

# Volcanic red-bed copper mineralisation related to submarine basalt alteration, Mont Alexandre, Quebec Appalachians, Canada

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**Abstract** Two types of native copper occur in Upper Silurian basaltic rocks in the Mont Alexandre area, Quebec Appalachians: (1) type 1 forms micrometric inclusions in plagioclase and is possibly magmatic in origin, whereas (2) type 2 occurs as coarse-grained patches rimmed by cuprite in altered porphyritic basalt. Type 1 has higher contents of sulphur (2,000–20,263 ppm) and arsenic (146–6,017 ppm), and a broader range of silver abundances (<65–2,186 ppm Ag) than type 2 (149–1,288 ppm S, <90–146 As, <65–928 ppm Ag). No mineral inclusions of sulphide or arsenide in native copper were observed at the electron-microprobe scale. Primary igneous fabrics are preserved, but the basaltic flows are pervasively oxidised and plagioclase is albitised. Chlorite replaces plagioclase and forms interstitial aggregates in the groundmass and has Fe/(Fe+Mg) ratios ranging from 0.29 to 0.36 with calculated temperatures between 155°C and 182°C. Copper sulphides in vacuoles and veinlets are associated with malachite, fibro-radiating albite and yarrowite ( $\text{Cu}_9\text{S}_8$  with up to 0.3 wt% Ag). Bulk-rock concentrations of thallium and lithium range from 70 to 310 ppb and 10 to 22 ppm, respectively, and thallium is positively correlated with  $\text{Fe}_2\text{O}_3$ . Such concentrations of thallium and lithium are typical of spilitisation during heated seawater–basalt inter-

action. Spilitisation is consistent with the regional geological setting of deepwater-facies sedimentation, but is different from current models for volcanic red-bed copper, which indicate subaerial oxidation of volcanic flows. The volcanic red-bed copper model should be re-examined to account for native copper mineralisation in basalts altered by warm seawater.

**Keywords** Native copper · Volcanic red beds · Spilitisation · Mont Alexandre · Quebec Appalachians · Canada

## Introduction

Volcanic red-bed copper deposits may be economically significant. For instance, the native copper district of northern Michigan (Keweenaw Peninsula) produced about 4.9 MT of copper metal from 1845 to 1967 (White 1968). Characteristically, this deposit type is hosted in volcanic sequences deposited in a subaerial environment, which is deemed essential for the reddening (oxidation) of the lavas (Kirkham 1995). Upper Silurian basaltic flows of the Mont Alexandre area, Quebec Appalachians, are pervasively oxidised towards the top of the sequence (Bédard 1986b) and host native copper mineralisation, and would thereby constitute an example of volcanic red-bed copper deposit. However, the basaltic lavas are not subaerial, but submarine and represent spilitised basalts.

This paper describes an occurrence of native copper from Mont Alexandre and aims at: (1) providing evidence that the reddening associated with the Mont Alexandre copper mineralisation is related to spilitisation, instead of subaerial oxidation; and (2) describing microscopic inclusions of native copper in plagioclase phenocrysts, presumably of magmatic origin, in low-Cu basalt.

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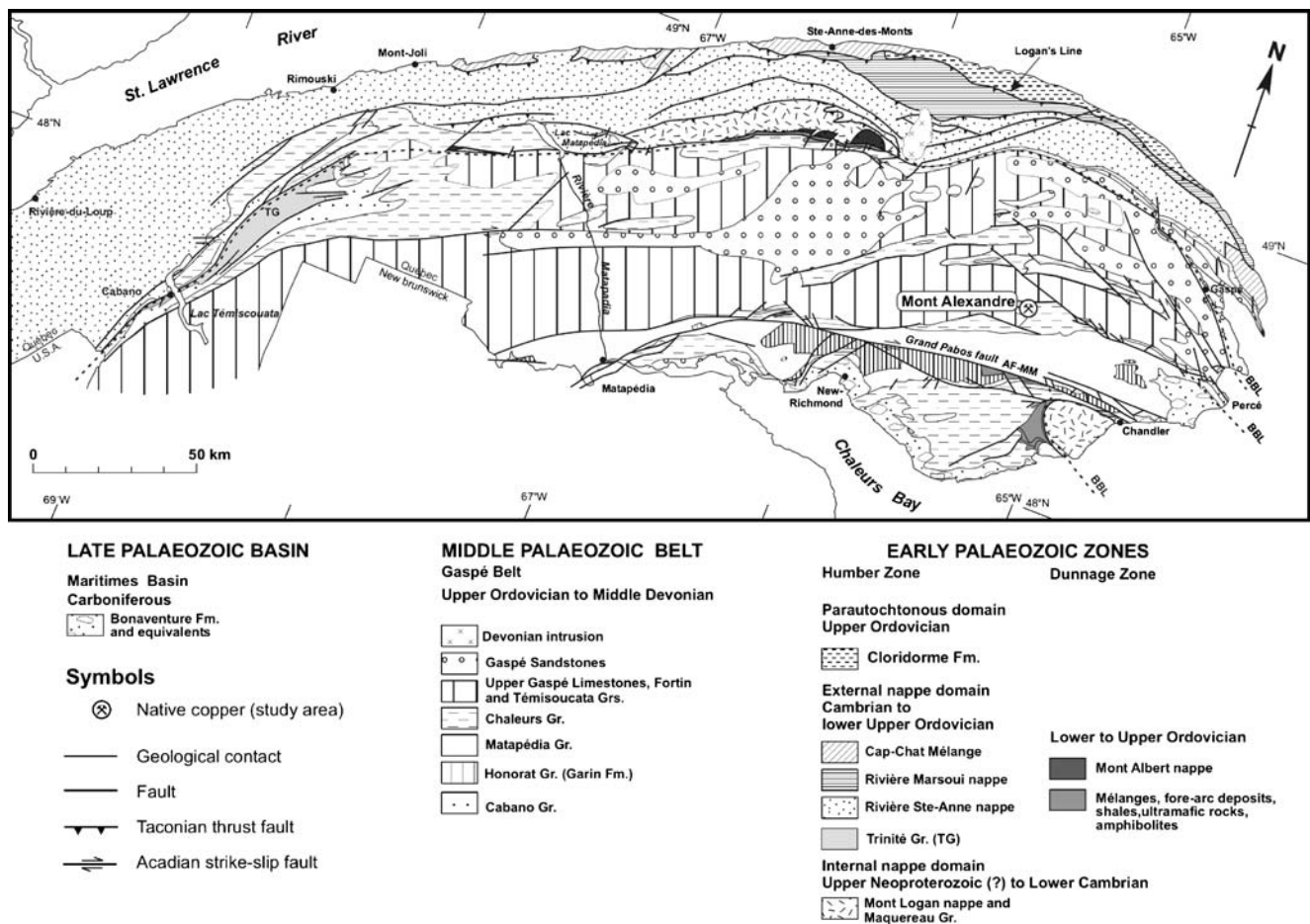
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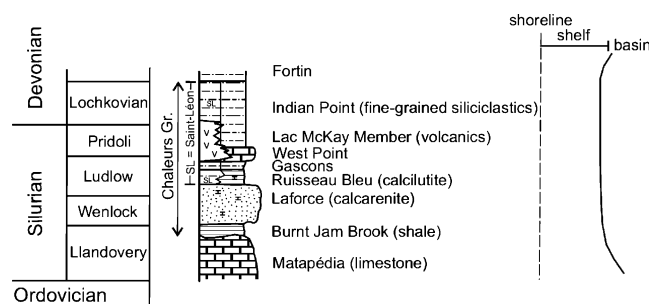
**Fig. 1** Location of the cupriferous occurrence investigated (Mont Alexandre) and major stratigraphic units of the Gaspé Appalachians (modified from Malo 2004)

