REE in carbonates from sediment-hosted Pb-Zn deposits, British Columbia, Canada

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Introduction

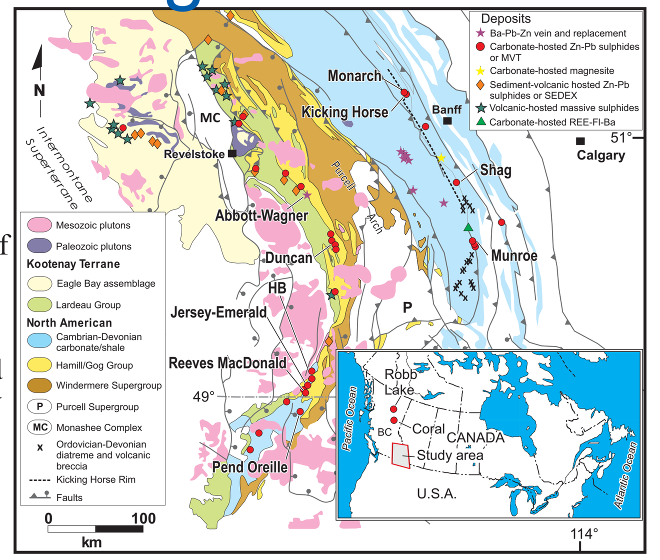
Paleozoic platform carbonate rocks of the Rocky Mountains host Mississippi Valley-type (MVT) deposits in the north, and in the south host MVT, magnesite, barite, and Rare Earth Element (REE)-Ba-F deposits. Farther to the west of the Rocky Mountains, the platform carbonate rocks of the Kootenay arc pericratonic terrane also host MVT deposits in addition to vein- and replacement-type Zn-Pb (±Ag, ±Au) deposits. Sparry dolomitization is commonly spatially associated with most of these deposits and is used as an exploration guide.

This is the first systematic study documenting REE variations in carbonate minerals from MVT deposits. In conjunction with tectonic, stratigraphic, structural, stable and radiogenic isotope, and petrographic studies it will help to constrain the genesis of MVT deposits and improve our knowledge of the metallogeny of the Kootenay arc and Rocky Mountains. It is based on more than 200 analyses by Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS), supported by electron microprobe work. Investigated samples are from the Munroe, Shag, Kicking Horse, Monarch, Coral and Robb Lake deposits in the Rocky Mountain belt, and from the Pend Oreille, Reeves MacDonald, Jersey-Emerald, HB, Duncan and Abbott-Wagner (a fracture-controlled replacement) deposits within the Kootenay arc.

In addition to high spatial resolution, LA-ICP-MS offers a further advantage over traditional whole rock analyses of carbonate concentrates: allowing the analyst to identify compositional artefacts from inclusions and interstitial material through careful examination for sharp compositional changes within the time-resolved spectrum of each analysis. Thus, selection of carbonate grains free of visible mineral inclusions, followed by examination of corresponding LA-ICP-MS spectra permits identification and rejection of 'contaminated' analyses, retaining only the analyses representing the trace element signature of carbonates. The high spatial resolution of the LA-ICP-MS method requires a large number of individual analyses to ensure that results are representative.

Geologic Setting

All of the deposits considered in this study are carbonate-hosted. They are all MVT as characterized by Leach et al. (2005) and Paradis et al. (2007), with the exception of Abbott-Wagner, (fracture-controlled replacement). All of the occurrences studied are in British Columbia, except for Pend Oreille (Washington state, USA). Deposits selected for this study are in the Rocky Mountain belt and the Kootenay arc. Kicking Horse, Monarch and Shag are spatially associated with the Kicking Horse Rim, a fault-bound Precambrian paleo-bathymetric high. Two deposits (Robb Lake and Coral) are located in the northern Rocky Mountains, outside the area depicted in Figure 1 (see inset).



Map showing the locations of the deposits studied in this work. The Robb Lake and Coral deposits are shown on the inset map.

Biostratigraphic ages of sedimentary rocks hosting these deposits vary from lower Cambrian to Upper Devonian. Radiometric ages are unavailable for most of the deposits we have studied as it is notoriously difficult to obtain ages from low temperature, sediment-hosted deposits. 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 calcsilicate minerals except where they are located in the contact metamorphic aureoles of Mesozoic intrusions (e.g., Jersey-Emerald deposit).

