Rare-earth element content of carbonate minerals in sediment-hosted Pb-Zn deposits, southern Canadian Rocky Mountains

G.J. Simandl^{1,2*}, R.J. D'Souza¹, S. Paradis³, and J. Spence²

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Abstract: Paleozoic platform carbonate rocks of the Rocky Mountains host Mississippi Valley–type (MVT), magnesite, barite, and REE-barite-fluorite deposits. Farther west, platform carbonate rocks of the Kootenay Arc host MVT and fracture-controlled replacement (FCR) deposits. This is the first systematic LA-ICP-MS study of carbonates in MVT and FCR deposits. We investigated seven MVT deposits in the Rocky Mountains, and five MVT deposits in the Kootenay Arc. None of the post-Archean Australian shale (PAAS)–normalized REE profiles show light REE (LREE) depletion and strong negative Ce anomalies characteristic of modern seawater: some profiles are nearly flat; others show depletion in LREE similar to seawater but without negative Ce anomalies; others are middle REE enriched. Carbonates with a strong positive Eu anomaly precipitated from or interacted with different fluids than carbonates with flatter profiles without a strong positive Eu anomaly. REE signatures reflect crystallization conditions of primary carbonates, and crystallization and re-equilibration conditions of carbonates with ambient fluids during diagenesis, deep burial, and/or metamorphic recrystallization. Chemical evolution of fluids along their migration path, fluid-to-rock ratio, fluid acidity, redox, and temperature also influence REE profile shape, which helps establish genetic and timing constraints on studied deposits and improves knowledge of the metallogeny of the Kootenay Arc and Rocky Mountains.

Résumé: Les roches carbonatées de plate-forme du Paléozoïque présentes dans les montagnes Rocheuses renferment des gîtes de type Mississippi-Valley (M-V), de magnésite, de barytine et d'ÉTR-barytinefluorite. Plus à l'ouest, les roches carbonatées de plate-forme de l'arc de Kootenay renferment des gîtes de type M-V ainsi que des gîtes de remplacement contrôlé par des fractures (RCF). Nous présentons ici la première étude systématique des carbonates des gîtes de type M-V et de RCF par LA-ICP-MS (spectrométrie de masse avec plasma à couplage inductif jumelée à l'ablation par laser). Nous avons étudié sept gîtes de type M-V dans les montagnes Rocheuses et cinq dans l'arc de Kootenay. Aucun des spectres des terres rares normalisés aux valeurs du shale australien post-archéen (PAAS) ne montre l'appauvrissement en terres rares légères ni la forte anomalie négative en Ce caractéristiques de l'eau de mer moderne : certains spectres sont presque plats; d'autres montrent un appauvrissement en terres rares légères semblable à l'eau de mer, mais sans l'anomalie négative en Ce; et d'autres montrent un enrichissement en terres rares intermédiaires. Les carbonates présentant une forte anomalie positive en Eu ont précipité à partir de fluides différents de ceux responsables des carbonates présentant des spectres plus plats sans forte anomalie positive en Eu, ou ont interagi avec de tels fluides. Les signatures des ÉTR reflètent les conditions de cristallisation des carbonates primaires, ainsi que les conditions de cristallisation et de rééquilibrage des carbonates avec les fluides ambiants pendant la diagenèse, l'enfouissement profond et/ou la recristallisation métamorphique. L'évolution chimique des fluides le long de leur voie de migration, le rapport fluide/roche, l'acidité du fluide, les conditions d'oxydoréduction et la température influent également sur la forme des spectres des ÉTR, ce qui aide à déterminer les contraintes génétiques et chronologiques relatives aux gîtes étudiés et améliore notre connaissance de la métallogénie de l'arc de Kootenay et des montagnes Rocheuses.

¹British Columbia Geological Survey, British Columbia Ministry of Energy, Mines and Petroleum Resources, P.O. Box 9333, Stn Prov Gov't, Victoria, British Columbia V8W 9N3

²School of Earth and Ocean Sciences, University of Victoria, P.O. Box 1700, Stn CSC, Victoria, British Columbia V8W 2Y2

³Geological Survey of Canada, 9860 West Saanich Road, Sidney, British Columbia V8L 4B2

^{*}Corresponding author: G.J. Simandl (email: <u>George.Simandl@gov.bc.ca</u>)

INTRODUCTION

Cambrian to Devonian carbonate rocks belonging to the North American Craton, particularly those in carbonate sequences of the Foreland Belt, can be traced from Yukon and the Northwest Territories southeast across British Columbia and beyond the Canada-U.S.A. border. These carbonate rocks host numerous sedimentary exhalative (SEDEX) and Mississippi Valley–type (MVT) deposits (Fig. 1). Kootenay Arc rocks of southeastern British Columbia host MVT, SEDEX, and volcanogenic massive-sulfide (VMS) deposits (Fig. 1), and do not have equivalents or correlative units in northern British Columbia. Authoritative coverage of the tectonic history of these belts and their origin is covered by Nelson et al. (2013).

Dolomitization of limestone and precipitation of openspace-filling carbonates, including sparry and saddle dolomite, reflects migration of fluids through a sedimentary sequence (e.g. Yao and Demicco, 1997; Morrow, 1998). Sparry dolomite is of particular interest to exploration companies and economic geologists because it is commonly used as an exploration guide for MVT (Zn-Pb) mineralization (Leach et al., 2005; Paradis et al., 2007) and in some cases may also be spatially related to economically significant magnesite (Simandl and Hancock, 1991; Simandl et al., 1991; Paradis and Simandl, 2018) and rare-earth element (REE)-fluorite-barite (Green et al., 2017; Hoshino et al., 2017; Akam et al., 2019) deposits. Although the timing of sparry dolomitization in British Columbia remains contentious, at least two periods of sparry dolomitization are proposed for the Western Canada Sedimentary Basin (Al-Aasm et al., 2000; Al-Aasm, 2003): the first coincides with the Antler Orogeny (370-340 Ma; Root, 2001) and the second coincides with the Columbian and Laramide orogenies (80-70 Ma; Symons et al., 1999). Nesbitt and Prochaska (1998) indicate that sparry dolomite formation probably preceded the Laramide Orogeny in southeastern British Columbia.

The REE content of carbonate rocks and mineral phases constituting these rocks have been used to establish the depositional environment of sedimentary carbonate rocks, determine the composition of diagenetic fluids (e.g. Himmler et al., 2010; Li et al., 2017; Phan et al., 2019), estimate the chemical composition of mineralizing fluids for a variety of deposit types (e.g. Dundee volcanogenic Fe-Zn deposit, China; Dilushi base metal–Cu-Ag sulfide deposit, Democratic Republic of Congo; Bracemac and McLeod VMS deposits in the Mattagami area, Canada; and Nkama stratiform Cu-Co deposit, Zambia (Debruyne et al., 2016)), and discriminate between biotic and abiotic carbonates (Guido et al., 2011).

In situ laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) analyses have been used to determine if carbonate precipitation occurred in equilibrium with seawater or anoxic porewater (e.g. Himmler et al., 2010) and to identify several generations of diagenetic dolomite (e.g. Zhang et al., 2014). Although it has been used to study the diagenesis of barren carbonate rocks (Mathieu et al., 2015; Hahn et al., 2018), this promising technique has not been systematically applied to study compositional differences among the different generations of dolomite in the MVT deposits of any major mining district. With regard to mineralized settings, the only published examples that we are aware of are a study on the Gays River MVT deposit in Nova Scotia (Kontak and Jackson, 1995); an M.Sc. thesis on the middle Ordovician dolomites of the upper Mississippi Valley (Callen and Herrmann, 2019); and, most recently, studies of the Storm Cu deposit in the Cornwallis district in the Canadian Arctic (Mathieu et al., 2018) and regional Zn-Pb occurrences in the same area (Mathieu et al., 2019). It is also noted that the study of Hahn et al. (2018) has relevance to mineralization in the Nanisivik zinc district given the spatial setting of the study. In addition to its high spatial resolution (less than tens of micrometres), LA-ICP-MS offers a further advantage over traditional whole-rock analyses of carbonate concentrates because it allows the analyst to identify compositional artefacts from inclusions and interstitial material through careful examination of compositional changes recorded by the time-resolved spectra. Thus, a careful petrographic-based selection of carbonate grains free of visible mineral inclusions, followed by critical examination of corresponding LA-ICP-MS spectra, permits identification and rejection of 'contaminated' analyses, allowing one to retain only the analyses representing the trace element signature of carbonates.

SEDIMENTARY-HOSTED DEPOSITS UNDER CONSIDERATION

All of the deposits considered in this study and described below are carbonate hosted and identified on Figure 1. They are all MVT deposits, as characterized by Leach et al. (2005) and Paradis et al. (2007), with the exception of Abbott-Wagner, which is a polymetallic, fracture-controlled replacement, Zn-Pb-Ag-Au sulfide deposit. All of the occurrences described below are located in British Columbia, with the exception of Pend Oreille, which is located in Washington state, U.S.A. (Fig. 1). Deposits selected for this study are located in the Rocky Mountains and the Kootenay Arc. The Kicking Horse, Monarch, and Shag deposits are associated with the Kicking Horse Rim, a fault-bound Precambrian paleobathymetric high. Two additional deposits, Robb Lake and Coral, are located in the northern Rocky Mountains, outside the area covered in Figure 1 (*see* Fig. 1 inset).

Biostratigraphic ages of sedimentary rocks hosting these deposits vary from lower Cambrian to Upper Devonian (Tables 1 and 2). Radiometric ages are unavailable for most of the deposits studied because it is notoriously difficult to obtain ages from low-temperature, carbonate-hosted ore deposits (e.g. Re-Os dating on pyrite and Rb-Sr dating



Figure 1. Geological map of the southern Rocky Mountains showing the locations of the deposits studied; the Robb Lake and Coral deposits are shown on the inset map. Abbreviations: MVT: Mississippi Valley–type; REE: rare-earth element; SEDEX: sedimentary exhalative.

on sphalerite; Paradis et al., in press). Although most carbonate rocks hosting the deposits are recrystallized and deformed, the regional metamorphic grade is typically in the sub-greenschist or lower greenschist facies. These deposits do not contain calc-silicate mineral assemblages, except where they are located in the contact metamorphic aureoles of Mesozoic intrusions (e.g. at the Jersey-Emerald deposit). In the sample descriptions that follow, we use the textural classification scheme of Sibley and Gregg (1987) to classify dolomite as planar-e (i.e. euhedral), planar-s (i.e. subhedral), and/or non-planar (i.e. anhedral); grain size is classified as fine (<0.05 mm), medium (0.05 to <0.4 mm), or coarse grained (\geq 0.4 mm).

Rocky Mountain MVT deposits

Munroe

Munroe is one of three stratabound Zn sulfide occurrences (Munroe, Boivin, Alpine) with similar characteristics located 120 km south-southeast of Banff (Fig. 1). The mineralization occurs in the overturned limb of an east-verging, asymmetrical anticline in the Upper Devonian Morro member of the Palliser Formation. Devonian rocks hosting the sulfide mineralization were thrust above Mississippian carbonate rocks, but are below Cambrian to Ordovician strata (Gibson, 1979a, b). Mineralization consists of pale yellow to orange sphalerite and subordinate pyrite disseminated in,

| Table 1. Summary of geology and mineralogy of analyzed samples from Rocky Mount | ain Mississippi Valley-type deposits. |
|---|---------------------------------------|
|---|---------------------------------------|

| Deposit | Sample number | Stratigraphic position | Host-rock age | Metamorphic grade | Ore mineralogy | Carbonate description |
|--------------------------|--------------------------------|--|---|---|---|---|
| Munroe | MUNR- 16-18T | Palliser Formation | Upper Devonian | Lower greenschist | sph and py disseminated in, and replacing, dolostone. Locally sph aggregates form layers alternating with sparry dol | saccharoidal dol: planar-e to planar-s (0.4–4 mm; 60 vol %), in irregular cm-scale lenses host dol: non-planar to planar-s (0.04–0.3 mm; 30 vol %) saddle dol: planar-e to planar-s (0.4–2 mm; 10–20 vol %) dol vein: microcrystalline (0.05 mm wide; <0.5 vol %), white, crosscutting sph and all other dol types |
| Shag | SHAG C4-7A | Waterfowl Formation | Middle to upper Cambrian | Lower greenschist | sph, gn, and minor py in a gangue of dol and qtz | sparry dol: planar-e (up to 5 mm) possible host dol: non-planar to planar-s (0.01–0.05 mm) |
| Monarch | MON- 16-5 | Cathedral Formation | Middle Cambrian | Lower greenschist | gn, sph, and py, disseminated in dolostone clasts; gn, sph, and py in sparry dol. Unconfirmed cp reported by Goranson (1937) | micritic matrix dol: non-planar to planar-s, (0.01–0.1 mm; 75 vol %) void-filling and void-lining sparry dol: planar-s to planar-e (0.1–2 mm; 10 vol %) |
| Kicking Horse | KICK-16- 11 | Cathedral Formation | Middle Cambrian | Lower greenschist | sph, gn, and py, disseminated in dolostone clasts; coarse- grained gn, sph, and py in sparry dol. | dol: planar-s (0.2–0.4 mm; 10 vol %) sparry dol: white, planar-e (0.8–9 mm; 65 vol %) |
| Coral | HDC TR 1a | Stone Formation (overlain by an unconformity) | Upper Silurian to Lower Devonian | Greenschist or sub-greenschist | sph with minor gn and py disseminated in dolomite fragments and in a white sparry dol | sparry dol: planar-e (2 mm; 10 vol %) sparry dol: planar-s (0.1–1 mm; 50 vol %) |
| Robb Lake | Robb Lake 3-1 | Muncho- McConnell Formation | Silurian to Devonian | Lower greenschist | matrix of breccias consisting of sparry dol, sph, gn, py, qtz, cal, and pyrobitumen | sparry dol: planar-s crystals (0.8–3 mm; 15 vol %) in mm-scale patches matrix dol: non-planar to planar-s (0.2–0.4 mm; 85 vol %) |
| Abbreviatio Carbonate | ons: cal: calo e grain-size | cite; cp: chalcopyri descriptions are | te; dol: dolom based on ma | ite; gn: galena; py: cro- and microsco | pyrite; qtz: quartz; sph: sphal pic analysis. | erite |

and replacing, a grey, supratidal, muddy to silty host dolostone. Locally, sphalerite aggregates form layers alternating with white sparry dolomite (Paradis and Simandl, 2019). Dolomite analyzed in this study comes from the Munroe occurrence (Table 1; Figure 1).