## Geological setting

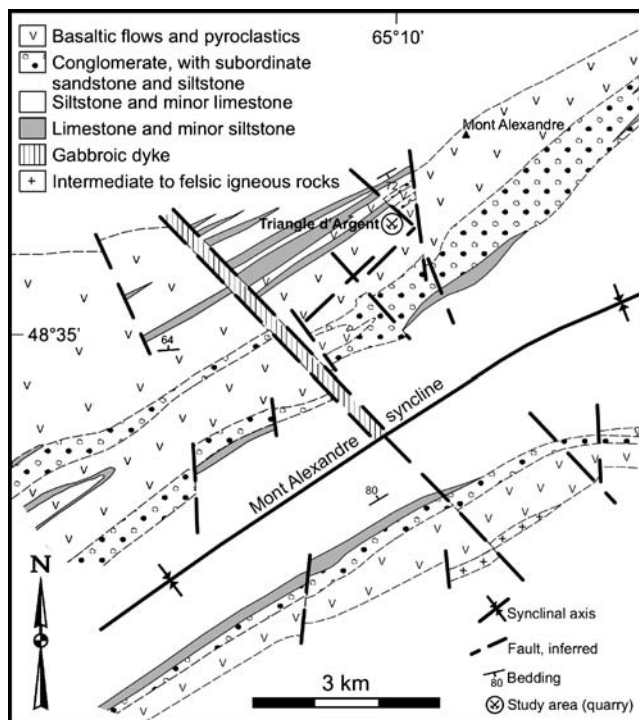
Mont Alexandre (Fig. 1) is the site of a major E–W-trending synclinal structure developed during the Acadian orogeny (Bourque and Lachambre 1980; Morin and Simard 1987). The Mont Alexandre syncline comprises calcilutite and calcareous conglomerate of the West Point Formation, overlain by fine-grained siliciclastic rocks (mudstone and sandstone) of the Lower Devonian Indian Point Formation of the Chaleurs Group (Fig. 2). Volcanic rocks transgress the West Point Formation into the Indian Point Formation. The volcanic pile is composed predominantly of basaltic flows of the Upper Silurian Lac McKay Member of the Saint-Léon Formation (Bourque 1975; Morin and Simard 1987). The mafic volcanism of the Lac McKay Member occurred in a basinal environment, interbedded with deepwater siliciclastic sediments (Bourque et al. 1995; Bourque 2001).

The Lac McKay lavas are mostly alkaline basalts (Laurent and Bélanger 1984; Bédard 1986b). The alkaline character is manifested by  $\text{Na}_2\text{O}$  contents from 3.0 to 6.9 wt% and normative albite, although the abnormally high

proportion of normative albite may be attributable to sodic alteration (Morin and Simard 1987). Primary flow textures are preserved, but the rocks are pervasively altered to secondary minerals, such as albite, chlorite, epidote, calcite and quartz (Bédard 1986a; Dostal et al. 1993). The lavas are more oxidised towards the top of the sequence (Bédard 1986b). The basalts were probably erupted during a tensional event in an orogenic foreland setting (Bédard



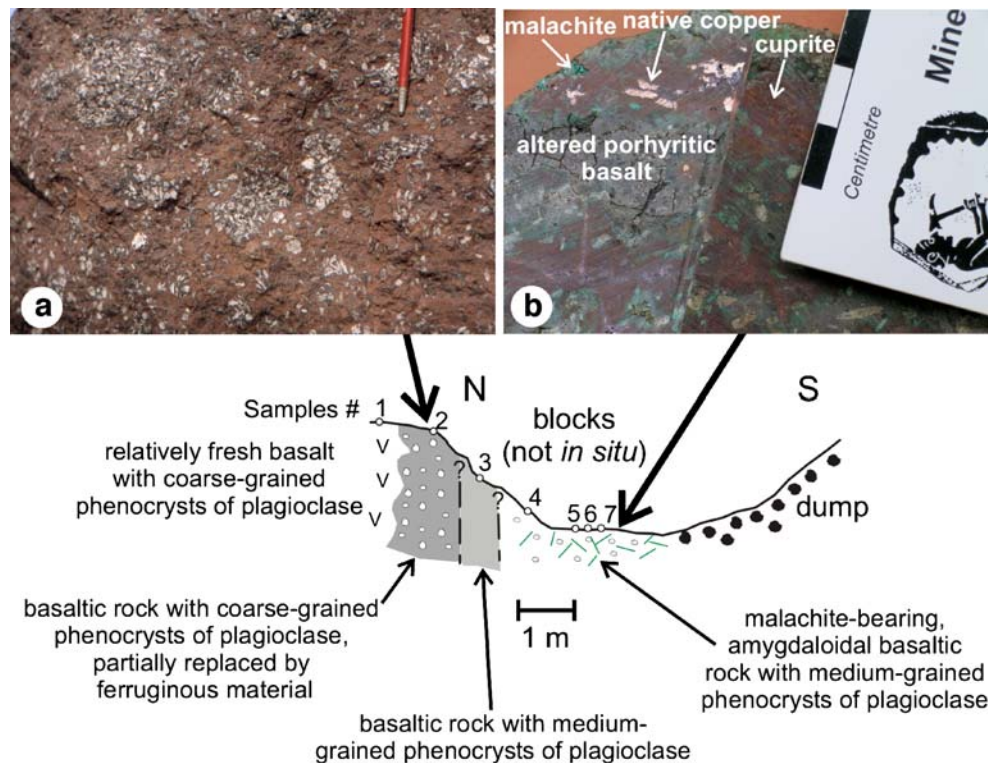
**Fig. 2** Depositional environments during Silurian time for the Mont Alexandre region (after Bourque and Lachambre 1980; Bourque 2001)



**Fig. 3** Location of the study area and simplified geological map of a portion of the Mont Alexandre syncline (modified after Duffours 2000)

1986b; Dostal et al. 1993) and are interpreted to represent an episode of intraplate volcanism during the Salinic disturbance (Malo 2001).

**Fig. 4** Schematic cross-section of the quarry working at Triangle d'Argent with the relative location of the samples investigated and listed in Table 3. The mineralisation is not in situ. **a** Ferruginous, brownish alteration isolates areas of relatively fresh porphyritic basalt, giving a breccia-like appearance. **b** Coarse-grained, type 2 native copper haloed by cuprite, which is surrounded by malachite



## Analytical techniques

Thin sections and slabs of selected samples were polished for optical microscopy and electron-microprobe analysis with a Cameca SX100 at the Laboratoire de Microanalyse, Université Laval (UL). Analytical conditions, standards and X-ray emission lines were as follows: (1) for native copper: 15 kV and 100 nA, pure metal ( $AgL\alpha$ ), pyrite ( $SK\alpha$ ),  $Se_{98}As_2$  ( $AsL\alpha$ ); (2) for copper sulphides: 15 kV and 20 nA, chalcopyrite ( $CuK\alpha$ ), haematite ( $FeK\alpha$ ), pyrite ( $SK\alpha$ ),  $Au_{80}Ag_{20}$  ( $AgL\alpha$ ); (3) for chlorite: 15 kV and 20 nA, diopside ( $SiK\alpha$ ,  $MgK\alpha$ ), rutile ( $TiK\alpha$ ), plagioclase ( $AlK\alpha$ ,  $CaK\alpha$ ), haematite ( $FeK\alpha$ ), ilmenite ( $MnK\alpha$ ), albite ( $NaK\alpha$ ), orthoclase ( $KK\alpha$ ) and fluorite ( $FK\alpha$ ).

Bulk-rock geochemical analyses for major and trace elements and assays for copper in mineralised samples were performed at the Activation Laboratories, Ontario, using the analytical methods described in Table 3.

