GS-11 Evidence for carbonatite magmatism at Paint Lake, Manitoba (parts of NTS 63O8, 63P5, 12)

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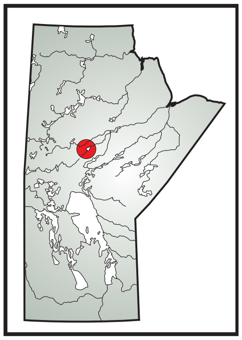

Summary

A swarm of subparallel, steeply dipping carbonate dikes is exposed on numerous small islands in the central part of Paint Lake in the Thompson Nickel Belt. This swarm of narrow discontinuous dikes has been traced over a distance of 21 km and is generally conformable with the regional structure/gneissosity. The contact between the dikes and their hostrocks is sharp and commonly interrupted by apophyses, embayments and stoping structures. The dikes show evidence of plastic flow accompanied by grain deformation and cataclasis. The principal constituent of all dikes is calcite enriched in Sr and rare earth elements (REE). The modal composition and texture of individual bodies vary from anchimonomineralic zones of coarse-grained calcite to fine-grained saccharoidal rocks with biotite-rich stringers to inequigranular, foliated varieties containing a large proportion of amphibole-group minerals, allanite, titanite, apatite, diopside and xenocrysts. Regardless of these textural variations, the rocks are consistently enriched in Sr and light REE, and have Y/Ho, Zr/Hf, Th/U and Nb/Ta ratios similar to the primitive-mantle values. The contents of chalcophile and high-field-strength elements are systematically low. Based on the available structural, petrographic and geochemical data, the dikes are interpreted here as calcite carbonatite of postorogenic affinity. The current situation on the REE market has led to a renewed interest in this commodity and intensified exploration for REE deposits worldwide. Carbonatite bodies produce, or are genetically associated with, the largest known deposits of REE ores.

Introduction

Mapping of the Paint Lake area by Couëslan (2008), aimed at detailing the character of the Archean basement of the Thompson Nickel Belt (TNB) and its cover sequence, revealed the presence of fine- to coarse-grained, pink carbonate rocks that were emplaced intrusively in orthogneiss and amphibolite of the Superior Boundary Zone, and were tentatively identified in that work as carbonatite-like rocks (subunit 8b). Subsequent mapping shows that these rocks extend beyond the area where they were initially recognized (Couëslan, 2009; Couëslan, GS-10, this volume, unit 10), forming a well-defined linear feature generally conformable with the regional metamorphic fabric. In addition, Couëslan (2009) described grey silicate-carbonate rocks (subunit 10a), which were previously identified as marble (Couëslan, 2008, subunit 4d) based on their similarity to the T3 member (siliceous dolomite) of the Thompson Formation in the Paleoproterozoic Ospwagan Group cover sequence (Bleeker and Macek, 1996). In the summer of 2009, further material was collected from unit 10, including the previously recognized and new localities on the islands in the central part of Paint Lake. A preliminary examination of the grey silicate-carbonate rocks (subunit 10a) showed their predominantly dolomitic composition, as well as extreme textural, modal and compositional variability, proper characterization of which would require an in-depth geochemical study. The currently available geochemical and mineralogical data are insufficient to classify these rocks unambiguously, or rule out a metasedimentary affinity. Consequently, this report will focus on the key features of the carbonate rocks of subunit 10b and their petrogenetic interpretation.

Geological overview of the Paint Lake area

Paint Lake is located along the northwestern margin of the Superior craton on the east side of the TNB, a segment of the Superior Boundary Zone (Figure GS-11-1). It is underlain by Archean granulite of the Pikwitonei Granulite Domain (PGD) that was reworked during the Paleoproterozoic Trans-Hudson orogeny (Hubregtse, 1980; Russell, 1981; Bleeker and Macek, 1996). The PGD consists dominantly of migmatitic intermediate to felsic enderbite and mafic granulite. Prior to Trans-Hudson orogenic overprint, two main tectonometamorphic events in the PGD resulted in two generations of isoclinal folding and widespread granulite-grade metamorphism at ca. 2690–2635 Ma, accompanied by the generation of pervasive orthopyroxene-bearing mobilizate (Hubregtse, 1980; Mezger et al., 1990; White et al., 1994; Böhm et al., 1999).

