	50B
	0.9038	749				
0.8984	0.8990	751	20	0.8969	572	40B
	0.8984	3125				
	0.8980	8010				

Ungavaite d_{obs} (Å)	d_{calc} (Å)	hkl	I_{meas}	Genkinite** d_{obs} (Å)	hkl	I_{meas}
				3.47	023	30
3.008	3.018*	008	90	3.020	025	90
					008	
				2.816	018	5
					125	
2.665	2.668*	222	10			
2.564	2.575	207	1			
	2.565	301				
2.399	2.398	312	5	2.454	033	20
2.353	2.341	313	1	2.367	034	5
2.263	2.268*	134	100	2.265	134	100
2.200	2.205*	209	5	2.204	029	20
2.147	2.146*	230	30	2.146	230	40
2.122	2.120*	129	10	2.120	129	40
2.073	2.074*	233	5	2.073	233	10
2.037	2.037	1111	1			
1.9994	2.0120	0012	5	2.013	0012	5
				1.979	1210	5
1.9404	1.9347	400	60	1.934	400	60
1.9047	1.9092*	2011	10	1.910	2011	50
1.8438	1.8424	404	1	1.854	142	5
1.8070	1.8104*	2210	10	1.812	2210	10
1.7808	1.7789	333	5			
	1.7851	2012				
1.7618	1.7628	3010	5			
	1.7587	1113				
1.7457	1.7494	415	1			
	1.7461	334				
	1.7436	406				
1.7308	1.7304	420	1	1.726	241	5
	1.7260	241				
1.7105	1.7129	422	1			
	1.7121	2211				
	1.7064	335				
1.6695	1.6744	0213	1			
	1.6717	3011				
1.6337	1.6290*	245	20	1.630	245	5
1.6158	1.6209	2212	1			
	1.6125	337				
1.5860	1.5897	246	1			
	1.5865	3012				
1.5521	1.5542	3112	5			
1.5046	1.5073	0313	5			
	1.5058	512				
	1.5012	428				
1.4827	1.4819	4110	1			
	1.4811	1016				
1.4765	1.4795	3113	1	1.467	2312	5
	1.4739	345				
1.4569	1.4595	1215	1			
	1.4590	2214				
	1.4554	3310				
	1.4547	1116				
	1.4542	249				
1.4089	1.4097	3114	1			
	1.4065	4110				
1.3886	1.3892*	517	1	1.389	157	10
1.3749	1.3774	515	10			
	1.3747	1117				
	1.3725	4112				
1.3644	1.3680	440	5	1.366	440	10
1.3585	1.3593	442	5	1.357	158	20
	1.3589	4211				
1.3383	1.3406	349				
	1.3398	0413				
1.3293	1.3272	530	1			
	1.3265	527				
1.3010	1.3030	4310	5	1.294	446	5
	1.3028	1118				
	1.3025	0316				
	1.3014	3313				

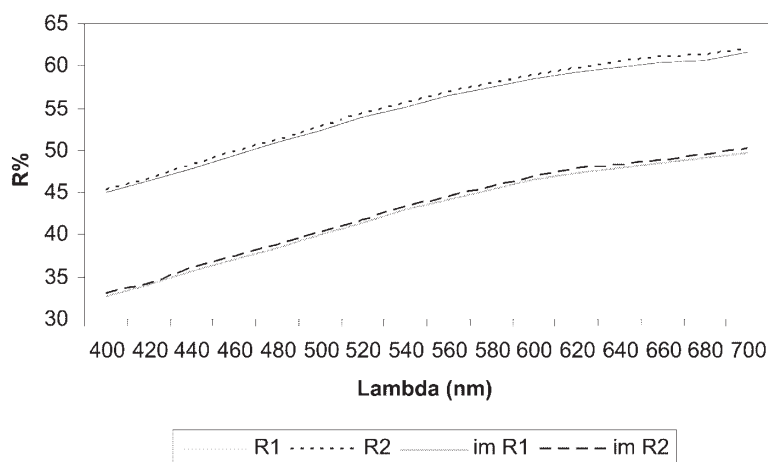* Reflections used for indexing. ** Cabri *et al.* (1977).

FIG. 2.   Reflectance spectra for ungavaite in air and in oil (im).

symmetry are only tentative for this mineral. These authors suggested that it is tetragonal, crystallizing in the possible space-groups $P4_12_12$, $P4_122$, $P4_32_12$, $P4_22_12$, or $P4_222$. By analogy, ungavaite is also considered to crystallize in one these space groups. Studies on the crystal structures of both genkinite and ungavaite have been initiated by the senior author. Unit-cell parameters for ungavaite, refined on the basis of 20 reflections over the 2θ range 34–162° for which unambiguous indexing was possible, are: a 7.7388 (4), c 24.145(1) Å, with $V = 1446.02(1)$ Å^3 and $Z = 8$. The Pearson Symbol Code (PSC) is tP56. The c:a ratio calculated from the unit-cell parameters is 3.1200.