Sulfide minerals in sample MUNR-16-18T (Table 1; Fig. 2a) predominantly form irregular lenses of dense clusters (0.4–0.8 mm) of pale to dark yellow sphalerite filling spaces and replacing the light grey to white saccharoidal dolomite, which replaces the dark grey host dolostone. In thin sections of MUNR-16-18T, vestiges of dark grey host dolostone are lens shaped and consist of fine- to medium-grained (0.04–0.3 mm; 25 volume per cent), planar-s dolomite. White, saccharoidal dolomite, consisting of coarse (0.4–2 mm; 60 volume per cent), planar-e to planar-s crystals,

replaces the host dolostone (Fig. 2a). Stylolites crosscut both previously described dolomite varieties. Both types of dolomite contain medium- to coarse-grained sphalerite (0.1-0.8 mm; <15 volume per cent). A third barren dolomite phase observed in hand specimen (not seen in thin section) consists of white, coarse (0.8-2 mm), planar-e to planar-s, saddle dolomite crystals $(10-20 \text{ volume per$ $cent})$ that fill voids and fractures. A fourth generation of dolomite occurs as white, sulfide-free, microcrystalline dolomite veinlets (<0.05 mm thick; <0.5 volume per cent). These veinlets crosscut sphalerite and all of the previously described dolomite types. Only the saccharoidal and fine- to medium-grained dolomite were analyzed using LA-ICP-MS.

| Deposit | Sample number | Stratigraphic position | Host-rock age | Metamorphic grade | Ore mineralogy | Carbonate description |
|------------------------------|--|---|---|--|---|---|
| Pend Oreille (Yellowhead) | 07-MET- 12A-3 07-MET- 12A-5 | Metaline Formation | Middle Cambrian to Lower Ordovician | Sub- greenschist to lower greenschist | | 07-MET-12A-3 void-lining sparry dol: planar-s to planar-e (0.1–1 mm; 2 vol %) void-filling sparry cal: anhedral (up to 1 cm; 5 vol %) 07-MET-12A-5 sparry dol: planar-s (0.8–3 mm; 65 vol %) dol: planar-s to non-planar (0.1–0.4 mm; 15 vol %) |
| Pend Oreille (Josephine) | MET-07-2 | Metaline Formation | Middle Cambrian to Lowery Ordovician | Sub- greenschist to lower greenschist | | dol: planar-s in dol-rich clasts (0.1– 0.7 mm; 90 vol %) |
| Reeves MacDonald | 2007-SP- 022-13b 2007-SP- 022-8 | Laib Formation (Reeves member limestone) | Lower Cambrian | Lower greenschist | py, sph, with minor gn and traces of cp forming lenses of massive to disseminated mineralization concordant with dolostone layering. | 2007-SP-022-13b cal: anhedral (0.9–4 mm 90 vol %), in cal-rich bands and lenses (cm-scale) cal: subhedral to anhedral (0.03–0.05 mm; 30 vol %), interstitial to py in py-rich bands (cm-scale), ± 'comb' texture 2007-SP-022-8 dol: planar-s (0.01–0.04 mm; 25 vol %) in mm-scale lenses cal: subhedral (0.2–0.6 mm; 15 vol %) in mm-scale lenses |
| Abbreviations: | asp: arsenop | yrite; cal: calcite; c | p: chalcopyrite; | dol: dolomite; gn: | galena; po: pyrrhotite; py | y: pyrite; sph: sphalerite; tr: trace |

Table 2. Summary of geology and mineralogy of analyzed samples from Kootenay Arc Mississippi Valley-type deposits.

Abbreviations: asp: arsenopyrite; cal: calcite; cp: chalcopyrite; dol: dolomite; gn: galena; po: pyrrhotite; py: pyrite; sph: sphalerite; tr: trace Carbonate grain-size descriptions are based on macro- and microscopic analysis.

Shag

The Shag deposit, 62 km south-southeast of Banff (Fig. 1), consists of 17 Zn-Pb (\pm Ag) occurrences within the Kicking Horse Rim. The mineralization is hosted in middle to upper Cambrian carbonate rocks of the Stephen, Eldon, and Waterfowl formations (Jensen, 1991). The main showings are BM, C-4, and Red Bed. Mineralization forms discontinuous, elongated lenses, pods, and layers in the upper part of dolostone units (Lenters, 1981) and consists of yellowish to orange sphalerite, galena, and minor pyrite in a gangue of dolomite and quartz (Drage and Paradis, 2018; Paradis and Simandl, 2019). In mineralized hand specimens, sulfide minerals are present replacing host dolostone, as disseminations in the dolostone, and filling open spaces.

Sample SHAG C4-7A is from the C4 occurrence, which is hosted by the Waterfowl Formation (Table 1). It shows replacement of the host dolostone by yellow granular sphalerite (≤ 1 cm across), large clots of galena (approximately 0.8 mm long), and white to pale grey sparry dolomite (Drage and Paradis, 2018). Sparry dolomite (<5 mm) with planar-e texture occurs adjacent to sulfide mineralization (Fig. 2b). Dolomite is also present as irregular patches of fine-grained (0.01–0.05 mm), planar-s to non-planar crystals, possibly vestiges of host dolostone, separated from sulfide mineralization by subhedral quartz crystals (0.2–0.5 mm; Fig. 2b).

Monarch and Kicking Horse

The Monarch and Kicking Horse Zn-Pb (\pm Ag, \pm Cd) deposits are located in the Kicking Horse Rim, approximately 60 km west-northwest of Banff. The deposits have been previously described by Allan (1914), Goranson (1937), Brown (1948), Ney (1954), Evans et al. (1968), Pană (2006), Vandeginste et al. (2007), and Drage and Paradis (2018). The orebodies, associated breccias, and dolomitized zones trend parallel to the Kicking Horse Rim (Fig. 1), a fault-controlled, paleotopographic high over which a carbonate platform-to-basin facies transition occurs (Aitken, 1971, 1997; McMechan and Macey, 2012). These deposits lie within a 60 m thick stratigraphic interval consisting of massive to thinly bedded, brecciated dolostone in the lower 125 m of the middle Cambrian Cathedral Formation, near the base of a brecciated and dolomitized alteration zone

| Deposit | Sample number | Stratigraphic position | Host-rock age | Metamorphic grade | Ore mineralogy | Carbonate description |
|---|-------------------------------|---|--------------------------------------|---|---|--|
| Jersey- Emerald | 08-SP- 75-T | Laib Formation (Reeves member limestone) | Lower Cambrian | Lower greenschist (with local contact metamorphic overprint) | sph, gn, py, and po with minor asp enclosed in dolomitized limestone. | cal matrix: anhedral (0.02–0.05 mm; 95 vol %), in cal-rich bands cal: subhedral (0.04–0.8 mm; 50 vol %), in cm-scale lenses in sulfide-rich bands |
| НВ | HB DUMP- 5 | Laib Formation (Reeves Member limestone) | Lower Cambrian | Lower greenschist | | matrix dol: non-planar to planar-s (0.04–0.1 mm 80 vol %), in dol- rich layervoid-lining dol: planar-s to planar-e (0.2–5 mm; 20 vol %), in dol-rich layer void-filling sparry cal: anhedral, (1–2 mm; trace), in cal-rich layer sparry cal: anhedral (0.4– 0.7 mm; 50 vol %), interstitial to py in sulfide-rich bands |
| Duncan | 08-SP-121 | Badshot Formation | Lower Cambrian | Middle to upper greenschist | py, sph, gn, and po forming bands, lenses. Trace cp, marcasite, pyrargyrite, and meneghinite reported by Muraro (1962). | cal matrix: anhedral (0.06–0.25 mm; 30 vol %) cal: anhedral (0.5–1 mm; trace), in mm-scale lenses |
| Abbott- Wagner (fracture- controlled replacement) | 08-SP- 155-C6 | Badshot and Index formations | Lower Cambrian to Devonian (?) | Lower greenschist | gn, sph, py, trace cp, and tetrahedrite in qtz-cal gangue replacing the dol matrix and cementing brecciated fragments of carbonate rocks and phyllites | sparry dol: planar-s (0.1–2 mm; 80 vol %) |
| Abbreviations: Carbonate gra | asp: arsenop ain-size desc | yrite; cal: calcite; c riptions are base | p: chalcopyrite; d on macro- an | dol: dolomite; gn d microscopic ar | : galena; po: pyrrhotite; p nalysis. | y: pyrite; sph: sphalerite; tr: trace |

Table 2 (cont.) Summary of geology and mineralogy of analyzed samples from Kootenay Arc Mississippi Valley-type deposits.

(Goranson, 1937; Brown, 1948; Hedley, 1954; Ney, 1957). Main sulfide minerals at Monarch and Kicking Horse are galena, sphalerite, and pyrite, with Monarch having a higher Pb content than Kicking Horse (Ney, 1954). Chalcopyrite, barite, and native silver were reported by Goranson (1937); however, their presence was not confirmed in samples studied by Drage and Paradis (2018). The mineralization is mainly hosted in two types of brecciated dolostone: a grey breccia and a white breccia (Ney, 1954). The grey breccia consists of pale grey, angular to subangular and minor rounded fragments of variable size (≤ 1 centimetre to several metres) in a darker grey dolomite matrix. The white breccia is defined as a stockwork of coarse-grained white dolomite veins crosscutting fragments and matrix of the light grey dolomite breccia. Breccias are described in detail by Ney (1954) and Drage and Paradis (2018). The East Monarch mineralized zone consisted of several en échelon orebodies over a length of 701 m. The West Monarch orebody (198 m west of the eastern mineralized zone) is 536 m long, 48 m wide, and averages 5.7 m in thickness (Goranson, 1937).

The Kicking Horse orebodies are on trend with those of Monarch. The No. 1 Kicking Horse orebody is 176 m long and flat-lying. In its southern part, it averages 12.1 m in width and 4.5 m in thickness. The No. 2 Kicking Horse or Western orebody is 426 m long and has a more irregular orientation and outline than the No. 1 orebody. Individual orebodies are suspected to be part of the same mineralizing system (Hedley, 1949). Together, the Monarch and Kicking Horse deposits (BC MINFILE 082N 019 and 082N 020) produced 25 124 kg (807 748 oz) of Ag, 71 315 t of Zn, 46 218 t of Pb, and 9016 kg of Cd from 826 180 t of ore mined (British Columbia Geological Survey, 1993).

The sample analyzed from the Monarch deposit (MON-16-5) is a pyrite-rich dolostone with a grey micritic matrix consisting of fine to medium (0.01-0.1 mm;75 volume per cent), non-planar to planar-s dolomite crystals (Fig. 2c). Sparry, white, planar-s to planar-e dolomite (0.1-0.7 mm; 15 volume per cent) fills voids entirely and lines pyrite-filled voids (Fig. 2c). Medium to coarse pyrite



Figure 2. Photomicrographs of dolomite from the Rocky Mountain Mississippi Valley–type deposits: **a)** Munroe deposit, sample MUNR-16-18T — coarse, saccharoidal dolomite and sphalerite within mediumgrained host dolostone (plane polarized light); **b)** Shag deposit, sample SHAG-C4-7A — coarse dolomite with quartz and sphalerite and fine-grained recrystallized vestiges of host dolostone (plane polarized light); **c)** Monarch deposit, sample MON-16-5 — sparry dolomite filling voids entirely (bottom left) and lining pyrite-filled voids (top centre) in fine- and medium-grained matrix dolomite (plane polarized light); **d)** Coral deposit, sample HDC Tr 1a — sparry dolomite adjacent to sphalerite and showing rhombohedral terminations in quartz (cross polarized light); **e)** Coral deposit, sample HDC Tr 1a — red sphalerite in the interstices of medium- and coarse-grained dolomite (plane polarized light); **f)** Robb Lake deposit, sample 3-1 — sparry dolomite and medium-grained matrix dolomite with trace amounts of disseminated pyrite (plane polarized light). Abbreviations: Dol: dolomite; Py: pyrite; Qtz: quartz; Sph: sphalerite; cg: coarse grained (≥ 0.4 mm); fg: fine grained (< 0.05 mm); ho: host dolostone; mat: matrix, mg: medium grained (≥ 0.05 and < 0.4 mm); sc: saccharoidal; sp: sparry.

crystals (0.1–2 mm; 10 volume per cent) mainly form disseminations, veinlets, and large irregular patches within the dolostone.

The sample analyzed from the Kicking Horse deposit (KICK-16-11) contains centimetre-scale aggregates of yellow and pale brown sphalerite and minor disseminated pyrite replacing heterogeneous grey dolomite and white sparry dolomite stringers. The grey dolomite consists of medium-grained (0.2–0.4 mm; 10 volume per cent) planar-s dolomite. White, sparry, planar-e dolomite crystals (0.8–9 mm; 65 volume per cent) are locally associated with late calcite and adjacent to large aggregates of yellow sphalerite (>1 cm; 15 volume per cent).

Coral

The Coral Zn-Pb deposit and related showings are located approximately 100 km north of the town of Mackenzie, British Columbia, and lie north of the main study area (Fig. 1 inset). Most of the mineralization is hosted in upper Silurian to Lower Devonian dolostones of the Stone Formation platform carbonate rocks (De Graaf et al., 2016). Sulfide mineralization consists of red and yellow sphalerite and minor galena, included in white sparry dolomite-quartz vein and breccia fillings, and as pyrite disseminated in a recrystallized dolostone matrix.

The analyzed sample (HDC TR 1a) is a mineralized, grey, coarse-grained, crystalline dolostone 'vein breccia': the sparry dolomite-quartz-sulfide veins crosscutting the dolostone resemble the crackle and mosaic mineralized breccias at Robb Lake (Paradis and Nelson, 2007). The sample has coarse sphalerite (0.4–0.9 mm; 20 volume per cent) concentrated adjacent to quartz (0.5–2.3 mm; 10 volume per cent) and sparry, planar-e, white dolomite (approximately 2 mm; 10 volume per cent) is seen with rhombohedral terminations in quartz (Fig. 2d). Additionally, red sphalerite (0.6–1 mm; 10 volume per cent) fills spaces between medium to coarse (0.1–1 mm; 50 volume per cent), planar-s, sparry dolomite crystals (Fig. 2e). Yellow sphalerite is a late phase and is only observed in association with quartz and white sparry dolomite.

Robb Lake

The Robb Lake Zn-Pb deposit is located in northeastern British Columbia, approximately 200 km northwest of Fort St. John, and is north of the main study area (Fig. 1 inset). The deposit consists of several interconnected beddingparallel and crosscutting breccias, stockworks, and fracture zones within the Silurian to Devonian Muncho-McConnell Formation (Paradis et al., 1999; Nelson et al., 2002; Paradis and Nelson, 2007). The matrix of mineralized breccias consists of sparry dolomite, sphalerite, galena, pyrite, quartz, calcite, and pyrobitumen (Nelson et al., 2002). Complex crosscutting relationships between breccias indicate multiple stages of brecciation and mineralization. The deposit has a resource of 6 500 000 t grading 7.11 weight per cent combined Pb and Zn (2.4 m mining width, 5 weight per cent cutoff grade; Consolidated Barrier Reef Resources, unpub. rept., 1984). Radiometric dating of sphalerite at Robb Lake gives an apparent age of 348 ± 130 Ma (Model 3 isochron from sphalerite residue; Nelson et al., 2002).

The analyzed sample (Robb Lake 3-1) is a rubble breccia from the Waterfall zone. The breccia is polymictic with highly angular to subangular fragments hosted by a fine-grained black carbonaceous fragmental matrix. The coarse-grained fragments consist of dolostone, white sparry dolomite, shaly mudstone, finely laminated shaly carbonate rock, chert, pyrobitumen-rich material, sulfide minerals, and fossils. In thin section, dolomite is the main constituent of the matrix and occurs as patches, up to 5 mm across, containing sparry, planar-s crystals (0.8–3 mm; 15 volume per cent) or as a matrix of medium, non-planar to planar-s dolomite crystals (0.2–0.4 mm; 85 volume per cent) with traces of fine to coarse pyrite (Fig. 2f).

Kootenay Arc MVT and fracture-controlled replacement (FCR) deposits

Pend Oreille

Pend Oreille, a carbonate-hosted Zn-Pb sulfide deposit in Washington State, U.S.A., approximately 275 km south-southeast of Revelstoke (Fig. 1), is the only basemetal mine with recent production in the historically prolific Kootenay Arc (Willenbrock, 2019). Mineralization is hosted in 915 to 1700 m thick, predominantly carbonate rocks of the middle Cambrian to Early Ordovician Metaline Formation (Table 2), which overlies shales and phyllites of the lower Cambrian Maitlen Formation (Park and Cannon, 1943; Yates and Robertson, 1958; Dings and Whitebread, 1965; Fischer, 1981, 1988; Bush et al., 1992). The Metaline Formation is itself generally conformably overlain by black, graptolitic, carbonaceous argillites and siltstones of the Ordovician Ledbetter Formation.

The mineralization consists of two spatially and lithologically distinct, stratabound, carbonate-hosted Zn-Pb types: Yellowhead and Josephine. Yellowhead sulfide mineralization consists of en échelon tabular to lens-shaped pyrite-sphalerite-rich orebodies composed mainly of colloform aggregates of pyrite, red to honey yellow sphalerite, and minor galena forming fine layers in a matrix of dolomite, calcite, phengite, jasperoid, quartz, and clay minerals (Morton, 1974, 1992; Bending, 1983; Colligan, 1984). In 2014, 6 to 8 t of Ge (5–10% of the total global Ge production) was expected to be recovered from Yellowhead ore as a byproduct of zinc mining (Burton and Smith, 2014). The Yellowhead mineralization is characterized by carbonate replacement and minor open-space–filling textures, indicating a diagenetic and epigenetic origin. The Josephine-type breccia zones lie exclusively near the top of the Metaline Formation, just below the Ordovician Ledbetter Formation. They are heterolithic and contain limestone, dolostone, silicified carbonate, quartzite, and black graptolitic shale fragments. The matrix of these breccias consists most commonly of sparry white dolomite; however, fine-grained dark grey dolomite and fine-grained jasperoid are also reported (Brown and Ahmed, 1986). Mineralization in these breccias is poor in pyrite and consists mainly of sphalerite and galena. The breccia bodies were interpreted as slumps and debris flows in a deep-water basin (McConnell and Anderson, 1968; Bush et al., 1992) or as solution collapse breccias (Morton, 1974; Zieg et al., 2000).