## Mineralisation

Native copper mineralisation has been known to be hosted in mafic volcanics of the Mont Alexandre area since 1936 (Fig. 3; Jones 1938; Duffours 2000). A quarry, in an area designated 'Triangle d'Argent', exposes basaltic rocks overprinted by alteration, which is more intense in the central, mineralised portion of the quarry (Figs. 3 and 4). The least-altered basalt, at the margin of the quarry and

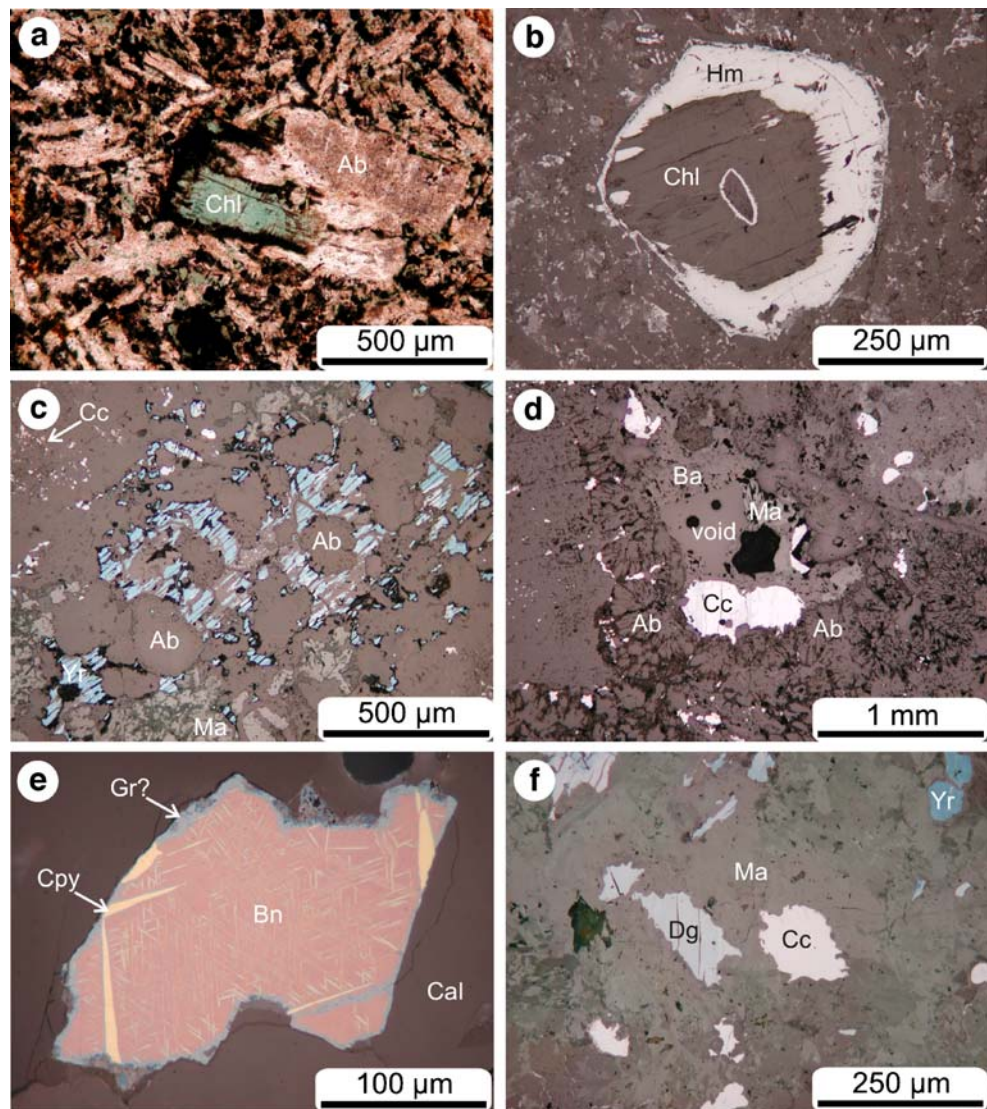
furthest from the mineralised central area, is characterised by coarse-grained phenocrysts of turbid plagioclase in a haematitic, cryptocrystalline groundmass. A ferruginous, aphanitic mass overprints the porphyritic basalt, imparting a brecciated aspect (Fig. 4a). This aphanitic material consists of fine-grained quartz, white mica, K-feldspar, haematite and zircon, and void-infilling aggregates of chlorite and calcite within a ferruginous groundmass.

Coarse-grained native copper mineralisation is found at the central part of the quarry (Fig. 4b) where plagioclase is albitised. Porphyritic basalts are vesicular and the vesicles are filled by calcite, chlorite and quartz. Chlorapatite occurs in basalt-hosted lithoclasts altered to epidote, calcite, haematite and albite. Pseudomorphic chlorite after feldspar and other igneous silicates are replaced by haematite (Figs. 5a, b). The chlorite has Fe/(Fe+Mg) ratios ranging from 0.29 to 0.36 (Table 1). This compositional range is similar to that of the chlorite investigated by Cathelineau

and Nieva (1985). Chlorite geothermometry using their equation yields temperatures between 155°C and 182°C.

Copper sulphides are present in sub-economic amounts (compared to native copper) in altered basalts without coarse-grained native copper. The most abundant copper sulphides are yarrowite and chalcocite. Yarrowite,  $\text{Cu}_9\text{S}_8$ , with up to 0.3 wt% Ag (Table 2), occurs mainly as independent crystals in veinlets of malachite and fibro-radiating albite (Fig. 5c). Yarrowite is also found as independent crystals in calcite-filled vesicles. Chalcocite is disseminated within the basaltic matrix (Fig. 5c) and co-exists with malachite and fibro-radiating albite, together with barite, as void infillings (Fig. 5d). Calcite-filled vesicles contain bornite, chalcopyrite, a Cu–S phase compositionally analogous to geerite,  $\text{Cu}_8\text{S}_5$  (Fig. 5e, Table 2), digenite, chalcocite, yarrowite (Fig. 5f) and covellite. Chalcopyrite forms exsolution spindles in a triangular or reticulated pattern in bornite (Fig. 5e).

**Fig. 5** Transmitted-light (a) and reflected-light (b–f, air) photomicrographs of altered basaltic rocks. **a** Albitised plagioclase (Ab) partially replaced by chlorite (Chl). **b** Haematite (Hm) substituting chlorite (Chl). **c** Veinlet of radiating albite (Ab), yarrowite (Yr) and malachite (Ma). Chalcocite (Cc) is disseminated in the adjacent groundmass. **d** Void infilling by radiating albite (Ab), barite (Ba), chalcocite (Cc) and malachite (Ma). **e** Chalcopyrite lamellae (Cpy) in bornite (Bn), rimmed by a Cu–S phase (geerite?, Gr?), in calcite (Cal) vesicle. **f** Digenite (Dg), chalcocite (Cc) and yarrowite (Yr) in malachite (Ma)



