

ANOMALOUSLY HIGH δD VALUES IN AN ARCHEAN FERROPICRITIC MELT: IMPLICATIONS FOR MAGMA DEGASSING

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ABSTRACT

In situ H isotope analysis of igneous amphibole from the Boston Creek ferropicrite, in the Abitibi Belt, Ontario, a 100-m-thick layered mafic-ultramafic unit, provides insights into the evolution of Archean mantle-derived hydrous melts in the crust. Ion-microprobe analyses of the ultramafic-rock-hosted interstitial igneous magnesiohastingsite indicate a wide range of δD values, from -47 to $+54\text{‰}$ and 2–3 wt% H₂O at the 100–1000 μm intragrain scale, but relatively uniform major-element and incompatible trace-element compositions. This wide range encompasses values significantly higher than the δD values of -50‰ for whole-rock samples, $<+10\text{‰}$ for igneous amphiboles from ultramafic sills, -80 to -30‰ values for hydrothermal-metamorphic fluids in the area, and -90 to -60‰ values for mantle materials. The anomalously high δD values cannot be attributed entirely to H loss from amphibole during secondary processes. The contrast with the relatively uniform magnesiohastingsite composition and H₂O and trace-element contents of the amphibole excludes the possibility that the δD values reflect variable fluid/mineral fractionation. The anomalously high δD values most plausibly record the composition of the ferropicritic melt from which the amphibole formed. Considering the widespread distribution and abundance of vesicles in the Boston Creek ferropicrite, these values can be explained by degassing of H relative to deuterium, perhaps by dissociation of H₂O during emplacement at shallow levels in the crust. The resulting increase in oxidation state of the residual degassed melt led to Fe–Ti oxide crystallization, which reduced the FeO content of the melt and triggered the Cu–PGE–Ag sulfide mineralization during formation of the magnetite gabbro host-rock.

Keywords: Abitibi belt, Archean, igneous magnesiohastingsite, H isotope, magmatic degassing, ferropicrite, platinum-group-element mineralization, Boston Creek, Ontario.

SOMMAIRE

Une analyse isotopique *in situ* de l'amphibole ignée provenant de la ferropicrite de Boston Creek, ceinture de l'Abitibi, en Ontario, une unité mafique-ultramafique de 100 m d'épaisseur, fournit une nouvelle information à propos de l'évolution de magmas archéens enrichis en H₂O, dérivés du manteau, et mis en place dans la croûte. Les analyses faites avec une microsonde ionique de la magnésiohastingsite interstitielle d'une roche ultramafique indique un grand intervalle de valeurs de δD , allant de -47 à $+54\text{‰}$ et une teneur de 2–3% H₂O (poids) à une échelle intragranulaire de 100 à 1000 μm , mais une composition relativement uniforme en termes des éléments majeurs et des éléments traces incompatibles. Ce grand intervalle dépasse largement les valeurs de δD obtenues pour les roches globales, -50‰ , les valeurs inférieures à $+10\text{‰}$ pour l'amphibole ignée des filons-couches ultramafiques, les valeurs entre -80 et -30‰ pour les fluides hydrothermaux-métamorphiques de la région, et les valeurs entre -90 et -60‰ pour les matériaux du manteau. Les valeurs de δD anormalement élevées ne sauraient être attribuées à la seule perte de H de l'amphibole au cours de sa recristallisation secondaire. Le contraste avec la composition et les teneurs en H₂O et

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en éléments traces relativement uniformes excluent la possibilité que les valeurs de δD témoignent d'un fractionnement variable entre phase fluide et minéral. C'est plutôt à la composition du magma ferropicritique à partir duquel l'amphibole s'est formée que nous attribuons les valeurs anomalement élevées en δD . Compte tenu de la distribution répandue et de l'abondance des bulles dans la ferropicrite de Boston Creek, ces valeurs semblent indiquer un dégazage de l'hydrogène par rapport au deutérium, possiblement par dissociation de H_2O pendant la mise en place du magma à faible profondeur dans la croûte. L'augmentation en degré d'oxydation du magma résiduel qui en résulte a causé la cristallisation d'un oxyde Fe-Ti, ce qui diminue la teneur en FeO du magma et déclenche une minéralisation en sulfures de Cu-PGE-Ag associée à la formation du gabbro à magnétite, la roche hôte.

(Traduit par la Rédaction)

Mots-clés: ceinture de l'Abitibi, archéen, magnésiohastingsite ignée, isotope de H, dégazage magmatique, ferropicrite, minéralisation en éléments du groupe du platine, Boston Creek, Ontario.

INTRODUCTION

Recent field, geochemical and experimental studies have led to the inference that some Archean ultrabasic melts were hydrous (Stone *et al.* 1997, Parman *et al.* 1997, Beresford *et al.* 2000). The H_2O may have been derived by melting of hydrous mantle or by assimilation of crustal material during ascent and emplacement of the magma (Stone *et al.* 2003, Inoue *et al.* 2000, Litasov *et al.* 2001, Parman *et al.* 2001, Wilson 2003). If magmatic, the presence of H_2O in the melts has major implications for the thermal evolution of the Earth (Grove & Parman 2004). However, the nature, composition and distribution of volatiles in the Archean mantle and ultramafic melts remain poorly constrained. An important step in advancing the understanding of putative hydrous source-rocks in the mantle and processes of "wet" melting is to first examine the effects of crustal-level processes, such as magmatic degassing and hydrothermal alteration, on volatile composition and distribution in ultramafic melts.

In this study, we present new data on the evolution of hydrogen isotope compositions in Archean mantle-derived melts emplaced in the crust. Ion-probe data are presented on the hydrogen isotope composition and H_2O and trace-element contents of relict igneous amphibole from the Boston Creek ferropicrite, exposed near Kirkland Lake, Abitibi Belt, Ontario. This major unit is a layered peridotite-gabbro and spinifex-textured body 100 m thick (Stone *et al.* 1995a, b), which contains magmatic Cu-PGE-Ag sulfide mineralization in magnetite gabbro (Stone *et al.* 1992, 1993, 1996). The nature and origin of anomalously high δD values, up to +54‰, are evaluated in the context of degassing during magmatic emplacement and postmagmatic hydrothermal alteration. The results have significant implications for the nature of Archean magmatic and postmagmatic processes and, possibly, for the origin of magnetite-gabbro-hosted Cu-PGE-Ag sulfide mineralization.

GEOLOGICAL SETTING

The Boston Creek ferropicrite crops out on the east flank of the Round Lake Dome, in the southern part of the Abitibi greenstone belt, Ontario (Fig. 1). As documented by Larson *et al.* (1998), the unit is folded about the dome and dips steeply to the east. It is cut by fault zones and appears to be structurally repeated in the hanging wall. The unit has also been metamorphosed under low-grade conditions. Regionally, the geological section has undergone hydrothermal alteration, regional deformation and epigenetic Cu-Au mineralization (Stone *et al.* 1987). The effects of deformation are present mainly on the upper and lower contacts of the ferropicrite unit, and primary igneous textures and minerals are well preserved internally within the unit. Consequently, research has focused on melt petrogenesis (Stone *et al.* 1995b), internal differentiation (Stone *et al.* 1995a), and magmatic Cu-PGE-Ag sulfide mineralization (Stone *et al.* 1996).