DISCUSSION

Geochemical implications

The geology, mineralogy, geochemistry, and genesis of Ni–Cu–PGE ore deposits associated with komatiites have been recently summarized by Lesher & Keays (2002). According to their classification scheme, the mineralized zones at the Mesamax Northwest deposit are most consistent with the Type-I (Stratiform Basal) type of ore, wherein massive sulfides, overlain by disseminated sulfides, occur in layers at or near the base of individual komatiitic units. These ore deposits are generally considered to have cooled quickly, in which case the process of fractional crystallization (and the resulting segregation of Cu-poor monosulfide solid-solution from a Cu–PGE-rich intermediate solid solution) are not considered to have played a major role in their genesis. The profile of graded massive to disseminated sulfide segregation that characterizes these ore deposits is believed to be the product of gravitational settling or flow-induced segregation. Whereas most of

the ore deposits in the Raglan area have geochemical features that are consistent with products of more evolved komatiitic basaltic magma, some of the more Cu-rich ore zones (*e.g.*, Cross Lake, Raglan, Quebec) have features that are more consistent with metal remobilization due to hydrothermal–metamorphic processes (Lesher & Keays 2002).

Ungavaite occurs at the Mesamax Northwest deposit in a thin zone (1–2 m) located between disseminated and massive sulfides. This zone is notable for its relatively high enrichment in Pd (tens of ppm on average, up to 150 ppm *versus* 3–10 ppm in both the disseminated and massive sulfide portions), an unusual assemblage of PGM dominated by Pd-rich antimonides (ungavaite, naldrettite, sudburyite) and an abundance of the chlorite-group mineral. These facts suggest that the mineralization may be the combined product of a hydrothermal fluid and associated Pd enrichment. The complete absence of Pt in all antimonides present, despite the presence of sperrylite and detectable Pt in whole-rock compositions from both the disseminated and massive sulfides, suggests that a strong Pt:Pd fractionation also occurred. The fact that the solubility of Pt (either as a chloride or bisulfide complex) is greater than, or equal to that of Pd (Wood 2002) might explain the Pt:Pd fractionation observed in the ungavaite-bearing zone. However, a complete understanding of the factors governing Pt:Pd solubilities is still lacking; this can only be considered as a working hypothesis, therefore. The source of the Sb in this zone is also intriguing. Antimonides associated with komatiite-hosted ore deposits are generally rare, but not unknown. Hudson & Donaldson (1984) have summarized the mineralogy of the Kambalda (type-I mineralization) Ni–Cu–PGE deposit. Kambalda is considered an example of type-I mineralization, consistent with that at the Mesamax

Northwest deposit. The listing of Hudson & Donaldson (1984) includes six antimonides (*e.g.*, sudburyite) and Sb-bearing minerals [*e.g.*, palladoarsenide, $Pd_2(As,Sb)$]. The implication is that the Sb mineralization observed at the Mesamax Northwest deposit is not unique. At Kambalda, Hudson & Donaldson (1984) noted that these antimonides, like most of the PGM found there, are products of the postmagmatic mobilization of PGE into reaction zones, mobilized sulfide veins and hydrothermal veins. They concluded that the PGM likely arose through the interaction of Te-, As- and Sb-rich fluids interacting with massive and net-textured sulfides. These fluids may have promoted the release of the PGE from pre-existing sulfides and ultimately, resulted in the crystallization of discrete platinum-group tellurides, arsenides and antimonides (Hudson & Donaldson 1984). The source of the unusual Te-, As-, Sb-bearing hydrothermal fluid at Kambalda is not known.

In the case of the unusual Pd–Sb mineralization of the Mesamax Northwest deposit, it was considered a possibility that the associated host-rocks (tholeiitic basalt, silicate-facies iron formation) might be responsible for the enrichment in Sb. However, preliminary data (J.E. Mungall, unpubl. data) indicate that this is unlikely, as the metasedimentary and metavolcanic rocks hosting the deposit typically contain Sb in very low concentrations (0.2–1 ppm). Antimony is a strongly chalcophile element, and the concentration of Sb in a sulfide liquid can be up to 1250 times that of a coexisting silicate melt (Klöck & Palme 1988). Whereas the komatiitic basalts may be generally considered unlikely sources for Sb (as they typically contain concentrations of Sb in the range of 0.02–0.5 ppm; Jochum & Hofmann 1997), calculations based on an immiscible sulfide liquid separating from the inferred parental magma at the Mesamax Northwest deposit using a sulfide/silicate mass ratio of 500 (Mungall & Keast 2003) would be expected to contain 35 ppm Sb (Campbell & Naldrett 1979). This value is greater than the average concentration, 5 ppm Sb, that characterizes most of the massive sulfides from the deposit. Consideration of the results from this modeling, in conjunction with the fact that Sb is highly mobile during low-temperature migration of fluid (Jochum & Verma 1996), suggest that the primary magmatic compositions of the komatiite basalts of the Mesamax Northwest deposit have been overprinted by a process (deuteric alteration, regional metamorphic fluids, *etc.*) that removed the Sb and Pd from the massive sulfides and redistributed them toward the margins of the body. The mechanism inducing precipitation of Pd and Sb at the contact with the enclosing silicate rocks is unknown, but may be related to changes in the oxidation or sulfidation state of the fluids that were transporting these elements. It may be notable that magnetite is ubiquitously associated with the Pd antimonides found in the contact zone.

