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REE and HFSE mobility due to protracted flow of basinal brines in the mesoproterozoic Belt-Purcell Supergroup, Laurentia

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ABSTRACT

Argillites from the Belt-Purcell Supergroup record three types of REE patterns. Type 1 (T1), near-primary compositional pattern is characterized by: (1) a PA-UCC-like REE pattern, and Th/Sc ratios reflecting a dominantly Paleoproterozoic catchment; (2) depletion of Ca, Sr and Na due to weathering in the provenance of the sediments; (3) variable depletion of Nb–Ta and Zr–Hf from winnowing of titanite and zircon, respectively, with Nb/Ta and Zr/Hf ratios similar to PA-UCC; and (4) K-enrichment, with variable Th/U and Ce/Ce* ratios from diagenesis. Sandstones with T1 patterns are compositionally equivalent to argillites diluted with quartz, and show the same four T1 compositional features, albeit at lower absolute abundances.

Relative to T1 argillites, Type 2 (T2) and Type 3 (T3) patterns both feature enriched and fractionated HREE, but T2 exhibits LREE depletion. Relative to T1 these constitute T2 low – ΣLREE/ΣHREE (15 ± 3) and T3 high – ΣLREE/ΣHREE (24 ± 3) patterns showing progressive enrichment of HREE, erratic ratios of Zr/Hf, Ti/Sm, Y/Ho, Y/Yb and Al/Yb. Collectively, T2 and T3 patterns record diagenetic transfer of REE as well as REE/HFSE and HFSE/HFSE fractionations. Such fractionations are more pronounced in sandstones due to greater hydraulic conductivity for diagenetic fluids.

Hence REE and HFSE patterns in the argillites and sandstones are interpreted as diagenetic processes superimposed on a PA-UCC provenance signature, specifically to pervasive and episodic migration of oxidizing-alkaline diagenetic basinal brines in the Belt-Purcell Supergroup. During these diagenetic processes Al, Th and Ga behaved isochemically.

Dominantly positive Ce anomalies coupled with mobility of U (as recorded by variable Th/U ratios) is consistent with oxidizing conditions, which may have been internally generated within the basin by reactions between clays and carbonate. Alkalinity of the fluids could have been promoted by some combination of: (1) enrichment of K as indicated by mass balance calculations and the presence of illite; (2) hydrothermal and/or diagenetic alteration of mafic igneous units lower in the stratigraphic sequence; and (3) dissolution of evaporitic units, evident in relict halite casts, in the Belt-Purcell sequence.

Supporting this interpretation, previous studies revealed two populations of monazite, differentiated in terms of texture, composition and age. Detrital monazites are >1400 Ma, whereas diagenetic monazites are euhedral and chemically distinctive, spanning ~1400–~300 Ma. The diagenetic monazites may record episodic brine activity for ~1000 Ma that induced T2 and T3 compositional features, and redistributed HREE and Zr–Hf at a basin scale.

1. Introduction

The rare earth elements (REEs), Th, Y, Co and Sc are in many cases conserved when transferred from provenance areas into fine-grained siliciclastic sedimentary sequences. Accordingly, these elements have been broadly used to address the provenance of sediments and sedimentary rocks (e.g., Taylor and McLennan, 1985, 1995; Cullers and Podkovyrov, 2002; McLennan et al., 2006; Chakrabarti et al., 2007). However, some studies describe processes that influence the fractionation of trace elements during transfer into the sedimentary budget, such as weathering, sedimentary sorting, and diagenesis (McDaniel et al., 1994; Nesbitt, 2003; Fralick, 2003; McLennan et al., 2003; Rudnick and Gao, 2003; Abanda and Hannigan, 2006).

Mathieu et al. (2001) documented large scale light rare earth element (LREE), U, Pb and P migration in the lower Proterozoic

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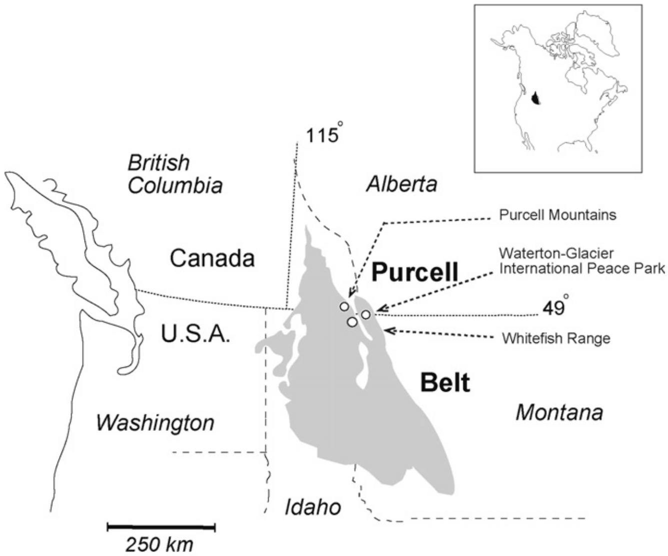

Fig. 1. Geographic extent of the Belt-Purcell Supergroup outcrops as shaded area spanning in the western Canada–USA border. Locations of the three areas sampled in the present study are marked as open circles.

sandstones of the Franceville Basin, Gabon, in relation to extensive accessory mineral alteration by highly saline oxidizing brines. Studies on the Paleoproterozoic Athabasca Basin, Canada, and McArthur Basin, Australia, revealed a protracted history of episodic basinal brine migration over hundreds of million years during which U, Y and REE may have been locally mobilized (Fayek and Kyser, 1997; Kyser et al., 2000; Alexandre et al., 2009).

