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Cycling of rare earth elements at the Precambrian-Cambrian boundary

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ABSTRACT

The Great Unconformity at the Precambrian-Cambrian boundary marks a global erosion surface, and a time gap which in places exceeded a billion years. The weathered sub-Cambrian rocks include abundant granites and pegmatites. These rocks and others were mineralized in several regions. The basal Cambrian sediments show that rare commodities including gold and rare earth elements (REEs) were concentrated from sub-Cambrian sources by both chemical and physical processes. The clay-rich unconformity in Europe demonstrates the weathering of Palaeoproterozoic pegmatites (~1.2 billion years older) and liberation of strontium and REEs to reprecipitate as authigenic phosphate minerals. This is consistent with a global strontium isotope excursion at the Precambrian-Cambrian boundary. The global extent of sub-Cambrian granites and pegmatites indicates a possible exploration play for REEs. More generally, the abundance of ores exposed on the surface globally, and examples of early Cambrian enrichment, indicate that the surface has high potential for exploration of rare elements.

1. Introduction

The Precambrian–Cambrian boundary represents one of the most globally significant episodes of change in the geological record. It was a time of both geochemical change and faunal evolution, which were probably linked to at least some degree (Wille et al., 2008; Peters and Gaines, 2012; Parnell et al., 2014; Medaris et al., 2018). The episode involved marine transgression across intensely weathered surfaces, which show extensive alteration and related planation to a degree unique in geological history. The altered surface can be traced across the Pan-African Orogen for 6000 km from Morocco to Oman (Avigad et al., 2005), across much of the Baltic region (Nielsen and Schovsbo, 2011), and over much of North America (Ambrose, 1964).

A previous investigation showed that there was a relatively high abundance of ore deposits on the sub-Cambrian surface, and that many of these deposits were weathered and even enriched before the subsequent peneplanation and transgression (Parnell et al., 2014). The wide variety of ore deposits exposed on the surface included gold, iron, copper and platinum group element (PGE) deposits (Fig. 1). The formation of palaeoplacers, and the supergene enrichment of ore bodies, both led to economic concentrations of metals, documented by Parnell et al. (2014). In addition to the direct evidence from metalliferous deposits on the sub-Cambrian surface, there is an implication of metal contribution from older deposits where they are truncated by the surface. For example, PGE-bearing deposits at Stillwater, Montana (Jackson, 1968) and Platinum City, Wyoming (Hausel, 1989) are both truncated by basal Cambrian sediments (Fig. 2), which indicates that PGEs were eroded and liberated into the surface environment. Similarly, banded iron formation in many countries is truncated by the sub-Cambrian surface (Fig. 3). Subsequently, further examples of mineralization of the unconformity have been described, including iron-manganese on the surface in Norway (Gabrielsen et al., 2015), and gold-bearing palaeoplacers in southern Sinai, Egypt (Saber, 2020). Other examples of gold-bearing palaeoplacer deposits in Cambrian sandstones occur in Saskatchewan (Rogers, 2011), South Dakota (Paterson et al., 1988), Wyoming (Hausel and Graves, 1996), Texas (Heylmun, 2001), the Siberian Platform (Konstantinovskii, 2001) and Spain (Pérez-García et al., 2000). As the exploration for pegmatites increases globally (Linnen et al., 2012; Steiner, 2019), more palaeoplacers are likely to be found (Fig. 4).

Given the evidence for diverse mineralization at the sub-Cambrian surface, it may be supposed that this setting may also be prospective for deposits of rare elements required for future technologies. Among the elements targeted to support the growth of future technologies, REEs are very highly valued (Liu and Chen, 2021; Balaram, 2023; Liu et al., 2023). This study seeks to:

(i) Assess if there is evidence for the concentration of REE deposits at the Precambrian-Cambrian boundary.