Analytical Methods

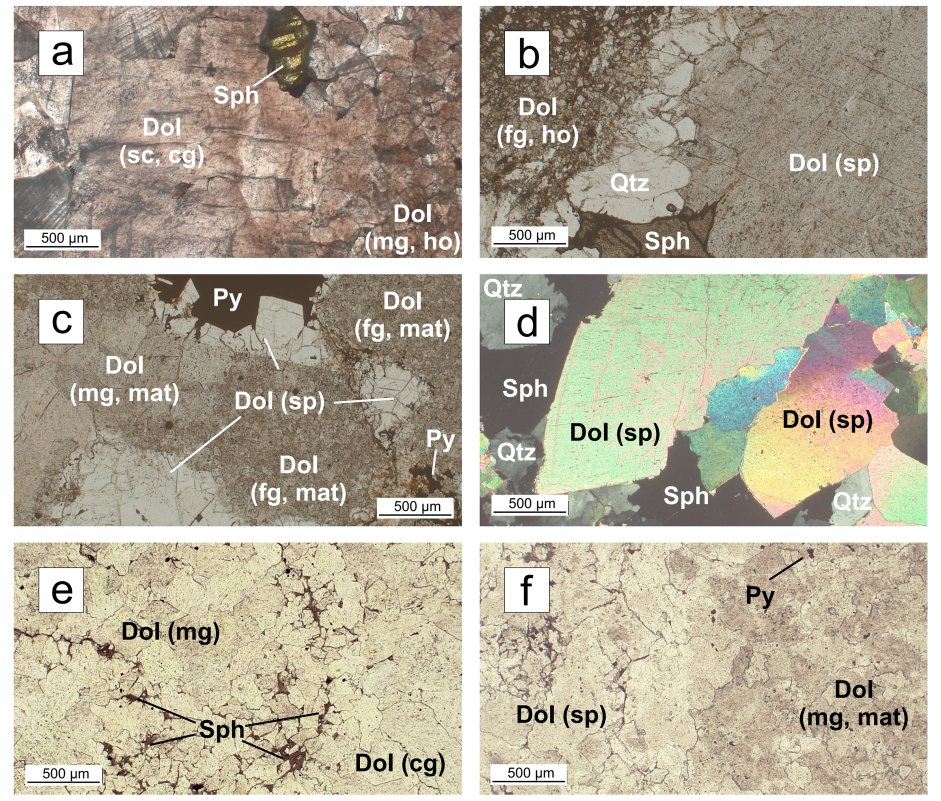
LA-ICP-MS analyses were carried out at the University of Victoria using a NewWave UP-213 (Nd-YAG laser, 213 nm) interfaced to either a Thermo-Fisher X-series 2 quadrupole ICP-MS or an Agilent 8800 triple quadrupole ICP-MS. Repeated analyses of the calibration standards (NIST 615, NIST 613, NIST 611) showed no measurable drift in instrument sensitivity over the course of each analytical session. The content of elements in the BCR2g standard thus obtained are within 15% (relative) of the GeoReM preferred value (Jochum et al., 2005) and repeated measurements over the course of each analytical session showed that analytical precision for the REE+Y is within 10% relative.

Definitions

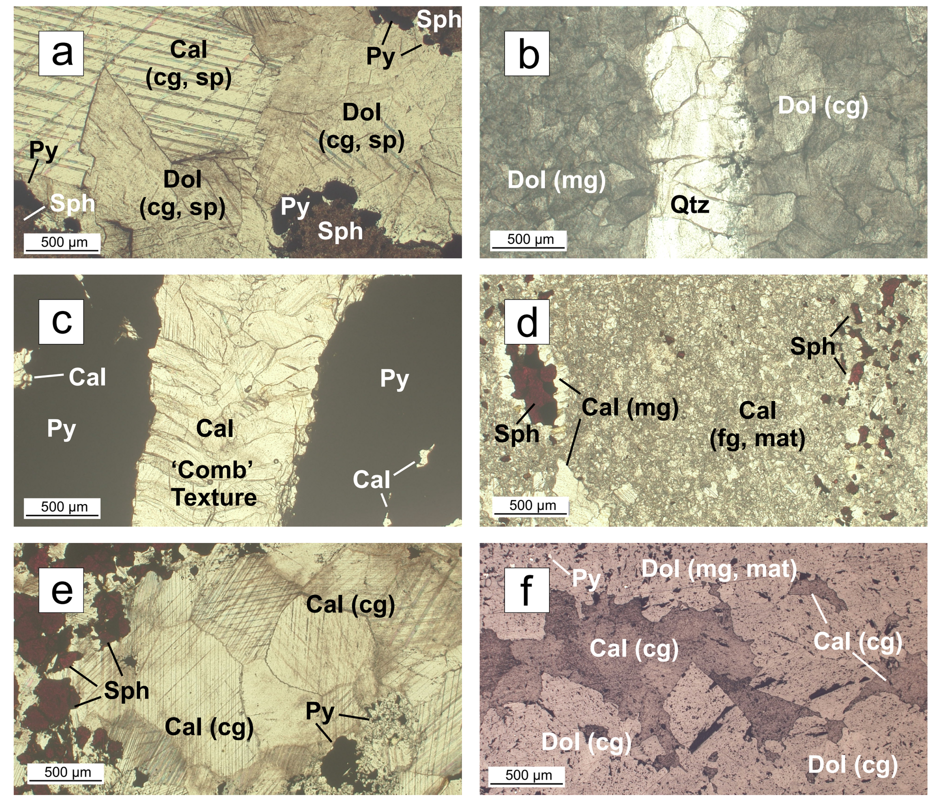
PAAS: Post-Archean Australian Shale
FCR: Fracture-controlled replacement deposit
LREE: Light Rare Earth Elements
MREE: Middle Rare Earth Elements
HREE: Heavy Rare Earth Elements
Pr Anomaly: $(Pr/Pr^*)_{PAAS} = Pr_{PAAS}/(\tfrac{1}{2}Ce_{PAAS} + \tfrac{1}{2}Nd_{PAAS})$
Ce Anomaly: $(Ce/Ce^*)_{PAAS} = Ce_{PAAS}/(\tfrac{1}{2}\cdot La_{PAAS} + \tfrac{1}{2}\cdot Pr_{PAAS})$
Eu Anomaly: $(Eu/Eu^*)_{PAAS} = Eu_{PAAS}/(\tfrac{2}{3}\cdot Sm_{PAAS} + \tfrac{1}{3}\cdot Tb_{PAAS})$
Values less than or greater than 1 indicate negative and positive anomalies, respectively, as proposed by Bau and Dulski (1996).