**Table 1** Electron-microprobe analyses of chlorite

| wt%                            | 1      | 2      | 3      | 4      | 5      |
|--------------------------------|--------|--------|--------|--------|--------|
| SiO <sub>2</sub>               | 32.80  | 33.60  | 33.91  | 32.05  | 31.30  |
| TiO <sub>2</sub>               | <0.07  | <0.07  | 0.31   | <0.07  | <0.07  |
| Al <sub>2</sub> O <sub>3</sub> | 15.58  | 14.70  | 15.00  | 14.86  | 15.54  |
| FeO                            | 19.17  | 17.76  | 16.79  | 18.17  | 19.71  |
| MnO                            | 0.30   | 0.23   | 0.25   | 0.30   | n.a.   |
| MgO                            | 19.16  | 21.58  | 20.83  | 22.03  | 19.36  |
| CaO                            | 0.27   | 0.38   | 0.45   | 0.25   | 0.20   |
| Na <sub>2</sub> O              | 0.06   | 0.08   | 0.11   | 0.07   | 0.04   |
| K <sub>2</sub> O               | 1.78   | 1.14   | 1.53   | 0.20   | 0.03   |
| F                              | <0.2   | <0.2   | 0.32   | <0.2   | n.a.   |
| –O≡F                           |        |        | 0.14   |        |        |
| Total                          | 89.13  | 89.45  | 89.37  | 87.93  | 86.18  |
| 28 O                           |        |        |        |        |        |
| Si                             | 6.585  | 6.644  | 6.702  | 6.450  | 6.459  |
| Al(IV)                         | 1.415  | 1.356  | 1.298  | 1.550  | 1.541  |
| Σ Z                            | 8.000  | 8.000  | 8.000  | 8.000  | 8.000  |
| Al(VI)                         | 2.271  | 2.070  | 2.196  | 1.974  | 2.239  |
| Ti                             | –      | –      | 0.047  | –      | –      |
| Fe                             | 3.218  | 2.937  | 2.774  | 3.058  | 3.401  |
| Mn                             | 0.051  | 0.038  | 0.042  | 0.052  | –      |
| Mg                             | 5.735  | 6.360  | 6.136  | 6.610  | 5.956  |
| Ca                             | 0.058  | 0.080  | 0.096  | 0.055  | 0.044  |
| Na                             | 0.024  | 0.029  | 0.041  | 0.027  | 0.015  |
| K                              | 0.455  | 0.286  | 0.385  | 0.052  | 0.008  |
| Σ Y                            | 11.812 | 11.800 | 11.717 | 11.827 | 11.662 |
| Fe/(Fe+Mg)                     | 0.36   | 0.32   | 0.31   | 0.32   | 0.36   |
| T (°C) <sup>a</sup>            | 168    | 162    | 155    | 182    | 181    |

n.a.: not analysed

<sup>a</sup> Temperature calculated using the equation by Cathelineau and Nieva (1985).**Native copper**

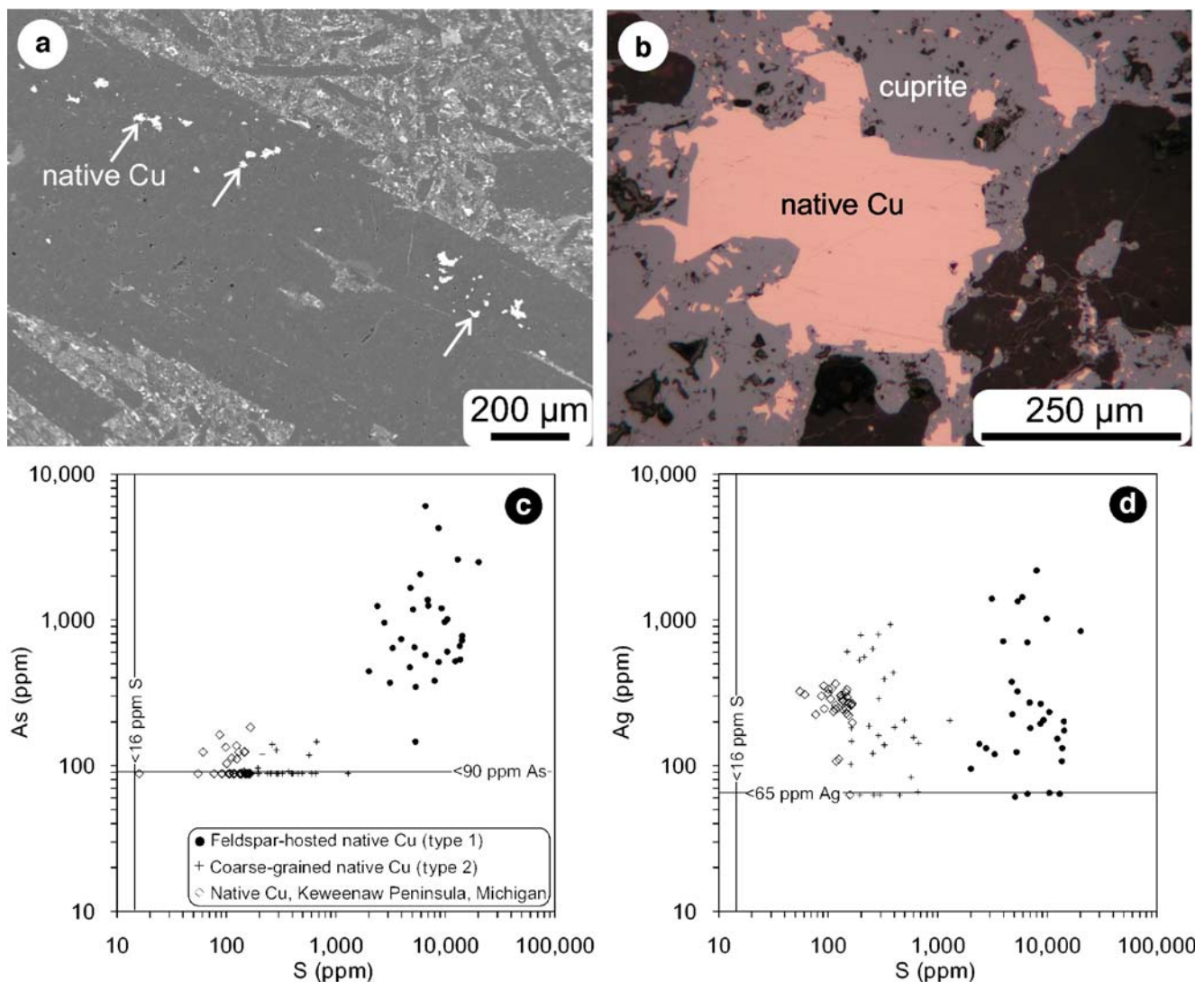
Two types of native copper can be distinguished on the basis of host mineral and trace element contents. Type 1 occurs as fine-grained, crystallographically oriented, mainly parallel to (001), inclusions (to ~50 µm in length) in laths of turbid feldspar in amygdaloidal porphyritic basalt (Fig. 6a). Type 2 native copper is characterised by cuprite-rimmed, coarse-

grained patches associated with malachite in altered basaltic rock (Figs. 4b and 6b). The feldspar-hosted, type 1 native copper is rich in sulphur (2,000–20,263 ppm) and arsenic (146–6,017 ppm) compared to type 2 native copper (149–1,288 ppm S, <90–146 As) (Fig. 6c). The silver content ranges from <65 (detection limit) to 2,186 ppm in type 1 and from <65 to 928 ppm in type 2 (Fig. 6d). A sample of coarse-grained native copper from the Keweenaw

**Table 2** Electron-microprobe analyses of copper sulphides

| wt%   | 1      | 2      | 3      | 4      | 5      | 6     | 7      | 8      | 9      | 10    |
|-------|--------|--------|--------|--------|--------|-------|--------|--------|--------|-------|
| S     | 30.86  | 31.16  | 31.32  | 25.54  | 25.91  | 34.88 | 32.25  | 20.88  | 20.95  | 24.21 |
| Cu    | 69.43  | 69.10  | 69.80  | 63.90  | 64.38  | 35.11 | 68.34  | 79.82  | 80.28  | 75.00 |
| Fe    | <0.03  | <0.03  | 0.16   | 10.66  | 10.96  | 29.08 | <0.03  | 0.42   | <0.03  | 0.51  |
| Ag    | 0.11   | 0.29   | 0.04   | 0.04   | <0.03  | <0.03 | 0.10   | <0.03  | 0.07   | 0.09  |
| Total | 100.40 | 100.56 | 101.31 | 100.14 | 101.25 | 99.07 | 100.69 | 101.13 | 101.30 | 99.79 |
| afpu  | 17     | 17     | 17     | 10     | 10     | 4     | 2      | 3      | 3      | 13    |
| S     | 7.958  | 8.013  | 7.989  | 3.996  | 4.005  | 2.013 | 0.966  | 1.020  | 1.022  | 5.046 |
| Cu    | 9.034  | 8.965  | 8.985  | 5.044  | 5.022  | 1.023 | 1.033  | 1.968  | 1.977  | 7.888 |
| Fe    | –      | –      | 0.023  | 0.958  | 0.972  | 0.964 | –      | 0.012  | –      | 0.061 |
| Ag    | 0.008  | 0.022  | 0.003  | 0.002  | –      | –     | 0.001  | –      | 0.001  | 0.005 |

apfu: atoms per formula unit; 1–3: yarrowite, Cu<sub>9</sub>S<sub>8</sub>; 4–5: bornite, Cu<sub>5</sub>FeS<sub>4</sub>; 6: chalcopyrite, CuFeS<sub>2</sub>; 7: covellite, CuS; 8–9: chalcocite, Cu<sub>2</sub>S; 10: geerite, Cu<sub>8</sub>S<sub>5</sub>



