Regional hydrothermal alteration and ¹⁸O-depletion of the ca. 620 Ma Huntington Mountain pluton and related rocks, Cape Breton Island, Canada

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ABSTRACT

The ca. 620 Ma Huntington Mountain pluton and East Bay Hills Group, which comprise part of the Avalonian Mira terrane, Cape Breton Island, Nova Scotia, Canada, are characterized by pervasive propylitic alteration (chlorite, epidote, sericite, and Fe-Ti oxides) and low $\delta^{18}O$ values (−3.8 to +6.2‰). This alteration is a product of interaction with hydrothermal fluids of meteoric and/or meteoric-seawater mixed origin at ~300 °C over a range of water/rock (w/r) ratios. Locally, the propylitic alteration was further overprinted by quartz-calcite-sericite alteration. Such samples have generally higher $\delta^{18}O_{WR}$ values (up to +9.5‰), reflecting interaction with evolved meteoric water at lower temperatures (~200 °C) and very low w/r ratios. The hydrothermal fluids responsible for widespread propylitic alteration of the Huntington Mountain-East Bay Hills complex (and regions beyond) likely entered the crust during initial rifting of the Mira terrane from Gondwana at ca. 575–550 Ma.

RÉSUMÉ

Le pluton du mont Huntington, apparu il y a quelque 620 Ma et la succession volcanique des collines East Bay, qui font partie du terrane Mira d'Avalon, sur l'île du Cap-Breton, en Nouvelle-Écosse, au Canada, se caractérisent par une altération propylitique envahissante (chlorite, épidote, séricite, et oxydes de fer et de titane), et des teneurs faibles en $\delta^{18}O$ (−3,8 à +6,2‰). Cette altération est le résultat de l'interaction de fluides hydrothermaux d'origine mixte météorique ou météorique et d'eau de mer, ou des deux, à une température d'environ 300 °C, selon divers rapports eau/roche. Au plan local, une altération de quartz-calcite-séricite s'est superposée à l'altération propylitique. Ces échantillons ont en règle générale des valeurs de $\delta^{18}O_{WR}$ supérieures (qui peuvent atteindre +9,5‰), ce qui rend compte de l'interaction de l'eau météorique évoluée à de basses températures (environ 200 °C) et de rapports eau/roche très faibles. Les fluides hydrothermaux à l'origine de l'altération propylitique très étendue du complexe du mont Huntington et des collines East Bay (et des régions au-delà) ont probablement pénétré la croûte terrestre au cours du soulèvement initial du terrane Mira, à l'époque du continent de Gondwana, il y a de cela entre 575 et 550 Ma.

[Traduit par la redaction]

INTRODUCTION

West Avalonia forms a fragmented belt along the eastern margin of the northern Appalachian orogen from Newfoundland to Massachusetts and records the complex tectonic history of several late Proterozoic magmatic arcs that evolved proximal to Gondwana (Murphy *et al.* 1990; Barr *et al.* 1998). Like other terranes in West Avalonia, the Mira terrane of southeastern Cape Breton Island is composed of mainly late Proterozoic volcanic-plutonic-sedimentary belts overlain by younger sedimentary cover sequences (Fig. 1).

The tectonic history of the Mira terrane, and especially its relationship to the Ganderian Bras d'Or and Aspy terranes of Cape Breton Island (Fig. 1), have been the subject of longstanding debate (Barr and Raeside 1989; Murphy *et al.* 1990; Barr *et al.* 1998). Potter *et al.* (2008a) added a new dimension to that discussion by showing the Mira terrane to have a distinctive low-¹⁸O signature relative to other peri-Gondwanan terranes of Cape Breton Island, and Potter *et al.* (2008b) expanded that observation to other West Avalonian terranes. Potter *et al.* (2008a, b) concluded that the Avalonian terranes underwent post-magmatic oxygen-

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isotope exchange with meteoric-dominated hydrothermal fluids across the region, and proposed that these fluids infiltrated the crust during regional transtensional faulting associated with initial rifting of Avalonia at ca. 600–550 Ma.

Here we evaluate the hypothesis of Potter *et al.* (2008a, b) through petrographic and stable isotope analysis of the ca. 620 Ma Huntington Mountain pluton and associated East Bay Hills Group from the Mira terrane (Fig. 1). More detailed examination of a single plutonic-volcanic complex allows testing for local versus regional patterns of hydrothermal alteration and ^{18}O-depletion that are essential in understanding the exact processes that lead to the noted ^{18}O-depletion observed on a regional-scale in Potter *et al* (2008a, b). We also examine the origin(s) of the hydrothermal fluid, and whether its presence in the Huntington Mountain – East Bay Hills area added to the potential for base- and precious-metal mineralization, as is sometimes the case for such mineral deposits associated with porphyry and epithermal systems (Lynch *et al.* 1990; Sillitoe and Hedenquist 2003; Richards 2009).

GEOLOGICAL SETTING

The Mira terrane is composed of mainly volcanic and plutonic rocks that form linear northeast-southwest trending belts separated by regional-scale faults and younger sedimentary cover sequences (Fig. 1). The majority of the Mira terrane rocks can be subdivided into four magmatic associations: the ca. 680 Ma Stirling Group, the ca. 620 Ma volcanic-plutonic units, which include the East Bay Hills Group and Huntington Mountain pluton, the ca. 575–560 Ma Coastal belt, and the ca. 380 Ma Devonian plutons (Barr *et al.* 1996).

The ca. 680 Ma Stirling Group consists primarily of andesitic to basaltic lapilli tuff with interbeds of tuffaceous arenite and laminated siltstone. Barr *et al.* (1996) interpreted it to have formed in an extensional basin within a volcanic arc. The Stirling Group contains zones of pyrite-rich, laminated litharenite-siltstone-chert-dolomite, which is host to the Mindamar Zn-Pb-Cu-Ag-Au deposit (interpreted as an exhalative volcanogenic massive sulphide deposit by Barr *et al.* 1996) (Fig. 1). The ca. 620 Ma volcanic-plutonic-sedimentary belts (East Bay Hills and Huntington Mountain – this study, Coxheath Hills, and Pringle Mountain Group and Chisholm Brook plutonic suite) are composed mostly of granitic to granodioritic rocks and andesitic to rhyolitic tuffs and flows (see next section for detailed descriptions). Barr *et al.* (1996) interpreted these high-K, calc-alkaline rocks to have formed in a subduction-related convergent margin setting. Mineralization includes sporadic Cu anomalies within an extensive shear zone in the Sporting Mountain
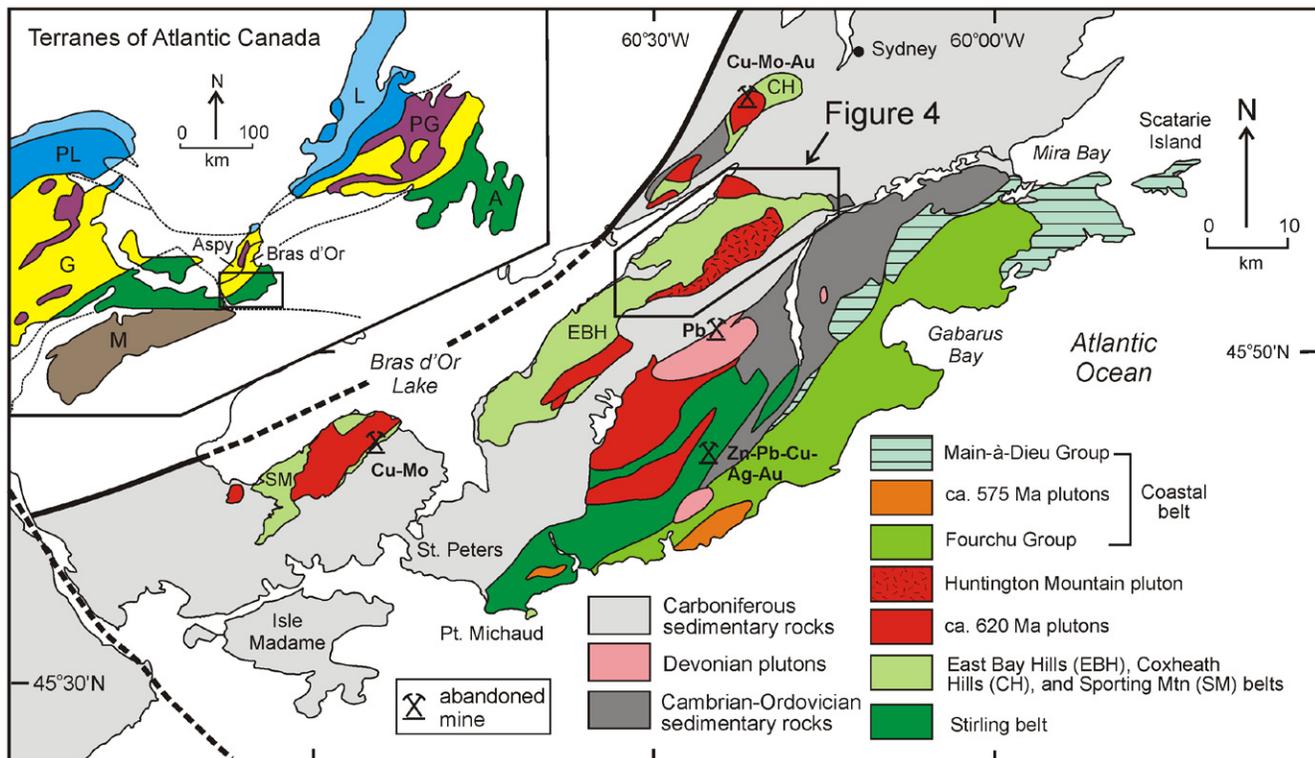