Experimental implications

One important goal of ongoing research into the crystal chemistry of the PGM is to ascertain conditions of formation. Mineral-synthesis experiments play an important role in this regard, although many such studies have a tendency to be overlooked, as they are not typically found in standard Earth Sciences journals. In the case of ungavaite, the first evidence we have as to the conditions under which it may have crystallized comes from studies made on the Pt-dominant analogue, genkinite. Synthetic genkinite has been synthesized at ~675°C in the ternary system Pt–Pd–Sb, in which $(Pt,Pd)_4Sb_3$ (major) + $(Pt,Pd)_7Sb_3$ (minor) or $(Pt,Pd)_4Sb_3$ (major) + $(Pt,Pd)Sb$ (minor) were produced (Cabri *et al.* 1977). It should also be noted that synthesis attempts in the Pt–Sb binary with a starting bulk-composition corresponding to Pt_4Sb_3 at 700°C were not successful, producing a combination of both Pt_3Sb_2 and $PtSb$. In both synthetic and natural genkinite, variations in Pt/(Pt + Pd) ratio are substantial, ranging from 0.60 to 0.68 in the synthetic and from 0.61 – 0.77 in the natural material (Cabri 2002). The question as to whether Pd is indeed essential to genkinite (and, by extension, whether Pt is essential to ungavaite) remains unresolved.

There is a paucity of synthesis experiments involving antimonides of Pd available in the literature (Makovicky 2002). Probably the most notable is that of Kim & Chao (1996), who investigated the system Pd–Pt–Sb over the range of 500–1000°C. The most salient findings of these authors (who noted the existence of seven unique Pd–Sb phases over this *T* range) are that: 1) PdSb (sudburyite?) develops at 800°C, 2) Pd_2Sb (naldrettite?) develops below 580°C (occurring along with either Pd_5Sb_2 or PdSb), and 3) in the subsystem Pd–Sb, Pd_2Sb (naldrettite?) develops between 570 and 500°C. These findings are consistent with those of Bälz & Schubert (1969), who were also able to synthesize Pd_2Sb at 500°C and noted that heating synthetic Pd_2Sb (naldrettite?) above 580°C resulted in the formation of Pd_5Sb_2 + hexagonal Pd_5Sb_3. Only El-Boragy & Schubert (1971), in their study of the system Pd–Sb–Te, investigated Pd–Sb phase relations below 400°C. Although they recognized more than 17 distinct phases, none of these correspond to any of the Pd–Sb minerals observed at the Mesamax Northwest deposit, including ungavaite. The relevance of these studies and how they relate to the genesis of the unusual Pd–Sb zone at the Mesamax Northwest deposit can be discerned when the modal distribution of Pd–Sb minerals is considered. In terms of modal abundance, naldrettite (Pd_2Sb) greatly predominates over sudburyite (PdSb), which predominates over ungavaite (Pd_4Sb_3); by implication, the prevailing conditions of formation must predominantly correspond to those of naldrettite. Given the data from the above experimental studies, we suggest that the Pd–Sb mineralization primarily developed over a range of 500–600°C,

possibly beginning as high as 800°C. The complete absence of a phase corresponding to ungavaite in any of the modern moderate- to high-temperature synthesis experiments [Pd–Pt–Sb: Cabri *et al.* (1977), Kim & Chao (1996), Pd–Sb–Te: Kim & Chao (1991)], in addition to that at low temperature (El-Boragy & Schubert 1971), is intriguing. The occurrence of ungavaite with a chlorite-group mineral implies that temperatures are unlikely to have exceeded ~600°C (assuming a Fe-rich composition for the chlorite-group mineral; James *et al.* 1976). Thus, one hypothesis must be that the mineral developed below 400°C. As workers have noted only solid phases to be stable below 400°C in many of the binary and ternary phase-diagrams involving Pd + Sb (*e.g.*, Kim & Chao 1991), the implication is that ungavaite may be a product of a solid-state transformation. Whereas 400°C may constitute an upper limit for the formation of ungavaite, the effect of trace elements (*e.g.*, Bi, Te, As, *etc.*) on its crystallization remains unknown. Regardless, the low abundance of ungavaite in the sample analyzed, relative to that of naldrettite and sudburyite, suggests that the physical–chemical conditions under which this mineral crystallized must have been very restricted.

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