Studies along twelve sections over a strike-length of 2.5 km indicate that the Boston Creek ferropicrite consists from base to top of a thin chilled margin, a thick peridotite layer, a thin clinopyroxenite layer, a thick complex gabbro layer, a very thick (30 m) clinopyroxene spinifex layer, and a thin upper vesicular chilled margin (Stone *et al.* 1995b, Crocket *et al.* 2005). The overprinting effects of deformation and limited exposure hamper determination of an extrusive *versus* a plutonic origin. Nevertheless, the anomalously large thickness of the spinifex-textured layer, extensive zones of vesiculation and presence of altered glass internally within the ferropicrite unit are features consistent with volcanic emplacement or shallow-level intrusion.

Geochemically, the Boston Creek ferropicrite unit has very high contents of Fe at high Mg, and low Al, high Ti, LREE, and Nb at low HREE, Y and Sc, and depleted Sm-Nd and Re-Os isotope compositions (Stone *et al.* 1995b, Walker & Stone 2001). The element enrichments, together with high initial values of ϵ_{Nd}

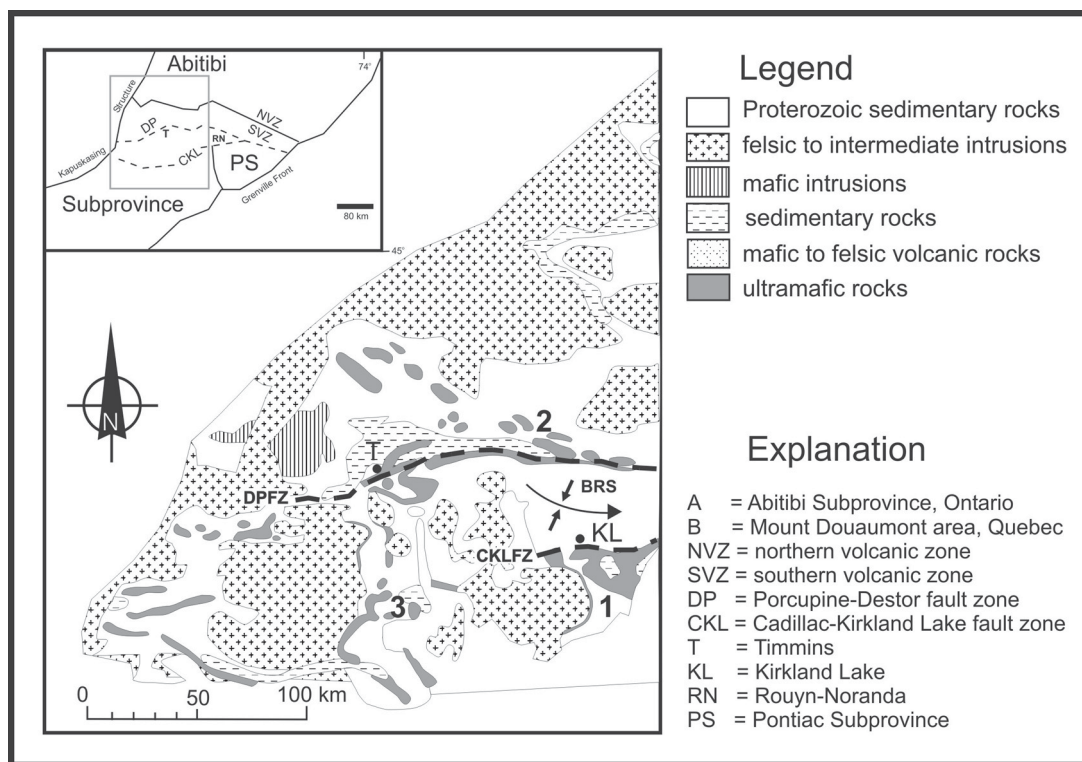


FIG. 1. The location and geological setting of the Boston Creek ferropicrite (BCF) in the Archean Abitibi greenstone belt, Ontario (Stone *et al.* 1987, Ayer & Trowell 2000). Legend: 1: location of the Boston Creek ferropicrite; 2 and 3: locations of ultramafic sills, Munro–McCool townships and Sothman Township, respectively (Stone *et al.* 2003).

(+2 to +3; Stone *et al.* 1995b) and low initial γ_{Os} (–4; Walker & Stone 2001) are characteristics of melting of depleted mantle metasomatically enriched in Nb–LREE and Fe–Ti by hydrous fluids.

Interestingly, the Boston Creek ferropicrite contains magmatic Cu–PGE–Ag sulfide mineralization in the margins of the gabbro layer (Fig. 2; Stone *et al.* 1992, 1993, 1996). The mineralization (up to ~2 ppm PGE + Ag + Au) is hosted in podiform bodies of vari-textured magnetite gabbro with up to 15–20 modal % magnetite + ilmenite and up to 20 modal % vesicles. Micrometric grains of Pd, Pt and Rh tellurides, bismuthotellurides and arsenides, Ag tellurides and selenides, and native Au and Au–Ag alloy occur in chalcopyrite and pyrite grains disseminated within lamellar intergrowths of magnetite and ilmenite and secondary silicates. The mineralization zones formed by *in situ* concentration of PGE–Ag–rich Fe–Cu sulfide with Fe–Ti oxide along the margins of internal dynamic melt-channels (Stone *et al.* 1996).

EXPERIMENTAL METHODS

The abundance and good preservation of relict igneous amphibole make the Boston Creek ferropicrite

ideal for petrographic and geochemical studies of this phase (Stone *et al.* 1995b, 2003). Igneous amphibole is widespread in the unit and present in minor to major modal amounts of relict grains of micrometric to millimetric size. The phase is most abundant in the ultramafic layers, where it forms interstitial grains up to 500 μm in diameter at the margin of metamorphic amphibole pseudomorphs of clinopyroxene grains (Fig. 3) and grains enclosing serpentine pseudomorphs of olivine grains. The preserved igneous textures and the very high Ti content of the magnesiohastingsite (see below) indicate a high-temperature origin (Spear 1981). The low-grade metamorphic amphibole has a much lower Ti content. The relict igneous amphibole analyzed for this study is from fine- to medium-grained rock in the transitional zone between the basal chilled margin below and the peridotite layer above. The lack of suitable standards precluded isotopic analysis of the metamorphic amphibole.

