Base-metal and REE anomalies in lower Palaeozoic sedimentary rocks of Amundsen Land, central North Greenland: implications for Zn-Pb potential

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During the 2013 field season, siliciclastic and carbonate rocks of the lower Palaeozoic sedimentary succession of the Franklinian Basin in Amundsen Land, central North Greenland, were collected for whole-rock geochemical analysis. These data are evaluated here in an attempt to identify possible hydrothermal signatures related to sediment-hosted Zn-Pb mineralisation, similar to that found in correlative strata at the large Citronen Fjord deposit located *c.* 100 km to the east-north-east. In this paper, we use the term Sedex in a broad sense to describe stratiform, sediment-hosted deposits that formed either by syngenetic (exhalative) processes or by sub-sea-floor replacement coeval with sedimentation (e.g. Emsbo *et al.* 2016); the term Mississippi Valley-type (MVT) is used for non-stratiform Zn-Pb deposits that formed epigenetically during late diagenesis or tectonism (e.g. Leach *et al.* 2010).

Regional setting

The Late Precambrian to Devonian Franklinian Basin extends *c.* 2000 km from the Canadian Arctic Islands to eastern North Greenland (Higgins *et al.* 1991). In eastern North Greenland, this basin fill overlies the Proterozoic Independence Fjord Group and the Hagen Fjord Group, corresponding to the passive continental margin of Laurentia. The Franklinian Basin is characterised by a transition from a deep-water trough, with mainly fine-grained siliciclastic strata, separated from shelf carbonates to the south (Fig. 1; Higgins *et al.* 1991). As summarised in Kolb *et al.* (2016), Zn-Pb mineralisation in the Franklinian Basin resulted from two different events: early exhalative and/or sub-sea-floor replacement in deep-water siliciclastic rocks, and late epigenetic MVT mineralisation in shelf carbonates. The present study concerns the potential for Zn-Pb mineralisation in the Lower Ordovician to Lower Silurian Amundsen Land Group, in Amundsen Land. In the study area, the Amundsen Land Group comprises black bedded chert and laminated mudstone, commonly siliceous, with subordinate thin-bedded siliceous turbidites and greenish siltstone; locally, thick redeposited chert and limestone conglomerate interbedded with thick calcareous turbidites are present (Friderichsen *et al.* 1982). The chert contains radiolarians (Higgins *et al.* 1991), implying that biogenic silica is responsible for the quartz-rich nature of these rocks, and the siliceous mudstone.

Approximately 100 km east-north-east of the study area, in northern Peary Land, correlative siliciclastic rocks host the large undeveloped, sediment-hosted Citronen Fjord deposit (Fig. 1; van der Stijl *et al.* 1998), with reported total resources (measured + indicated + inferred), at a 2.0% Zn cut off, of 132 Mt with 4.0% Zn and 0.4% Pb (Ironbark Zinc