Recent Re-Os geochronometry on pyrite from the Yellowhead sulfide mineralization provides an age of 515 ± 23 Ma, consistent with the middle Cambrian to Early Ordovician stratigraphic age of the carbonate rocks of the Metaline Formation (Paradis et al., in press); therefore, the Yellowhead mineralization was likely emplaced soon after the deposition of the carbonate rocks, suggesting that it is diagenetic. This ore style is similar to Irish-type mineralization, which was described by Wilkinson (2014), although an MVT genetic model cannot be ruled out.

Two samples from the Yellowhead-type mineralization (07-MET-12A-3 and 07-MET-12A-5) and one sample from the Josephine-type mineralization (MET-07-2) were selected for analysis (Table 2). The Yellowhead-type samples show fine colloform and botryoidal textures of pyrite and honey yellow sphalerite with minor galena forming fine layers and aggregates in a dolomite and calcite gangue. Yellowhead sample 07-MET-12A-3 shows centimetre-scale voids in sphalerite with cores of anhedral, coarse, sparry calcite (up to 1 cm; 5 volume per cent). This calcite is lined with sparry dolomite crystals (0.1–1 mm; 2 volume per cent) grading from coarse and planar-e (directly adjacent to the calcite; Fig. 3a), to medium and planar-s (away from the calcite core). Dolomite in sample 07-MET-12A-5 occurs as coarse (0.8-3 mm; 5 volume per cent), sparry, planar-s crystals and as medium-grained (0.1–0.4 mm; 15 volume per cent) planar-s to non-planar dolomite. Both types of dolomite in this sample are in sharp contact with pyrite (20 volume per cent), but only the medium-grained dolomite is immediately adjacent to, and in gradational contact with, sphalerite (60 volume per cent).

The sample of the Josephine-type mineralization (MET-07-2) is brecciated, pyrite-rich, silicified dolomitic limestone. Pyrite (30 volume per cent) forms veinlets and veins (0.02-5 mm thick) crosscutting or replacing subangular, centimetre-scale, dolomite-rich (65 volume per cent) or quartz-rich (5 volume per cent) fragments. The quartz-rich clasts contain 90 volume per cent anhedral quartz (0.01-0.6 mm) with nonplanar to planar-s, coarse (approximately 0.5 mm; 10 volume per cent) dolomite and trace pyrite. Within the dolomite-rich clasts, dolomite occurs as medium to coarse (0.1-0.7 mm; 90 volume per cent) planar-s crystals,

crosscut by irregular, 0.2 to 0.9 mm thick quartz veins (10 volume per cent; Fig. 3b) that are themselves crosscut by minor pyrite veinlets (0.02–0.05 mm wide) branching off larger pyrite veins surrounding the clasts.

Reeves MacDonald

The Reeves MacDonald MVT deposit, 225 km south-southeast of Revelstoke (Fig. 1), consists of several ore zones (e.g. Reeves, MacDonald, O'Donnell, Annex, Point, Prospect, B.L., No. 4, and Red Bird) that are the faulted and folded portions of a single large orebody (Fyles and Hewlett, 1959; Gorzynski, 2001). Ore zones consist of stratabound sulfide lenses and layers of massive to disseminated mineralization, parallel to compositional layering within medium to dark grey dolostone. The orebodies, their enveloping dolostone, and the limestone host rock (Reeves member, lower Cambrian Laib Formation) were folded and metamorphosed to lower greenschist facies (Table 2). Layering within the orebodies varies from millimetre- to centimetre-scale and can be continuous over tens of metres or discontinuous and highly contorted. Breccias occur mainly on synclinal fold limbs with sulfide minerals forming the matrix and supporting rounded to platy fragments of dolomite, limestone, and quartz (Paradis et al., 2011).

Anhedral quartz (0.01–0.4 mm) in pockets surrounded by sulfide minerals, is a minor constituent of the rock (5 volume per cent). Sulfide minerals are present in well-defined, branching bands composed of cubic to rounded pyrite (50 volume per cent) with platy sphalerite (5 volume per cent) and galena (trace) interstitial to pyrite. Sulfide minerals include pyrite, honey-coloured to brown sphalerite, minor galena, and traces of chalcopyrite. Copper and cadmium contents are typically less than 0.5 weight per cent and 1 g/t, respectively (Paradis et al., 2011). Near the surface, sulfide ore weathers to a gossan of limonite, hematite, and goethite, with variable amounts of hemimorphite, cerussite, and possibly smithsonite (Paradis et al., 2011, 2015), although only sulfide ore was mined.

Samples (2007-SP-022-13b and 2007-SP-022-8) used for analysis are mineralized, tectonically deformed limestone with discontinuous bands and stringers of pyrite with minor sphalerite and traces of galena. In sample 2007-SP-022-13b, the centimetre-scale, carbonate-rich bands and lenses consist of coarse (0.9–4 mm; 90 volume per cent), anhedral crystals of calcite with 10 volume per cent of sulfide minerals in stringers and millimetre-scale layers. In centimetrescale pyrite-rich bands, calcite is interstitial to pyrite grains as fine (0.03–0.05 mm; 30 volume per cent) subhedral to anhedral crystals, in places forming a 'comb' texture of elongated crystals (0.05×0.01 mm; Fig. 3c) oriented at a high angle to fracture walls in pyrite. In sulfide-rich sample 2007-SP-022-8, dolomite occurs exclusively as fine (0.01– 0.04 mm; 25 volume per cent), planar-s crystals, whereas



Figure 3. Photomicrographs of carbonates from the Kootenay Arc Mississippi Valley–type deposits: **a**) Pend Oreille deposit, sample 07-MET-12A-3 (Yellowhead-type mineralization) — sparry calcite surrounded by sparry dolomite, which is itself adjacent to pyrite and sphalerite (plane polarized light); **b**) Pend Oreille deposit, sample MET-07-2 (Josephine-type mineralization) — medium- and coarse-grained dolomite from a dolomite-rich clast crosscut by a quartz vein (plane polarized light); **c**) Reeves MacDonald deposit, sample 2007-SP-022-13b — 'comb' texture calcite crosscutting a pyrite-rich band (plane polarized light); **d**) Jersey-Emerald deposit, sample 08-SP-75-T — fine-grained, matrix calcite with red to brown sphalerite rimmed by medium-grained calcite (not analyzed in this study) in a calcite-rich layer (plane polarized light); **e**) Jersey-Emerald deposit, sample 08-SP-75-T — coarse-grained calcite with red to brown sphalerite and pyrite in a sulfide-rich band (plane polarized light); **f**) HB deposit, sample HB DUMP-5 — a coarse-grained calcite-filled void surrounded by coarse- and medium-grained dolomite and trace pyrite (reflected light). Abbreviations: Cal: calcite; Dol: dolomite; Py: pyrite; Qtz: quartz; Sph: sphalerite; cg: coarse-grained (≥ 0.4 mm); fg: fine-grained (< 0.05 mm); mat: matrix; mg: medium-grained (≥ 0.4 mm); sp: sparry.

calcite occurs as medium to coarse, subhedral crystals (0.2–0.6 mm; 15 volume per cent), and both types of dolomite form millimetre- to centimetre-scale lenses.

Jersey-Emerald

The Jersey-Emerald deposit is 220 km south-southeast of Revelstoke (Fig. 1). Production from the adjacent Jersey and Emerald Zn-Pb mines accounted for a combined production of more than 4830000 t grading 1.95 weight per cent Pb and 3.83 weight per cent Zn (Giroux and Grunenberg, 2014). Mineralization occurs within a dolomitized zone near the base of the Reeves member limestone, Laib Formation (Table 2). Five Zn-Pb-bearing dolomite-hosted horizons, ranging in thickness from 0.3 to 9 m, were recognized in the mine. Mineralization forms stratabound tabular and lensshaped bodies consisting of sphalerite, galena, pyrite, and pyrrhotite with minor arsenopyrite. Mineralogically, ore from the Jersey-Emerald deposit is similar to the adjacent Reeves MacDonald and HB deposits. According to Fyles and Hewlett (1959), mineralization is structurally controlled by phase II secondary folding and massive-sulfide mineralization is locally brecciated.

Where Reeves member limestone and dolomite are in proximity to mid-Cretaceous Emerald and Dodger granitic stocks, W and Mo skarns are related to contact metasomatism. Several poorly characterized, potentially skarn-related gold occurrences in proximity to Zn-Pb deposits and skarn mineralization have been identified, and some have been historically mined (Dandy, 1977; Giroux and Grunenberg, 2014).

The sample (08-SP-75-T) used for analysis is a greywhite limestone with alternating, irregular centimetre-scale carbonate- and sulfide-rich layers. The carbonate-rich layers are dominantly (95 volume per cent) composed of fine-grained (0.02-0.05 mm), anhedral calcite with minor (5 volume per cent) red to brown sphalerite in irregular patches (0.03-0.5 mm) rimmed with fine- to medium-grained (0.03–0.1 mm) subhedral to euhedral calcite (Fig. 3d). The sulfide-rich bands contain up to 30 volume per cent red to brown, anhedral sphalerite (0.2-1.4 mm), 20 volume per cent galena (0.2–1.4 mm), and traces of pyrite (0.4–0.8 mm), with coarse-grained (0.5-3 mm; 50 volume per cent), subhedral calcite interstitial to sulfide grains or as irregular lenses up to 1 cm long. The typical relationship between sphalerite and coarse-grained, subhedral calcite analyzed in this study is shown in Figure 3e.

HB

The HB deposit consists of the HB and Garnet orebodies hosted by the Reeves member of the lower Cambrian Laib Formation (Table 2). The orebodies in limestone/ dolostone beds are 215 km south-southeast of Revelstoke (Fig. 1), on the west limb of a broad synclinorium (Paradis et al., 2011). Most of the mineralization at HB is contained

in three elongated, steeply dipping, crudely ellipsoid bodies and two gently dipping, tabular sulfide breccia bodies. Sulfide minerals in the steeply dipping bodies are controlled by cleavage and form discontinuous stringers in the host dolomitic limestone (MacDonald, 1973). Mineralization, located within tabular breccia zones that follow layering, consists of pyrite, subordinate sphalerite, galena, and locally minor pyrrhotite. The ore zone is enveloped by a broad zone of dolomitization, in turn separated from the host limestone by a narrow, silica-rich zone. The northern portions of the mineralized zones are exposed at the surface and oxidized to a depth of 100 m (Fyles and Hewlett, 1959). The main non-sulfide ore minerals in the oxidized zone are hemimorphite (Zn₄Si₂O₇(OH)₂·H2O), cerussite (PbCO₃), and goethite FeO(OH) (Paradis et al., 2011). Fyles and Hewlett (1959) also reported several uncommon Zn- and Pb-bearing phosphate minerals. A selected sample from the oxidized zone contains 30.6 weight per cent Zn, 5.1 weight per cent Pb, and 19.3 weight per cent Fe (Paradis et al., 2015).

The analyzed sample (HB DUMP-5) from scree below the main mine adit consists of alternating centimetre-scale, carbonate-rich layers and millimetre- to centimetre-scale sulfide-rich layers. The sulfide-rich layers are oriented parallel to sub-parallel to compositional layering of the carbonate host rock, although a few sulfide-rich bands crosscut layers in the host rock. The carbonate-rich bands consist mainly of fine- to medium-grained (0.04-0.1 mm; 80 volume per cent), non-planar to planar-s dolomite matrix with anhedral quartz (0.04–0.1 mm; trace). The carbonate-rich bands also contain millimetre-scale voids filled with anhedral, coarse calcite (1-2 mm; trace). These voids are lined with medium to coarse (0.2–5 mm; 20 volume per cent), planar-s to planar-e dolomite with trace interstitial anhedral pyrite (0.01-0.03 mm) as shown in Figure 3f. The sulfide-rich layers are composed of ragged, platy sphalerite (25 volume per cent); subhedral pyrite (20 volume per cent); and irregular, platy galena (5 volume per cent), and anhedral, sparry calcite (0.4-0.7 mm; 50 volume per cent) is the main gangue mineral.

Duncan

The Duncan MVT deposit, located 115 km southeast of Revelstoke (Fig. 1), consists of the Duncan #1 to #4 zones and the main Duncan #5 to #8 zones. These zones are hosted in a thick section of dolomitized or silicified carbonates of the lower Cambrian Badshot Formation (Table 2). Carbonate rocks hosting mineralization were faulted and folded and have been interpreted as an "extensively brecciated and locally dolomitized bank-margin facies developed on a shoal complex" (Höy, 1982). The massive or layered dolomite is similar in texture to that of dolomites enclosing the sulfide deposits in the Salmo area (i.e. Reeves MacDonald, Jersey-Emerald, and HB). The sulfide bodies are vertical lenses and sheets with gradational but well-defined margins. The orientation of the sulfide bodies mimics that of enclosing formations, with steep dips and low-angle plunges to the north (Fyles, 1964), parallel to the most prominent lineation and phase II fold axes in the surrounding rocks. The deposit has not been mined, but the main mineralized zones (Duncan #5 to #8) have pre–NI 43-101 reserves of 9 000 000 t grading 2.7 weight per cent Pb and 2.9 weight per cent Zn (Muraro, 1962). Mineralization consists of bands and lenses of fine pyrite with subordinate sphalerite, galena, and pyrrhotite and minor chalcopyrite, marcasite, pyrargyrite, and meneghinite (Muraro, 1962).

The sample (08-SP-121) used for analysis is from the Duncan #1 zone and consists of a medium- to coarsegrained polycrystalline aggregrate of sphalerite (0.3-1 cm; 60 volume per cent) and galena (0.08-2.4 mm; 10 volume per cent) with trace pyrite and pyrrhotite in a calcite matrix (30 volume per cent). The matrix is dominantly medium (0.06-0.25 mm), anhedral calcite, with millimetre-scale lenses of coarse (0.5-1 mm; trace), anhedral calcite.

Abbott-Wagner

The Abbott-Wagner deposit is a polymetallic FCR Zn-Pb-Ag-Au sulfide deposit located approximately 98 km east-southeast of Revelstoke (Fig. 1). It is hosted in the basal part of the Index Formation and the upper part of the lower Cambrian Badshot Formation (Table 2; Paradis et al., 2019). Mineralization occurs as sulfide-rich quartz veins in calcareous and carbonaceous phyllites and phyllitic schists of the Index Formation, and as lenses of massive to semi-massive sulfide minerals replacing carbonate rocks of the Badshot Formation. The total historical mineral resource is estimated at 296 650 t grading 7.81 weight per cent Pb, 6.39 weight per cent Zn, and 295 g/t Ag (9.5 oz/t; Kjosness, 2006). The LA-ICP-MS analysis of the pyrite from this deposit indicates it contains up to 0.22 ppm Au (Paradis et al., this volume). The replacement-style mineralization in this deposit consists of clustered and disseminated galena, sphalerite, and pyrite, with trace chalcopyrite and tetrahedrite in quartzcalcite gangue replacing the dolomite matrix and cementing brecciated fragments of carbonate rocks and phyllites.

The sample (08-SP-155-C6) selected for analysis is a polycrystalline mass of sphalerite (0.02–1 cm; 10 volume per cent), pyrite (0.2–2 mm; 5 volume per cent), galena (0.6–3 mm; 5 volume per cent), and traces of chalcopyrite in a gangue of dolomite (80 volume per cent) and trace quartz (0.08–0.5 mm). The dolomite gangue consists of medium to coarse, sparry (0.1–2 mm), planar-s crystals adjacent to sulfide minerals.