Abbreviations

Cal – calcite; **Dol** – dolomite; **Py** – pyrite; **Qtz** – quartz; **Sph** – sphalerite; **fg** – fine grained (< 0.05 mm); **mg** – medium-grained (0.05 – 0.4 mm); **cg** – coarse-grained (> 0.4 mm); **ppl** – plane polarized light; ; **rl** – reflected light; **xpl** – cross-polarized light; **ho** – host; **mat** – matrix; **sc** – saccharoidal; **sp** – sparry; **adj** – adjacent.



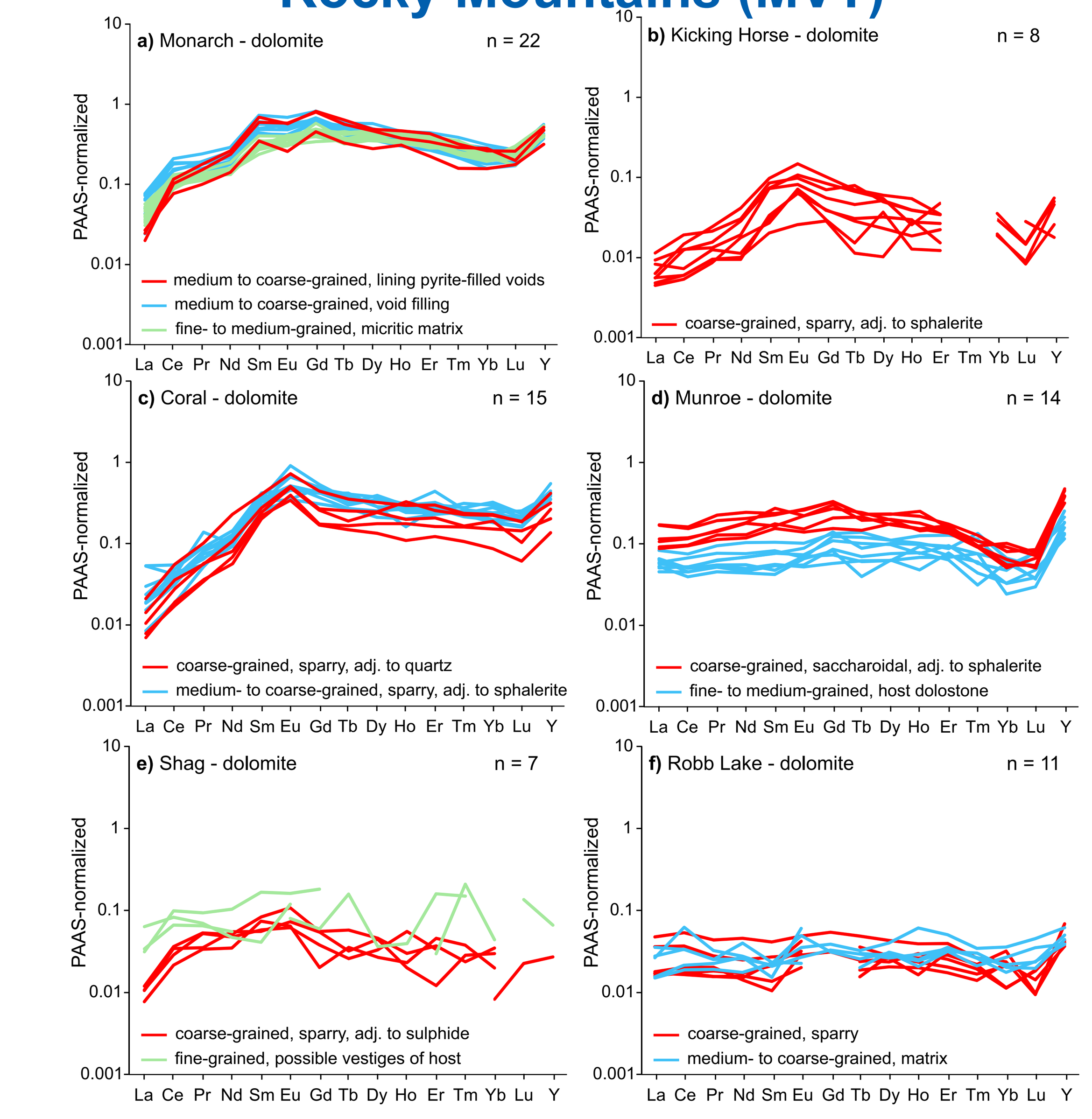
Microphotographs of dolomite from the Rocky Mountain MVT deposits. (**a**) Munroe deposit, sample MUNR-16-18T (ppl); (**b**) Shag deposit, sample SHAG-C4-7A (ppl); (**c**) Monarch deposit, sample MON-16-5 (ppl); (**d**) Coral deposit, sample HDC Tr 1a (xpl); (**e**) Coral deposit, sample HDC Tr 1a (ppl); (**f**) Robb Lake deposit, sample 3-1(ppl).