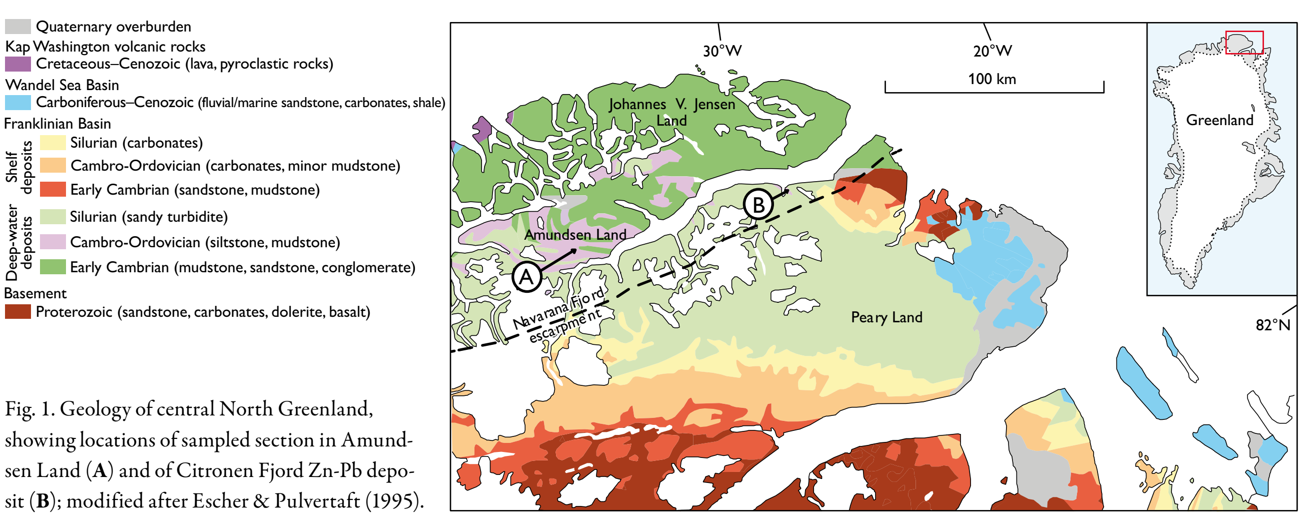

Fig. 1. Geology of central North Greenland, showing locations of sampled section in Amundsen Land (**A**) and of Citronen Fjord Zn-Pb deposit (**B**); modified after Escher & Pulvertaft (1995).

2012). In the model of Slack *et al.* (2015), this deposit formed predominantly by exhalative processes.

Younger epigenetic, carbonate-hosted, MVT Zn-Pb occurrences, found in the carbonate shelf in southern Peary Land, are related to the migration of basinal brines expelled by tectonism and/or hydraulic head caused by Ellesmerian orogenic uplift during the Middle to Late Devonian (Rosa *et al.* 2016). In Amundsen Land, no carbonate shelf exists, so this mineralisation style is not expected to be present, although effects of the Ellesmerian orogeny are well expressed by open to recumbent folds and local thrust faults.

Methods

All samples were collected along one section across strata of the Amundsen Land Group at WGS84 longitude 35°.3647 W and latitude 82°.9655 E (Fig. 1). Twenty-two samples of silty limestone, dolomitic mudstone and mudstone were analysed using a variety of methods. All data are from Acme Analytical Laboratories Ltd. in Vancouver, British Columbia (Canada), except Y and rare-earth elements (REE) that were determined at Activation Laboratories Ltd. in Ancaster, Ontario (Canada). Detailed information on methods, standards, and uncertainties are given on the respective web sites (*www.acmelab.com; www.actlabs.com*). Complete analyses of all 22 samples are available in *Appendix A* (online Excel file).

Results

Several samples have distinctive bulk compositions. For major-element oxides, one of three grey mudstones contains slightly high $Fe_2O_3^T$ (7.83 wt%) relative to average shale (6.75 wt%; Appendix IV in Krauskopf & Bird 1995); this sample also has elevated MnO (0.14 wt%) in contrast to the other samples that contain <0.05 wt% MnO. The three mudstones have uniformly low total S and organic C (<0.8 wt% and <0.7 wt%, respectively). For metals of economic and exploration interest, one mudstone sample is noteworthy for having slightly anomalous Zn (174 ppm), Pb (29.6 ppm), Ni (75.0 ppm) and As (24.7 ppm) relative to average concentrations in shale (Zn = 95 ppm; Pb = 20 ppm; Ni = 68 ppm; As = 13 ppm; Krauskopf & Bird 1995, Appendix IV). One sample of silty limestone has the highest total S (1.27 wt%) and Pb (63.0 ppm) among all 22 analysed samples, the latter concentration being highly anomalous relative to the average of 3.1 ppm Pb for unaltered limestone (Hartree & Veizer 1982).

Abundances of REE vary greatly from 0.6–2.0 × average Post-Archaean Australian Shale (PAAS; Fig. 2). Most of the mudstone and all of the carbonate-rich samples (silty limestone, dolomitic limestone, calcareous shale) display