The Archean granulite was unconformably overlain by the Ospwagan Group supracrustal sequence, a platform rift-drift succession of clastic and chemical sedimentary rocks overlain by coarse clastic-flow deposits and mafic-ultramafic volcanic assemblages, deposited between ca. 2100 and 1880 Ma (Bleeker and Macek, 1996; Zwanzig et al., 2007). Subsequent Hudsonian tectonometamorphic

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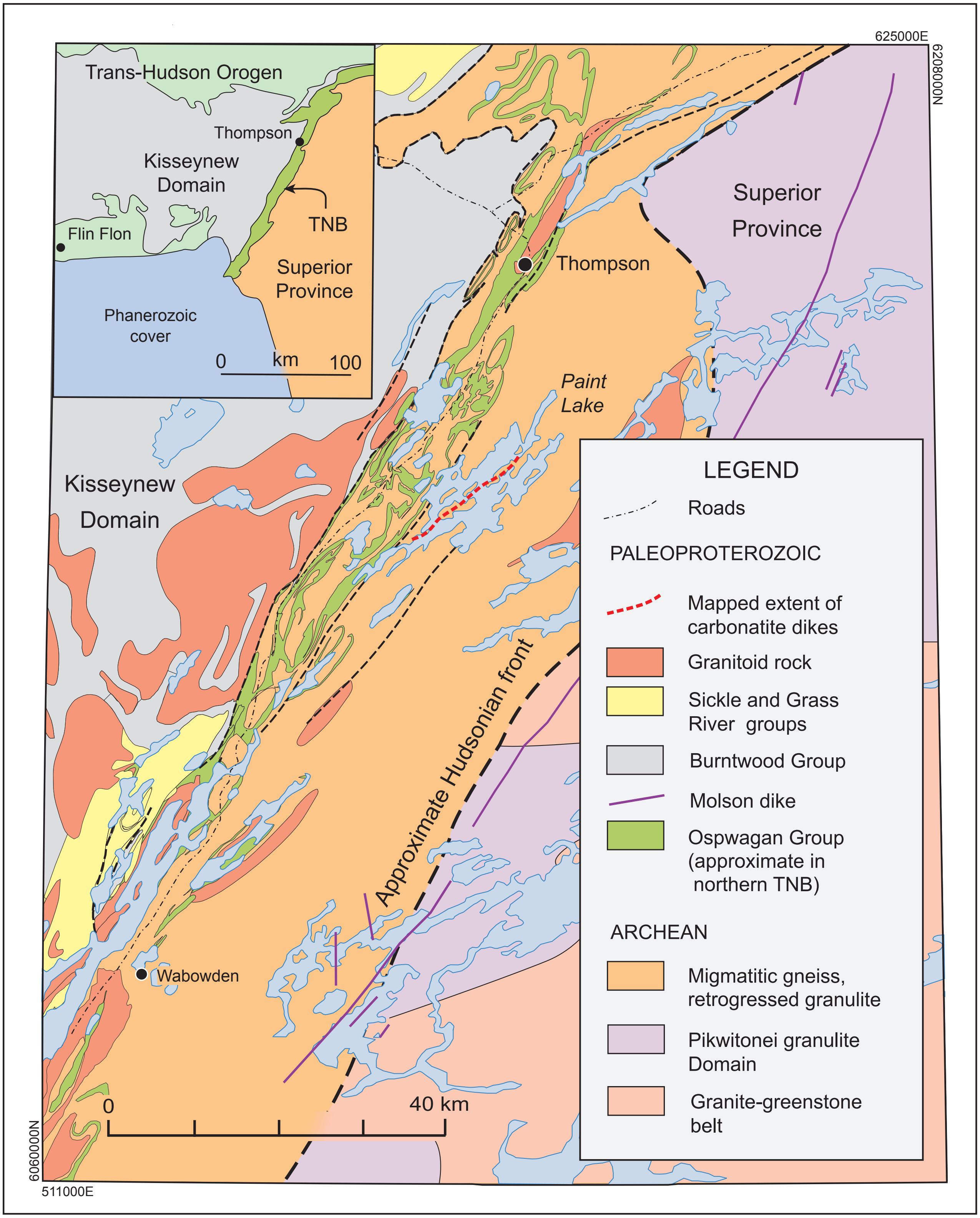

***Figure GS-11-1:** Simplified geology of the Thompson Nickel Belt, with extent of mapped carbonatite dikes and alkali metasomatism indicated by broken red line.*

events consist of D_1 nappe development followed by tight to isoclinal, likely recumbent, folds during the D_2 event. Peak thermal metamorphism was likely coeval with, and outlasted, the D_2 event (Bleeker and Macek, 1996). Peak Hudsonian metamorphism in the TNB reached middle to upper amphibolite-grade, and locally granulite-grade conditions from ca. 1810 to 1770 Ma (Machado et al., 1990; Schneider et al., 2007; Couëslan et al., 2007).

The Hudsonian D_3 event began at ca. 1770 Ma, forming upright, northeast-trending, doubly plunging folds that are the most obvious structures present in the TNB. Extensive zones of mylonitization are confined to shear zones roughly parallel to the limbs of these upright folds (Bleeker and Macek, 1996). Widespread emplacement of pegmatite dikes, associated with hydrous, retrogressive, amphibolite- to upper greenschist–grade metamorphism, occurred from ca. 1785 to 1765 Ma and continued locally as late as ca. 1725 Ma (Machado et al., 1990; Bleeker and Macek, 1996).

