



## Archean cherts in banded iron formation: Insight into Neoproterozoic ocean chemistry and depositional processes

P.C. Thurston<sup>a,\*</sup>, B.S. Kamber<sup>a,1</sup>, M. Whitehouse<sup>b</sup>

<sup>a</sup> Laurentian University, Sudbury, ON, Canada P3E 2C6

<sup>b</sup> Swedish Natural History Museum, Stockholm, Sweden

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### ABSTRACT

This study reports new REE+Y and  $\delta^{34}\text{S}$  isotope sulfur data for Archean banded iron formation and volcanoclastic rocks with cherty bed tops in the Neoproterozoic Abitibi greenstone belt of Canada. The data were analyzed with a view to better constrain Neoproterozoic ocean chemistry, atmospheric conditions prevalent during weathering and transport, the development of Algoma-type banded iron formation and the overall process of stratigraphic development of greenstone belts. The Abitibi greenstone belt consists of 7 mafic to felsic volcanic cycles, each capped by a sedimentary interface zone consisting of chemical and minor clastic metasediments. We concentrated sampling on the iron formation capping the ca. 2730 Ma Deloro assemblage as it occurs over a wide area (300 km  $\times$  600 km) and because there is a substantial depositional gap prior to deposition of the overlying volcanic rocks. Volcanoclastic rocks within the ca. 2710 Ma Tisdale assemblage were also sampled.

Chemical analyses focussed on the  $\text{SiO}_2$ -rich portion of the samples and were conducted by laser ablation ICP-MS. In situ analysis of S isotopes was obtained for pyrite by ion probe. REE data display four types of patterns: (1) hydrothermally influenced marine hydrogenous sediment, (2) contaminated, hydrothermally influenced marine hydrogenous sediment, (3) hydrothermally dominated patterns, and (4) replacement patterns indicating silicification of precursor volcanic units. Contamination and/or the presence of non-chert components were documented with Th, U and Zr content. Non-chert components were defined as: (1) phosphates that led to elevated Th/U, (2) clastic detritus leading to flat shale normalized REE patterns, and (3) volcanic detritus leading to elevated values for Zr. No meaningful difference in REE+Y geochemistry as a function of elevated Th/U was found implying that phosphates have the same REE patterns as the host chert. The cherts within banded iron formation exhibited stratigraphic variation in several localities, progressing from replacement chemistry (flat REE profile) at the base, hydrogenous sediment geochemistry (positive La, Gd, Y/Ho anomalies) in the middle part and hydrothermal patterns (depleted LREE, elevated positive Eu anomalies) in the upper part. The upper parts of some units also display +Ce anomalies possibly reflective of more oxygenated water also supported by S isotope data. A consistent increase in Pr/Yb in the upper parts of units is postulated to reflect shallowing upward of depositional depth to an unknown extent but not above storm wave base. A number of samples with flat REE patterns lacking La and Gd anomalies represent hydrothermal deposition with the largest Eu/Eu\* values recorded for Archean iron formation. The main contribution of the Abitibi banded iron formations is that they provide a deeper water perspective on Archean ocean chemistry. The resulting picture is that of slow BIF accumulation, a generally strong hydrothermal input of REE and complex oceanic cycling, possibly involving a chemocline above the sampled water depth.

The new sulfur isotope data show a greater extent of mass independent fractionation than previously recorded for the Neoproterozoic, with  $\Delta^{33}\text{S}$  ranging from  $-1.4$  to  $+4.2\%$ . The strongly MIF positive source ( $\Delta^{33}\text{S} = +4\%$ ) was apparently similar to Paleoproterozoic values.

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### 1. Introduction

The geochemistry of banded iron formation in a large greenstone belt, such as the Abitibi, may contain information about the water mass from which the sediment formed, atmospheric conditions that prevailed during weathering and transport of dissolved species from land to sea (e.g., U, Th, the rare earth elements

\* Corresponding author. Tel.: +1 705 675 1151; fax: +1 705 671 3878.