Microphotographs of carbonates from the Kootenay arc MVT deposits. (**a**) Pend Oreille deposit, sample 07-MET-12A-3 (Yellowhead-type mineralization; ppl); (**b**) Pend Oreille deposit, sample MET-07-2 (Josephine-type mineralization; ppl); (**c**) Reeves MacDonald deposit, sample 2007-022-13b (ppl); (**d**) Jersey-Emerald deposit, sample 08SP75-1 (ppl); (**e**) Jersey-Emerald deposit, sample 08SP75-1 (ppl); (**f**) HB deposit, sample HB-DUMP-5 (rl).

PAAS normalized REE Patterns

Rocky Mountains (MVT)

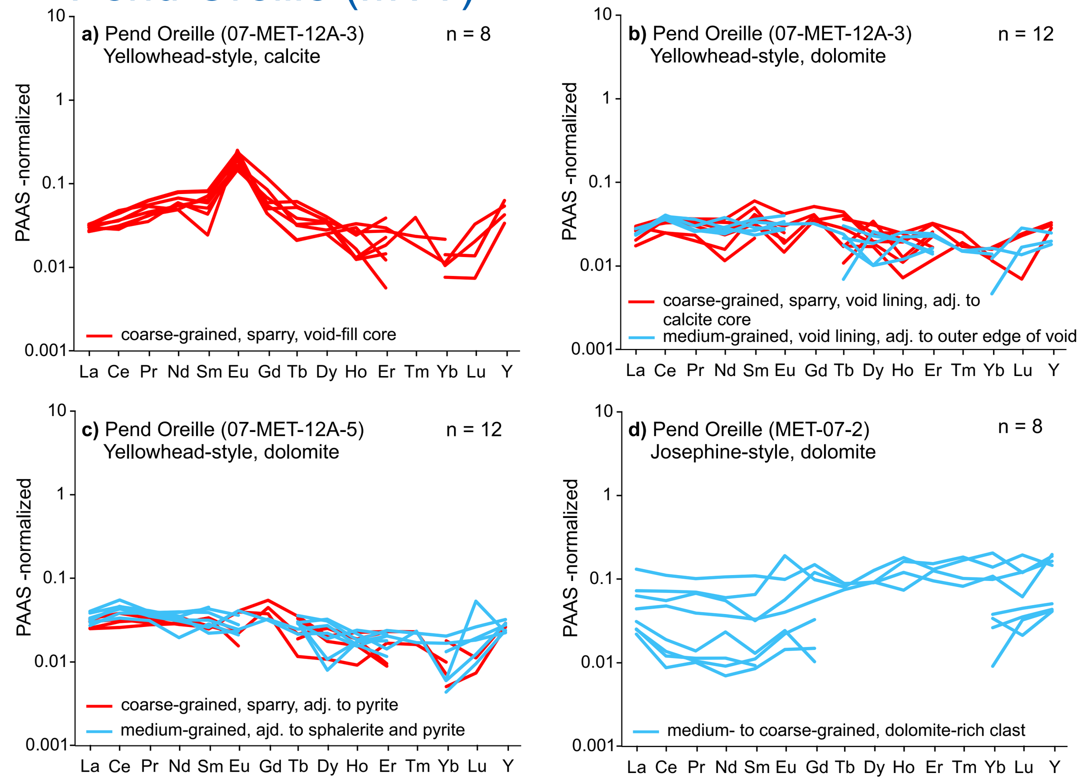


PAAS-normalized REE profiles of carbonates from MVT deposits, (**a**) Monarch (**b**) Kicking Horse (**c**) Coral (**d**) Munroe (**e**) Shag (**f**) Robb Lake, within the Rocky Mountains.

All dolomite, irrespective of texture, from the Monarch, Kicking Horse and Coral deposits show similar convex-upward REE profiles with steep positive