The Paint Lake area is underlain by a variety of Archean and Proterozoic rocks that are outlined in greater detail in Couëslan (2008; GS-10, this volume; 2009). Archean multicomponent gneiss is the dominant rock type. It consists of varying proportions of hornblende gneiss, biotite gneiss, plagioclase amphibolite, leucogranodiorite, granodiorite, aplite, pegmatite and assorted ultramafic blocks and boudins, all of which occur as intermixed, highly attenuated, centimetre- to metre-scale bands. Other Archean phases consist of variably retrogressed enderbitic gneiss, and layered metagabbro and leucocratic metagabbro. A suite of supracrustal rocks, tentatively identified as Archean, is present as disrupted belts along the east and west shores of the lake and as a continuous belt through the central islands. The supracrustal suite consists dominantly of metagreywacke and metapsammite, with minor iron formation and rare metapelite and possible metavolcanics. Discontinuous bands and boudins of plagioclase amphibolite are present in most outcrops and likely represent mafic rocks of various ages, including Paleoproterozoic dikes. Granodiorite and leucogranodiorite occur as dikes and larger intrusive bodies that are potentially Proterozoic. A quartz-saturated melasyenite intrusion is present in the southwest corner of the lake and is also likely Proterozoic. Ospwagan Group supracrustal rocks are present as a narrow band along the west shore of the lake. Simple quartz-feldspar, pink pegmatite dikes are present in almost all outcrops. The majority of pegmatite dikes are foliated to mylonitic and oriented subparallel to regional structures and gneissosity; later massive dikes, however, locally crosscut the regional structures at a high angle. Rare plagioclase-rich, white pegmatite dikes are locally present and spatially associated with carbonatite dikes.

Field relations and petrography

The carbonate rocks of subunit 10b (Couëslan, GS-10, this volume) occur as a swarm of subparallel dikes that extends at least 21 km through the central islands of Paint Lake. The swarm has been traced up to the northern edge of the currently mapped area (Couëslan, 2009), and may continue beyond. The dikes are generally oriented subparallel to the regional structure/gneissosity, with an overall trend of 040° and a subvertical dip. In outcrop, weathered surfaces of the dikes are recessed and characterized by a chalky, yellow-orange coating. The colour of fresh rock is bright pink but grades into milky white with rusty streaks near the surface and along fractures. Individual dikes are small and have a highly variable thickness along strike, which generally does not exceed 1 m but locally reaches 2.75 m (Figure GS-11-2a, b). The dikes exhibit conspicuous metamorphic (micro)textures, including foliation, cataclasis, twinning and ductile deformation of calcite (Figures GS-11-2c, -3a). The texture of the dikes is highly variable, ranging from anchimonomineralic zones of coarse-grained mosaic-textured calcite to fine-grained saccharoidal rocks with biotite-rich stringers to inequigranular foliated varieties containing a large modal proportion of silicate minerals and apatite. Contacts between the dikes and their hostrocks are sharp but irregular and commonly interrupted by apophyses, embayments and stoping structures (Figure GS-11-2b).

The dikes consist predominantly of calcite and contain subordinate amounts of (in order of decreasing abundance) amphibole, biotite, apatite, titanite, allanite, diopside, magnetite and sulphides (Figure GS-11-3a–c). Anhedral grains of quartz and feldspar are also common (Figure GS-11-3d), but probably represent xenocrysts derived from the wallrock gneiss and amphibolite. Calcite grains range from 50 µm to 3 cm in size; in contrast to the

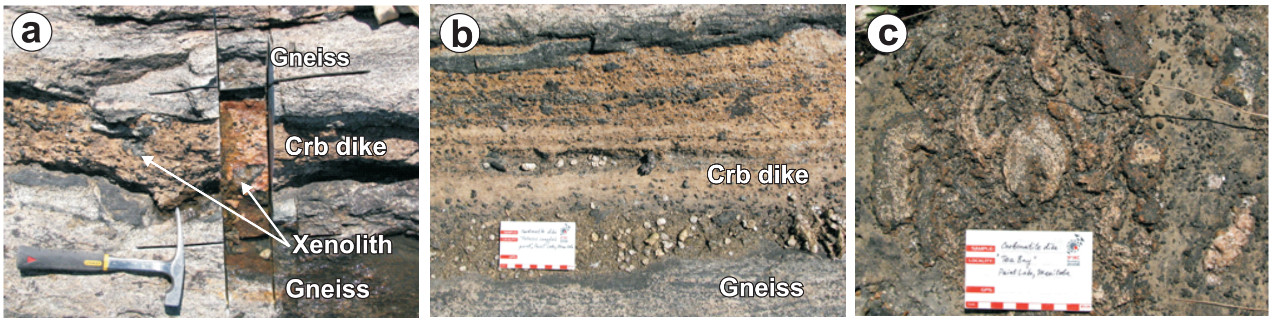

***Figure GS-11-2:** Field relations of the carbonate rocks (subunit 10b) at Paint Lake: **a)** Carbonate (Crb) dike emplaced concordantly in Archean gneiss; note xenoliths of the hostrock within the dike and dark amphibole-rich metasomatic haloes around the xenoliths and along the contact; **b)** foliated carbonate (Crb) dike showing structures similar to those in (a); **c)** deformed and metasomatized xenoliths of gneiss exposed on a recessed surface of weathered carbonatite.*