Fig. 1. Geological map of the Mira terrane, Cape Breton Island (modified from Barr *et al.* 1996), and the location of the Huntington Mountain pluton and East Bay Hills Group. Inset map shows major components of the northern Appalachian orogen after Hibbard *et al.* (2006). Abbreviations: A, Avalonia; G, Ganderia; L, Laurentia; M, Meguma; PG, peri-Gondwanan; PL, peri-Laurentian terranes.

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pluton and the Coxheath porphyry-style Cu-Mo-Au deposit located in the Coxheath Hills Group and comagmatic Coxheath Hills pluton (Barr et al. 1996; Lynch and Ortega 1997; Kontak *et al.* 2003) (Fig. 1).

The volcanic-sedimentary sequences of the ca. 575–560 Ma Coastal Belt are subdivided into the Fourchu and Main-à-Dieu groups. The Fourchu Group consists of mainly dacitic tuffs and flows, with minor basaltic to rhyolitic tuffs and flows and tuffaceous sedimentary rocks, and was interpreted by Barr *et al.* (1996) to represent a volcanic-arc setting. The Main-à-Dieu Group consists of mainly tuffaceous sedimentary and epiclastic rocks, with minor basaltic and rhyolitic flows, interpreted by Barr *et al.* (1996) to have formed in an intra-arc extensional setting. Given their close stratigraphic association, the Fourchu and Main-à-Dieu groups are inferred to be different facies formed more or less coevally (Barr *et al.* 1998). The ca. 380 Ma Devonian plutons are composed mostly of monzogranite and are interpreted to have formed in an anorogenic, within-plate setting (Barr and Macdonald 1992).

Geology of the Huntington Mountain area

The ca. 620 Ma Huntington Mountain pluton intruded the northeastern part of the East Bay Hills Group (Fig. 1). The pluton is dominated by diorite, but also contains granodiorite, leucogranite, monzogranite, and syenogranite. The East Bay Hills Group forms an elongate belt along and inland from the southeastern shore of Bras d'Or Lake. This group is dominated by andesitic to dacitic rocks with lesser quantities of basaltic to rhyolitic tuffs and flows and epiclastic sedimentary rocks. Field relationships suggests that the Huntington Mountain diorite was emplaced first, followed by granodiorite, leucogranite, and syenogranite; the small body of monzogranite may have been emplaced at some time between the granodiorite and syenogranite (Barr *et al.* 1996). Earlier basaltic, andesitic-dacitic, and dacitic rocks in the East Bay Hills Group have a thermal overprint attributed to pluton emplacement. Minor pyrite, chalcopyrite, and malachite in the basaltic rocks are associated with the Huntington Mountain pluton (Barr et al. 1996). Later basaltic andesite and rhyolite are considered to be coeval with pluton emplacement as all units are dated at ca. 620 Ma (Barr *et al.* 1990; Keppie *et al.* 1990; Bevier *et al.* 1993). All rocks in the study area are characterized by some degree of post-magmatic alteration.

METHODS

A representative range of pristine to moderately altered volcanic and plutonic rocks were collected (65 in total) in the Huntington Mountain area. These were discriminated in the field on the basis of visible turbid feldspar, veining, and alteration minerals (chlorite, epidote, quartz, calcite, pyrite, and ilmenite). The nature of the alteration was confirmed by petrographic examination of thin sections. A portion of each sample was crushed for mineral separation and powder X-ray diffraction (pXRD). Standard mineral separation techniques (magnetic and heavy liquid separation, hand-picking) were used to isolate primary and secondary phases. Separate purity was assessed using high-brilliance pXRD (Rigaku rotating anode diffractometer, CoKα radiation at 160 kV and 45 mA). Purity was better than 90% for most separates and >95% for quartz. Feldspar separates consisted of alkali feldspar, either albitic plagioclase or potassium feldspar, or mixtures of both.

Stable isotopic compositions are reported in δ-notation relative to VSMOW for hydrogen and oxygen and VPDB for carbon (Coplen 1996). Oxygen was liberated from silicates by overnight reaction with ClF^3 at 550 °C in sealed Ni reaction vessels, following the method of Clayton and Mayeda (1963), as modified by Borthwick and Harmon (1982). The released oxygen was converted to CO_2 over a red-hot carbon rod and its oxygen isotopic composition measured using a dual-inlet DeltaPlus XL stable isotope ratio mass-spectrometer. The $\delta^{18}O$ values of an internal laboratory standard quartz, NBS-30 (biotite) and NBS-28 (quartz) were +11.4 ± 0.2‰, +5.1 ± 0.1‰, and +9.7 ± 0.3‰, respectively, which compares well with their accepted values of +11.5‰, +5.1‰, and +9.6‰. Sample reproducibility was generally better than ±0.2‰.

Hydrogen was extracted from hydrous silicates following the methods of Bigeleisen *et al.* (1952), as modified by Vennemann and O'Neil (1993). Following drying at 105 °C overnight under vacuum, samples were heated to ~1200 °C using an oxygen-methane torch. Released hydroxyl groups were then converted to H_2O by reaction with copper oxide at 400–600 °C, and H^2O then reduced to H_2 over Cr at 900 °C. Stable hydrogen-isotope compositions were measured using a dual-inlet VG Prism-II stable isotope ratio mass-spectrometer calibrated to VSMOW and SLAP using four in-house water standards. A δ^2H value of –55 ± 5‰ was obtained for kaolinite KGa-1 (accepted value = –57‰). Sample reproducibility was generally better than ±5‰.

Calcite was placed in glass reaction vials and dried at 60 °C for 12 hours. It was then reacted under vacuum with orthophosphoric acid at 90 °C for 10 minutes using a MultiPrep autosampler attached to a dual-inlet VG Optima stable isotope ratio mass-spectrometer. During this study, laboratory standard calcite had $\delta^{18}O$ and $\delta^{13}C$ values of +26.2

± 0.1‰ and +0.7‰ ± 0.1‰, respectively (accepted values, +26.2‰ and +0.8‰). Sample reproducibility for both oxygen and carbon isotopic compositions was generally better than ±0.1‰.

RESULTS

Petrography

Plagioclase and hornblende are the main primary minerals in the Huntington Mountain diorite and granodiorite; K-feldspar, quartz, and biotite occur in lesser quantities. Primary phases in the leucogranite are dominantly perthitic K-feldspar, quartz, and plagioclase, and in the syenogranite, K-feldspar, quartz, and plagioclase. These rocks have undergone weak to strong secondary alteration. Basaltic to andesitic rocks of the East Bay Hills Group are typically aphanitic and massive, with slight to moderate porphyritic textures. Phenocrysts consist mostly of plagioclase and rarely, clinopyroxene. Plagioclase-rich groundmass is commonly overprinted by secondary phases and in a few localities, all primary features have been obscured. Dacite is typically aphanitic to weakly porphyritic, consisting mainly of plagioclase phenocrysts suspended in a plagioclase-rich groundmass with minor quartz. Dacite typically exhibits moderate to strong alteration. Rhyolite samples are dominated by ash to lapilli crystal tuff; aphanitic to weakly porphyritic flow-banded pyroclastic beds are also present. Rhyolite consists of feldspar microlites, quartz, and minor K-feldspar, and exhibits only weak alteration.

Three main alteration types were observed. Type 1 consists of fine-grained chlorite, epidote, sericite, and Fe-Ti oxides (Figs. 2a, b, c), which are characteristic of propylitic alteration (Meyer and Hemley 1967). This alteration is widespread and varies in intensity from weak to strong (partial to complete replacement of primary phases). Type 2 consists of fine- to coarse-grained, anhedral quartz, sericite, and calcite, with minor Fe-oxides. This moderate to strong alteration is highly localized, and has partially to completely replaced primary minerals and textures (Fig. 2d). Type 2 alteration appears to overprint the propylitic alteration (Fig. 2e). Type 3, which was observed only rarely, is typical of phyllic alteration (Meyer and Hemley 1967). Most primary minerals have been moderately to strongly overprinted by fine-grained euhedral quartz, sericite, and pyrite (Fig. 2f). Type 3 alteration occurs mainly in the contact zone between the Huntington Mountain pluton and East Bay Hills Group, suggesting its development during contact metamorphism. Contact metamorphic features in the East Bay Hills dacite, including hornfelsic texture and pyrite mineralization, were previously reported by Barr *et al.* (1996). Such alteration is a common product of interaction with magmatic-dominated fluids in the hottest parts of a hydrothermal system (~ 350–500 °C; Harris and Golding 2002).