ANALYTICAL METHODS

Polished thin $(35 \ \mu m)$ and thick $(100 \ \mu m)$ sections made from a suite of representative samples from sulfide deposits of the Kootenay Arc and the Rocky Mountains were examined in detail with a petrographic microscope to document the minerals and carbonate textures present and to identify suitable (inclusion-free and with no visible interstitial material) carbonate grains for LA-ICP-MS analysis. To obtain representative analyses, we selected two or three widely spaced areas for each carbonate texture per thin section.

The Ca content of the analyzed phases, which was used as the internal standard for the LA-ICP-MS data reduction (*see* below), was determined with wavelength dispersive spectrometry analysis using the electron microprobe at The University of British Columbia.

Electron probe micro-analyses of carbonates for Ca, Mg, Fe, Mn, Sr, and Ba were done on a fully automated CAMECA SX-50 instrument, operating in wavelength-dispersion mode with the following operating conditions: 15 kV excitation voltage, 10 nA beam current; 20 s peak count time (except Sr: 40 s peak count time); 10 s background count time (except Sr: 20 s background count time); and 10 μ m spot diameter. Data reduction was done using the 'PAP' $\phi(\rho Z)$ method (Pouchou and Pichoir, 1985). Oxygen content was determined by stoichiometry and C content by difference. For the elements considered, the following standards, X-ray lines, and crystals were used: dolomite, MgKa, TAP; calcite, CaKa, PET; rhodochrosite, MnKa, LIF; siderite, FeKa, LIF; synthetic Sr titanite, SrLa, TAP; barite, BaLa, PET.

The LA-ICP-MS analyses were carried out at the University of Victoria's School of Earth and Ocean Sciences using a New Wave UP-213 (Nd-YAG laser, 213 nm) interfaced to 1) a Thermo Fisher XSeries 2 quadrupole ICP-MS, or 2) an Agilent 8800 triple quadrupole ICP-MS (used for one day, only five samples). The Agilent 8800 was operated in single quadrupole, no-gas mode and was only used when the Thermo Fisher XSeries 2 was not available.

The following laser conditions were used for all analyses: He carrier gas (0.7 L/min), 55 μ m spot diameter, 5 Hz laser firing frequency, and 0.4 J/cm² fluence. Analyses carried out on thick sections used four passes along a 200 μ m line at a speed of 20 μ m/s. On the thin sections, to avoid ablating though the sample, either two passes along a 400 μ m line or, where grain size permitted, a single pass along an 800 μ m line were used. Each analysis included: 30 s gas blank, 5 s laser warmup (laser fires against a shutter to stabilize the energy output), and 40 s analysis time, plus 30 s of monitored washout time to ensure signals returned to acceptable background levels before setting up the next analysis.

At the beginning and end of each analysis session, and after every 16 analyses, standards were run in the following order: NIST 615, NIST 613, NIST 611, and BCR2g (*see* Jochum et al. (2005) for concentrations and contents). Following every sample change, a 120 s gas blank was run and evaluated to ensure the sample chamber and carrier line were fully purged before continuing the session. Repeated analyses of the calibration standards showed no measurable drift in instrument sensitivity over the course of each analytical session. The following isotopes were measured, with a dwell time of 10 ms on each, resulting in an overall mass sweep time of 500 ms: ²⁵Mg, ⁴³Ca, ⁵¹V, ⁵⁵Mn, ⁵⁷Fe, ⁶⁶Zn, ⁸⁵Rb, ⁸⁸Sr, ⁸⁹Y, ⁹⁰Zr, ⁹³Nb, ¹³⁷Ba, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁵¹Eu, ¹⁵⁷Gd, ¹⁵⁹Tb, ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁶Er, ¹⁶⁹Tm, ¹⁷²Yb, ¹⁷⁵Lu, ¹⁷⁸Hf, ¹⁸¹Ta, ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb, ²³²Th, and ²³⁸U.

Following data acquisition, background and sample time intervals were selected in Thermo PlasmaLab v. 2.6.1.335 for data collected with the XSeries 2, and in Microsoft[®] Excel[®] for data collected with the Agilent 8800. All data reduction calculations were done in Microsoft Excel. In each case, care was taken to examine the time-resolved profile of each analyte in each sample to detect deviations from the ideal plateau-shaped spectra regions representing chemically homogeneous material. Features like isolated or repeating peaks or troughs in one or more elements in the analytical spectra may indicate that the laser traverse intersected a solid or fluid inclusion or a grain boundary with an adjacent non-carbonate phase. Where such peaks were observed, only the 'peak-free' portion of the spectra was used, or the analysis was rejected.

Glass standards NIST 615, 613, and 611 were used as the calibration standards and the 30 s gas blank from each sample was subtracted from the corresponding sample signal. Calcium was used as the internal standard (sample Ca contents determined by electron probe). Accuracy and precision were determined by repeat analysis of the BCR-2G standard. The elemental contents in the BCR-2G standard obtained were within 15% (relative) of the GeoReM preferred value (Jochum et al., 2005) for this glass standard and repeated measurements over the course of each analytical session showed that analytical precision for the REE + Y was within 10% (relative). The data were filtered using a quantification limit defined as the value of $10 \times$ the standard deviation for the gas blank (Longerich et al., 1996).

RESULTS

This section covers the results of LA-ICP-MS analyses of carbonate minerals in samples selected from the previously described carbonate-hosted deposits, with the emphasis on the REE data. Rare-earth elements are traditionally classified into a light REE group (La to Gd), containing unpaired f-orbital electrons, and a heavy group (Tb to Lu), containing paired f-orbital electrons (Generalic, 2019). In this paper, Y is separated from the REE and added to end of the normalized plots, and Sc is not discussed as it does not fit into either the light or heavy REE groups. To facilitate description of the normalized REE profiles presented, we define the light REE (LREE) as La to Nd, middle REE (MREE) as Sm to Gd, and heavy REE (HREE) as Tb to Lu. The REE content of the analyzed samples is normalized against those of post-Archean Australian shale (PAAS; McLennan, 1989) and normalized element abundances are referred to with a subscript N (e.g. La_N). The Ce anomaly (Ce-Ce*) is defined as $CeN/((\frac{1}{2} \cdot La_{N}) + (\frac{1}{2} \cdot Pr_{N}))$ and the Eu anomaly (Eu-Eu*) as

 $Eu_{N}/((?_{3} \cdot Sm_{N}) + (!_{3} \cdot Tb_{N}))$, where values less than and greater than 1 indicate negative and positive anomalies, respectively, as proposed by Bau and Dulski (1996). We chose to use the same Eu anomaly formula as Bau and Dulski (1996) so that data are directly comparable to the results presented in Webb et al. (2009), Jiang et al. (2015), Callen and Herrmann (2019), and Kraemer et al. (2019). The background Gd in the LA-ICP-MS system at the University of Victoria is systematically higher (by a factor of 2–5) than other REE in all our analyses, meaning that a portion of our Gd analyses are below quantification limits. Thus, using Gd would have precluded calculation of Eu anomalies for a substantial portion of our analyses (the same as in Bau and Dulski, 1996). Uncertainties are provided for average values at the level of 1 standard deviation.

The REE content of carbonates varies widely among deposits (Table 3). The results of the analyses from the MVT deposits in the Rocky Mountains and the Kootenav Arc are summarized in Tables 4 and 5, respectively. Overall, we identified six types of PAAS-normalized REE profile categories (A through F), based on visual observations, which allows for a general comparison between carbonate analyses of the different samples and deposits. The terminology describing the strength of the anomalies (either Ce or Eu) and the gradient of the slopes on REE profiles is traditionally qualitative. It is common practice in scientific papers describing chondrite- or PAAS-normalized profiles to base these descriptions on visual examination. In this study, we were more thorough, providing the mean and standard deviation of both the anomalies and La-Nd, Sm-Gd, and Tb-Lu ratios, permitting characterization of REE profiles in terms of their LREE, MREE, and HREE segments. This provides the reader with exact information.

Rocky Mountain MVT deposits

Munroe

Coarse, saccharoidal dolomite from sample MUNR-16-18T has higher average ΣREE , $\Sigma LREE$, $\Sigma MREE$, and Σ HREE content compared to the fine- to medium-grained dolomite mass interpreted to correspond to the host dolostone (Table 4). The same is true for Y content. Correspondingly, the coarse, saccharoidal and fine- to medium-grained dolomite have parallel, flat to slightly convex upward REE + Y profiles (category B, Table 4; Fig. 4). This similarity is reflected in the LREE, MREE, and HREE slopes for the coarse, saccharoidal dolomite (La_N-Nd_N = 0.7 ± 0.1 ; Sm_N- $Gd_{N} = 0.8 \pm 0.2$; $Tb_{N}-Lu_{N} = 3.2 \pm 0.9$), which are within error of those for the host dolomite (La_N-Nd_N = 1.0 ± 0.2 ; $\text{Sm}_{_{N}}\text{-Gd}_{_{N}} = 0.7 \pm 0.1$; $\text{Tb}_{_{N}}\text{-Lu}_{_{N}} = 1.8 \pm 0.6$). The Ce anomaly is slightly negative for the coarse saccharoidal dolomite (Ce-Ce^{*} = 0.9 ± 0.1), whereas the Eu anomaly is weakly positive to weakly negative (Eu-Eu* = 1.0 ± 0.2) and both are within error of the Ce and Eu anomalies in host dolomite (Ce-Ce* = 0.9 ± 0.1 ; Eu-Eu* = 1.0 ± 0.3).

| Belt | Rockies | Rockies | Rockies | Rockies | Rockies | Rockies | Kootenay | Kootenay | Kootenay | Kootenay | Kootenay | Kootenay |
|-------------------|-----------------|--------------|--------------|------------------|------------------|----------------|------------------|------------------|--------------|--------------|-------------------|--------------------|
| Deposit | Munroe | Monarch | Coral | Robb Lake | Kicking Horse | Shag | Pend Oreille | Pend Oreille | HB | HB | Abbott- Wagner | Jersey- Emerald |
| Mineral | Dolomite | Dolomite | Dolomite | Dolomite | Dolomite | Dolomite | Calcite | Dolomite | Calcite | Dolomite | Dolomite | Calcite |
| Sample | MUNR- 16-18T | MON- 16-5 | HDCTr1a | Robb Lake 3-1 | KICK- 16-11 | SHAG- C4-7A | 07-MET- 12A-3 | 07-MET- 12A-3 | HB DUMP-5 | HB DUMP-5 | 08SP155- C6 | 08-SP- 75-T |
| Analysis # | C2-L4 | C3-L6 | C1-L4 | C4-L4 | C2-L1 | C3-L3 | C2-L9 | C3-L1 | C4-L3 | C2-L7 | C4-L2 | C4-L5 |
| ²⁵ Mg | 166 000 | 127 000 | 155 000 | 166 000 | 152 000 | 144 000 | 1730 | 156 000 | 9700 | 123 000 | 95 000 | 14 800 |
| ⁴³ Ca | 217 000 | 217 000 | 217 000 | 217 000 | 217 000 | 217 000 | 400 000 | 217 000 | 400 000 | 217 000 | 217 000 | 400 000 |
| ⁵¹ V | 1.22 | bql | 4.2 | 4.9 | bql | bql | bql | 4.2 | 3 | 10.2 | 20.6 | bql |
| 55Mn | 390 | 4400 | 950 | 1990 | 2040 | 570 | 138 | 570 | 217 | 460 | 25 500 | 167 |
| ⁵⁷ Fe | 288 | 24 700 | bql | bql | 17 900 | 5500 | 292 | 8900 | bql | 7000 | 39 000 | bql |
| 66Zn | 390 | 32 | 1380 | 278 | 59 | 310 | 54 | 85 | 111 | 48 | 2410 | bql |
| ⁸⁵ Rb | 1.69 | bql | bql | bql | bql | bql | bql | bql | bql | bql | bql | bql |
| ⁸⁸ Sr | 33 | 49 | 48 | 36 | 51 | 41 | 710 | 36 | 230 | 82 | 89 | 1120 |
| ⁸⁹ Y | 6.8 | 11 | 14.8 | 1.07 | 1.38 | 0.72 | 1.17 | 0.49 | 19.3 | 2.17 | 28.7 | 4.6 |
| ⁹⁰ Zr | 3.3 | 0.73 | 5.6 | 0.96 | 0.056 | 0.188 | 0.104 | 0.58 | bql | bql | bql | bql |
| ⁹³ Nb | 0.33 | bql | 0.206 | 0.06 | bql | bql | bql | 0.006 | bql | bql | bql | bql |
| ¹³⁷ Ba | 5.5 | 0.69 | 11.2 | 11 | 6.6 | 4.7 | 9.4 | 8.7 | 13.2 | 95 | 12.7 | 2470 |
| ¹³⁹ La | 3.1 | 2.77 | 1.13 | 0.6 | 0.217 | 0.4 | 1.16 | 0.93 | 6.1 | 4.8 | 2.2 | 8.1 |
| ¹⁴⁰ Ce | 5.9 | 11.6 | 3.3 | 1.74 | 1.01 | 2.25 | 2.31 | 3.1 | 10.6 | 6.5 | 7.8 | 13.1 |
| ¹⁴¹ Pr | 0.83 | 1.57 | 0.58 | 0.201 | 0.14 | 0.45 | 0.38 | 0.24 | 1.21 | 0.57 | 1.26 | 1.28 |
| ¹⁴⁶ Nd | 3.5 | 7.1 | 3.4 | 0.92 | 0.99 | 1.58 | 1.69 | 0.83 | 4.3 | 1.92 | 7.1 | 4.2 |
| ¹⁴⁷ Sm | 0.58 | 2.32 | 1.61 | 0.086 | 0.42 | 0.32 | 0.137 | 0.188 | 0.52 | 0.211 | 2.05 | 0.51 |
| ¹⁵¹ Eu | 0.109 | 0.44 | 0.49 | 0.066 | 0.118 | 0.065 | 0.279 | 0.035 | 0.262 | 0.085 | 3.1 | 0.49 |
| ¹⁵⁷ Gd | 0.62 | 2.72 | 1.97 | bql | 0.4 | 0.173 | 0.238 | 0.152 | 0.88 | bql | 4 | 0.6 |
| ¹⁵⁹ Tb | 0.106 | 0.35 | 0.24 | 0.023 | 0.053 | 0.020 | 0.041 | 0.019 | 0.105 | 0.028 | 0.55 | 0.075 |
| ¹⁶³ Dy | 0.51 | 1.79 | 1.59 | 0.134 | 0.261 | 0.152 | 0.175 | 0.048 | 0.95 | 0.121 | 4.1 | 0.48 |
| ¹⁶⁵ Ho | 0.1 | 0.35 | 0.239 | 0.024 | 0.026 | 0.054 | 0.013 | 0.022 | 0.31 | 0.029 | 0.91 | 0.118 |
| ¹⁶⁶ Er | 0.247 | 0.85 | 0.68 | 0.092 | 0.139 | 0.094 | 0.053 | 0.066 | 0.91 | 0.117 | 2.23 | 0.33 |
| ¹⁶⁹ Tm | 0.054 | 0.11 | 0.1 | 0.009 | 0.014 | 0.008 | 0.016 | 0.006 | 0.136 | 0.009 | 0.36 | 0.05 |
| ¹⁷² Yb | 0.187 | 0.54 | 0.55 | 0.077 | 0.087 | 0.023 | 0.03 | 0.047 | 0.82 | 0.04 | 2.01 | 0.242 |
| ¹⁷⁵ Lu | 0.023 | 0.089 | 0.083 | 0.015 | 0.007 | 0.010 | 0.009 | 0.006 | 0.137 | 0.006 | 0.267 | 0.035 |
| ¹⁷⁸ Hf | 0.091 | 0.023 | 0.047 | 0.024 | bql | bql | bql | bql | 0.006 | 0.003 | bql | bql |
| ¹⁸¹ Ta | 0.016 | 0.001 | 0.033 | 0.036 | 0.004 | bql | bql | 0.001 | bql | 0.005 | 0.005 | bql |
| Pb total | bql | 60 000 | 720 | 105 | 20.5 | 870 | 41 | 73 | 179 | 94 | 570 | 35 |
| ²³² Th | 0.238 | 1.07 | 0.68 | 0.07 | 0.047 | bql | bql | 0.030 | bql | 0.052 | 0.09 | 0.003 |
| ²³⁸ U | 0.106 | 0.39 | 0.92 | 0.56 | 0.005 | bql | 0.254 | 0.195 | 0.085 | 0.154 | 0.127 | 0.001 |
| Notes: all el | ement cor | centration | s are in par | ts per milli | on: Pb tota | al = 206Pb + | 207Pb + 208Pt | <u></u> | | | | |