E-mail address: [pthurston@laurentian.ca](mailto:pthurston@laurentian.ca) (P.C. Thurston).

<sup>1</sup> Now at: Trinity College, Dublin, Ireland.

(REE)), the significance of Archean Algoma-type iron formation (Gross, 1965) in general, and the overall history of greenstone belt development. The Abitibi greenstone belt forms the eastern part of the Wawa-Abitibi terrane, the youngest granite-greenstone sub-province within the Superior Province (Percival, 2007). It is widely regarded as a purely oceanic terrane (Dimroth et al., 1982; Desrochers et al., 1993; Kimura et al., 1993; Ludden and Peloquin, 1996) either built autochthonously (Ayer and Trowell, 2002b; Thurston, 2002; Ayer et al., 2006) or as a stack of accreted oceanic terranes (Jackson and Fyon, 1991; Desrochers et al., 1993). In common with many Archean greenstone belts worldwide, the Abitibi stratigraphy is divided into a sequence of volcanic units and syn- to post-tectonic successor basins (Fig. 1). In the Abitibi, the volcanic units comprise the Keewatin stratigraphy containing very few shallow water sedimentary units prior to development of successor basins (known as the Timiskaming-type). In contrast the Archean greenstones of the Zimbabwe craton (Martin et al., 1993), the Slave craton (King and Helmstaedt, 1997), the West African shield (Attoh and Ekwueme, 1997), the Pilbara craton (Barley, 1997), and the Tanzanian craton (Borg and Shackleton, 1997) have abundant sedimentary deposits and hence continental detritus. This lack of sedimentary material, particularly of continental provenance, strongly suggests that the Abitibi greenstone belt developed in a marine environment relatively distant from continental land masses (Desrochers et al., 1993; Ayer et al., 2002a). This is also consistent with the non-radiogenic isotope composition of volcanic rocks and the lack of >2.8 Ga inherited zircon (Ketchum et al., 2008).

A final important aspect of Abitibi greenstone belt volcanism is that it spans a period of about 90 My with most volcanism occurring in the interval 2750–2700 Ma (Thurston et al., 2008). Each of the mafic-felsic volcanic cycles is capped by a sedimentary interface zone (SIZ) dominated by chemical sedimentary rocks (Fig. 1). Collectively, these attributes make the Abitibi greenstone belt an ideal environment to record changes in Neoproterozoic open ocean chemistry, unlike, for example the Zimbabwean belts that record localized shallow water environments, including epi-continental seas, potentially misleading our understanding of the global picture of ocean chemistry in the Neoproterozoic. Regardless of the attractiveness of the Abitibi belt's tectonic setting for geochemical investigation, few studies have attempted to extract paleoenvironmental information from Abitibi cherts and BIFs. The present report aims to address this shortage by providing in situ trace element and S-isotope data on carefully studied and selected Abitibi BIFs.

## 2. Regional geology

The Abitibi greenstone belt volcanic units have been divided by Ayer et al. (2002a) into 7 lithotectonic assemblages. These include, stratigraphically arranged: (1) pre-2750 Ma (small scattered units), (2) the 2750–2735 Ma Pacaud assemblage, (3) 2734–2724 Ma Deloro assemblage, (4) 2723–2720 Ma Stoughton-Roquemaure assemblage, (5) 2719–2711 Ma Kidd-Munro assemblage, (6) 2710–2704 Ma Tisdale assemblage and (7) 2704–2695 Ma Blake River Group (Fig. 1). The subdivision into these intervals is underpinned with more than 450 high-precision (typically 1–2 Ma) U–Pb zircon ages from a region in excess of 250,000 km<sup>2</sup>. About 20% of the U–Pb zircon age determinations acquired over the last decade by the single grain TIMS or the SIMS (SHRIMP) method display evidence for isotopic inheritance, in which the inherited ages represent the age of subjacent, underlying stratigraphic units (Ayer et al., 2002a, 2005; Thurston et al., 2008). The major exception to this situation is the region west and south of Timmins where Ketchum et al. (2008) have documented the presence of ca. 2.8 Ga isotopic inheritance which is interpreted to represent the presence of subjacent older continental crust. Possible remnants of this older crust

exist in the western extension of the Abitibi greenstone belt in the Wawa area where 2.89 Ga volcanism and plutonism occur.