Stable isotope compositions

The $\delta^{18}O_{WR}$ results for the Huntington Mountain pluton range from −1.5 to +7.1‰ (Table 1a, Fig. 3a, 4): diorite and granodiorite, −1.5 to +4.5‰; syenogranite, −1.2 to +6.2‰; leucogranite, +3.8 to +7.1‰ (except for one sample, +0.2‰). Two leucogranite samples have $\delta^{2}H_{WR}$ values of −60 and −56‰, whereas values are lower for other plutonic rock types (−78 to −61‰). The East Bay Hills Group has a wider range of $\delta^{18}O_{WR}$ values (−3.8 to +9.5‰) than the plutonic suite: rhyolite-andesite and dacite, −3.8 to +6.5‰; basaltic rocks, −1.9 to +9.5‰; rhyolite, +4.6 to +6.9‰ (Table 1b, Fig. 3b). The $\delta^{2}H_{WR}$ values of the volcanic rocks range from −93 to −70‰. In Figure 4 no clear pattern is observed between $\delta^{18}O_{WR}$ values and the intrusive sequence and/or rock types in this complex.

Primary quartz (qtz) in the plutonic rocks has $\delta^{18}O_{qtz}$ values ranging from +0.5 to +7.0‰, with leucogranite having higher values (≥ +4.8‰) than other rock types. The pattern for alkali feldspar (fs) is similar (leucogranite $\delta^{18}O_{fs}$, +4.4 to +6.0‰; other rock types, +1.4 to +4.6‰). Hornblende (hbl) has $\delta^{18}O_{hbl}$ values of +1.4 to +5.5‰. The $\delta^{18}O$ values for phenocrysts from volcanic samples also vary widely: quartz, −1.5 to +8.2‰; alkali feldspar, −0.3 to +6.5‰.

Chlorite (chl) $\delta^{18}O_{chl}$ values vary widely: granodiorite, syenogranite and andesite, −6.3 to −4.0‰; diorite and leucogranite (−5.2 to +3.3‰). The $\delta^{2}H_{chl}$ values for all rock types range from −77 to −69‰. Disseminated secondary quartz from a diorite sample affected by phyllic alteration has a $\delta^{18}O_{qtz}$ value of +3.3‰, whereas values for basaltic to andesitic rocks and leucogranite affected by quartz-sericite-calcite alteration are much higher (+11.1 to +15.1‰). Disseminated calcite (cal) from plutonic rocks has $\delta^{18}O_{cal}$ values of +5.4 to +8.4‰, and from volcanic rocks, +5.8 to +11.7‰. Disseminated calcite from the plutonic rocks has $\delta^{13}C_{cal}$ values of −3.8 to +0.1‰; values for the volcanic rocks are lower (−7.2 to −4.5‰).

Rare vein quartz associated with phyllic alteration of diorite has a $\delta^{18}O_{qtz}$ value of −2.1‰. Veins are more abundant in the volcanic rocks, with $\delta^{18}O_{qtz}$ values ranging from +6.1 to +10.5‰. Vein calcite $\delta^{18}O_{cal}$ and $\delta^{13}C_{cal}$ values range from +6.0 to +14.3‰, and −7.4 to −3.2‰, respectively. As for the disseminated calcite, the vein calcite samples most enriched in ^{18}O are also the most depleted of ^{13}C.
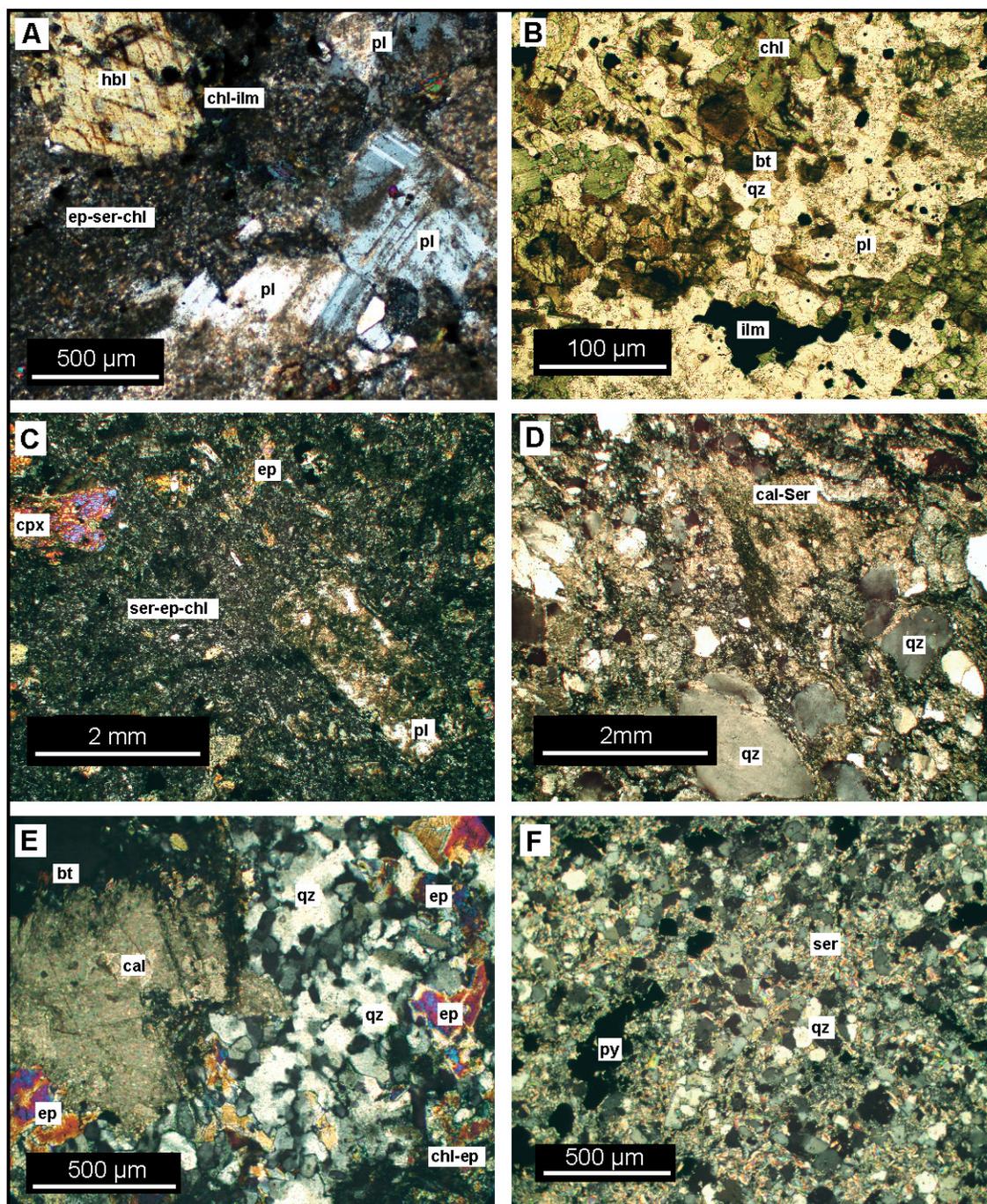
Fig. 2. Photomicrographs of the Huntington Mountain pluton and East Bay Hills Group: (A) CBI-6-6-86, diorite partially replaced by chlorite-epidote-sericite-ilmenite; (B) CBI-6-6-87, diorite with replacement of biotite by chlorite-ilmenite; (C) CBI-6-6-39, porphyritic basalt with sericitized plagioclase, rare clinopyroxene phenocrysts, and epidote-chlorite-sericite alteration; (D) CBI-6-6-11, basalt overprinted by quartz-calcite-sericite alteration; (E) CBI-6-6-25/26, chlorite-epidote overprinted by fine-grained quartz, which is overprinted in turn by calcite; and (F) CBI-6-6-103, diorite replaced by quartz-sericite-pyrite. Abbreviations: bt - biotite, cal - calcite, chl - chlorite, cpx - clinopyroxene, ep - epidote, hbl - hornblende, ilm - ilmenite, pl - plagioclase, py - pyrite, qz - quartz, ser - sericite.

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Table 1a. Oxygen- and hydrogen-isotope results for the Huntington Mountain pluton.