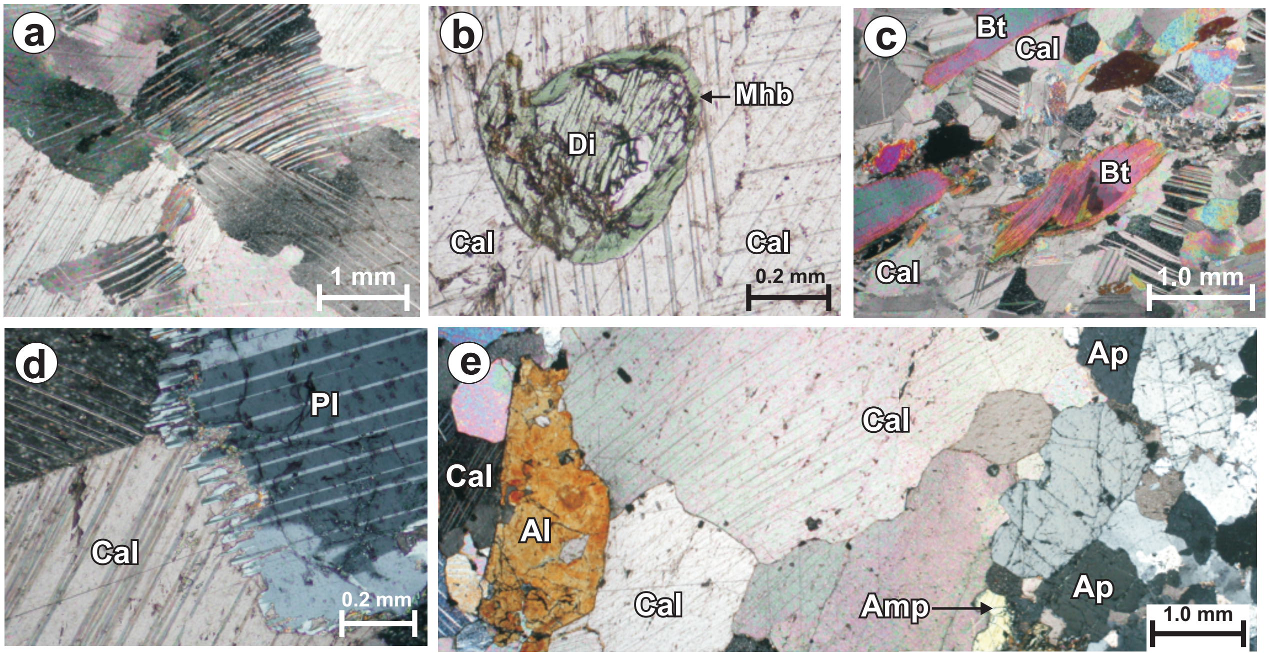

***Figure GS-11-3:** Major textural and mineralogical characteristics of the carbonate rocks (subunit 10b) from Paint Lake: **a)** polysynthetically twinned and plastically deformed calcite showing serrated margins and grain reduction, under cross-polarized light (XPL); **b)** diopside (Di), rimmed by magnesiohornblende (Mhb), and calcite (Cal), under plane-polarized light (PPL); **c)** deformed crystals of biotite (Bt) embedded in fine-grained calcite (Cal) under XPL; **d)** plagioclase xenocryst (Pl) mantled by albite at the contact with calcite (Cal), under XPL; **e)** cross-section through marginal zone of a carbonate dike showing an apatite-amphibole (Ap, Amp) aggregate near the contact and a subhedral crystal of allanite (Al), under XPL.*

saccharoidal calcite, larger grains are strongly deformed and aligned subparallel to the foliation (Figure GS-11-3a). The marginal zones of the dikes are composed of a calcite-apatite-amphibole aggregate up to several centimetres in thickness and contain a higher proportion of titanite, allanite and xenocrysts relative to the interior of the dikes (Figure GS-11-3e). The dike swarm is accompanied by a zone of alkali metasomatism that is present along the entire strike length of the swarm. The normally grey hornblende and biotite gneisses become pink as plagioclase feldspar is replaced by microcline, and dark metamorphic amphibole (ranging from magnesiohastingsite to edenite in composition) and biotite are replaced by light green actinolite and, locally, clinopyroxene. Amphibolite is even more susceptible to metasomatism, and transforms into a light green, medium- to coarse-grained apatite-amphibole aggregate at the contact with the carbonate dikes.

Locally, the carbonate dikes crosscut foliated dikes of pink granitic pegmatite and, in turn, are crosscut by later-emplaced, weakly foliated to massive pegmatite dikes. This suggests a time of carbonate dike emplacement between ca. 1785 and 1725 Ma.