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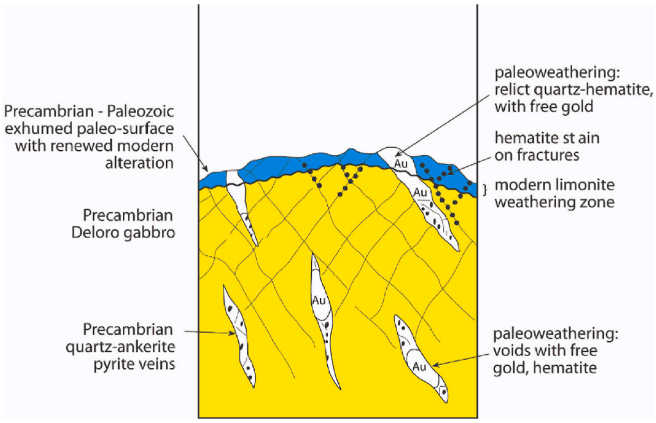

Fig. 1. Cross-section through Ontario gold-bearing deposit, showing supergene enrichment below sub-Cambrian surface (after Di Prisco and Springer, 1991). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(ii) Deduce whether these deposits indicate viable strategies for the exploration of REEs.

(iii) Test if a known example of the palaeo-weathered sub-Cambrian surface holds evidence for REE weathering and/or concentration in the detailed mineralogy. The rock has a robust Ar—Ar age of 542.6 ± 0.4 Ma (i.e, precisely the Precambrian-Cambrian boundary), so the alteration is not overprinted by younger events (Parnell et al., 2014).

2. Methodology

Phyllosilicate-rich rock was collected from the sub-Cambrian surface in Scotland (Ceannabeinne; United Kingdom national grid reference NC 437662), where the Lewisian rock below Cambrian sandstone was substantially altered. A petrographic study was made in support of understanding the processes that occurred at the Precambrian-Cambrian boundary. The rock sampled in Scotland represents a style of alteration at the boundary that is found globally, including in North America (Buckwalter, 1963; Simpson et al., 2002) and Asia (Kim and Lee, 2003). Measurements were performed at the University of Aberdeen ACEMAC Facility using a Zeiss Gemini field emission gun scanning electron microscope (FEG-SEM) on polished blocks of the phyllosilicate-rich rock.

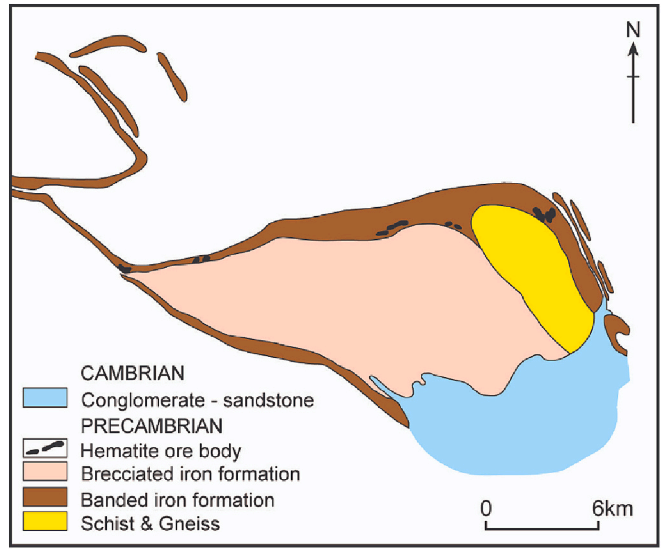

Fig. 3. Exposure of banded iron formation on sub-Cambrian surface, Mauritania (after Baldwin and Gross, 1967).

Samples were carbon coated and analysed at 20 kv, with a working distance of 10.5 mm. Mineral phases identified in samples were analysed using Oxford Instruments EDS X-ray analysis, focussing on phases that contained REEs and strontium. The standards used were a mixture of natural minerals, metal oxides and pure metals, as calibrated by the factory. Oxygen contents were determined by stoichiometry.