**Fig. 6** **a** Backscattered electron (BSE) image of type 1 native copper (arrows) along the *c*-axis of a plagioclase phenocryst (dark grey). The groundmass of the basaltic rock is spotted with titanium oxide and

haematite (white). **b** Reflected-light photomicrograph (air) of coarse-grained, type 2 native copper, which is replaced by cuprite. **c** S vs As and **d** S vs Ag plots of electron-microprobe analyses of native copper

Peninsula of northern Michigan was analysed for comparison. It has lower concentrations in silver, arsenic and sulphur than type 1 native copper, but which are comparable to those of type 2 native copper (Figs. 6c, d).

### Bulk-rock geochemistry

Samples representing a profile from the relatively least-altered basalt at the margin to the mineralised central portion of the quarry were analysed for major and trace elements (Table 3). Trace element analyses show that the basalts plot with other data from the Upper Silurian Lac McKay Member (Bédard 1986a, b; Dostal et al. 1993; Laurent and Bélanger 1984) at the intersection of the andesite/basalt–alkali basalt–trachy-andesite fields in a Zr/TiO<sub>2</sub> vs Nb/Y diagram (Fig. 7a). The basalts display a calc-alkaline affinity in the Y vs Zr diagram

(Fig. 7b) and plot in the arc-basalt field in the Zr–Th–Nb diagram (Fig. 7c). Fe<sub>2</sub>O<sub>3</sub>/FeO ratios are greatest (~10) at the quarry margin and reach zero in the type 2 native copper-rich sample at the central part of the quarry, where the highest copper contents occur. Sodium is progressively enriched towards the centre of the quarry, but is depleted in the type 2 native copper-rich sample (Fig. 8).

Lithium concentrations range from 10 to 22 ppm and are higher than those of fresh mid-ocean ridge basalt (MORB) (4.5±1.5 ppm Li; Staudigel 2003). The relatively least-altered basalt, at the quarry margin, and the type 2 native copper-rich sample, at the quarry centre, have the highest lithium abundances (Fig. 8). Thallium contents vary from 70 to 310 ppb and co-vary with Fe<sub>2</sub>O<sub>3</sub> (Fig. 9). The samples are enriched in thallium relative to unaltered oceanic basaltic glasses, which generally contain less than 13 ppb Tl (McGoldrick et al. 1979).

**Table 3** Bulk-rock chemical analyses

| Analytical method |   | 1     | 2     | 3     | 4     | 5     | 6       | 7       |
|-------------------|---|-------|-------|-------|-------|-------|---------|---------|
| (wt%)             |   |       |       |       |       |       |         |         |
| Na                | 1 | 2.83  | 2.44  | 2.42  | 2.75  | 3.17  | 4.11    | 1.14    |
| Mg                | 5 | 2.57  | 1.14  | 2.49  | 1.32  | 1.25  | 1.25    | 0.61    |
| Al                | 5 | 4.11  | 2.18  | 4.71  | 2.55  | 2.74  | 2.33    | 2.45    |
| P                 | 5 | 0.222 | 0.191 | 0.331 | 0.313 | 0.277 | 0.250   | 0.791   |
| S                 | 5 | <0.01 | <0.01 | <0.01 | <0.01 | 0.01  | 0.19    | <0.01   |
| K                 | 5 | 1.49  | 1.52  | 1.20  | 1.43  | 1.22  | 0.16    | 0.50    |
| Ca                | 5 | 5.47  | 2.88  | 5.21  | 5.19  | 5.99  | 1.57    | 1.61    |
| Ti                | 5 | 0.95  | 0.81  | 1.24  | 1.18  | 1.11  | 0.76    | 0.55    |
| FeO               | 9 | 3.03  | 0.70  | 3.46  | 4.49  | 1.50  | 3.33    | 4.24    |
| Fe                | 1 | 5.06  | 5.67  | 5.80  | 4.21  | 4.47  | 3.12    | 2.68    |
| Cu                | 7 | n.a.  | n.a.  | n.a.  | 0.03  | n.a.  | 2.53    | 19.90   |
| (ppb)             |   |       |       |       |       |       |         |         |
| Au                | 8 | 24    | 21    | 27    | 39    | 38    | 40      | 42      |
| Pt                | 8 | <0.5  | 0.8   | <0.5  | <0.5  | <0.5  | 1.0     | 0.6     |
| (ppm)             |   |       |       |       |       |       |         |         |
| Ag                | 2 | 0.10  | 0.15  | 0.17  | 0.11  | 0.34  | 4.58    | 26.2    |
| Be                | 3 | 1.7   | 2.3   | 3.1   | 3.7   | 2.4   | 1.0     | 1.3     |
| Li                | 6 | 22.1  | 10.1  | 9.6   | 11.3  | 11.9  | 9.7     | 20.5    |
| Sc                | 1 | 15.1  | 13.0  | 16.7  | <0.1  | 13.6  | 13.6    | 9.1     |
| V                 | 5 | 191   | 118   | 223   | 208   | 180   | 199     | 123     |
| Cr                | 2 | 23    | 31    | 21    | 17    | 16    | 20      | 17      |
| Mn                | 5 | 1,210 | 1,030 | 957   | 759   | 842   | 551     | 564     |
| Co                | 2 | 25    | 18    | 23    | 25    | 24    | 19      | 17      |
| Ni                | 2 | 47.0  | 40.9  | 22.9  | 29.8  | 22.3  | 19.1    | 25.8    |
| Cu                | 3 | 77    | 248   | 32    | 252   | 1,390 | >10,000 | >10,000 |
| Zn                | 2 | 105.0 | 56.4  | 97.4  | 59.2  | 52.3  | 58.5    | 71.9    |
| Ga                | 6 | 19.8  | 21.1  | 22.4  | 24.0  | 20.2  | 19.9    | 16.0    |
| Ge                | 6 | 0.2   | 0.2   | 0.3   | 0.4   | 0.4   | 0.2     | 0.1     |
| As                | 1 | <0.5  | <0.5  | 2.2   | <0.5  | <0.5  | 2.1     | 9.5     |
| Se                | 2 | <0.1  | <0.1  | 0.6   | 1.1   | 0.5   | 0.2     | 1.1     |
| Rb                | 2 | 6.8   | 12.8  | 2.4   | 9.7   | 17.8  | <0.2    | 7.8     |
| Sr                | 6 | 973   | 559   | 1,070 | 960   | 849   | 324     | 321     |
| Y                 | 6 | 21.5  | 18.1  | 27.7  | 28.7  | 28.8  | 17.8    | 11.7    |
| Zr                | 6 | 247   | 210   | 339   | 371   | 333   | 302     | 158     |
| Nb                | 6 | 27.8  | 24.4  | 44.1  | 44.9  | 35.8  | 18.3    | 5.1     |
| Mo                | 4 | 2     | 1     | 2     | 2     | <1    | 3       | 4       |
| Cd                | 3 | 0.3   | <0.1  | <0.1  | <0.1  | <0.1  | 0.2     | <0.1    |
| Sn                | 6 | 2     | 2     | 3     | 2     | 2     | 1       | <1      |
| Sb                | 1 | <0.1  | 0.3   | 0.3   | <0.1  | <0.1  | <0.1    | 0.1     |
| Te                | 6 | 0.3   | 0.1   | 0.2   | 0.3   | 0.2   | 0.2     | 0.1     |
| Cs                | 2 | 0.20  | 0.50  | 0.17  | 0.30  | 0.14  | 0.09    | 0.57    |
| Ba                | 2 | 640   | 486   | 680   | 500   | 680   | 1,500   | 208     |
| La                | 1 | 48.8  | 48.8  | 80.0  | <0.5  | 69.8  | 58.7    | 37.3    |
| Ce                | 1 | 67    | 78    | 137   | 113   | 118   | 82      | 66      |
| Pr                | 6 | 15.1  | 10.6  | 22.6  | 22.1  | 22.4  | 14.3    | 8.7     |
| Nd                | 6 | 53.9  | 40.0  | 80.5  | 80.8  | 81.7  | 54.1    | 32.6    |
| Sm                | 1 | 4.3   | 5.4   | 7.8   | 6.8   | 7.1   | 5.0     | 3.8     |
| Eu                | 6 | 2.30  | 1.80  | 3.03  | 2.92  | 3.06  | 2.08    | 1.21    |
| Gd                | 6 | 7.5   | 6.3   | 10.2  | 10.1  | 10.4  | 7.1     | 4.2     |
| Dy                | 6 | 6.0   | 5.3   | 7.2   | 7.2   | 7.1   | 5.2     | 3.3     |
| Tb                | 6 | 1.0   | 0.9   | 1.2   | 1.2   | 1.3   | 0.9     | 0.5     |
| Ho                | 6 | 1.1   | 1.0   | 1.3   | 1.3   | 1.3   | 0.9     | 0.6     |
| Er                | 6 | 3.3   | 2.9   | 3.7   | 3.8   | 3.7   | 2.8     | 1.7     |
| Tm                | 6 | 0.4   | 0.4   | 0.5   | 0.5   | 0.5   | 0.4     | 0.2     |
| Yb                | 6 | 2.6   | 2.4   | 2.8   | 2.9   | 3.1   | 1.6     | 1.5     |