Major-element compositions of the igneous amphibole were determined with a JEOL JXA–8600/3 electron probe micro-analyzer at the University of Alabama (Tuscaloosa). The analyses were generated with a beam size of 1 μm , Faraday cup current of 20 nA, an accelera-

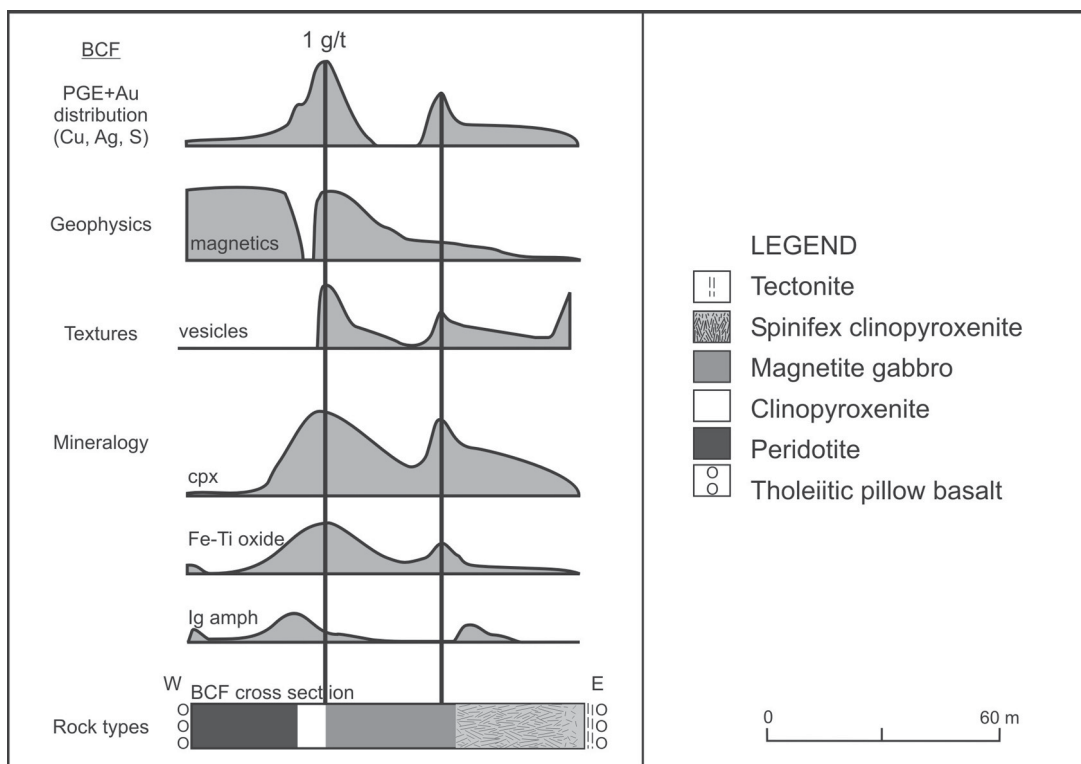


FIG. 2. The internal setting of the disseminated Cu–PGE–Ag sulfide mineralization in the lower and upper margins of the central magnetite gabbro layer. The position of the mineralization coincides with markedly higher allied metal contents, positive magnetic susceptibility, and higher modal proportions of vesicles, clinopyroxene and magnetite + ilmenite.

ting voltage of 15 kV, and wavelength-dispersion techniques. Natural silicate, oxide, and phosphate minerals and glass were utilized as standards. Replicate analyses of the standards indicate accuracy and precision errors of ≤ 0.5 wt% in relative value. The analytical results were reduced employing the recommendations of Leake *et al.* (1997). The procedure employed for calculation of Fe^{3+} and Fe^{2+} is that of Rock & Leake (1997), and produces values close to those accurately measured in 80% of the compositions studied.

The igneous amphibole was analyzed *in situ* for H_2O , D/H ratio and trace elements on a modified CAMECA IMS 3f ion microprobe at the CRPG–CNRS (Nancy). The H_2O analyses were carried out following the techniques of Deloule *et al.* (1991a, 1995). The analytical uncertainty is $<10\%$ in relative value. The analytical procedure for the hydrogen isotope analysis is that of Deloule *et al.* (1991b). A negative primary oxygen beam is focused to 10 μm on carefully selected spots on the amphibole grains. Standards are analyzed prior to and following analysis of each sample. The standards are utilized to establish the relationship of the mean mass-

to-charge ratio (M/C) of the octahedrally coordinated cations and the instrumental D/H fractionation factor. The precision for the δD values measured through this calibration method, calculated from replicate analysis of standard minerals, is better than $\pm 12\%$, including the possible spatial heterogeneity of the standards. For amphibole, ion-probe measurements of D/H are independent of crystallographic orientation, at least to the analytical precision of the probe (*cf.* Deloule *et al.* 1991b). The concentration of the rare-earth elements (REE) and of the high field-strength elements (HFSE) were obtained following the techniques of Gurenko & Chaussidon (1995). Replicate analyses of the Kakanui clinopyroxene standard indicate an accuracy of ± 5 – 15% for Ba, Sr, La, Ce, Nd, Sm, and Dy, and ± 15 – 25% for Nb, Gd, Er and Yb.

RESULTS

Geochemical analyses of petrographically similar grains of relict igneous amphibole indicate relatively uniform intragrain and intergrain contents of major

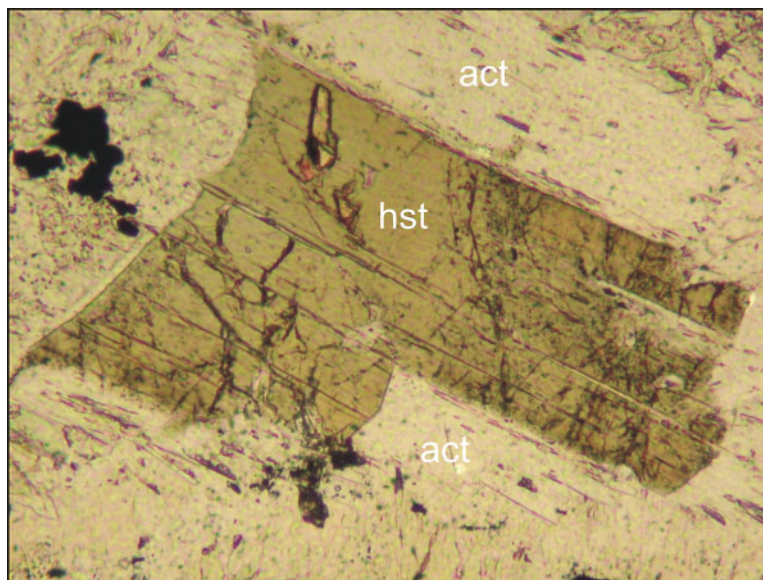


FIG. 3. Large relict igneous amphibole (hst) and finer-grained secondary metamorphic amphibole (act) due to alteration at the margins of replaced clinopyroxene (plane-polarized light, field of view: 1.2 mm). Symbols: hst: magnesiohastingsite, act: actinolite.

elements, trace elements and H₂O, but markedly variable δ D compositions (Tables 1–3). Contents of total iron oxide (12 wt% FeO), magnesium oxide (13 wt% MgO), aluminum oxide (11–12 wt% Al₂O₃), and titanium oxide (3 wt% TiO₂) are high relative to silicon oxide (41–43 wt% SiO₂), and the grains lack zonation (Table 1). Contents of Fe³⁺ are greater than ^{VI}Al (Fig. 4) and, in the classification scheme of Leake *et al.* (1997), the igneous amphibole is magnesiohastingsite in composition. Primitive mantle-normalized profiles peak at Nb–La and show strong enrichment in the light REE (LREE) relative to the heavy REE (HREE) [(La/Yb)_n between 10 and 15] (Table 2, Fig. 5). These profiles are similar to those for the ferropicrite whole-rock samples (Stone *et al.* 1995b), but differ from the flatter [(La/Yb)_n in the range 0.6–5.0] and more irregular profiles (*e.g.*, negative Sr anomalies) for the Archean ultramafic sills in the area (Fig. 5). The contents of H₂O range from 1.7 to 4.1 wt% (Table 3). With a mean value of 2.6 ± 0.6 wt%, the H₂O contents are at the high end for igneous amphiboles.