3. Results and discussion

3.1. REE and strontium deposition on the Precambrian-Cambrian surface, Scotland

Evidence for the mobility and concentration of REEs and strontium at the Precambrian-Cambrian boundary peneplain is recorded in Scotland. The unconformity surface is marked by a concentration of phyllosilicate (pinite, a massive variety of muscovite, probably metamorphosed from illite), coloured variably green, yellow and pink (Figs. 5, 6). The mineralized unconformity can be traced over a strike length exceeding 40 km (Peach et al., 1907). The layer of phyllosilicate occurs between

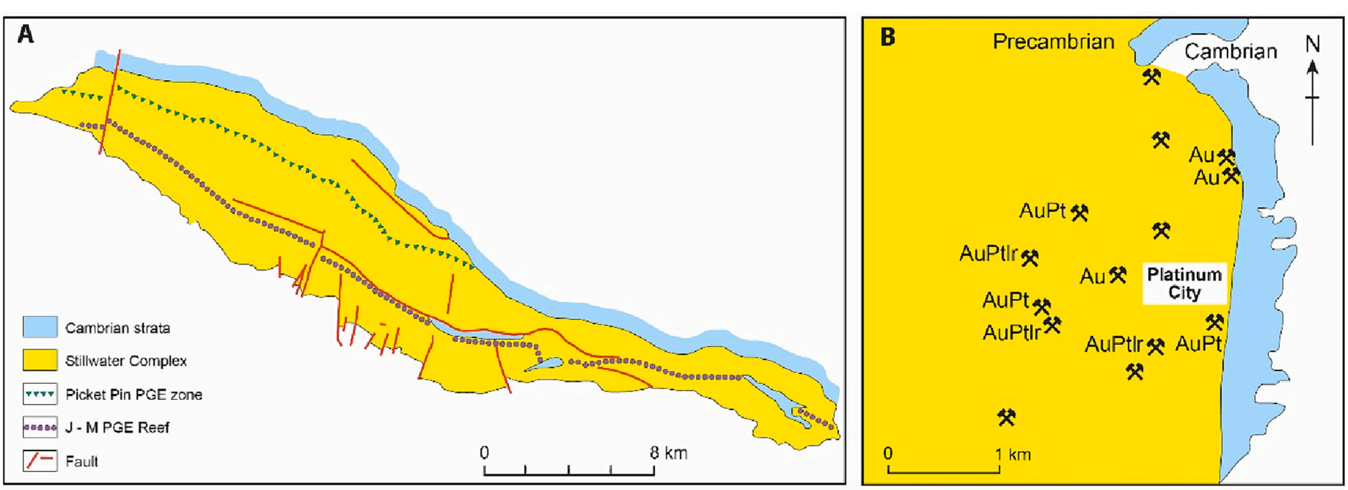

Fig. 2. Exposure of ore deposits on sub-Cambrian surface. Platinum-bearing ore deposits, truncated by sub-Cambrian surface and overlain by basal Cambrian sediments, imply erosion and liberation of PGEs into surface environment. (A) Stillwater ore deposit, Montana, where PGE-rich zones are truncated by Cambrian sediments (after Jackson, 1968); (B) Platinum-Iridium-Gold deposits, Platinum City district, Wyoming (after Hausel, 1989). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Archean Lewisian gneisses with abundant Palaeoproterozoic pegmatites and Lower Cambrian sandstones (Russell and Allison, 1985; Allison et al., 1992; Ferguson et al., 1998; Parnell et al., 2014). Regional geochemical mapping shows the imprint of the pegmatites in the basement in stream sediment samples (Institute of Geological Sciences, 1982). The pegmatites include a range of rare elements, including REEs (Shaw et al., 2016). The pinite forms a layer on the peneplain surface, rarely exceeding 1.0 m, but also penetrates downwards into the underlying pegmatites to a depth over 2.0 m, which were therefore altered to at least this depth. Abundant feldspar in the pegmatite is extensively altered to pinite, predominantly coloured green (Fig. 5). Only quartz survives from the original mineralogy in the most altered pegmatite. The pinite is dated at 542 Ma (Parnell et al., 2014), i.e., precisely at the Precambrian-Cambrian boundary (Fig. 7). The high precision date indicates that the pinite has not been altered by subsequent alteration; and pinitized clasts are also found as clasts in the overlying Cambrian sandstone. Detailed petrographic study by electron microscopy shows that REEs and strontium were concentrated as authigenic phosphates.