Table 3. Representative elemental analyses from the Rocky Mountain and Kootenay Arc deposits

Notes: all element concentrations are in parts per million; Pb total = ²⁰⁶Pb + ²⁰⁷Pb + ²⁰⁸Pb Abbreviations: bql: below quantification limit

Table 4. Summary of laser-ablation inductively coupled plasma mass spectrometry analyses of carbonates from Rocky Mountain Mississippi Valley-type deposits, showing rare-earth element (REE), light REE (LREE), medium REE (MREE), and heavy REE (HREE) content, Ce and Eu anomalies, and post-Archean Australian shale (PAAS)-normalized La-Nd, Sm-Gd, and Tb-Lu ratios.

| shape | | 7 | Сп, - | | | | \rangle | | ant samples |
|--------------|-----------------------|---|---|-------------------------------|---|--|------------------------|---------------------------|--|
| REE profile | | 8 | - - - - - - - - - - - - - - - - - - - | | En | ບ | | En - Ea - Fa - | yses of the differe |
| (n) | ъ | 0.9 | 0.6 | I | I | 0.5 | 0.2 | 0.2 | anal |
| É L | × | 3.2 | 1.8 | | I | 2.4 | 2.2 | 1.7 | onate |
| Ę (Đ | ъ | 0.2 | 0.1 | 1.2 | I | 0.1 | 0.1 | 0.1 | carbo |
| လွှစ | × | 0.8 | 0.7 | 1.9 | 0.9 | 0.8 | 0.8 | 0.7 | ective |
| (pv- | ь | 0.1 | 0.2 | 0.02 | 0.5 | 0.1 | 0.1 | 0.1 | respe |
| (La. | × | 0.7 | 1.0 | 0.2 | 0.8 | 0.1 | 0.3 | 0.3 | e. files, arisor |
| -n: (*r | ъ | 0.2 | 0.3 | 0.2 | I | 0.1 | 0.1 | 0.1 | E pro |
| ШШ | × | 1.0 | 1.0 | 1.3 | 2.2 | 0.9 | 1.0 | 1.0 | eral c |
| (ce*) | ь | 0.1 | 0.1 | 0.3 | 0.2 | 0.0 | 0.1 | 0.1 | mite of the |
| (Ce- | × | 0.9 | 6.0 | ÷. | 1.4 | 1.2 | 1.3 | 1.3 | tions |
| , Ê | ъ | 1.5 | 1.2 | 0.1 | 0.3 | 2.8 | 1.7 | 1.5 | E por |
| ≻ dd) | × | 10.6 | 4.6 | 0.7 | 1.7 | 11.5 | 12.2 | 12.0 | nly; g hed HRE |
| Щ (г | ь | 0.2 | 0.2 | 0.1 | 0.3 | 1.2 | 0.7 | 0.4 | cite o grair , and , and |
| ∑HR (pp | × | 2.0 | 1.0 | 0.4 | 0.5 | 4.4 | 4.6 | 4.3 | e: cal edium |
| Щ е | ь | 0.6 | 0.3 | 0.1 | 6.0 | 2.1 | 1.0 | 0.5 | y; blu g: me g: me g: me g: blu |
| ∑MR (ppi | ix | 2.6 | 6. 0 | 9.0 | 6.0 | 9.6 | 6.5 | 4.1 | ed; m ed; m on E pro sual (|
| ЩĈ | ь | 5.5 | 5.1 | 6. 0 | 2.1 | 3.9 | 4.4 | 1.8 | olomit grain alizati s of th d RE on vi |
| ∑LRI (ppr | × | 21.6 | 9.2 | 4.7 | 10.9 | 16.8 | 23.6 | 16.1 | ed: fine ineraninera slants nalize ased |
| шç | ь | 0.2 | i S | 1.0 | 2.7 | 7.1 | 5.4 | 2.4 | ws: rews: re |
| ∑RE (ppn | × | 26.1 | 1.1 | 5.7 | 12.2 | 27.7 | 34.8 | 24.5 | as follo e graine phine-t presen PAAS ies (A- |
| | Texture | cg/ saccharoidal, adj. to sphalerite | fg-mg/host dolostone | cg/sparry, adj. to sulfide | fg/possible vestige of host dolostone | mg-cg/lining pyrite-filled voids | mg-cg/ void filling | fg-mg/ micritic matrix | bes are coloured a lacent; cg: coarse aralization; ^b Josel d Tb-Lu ratios re alized composite six shape categor |
| | Mineral | Dolomite | Dolomite | Dolomite | Dolomite | Dolomite | Dolomite | Dolomite | profile shar ins: adj.: adj id-type mine Sm-Gd, an strate gener identified s ts. |
| Denocit | ueposit (sample #) | Munroe (MUNR 16-18T) | Munroe (MUNR 16-18T) | Shag (SHAG C4-7A) | Shag (SHAG C4-7A) | Monarch (MON 16-5) | Monarch (MON 16-5) | Monarch (MON 16-5) | Note: REE Abbreviatio ^a Yellowhea The La-Nd, Graphs illus Overall, we |

| deposits Australis | (cont.) ou t, showing r an shale (P/ | are-earth elemer AAS)–normalizeo | t La-No | l indu ≡), ligl d, Sm | Ht RE-Gd, a | and T | P-Lu | medi ratios | al El | de N EE V | IREE |), and | heav | y RE | E (HE | | conte | L Q I | and and | Eu al | n mai | ississippi valiey-rype ies, and post-Archean | |
|---|--|---|--|---|---|--|---|--|-----------------------------------|---|-----------------------------------|----------------|--------------------------|----------|-----------------------|--------------------------|------------------|---------|-----------------|----------|------------|---|---|
| Denosit | | | ∑Rf (ppi | ₩ ê | ∑LR (pp | n) E | ZMF (pp | m) (E | ∑н Прр | Ш Ш | Y Y | بر | (Ce-C | ;e*) | Eu, | | (La-N | d) | (Sm- Gd) | <u> </u> | p-Lu) | REE profile shape | |
| (sample #) | Mineral | Texture | × | ь | × | ь | IX | ь | × | ь | × | ь | × | ь | × | ь | IX | ь | | × | ь | | |
| Kicking Horse (KICK- 16-11) | Dolomite | cg/sparry, adj. to sphalerite | 3.0 | 1.3 | 2.0 | 0.0 | 0.7 | 0.3 | 0.4 | 0.2 | 1.0 | 0.4 | 6. 0 | 0.2 | 1.8 | 0.5 | .4 | <u></u> | <u> </u> | ي ب | 1.9 | Eu Luy | |
| Coral (HDC Tr 1a) | Dolomite | cg/sparry, adj. to quartz | 13.0 | 5.9 | 7.1 | 4.0 | 3.2 | 1.1 | 2.7 | 0.9 | 7.2 | 2.9 | 6.0 | 0.1 | 2.0 | 0.2 | 0.1 0 | 02 1 | | | 7 0.5 | A (| |
| Coral (HDC Tr 1a) | Dolomite | mg–cg/ sparry, adj. to sphalerite | 16.8 | 2.1 | 8.6 | 1.6 | 4.5 | 9.0 | 3.7 | 0.5 | 11.2 | 1.5 | 8.0 | 0.2 | 1.6 | 0.5 | 0.0 | 0 | 0 8 | | 0.2 | La Eu LuY | |
| Robb Lake (Robb Lake 3-1) | Dolomite | cg/sparry | 4.7 | 2.5 | 4.1 | 2.2 | 0.2 | 0.2 | 0.3 | 0.1 | 1 2 | 0.3 | | 0.1 | 1.5 | 0.5 | <u> </u> | 0 | 0 8 | - - | 00 1.00 | | |
| Robb Lake (Robb Lake 3-1) | Dolomite | mg–cg/ matrix | 5.5 | .1. | 4.8 | 1.8 | 0.3 | 60.0 | 0.4 | 0.1 | د . دن | 0.3 | | 0.4 | 1.7 | 0.8 | 6.0 | | .0 9 | | 0.0 | La Eu LuY | |
| Note: REE Abbreviatio ^a Yellowhea The La-Nd, Graphs illu: Overall, we and deposi | profile shat ns: adj.: ad d-type min Sm-Gd, ar strate genel identified s ts. ries A, B, a | bes are coloured jacent; cg: coars eralization; ^b Jose nd Tb-Lu ratios re ralized composite six shape categoi and C appear in th | e grair e grair ephine- epresel e PAA ries (A | ed; fg ied; fg type r rtthe S-norn ole (se | ed: d j: fine slant: nalize based | olomi grair alizat s of th s of th ed RE ed RE l on v | te onl ion ion E pro isual isual | ly; blu ng: me iEE, N offiles. obser | e: cal edium IREE vatior | cite o , and , and ns, wh cateç | nly; gi ied HREE iich al | Feen: Foort | dolon ions c for a | of the a | nd ca REE al co | lcite. profil mpar | es, re ison t | spect | ively. en ca | | te aus | alyses of the different samples | 0 |

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Table 5. Summary of laser-ablation inductively coupled plasma mass spectrometry carbonate analyses from Kootenay Arc Mississippi Valley–type and fracture-con-trolled replacement deposits, showing rare-earth element (REE), light REE (LREE), medium REE (MREE), and heavy REE (HREE) content, Ce and Eu anomalies, and post-Archean Australian shale (PAAS)–normalized La-Nd, Sm-Gd, and Tb-Lu ratios.

| : profile shape | | positive LREE slope. | Eu LuY | Eu LuY | | Eu LuY | nverse) Eu LuY | different samples |
|-----------------|------------|--|---|--|--|--|---|--|
| REE | | | <u>a</u> LL | | | - - - - | | is of the |
| -Lu | ь | 4. | 0.2 | 0.9 | 0.5 | 1.0 | 0.5 | lalyse |
| (Tb | × | 2.7 | 1.7 | 1.3 | 2.3 | 1.7 | 0.8 | ate ar |
| -Gd) | ь | 0.4 | 0.3 | 1 | 0.1 | 0.1 | 0.3 | arbona |
| (Sm | × | 1.0 | 1.0 | 1.0 | 0.6 | 0.9 | 0.6 | tively |
| (pN- | ь | 0.1 | 0.6 | 0.1 | 0.1 | 0.3 | 8. O | espec |
| (La | × | 0.5 | 1.2 | 0.9 | 0.9 | 1.0 | 1.8 | es, re |
| | ь | 1.6 | 0.2 | 0.2 | 0.6 | 0.4 | 6.0 | cite. profil |
| | × | 4.0 | 0.7 | 1.2 | 1.1 | 1.0 | 4. | d cal |
| -Ce*) | ь | 0.1 | 0.2 | 0.1 | 0.1 | 0.1 | 0.2 | the F |
| Č. | × | 6.0 | 1.2 | 1.4 | 1.1 | 1.2 | 0.8 | olomi ns of |
| , î | ь | 0.4 | 0.1 | 0.1 | 0.1 | 0.1 | 5.0 | en: d |
| dd) | IX | 1.3 | 0.8 | 0.6 | 0.7 | 0.7 | 3.0 | y; gred d REE p |
| M) | ь | 0.1 | 0.05 | 0.03 | 0.1 | 0.1 | 0.7 | te onl graine and H and H |
| H] (pi | × | 0.3 | 0.3 | 0.2 | 0.2 | 0.2 | 0.0 | calci calci ium g tium g |
| a de | ь | 0.2 | 0.1 | 0.1 | 0.1 | 0.1 | 0.5 | blue: med ;, MR ssrva |
| M⊠ M | × | 0.0 | 0.4 | 0.2 | 0.3 | 0.3 | 0.6 | : mg: Buly; CREE Profile |
| Щ _е | ь | | 0.9 | 0.3 | 0.6 | 0.9 | 5.9 | mite a ained ation f the l XEE |
| ∑LR (ppi | × | <u>6</u> .8 | 4.8 | 5.3 | 5.0 | 6.2 | 7.2 | : dolo ine gra neraliz ants of lized F sed on |
| ЩÊ | ь | 4. | 1.0 | 0.3 | 0.7 | 0.9 | 7.0 | vs: red d; fg: f pe min the sla norma |
| ∏ R | × | 8.0 | 5.4 | 5.8 | 5.5 | 6.7 | 8.7 | s follov graine nine-ty resent PAS- |
| | Texture | cg/sparry, void- fill core | cg/sparry, void lining adj. to calcite core | mg/ void lining, away from calcite core | cg/sparry, adj. to pyrite | mg/adj. to sphalerite and pyrite | mg-cg/dolomite- rich clast | es are coloured a: acent; cg: coarse rralization; ^b Josepl d Tb-Lu ratios repi alized composite F ix shape categorie |
| | Mineral | Calcite | Dolomite | Dolomite | Dolomite | Dolomite | Dolomite | increating the second stands of the second stands o |
| Denocit | (sample #) | Pend Oreille ^ª (07MET- 12A-3) | Pend Oreille ^a (07MET- 12A-3) | Pend Oreille ^ª (07MET- 12A-3) | Pend Oreille ^a (07MET- 12A-5) | Pend Oreille ^a (07MET- 12A-5) | Pend Oreille ^b (MET-07-2) | Note: REE p Abbreviation ^a Yellowhead The La-Nd, § Graphs illust Overall, we i |

| vrc Mississippi Valley–type and frac- y REE (HREE) content, Ce and Eu | -Gd) (Tb-Lu) REE profile shape | α X α | 0.1 1.3 0.7 | 0.03 1.1 0.3 D (negative LREE slope) | 0.004 0.6 0.1 La Eu LuY | 0.2 2.9 1.3 D (positive LREE slope) | 0.3 3.2 - La Eu LuY | 0.2 2.9 2.0 D (negative LREE slope) | 0.2 1.3 0.3 |
|--|--------------------------------|-------------|---|--|---|--|---|--|------------------------------------|
| enay A heavy | (Sm | × | 0.8 | 0.8 | 0.3 | 6.0 | 0.9 | 0.9 | 0.9 |
| , and | (pN- | ь | 1.1 | 0.4 | 0.7 | 0.2 | 0.2 | 0.4 | 0.1 |
| from REE) | (La | × | 4.8 | 3.2 | 5.9 | 0.8 | | 1.9 | 1.3 |
| /ses ≣ (MI | Eu- | ь | 0.8 | 0.2 | 0.0 | 0.7 | 1.0 | . 0.9 | 0.6 |
| anal) REI ເ | | × | 2.6 | 2 2.0 | 3.5 | 2.7 | 5.8 | 4.4 | 4 2.6 |
| nate edium os. | e, | ь | 0.0 | 0.02 | 0.1 | 0.1 | 0.1 | 0.1 | 0.0 |
| carbo :), me u ratio | Ű | × | 0.6 | 0.7 | 0.7 | 0.0 | 1.0 | 0.9 | 1.1 |
| etry o _REE Tb-Lu | , ma | ь | 0.5 | 0.8 | 0.6 | 0.0 | 0.1 | 0.8 | 0.4 |
| EE (I and | đ | × | 1.2 | 2.2 | 2.8 | 4.0 | 1.6 | 4.2 | 2.8 |
| s spec ght R n-Gd, | m) Sm) | ь | 0.1 | 0.2 | 0.1 | 0.2 | 0.1 | 0.1 | 0.2 |
| mas E), li Id, Sr | н Ц С | × | 0.3 | 0.4 | 0.6 | 0.7 | 0.3 | 1.2 | 0.8 |
| isma t (RE La-N |) REE | ь | 0.1 | 0.1 | 0.1 | 0.3 | 0.2 | 0.2 | 0.1 |
| d pla ment lized | M] (pk | × | 0.3 | 0.4 | 0.2 | 1.4 | 0.7 | 1.7 | 0.9 |
| ouple h ele orma | Щ Э | ь | 3.7 | 1.8 | 0.4 | 1.8 | 0.4 | 2.4 | 1.7 |
| vely co e-eart AS)–n | ∑LR (pp | × | 12.6 | 12.0 | 2.9 | 13.4 | 7.8 | 28.5 | 15.9 |
| inducti ing rai ile (PA | EE (| ъ | 3.8 | 1.9 | 0.3 | 1.6 | 0.5 | 2.6 | 1.9 |
| ation show an sha | R Ppp | IX | 13.1 | 12.8 | 3.8 | 15.5 | 8.8 | 31.4 | 17.5 |
| nmary of laser-abl acement deposits, -Archean Australia | | Texture | cg/in calcite-rich layer | mg–cg/ interstitial to pyrite in pyrite- rich layer | mg–cg/in pyrite- rich layer, 'comb' texture | mg–cg/ Iens | fg/lens | cg/lens in sulfide-rich band | fg/matrix in calcite-rich layer |
| cont.) Sun rolled repla s, and post | | Mineral | Calcite | Calcite | Calcite | Calcite | Dolomite | Calcite | Calcite |
| Table 5 (ture-conti anomalie: | | (sample #) | Reeves MacDonald (2007SP- 022-13b) | Reeves MacDonald (2007SP- 022-13b) | Reeves MacDonald (2007SP- 022-13b) | Reeves MacDonald (2007SP- 022-8) | Reeves MacDonald (2007SP- 022-8) | Jersey- Emerald (08-SP-T-75) | Jersey- Emerald (08-SP-T-75) |

19 È NA:O < 2 4 --4 -4 ÷ 4 4 4 0

Note: REE profile shapes are coloured as follows: red: dolomite only; blue: calcite only; green: dolomite and calcite. Abbreviations: adj.: adjacent; cg: coarse grained; fg: fine grained; mg: medium grained

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^a Yellowhead-type mineralization; ^b Josephine-type mineralization

The La-Nd, Sm-Gd, and Tb-Lu ratios represent the slants of the LREE, MREE, and HREE portions of the REE profiles, respectively. Graphs illustrate generalized composite PAAS-normalized REE profiles. Overall, we identified six shape categories (A–F), based on visual observations, which allows for a general comparison between carbonate analyses of the different samples and deposits.