LREE slopes and shallower MREE to HREE slopes. A positive Eu anomaly is exhibited in Kicking Horse (weaker) and Coral (stronger).

Munroe, Shag and Robb lake exhibit relatively flat profiles. Munroe and Shag have a slightly convex-upward shape that is not observed at Robb Lake. Shag has a slight negative LREE slope.

Pend Oreille (MVT)



PAAS-normalized REE profiles for calcite and dolomite from the Yellowhead- (**a, b, c**) and Josephine-type mineralization (**d**) from Pend Oreille in the Kootenay arc

(a) Sparry calcite in Yellowhead-type mineralization (sample 07-MET-12A-3) show REE profiles with a positive LREE to MREE slope and a steeper, negative MREE to HREE slope, with a positive Eu anomaly.

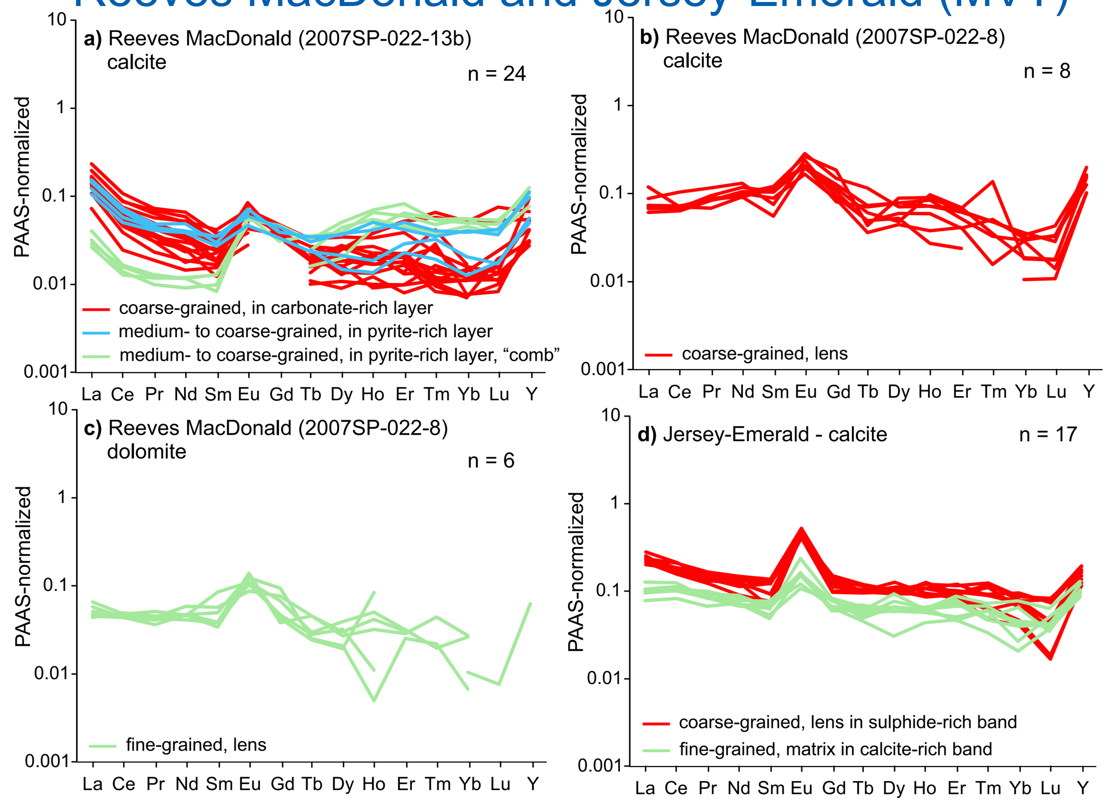
(b) Dolomite in Yellowhead-type mineralization (sample 07-MET-12A-3) has an overall flat to slightly negative sloping REE profile.