In contrast to the major- and trace-element and H₂O contents, the δ D compositions at the same four spots on the amphibole grains show marked heterogeneity (Table 3). The δ D values for three points on grain 1a vary from +22‰ to +54‰, four points on grain 1b vary from –28‰ to +7‰, three points on grain 2a vary from –4‰ to +21‰, and three points on grain 3b/a vary from –47‰ to –4‰. Overall, the δ D values measured

for the amphibole grains range from –47‰ to +54‰ (Fig. 6). This range is much higher than the δ D values of –50‰ for whole-rock samples (mixture of relict igneous and secondary metamorphic minerals), values for hydrothermal-metamorphic fluids in the area (–80 to –30‰; McCuaig & Kerrich 1998) and elsewhere (Taylor 1974), and range of generally acceptable values for mantle materials (–90 to –60‰; Sheppard & Epstein 1970, Taylor, H.P. 1986, Garcia *et al.* 1989). The variations at the grain scale are well beyond analytical error (12‰). They cannot be attributed to variations in the instrumental mass-fractionation factor applied to the raw ion-probe D/H measurements, because of the uniform major-element and incompatible trace-element contents of the grain spots analyzed.

The magnitude of the δ D variation within single grains of amphibole from the ferropicrite resembles that of igneous amphiboles from other ultramafic rocks elsewhere (Fig. 7, Deloué *et al.* 1991a, Wagner *et al.* 1996, Valley *et al.* 1998, Stone *et al.* 2003), though it is smaller than that for the Cenozoic Nushan amphibole (–94 to 46‰; Xia *et al.* 2002). Seven of the thirteen points gave positive δ D values, up to +54‰, much higher than the +8‰ value of the inclusion amphibole in ultramafic sills of this area (Stone *et al.* 2003) and the +8‰ value of megacryst amphibole from the Cima basanite (Boettcher & O’Neil 1980), though similar to the +46‰ value for Nushan amphibole (Xia *et al.* 2002) (Fig. 7). Indeed, the ultramafic sills in the area under-

went low-grade metamorphism, like the Boston Creek ferropicrite, yet have significantly more negative (*i.e.*, lighter) or "normal" δD values. Consequently, the less negative and positive δD values for the ferropicrite unit are significantly anomalous and warrant further study.

DISCUSSION

The wide range of δD values for the igneous amphibole from the Boston Creek ferropicrite contrasts with the relatively uniform contents of major and trace elements and H_2O in the grains. The unaltered nature of the analyzed amphibole and their distinctive δD values (-47 to $+54\text{‰}$), compared to the whole-rock values (-50‰) and to amphibole from similarly altered

and metamorphosed ultramafic sills in the area (-125 to $+10\text{‰}$), exclude the possibility that the δD variations reflect hydrogen exchange during postmagmatic hydrothermal and metamorphic processes (*e.g.*, Xia *et al.* 2002, Stone *et al.* 2003). For example, the δD mean value of -80‰ for relict igneous amphibole from

TABLE 1. MAJOR- AND MINOR-ELEMENT COMPOSITION OF THE IGNEOUS AMPHIBOLE FROM THE BOSTON CREEK FERROPICRITE¹

Grain <i>n</i>	1a	1b	2	3	s.d.	s.d.	s.d.
	ave.	ave.					
SiO ₂ wt%	41.82	42.24	0.17	42.35	0.30	43.32	0.54
TiO ₂	3.27	3.27	0.19	3.31	0.27	2.88	0.17
Al ₂ O ₃	12.02	11.83	0.51	11.71	0.44	10.86	0.49
Cr ₂ O ₃	0.03	0.03	0.04	0.07	0.06	0.02	0.02
Fe ₂ O ₃ ²	3.49	4.23	1.24	5.21	1.15	4.93	0.98
FeO	8.83	7.84	0.59	7.09	1.14	7.25	0.85
MgO	12.88	13.10	0.19	13.18	0.15	13.52	0.31
MnO	0.07	0.12	0.02	0.12	0.02	0.12	0.02
NiO	0.10	0.06	0.02	0.07	0.03	0.06	0.03
CaO	10.99	10.97	0.38	10.80	0.09	10.79	0.13
Na ₂ O	3.24	2.85	0.36	2.83	0.35	2.88	0.18
K ₂ O	0.48	0.50	0.05	0.47	0.05	0.45	0.05
F	<0.05	<0.05		<0.05		<0.05	
Cl	0.03	0.02	0.00	0.02	0.01	0.02	0.01
H ₂ O ³	2.01	2.01	0.01	2.01	0.01	2.01	0.01
Total	99.24	99.07		99.23		99.09	
Si <i>apfu</i>	6.17	6.21		6.21		6.35	
^{IV} Al	1.83	1.79		1.79		1.65	
^{VI} Al	0.26	0.26		0.23		0.22	
Ti	0.36	0.36		0.37		0.32	
Fe ³⁺	0.39	0.47		0.57		0.54	
Cr	0.00	0.00		0.01		0.00	
Mg	2.83	2.87		2.88		2.95	
Fe ²⁺	1.09	0.96		0.87		0.89	
Mn	0.01	0.01		0.01		0.02	
Ni	0.01	0.01		0.01		0.01	
Ca	1.75	1.75		1.72		1.72	
Na	0.94	0.82		0.82		0.83	
K	0.09	0.10		0.09		0.09	
F							
Cl	0.01	0.01		0.01		0.01	
Total	15.75	15.63		15.59		15.59	
Mg# ⁴	65.4	66.4		66.3		67.0	
N _{Oct} ⁵	4.96	4.96		4.95		4.95	
M/C ⁶	16.0	15.7		15.6		15.6	

¹ The analyses were made by electron-microprobe wavelength-dispersion (WDS) techniques.

² The amounts of Fe³⁺ and Fe²⁺ are calculated assuming 23 O per formula unit and a total of 13 cations excluding Ca, Na and K.

³ The amount of H₂O is calculated assuming stoichiometry.

⁴ Mg# = 100 * Mg / (Mg + Fe²⁺ + Fe³⁺ + Mn + Ni).