**Table 3** (continued)

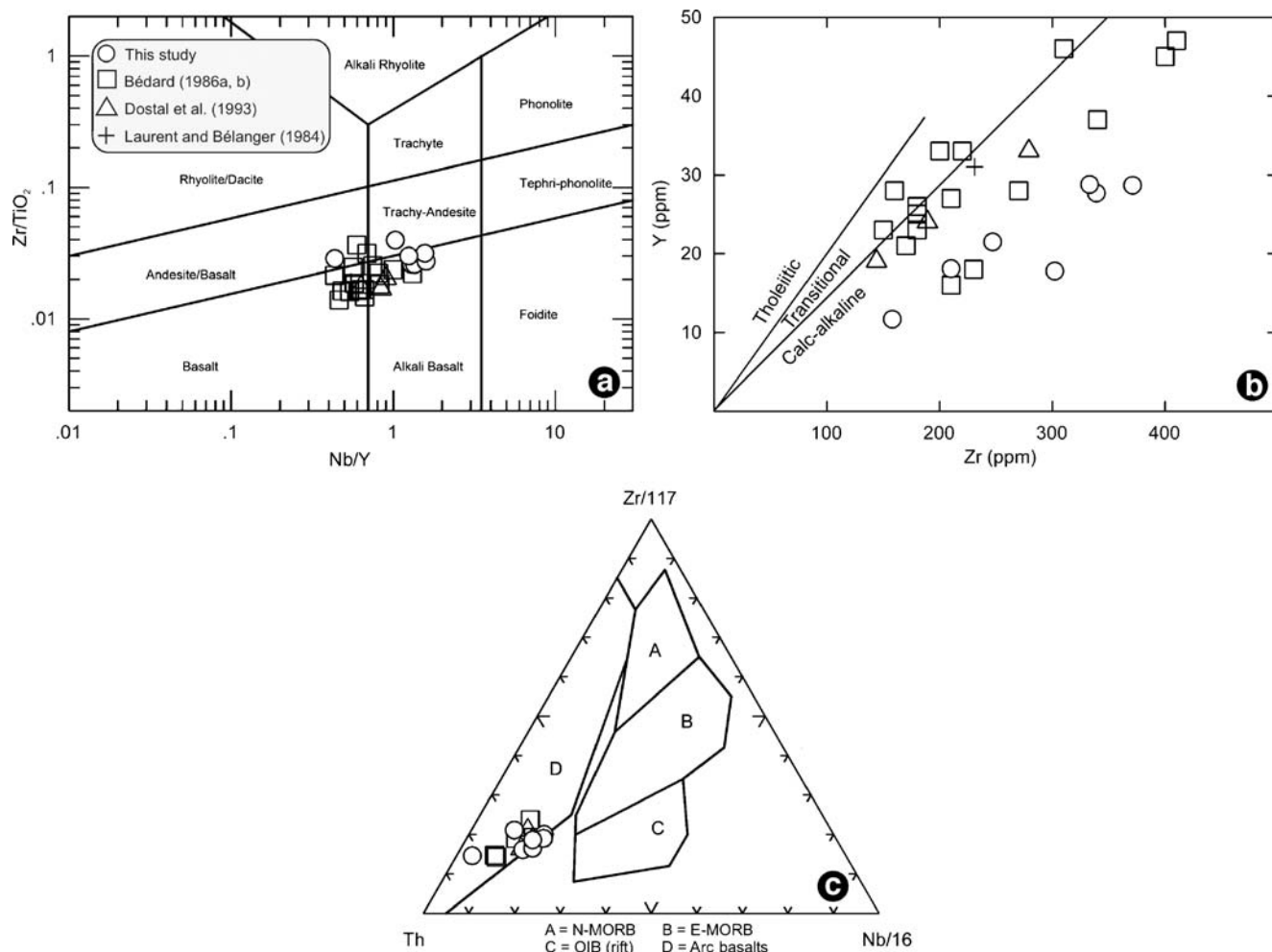
| Analytical method |   | 1    | 2    | 3    | 4    | 5    | 6    | 7    |
|-------------------|---|------|------|------|------|------|------|------|
| Lu                | 1 | 0.28 | 0.32 | 0.31 | 0.26 | 0.29 | 0.22 | 0.16 |
| Hf                | 6 | 5.5  | 5.4  | 7.4  | 7.3  | 7.3  | 6.0  | 3.5  |
| Ta                | 2 | 2.3  | 2.2  | 2.1  | 1.6  | 2.2  | 1.0  | <0.1 |
| Tl                | 6 | 0.19 | 0.31 | 0.11 | 0.12 | 0.18 | 0.10 | 0.07 |
| Pb                | 3 | 31.8 | 21.8 | 11.4 | 20.0 | 22.6 | 19.1 | 5.8  |
| Bi                | 3 | 0.2  | 0.1  | <0.1 | <0.1 | 0.2  | 1.8  | 0.1  |
| Th                | 2 | 6.7  | 7.8  | 11.9 | 10.7 | 10.2 | 8.5  | 7.6  |
| U                 | 2 | 2.4  | 2.0  | 1.3  | 2.7  | 3.0  | 2.3  | 2.2  |

Analytical methods: 1, INAA; 2, INAA/total digestion ICP-MS; 3, total digestion ICP/total digestion ICP-MS; 4, INAA/total digestion ICP; 5, total digestion ICP; 6, total digestion MS; 7, ICP-OES; 8, FA-MS; 9, titration.