Only categories A, B, and C appear in this table (see Table 5 for the remaining categories).

| /pe and frac- | , Ce and Eu | |
|-----------------|----------------|----------------|
| sippi Valley-ty | IREE) content | |
| ay Arc Missis | neavy REE (H | |
| from Kooten | REE), and I | |
| ite analyses | lium REE (M | S. |
| letry carbona | (LREE), mec | id Tb-Lu ratio |
| ass spectrom |), light REE | d, Sm-Gd, ar |
| d plasma m | ement (REE | alized La-No |
| tively couple | rare-earth el | PAAS)-norm |
| blation induc | ts, showing I | alian shale (|
| iry of laser-a | ment deposi | rchean Austr |
| ont.) Summa | olled replace. | , and post-A |
| Table 5 (co | ture-contro | anomalies |

| | • | | | | | | | | | | | | | _ | | | | | | _ | | | |
|---|--|---|--|--|--|---|---|-------------------|----------------------------------|---|--|--------|------------------------------|------------------------|-------------|----------------|--------|-------|-------|----------|----------|------------|-----------------------|
| Denosit | | | ∑R (pp | Шę | ∑LR (pp | л) Е | MZ (pp | n) KE | ZHR (pp | m) EE | , rad | . î | (Ce-C | Ce*) | ЩÜ | + (| (La-I | (bl | (Sm-G | () () | Гb-Lu | RE | E profile shape |
| (sample #) | Mineral | Texture | × | ь | × | ъ | × | ъ | × | ь | x | ъ | × | ь | × | ь | × | ъ | × | ь | N X | | |
| HB (HB DUMP-5) | Calcite | cg/sparry, interstitial to sulfides in sulfide-rich layer | 27.9 | 4.3 | 23.3 | 3.5 | 1.7 | 0.3 | 2.9 | 0.7 | 16.5 | 3.0 | 0.9 | 0.1 | 1.9 | 0.4 | 1.5 | 0.3 | 0.6 | | .6 | ш \ | |
| HB (HB DUMP-5) | Calcite | mg/void-fill in carbonate-rich layer | 24.8 | 5.8 | 20.3 | 4.9 | 1.7 | 0.3 | 2.8 | 0.6 | 16.8 | 3.5 | 0.9 | 0.05 | 1.6 | 0.2 | 1.2 | 0.1 | 0.6 | .1 | .0 .0 | | Eu LuY |
| HB (HB DUMP-5) | Dolomite | mg-cg/ lining voids in carbonate-rich layers | 14.7 | 4.3 | 13.8 | 4.0 | 0.5 | 0.2 | 0.4 | 0.2 | 2.1 | 0.6 | 1.1 | 0.2 | 2.3 | 0.6 | 2.1 | 0.5 | 0.7 0 | | 2 - | | (negative LREE slope) |
| Duncan (08SP-121) | Calcite | cg/ lenses in matrix | 6.6 | 1.6 | 7.9 | 1.6 | 1.0 | 0.2 | 1.0 | 0.1 | 3.6 | 0.5 | 0.8 | 0.1 | 1.9 | 0.8 | 1.4 | 0.5 | 8.0 | .3 | 0. | D / | (negative LREE slope) |
| Duncan (08SP-121) | Calcite | mg/ matrix | 20.4 | 3.1 | 18.5 | 3.3 | 0.9 | 0.3 | 1.1 | 0.3 | 3.7 | 1.6 | 0.9 | 0.1 | 2.0 | 0.7 | 2.1 | 0.2 | 1.0 | .4 | .5 0. | | Eu |
| Abbott- Wagner (08SP- 155-C6) | Dolomite | mg–cg/sparry, adj. to sulfide | 29.9 | 10.8 | 14.8 | 6.2 | 7.1 | 2.4 | 6.7 | 3.0 | 21.1 | 8.1 | 6.0 | 0.1 | 5.1 | 0.8 | 0.3 | 0.1 | 9.0 | | .5 | | (positive Eu anomaly) |
| Note: REE r Abbreviatior ^a Yellowhead The La-Nd, Graphs illus Overall, we and depositi | orofile shat profile shat stadj.: adj. sm-Gd, ar sm-Gd, ar trrate genel identified s s. | bes are coloured as jacent; og: coarse of eralization; ^b Josepl nd Tb-Lu ratios repr ralized composite F six shape categorie and C appear in thi | s follov graine hine-ty resent >AAS-I is (A-F | the sk the sk norma F), bas (see) | : doloi ine gra neraliz ants of lized F sed on Table (| mite o ation ation The I REE visua | , mg: , mg: | MR MR Serva | calcit um g EE, a ions, | e only rained nd HF whicl atego | /; gree d REE p h allo∖ ries). | en: dc | olomite ns of t r a ge | e and he R neral | com EE calc | ite. rofile | s, res | pecti | vely. | onate | analy | ses of the | e different samples |

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Figure 4. Post-Archean Australian shale (PAAS)–normalized rare-earth element (REE) + Y profiles for dolomite from the Munroe deposit showing a flat to slightly convex upward shape regardless of dolomite texture.

Shag

Coarse, sparry dolomite from sample SHAG-C4-7A has $\sum \text{REE} = 5.7 \pm 1.0 \text{ and } \text{Y} = 0.7 \pm 0.1 \text{ ppm}$ (Table 4). Most of the REE detected are LREE (Σ LREE = 4.7 ± 0.9 ppm), whereas the MREE and HREE content is minor (Σ MREE = 0.6 ± 0.1 ppm; Σ HREE = 0.4 ± 0.1 ppm). The REE + Y profiles are convex upward (category A, Table 4; Fig. 5), with a consistent positive LREE slope (La_N-Nd_N = 0.2 ± 0.02) and a variable negative MREE slope (Sm_N - Gd_N = 1.9 ± 1.2). Lutetium content is above the quantification limit for only one analysis, giving an HREE slope (Tb_N-Lu_N) of 1.1. The sparry dolomite shows weakly negative to positive Ce-Ce* (1.1 ± 0.3) and positive Eu-Eu* (1.3 ± 0.2) . The data for the fine-grained dolomite in this sample, possibly representing vestiges of host material, show that $\sum \text{REE} (12.2 \pm 2.7 \text{ ppm})$ is dominated by LREE (10.9 ± 2.1 ppm). The data for MREE and HREE are highly variable (Table 4; Fig. 5) and of poor quality (0.9 \pm 0.9 ppm and 0.5 \pm 0.3 ppm, respectively) because these elements are near or below quantification limits. The REE profiles for fine-grained dolomite are much flatter than those of coarse sparry dolomite. They have $La_N-Sm_N = 0.8 \pm 0.5$ and $Sm_N-Gd_N = 0.9$. The Tb_N-Lu_N was impossible to determine because HREE were below the limit of quantification (Table 4; Fig. 5). The fine-grained dolomite shows positive Ce anomalies (Ce-Ce^{*} = 1.4 ± 0.2) and the Eu anomaly is positive in the only available measurement of it $(Eu-Eu^* = 2.2).$

Monarch and Kicking Horse

In the Monarch sample (MON-16-5), the micritic, matrix dolomite has $\sum REE = 24.5 \pm 2.4$ ppm with high $\sum LREE$ (16.1 ± 1.8 ppm), $\sum MREE$ and $\sum HREE$ content similar to one another (4.1 ± 0.5 ppm and 4.3 ± 0.4 ppm, respectively),



Figure 5. Post-Archean Australian shale (PAAS)–normalized rare-earth element (REE) + Y profiles for dolomite from the Shag deposit. Coarse dolomite shows a slightly convex upward REE profile. Fine-grained dolomite, possibly representing vestiges of host material, shows consistently higher light REE content than the coarse dolomite; the middle REE and heavy REE data for fine-grained dolomite are more erratic but may nevertheless indicate the order of magnitude.

and $Y = 12.0 \pm 1.5$ ppm. The REE + Y profiles are convex upward (category C, Table 4; Fig. 6a), with positive LREE and MREE slopes and a negative HREE slope (Table 4). The Ce and Eu anomalies of micritic dolomite are positive. In sample MON-16-5, the REE content of the medium to coarse dolomite that fills voids entirely is slightly higher than that of the micritic matrix dolomite and the medium to coarse dolomite that lines pyrite-filled voids (Table 4); however, these contents are within the margin of error of each other. Similarly, the Y contents of all three dolomite types in this sample are within the margin of error of one another (Table 4). The REE + Y profile for void-filling dolomite is convex upward (category C, Table 4; Fig. 6a) and very similar to the REE + Y profile for the matrix dolomite. In detail, the LREE, MREE, and HREE slopes, as well as Ce and Eu anomalies for all three dolomite types in this sample, are within the margin of error of each other (Table 4).

In the Kicking Horse sample (KICK-16-11), medium to coarse dolomite was not analyzed because sufficiently large areas free of inclusions and interstitial material could not be found. The REE profiles for sparry, coarse dolomite analyzed from this sample (category A, Table 4; Fig. 6b) are very similar in shape to those of the dolomite from Monarch, sample MON-16-5 (Fig. 6a), but the REE + Y content is approximately ten times lower (Table 4). The REE + Y profile for dolomite from KICK-16-11 is convex upward, with $La_N-Nd_N = 0.4 \pm 0.2$, $Sm_N-Gd_N = 1.0 \pm 0.2$, and $Tb_N-Lu_N = 3.7 \pm 1.9$. Unlike the dolomite in the Monarch sample, Ce anomalies for dolomite from Kicking Horse vary from weakly negative to slightly positive (0.9 ± 0.2) and Eu anomalies are weakly to moderately positive (1.8 ± 0.5).



Figure 6. Post-Archean Australian shale (PAAS)–normalized rare-earth element (REE) + Y profiles for dolomite from the Monarch and Kicking Horse deposits: **a)** Monarch — irrespective of texture, all dolomites show similar convex upward REE profiles with steep positive light REE slopes and shallower negative middle REE to heavy REE slopes; **b)** Kicking Horse — similar REE + Y profile shape to the Monarch deposit; however, REE contents are an order of magnitude lower and show positive Eu anomalies (see Table 4).

Coral

Sample HDCTr1a from Coral contains sparry dolomite as both medium to coarse planar-s crystals and as coarse, planar-e crystals adjacent to quartz. Both types of dolomite have similar REE profiles and very similar REE content (Table 4; Fig. 7). The medium to coarse dolomite has $\sum \text{REE} = 16.8 \pm 2.1 \text{ ppm}$ ($\sum \text{LREE} = 8.6 \pm 1.6 \text{ ppm}$, $\sum \text{MREE} = 4.5 \pm 0.6 \text{ ppm}$, $\sum \text{HREE} = 3.7 \pm 0.5 \text{ ppm}$); and $Y = 11.2 \pm 1.5 \text{ ppm}$, with convex-upward REE + Y profiles [La_N-Nd_N = 0.2 \pm 0.1; Sm_N-Gd_N = 0.8 \pm 0.2; Tb_N-Lu_N = 1.6 \pm 0.2; category A, Table 4]). The Ce anomalies for the medium to coarse dolomite are negative (0.8 \pm 0.2), whereas Eu anomalies are weakly to strongly positive (1.6 \pm 0.5). The coarse dolomite that is adjacent to quartz has slightly lower REE content ($\sum \text{REE} = 13.0 \pm 5.9 \text{ ppm}$, $\sum \text{LREE} = 7.1 \pm 4.0 \text{ ppm}$, $\sum \text{MREE} = 3.2 \pm 1.1 \text{ ppm}$, $\sum \text{HREE} = 2.7 \pm 1.1 \text{ ppm}$, $\sum \text{HREE} = 2.7 \pm 1.1 \text{ ppm}$, $\sum \text{HREE} = 2.7 \pm 1.1 \text{ ppm}$.

0.9 ppm) and Y (7.2 \pm 2.9 ppm) but all are within the margin of error of the medium to coarse dolomite that occurs far away from quartz. The REE + Y profiles and Ce and Eu anomalies for coarse sparry dolomite are similar to those of the medium to coarse dolomite (Fig. 7); however, the intensity of Eu anomalies in the coarse, sparry dolomite is more consistent.

Robb Lake

Sparry, coarse dolomite in the Robb Lake sample (Robb Lake 3-1) has $\sum REE = 4.7 \pm 2.5$ ppm, dominated by LREE (4.1 \pm 2.2 ppm) with minor MREE (0.2 \pm 0.2 ppm) and HREE (0.3 \pm 0.1 ppm; Table 4). Yttrium is present at 1.2 ± 0.3 ppm. The resulting REE + Y profiles are flat to slightly negatively sloping (category B, Table 4; Fig. 8; $La_{N}-Nd_{N} = 1.1 \pm 0.2$, $Sm_{N}-Gd_{N} = 0.8 \pm 0.1$, $Tb_{N}-Lu_{N} =$ 2.6 ± 1.8), with weak positive Ce anomalies (1.1 ± 0.1) and weak to strong positive Eu anomalies (1.5 ± 0.5) . The medium- to coarse-grained dolomite matrix has similar REE and Y content to the sparry dolomite (Table 4), but the REE + Y profiles (Fig. 8) are generally slightly flatter, especially in the HREE portion of the profile. The medium- to coarse-grained dolomite matrix shows weakly negative to positive Ce anomalies (1.3 ± 0.4) and weakly negative to strongly positive Eu anomalies (1.7 ± 0.8) .