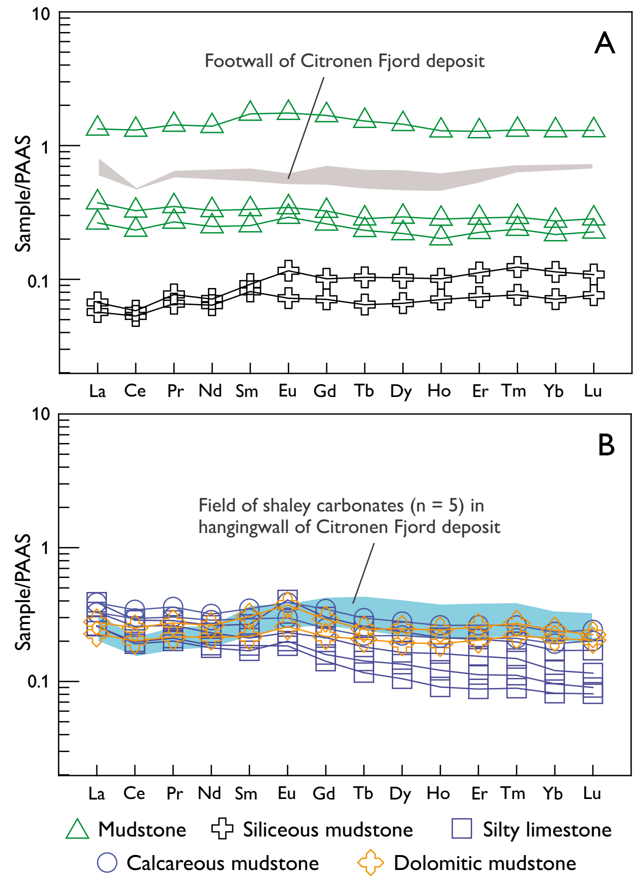

Fig. 2. Plots of rare-earth element concentrations of representative samples of early Palaeozoic sedimentary rocks from Amundsen Land Group in Amundsen Land. **A:** mudstone and siliceous mudstone. **B:** Calcareous mudstone, dolomitic mudstone, and silty limestone. Field of samples hosting the Citronen Fjord deposit are included (Slack *et al.* 2015), for comparison; note that small positive Eu anomalies for these samples (1.16-1.29) are not evident due to overlapping patterns. Normalisations are to average Post-Archean Australian Shale (PAAS); data from Taylor & McLennan (1985).

relatively flat PAAS-normalised patterns, which are typical of sedimentary rocks from throughout the geological record (e.g. McLennan 1989). However, one mudstone and both siliceous mudstone samples show slight depletion of light rare-earth elements (LREE). Most of the silty limestone samples display slight enrichment of LREE. Calculated Eu anomalies (Eu/Eu*), relative to PAAS, range from 0.90 to 1.51; 20 of 22 samples have positive anomalies, the three highest values (1.41–1.51) occurring in silty limestone. These Eu anomalies are not an analytical artifact of Ba interference on Eu (e.g. Slack *et al.* 2004), because no correlation exists between Eu/Eu* and Ba. Also important is the fact that all samples display small negative Ce anomalies (Ce/Ce*), which relative to PAAS vary from 0.81 to 0.95; most are true anomalies (i.e., unrelated to anomalous La enrichment), based on a discriminant plot of Pr/Pr* vs Ce/Ce* (Fig. 3).

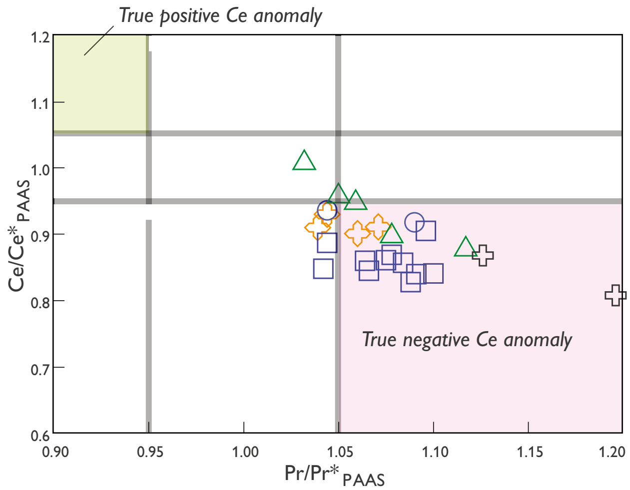

Fig. 3. Plot of Ce anomaly (Ce/Ce*) vs Pr anomaly (Pr/Pr*) for analysed samples of early Palaeozoic sedimentary rocks from the Amundsen Land Group in Amundsen Land. Data are normalised to PAAS. Fields after Bau & Dulski (1996). Symbols as in Fig. 2.

Discussion

The presence in one mudstone sample of slightly high $Fe_2O_3^T$, Zn, Pb, Ni and As is permissive evidence of a hydrothermal component being present in the basin. The small LREE depletion in this sample and in the two siliceous mudstone samples (Fig. 2A), likely reflects the dissolution of detrital apatite, which in low-temperature sedimentary environments occurs by interaction with acidic fluids and not typical seawater-derived pore fluids (see Slack *et al.* 2017).