(c) Both dolomite types in Yellowhead-type mineralization (sample 07-MET-12A-5) have flat to slightly negative sloping REE profiles, regardless of texture.

(d) Dolomite in Josephine-type mineralization (sample MET-07-2) shows an overall positively sloping REE profile with a flat to convex-upward profile in the LREE.

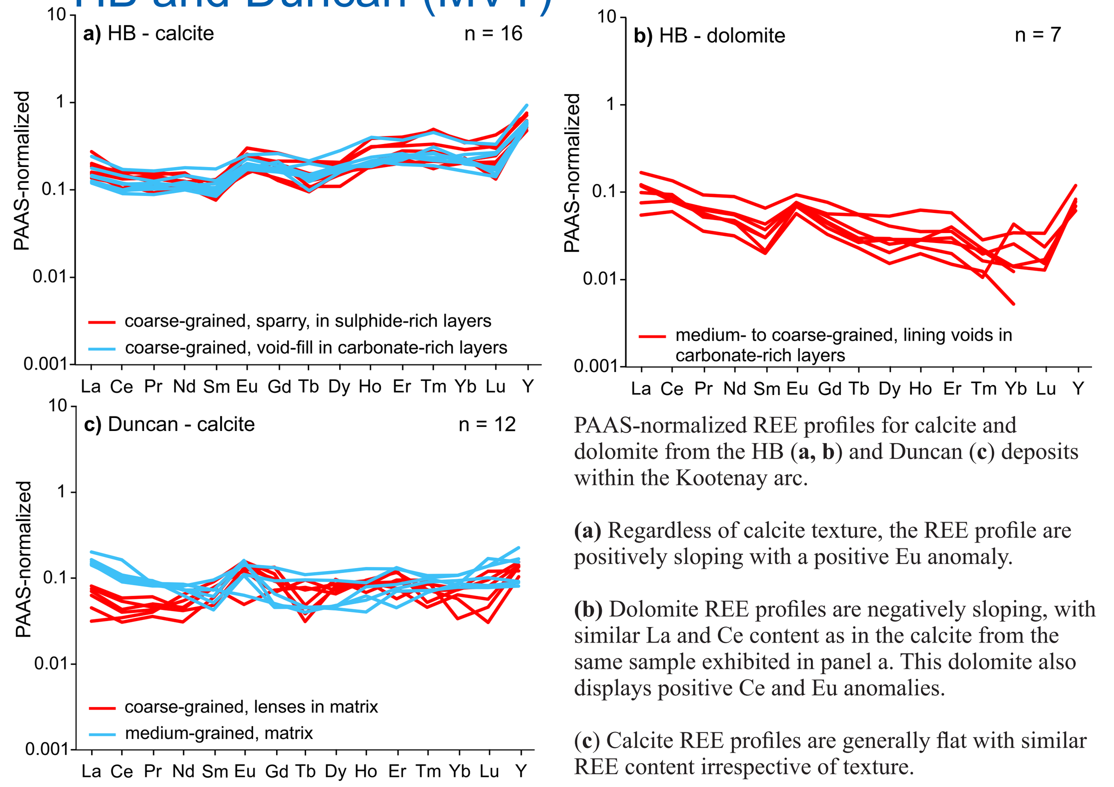
Kootenay Arc

Reeves MacDonald and Jersey-Emerald (MVT)



PAAS-normalized REE profiles for calcite and dolomite from the Reeves MacDonald (**a, b, c**) and Jersey-Emerald (**d**) deposits within the Kootenay arc. (**a**) In sample 2007SP-022-13b, calcite shows negative sloping LREE profiles and flat to slightly negative or positive MREE to HREE profiles, except where present with the "comb" texture which exhibits positive MREE to HREE slopes 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**) Dolomite from sample 2007SP-022-8 has a similar REE profiles to calcite from this sample, but with slightly lower overall content; **d)** All calcite, irrespective of texture, from the Jersey-Emerald deposit has a generally flat to slightly negative overall slope.

HB and Duncan (MVT)



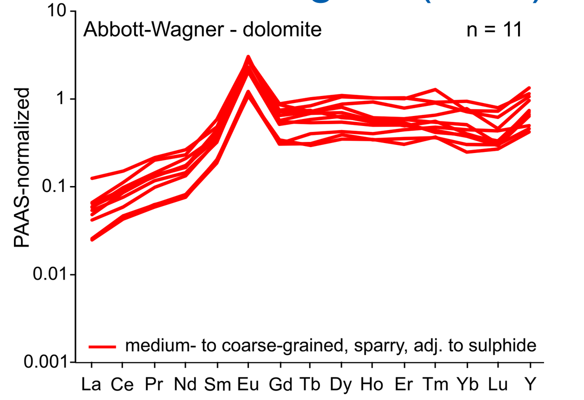
PAAS-normalized REE profiles for calcite and dolomite from the HB (**a, b**) and Duncan (**c**) deposits within the Kootenay arc.