Kootenay Arc MVT and FCR deposits

Pend Oreille

In the Yellowhead-type mineralization sample (07-MET-12A-3) from Pend Oreille, sparry calcite fills dolomite-lined voids in sulfide minerals (Fig. 3a). The total REE content in calcite is 8.0 ± 1.4 ppm ($\Sigma LREE = 6.8 \pm 1.1$ ppm, \sum MREE = 0.9 ± 0.2 ppm, \sum HREE = 0.3 ± 0.1 ppm) and $Y = 1.3 \pm 0.4$ ppm. The corresponding REE + Y profiles are convex upward (category D, Table 5; Fig. 9a), and show weak positive to weak negative Ce anomalies (0.9 ± 0.1) and strong positive Eu anomalies (4.0 ± 1.6) . Dolomite is sparry and coarse adjacent to the calcite core and mediumgrained adjacent to sulfide minerals at the outer edge of the voids. Sparry, coarse-grained dolomite has REE and Y contents within the margin of error of medium-grained dolomite (Table 5) and the two REE + Y profiles are parallel and overlapping (category F, Fig. 9b). The only difference between these two types of dolomite is their Eu anomalies (Table 5, Fig. 9b).

In sample 07-MET-12A-5 (Yellowhead-type mineralization), sparry dolomite occurs adjacent to pyrite only. It has total REE and Y content ($\sum REE = 5.5 \pm 0.7$ ppm, Y = 0.7 ± 0.1 ppm) similar to medium-grained dolomite, which is adjacent to both pyrite and sphalerite (Table 5). The REE + Y profiles (Fig. 9c) of sparry and medium-grained dolomite are



Figure 7. Post-Archean Australian shale (PAAS)–normalized rare-earth element (REE) + Y profiles for dolomite from the Coral deposit showing similar steep positive light REE to middle REE (MREE) slopes, shallow MREE to heavy REE slopes, and a positive Eu anomaly, irrespective of texture (*see* Table 4).



Figure 8. Post-Archean Australian shale (PAAS)–normalized rare-earth element (REE) + Y profiles for dolomite from Robb Lake showing overlapping flat REE profiles regardless of texture.

similar (category F, Table 5). Dolomite analyses from both samples of Yellowhead-type mineralization are within the margin of analytical error of one another.

In the Josephine-type mineralization sample (MET-07-2), medium to coarse dolomite has variable REE and Y content ($\sum REE = 8.7 \pm 7.0$ ppm, Y = 3.0 ± 2.0 ppm), within the margin of error of dolomite from Yellowhead-type mineralization (Table 5). The REE profiles for dolomite from the Josephine-type mineralization differ from those of Yellowhead-type dolomite in their positive MREE (Sm_N-Gd_N = 0.6 ± 0.3) and HREE (Tb_N-Lu_N = 0.8 ± 0.5) slopes, weak negative to positive Ce anomalies (0.8 ± 0.2), and variable negative to positive Eu anomalies (1.4 ± 0.9; Table 5; Fig. 9c, d).

Reeves MacDonald

The calcite-rich layer in sample 2007SP-022-13b consists of coarse calcite with $\Sigma REE = 13.1 \pm 3.8$ ppm and Y = 1.2 ± 0.5 ppm. These REE and Y contents are within error of calcite in the pyrite interstices of the pyrite-rich layer (Table 5, Fig. 10a), except where present in the comb texture (Fig. 3c), which has lower total REE (especially LREE) and slightly higher HREE and Y ($\sum REE = 3.8 \pm 0.3$ ppm, $Y = 2.8 \pm 0.6$ ppm; Table 5). Overall, calcite in the carbonaterich layer has LREE-enriched profiles with negative Ce anomalies and positive Eu anomalies (category D, Table 5; Fig. 10a). These profiles overlap those corresponding to calcite filling the interstices between sulfide grains (Table 5, Fig. 10a). The REE profile of calcite displaying comb textures is S-shaped (La_N-Nd_N = 2.9 \pm 0.7, Sm_N-Gd_N = 0.3 \pm 0.004, Tb_N -Lu_N = 0.6 ± 0.1), though the Ce and Eu anomalies are similar to calcite with other textures in this sample (Ce-Ce^{*} = 0.7 ± 0.1 , Eu-Eu^{*} = 3.5 ± 0.9).

Sample 2007SP-022-8 from Reeves MacDonald is sulfide rich and contains lenses of medium- to coarse-grained calcite and fine-grained dolomite. The calcite has a total REE content of 15.5 ± 1.6 ppm (Σ LREE = 13.4 ± 1.8 ppm, Σ MREE = 1.4 ± 0.3 ppm, Σ HREE = 0.7 ± 0.2 ppm) and Y = 4.0 ± 0.9 ppm (Table 5). The REE + Y profiles of calcite (Fig. 10b) show flat to slightly positive LREE and MREE slopes, steep negative HREE slopes, and weak negative Ce and strong positive Eu anomalies (Ce-Ce* = 0.9 ± 0.1 , Eu-Eu* = 2.7 ± 0.7). Compared to calcite, dolomite in this sample has a lower average total REE (Σ REE = 8.8 ± 0.5 ppm, with Lu above the quantification limit (0.003 ppm) in only one analysis) and Y content (1.6 ± 0.1 ppm). The REE + Y profiles for dolomite (Fig. 10c) are similar to those of calcite (category D, Table 5; Fig. 10b).

Jersey-Emerald

Sample 08-SP-75-T from the Jersey-Emerald deposit contains two distinct varieties of calcite: 1) coarse calcite forming lenses in sulfide-rich bands and 2) fine-grained calcite in calcite-rich layers. The coarse, sulfide-related calcite has higher REE and Y content ($\sum REE = 31.4 \pm 2.6 \text{ ppm}$, $\sum LREE = 28.5 \pm 2.4 \text{ ppm}$, $\sum MREE = 1.7 \pm 0.2 \text{ ppm}$, $\sum HREE =$ $1.2 \pm 0.1 \text{ ppm}$, $Y = 4.2 \pm 0.8 \text{ ppm}$) than the fine-grained matrix calcite (Table 5; Fig. 11). The weakly negative sloping REE+Y profiles for coarse calcite are similar to the profiles for fine-grained calcite (category D, Table 5; Fig. 11). Both coarse and matrix calcite have non-existent to weak Ce anomalies (Ce-Ce* = 0.9 \pm 0.1 and 1.1 \pm 0.04, respectively). Coarse calcite crystals are characterized by stronger positive Eu anomalies than the matrix calcite (Eu-Eu* = 4.4 \pm 0.9 and 2.6 \pm 0.6, respectively).



Figure 9. Post-Archean Australian shale (PAAS)–normalized rare-earth element profiles for calcite and dolomite from Yellowhead- and Josephine-type mineralization from the Pend Oreille deposit: **a)** Yellowhead-type mineralization, sample 07-MET-12A-3 — sparry calcite showing REE profiles with a positive light REE (LREE) to middle REE (MREE) slope, a steeper, negative MREE to heavy REE slope, and a positive Eu anomaly; **b)** Yellowhead-type mineralization, sample 07-MET-12A-3 — dolomite showing a flat to slightly negative sloping REE profile; **c)** Yellowhead-type mineralization, sample 07-MET-12A-5 — both dolomite types have flat to slightly negative sloping REE profiles, regardless of texture; **d)** Josephine-type mineralization, sample MET-07-2 — dolomite showing an overall positive-sloping REE profile with a nearly flat to convex downward LREE segment.

HB

Calcite in sample HB DUMP-5 is part of sulfide-rich layers (filling interstices between pyrite crystals) or filling voids within a dolomite matrix in carbonate-rich layers (Fig. 3f). The REE and Y content in calcite is similar between sulfide interstices ($\sum REE = 27.9 \pm 4.3$ ppm, Y = 16.5 ± 3.0 ppm) and void-filling crystals in the carbonate-rich layers ($\sum REE = 24.8 \pm 5.8$ ppm, Y = 16.8 ± 3.5 ppm; Table 5; Fig. 12a). The REE profiles and slopes for sparry interstitial calcite are similar to those of void-filling calcite. Both calcite varieties have identical Ce anomalies (0.9 ± 0.05) and their Eu anomalies are also within the margin of error of one another (category E, Table 5). Fine- to medium-grained dolomite making up the matrix of the carbonate-rich layers could not be analyzed due to a high abundance of microscopic impurities. Medium- to coarse-grained planar-s to planar-e crystals of dolomite lining calcite-filled voids have $\sum \text{REE} = 14.7 \pm 4.3 \text{ ppm}$ and $Y = 2.1 \pm 0.6 \text{ ppm}$. The corresponding dolomite REE + Y profiles have negative slopes (category D, Table 5; Fig. 12b) with weak negative to weak positive Ce anomalies (1.1 ± 0.2) and positive Eu anomalies (2.3 ± 0.6) .

Duncan

Calcite in sample 08SP-121 from the Duncan deposit occurs as medium and coarse crystals intimately mixed with sulfide minerals. The medium-grained matrix calcite has higher $\sum \text{REE}$ (20.4 ± 3.1 ppm) than the coarse calcite in lenses within the matrix (9.9 ± 1.6 ppm). This difference is due to higher $\sum \text{LREE}$ (18.5±3.3 ppm) in the medium-grained calcite relative to the coarse calcite (7.9 ± 1.6 ppm);



Figure 10. Post-Archean Australian shale (PAAS)–normalized rare-earth element (REE) profiles for calcite and dolomite from the Reeves MacDonald deposit: **a**) calcites in sample 2007SP-022-13b show negative-sloping light REE (LREE) profiles and flat to slightly negative or positive middle REE (MREE) to heavy REE (HREE) profiles, except where it displays the 'comb' texture, which has a positive MREE to HREE slope and strong positive Eu anomalies; **b**) calcite in sample 2007SP-022-8 shows flat to slightly positive sloping LREE to MREE profiles with steep negative MREE to HREE profiles and strong positive Eu anomalies; **c**) dolomites from sample 2007SP-022-8 have a similar REE profile to calcite from the same sample, but with slightly lower overall content.



Figure 11. Post-Archean Australian shale (PAAS)–normalized rare-earth element (REE) profiles for calcite from the Jersey-Emerald deposit have a generally flat to slightly negative slope regardless of texture, although the fine-grained matrix calcite has slightly lower REE content and a shallower light REE to middle REE slope compared to the coarse-grained calcite interstitial to the sulfide minerals in the sulfide-rich bands.

both types of calcite have similar \sum MREE, \sum HREE, and Y contents (Table 5; Fig. 13). The REE + Y profiles (Fig. 13) of the medium-grained calcite have a more negative LREE slope compared to the coarse calcite, though they are within the margin of error of each other (category D, Table 5). The MREE and HREE slopes of the medium-grained calcite (Sm_N-Gd_N = 1.0 ± 0.4, Tb_N-Lu_N = 0.5 ± 0.2) are within the margin of error of the coarse calcite (Sm_N-Gd_N = 0.6 ± 0.2 , Tb_N-Lu_N = 0.8 ± 0.3). The Ce anomalies for the medium and coarse calcite are weakly negative (0.9 ± 0.1 and 0.8 ± 0.1, respectively; Fig. 13) and within margin of error, whereas the Eu anomalies are strongly positive (2.0 ± 0.7 and 1.9 ± 0.8, respectively) and within the margin of error of each other.

Abbott-Wagner

Sparry dolomite in the Abbott-Wagner sample (08SP-155-C6) has total REE = 29.9 ± 10.8 ppm (\sum LREE = 14.8 ± 6.2 ppm, \sum MREE = 7.1 ± 2.4 ppm, \sum HREE = 7.9 ± 3.0 ppm) and Y = 21.1 ± 8.1 ppm (Table 5). The REE + Y profiles of this dolomite have steep positive LREE and MREE slopes (La_N-Nd_N = 0.3 ± 0.1, Sm_N-Gd_N = 0.6 ± 0.1) and flat to weakly negative HREE slope (Tb_N-Lu_N = 1.5 ± 0.5; category A, Table 5; Fig. 14). Dolomite from this sample shows weak negative Ce anomalies (0.9 ± 0.1) and strong positive Eu anomalies (Table 5; Fig. 14).



Figure 12. Post-Archean Australian shale (PAAS)–normalized rare-earth element (REE) profiles for calcite and dolomite from the HB deposit: **a)** regardless of calcite texture, the REE profiles have a positive slope with a positive Eu anomaly (Table 5); **b)** dolomite REE profiles have a negative slope, with similar La and Ce content to in the calcite from this sample. This dolomite also displays positive Ce and Eu anomalies.

DISCUSSION

Rare-earth element signatures of carbonates

Typical shallow oxic seawater has an MREE- and HREE-enriched PAAS-normalized REE pattern with distinct negative Ce and positive Y anomalies (Fig. 15a) and in some cases positive Gd anomalies with relative depletion in LREE, as described by Bau and Dulski (1996), Bau et al. (2003), and Tostevin et al. (2016). The REE patterns of calcite and other carbonates are commonly influenced by the composition of the fluid from which they crystallized and by ambient physicochemical depositional conditions (Bau and Möller, 1992; Tostevin et al., 2016); consequently, PAAS-normalized REE patterns characteristic of seawater may be preserved in marine sediments and many sedimentary carbonate rocks (e.g. carbonate ooids (Li et al., 2019); biotic and abiotic carbonates (Guido et al., 2011); reef carbonates



Figure 13. Post-Archean Australian shale (PAAS)–normalized rare-earth element (REE) profiles for calcite from the Duncan deposit are generally flat with similar REE content irrespective of texture.



Figure 14. Post-Archean Australian (PAAS)–normalized rare-earth element (REE) profiles for dolomite from the Abbott-Wagner deposit show positive light REE to middle REE (MREE) slopes with flat MREE to heavy REE (HREE) slopes and a positive Eu anomaly.

(Northdurft et al., 2004); and carbonate host rocks to MVT Zn-Pb deposits (Bau et al., 2003)). These primary signatures may survive diagenesis, including recrystallization and dolomitization, if fluid-rock ratios are low to moderate (Banner and Hanson, 1990; however, in many cases they are expected to be modified or completely obliterated (e.g. Zhang et al., 2014). Anomalous La concentrations have been reported in some recent seawaters, marine metalliferous sediments, and high-temperature hydrothermal fluids (Bau and Dulski, 1996). In such situations, the interpretation of Ce anomalies may become problematic. To circumvent this issue, Bau and Dulski (1996) introduced Pr-Pr*, defined as $Pr_N/((\frac{1}{2} \cdot Ce_N) + (\frac{1}{2} \cdot Nd_N))$, and used it to identify false Ce anomalies (Fig. 15).



Figure 15. a) Post-Archean Australian (PAAS)–normalized rare-earth element (REE) profiles for seawater from the western North Pacific (Alibo and Nozaki, 1999) showing the distinct negative Ce anomaly and light REE depletion relative to heavy REE, porewater from marine sediments on the California margin (Haley et al., 2004), hydrothermal vent (black/grey smoker) fluids from Manus Basin (Craddock et al., 2010), sparry calcite from the Dirtlow open pit in the South Pennine Orefield (Bau et al., 2003), cold seep carbonates from northern Apennines, and calcite from the volcanogenic massive-sulfide Bracemac-McLeod deposits (Genna et al., 2014); **b)** a binary plot showing how true Ce and La anomalies are distinguished using the relationship between PAAS-normalized Ce and Pr anomalies, *after* Bau and Dulski (1996); **c)** the effect of progressive contamination of stromatolite analyses by shale on the PAAS-normalized REE profile (van Kranendonk et al., 2003).