⁵ N_{Oct} = ^{VI}Al + Ti + Cr + Fe³⁺ + Fe²⁺ + Mg + Mn + Ni.

⁶ M/C = mean mass-to-charge ratio of the octahedrally coordinated cations.

TABLE 2. TRACE-ELEMENT CONTENTS OF THE IGNEOUS AMPHIBOLE, AS MEASURED BY ION PROBE

Grain Spot	1b	1b	1b	2a	2b	3b	3b
	1	2	3	1	1	1	2
Ba ppm	158	234	541	234	154	173	170
Nb	67.9	119	97.9	85.6	65.1	100	55.5
La	60.4	69.0	62.8	78.8	43.7	49.6	60.9
Ce	184	262	211	220	154	164	190
Pr	18.4	27.6	22.5	20.0	15.4	16.0	17.3
Sr	1057	1362	1171	1526	1020	1126	1154
Nd	71.2	112.6	89.2	76.2	60.2	55.4	63.4
Sm	12.3	22.4	18.9	14.4	11.0	10.7	11.3
Eu	2.2	6.2	5.9	3.6	6.7	3.6	3.4
Zr	250	366	390	294	160	304	187
Hf	4.0	<1.00	2.5	2.5	1.7	2.3	3.0
Ti	17187	18752	20114	23827	10872	18523	14314
Gd	9.6	19.1	12.3	11.6	7.0	9.1	8.5
Dy	10.4	17.4	13.2	10.3	7.1	8.3	8.8
Y	59.9	99.1	66.5	65.6	44.7	53.7	52.0
Er	4.6	7.2	6.0	5.6	3.6	3.8	4.1
Yb	4.0	5.0	4.0	4.0	3.1	2.9	3.2
Lu	0.3	0.5	0.4	0.4	0.2	0.2	0.3
V	325	243	256	342	170	247	211
Sc	26.9	13.4	13.1	21.0	15.3	13.6	17.7
(La/Yb) _n	10.71	9.93	11.25	14.10	10.05	12.25	13.50
(La/Sm) _n	3.16	1.99	2.15	3.55	2.56	2.99	3.49
(Gd/Yb) _n	1.97	3.16	2.54	2.39	1.85	2.60	2.18

TABLE 3. AMOUNT OF H₂O AND H ISOTOPE COMPOSITIONS OF IGNEOUS AMPHIBOLE FROM THE BOSTON CREEK FERROPICRITE

Area, grain	Spot	X μm	Y μm	H ₂ O wt%	D/Hc	s.d.	M/C	D/Hv	D _{SMOW} ‰
1 a	1	-3126	-3919	2.73	106.5	1.1	16	164.2	54
	2	-3381	-3884	2.09	103.3	1.2	16	159.2	22
	3	-6040	-2265	n.d.	105.2	1.1	16	162.1	40
							average		38
1 b	4	-5577	-3164	1.65	100.0	1.1	16	152.9	-18
	5	-5654	-3000	4.05	99.0	1.1	16	151.4	-28
	6	-6562	-2178	2.59	102.5	1.3	16	156.8	6
	7	-5819	-1846	1.93	102.5	1.2	16	156.8	7
							average		-8
2 a	1	2470	-4661	2.58	104.3	1.1	16	159.1	21
	2	2386	-4324	2.41	103.8	1.3	16	158.3	16
	3	2608	-4300	3.07	101.7	1.2	16	155.2	-4
							average		11
3 b/a	1	3390	4860	2.43	101.7	1.2	16	155.1	-4
	2	3590	5025	2.94	100.4	1.2	16	153.1	-17
	3	3650	5178	2.85	97.3	1.1	16	148.5	-47
							average		-23

The analyses were made by ion-probe techniques. D/Hc: D/H value measured by ion probe; D/Hv: D/H value corrected for instrumental fractionation. The standard deviation, s.d., includes statistical and calibration errors. M/C: mean mass-to-charge ratio of the octahedrally coordinated cations.