The phosphates occur in clusters within the pinite. Most phosphate crystals measure 10 to 50 μm, but some reach 100 μm size. They have a variable chemistry, in particular the presence/absence of REEs and exhibiting a wide range of strontium contents (8.7 to 19.4 wt% SrO). They are attributable to the family of APS (aluminium phosphate sulphate) minerals, i.e. they represent a concentration of phosphorus, sulphur, and variable amounts of strontium and REEs. The major variations in the APS solid solution series are in the relative proportions of the end members svanbergite ($SrAl_3[PO_4,SO_4]OH_6$), florencite ($REEAl_3(PO_4)_2OH_6$) and goyazite ($SrAl_3(PO_3{\cdot}(O_{0.5}(OH)_{0.5}))_2(OH)_6$). They are commonly associated with calcium- and barium-bearing equivalents woodhouseite $CaAl_3(PO_4)(SO_4)(OH)_6$, crandallite $CaAl_3(PO_4)(PO_3OH)(OH)_6$ and gorceixite $BaAl_3(PO_4)(PO_3OH)(OH)_6$. The REE-bearing crystals in the Scottish pinite have similar strontium and total REE contents (Table 1), and are intermediate in composition between svanbergite and florencite, but additionally have some calcium substitution. In many cases the crystals are zoned, and have a REE-bearing core, followed by zones of increasing strontium content but without REEs (Figs. 8, 9). The REEs identified are praseodymium, neodymium, samarium and gadolinium, which are present at a concentration that could be resolved by the analytical system. It is likely that lower concentrations of other REEs are also present. Most analyses of the non-REE phases include high levels of sulphur and at least some calcium, placing them intermediate between svanbergite and woodhouseite (Table 1). The evolution of mineralogy implies not just that strontium was available and mobile, but there was a progressive increase in strontium availability.

In some cases, the APS minerals are associated with authigenic bladed masses of the aluminium oxy-hydroxide mineral diaspore (Fig. 8). Diaspore typically occurs in weathering horizons (Mordberg, 1999; Cloutis and Bell, 2000), and the association of strontium-rich APS minerals with diaspore is recorded in numerous alteration profiles elsewhere (Mordberg, 1999; Milu et al., 2004; Voudouris and Melfos, 2012; Hikov and Velinova, 2018). Another alteration profile of similar age (late Neoproterozoic) on apatite-rich basement in the Baltic region contains APS minerals like the example in Scotland (Vircava et al., 2015).

Additionally, the pinite contains sub-millimetre size aggregates of tourmaline (Fig. 8). The tourmaline is described by Ferguson et al. (1998), who suggested that the boron required for tourmaline formation