Sample	Map Unit	[a]Alteration	$\delta^{18}O_{wr}$	$\delta^{2}H_{wr}$	$\delta^{18}O_{qtz}$	$\delta^{18}O_{fs}$	$\delta^{18}O_{hbl}$	$\delta^{18}O_{chl}$	$\delta^{2}H_{chl}$	$\delta^{18}O_{ser}$	$\delta^{2}H_{ser}$	$\delta^{18}O_{cal}$	$\delta^{13}C_{cal}$
Huntington Mountain pluton													
CBI-8-5-23	Leucogranite	1 - weak	5.9	-	6.4	5.2	-	[b,1]1.0	-	-	-	-	-
CBI-6-6-81	Leucogranite	1 - weak	5.8	-	6.2	5.0	-	[b,1]-1.2	-	-	-	-	-
CBI-6-6-105	Leucogranite	1 - weak to moderate	3.8	-56	4.8	4.4	-	[b,1]-3.3	-	-	-	-	-
CBI-6-6-106	Leucogranite	1 - weak	5.4	-	7.0	5.2	-	[b,1]-0.2	-	-	-	-	-
[d]EB91-014	Leucogranite	2 - undetermined	7.1	-60	[b]15.1	6.0	-	-	-	-	-	[b]8.4	[b]-3.8
[d]F16C-1582	Leucogranite	1 - undetermined	0.2	-	-	-	-	-	-	-	-	-	-
CBI-6-6-54	Syenogranite	1 - weak to moderate	6.2	-71	4.3	3.5	-	[b,1]-4.8	-	-	-	-	-
CBI-6-6-55	Syenogranite	1- moderate to strong	1.4	-61	0.5	1.8	-	[b,1]-6.3	-	-	-	-	-
[d]F16C-1631	Syenogranite	1 - undetermined	4.3	-	-	-	-	-	-	-	-	-	-
[d]F16C-1635	Syenogranite	1 - undetermined	-1.2	-70	-	-	-	-	-	-	-	-	-
[d]F16C-1782	Syenogranite	1 - undetermined	5.5	-	-	-	-	-	-	-	-	-	-
CBI-8-5-21	Granodiorite	1 - moderate	-	-	1.3	2.9	-	[b,1]-4.0	-	-	-	-	-
CBI-8-5-22	Granodiorite	1 - moderate	1.2	-62	1.5	3.1	-	[b,1]-5.3	-	-	-	-	-
CBI-8-5-25	Diorite	1 - moderate	2.7	-69	-	2.5	3.9	[b,1]-0.8	[b,1]-73	-	-	-	-
CBI-8-5-26	Diorite	1 - moderate	-	-	-	3.6	-	-	-	-	-	-	-
CBI-8-5-27A	Diorite	1 - weak to moderate	-	-	4.8	3.8	-	[b,1]-1.7	-	-	-	-	-
CBI-8-5-27B	Diorite	1 - weak to moderate	-	-	-	-	-	[b,1]-1.0	-	-	-	-	-
CBI-6-6-56	Diorite	1 - moderate to strong	1.7	-72	-	2.5	1.7	[b,1]-5.2	[b,1]-73	-	-	-	-
CBI-6-6-82	Diorite	1 - moderate	3.8	-	-	3.9	4.6	[b,1]0.1	-	-	-	-	-
CBI-6-6-83	Diorite	1 - moderate	4.5	-78	-	4.3	5.5	[b,1]3.3	[b,1]-69	-	-	-	-
CBI-6-6-84	Diorite	1 - moderate to strong	2.2	-	-	2.4	3.5	-	-	-	-	-	-
CBI-6-6-86	Diorite	1 - moderate	3.6	-69	-	4.6	3.3	[b,1]0.6	[b,1]-77	-	-	-	-
CBI-6-6-87	Diorite	1 - moderate	3.6	-	-	3.8	4.5	-	-	-	-	-	-
CBI-6-6-102	Diorite	1 - strong, 2 - weak, 3 - moderate	1.0	-	-	*1.4	1.4	-	-	[b,1,*]1.4	[b,1,*]-73	[b,2]5.4	[b,2]0.1
CBI-6-6-103	Diorite	3 - strong	1.9	-	[b,3]3.3	-	-	-	-	[b,1]2.0	[b,1]-61	-	-
CBI-6-6-104	Diorite	1 - strong, 3 - moderate	-1.5	-68	[c,1]-2.1	-	-	-	-	-	-	-	-
[d]F16C-1751	Diorite	1 - undetermined	3.1	-	-	-	-	-	-	-	-	-	-

Notes: cal = calcite, chl = chlorite, fs = feldspar, hbl = hornblende, qtz = quartz, ser = sericite; a = alteration types: (1) propylitic, (2) quartz, sericite and calcite, and (3) phyllic; b = disseminated secondary mineral; c = vein mineral; d = previously reported by Potter *et al.* (2008a); * = ser>fs mixture taken from Table 1b.
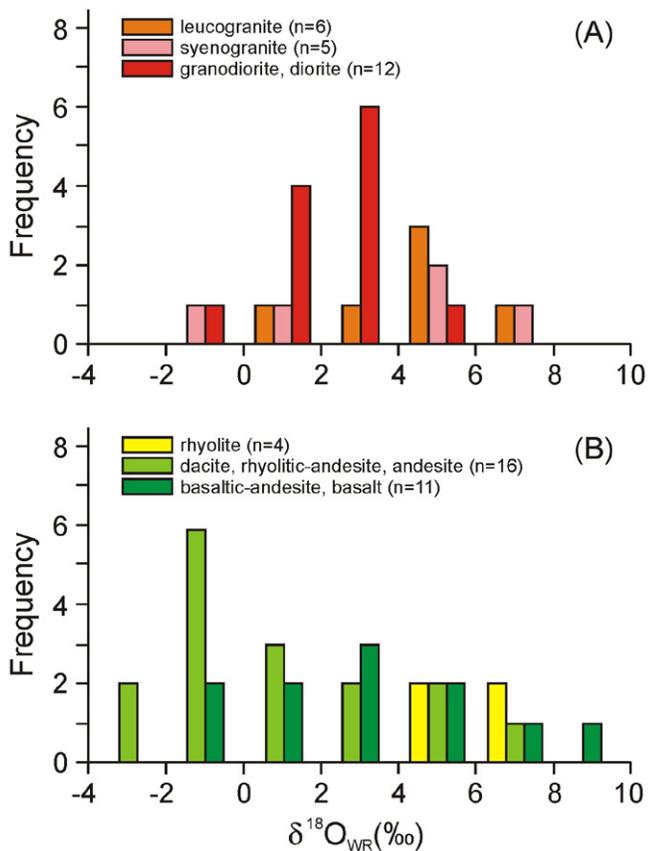
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Fig. 3. Distribution of $\delta^{18}O_{WR}$ values for various rock types in the Huntington Mountain pluton (A) and the East Bay Hills Group (B).

DISCUSSION

Fluid composition

Most Huntington Mountain area samples have $\delta^{18}O_{WR}$ values that are lower than typical for "normal" (+6 to +10 ‰, Taylor 1974) igneous rocks, thus following the pattern of ^{18}O-depletion reported for the Avalon terrane by Potter *et al.* (2008a, b). Most commonly, igneous rocks with abnormally low $\delta^{18}O$ values have experienced post-crystallization alteration (see Taylor 1974), but crystallization from a low-^{18}O magma (see Taylor 1986; Bindeman and Valley 2000) cannot be ruled out a priori. In the latter case, high-temperature oxygen isotopic equilibrium should produce primary compositions in which (i) $\delta^{18}O_{qtz} > \delta^{18}O_{fs} > \delta^{18}O_{hbl}$, and (ii) values of $\Delta^{18}O_{qtz-fs}$ and $\Delta^{18}O_{fs-hbl}$ ($\Delta_{a-b} = \delta_a - \delta_b$) are small and positive (~+1 to +2 ‰, Taylor and Epstein 1962). Hydrothermally altered igneous rocks, by comparison, typically lack consistent high-temperature oxygen-isotope equilibrium between coexisting primary phases (Criss and Taylor 1986; Liu 2000). While some samples from the

study area have $\Delta^{18}O_{mineral1-mineral2}$ values within the range of magmatic systems, others – most particularly diorite, granodiorite, and syenodiorite – display oxygen isotopic disequilibrium, as manifested by negative values for $\Delta^{18}O_{qtz-fs}$ and $\Delta^{18}O_{fs-hbl}$. Such reversals are a hallmark of post-crystallization, hydrothermal alteration.