(a) Regardless of calcite texture, the REE profile are positively sloping with a positive Eu anomaly.

(b) Dolomite REE profiles are negatively sloping, with similar La and Ce content as in the calcite from the same sample exhibited in panel a. This dolomite also displays positive Ce and Eu anomalies.

(c) Calcite REE profiles are generally flat with similar REE content irrespective of texture.

Abbott-Wagner (FCR)

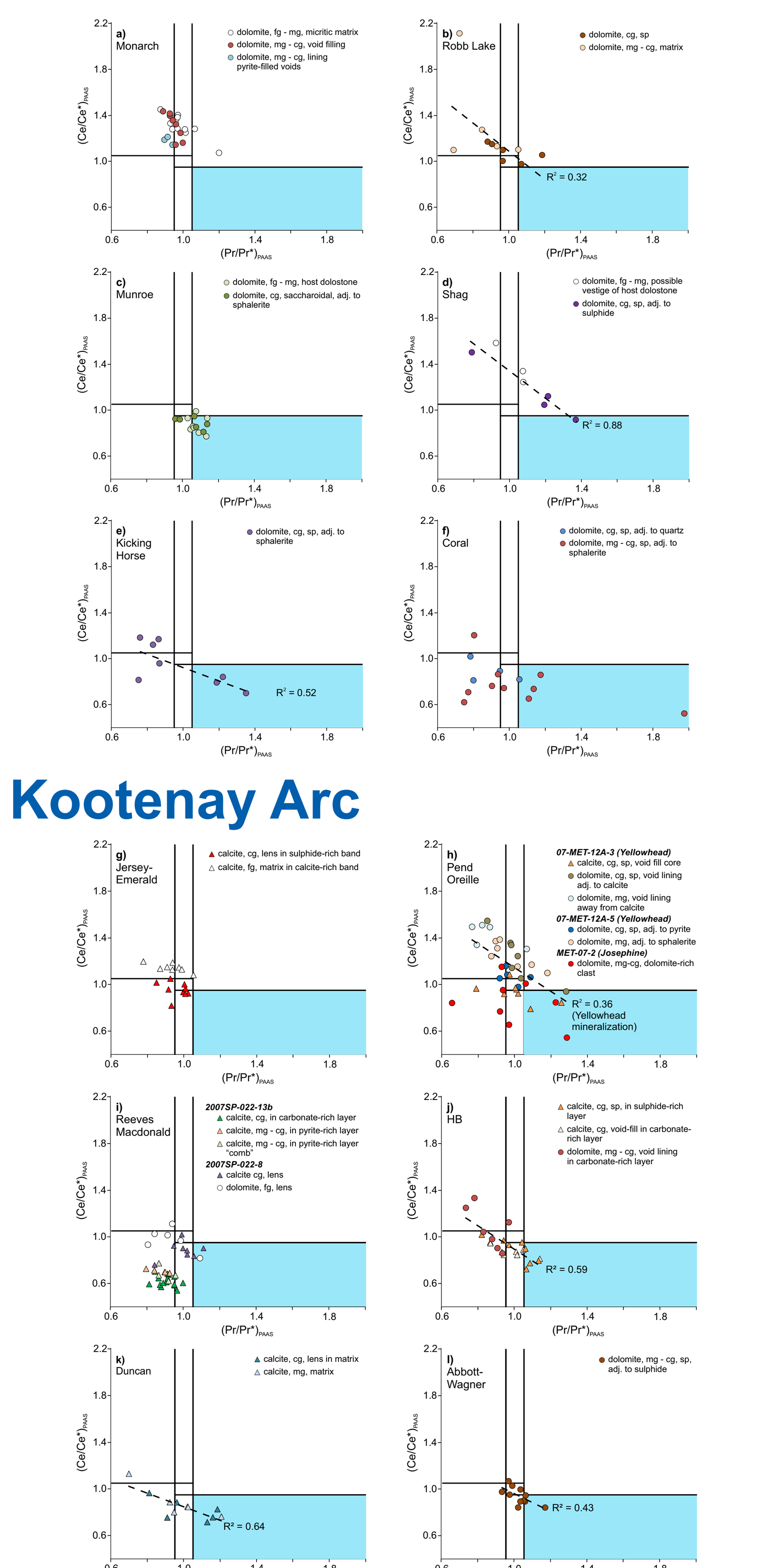


PAAS-normalized REE profiles for dolomite from the fracture-controlled replacement deposit (FCR), Abbott-Wagner, in the Kootenay arc show positive LREE to MREE slopes with flat MREE to HREE profiles, and a positive Eu anomaly.