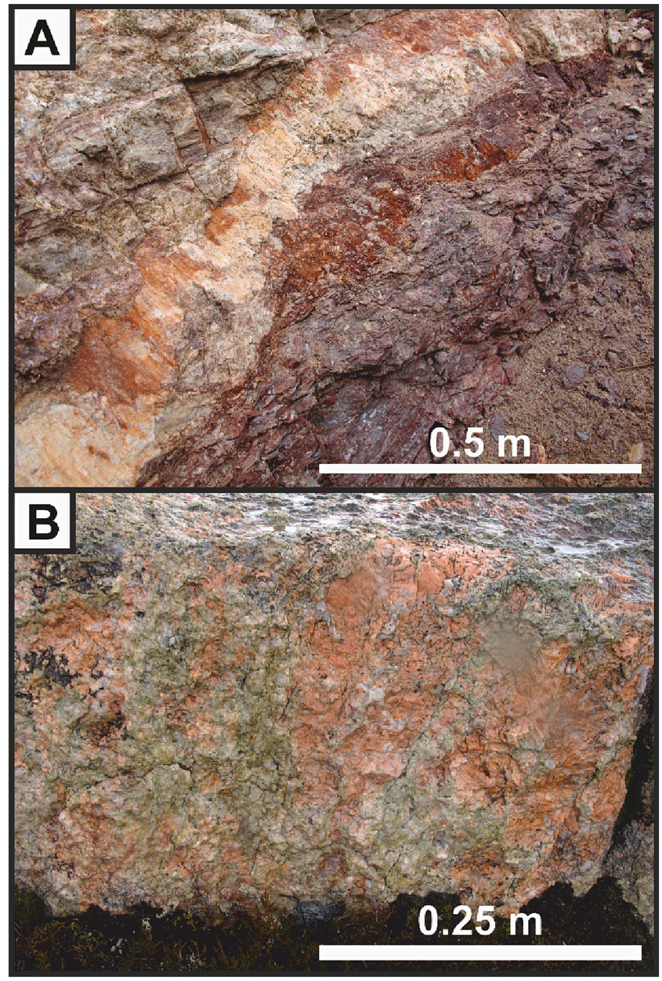

Fig. 5. Field images of alteration profile at Precambrian-Cambrian boundary, Scotland. A, Coloured phyllosilicate layer on Lewisian gneiss basement, overlain by Cambrian sediments. B, Pegmatite (pink, feldspathic), impregnated by alteration phyllosilicates (green). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

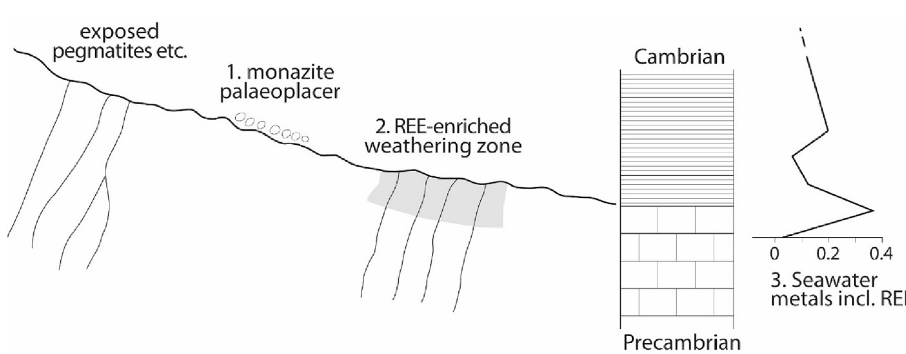

Fig. 4. Schematic evolution of REEs at sub-Cambrian surface. Exposed REE-bearing pegmatites weathered to form (1) monazite placers, (2) weathered supergene ores, followed by Cambrian transgression and (3) enrichment of REEs in earliest Cambrian sediments.

Fig. 6. Slab of altered Precambrian gneiss at Precambrian-Cambrian boundary, Scotland, coloured green by chromium-rich fuchsite. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

was introduced from seawater during the post-unconformity Cambrian transgression. If the strontium and REEs were derived from weathering of the sub-Cambrian basement, it is likely that this was also the source of the boron. Regardless of the origin of the boron, the diverse mineralogy emphasizes that a range of trace elements was concentrated at the Precambrian-Cambrian boundary.

3.2. REE concentration: weathered granites and pegmatites

The rocks below the surface include many outcrops of granite, and particularly pegmatite, at the surface (Fig. 4). Commonly, granites are relatively resistant, and are the rocks at which downward erosion terminates or is slowed down, which increases their proportional outcrop. They also form topographic highs above peneplains (inselbergs). Granites and pegmatites at the sub-Cambrian surface were exposed to prolonged alteration. The fate of granites during weathering varies with climatic conditions, which control the relative importance of mechanical erosion and chemical alteration. Mechanical erosion favours the formation of placer deposits, while leaching favours the formation of new minerals by remobilization. Rare earth elements could be concentrated by either process, described in an ore deposit model (Dill, 2017).