The following elements were sought, but were not detected (analytical method in parenthesis): Re, <0.001 ppm (6); Ir, <5 ppb (1); Hg, <1 ppm (1); W, <1 ppm (1); In, <0.1 ppm (6); Br, <0.5 ppm (1); Pd, <0.5 ppb (8).

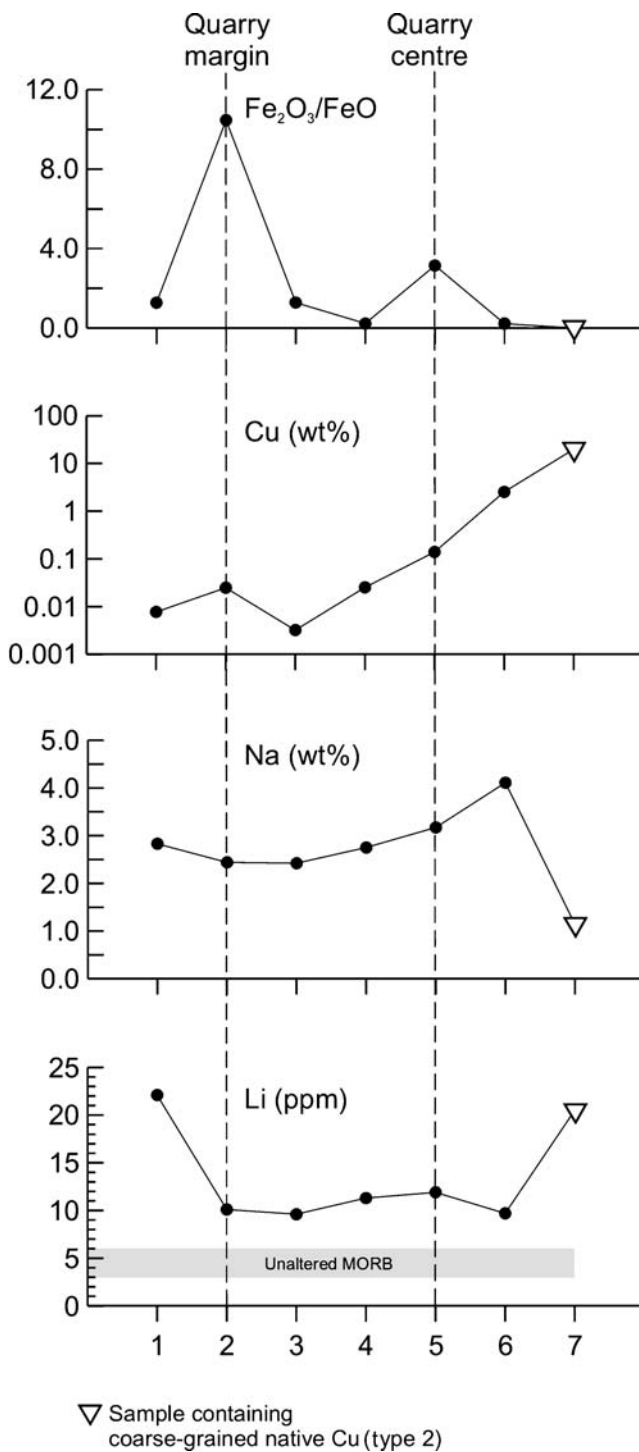
Sample numbers correspond to those indicated in Fig. 4.

n.a.: not analysed

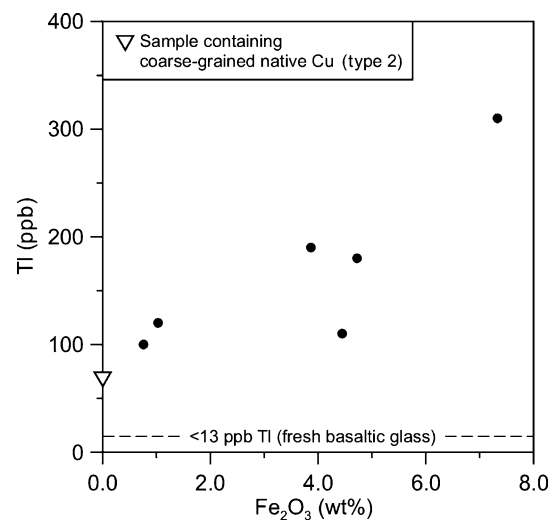


**Fig. 7** Geochemistry of Mont Alexandre and other basalts from the Lac McKay Member. **a** Classification using the  $Zr/TiO_2$  vs  $Nb/Y$  diagram (Winchester and Floyd 1977; Pearce 1996). **b** The  $Y$  vs  $Zr$

diagram to discriminate affinity (MacLean and Barrett 1993). **c** The  $Th-Zr-Nb$  diagram with the fields for different tectonic settings from Wood (1980)



**Fig. 8** Variation of bulk-rock contents of  $\text{Fe}_2\text{O}_3/\text{FeO}$ , Cu, Na and Li from the margin to the centre of the quarry. Numbers refer to samples located in Fig. 4. Lithium abundance of unaltered MORB used as reference from Staudigel (2003)



**Fig. 9** Distribution of  $\text{Fe}_2\text{O}_3$  and TI in the basaltic rocks (Table 3; Fig. 4). Unaltered oceanic basaltic glasses contain less than 13 ppb TI (McGoldrick et al. 1979)

## Discussion

### Volcanic red-bed copper and spilitisation

The cupriferous occurrence investigated here and those described by Duffours (2000) could be classified as ‘volcanic red-bed copper’ (Kirkham 1995). According to the model proposed by Kirkham (1995), a significant part of the volcanic pile must be subaerial to account for the oxidation of the volcanic flows. However, as pointed out by Bédard (1986b), the oxidation of the Upper Silurian Lac McKay lavas cannot be subaerial because the lavas are interbedded with deepwater sediments (Bourque et al. 1995; Bourque 2001). Bédard (1986b) argued that the oxidation could be magmatic, but such an origin is unsuitable to explain the high proportion of normative albite (Morin and Simard 1987) and the post-chlorite oxidation (Fig. 5b). The latter also conflicts with Duffours’ suggestion that, in the Mont Alexandre area, the spatial association of haematite and chlorite is fortuitous.

Albitisation, chloritisation and post-chlorite haematitic alteration of the Mont Alexandre basaltic rocks are interpreted here to result from circulating heated seawater causing spilitisation, as previously proposed elsewhere (e.g. Spooner and Fyfe 1973; Munhá and Kerrich 1980). Spilitisation provides an explanation not only for the sodic enrichment, but also for the copper depletion (Dostal et al. 1993) in the Late Silurian–Early Devonian basalts of the Gaspé Peninsula. Copper is leached from hydrothermally altered basalts of the oceanic crust (e.g. Humphris and Thompson 1978a; Wheat et al. 2002). Other alternatives for copper leaching from basalts are burial metamorphism and diagenetic reddening, as suggested for the Keweenaw basalts (Jolly 1974; Brown 2006). These alternatives are

considered unlikely, given the submarine environment at Mont Alexandre. Spilitisation agrees with the regional geological setting of deepwater-facies sedimentation.