Schieber (1988) presented the first geochemical study on the redistribution of REE during diagenesis of carbonate rocks in the Belt-Purcell sequence. This study builds on earlier geochemical studies that related REE patterns with source area, weathering intensity and tectonic activity for the Belt-Purcell sedimentary sequence (Schieber, 1986, 1990, 1992). A recent geochemical and monazite geochronological study of argillites and sandstones of the Mesoproterozic Belt-Purcell Supergroup revealed a primary population of samples with REE patterns comparable to post-Archean upper continental crust (PA-UCC; cf. Rudnick and Gao, 2003; Hu and Gao, 2008), whereas a secondary population of samples is characterized by systematic enrichment of heavy rare earth elements (HREE) relative to LREE, and fractionation of high field strength elements (HFSE), when normalized to PA-UCC. That study identified both detrital monazite as well as precipitation of texturally and compositionally distinct diagenetic monazite [(Ce, La, Y, Th) $(PO)_4$] retaining secondary ages spanning ~1000 Ma and secondary LREE/HREE fractionation. The diagenetic monzites were interpreted to have formed during episodic migration of basinal brines in response to distal tectonic events (González-Álvarez et al., 2006).

This paper builds on the above study, and reports an extensive database of major and trace elements for siliciclastic rocks at three locations (Waterton-Glacier International Peace Park, the Purcell Mountains and Whitefish Range) in the Belt-Purcell Supergroup. Each location sampled covers the complete stratigraphic section of the Supergroup (Figs. 1 and 2). The aim of is this paper is to further evaluate the primary characteristics and scale of possible secondary trace element mobility during diagenesis in the Belt-Purcell basin.

Based on the combination of dominantly Paleoproterozoic detrital zircon and monazite ages (Ross and Villenueve, 2003) with a primary population of samples having compositions close to PA-UCC, it is assumed the PA-UCC composition reflects that of the sedimentary package. This constraint permits quantifying geochemical variations in secondary populations of zircon and monazite in the Belt-Purcell sequence, caused by diagenetic basinal brine activity, using well established chemical mass balance calculations (Pettke et al., 2005). The nature of the brines involved in secondary diagenetic element mobility is addressed by comparison with modern alkaline brines having high aqueous solubility of REE and HFSE from the East African Rift (Kerrich et al., 2002), and in conjunction, brine activity is linked to the genesis of previously reported diagenetic monazite grains (González-Álvarez et al., 2006).

2. Geological setting

This Laurentian Mesoproterozoic sedimentary sequence has been named the Belt Supergroup in the United States, whereas its Canadian counterpart is referred to as the Purcell Supergroup (Fig. 1). The Belt-Purcell basin was generated by intracontinental rifting at ~1500 Ma (Hoffman, 1991; Ross et al., 1991; Chandler, 2000; Price and Sears, 2000).

The Belt-Purcell Supergroup has been divided into four major stratigraphic divisions (Fig. 2A). (1) The lower Belt-Purcell, comprising fluvial to deltaic and fine-grained marine turbiditic facies, up to 12 km thick (e.g., McMechan, 1981; Cook and Van Der Velden, 1995; Lydon et al., 2000). This unit grades upwards into (2) the Ravalli Group, composed dominantly of fine-grained siliciclastic facies, with interbedded units of medium to coarse sandstone, which are more pronounced towards the upper part of the sequence. These facies are interpreted as prograding alluvial aprons, playas and sheet-floods by Winston (1986, 1990), whereas in the northwest of the basin McMechan (1981) interpreted these facies as subtidal to intertidal facies. In turn, the Ravalli Group grades upwards into (3) the middle Belt-Purcell carbonate-dominated unit for which there are multiple interpretations of depositional environment (Frank et al., 1997 and references therein). The upper Belt-Purcell sequence is represented by (4) the Missoula Group that comprises siliciclastic facies interpreted as alluvial in origin (e.g., Whipple et al., 1984, 1997).

Sears et al. (2004) viewed the large volume of siliciclastic detritus as reflecting fluvial transport from a low relief, continental-scale catchment. Lower units were deposited during active rifting, whereas the upper Belt-Purcell is considered to record basinal subsidence from thermal contraction of the lithosphere (Sears and Price, 2000; Lydon, 2000).

Stratigraphically, the Belt-Purcell Supergroup thickens to the west and southwest reaching a maximum of ~17 km (Fig. 2A; e.g., Harrison, 1972; Whipple et al., 1984). Four main source areas are considered to have contributed to the Belt-Purcell sedimentary package based on a combination of paleocurrent directions, geochemical compositions and age distributions of detrital minerals. These source areas are: (1) the Paleoproterozoic Trans-Hudson orogen to the east; (2) the late Archean Dillon block to the south; (3) the Mesoproterozoic Mojave and/or Yavapai Province for the Missoula Group from the southeast; and (4) an unknown Proterozoic craton from the west, possibly Australia (e.g., Ross and Villenueve, 2003; Sears et al., 2004; González-Álvarez et al., 2006; Canil, 2008). The eastern sources contributed mainly coarse sediments (sands) to the Belt-Purcell basin, and the western sources fine-grained sediments (silts and clays). Both facies interfinger throughout the stratigraphic sequence (e.g., Frost and Winston, 1987; Winston, 1990).

The duration of sedimentation of the Belt-Purcell Supergroup was ≤75 Ma. A maximum age of sedimentation is estimated at 1468 ± 2 Ma and 1469 ± 3 Ma by U–Pb from zircons in sills located near the base of the Belt-Purcell sequence (Fig. 2A; Anderson and Davis, 1995). This age excludes hidden strata located below the Aldridge Formation but above the basement (Lydon, 2000). The