Mineral chemistry

Calcite, the principal constituent of the subunit 10b dikes, was examined in detail using ultraviolet fluorescence, cathodoluminescence (CL), back-scattered-electron imaging (BSE), electron-microprobe analysis (EMPA) and laser-ablation inductively coupled plasma–mass spectrometry (LA-ICP-MS). The mineral shows complex zoning in CL and BSE images arising from variations in MgO and FeO contents (0.3–0.7 and 0.4–0.8 wt. %, respectively); the MnO content is consistently low, whereas SrO is consistently high (<0.3 and 0.5–0.6 wt. %, respectively). The Mg, Mn and Sr values determined by LA-ICP-MS are in accord with those obtained by EMPA. Additionally, we measured the abundances of Na, Rb, Ba, Y, total rare earth elements (ΣREE = La to Lu), Th and U. Only the Ba, Y and ΣREE levels are consistently above their lower limit of detection (i.e., 8–48 ppm Ba, 81–111 ppm Y, 183–481 ppm ΣREE). The Y/Ho ratio ranges between 26 and 31, and the La/Yb ratio normalized to the chondrite composition (La/Yb$_{CN}$; Anders and Grevesse, 1989) varies between 1.2 and 5.2 (Figure GS-11-4).

Amphibole-group minerals and biotite are the most common mafic constituents of the subunit 10b dikes. The modal content of amphiboles typically does not exceed 15%, but may increase to 50% near dike selvages and in dikes containing a large proportion of wallrock xenoliths. These minerals cover a range of compositions from magnesiohastingsite to edenite to magnesiohornblende to alkali-Al-Fe–rich actinolite (mg# 0.75–0.76, 0.7–0.9 wt. % Na_2O+K_2O, 2.5–3.1 wt. % Al_2O_3) to alkali-Al-Fe–poor actinolite (mg# 0.77–0.78, ≤ 0.6 wt. % Na_2O+K_2O, ≤2.4 wt. % Al_2O_3). Most amphibole crystals contain inclusions of, or are intergrown with, quartz, feldspar and