Ce Anomaly

Rocky Mountains

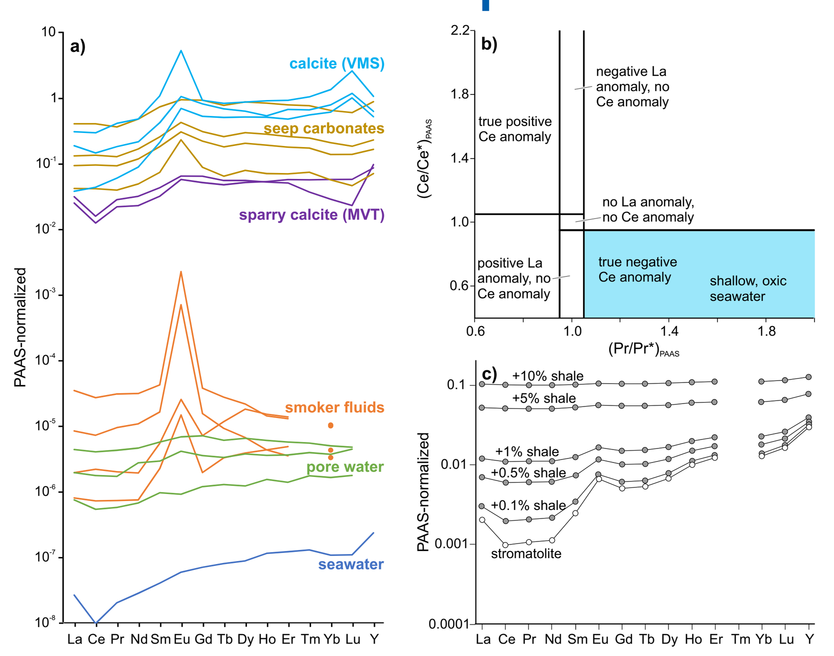
Kootenay Arc



PAAS-normalized Ce anomalies versus Pr anomalies for the Rocky Mountain and Kootenay arc MVT deposits. Rocky Mountain deposits: (**a**) Monarch, (**b**) Robb Lake, (**c**) Munroe, (**d**) Shag, (**e**) Kicking Horse, (**f**) Coral. No analyses from the Monarch or Robb Lake deposits plot within the seawater field (pale blue, lower right quadrant), however over half of the analyses from Munroe plot in this field. Only a minority of analyses from the other deposits plot in the seawater field. Kootenay arc deposits: (**g**) Jersey-Emerald, (**h**) Pend Oreille, (**i**) Reeves MacDonald, (**j**) HB, (**k**) Duncan, (**l**) Abbott-Wagner. Analyses from the Jersey-Emerald deposit plot exclusively outside the seawater field and a minority of analyses from all Kootenay arc deposits studied plot within this field.

The negatively sloping arrays of correlated analyses from Robb Lake, Shag, Kicking Horse, Pend Oreille (Yellowhead mineralization), HB, Duncan and Abbott-Wagner likely indicate post-depositional overprint by reduced fluids.

Guide to Interpretation



(**a**) PAAS-normalized REE profiles for seawater from the western North Pacific (Alibo and Nozaki, 1999) showing the distinct negative Ce anomaly and LREE depletion relative to HREE, pore water from marine sediments on the California margin (Haley et al., 2004), hydrothermal vent 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 sulphide 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).

Summary

1. This study shows that calcite and dolomite from the studied carbonate-hosted Zn-Pb deposits display significant differences in REE content, in the overall shape of PAAS-normalized REE plots, and in the intensity of Eu, Ce, and Pr anomalies. In the case of fine-grained carbonates, these variations are probably due, at least in part, to modification of the REE signature corresponding to original carbonates by later diagenetic, dolomitizing, hydrothermal, contact metamorphic and/or regional metamorphic overprint.

2. Approximately 85% of carbonate minerals analysed plot outside of the shallow seawater field on PAAS-normalized Ce to Pr anomaly diagrams, indicating post-depositional re-equilibration, crystallization from hydrothermal fluids or metamorphic overprint.

3. Strong positive Eu anomalies, particularly if associated with convex upward patterns are interpreted to mark the influence of hot (>200°C) hydrothermal fluids and correspond to carbonates precipitated from, or recrystallized in the presence of ambient hydrothermal fluids.

4. To fully appreciate the significance of these observations, including trends on Ce to Pr (PAAS-normalized) anomaly diagrams, the results presented here will need to be interpreted in conjunction with: the corresponding detailed major element analyses; detailed paragenetic studies; C, O, and Sr isotopes and clumped C and O isotopes; radiogenic isotopes; and fluid inclusion results.

Acknowledgements

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