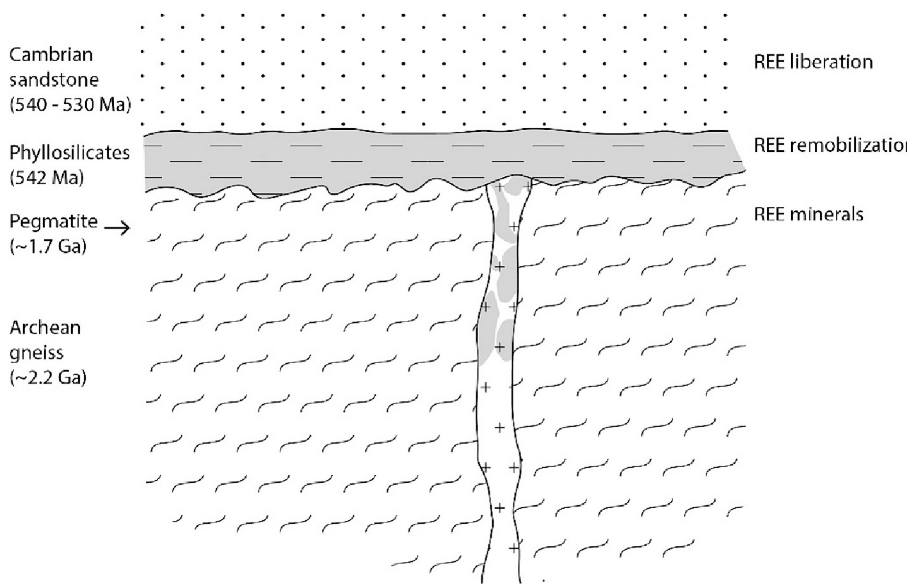

Fig. 7. Schematic section of alteration profile at Precambrian-Cambrian boundary, Scotland. Archean gneiss and Proterozoic pegmatite were altered to phyllosilicates at 542 Ma before transgression by Cambrian sandstone.

Table 1
Sample analyses for zoned mineral (Fig. 9) in altered phyllosilicate, Precambrian-Cambrian boundary, Scotland. Core is intermediate florencite-svanbergite, inner zone is intermediate woodhouseite-svanbergite, and outer zone is closest to svanbergite. Proportion of strontium increases progressively outwards.

	Core				Inner				Outer			
	1	2	3	4	5	6	7	8	9	10	11	12
F	0.96	1.11	1.25	0.43								
Al_2O_3	33.08	32.98	33.75	33.50	34.90	35.45	35.13	35.40	34.54	34.45	35.28	35.22
P_2O_5	26.07	25.77	26.59	24.13	17.59	17.44	17.87	17.91	17.22	16.95	17.34	17.56
SO_3	5.85	5.63	5.69	7.85	17.64	18.31	16.88	17.99	18.31	18.29	18.59	18.58
CaO	3.35	3.52	3.36	2.64	5.63	5.42	5.67	4.98	2.43	2.28	2.14	2.22
SrO	8.85	8.71	9.73	9.81	12.80	13.07	12.24	14.05	18.57	18.76	19.26	19.35
BaO	0.00	0.00	0.00	0.00	0.00	0.28	0.83	0.00	0.00	0.00	0.00	0.00
La_2O_3	1.01	1.10	1.18	2.15								
Ce_2O_3	2.45	2.35	2.84	3.75								
Pr_2O_3	0.56	0.70	0.76	0.72								
Nd_2O_3	4.80	4.80	4.17	3.74								
Sm_2O_3	1.55	1.46	1.03	0.84								
Gd_2O_3	0.00	0.56	0.54	0.00								
-O ≡ F	−0.40	−0.47	−0.53	−0.18								
Total	88.13	88.22	90.36	89.38	88.55	89.97	88.62	90.33	91.07	90.74	92.62	92.93