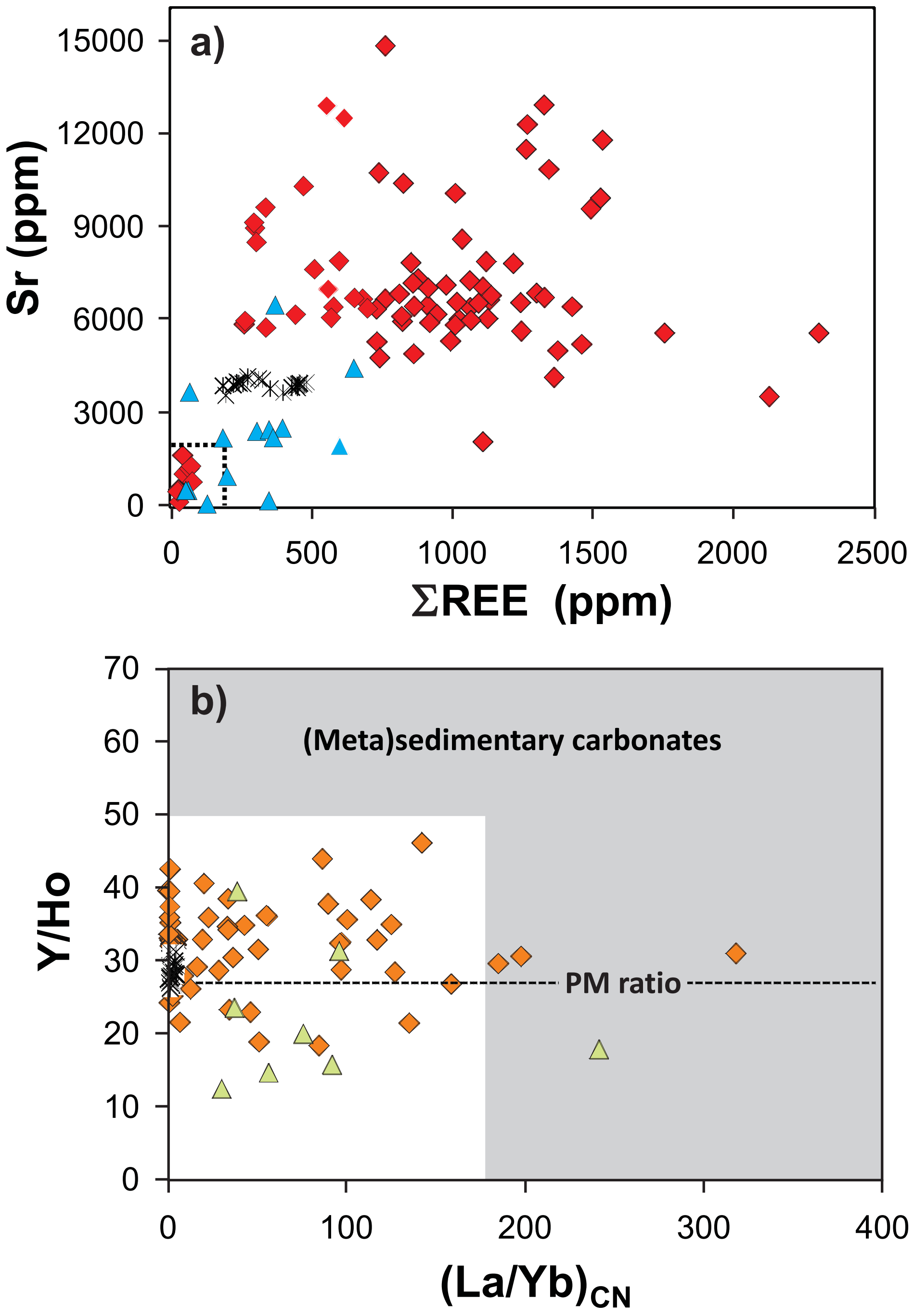

***Figure GS-11-4:** Trace-element composition of major carbonates from the Paint Lake carbonate rocks (asterisks), calcite carbonatites (diamonds) and dolomite carbonatites (triangles). The dashed box in the lower left corner of **(a)** indicates the inferred extent of Sr and ΣREE values in sedimentary carbonates. The shaded areas in **(b)** are the inferred Y/Ho and* $(La/Yb)_{CN}$ *ratios in (meta)sedimentary calcite based on the data of Zhong and Mucci (1995) and Bau (1996), and the dashed line corresponds to the Y/Ho ratio of the primitive mantle (PM; McDonough and Sun, 1995). The published data (diamonds and triangles) are from Hornig-Kjarsgaard (1998), Dawson and Hinton (2003) and Xu et al. (2007, 2008).*

biotite, and show evidence of resorption and chemical re-equilibration, indicating that these are xenocrysts derived from the metamorphic wallrocks. Only reaction rims of magnesiohornblende on resorbed diopside crystals (Figure GS-11-3b) can be unambiguously identified as primary. This magnesiohornblende is compositionally indistinguishable from some of the discrete resorbed amphibole grains in the carbonate mesostasis (mg# 0.67–0.70, 0.8–1.6 wt. % Na_2O+K_2O, 3.2–5.3 wt. % Al_2O_3, 0.2–0.4 wt. % F, ~0.3 wt. % TiO_2), implying that these crystals may be either phenocrysts or re-equilibrated xenocrysts.

Biotite commonly occurs in stringers of fine-grained calcite in foliated carbonate rocks; biotite crystals are typically bent and show a ‘whisk-tail’ texture (Figure GS-11-3c). The mineral is not zoned and shows little intergranular variation in composition (mg# 0.65–0.74, 14.3–14.6 wt. % Al_2O_3, 1.8–2.3 wt. % TiO_2, 0.7–1.0 wt. % F).

Whole-rock geochemistry

Several samples of fresh pink carbonate rock of variable texture and modal composition were analyzed for major and trace elements using a combination of x-ray fluorescence and tetraborate-fusion inductively coupled plasma–mass spectrometry. The major-element composition is variable (6.0–24.6 wt. % SiO_2, 0.03–0.13 wt. % TiO_2, 0.73–0.95 wt. % Al_2O_3, 1.8–6.5 wt. % Fe_2O_3, 1.8–5.9 wt. % MgO, 38.2–48.9 wt. % CaO, 0.15–0.28 wt. % MnO, 0.04–0.18 wt. % Na_2O, 0.02–0.34 wt. % K_2O, 0.04–0.51 wt. % P_2O_5), as can be expected from the modal variations of the examined samples, whereas the trace-element compositions of all samples show a number of consistent trends, including

- low levels of compatible trace elements (Cr, Co, Ni and Sc) and chalcophile elements (Cu, Zn, Ge, In, Sn, Bi, Mo, As and Sb);
- elevated levels of incompatible trace elements (Figure GS-11-5), particularly Sr (3120–3930 ppm) and ΣREE (540–2170 ppm);
- enrichment in light REE over heavy REE (i.e. $[La/Yb]_{CN}$ = 12–54);
- anomalously low abundances of high-field-strength elements (HFSE = Ti, Zr, Hf, Nb and Ta) and K relative to other incompatible trace elements on spider diagrams (Figure GS-11-5);
- primitive mantle–like Y/Ho, Zr/Hf, Th/U and Nb/Ta ratios (averaging 28, 34, 3.2 and 22, respectively);
- high Rb/K and Ga/Al ratios that far exceed primitive-mantle values (averaging 0.022 and 0.0015, respectively).