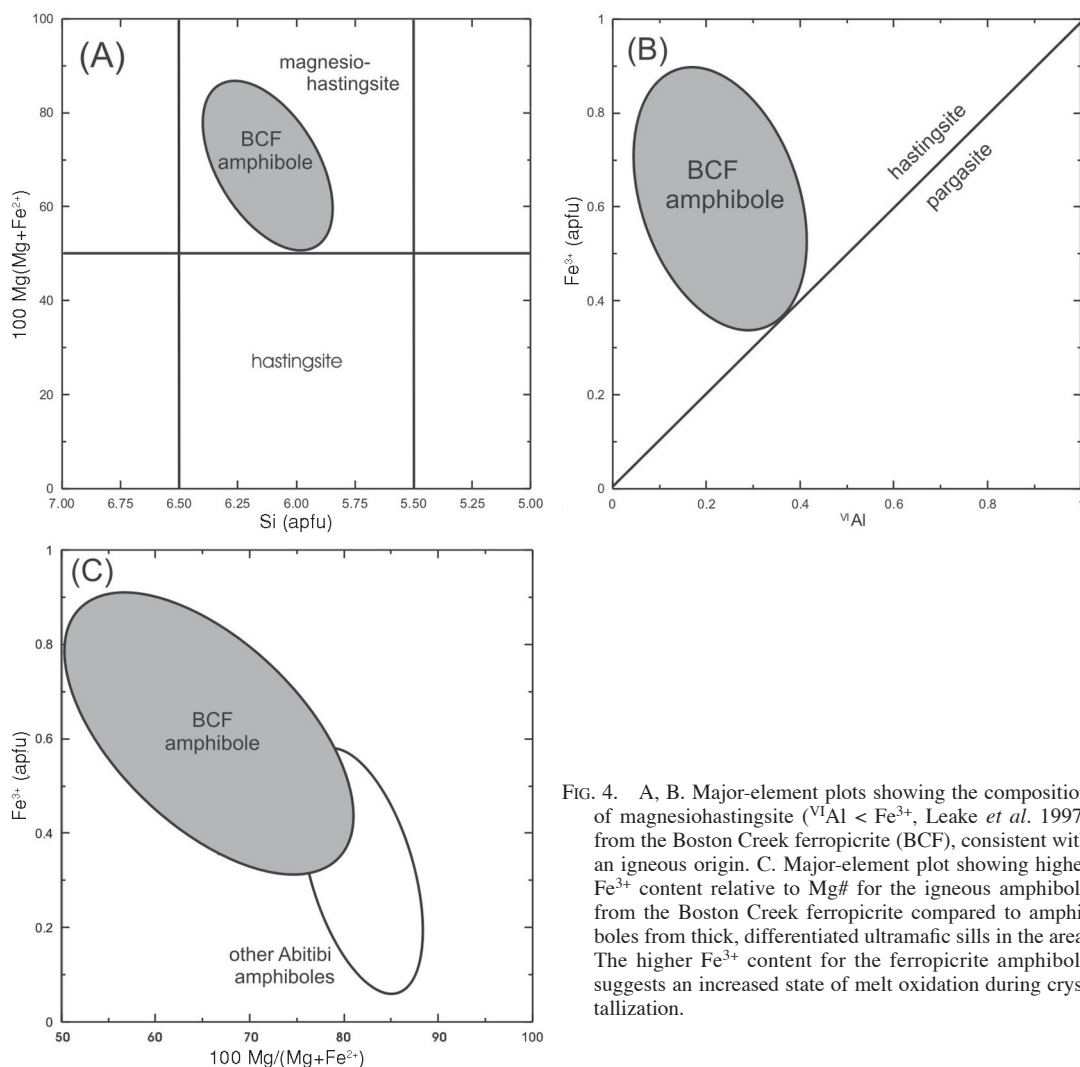


FIG. 4. A, B. Major-element plots showing the composition of magnesianhastingsite ($VIAl < Fe^{3+}$, Leake *et al.* 1997) from the Boston Creek ferropicrite (BCF), consistent with an igneous origin. C. Major-element plot showing higher Fe^{3+} content relative to $Mg\#$ for the igneous amphibole from the Boston Creek ferropicrite compared to amphiboles from thick, differentiated ultramafic sills in the area. The higher Fe^{3+} content for the ferropicrite amphibole suggests an increased state of melt oxidation during crystallization.

the basal chilled margin of a major ultramafic unit in Sothman Township (*i.e.*, Location 3 in Fig. 1) is much more strongly negative than any of the values for the Boston Creek ferropicrite. Furthermore, hydrogen exchange with meteoric water would result in negative, not positive δD values. Consequently, the δD values for the amphibole in the ferropicrite most probably record a magmatic process.

Magma degassing

Considering the nature and abundance of vesicles within the Boston Creek ferropicrite, the anomalously high δD values can plausibly be explained by H loss through degassing prior to or during crystallization.

Large inter-species fractionation-factors are expected; thus it is possible to cause significant variation in δD by fractionation among different hydrogen species (*e.g.*, H_2O , H_2 , H_2S , HCl) during degassing. Laboratory studies (Pineau *et al.* 1998) indicate hydrogen isotopic fractionation between water vapor (H_2O) and melt ($\Delta D_{H_2O-melt}$) can exceed +40‰. Hydrogen isotopic fractionation-factors between reduced gases (*e.g.*, H_2 , H_2S , HCl) and melt can be less than -150‰ (Pineau *et al.* 1998, Xia *et al.* 2002). In more recent terranes, outgassing of H is common during basalt emplacement (Sato & Wright 1966, Mathez 1984, Christie *et al.* 1986).

The proposed process of degassing in Boston Creek ferropicrite can be modeled to explain the H isotope compositions of its igneous amphibole. Partial melting

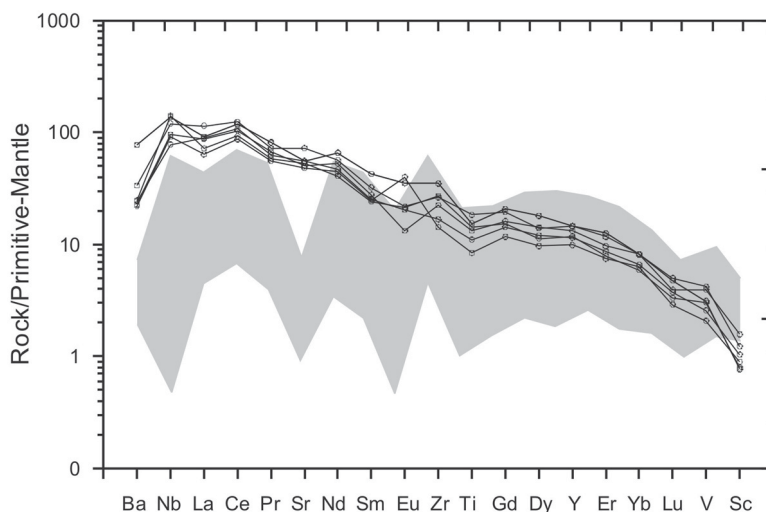


FIG. 5. Primitive mantle-normalized trace-element concentrations of the igneous amphibole from the Boston Creek ferropicrite. The shaded field represents the levels of trace elements of igneous amphiboles from ultramafic sills in the area (Stone *et al.* 2003). The normalization values are those of McDonough & Frey (1989) and Sun & McDonough (1989).

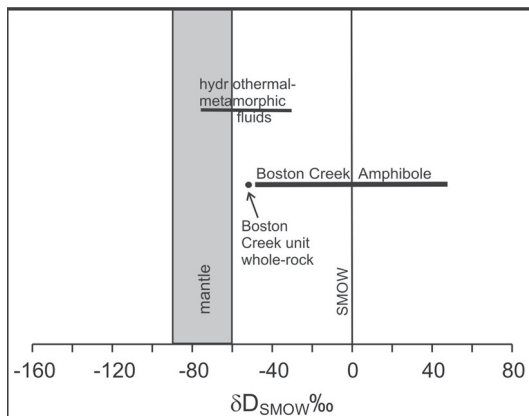


FIG. 6. Schematic summary of the range of values for $\delta D\text{‰}$ determined *via in situ* SIMS analyses of the igneous amphibole from the Boston Creek ferropicrite compared to whole-rock values (W.E. Stone, unpubl. data), hydrothermal-metamorphic fluids (-80 to -30‰ ; McCuaig & Kerrich 1998) in the area, mantle materials (-90 to -60‰), and seawater (SMOW) (Sheppard & Epstein 1970, Taylor, H.P. 1974, 1986, Garcia *et al.* 1989).

in the mantle would impart a primary hydrogen-isotope composition on the melt. Gases escaped from the magma either as aqueous vapor (H_2O) or reduced species (*e.g.*, H_2 , H_2S , HCl , *etc.*) during emplacement. For H_2O , the H isotope fractionation between H_2O and magma is positive ($\Delta\text{H}_{\text{gas/melt}} > 0$), such that the escaping gas would be enriched in D and the residual magma progressively depleted in D during degassing. In this process, the δD values of the residual melt shift from an initial mantle value to more negative values. Obviously, this model cannot explain the anomalously high δD values.