The geochemical data for this mudstone sample, namely elevated MnO together with very low Mo, record sedimentation and early diagenesis in oxic bottom waters (e.g. Slack *et al.* 2017). Oxic bottom waters are consistent with the presence of small negative Ce anomalies in this sample, in both siliceous mudstone samples, and in most of the carbonate-rich rocks. These conditions, as well as the apparently low availability of H_2S in pore fluids beneath the palaeo-sea floor (total S <0.8 wt%), were also proposed by Slack *et al.* (2015) for the host sedimentary rocks during initial formation of the Citronen Fjord deposit. However, according to their model for that deposit, only after emplacement of debris flows that physically restricted the local basin and sealed off communication with the larger oxic ocean, did the venting of hydrothermal fluids turn the bottom waters anoxic and possibly locally very reducing (euxinic) and allow for sulphide preservation. If this model for the redox evolution of the Citronen Fjord deposit is correct, an analogous scenario for Amundsen Land (this study) hinges on verifying the local presence of anoxic to euxinic bottom waters, a requirement as yet unachieved, without supporting evidence from additional sampling and analyses.

The presence of small positive Eu anomalies in most samples is consistent with a hydrothermal component (e.g. Lottermoser 1992). However, other non-hydrothermal processes can also create small positive Eu anomalies in sedimentary rocks, both siliciclastic and carbonate. For example, in organic-rich black shales, small positive Eu anomalies may form diagenetically in euxinic pore fluids (Slack *et al.* 2017, and references therein), but no evidence of such fluids exists in the geochemically anomalous mudstone, based on its elevated MnO (0.14 wt%) coupled with low organic C (0.37 wt%) and very low Mo (1.75 ppm) contents, which together indicate oxic (not anoxic or euxinic) bottom waters and pore fluids (see Slack *et al.* 2017). Furthermore, TOC values lack any correlation with metal concentrations. The relatively high $Fe_2O_3^T$ content of this mudstone sample could be a hydrothermal signature, but might also reflect a detrital component derived from a Fe-rich source area. Regarding the positive Eu anomalies present in all of the carbonate samples, a possible non-hydrothermal origin for this anomaly may be related to a large clay component (Tostevin *et al.* 2016), but this explanation is ruled out by the fact that the samples with the highest Eu/Eu* values (1.41–1.51) have uniformly low Al_2O_3 (0.49–0.62 wt%). Given these observations, we conclude that the small positive Eu anomalies reflect a hydrothermal signature, involving the passage of reduced fluids that preferentially carried Eu^{2+} (Bau 1991). Importantly, a hydrothermal origin has also been proposed by several workers for positive Eu anomalies in the carbonate gangue and carbonate-rich wall rocks and country rocks of several stratiform Sedex deposits (e.g. Slack *et al.* 2004; Frimmel 2009).

The inferred hydrothermal component in the early Palaeozoic siliciclastic and carbonate rocks of the studied section can be ascribed to either a distal or a proximal source, or both. In the case of a distal source, the likely prolonged (*c.* 10^5–10^6 y) venting of hydrothermal fluids into seawater to form the Citronen Fjord deposit could account for the Eu incorporated into the distal mudstones and carbonates of Amundsen Land during sedimentation, by mixing of hydrothermally derived Eu with seawater. In the latter case, involving a proximal source, the observed base-metal and REE anomalies – both Eu and LREE – in the samples analysed here could record a hydrothermal signature from a local system of either syngenetic or epigenetic origin. Given the apparent lack of organic-rich black shales in the study area with anoxic or euxinic redox signatures, a syngenetic origin for this postulated Zn-Pb mineralisation is considered unlikely, either by purely exhalative or downward-penetrating brine processes (Emsbo *et al.* 2016; Sangster 2018). The occurrence of undiscovered MVT Zn-Pb deposits is also possible (Rosa *et al.* 2016), but this type of mineralisation is characterised by negative, not positive, Eu anomalies in carbonate host rocks and gangue minerals (e.g. Graf 1984; Souissi *et al.* 2013).

In summary, considering all available field and geochemical data, including the lack of evidence for anoxic or euxinic bottom waters during sedimentation, we suggest that the base-metal and REE anomalies highlighted in this study from the Amundsen Land Group, in Amundsen Land, favour a potential for local Sedex Zn-Pb mineralisation that formed mainly by the sub-sea-floor replacement of carbonate-rich sediments. Additional sampling and geochemical analysis are recommended for the study area, in order to better evaluate this mineral potential.

Acknowledgements

This work was financially supported by GEUS and the Ministry of Mineral Resources of Greenland, through the Nordzinc project. Additional support was provided by the Northwest Territories Geological Survey, Canada. Per Kalvig and Erik Vest Sørensen of GEUS are acknowledged for collaboration during field work. We thank Hartwig Frimmel (University of Würzburg) and Steve Piercey (Memorial University of Newfoundland) for helpful reviews.

Online Appendix A: *Whole-rock analyses of early Palaeozoic sedimentary rocks from the Amundsen Land Group in Amundsen Land.*

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