Discussion

Discrimination between carbonatites and texturally similar metamorphic, contact-metasomatic and hydrothermal rocks is difficult, even in cases where the intrusive mode of emplacement can be established unambiguously. Metamorphic remobilization of non-igneous carbonate rocks, involving their deformation, cataclasis and plastic flow in the presence of pressure gradient, obliterates primary textures, facilitates mineral reactions and produces

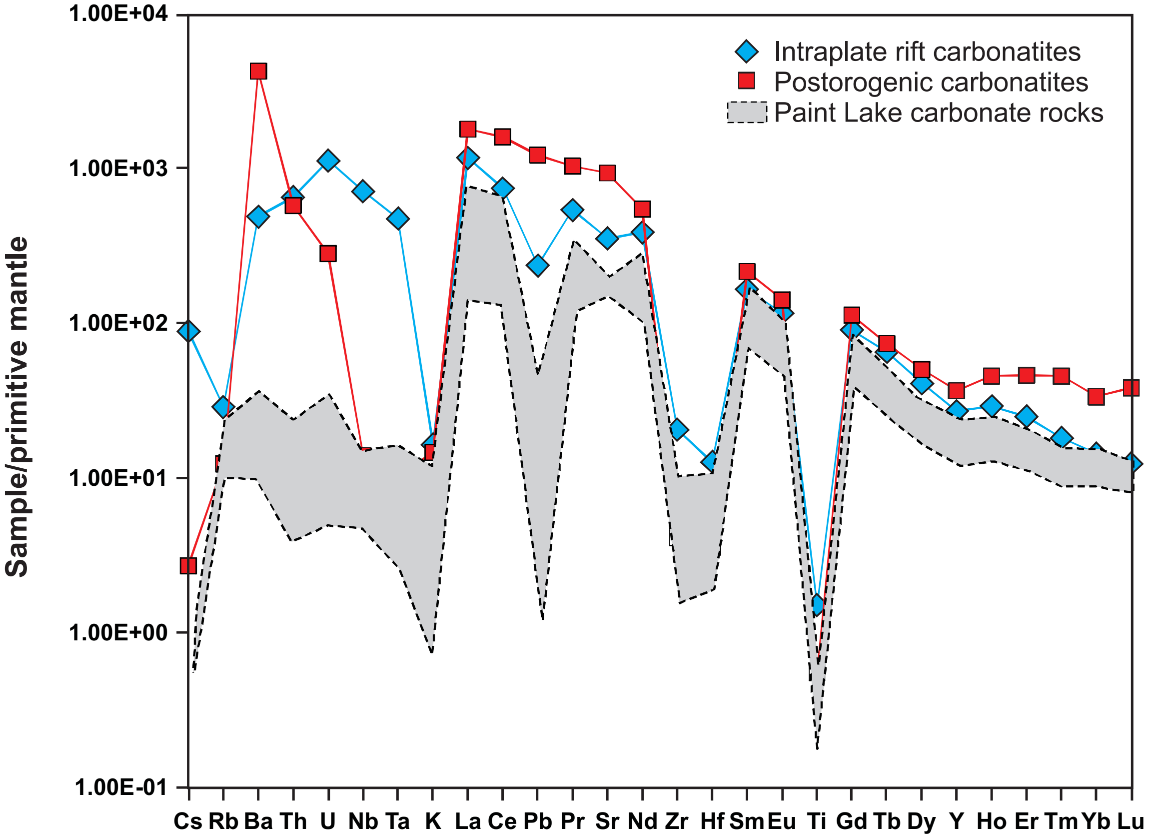

Figure GS-11-5: *Abundances of selected trace elements in the Paint Lake carbonate rocks (shaded field) normalized to the primitive mantle of McDonough and Sun (1995); average trace-element compositions of calcite carbonatites emplaced in intracontinental-rift and postorogenic settings (Chakhmouradian, unpublished data, 2009) are shown for comparison.*

intrusive bodies that can be mistaken for carbonatites (for discussion, *see* Chakhmouradian et al., 2008b). Minerals such as apatite, titanite and allanite are not reliable indicators of carbonatite magmatism because they also occur in marbles metasomatized by fluids derived from granitic or alkaline magmas (e.g., Gieré, 2007). Geochemically, calcitic metasedimentary rocks exhibit much lower levels of Sr and ΣREE (<1200 and 130 ppm, respectively) compared with calcite carbonatites from different tectonic settings, more than 94% of which contain >1200 ppm Sr and more than 98% of which contain >130 ppm ΣREE (Chakhmouradian, unpublished data, 2009).