The leucogranite and rhyolite exhibit the least alteration and, except for one sample, have relatively high $\delta^{18}O_{WR}$ values ($\geq$ +4‰); samples of mafic to intermediate composition, in which mineral phases are more susceptible to alteration, generally have lower $\delta^{18}O_{WR}$ values (Fig. 3, Table 1a, b). The few samples retaining mineralogical and textural characteristics of phyllic alteration have among the lowest $\delta^{18}O_{WR}$ (<2‰) and $\delta^{18}O_{qtz}$ values (<3‰, Fig. 5, Table 1a, b), despite their potential association with magmatic fluids during contact metamorphism. The isotopic results suggest that these samples were overprinted by low-^{18}O hydrothermal fluids.

Samples affected by moderate to strong propylitic alteration display the largest range of $\delta^{18}O_{WR}$ values, with the majority falling between –2 and +4‰ (Fig. 5); primary quartz affected by propylitic alteration likewise has a wide range of $\delta^{18}O_{qtz}$ values (–2 to +7‰, Table 1a, b). Samples moderately to strongly affected by the later quartz-sericite-calcite alteration have higher $\delta^{18}O_{WR}$ values (+4 to +10‰, Fig. 5), as does associated vein quartz ($\delta^{18}O_{qtz}$ = +6 to +11‰) (Table 1a, b). The δ^2H_{WR} values (–93 to –56‰) fall close to or within the normal range for igneous rocks (–85 to –50‰, Sheppard 1986). However, interaction with mid- to low-latitude meteoric water or seawater can also produce such compositions (Longstaffe 1982). With the exception of hornblende, hydrous minerals in the Huntington Mountain area are of secondary origin (chlorite > epidote > sericite). Where comparisons are possible, the δ^2H_{chl} values are very similar to the δ^2H_{WR} values (Table 1a, b), indicating that chlorite – and fluids that formed it – control the bulk hydrogen-isotope composition of most samples.

The oxygen isotopic results for minerals formed and/or re-equilibrated during both the propylitic and quartz-sericite-calcite alteration stages have been used to estimate fluid $\delta^{18}O$ values (Fig. 6). Over the 300–450 °C temperature range typical for propylitic alteration (Ferry 1985; Criss and Taylor 1986), $\delta^{18}O_{H2O}$ values range from –9 to –2‰ at 300 °C, to –5 to +1‰ at 450 °C (Fig. 6a). Coexisting propylitic quartz and chlorite for syenogranite and granodiorite samples (CBI-6-6-55 and CBI-8-5-22) yield virtually identical $\delta^{18}O_{H2O}$ values of –6 to –5‰ at 300 °C as does coexisting secondary feldspar and chlorite for andesite sample CBI-6-6-52 (Fig. 6a). Hence we use 300 °C as the propylitic alteration temperature in the discussion that follows. These results suggest that meteoric water ($\delta^{18}O_{H2O}$ < 0‰) comprised a significant fraction of the propylitic alteration fluid. Some estimates based on brachiopod carbonate suggest $\delta^{18}O$ values of –8 to –6‰ for late
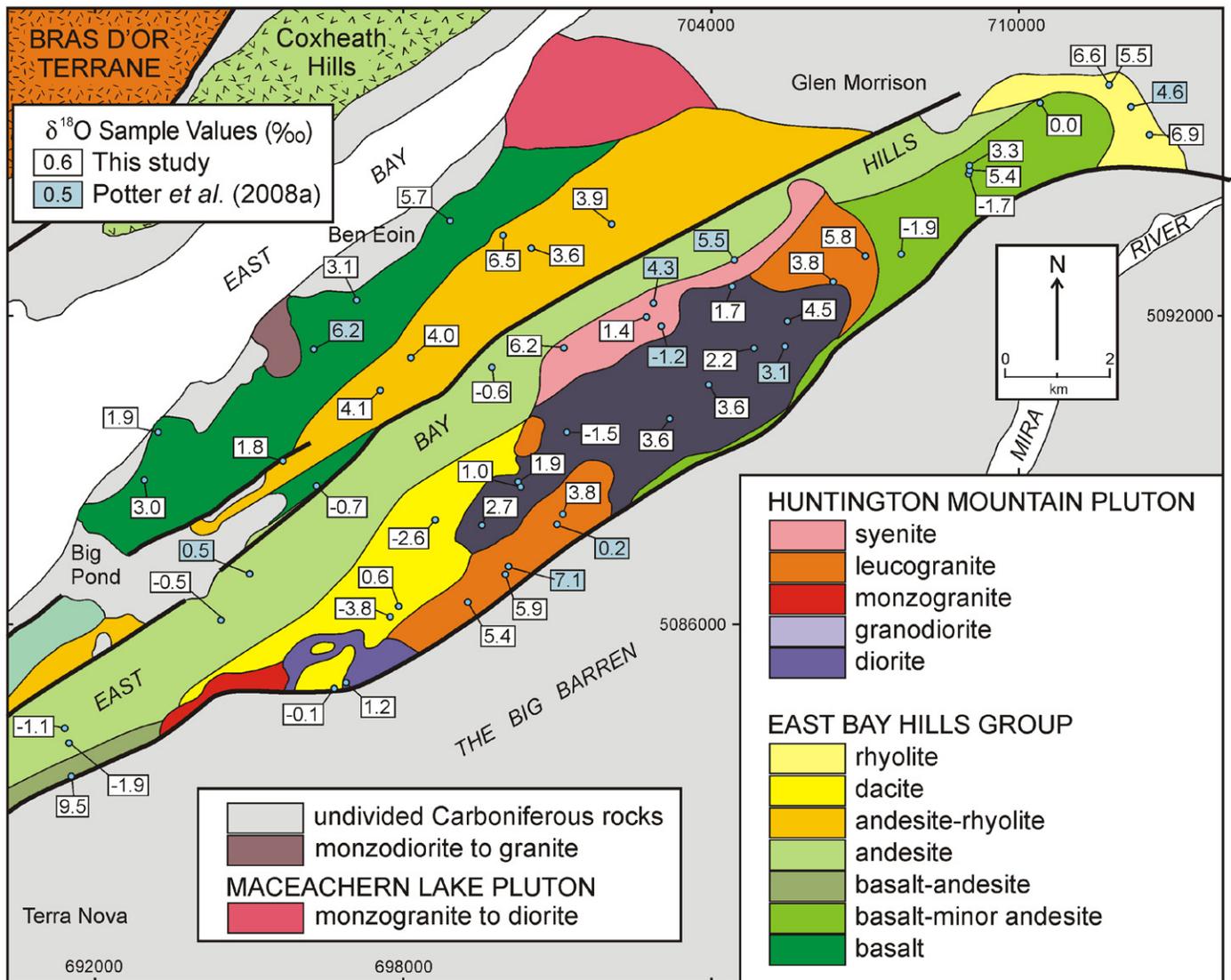
Fig. 4. Geologic map of the Huntington Mountain pluton and East Bay Hills Group, including $\delta^{18}O_{WR}$ values of samples from this study and Potter *et al.* (2008a). Map is after Barr *et al.* (1996).

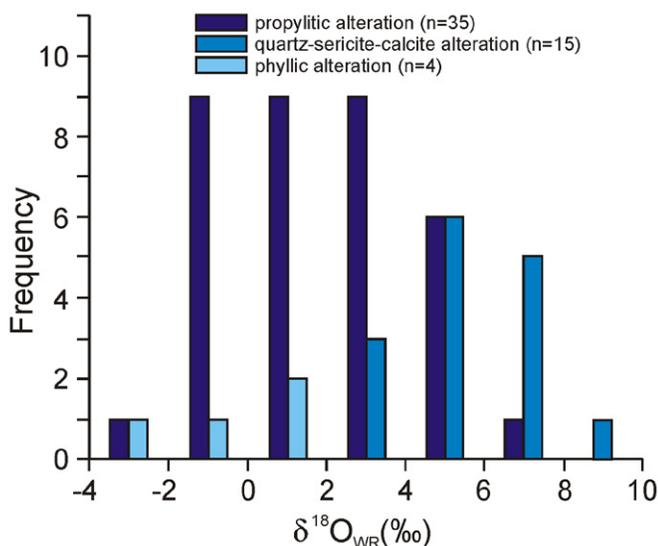**Fig. 5.** Distribution of $\delta^{18}O_{WR}$ values by alteration type: propylitic, quartz-sericite-calcite, and phyllic. The samples retaining mineralogical characteristics of phyllic alteration appear to have been isotopically overprinted during later propylitic alteration.

Precambrian-early Cambrian seawater (Veizer *et al.* 1986). However, evidence from ophiolite, greenstone, and massive sulphide deposits overwhelmingly suggests open ocean $\delta^{18}O$ values that varied no more than ±2‰ from its present composition since at least 3 Ga (Muehlenbachs 1986; Johns *et al.* 2006). Accordingly, we accept a seawater $\delta^{18}O$ value of 0‰ in the discussion that follows.

Quartz-sericite-calcite alteration is generally known to occur at temperatures ranging from 200 to 300 °C (Ferry 1985; Criss and Taylor 1986). For the Huntington

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Table 1b. Oxygen- and hydrogen-isotope results for the East Bay Hills Group.