Regardless of the presence of older zircon from the NW Abitibi belt, the extensive U/Pb zircon database confirms that the individual units defined above extend over the full extent of the Abitibi greenstone belt (Fig. 1) and that the volcanic episodes represented by the units were short-lived and separated by periods of quiescence. The older (>2.73 Ga) assemblages are preserved either on the flanks of batholiths or in the cores of regional anticlinoria. For example, the ~2750 Ma Pacaud assemblage is preserved only as remnants on the margin of the Round lake batholith, but the areal extent of units with ~2750 Ma xenocrysts clearly suggests it had greater extent than presently preserved (Ayer et al., 2005). Two important features of the Abitibi bear on its origin and development: (1) there is no large-scale tectonic transport of stratigraphy (Snyder et al., 2008), and (2) diking relationships indicate that stratigraphy developed autochthonously (Ayer et al., 2005). Examination of intact stratigraphic sequences on the margins of synvolcanic batholiths confirms the presence of depositional gaps of up to 20 My (e.g. south of Timmins; Thurston et al., 2008) and on the west flank of the Kenogamissi batholith (Heather, 2001). The geochemistry of the thin sedimentary veneers that developed during periods of volcanic quiescence may therefore help to reconstruct the environment in which the Abitibi formed. The metamorphic grade of the Abitibi greenstone belt ranges from subgreenschist to greenschist grade with local development of higher grade zones on the margins of the major batholiths (Easton, 2001 and references therein).

## 3. Samples and analytical details

### 3.1. Samples

The bulk of sampling was concentrated in the 2734–2724 Ma Deloro assemblage because it underlies a depositional gap both west (Thurston et al., 2008) and east (Heather, 2001) of the synvolcanic Kenogamissi batholith (Benn, 2008). Thus, this sequence may preserve evidence of the character of the Archean ocean over a ca. 20 My period (i.e. after the >2735 Ma Pacaud assemblage through to the 2724 Ma age of the youngest Deloro assemblage units) (Thurston et al., 2008). On both sides of the batholith, the mafic base of the assemblage is overlain by several hundred meters of dacite-rhyolite with three intercalated banded iron formations. Recent mapping on the east side shows that the lowest iron formation consists from base to top of 0.5–5 m of oxide facies micritic iron formation with magnetite-rich bands 1–10 cm thick intercalated with felsic tuff with minor amounts of magnetite-rich and jasper beds (Houlé, 2006). The middle iron formation is 5–40 m thick and consists of intercalated oxide and chert microbands with the upper part of the unit consisting of sulfide ± magnetite-rich bands intercalated with chert-magnetite bands. The upper unit is represented by a meter-scale sedimentary rock consisting of graphitic and sulfidic argillite with minor intercalated chert bands which grades southward into intercalated, chert and oxide bands. On a local scale, the three units are not continuous along strike; in particular the upper unit may have been eroded or tectonically displaced but the package of three units does persist in general over several hundred km around the Kenogamissi batholith (Thurston et al., 2008).

Analytical results for all determinations except S isotope samples are listed in Table 1. UTM coordinates for all samples are listed in Table 2. Most samples are from the uppermost of the three iron formations of the Deloro assemblage south of Timmins (Figs. 1 and 2). As shown in Fig. 3, this iron formation is 2–3 m thick with a ca. 30 cm thick parallel laminated chert (Photo 1) overlain by oxide facies iron formation (Photo 2), heterolithic pyroclastic

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