In terms of their Sr and REE abundances, the Paint Lake carbonate rocks fall well within the carbonatite range. The trace-element composition of carbonate minerals has been used as an indicator of their carbonatitic origin (e.g., Moine et al., 2004; Wall et al., 2008). The calcite samples examined in this study show the same levels of Sr-REE enrichment as Mg-rich (i.e., >0.4 wt. % MgO) calcite from carbonatites (Hornig-Kjarsgaard, 1998; Figure GS-11-4). There is a paucity of published data on the trace-element composition of (meta)sedimentary calcite, but the overall low levels of Sr and REE, and low partition coefficients of these elements in seawater (Zhong and Mucci, 1995; Chester, 2003; Nehrke et al., 2007) imply that the Sr and REE abundances in sedimentary calcite do not significantly exceed their whole-rock levels. Different complexing behaviour of Y relative to Ho results in extreme fractionation of these elements in aqueous systems (Bau, 1996), which is not observed in the Paint Lake samples. Both whole-rock and LA-ICP-MS analyses gave Y/Ho ratios similar to the primitive-mantle value (~28) and that characteristic of igneous rocks, including carbonatites (Chakhmouradian et al., in press). In terms of its trace-element signature, the calcite examined in this study is very similar to that from carbonatites in the Lesser Qinling Orogen in China, which were interpreted as cumulates (Xu et al., 2007).

The trace-element patterns of the Paint Lake carbonate dikes and calcite carbonatites from two major types of intracontinental settings are compared in Figure GS-11-5. In common with carbonatites, the examined carbonate rocks exhibit enrichment in light REE relative to heavy REE, high Ga/Al and primitive Y/Ho ratios, and prominent K, Zr-Hf and Ti negative anomalies. Geochemically, the subunit 10b rocks resemble postorogenic carbonatites, characterized by depletion in Nb+Ta (in addition to other HFSE) and Cs, and primitive-mantle–like Zr/Hf, Th/U and Nb/Ta ratios (Chakhmouradian et al., 2008b). The only significant difference lies in the lower levels of Ba, Th and U measured in the Paint Lake samples (64–235, 0.3–1.9 and 0.1–0.7 ppm, respectively) compared with the *average* postorogenic calcite carbonatite (Figure GS-11-5). It is noteworthy, however, that carbonatites with comparable and lower levels of these elements are known from other localities, including Naantali in Finland (Woodard and Hölttä, 2005) and Huanglongpu in the aforementioned Lesser Qinling Orogen (Xu et al., 2007).

In summary, the Sr-REE–enriched carbonate rocks exposed in the central part of Paint Lake (subunit 10b of Couëslan, 2009; Couëslan, GS-10, this volume) can be tentatively identified as calcite carbonatites emplaced in a postcollisional continental setting and tectonically remobilized after the peak of Hudsonian metamorphism. Although a hydrothermal origin cannot be completely ruled out at this time, it is unlikely, given the extremely low concentrations of chalcophile elements in all analyzed dikes and the lack of associated sulphide±fluorite±barite mineralization. A stable and radiogenic isotope study of these rocks is presently being undertaken to constrain their source and age.

Economic considerations

Potential implications of the present work extend well beyond the task of providing a petrologically accurate map for the Paint Lake area (Couëslan, 2009). Carbonatites are economically important igneous rocks that produce, or are genetically associated with, the largest known deposits of rare earth element (REE) ores. For example, carbonatites of the Himalayan collision zone host some of the largest REE deposits in China, including Maoniuping and Dalucao (Hou et al., 2006; Xu et al., 2008). With a reserve of at least 1.2 million tonnes REE_2O_3 and an average grade of 2.9 wt. % REE_2O_3, the Maoniuping deposit is the second largest of its kind in China (Hou et al., 2009). The recent revival of interest in these commodities, driven by supply-demand asymmetry on the current REE market (Cox, 2008; Vulcan, 2008; McClearn, 2009), led to the launch of new exploration programs at the known REE mineralization sites (Halpin et al., 2007; Molycorp Minerals LLC, 2009) and discovery of new potential exploration targets in North America and beyond (Mumin, 2002; Commerce Resources Corp., 2009; Hudson Resources Inc., 2009).

The detailed work of Mumin (2002) and Chakhmouradian et al. (2008a, b, in press) shows that the central part of Manitoba experienced several episodes of carbonatite magmatism involving different mantle sources and geodynamic settings. In this context, it is important to note that carbonatites had not been known in this part of the Canadian Shield prior to this work, so there had been no exploration activity targeting REE or any other carbonatite-related resources in the province. This report expands our understanding of the distribution and emplacement styles of Manitoba carbonatites, showing that the Superior Boundary Zone was a setting favourable for the emplacement of carbonatites with a postorogenic geochemical signature (i.e., similar to those found in the Himalayan and Lesser Qinling collision zones in China).

The discrepancy between the REE budget of the rock-forming calcite, containing <500 ppm ΣREE and showing relatively flat REE patterns [$(La/Yb)_{CN} \leq 5$], and whole-rock samples that are strongly enriched in light REE [>500 ppm ΣREE, $(La/Yb)_{CN} \geq 12$] indicates that a large proportion of these elements remains unaccounted for. At present, it is unknown whether REE substitute for Ca in the common accessory constituents of the Paint Lake rocks (apatite, titanite and allanite), or reside predominantly in an as-yet unidentified host phase or phases amenable to economic extraction. Further exploration and a detailed mineralogical study are required to identify the principal REE minerals in these rocks and their distribution among the texturally diverse types of carbonatite.

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