Sample	Map Unit	[a]Alteration	$\delta^{18}O_{wr}$	$\delta^{2}H_{wr}$	$\delta^{18}O_{qtz}$	$\delta^{18}O_{fs}$	$\delta^{18}O_{hbl}$	$\delta^{18}O_{chl}$	$\delta^{2}H_{chl}$	$\delta^{18}O_{ser}$	$\delta^{2}H_{ser}$	$\delta^{18}O_{cal}$	$\delta^{13}C_{cal}$
East Bay Hills Group													
CBI-8-5-30	Rhyolite	1 - weak, 2 - moderate	6.6	-	8.2	6.5	-	-	-	-	-	-	-
		2 - qtz-cal vein	-	-	[c,2]10.1	-	-	-	-	-	-	[c,2]12.1	[c,2]-7.3
CBI-6-6-17	Rhyolite	1 - weak, 2 - moderate	5.5	-	-	-	-	-	-	-	-	[b,2]9.4	[b,2]-5.0
		2 - qtz-cal vein	-	-	[c,2]9.1	-	-	-	-	-	-	[c,2]7.3	[c,2]-5.2
CBI-6-6-80	Rhyolite	1 - weak, 2 - moderate	6.9	-	-	-	-	-	-	-	-	-	-
[d]FS91-53	Rhyolite	2 - undetermined	4.6	-	-	-	-	-	-	-	-	-	-
CBI-8-5-28	Dacite	1 - strong, 3 - moderate	-2.6	-70	-1.5	-	-	-	-	-	-	-	-
CBI-6-6-98	Dacite	1 - moderate	-0.1	-	-	-	-	-	-	-	-	-	-
CBI-6-6-99	Dacite	1 - strong	0.6	-	-	-	-	-	-	-	-	-	-
CBI-6-6-101	Dacite	1 - strong	-3.8	-	-	-	-	-	-	-	-	-	-
CBI-6-6-93	Andesite-Rhyolite	1 - moderate, 2 - weak	1.8	-	-	-	-	-	-	-	-	-	-
CBI-6-6-94	Andesite-Rhyolite	1 - weak, 2 - moderate	4.1	-	-	-	-	-	-	-	-	-	-
CBI-6-6-95	Andesite-Rhyolite	2 - qtz-cal vein	-	-	[c,2]7.7	-	-	-	-	-	-	-	-
CBI-6-6-96	Andesite-Rhyolite	1 - weak, 2 - moderate	4.0	-	-	-	-	-	-	-	-	-	-
CBI-6-6-118	Andesite-Rhyolite	1 - weak, 2 - moderate	3.6	-	-	-	-	-	-	-	-	-	-
CBI-6-6-119	Andesite-Rhyolite	1 - weak, 2 - moderate	3.9	-77	-	-	-	-	-	-	-	[c,2]6.0	[c,2]-3.2
CBI-6-6-121	Andesite-Rhyolite	1,2 - weak to moderate	6.5	-	-	-	-	-	-	-	-	-	-
CBI-6-6-50	Andesite	1 - moderate to strong	-0.5	-	-	-	-	-	-	-	-	-	-
CBI-6-6-51	Andesite	1 - moderate to strong	-0.7	-	-	-	-	-	-	-	-	-	-
CBI-6-6-52	Andesite	1 - moderate to strong, 2 - weak	-0.6	-	[b,2]11.1	-0.3	-	[b,1]-5.3	[b,1]-69	-	-	-	-
CBI-6-6-89	Andesite	1 - moderate to strong	-1.1	-	-	-	-	-	-	-	-	-	-
CBI-6-6-90	Andesite	1 - moderate, 2 - weak	-1.9	-	-	-	-	-	-	-	-	-	-
[d]EB87-037	Andesite	1 - undetermined	0.5	-82	-	-	-	-	-	-	-	-	-
CBI-6-6-11	Basalt-Andesite	2 - strong	9.5	-93	[b,2]11.7	-	-	-	-	-	-	[b,2]9.8	[b,2]-4.5
CBI-6-6-88	Basalt-Andesite	1 - strong	-1.9	-79	-	-	-	-	-	-	-	-	-
CBI-6-6-110	Basalt-Andesite	1 - strong	0.0	-	-	-	-	-	-	-	-	-	-
CBI-6-6-111	Basalt-Andesite	1 - weak to moderate, 2 - weak	3.3	-	[#]6.4	[#]3.3	-	-	-	-	-	-	-
CBI-6-6-112	Basalt-Andesite	1 - strong, 2 - weak	-1.7	-	-	-	-	-	-	-	-	-	-
CBI-6-6-112A	Basalt-Andesite	2 - qtz-cal vein	-	-	[c,2]8.6	-	-	-	-	-	-	-	-
CBI-6-6-112B	Basalt-Andesite	2 - qtz-cal vein	-	-	[c,2]10.5	-	-	-	-	-	-	[c,2]14.3	[c,2]-7.4
CBI-6-6-112C	Basalt-Andesite	2 - qtz-cal vein	-	-	[c,2]7.9	-	-	-	-	-	-	-	-
CBI-6-6-114	Basalt-Andesite	1 - weak, 2 - moderate	5.4	-	-	-	-	-	-	-	-	-	-
CBI-6-6-38	Basalt	2 - qtz-cal vein	-	-	[c,2]6.1	-	-	-	-	-	-	-	-
CBI-6-6-39	Basalt	1 - moderate, 2 - weak	3.0	-	-	-	-	-	-	-	-	-	-
CBI-6-6-40	Basalt	1 - moderate, 2 - weak	1.9	-70	-	-	-	-	-	-	-	-	-
CBI-6-6-107	Basalt	1 - weak, 2 - moderate	3.1	-	-	-	-	-	-	-	-	[b,2]11.7	[b,2]-7.2
CBI-6-6-122	Basalt	2 - moderate to strong	5.7	-	-	-	-	-	-	-	-	[b,2]5.8	[b,2]-4.5
[d]MT6-397	Basalt	2 - undetermined	6.2	-	-	-	-	-	-	-	-	-	-

Notes: cal = calcite, chl = chlorite, fs = feldspar, hbl = hornblende, qtz = quartz, ser = sericite; a = alteration types: (1) propylitic, (2) quartz, sericite and calcite, and (3) phyllic; b = disseminated secondary mineral; c = vein mineral; d = previously reported by Potter *et al*. (2008a); # = porphyritic quartz-feldspar rhyolite.

Mountain area, calculated $\delta^{18}O_{H2O}$ values at 200 °C, with two exceptions, are ≤0‰ (range: –4 to +0‰, Fig. 6b). At 300 °C, calculated $\delta^{18}O_{H2O}$ values are >0‰, with most ranging from 0 to +5‰, Fig. 6b). Vein calcite from volcanic samples CBI-8-5-30 and CBI 6-6-112B yields anomalously high $\delta^{18}O_{H2O}$ values; they also have the lowest $\delta^{13}C$ values measured in this study. Oxygen isotopic disequilibrium in these veins is indicated by negative $\Delta^{18}O_{qtz-cal}$ values, and in sample CBI-6-

6-112B, by the occurrence of calcite as a vug-filling in quartz. We conclude that calcite in these veins formed from fluids unrelated to quartz-sericite-calcite alteration. Two other vein samples from volcanic rocks (CBI 6-6-17 and CBI 6-6-11), however, have textures characteristic of quartz-calcite co-precipitation. Assuming isotopic equilibrium, temperatures of 220 to 230 °C and $\delta^{18}O_{H2O}$ values of –1 to +1‰ are obtained for these samples using the quartz-calcite oxygen-isotope