The visual assessment of normalized REE profiles is convenient for comparing homogeneous data sets, or for comparing such profiles to the seawater REE profile if the number of analyses is small. For example, qualitatively, one could suggest that none of the PAAS-normalized REE profiles from the Kootenay Arc and Rocky Mountains have overall patterns similar to seawater (Fig. 15a); however, where large numbers of profiles are involved, the PAASnormalized Ce-Ce* versus Pr-Pr* plots (Bau and Dulski, 1996) are more effective for comparing the data (Fig. 15b). This plot is a convenient tool for summarizing and discussing the fluid oxidation state at the time of carbonate precipitation, their recrystallization, or the characteristics of fluids that interacted with the original carbonate precipitates during or after diagenesis. Essentially, carbonates that retain the shallow (oxic) seawater signature plot in the lower-right quadrant of the PAAS-normalized Ce-Ce* versus Pr-Pr* diagram (pale blue field in Fig. 15b). Carbonates precipitated in a deeper marine (i.e. more reducing) environment and those that re-equilibrated with, or precipitated directly from, magmatic, metamorphic, or hydrothermal fluids, will plot outside this field. The PAAS-normalized Ce-Ce* versus Pr-Pr* diagrams for carbonates from the Rocky Mountains (Fig. 16) and Kootenay Arc deposits (Fig. 17) clearly indicate that no carbonate analyses from Monarch (Fig. 16a), Robb Lake (Fig. 16b), and Jersey-Emerald (Fig. 17a) plot within the typical shallow seawater field, whereas 9 out of 14 analyses from the Munroe deposit do (Fig. 16c). Only a minority



Figure 16. Binary plots showing the relationship between post-Archean Australian shale (PAAS– normalized Ce and Pr anomalies background from Bau and Dulski (1996)) for the Rocky Mountain Mississippi Valley–type deposits studied: **a)** Monarch, **b)** Robb Lake, c) Munroe, **d)** Shag, **e)** Kicking Horse, and **f)** Coral. No analyses from the Monarch or Robb Lake deposits plot within the seawater field (light blue, lower right quadrant); however, more than half of the analyses from Munroe plot in this field. Only a minority of analyses from the other deposits plot in the seawater field. The negatively sloping arrays of correlated analyses from Robb Lake, Shag, and Kicking Horse likely indicate post-depositional overprint by reduced fluids. Abbreviations: cg: coarse grained; fg: fine grained; mg: medium grained; sp: sparry.



Figure 17. Binary plots showing the relationship between PAAS-normalized Ce and Pr anomalies (background from Bau and Dulski (1996)) for the Kootenay Arc Mississippi Valley–type (MVT) and fracturecontrolled replacement (FCR) deposits studied: **a)** Jersey-Emerald (MVT), **b)** Pend Oreille (MVT), **c)** Reeves MacDonald (MVT), **d)** HB (MVT), **e)** Duncan (MVT), and **f)** Abbott-Wagner (FCR). Analyses from the Jersey-Emerald deposit plot exclusively outside the seawater field (pale blue, lower right quadrant) and a minority of analyses from all Kootenay Arc deposits studied plot within this field. The Pend Oreille (Yellowhead mineralization), HB, Duncan, and Abbott-Wagner deposit analyses show negatively sloped arrays. Abbreviations: cg: coarse grained; fg: fine grained; mg: medium grained; sp: sparry.

of carbonate analyses from Shag (Fig. 16d), Kicking Horse (Fig. 16e), Coral (Fig. 16f), Pend Oreille (Fig. 17b), Reeves MacDonald (Fig. 17c), HB (Fig. 17d), Duncan (Fig. 17e), and Abbott-Wagner (Fig. 17f) plot in the shallow seawater field. Overall, less than 15% of carbonate analyses from the Kootenay Arc and Rocky Mountain deposits plot in the field of shallow, oxic seawater based on PAAS-normalized CeN-Ce* versus Pr-Pr* plots. Because this study is the first systematic, multi-deposit, LA-ICP-MS-based examination of carbonate minerals from MVT settings, it remains to be determined if the same findings apply to MVT districts worldwide.

Our pioneering study shows that clusters of analyses from several deposits, including Pend Oreille (Yellowheadtype mineralization), HB, Duncan, Abbott-Wagner, Shag, Kicking Horse, and possibly Robb Lake, show significant negative correlation of Ce-Ce* with Pr-Pr*, with coefficients of determination (R2) ranging from 0.32 (Robb Lake) to 0.88 (Shag). Such a relationship is not previously documented or discussed in studies covering MVT-related carbonates. These trends suggest that the composition of carbonates in these deposits evolved toward the central field of the PAASnormalized Ce-Ce* versus Pr-Pr* diagrams, reflecting more reducing conditions. This may indicate one or more of the following: a) post-depositional overprint of the original carbonates by basinal, hydrothermal, or metamorphic fluids; b) evolution in the characteristics of hydrothermal formation waters; and c) variation in fluid-to-rock ratio, possibly related to changes in permeability. To fully recognize and appreciate the significance of these trends, the REE data set presented here must be interpreted in conjunction with the results of detailed paragenetic studies, C-O and Sr isotope analyses, clumped C and O isotope analyses, and fluid-inclusion studies, where possible.

We have thus far addressed features related to Ce anomalies that provide information regarding fluid redox conditions; however, the presence or absence of Eu anomalies is also significant. For example, convex upward REE patterns with positive Eu anomalies (e.g. Fig. 15a) have been reported in hydrothermal fluids and in carbonates and fluorite formed from acidic crustal fluids (Möller and Moretani, 1983; Michard, 1989; Bau and Möller, 1992; Lüders et al., 1993; Ohr et al., 1994; Douville et al., 1999; Hecht et al., 1999; Bau et al., 2003). Positive Eu anomalies in fluids can also be produced through water-rock interaction at temperatures exceeding 200°C (Sverjensky, 1984; Bau, 1991; Bau et al., 2003). Under such conditions, Eu³⁺ ions are reduced to Eu²⁺ ions, which are preferentially incorporated into and transported by fluids (Bau, 1991; Bau and Möller, 1992, Bau et al., 2003; Voigt et al., 2017). These fluids retain the excess Eu as they migrate to cooler, oxidized geological settings where precipitating carbonates can incorporate Eu as Eu³⁺ (Bau et al., 2010). Oxidized Eu (i.e. Eu^{3+}) has a smaller ionic radius compared to Eu²⁺ and is thus preferentially incorporated into carbonate minerals such as calcite, where it substitutes for Ca²⁺ through coupled substitution involving Na⁺ to maintain the charge balance (Lüders et al., 1993; Hellebrandt et al., 2016), resulting in a positive Eu anomaly. It is unlikely that such positive Eu anomalies will form in carbonate minerals during low-temperature water-rock interaction (Bau, 1991; Bau and Möller, 1992; Bau et al., 2003), except in reducing environments where the concentration of H2S in the fluid exceeds that of SO₄ (Möller and Moretani, 1983; Lüders et al., 1993). Nevertheless, Eu anomalies could be produced by water-rock interaction (Jiang et al., 2015) in closed-system basins if burial temperatures exceed the 200 to 250°C range.

Carbonates from several deposits, such as Coral (Fig. 7), Robb Lake (Fig. 8), Pend Oreille (Fig. 9a), Reeves MacDonald (Fig. 10), Jersey-Emerald (Fig. 11), and Abbott-Wagner (Fig. 14), show strong positive Eu anomalies. These anomalies may be attributed to precipitation of carbonates from hot hydrothermal fluids, or by incorporation of Eu³⁺ into the carbonate structure during dolomitization or metamorphic recrystallization.

Analyses from Monarch (dolomite), Yellowhead-type mineralization from Pend Oreille (calcite), and Reeves MacDonald (dolomite and calcite) show an overall convex upward pattern, which is commonly observed in minerals precipitated from hot hydrothermal fluids exceeding the 200 to 250°C temperature range (e.g. Sverjensky, 1984; Bau et al., 2003). This is the best explanation for samples with profiles showing both the convex upward pattern and a positive Eu anomaly; however, convex upward patterns without positive Eu anomalies were also reported from cold seeps from methane-derived authigenic carbonates (e.g. Wang et al., 2015).

In many areas of the Rocky Mountains and in the Kootenay Arc, metamorphic conditions attained or exceeded lower greenschist facies (Tables 1 and 2), thus temperatures during metamorphism exceeded the 200 to 250°C range needed to produce Eu anomalies by water-rock interaction.

Possible interference

Caution must be exercised in interpreting the Eu anomalies that we report from these MVT- and FCR-related carbonates. Europium anomalies can be produced as an analytical artefact due to ¹³⁵Ba¹⁶O⁺ polyatomic interference on ¹⁵¹Eu during ICP-MS analyses (Jarvis et al., 1989; Dulski, 1994; Slack et al., 2004; Zwahlen et al., 2019). Mississippi Valley-type deposits are commonly rich in Ba in the form of barite (Paradis et al., 2007). Thus, theoretically, analysis of a carbonate mineral with a high Ba content may lead to an exaggerated Eu content due to 135Ba16O+ polyatomic interference. For this reason, we systematically considered Eu and Ba contents and their covariation in the carbonates that we analyzed on a deposit-by-deposit basis. In general, the Ba content in calcite and dolomite ranges from 1 to 250 ppm, except in the Jersey-Emerald and Reeves MacDonald deposits, where the Ba content reaches 2500 and 7500 ppm,

Figure 18. Binary plots of Eu versus Ba content to assess the potential impact of ¹³⁵Ba¹⁶O⁺ polyatomic interference on Eu analyses of the **a**) Jersey-Emerald, **b**) HB, **c**) Pend Oreille, and **d**) Reeves MacDonald deposits. The high correlation between Eu and Ba in the Jersey-Emerald deposit is likely to be an artefact of Ba-rich calcite and Ba-poor dolomite. The increase in Eu in analyses from HB is small compared to the increase in Ba, indicating that ¹³⁵Ba¹⁶O⁺ interference is minor. In the Reeves MacDonald deposit and the Josephine-type mineralization at Pend Oreille, however, the Eu content increases significantly with increasing Ba, implying that ¹³⁵Ba¹⁶O⁺ interference may be significant. Abbreviations: cg: coarse grained; fg: fine grained; mg: medium grained; sp: sparry.

respectively. Comparison of Ba content with Eu-Eu* using the whole data set further indicates that there is no significant polyatomic interference ($R^2 = 0.0682$, slope = 0.0003), indicating no Ba–Eu-Eu* relationship.

In most of the studied deposits, the effect of $^{135}Ba^{16}O^+$ interference on measured ^{151}Eu can be considered nonexistent or negligible, especially where Ba content is low and Eu content is relatively high; however, analyses of carbonates from four deposits (Jersey-Emerald, HB, Pend Oreille, and Reeves MacDonald) show non-negligible correlation as expressed through the coefficient of determination (R²) between Ba and Eu in carbonate minerals. At Jersey-Emerald (R² = 0.86 for all calcite samples), HB (R² = 0.57 for dolomite), Pend Oreille (R² = 0.96 for dolomite from Josephine-type mineralization), and Reeves MacDonald ($R^2 = 0.86$ for all carbonates; $R^2 = 0.49$ for only Ba-rich sample 2007SP-022-8), the possibility that ¹³⁵Ba¹⁶O⁺ polyatomic interference may contribute to the observed Eu anomalies (Fig. 18a, b, c, and d) cannot be entirely eliminated. For the Jersey-Emerald deposit (Fig. 18a), the R^2 value is probably an artefact of data clustering caused by two petrographically indistinguishable generations of carbonate minerals (i.e. two populations rather than a single oval-shaped 'cloud' of data): Ba-rich (sulfide-related) and Ba-poor (unmineralized) calcite. The statistically significant coefficient of determination between Ba and Eu for dolomite analyses from the HB deposit (Fig. 18b) corresponds to little change in Eu (0.06–0.33 ppm) and a large change in Ba

Figure 19. Binary plots of Th content versus total rare-earth element (REE) content to evaluate possible contamination of carbonate analyses by submicroscopic clay particles. Only the **a**) Munroe, **b**) Monarch, and **c**) Coral deposits have analyses above the threshold Th content of 0.2 ppm, where clay contamination severely impacts the measurable REE content of carbonates. Of these three deposits, only analyses from Coral show the expected positive correlation of Th with total REE that is indicative of clay contamination. Abbreviations: fg: fine grained; mg: medium grained; cg: coarse grained; sp: sparry.

content (13–244 ppm), implying that the effect of ¹³⁵Ba¹⁶O⁺ interference, if present, was minimal. Analyses of carbonates from Pend Oreille (Josephine-type mineralization; Fig. 18c) and Reeves MacDonald (Fig. 18d) indicate that increases in the Ba content are accompanied by relatively large increases in Eu, implying that ¹³⁵Ba¹⁶O⁺ interference in these analyses cannot be discounted. These findings are further supported by the use of the purely analytical approach (S. Jackson, pers. comm., 2019) of considering the likely effect of the BaO interference on Eu using a ThO-Th ratio of 0.5% (typical for LA-ICP-MS). Given that Ba forms oxides approximately 50 times less vigorously than Th, BaO-Ba would be approximately 0.01%. The abundance of ¹³⁵Ba is 6.6% of all Ba and ¹⁵¹Eu is 48% of all Eu, effectively further attenuating the interference seven-fold; therefore, the effective interference of BaO is on the order of 0.0014%. Thus, a sample with 7000 ppm Ba might have produced an interference equivalent to approximately 0.1 ppm of Eu; this is similar to our data for the Reeves MacDonald calcite. It also suggests that the interference is probably not significant in the other deposits.

Assessment of possible contaminants

One of the main advantages of the LA-ICP-MS method over solution ICP-MS analyses of whole rock or mineral concentrates is that the analyst can carefully select grains for analysis and avoid, or at least significantly reduce, the contamination of carbonate analyses by microscopic clay or other detrital particles. Contamination by clay particles (richer in REE than calcite or dolomite) on whole-rock analyses of carbonate-rich rocks results in flattened PAASnormalized REE plots, in particular, the LREE part of the diagram (e.g. Fig. 15c). As per Callen and Herrmann (2019), contamination by clay can be detected on the carbonate REE profiles if Th content exceeds a threshold value of 0.2 ppm. Thorium content is below 0.2 ppm in carbonate samples from all the deposits that we considered here, except for Munroe, Monarch, and Coral (Fig. 19). Of these three deposits, only the data from Coral show a positive correlation between Th and $\sum \text{REE}$ (R² = 0.49 for coarse dolomite), as would be expected by progressive clay contamination. Data from the Monarch and Munroe deposits show no systematic covariation of Th and \sum REE, implying that the high Th in these analyses is not likely due to contamination by clay particles. This indicates that our flat REE profiles for dolomite from Reeves MacDonald, Pend Oreille (Yellowhead-type mineralization), Robb Lake, and possibly Munroe are unlikely to reflect contamination of carbonates by microscopic or submicroscopic clay particles. Similarly, the flat REE profiles for calcite from Jersey-Emerald, HB, and Duncan are most likely not an artefact of contamination by clay particles.

CONCLUSIONS AND SUMMARY

This study, based on 218 LA-ICP-MS carbonate analyses from 12 deposits, demonstrates that calcite and dolomite from carbonate-hosted Zn-Pb deposits of the Kootenay Arc and Rocky Mountains display significant differences in REE content, overall patterns of PAAS-normalized REE plots, and intensity of Eu, Ce, and Pr anomalies. In the case of fine-grained carbonates, these variations are probably due, at least in part, to the modification of the REE signature of the original carbonates by interaction with fluids during one or more of the following overprints: later diagenetic, dolomitizing, hydrothermal, contact metamorphic, and/or regional metamorphic.

Most (approximately 85%) of the carbonate minerals analyzed plot outside of the field corresponding to shallow oxic seawater on a Ce-Ce* versus Pr-Pr* (PAAS-normalized) diagram, indicating post-depositional re-equilibration related to one or more processes (e.g. crys-tallization from hydrothermal fluids, or crystallization or re-crystallization under a partially open system from, or in the presence of, metamorphic fluid).

In general, carbonates with strong positive Eu anomalies, particularly those associated with convex upward patterns (increase in MREE and HREE), indicate precipitation from, or recrystallization in the presence of, hot (>200°C) hydrothermal fluids.

To determine if regional metamorphic fluids may have contributed to the anomalous PAAS-normalized REE patterns, more carbonates from country rock samples should be analyzed for their REE content. The LA-ICP-MS analytical data do not significantly indicate ¹³⁵Ba¹⁶O⁺–Eu interference; consequently, the data presented here are free of spurious positive Eu anomalies.

Furthermore, with the possible exception of carbonate analyses from the Coral deposit, contamination by clay particles did not have a significant effect on the PAAS-normalized carbonate REE profiles.

Full understanding of these observations, including the trends on Ce-Ce* versus Pr-Pr* (PAAS-normalized) diagrams, requires interpretation in conjunction with corresponding detailed major element analyses; detailed paragenetic studies; C, O, and clumped C and O isotope analyses; Sr and other radiogenic isotope analyses; and fluid-inclusion petrography and microthermometry.

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