Hydrothermal alteration by heated seawater at Mont Alexandre is indicated by the relatively high content of lithium in the altered basaltic rocks, compared to unaltered MORB (Chan et al. 2002; Staudigel 2003). Lithium is sensitive to the basalt–seawater interaction because it is removed from seawater and incorporated into alteration minerals at temperatures up to about 150°C (Seyfried et al. 1984; Chan et al. 2002). The upper volcanic rocks (275–594 m below the seafloor) of hole 504B near the Costa Rica Rift are altered by circulating seawater at temperatures of up to 150°C and are enriched in lithium (6–27 ppm) (Chan et al. 2002). Like lithium, thallium is a sensitive indicator of basalt–seawater interaction, as it is extracted from seawater by secondary silicate phases and by co-precipitation with iron and manganese oxides and hydroxides (McGoldrick et al. 1979). Thallium is such a diagnostic element for seawater interaction that additions of marine ferromanganese precipitates, which scavenge thallium from seawater, into the mantle can explain the pronounced thallium-isotope variations recorded in ocean-island basalts (Nielsen et al. 2006). Figure 9 suggests the incorporation of thallium into the Mont Alexandre lavas during haematitic alteration by seawater.

Another line of evidence suggesting basalt–seawater interaction is the chlorite-bearing alteration assemblage. The Mont Alexandre chlorite is as rich in magnesium as that from spilitised basalt (e.g. Alt et al. 1996) and hence requires a source of magnesium, such as seawater (Humphris and Thompson 1978b). Both the lithium and thallium enrichments and chlorite geothermometry (155–182°C; Table 1) are consistent with hydrothermal alteration by seawater.

Evidence of native copper in spilitised rocks can be found in earlier works (Hussak 1906). A.C. Lane (cited in Lindgren 1933 and Cornwall 1956) assumed that disseminated magmatic copper had been leached from the cooling Keweenawan lavas of Michigan by seawater, precipitating native copper in permeable zones. Nonetheless, subaerial volcanism is a requisite for the current genetic model for volcanic red-bed copper with the argument that lavas erupted under significant water depths would retain some of their sulphur, and this would inhibit later leaching of metals (Kirkham 1995).

It is interesting to make an analogy with the reddening model for sediment-hosted stratiform copper deposits (Brown 2005), which involves progressively less oxidising groundwater infiltrating sediments that are reddened until the pore solution attains optimal conditions to leach and transport trace amounts of copper from oxidised sediments (cf. Brown 2006). Seawater could play the same role as groundwater in continental settings to leach and transport copper from basalts during spilitisation.

## Copper sulphides

There is a long-standing controversy with regard to the metastability of yarrowite (Whiteside and Goble 1986). Yarrowite is a variety of *blaubleibender* covellite that replaces copper and copper–iron sulphides by selective removal of copper (Goble 1980). *Blaubleibender* covellite was synthesised at temperatures below 157°C (Vaughan and Craig 1978). Contrary to the yarrowite found as a replacement of roxbyite, a Cu–S mineral formed at low temperatures (<50°C, Gablina et al. 2006), the Mont Alexandre yarrowite forms independent crystals without relics of a precursor sulphide such as roxbyite. It is thus suggested that the Mont Alexandre yarrowite is a primary stable phase that probably precipitated from a low-temperature aqueous solution, i.e. not an alteration of a pre-existing Cu-rich sulphide.

The bornite-hosted chalcopyrite spindles (Fig. 5e) possibly represent exsolution intergrowths produced by rapid cooling (Uytenbogaardt and Burke 1971; and references therein) rather than replacement lamellae as previously interpreted by Duffours (2000).

## Feldspar-hosted, type 1 native copper

Albitised plagioclase hosts micrometric platelets of native copper distributed along (001) planes of feldspar in spilitic lavas from Mont Alexandre. Crystallographically oriented inclusions of native copper in fresh labradorite phenocrysts are considered to be magmatic, formed by exsolution from the feldspar (Hofmeister and Rossman 1985; Kimata et al. 1997). Similarly, a magmatic origin is favoured for the feldspar-hosted native copper documented here. It is nonetheless conceivable that native copper was introduced during plagioclase alteration, as suggested by the occurrence of native copper in analcite pseudomorphs after plagioclase phenocrysts in spilitic basalts from DSDP Site 417 (Alt and Honnorez 1984). There, however, native copper is also disseminated in the groundmass, which is not the case at Mont Alexandre. The Mont Alexandre feldspar-hosted native copper has distinctly higher sulphur and arsenic contents, and a broader range of silver content than the coarse-grained, cuprite-rimmed, type 2 native copper (Fig. 6). A magmatic origin for the feldspar-hosted native copper is compatible with copper, sulphur, silver and other metals that line vacuoles in melt inclusions in phenocrysts of volcanic rocks (Yang and Scott 1996).

## Coarse-grained, type 2 native copper

Type 2 native copper differs from the feldspar-hosted, type 1 native copper (1) in grain size with patches attaining a few centimetres in length and (2) in mineral chemistry

(Fig. 6). Its partial oxidation to cuprite is likely related to recent meteoric weathering. The type 2 native copper-bearing sample has virtually no ferric iron (Fig. 8), despite the pervasive haematitic alteration of the enclosing basalt. This situation is analogous to the bleached (dehaematitised) conglomerates highly mineralised in native copper from the Keweenaw district (Fig. 5 of Brown 2006). The absence of ferric iron can be explained either (1) by haematite-mediated oxidation of sulphide sulphur to sulphate in acidic solutions with removal of iron and sulphate as iron salt (R.C. Wells, cited in Lindgren 1933) or (2) by destabilisation of haematite in a highly reduced fluid capable of depositing native copper (Brown 2006). The removal of iron implied by the first hypothesis is perhaps expressed in the low total iron content of the type 2 native copper-bearing sample, which has the lowest value of all samples analysed (Table 3).

A possible analogue to the type 2 native copper is the epigenetic native copper hosted by spilitised basaltic flows from La Désirade, Lesser Antilles, where it is associated with flows extensively haematitised by heated, oxygenated seawater (Nagle et al. 1973). A similar epigenetic native copper mineralisation is known in tholeiitic flows from site 642 in the North Atlantic (LeHuray 1989). In contrast to La Désirade, an ephemeral period of subaerial weathering is believed to account for the haematitic alteration at site 642 before basalt–seawater interaction (LeHuray 1989). At Mont Alexandre, the haematitic alteration can be suitably explained by spilitisation in accord with a submarine environment.

### Implications for exploration

Economically important cupriferous deposits in the Gaspé Peninsula are associated with porphyritic intrusions and skarns, particularly in the Murdochville area (e.g. Bellehumeur and Valiquette 1993). There are, nevertheless, several occurrences of volcanic-hosted copper in Mont Alexandre area (Duffours 2000) that remain poorly recorded despite their potential for the mineral diversification in the region. Although several studies have focused on the petrogenesis of the Silurian–Devonian volcanic rocks in the Gaspé Peninsula (e.g. Laurent and Bélanger 1984; Bédard 1986a, b; Dostal et al. 1993), no allusion to spilitisation has been made.

Our investigation of a quarry for native copper in basaltic flows has indicated that the rocks are spilitised and enriched in thallium. This finding is relevant to exploration given that an ore-forming process mediated by seawater is expected to produce haloes of thallium enrichment within and around the orebody (McGoldrick et al. 1979; Murao and Itoh 1992). Thallium dispersion haloes may be as broad as 250 m from the ore, as revealed from

stratiform sediment-hosted Zn–Pb–Ag deposits (Large and McGoldrick 1998; Large et al. 2000).

### Conclusion

The main conclusions of this study are: (1) Upper Silurian basaltic lava of the Mont Alexandre area contains magmatic native copper included in plagioclase; (2) the oxidation of the basaltic flows is not related to the subaerial environment but to heated seawater–basalt interaction (spilitisation); (3) spilitisation can explain the anomalous sodium content and copper depletion reported in previous studies; and (4) copper and silver were possibly leached from basalts during spilitisation and ultimately deposited as argentiferous native copper.

This study prompts the re-examination of the current volcanic red-bed copper model, demonstrating that not only subaerial basaltic settings are favourable for this deposit type. Submarine arc basalts oxidised by warm seawater may also be a suitable setting.

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