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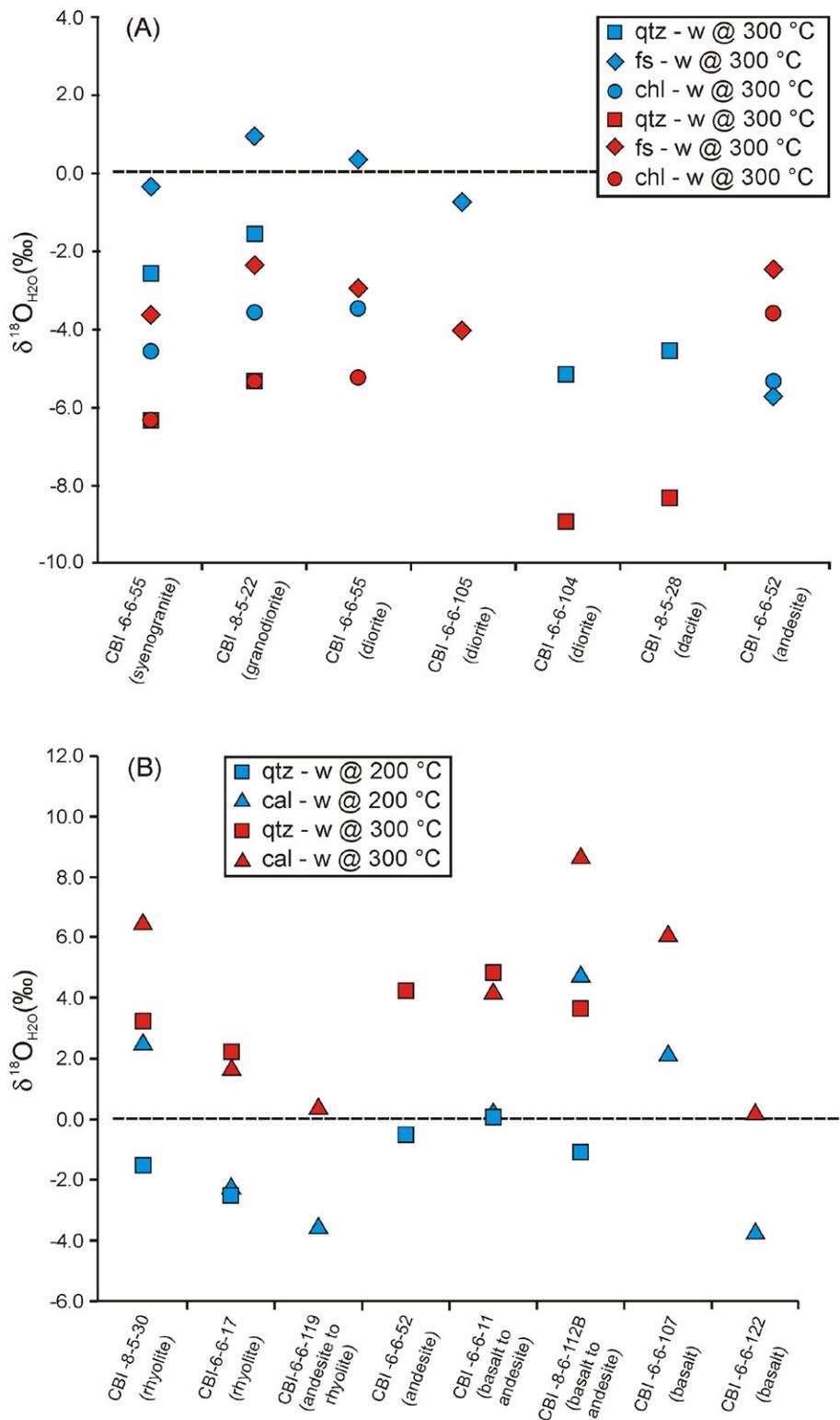
Fig. 6. Hydrothermal fluid compositions ($\delta^{18}O_{H2O}$) for: (A) propylitic assemblage minerals at 300 and 450 °C, and (B) quartz-sericite-calcite assemblage minerals at 200 and 300 °C. The mineral-H_2O oxygen-isotope geothermometers utilized are: calcite-H_2O (Friedman and O'Neil 1977), chlorite-H_2O (Wenner and Taylor 1971), alkali feldspar-H_2O (O'Neil and Taylor 1967) and quartz-H_2O (Matsuhisa *et al.* 1979). Abbreviations: cal - calcite, chl - chlorite, fs - feldspar, qtz - quartz.

geothermometer. The apparent trend towards higher $\delta^{18}O_{H2O}$ values from propylitic (–6‰) to quartz-sericite-calcite (0‰) alteration is suggestive of either ^{18}O-enrichment of meteoric water during water-rock interaction and/or an increasing contribution of seawater (~0‰) as the system cooled and waned. Combined consideration of the hydrogen- and oxygen-isotope compositions of altered whole-rock samples and associated chlorite allows evaluation of these two possibilities. Figure 7 compares propylitic fluid hydrogen- and oxygen-isotope compositions at 300 °C for chlorite and whole-rock samples to results calculated for a range of molar oxygen water/rock (w/r) ratios in a simple hydrothermal system (following Ohmoto and Rye 1974; see caption to Figure 7 for details). The oxygen- and hydrogen-isotope compositions predicted for meteoric water at ~560 Ma, based on Avalonia paleolatitude estimates (Murphy et al. 2004) closely match the values calculated using the Ohmoto and Rye (1974) model (see caption to Figure 7 for details). Fluid compositions for chlorite range from –5.3‰ $\delta^{18}O_{H2O}$ and –37‰ δ^2H_{H2O}, which cluster near the Global Meteoric Water Line (GMWL; Craig 1961) at very high w/r ratios, to +3.3‰ $\delta^{18}O_{H2O}$ and ~ –33‰ δ^2H at very low w/r ratios. Many whole-rock samples follow the same trend. This shift away from the GMWL towards higher $\delta^{18}O_{H2O}$ values at lower w/r ratios is typical of many modern geothermal systems. Meteoric-dominated hydrothermal fluids become enriched in ^{18}O as w/r ratios decrease whereas δ^2H_{H2O} values are largely unchanged, except at very low w/r ratios, because of the low initial molar hydrogen content of the rock (Craig 1963; Taylor 1974; Longstaffe 1989; Cole 1994). Addition of seawater as the hydrothermal fluid evolved would not produce such a pattern. One sample (CBI-6-6-11), which is dominated by the lower temperature quartz-sericite-calcite alteration, plots just beyond the end of the trend calculated for propylitic alteration at very low w/r ratios (<0.001). This positioning is consistent with a waning flux of hydrothermal fluid.

Seawater may have been important earlier in the alteration history at higher w/r ratios. A handful of samples, including some with sericite as the main hydrous phase, have δ^2H_{H2O} values plotting well above the meteoric-hydrothermal fluid w/r trend-line for 300 °C (Fig. 7). Such compositions could indicate alteration of these samples at >300 °C. Calculated δ^2H_{H2O} values at 450 °C for these samples would plot closer to the trend-line, albeit at higher $\delta^{18}O_{H2O}$ values and lower w/r ratios. However, the main alteration phases in two of these samples (CBI-6-6-55 and CBI-8-5-22) are in oxygen isotopic equilibrium at 300 °C. An alternate explanation is that the hydrothermal fluid affecting these samples comprised a mixture of seawater and (evolved) meteoric water (Fig. 7). Based on petrographic, isotopic and fluid-inclusion thermometric data, Potter et al. (2012) have suggested that seawater was a significant component of the hydrothermal fluid associated with early vein assemblage formation during the Mira terrane alteration.

The carbon isotopic compositions of disseminated and vein calcite samples (–7.4 to +0.1‰) are not uniquely diagnostic of a particular source (e.g., seawater, magmatic fluids, organic matter oxidation). Further confounding the situation is that Neoproterozoic marine carbonates at 575–550 Ma ranged widely in $\delta^{13}C$ (–6 to +4‰) (Des Marais 2001, Deines 2002). The majority of samples analyzed here lie within this range (–5.2 to +0.1‰); only those samples with the very highest $\delta^{18}O$ values, and which are unrelated to propylitic or quartz-sericite-calcite alteration, have lower $\delta^{13}C$ values.

Local versus regional alteration and mineralization potential

Potter et al. (2008a) proposed two scenarios to explain the regional low-^{18}O character of the Mira terrane: (1) a series of local meteoric water-dominated geothermal systems associated with convergent subduction, associated volcanism, and emplacement of individual plutons, or (2) a single event involving regional infiltration of hydrothermal fluids during transcurrent rifting of Avalonia at the Gondwanan margin at ca. 575–550 Ma. Potter et al. (2008a, b) preferred the second model, given the widespread ^{18}O-depletion of Avalonia, and absence of such ^{18}O-depletion for the associated inboard Neoproterozoic peri-Gondwanan terranes of the region (e.g., Bras d'Or terrane).