Alternatively, for reduced species, the H isotope fractionation between gas and magma is negative ($\Delta\text{H}_{\text{gas/melt}} < 0$), such that escaped H gas would be isotopically lighter, with a lower δD value and residual H_2O isotopically heavier, with a higher δD . In this model, the values of δD for the residual magma shift from an initial mantle-type value to progressively higher and ultimately positive values during exsolution and degassing of volatiles, and the residual magma becomes more oxidized. This model explains the anomalously high δD values for the Boston Creek ferropicrite. Following Xia *et al.* (2002), the magnitude of change in the δD values can be modeled *via* the Rayleigh distillation equation

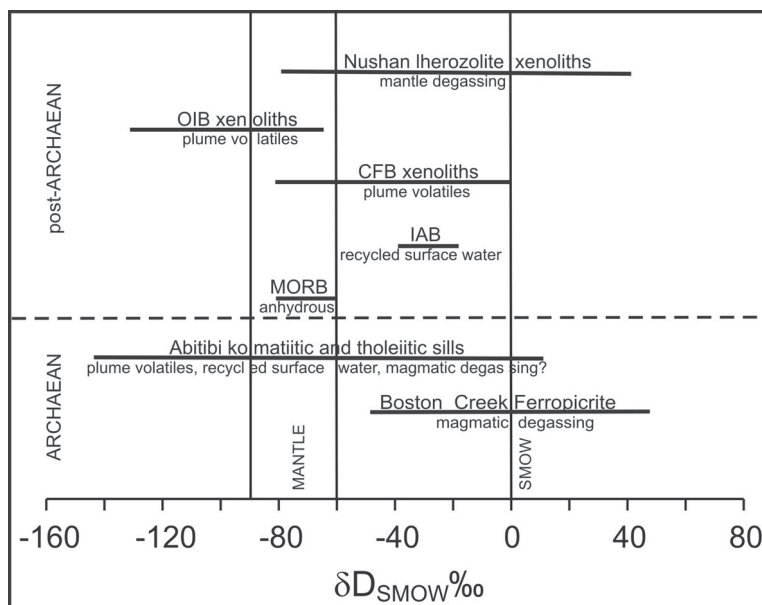


FIG. 7. Variation in $\delta D\text{‰}$ values for igneous amphibole from the Boston Creek ferropicrite compared to other major rock-types globally. Values for the ferropicrite amphibole exceed SMOW and igneous amphiboles from other Abitibi units, and even the Nushan xenoliths (Delouie *et al.* 1991a, 1995, Wagner *et al.* 1995, Valley *et al.* 1998, Xia *et al.* 2002, Stone *et al.* 2003). Acronyms: MORB: mid-ocean-ridge basalts, IAB: island-arc basalt, CFB: continental flood basalt, and OIB: ocean-island basalt.

$R = R_0 \times f^{\alpha_{\text{gas-melt}} - 1}$, with R and R_0 representing the residual and initial ratios of the heavy to light isotopes, f is the fraction of H_2O in the residual melt, and $\alpha_{\text{gas-melt}}$ is the H isotope fractionation-factor. The isotope fractionation between gas and melt ($\Delta D_{\text{gas-melt}}$) is assumed to be -130‰ and -220‰ at 1000° and 700°C , respectively (Taylor, B.E. 1986). The primary δD of magma is set at -60‰ , a generally acceptable mantle-type value (Sheppard & Epstein 1970, Taylor, H.P. 1986). If the fraction of residual H_2O in the melt (f) is 0.41 and 0.57, respectively, the value of the model ratio δD is $+50\text{‰}$ (Table 4, Fig. 8), in agreement with the highest value determined for Boston Creek amphibole. The fractionation factor between amphibole and melt is minor (Xia *et al.* 2002), such that the δD values for the amphibole should be similar to that of the parental melt.

Oxidation and PGE mineralization

A potential mechanism for the degassing of H from the Boston Creek ferropicrite is dissociation of H_2O , as follows: $\text{H}_2\text{O}_{(\text{melt})} \rightarrow \text{H}_{2(\text{gas})} + \frac{1}{2}\text{O}_{2(\text{melt})}$ (Sato & Wright 1966, Mathez 1984). The preferential loss of H as H_2 relative to H_2O would result in oxidation of the residual degassed melt. Oxidation during progressive or episodic degassing is consistent with four major

features of the ferropicrite unit: (1) Fe^{3+} -enriched magnesiohastingsite composition of the igneous amphibole (*e.g.*, Semet & Ernst 1981), (2) high bulk modal abundance of magnetite + ilmenite (up to 20 modal %; Stone *et al.* 1995b), (3) values of the ratio Fe^{3+} :total iron of 0.25 for whole-rock samples (Stone 1985), and (4) high contents of Pt in chromite (Stone & Crockett 2003). The proposed oxidation of the residual melt is significant, because it could be a controlling factor in the origin of the Cu-PGE-Ag sulfide mineralization within the gabbro layer.

The close spatial association of the PGM, Ag minerals and Cu-Fe sulfides with magnetite + ilmenite and vesicles within the magnetite gabbro host-rock all support a strong role for melt oxidation in the mineralization. Indeed, section 9, the most highly mineralized of the twelve sections studied (Stone *et al.* 1995a, 1996), is also the most highly vesicular (Fig. 9). The vesicles could represent, at least in part, volatiles derived by compaction of the underlying amphibole-bearing ultramafic cumulates and percolation of the hydrous interstitial melt upward to the interior level of formation of the gabbro layer. The medium-grained nature of the amphibole-bearing ultramafic rocks suggests that they may not have been fully crystallized during the formation of the magnetite gabbro.

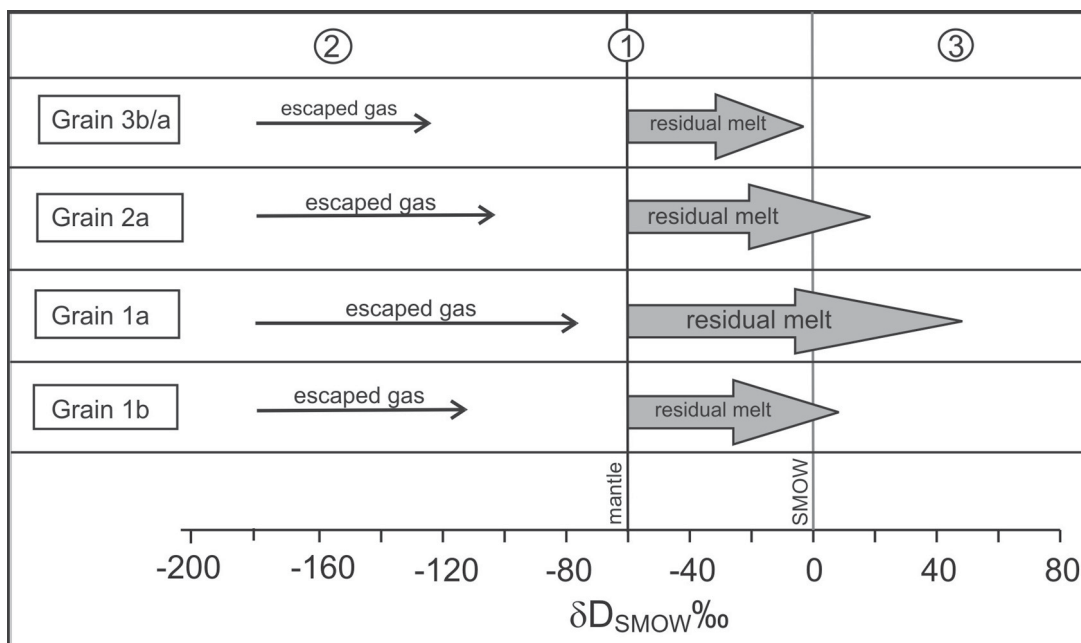


FIG. 8. Magmatic degassing model for the Boston Creek ferropicritic melt at 1000°C. Partial melting in the mantle imparts a primary magmatic δD value of -60‰ on the magma (1). Gases escaped from the melt as the reduced species H during magmatic emplacement (2). The gas/melt fractionation-factor for the H isotope is negative, and the escaped H gas is isotopically lighter, with lower δD values, whereas the residual H_2O is heavier, with higher δD values. With progressive exsolution of volatiles, δD values for degassed melt shifted from the initial mantle-type value to progressively higher and, in some grains, a positive value (3).