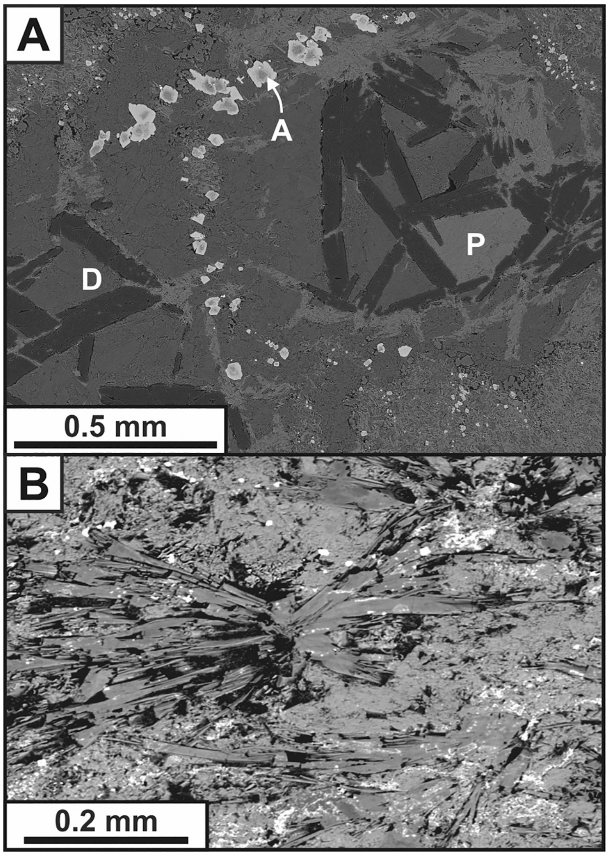

Fig. 8. Backscattered electron images of altered phyllosilicate layer, Precambrian-Cambrian boundary, Scotland. A, Phyllosilicate containing crystals of APS mineral (A), pyrophyllite (P) and diaspore (D); B, Radiating crystals of authigenic tourmaline.

Studies in numerous parts of the world show that rare earth elements become concentrated and/or fractionated during weathering processes in granites (e.g., Sanematsu et al., 2009; Foley and Ayuso, 2015; Padrones et al., 2017; Fu et al., 2019; Sababa et al., 2021). The vein-like morphology of pegmatites makes them pathways for the penetration of weathering (Dill et al., 2015; Dill, 2017), which could lead to their preferential alteration.

Three examples reviewed from recent literature demonstrate the potential of the Precambrian-Cambrian boundary for the concentration of REEs.

In the southern Sinai, Egypt, recent discoveries of gold in basal Cambrian sandstones have been attributed to derivation from the underlying basement (Alshami, 2019; Surour et al., 2003; Saber, 2020). The gold is accompanied by monazite, and an abundance of Neoproterozoic pegmatites immediately beneath the sandstone-basement unconformity (Abdelfadil et al., 2016) suggests the potential for REE resources. Monazite from these rocks is a known source of REEs and radio-elements in modern placers (Surour et al., 2003; El Ghaffar, 2018), so they were probably an equally fertile source during the early Cambrian.

The Damaran Orogen, Namibia, includes valuable mineralized pegmatites of late Neoproterozoic age (Fuchsloch et al., 2018; Ashworth et al., 2020). The basement surface was conspicuously incised before infill by Lower Cambrian sediments (Saylor and Grotzinger, 1996). Cambrian sediments derived from the orogen contain beds rich in heavy minerals with an order of magnitude greater REE content than other beds (Blanco et al., 2014).