The observations reported here for the Huntington Mountain pluton and East Bay Hills metavolcanic rocks are not typical of a localized hydrothermal system. The putative concentric pattern of progressively cooler alteration zones (potassic, phyllic, propylitic, argillic; Meyer and Hemley 1967; Sheppard et al. 1971; Taylor 1997) that would have been associated with emplacement at ca. 620 Ma is absent – or at the very least – not preserved at present exposure levels. Nor is there a zonation of oxygen isotopic compositions that would be predicted for intrusion-driven water-rock interaction – magmatic fluids near the intrusive centres followed progressively outwards by ^{18}O-depletion (propylitic alteration) and then ^{18}O-enrichment (argillic alteration), as meteoric-hydrothermal waters became dominant in the cooling system through circulatory fluid flow above the brittle-ductile boundary as is evident in the distribution of $\delta^{18}O_{WR}$ values in Figure 4. The minor variations in alteration assemblages across the study area and the absence of any systematic patterning of $\delta^{18}O$ values are more consistent with the regional model for ^{18}O-depletion across West Avalonia, in which fluid infiltration into deep extensional basins occurred during transition from a subduction to a transtensional rifting environment (Potter et al. 2008a, b). In this model, initial rifting of West Avalonia resulted
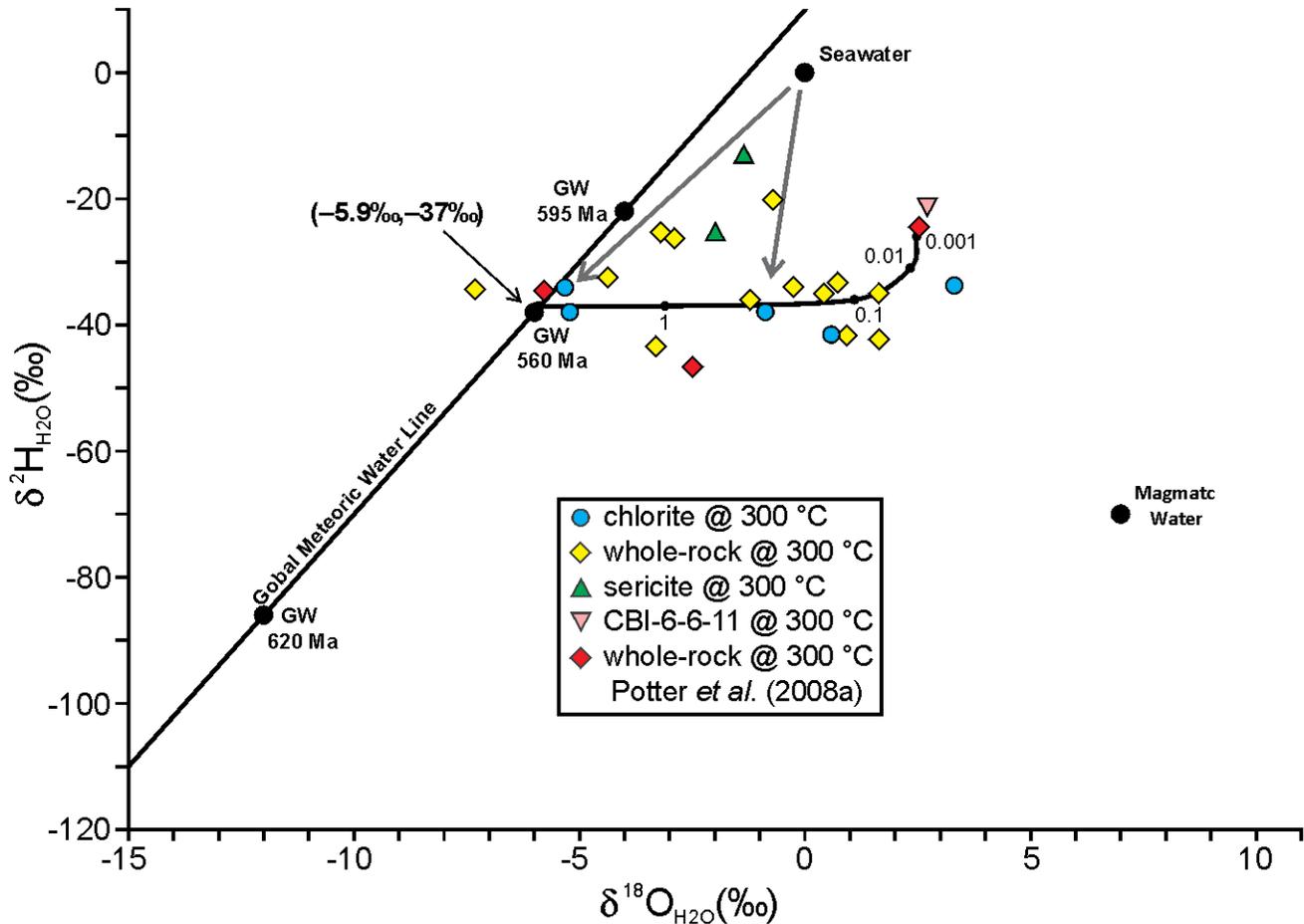
Fig. 7. Hydrogen- and oxygen-isotope compositions of the propylitic alteration fluid. The δ^2H_{H2O} and $\delta^{18}O_{H2O}$ values for chlorite were calculated at 300 °C using the chlorite-H_2O oxygen- and hydrogen-isotope geothermometers of Wenner and Taylor (1971) and Graham *et al.* (1984), respectively. Fluid compositions (δ^2H_{H2O} and $\delta^{18}O_{H2O}$) for sericite were calculated at 300 °C (sample CBI-6-6-11 at 200 °C) using the muscovite-H_2O oxygen- and hydrogen-isotope geothermometers of Friedman and O'Neil (1977) and Suzuoki and Epstein (1976), respectively. The fluid compositions (δ^2H_{H2O} and $\delta^{18}O_{H2O}$) for whole-rock samples were calculated at 300 °C using the oxygen-isotope rock-H_2O geothermometers (granite-water, granodiorite-water, diorite-water, rhyolite-water, andesite-water and basalt-water, as appropriate) of Zhao and Zheng (2003) and the hydrogen-isotope chlorite-H_2O geothermometer of Graham et al. (1984). The molar oxygen w/r ratio line was calculated for 300 °C following Ohmoto and Rye (1974). This calculation assumes interaction with meteoric water by an igneous rock originally equilibrated with a felsic to intermediate magmatic fluid of $\delta^2H_{H20} = -70‰$ and $\delta^{18}O_{H20} = +7‰$. We used initial δ^2H_{H2O} and $\delta^{18}O_{H2O}$ values of −37 and −5.9‰ for the hydrothermal fluid, as inferred from the mean whole-rock and chlorite δ^2H_{H2O} values produced during interaction with meteoric water and the corresponding $\delta^{18}O_{H2O}$ value calculated using the equation for the Global Meteoric Water Line (GMWL) (Craig 1961). Meteoric water compositions (GW) for 620 Ma, 595 Ma, and 560 Ma were inferred using the paleolatitude estimates for Avalonia of Murphy et al. (2004) and values of $\delta^{18}O$ and δ^2H for meteoric water currently typical of these latitudes.

in the formation of large-scale extensional fault networks, which provided conduits for deep infiltration of meteoric water (and/or seawater during earlier stages). Continued volcanism during the initial stages of rifting served to heat and circulate these fluids. Direct evidence exists throughout West Avalonia for extensional-related volcanism and associated transtensional faulting, including volcanic-sedimentary sequences of the ca. 575–560 Ma Coastal Belt in the Mira terrane, the ca. 560–550 Ma Coldbrook Group of the Caledonia terrane in New Brunswick, and the ca. 580–570 Ma and younger units of the Avalon terrane in Newfoundland (Barr *et al.* 1996; O'Brien *et al.* 1996).

Many economic accumulations of base and precious metals are known to form in epithermal systems, commonly as the product of circulation of metal-laden hydrothermal fluids associated with pluton emplacement. To the best of our knowledge, the Huntington Mountain pluton and East Bay Hills Group are barren of significant mineralization (Barr et al. 1996). The hydrothermal fluids responsible for regional ^{18}O-depletion may not have been metal-rich, perhaps because of the lack of a magmatic fluid component. The δ^2H_{H2O} and $\delta^{18}O_{H20}$ values calculated for the Huntington Mountain alteration assemblages certainly do not reveal any strong association with magmatic water (Fig. 7). Alternatively or additionally, it may be that the processes needed to focus the flow of the hydrothermal fluids and/or precipitate metals efficiently were not operating in this system (Simmons and Brown 2007). Whether regional movement of hydrothermal fluids of meteoric/seawater origin lead to leaching and/or redistribution of pre-existing metals of economic interest in this area, and hence, West Avalonia more widely is worthy of further enquiry.

CONCLUSIONS

The ca. 620 Ma cogenetic Huntington Mountain pluton and East Bay Hills Group comprise rocks of mainly intermediate composition (mostly diorite and andesite), which have undergone regional propylitic alteration and more localized overprinting by quartz-sericite-calcite alteration. These rocks are most commonly characterized by anomalously low $\delta^{18}O$ values, which are attributed to propylitic alteration at ~ 300 °C from fluids of dominantly meteoric ± seawater origin over a range of w/r ratios. Lower temperatures (~200 °C), lower w/r ratios and higher $\delta^{18}O_{H2O}$ values characterized the evolved meteoric hydrothermal water responsible for later, more localized quartz-sericite-calcite alteration. The widespread ^{18}O-depletion, which is also characteristic of other Neoproterozoic rocks from the Mira terrane, likely occurred at ca. 575–550 Ma during large-scale transtensional faulting and extensional-related volcanism, during initial rifting of Avalonia from Gondwana. This

alteration appears not to be associated with mineralization in the Huntington Mountain pluton or East Bay Hills Group.

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