The relationship envisaged between the Cu-PGM-Ag mineralization and oxidation of the melt is represented in Figure 10. Laboratory experiments (Haughton *et al.* 1974) indicate that the S and FeO contents of basaltic melts in equilibrium with Fe-S-O liquids and varying $f(O_2)$ and $f(S_2)$ show a strong positive correlation. Evidently, the FeO content of a basaltic melt exerts a strong influence on the solubility of sulfur and, therefore, PGE and related metals (Poulsen & Ohmoto 1990, Fleet *et al.* 1991). The experiments also indicate a strong controlling role for temperature. Any significant reduction in FeO content and temperature markedly decreases the solubility of sulfur in the melt and promotes sulfide mineralization.

In this scenario, oxidation of the degassed residual melt in the interior of the Boston Creek ferropicrite led to Fe-Ti oxide crystallization during formation of the gabbro layer. The resulting decrease in FeO content triggered sulfide supersaturation and the Cu-PGE-Ag mineralization. In addition, the dynamic or turbulent magmatic environment promoted by the degassing had the capacity to concentrate Fe-Ti oxide and form sulfide highly enriched in PGE and Ag. Therefore, the high volatile and FeO contents and extensive degassing-

related oxidation altogether are major controlling factors in the origin of magnetite-gabbro-hosted Cu-PGE-Ag sulfide mineralization.

Depth of degassing

Degassing of the Boston Creek ferropicritic magma could have occurred at depth in the mantle or at more shallow levels in the crust. The high δD values found for the Nushan xenoliths have been attributed to degassing processes in the mantle (Xia *et al.* 2002). The Boston Creek ferropicritic melt might possibly have degassed in the mantle. However, development of the extensive zones of vesiculation in the upper chilled margin (Crocket *et al.* 2005) and in the central gabbro layer renders degassing at crustal levels more plausible. The anomalously high δD values relative to ultramafic sills in the area (Stone *et al.* 2003) can be explained if the Boston Creek ferropicrite was emplaced at higher levels in the crust and contained higher volatile contents in the initial melt. Lower confining pressures during hypabyssal intrusion or volcanic flow favor enhanced degassing relative to the deeper-level intrusions. Higher contents of volatiles in the parental ferropicritic melt are



FIG. 9. Vesicular magnetite gabbro, host rock of magmatic Cu–PGE–Ag sulfide mineralization internally within the Boston Creek ferropicrite. Note the high abundance of vesicles, very coarse-grained clinopyroxene and fine-grained plagioclase (now albite). In thin sections, the vesicles are filled by calcite with or without pyrite.

consistent with the higher abundances of amphibole and vesicles, evidence for enhancement of clinopyroxene relative to plagioclase and orthopyroxene in the crystallization sequence (Stone *et al.* 1995a) and, perhaps, the anomalous thickness (>30 m) of the clinopyroxene spinifex layer. Indeed, high volatile contents appear to be characteristics of ferropicritic melts (*e.g.*, Hanski 1992).

CONCLUSIONS

This study of the δD values and H_2O and trace element contents of igneous amphibole from the Boston Creek ferropicrite, Archean Abitibi belt (Ontario), leads to the following conclusions:

1. The contrast with the uniform major-element and trace-element compositions and H_2O content of the igneous amphibole, the negative δD values for whole-rock samples, and the negative δD values for igneous amphiboles from similarly altered ultramafic sills in the area, indicates that the heterogeneous and high values of δD for the ferropicrite unit can best be attributed to magmatic processes.

2. The anomalously high δD values, in conjunction with the development of extensive zones of vesiculation are explained by outgassing of hydrogen during emplacement of the ferropicritic melt at high levels in the crust.

3. Outgassing of hydrogen *via* dissociation of H_2O resulted in oxidation and probably cooling of the degassed residual melt in the interior of the ferropicrite unit. The resulting crystallization of Fe–Ti oxide reduced the FeO content of the melt and triggered Cu–PGE–Ag sulfide mineralization.

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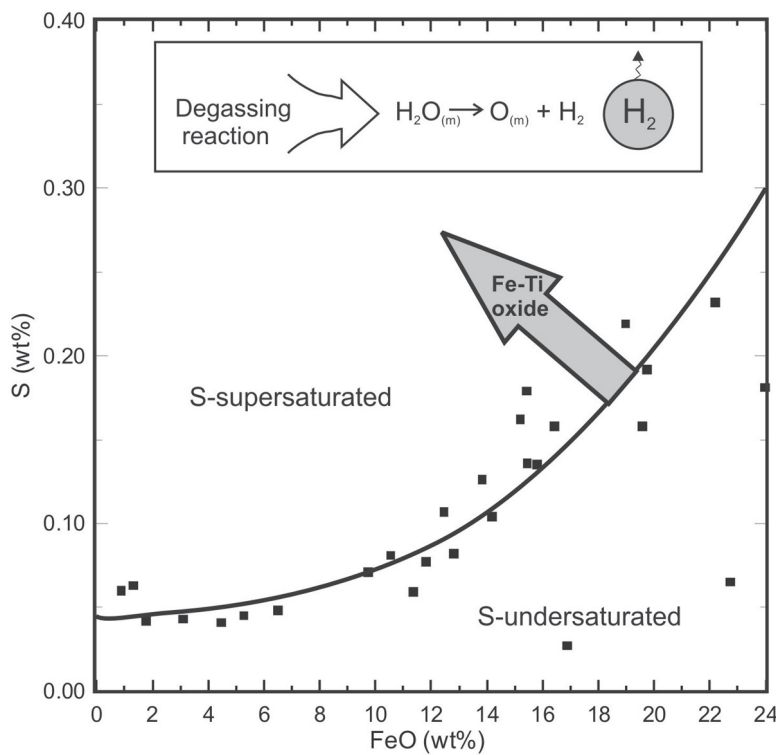


FIG. 10. The strong positive correlation of S and FeO contents of basaltic melts in equilibrium with Fe–S–O liquids at 1200°C and varying $f(\text{O}_2)$ and $f(\text{S}_2)$ in laboratory experiments (Haughton *et al.* 1974). The black squares represent the experimental data of Haughton *et al.* (1974). In this model, Fe–Ti oxide crystallization markedly reduced the FeO content of the melt, which triggered S-supersaturation and Cu–PGE–Ag mineralization in magnetite gabbro internally within the Boston Creek ferropicrite.

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