In addition to the gold accumulations in the Cambrian Flathead Formation, Wyoming, occurrences of the sandstone contain major resources of monazite, up to 20 lb./ton (about 10 kg/t) (McKinney and Horst, 1953). The underlying Archean basement is rich in granites and pegmatites. The deposits in the Bald Mountain region were originally evaluated as a thorium resource, but they have since been re-evaluated for their REE concentration (Sutherland et al., 2013).

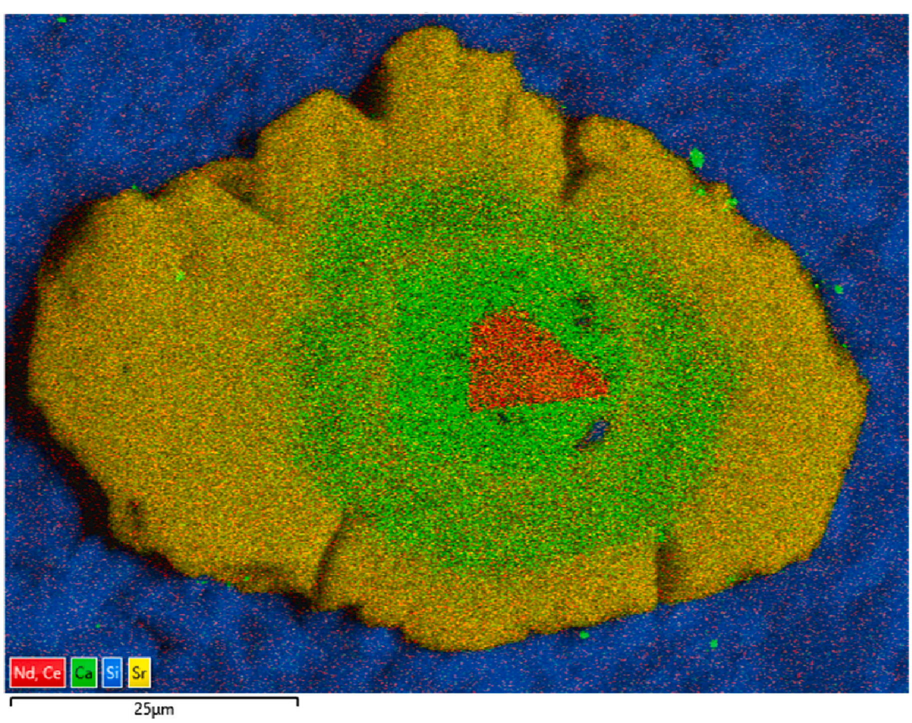

Fig. 9. Combined multi-layer electron image of APS mineral grain in altered phyllosilicate, Precambrian-Cambrian boundary, Rispond, Scotland. Grain is zoned from REE-rich phosphate core, outwards to zones with increasing strontium content.

3.3. REE concentration: weathered iron formation

Another distinct Precambrian rock type that is commonly REE-rich is magnetite iron ore. Banded iron formation is widely distributed in the Precambrian (Klein, 2005), and it has been mined on most continents. The magnetite is commonly accompanied by apatite, which makes the ore rich in phosphorus, strontium and REEs. Large bodies of the iron ore form prominent hills on the sub-Cambrian surface, like granites (Chan et al., 1991). Ores in three regions show that the REE contents reach economic importance.

In Missouri, the Pea Ridge iron ore deposit is high in apatite, and has been assessed for reworking of tailings to extract REEs (Whitten and Yancey, 1990; Nuelle et al., 1991; Seeger, 2000). Boulders of ore in unconformably overlying basal Cambrian sediments show that the ore metals were released at the surface.

In the Adirondack Mountains, New York, and adjacent Ontario, Precambrian iron ores are widespread, and again tailings have been assessed as a source of REEs (Lupulescu et al., 2015; Taylor et al., 2019; Shah et al., 2021). The Adirondacks formed a topographic high during Cambrian sedimentation, and there is a prominent planar Precambrian-Cambrian unconformity which implies exposure of the REE-bearing ores at the Cambrian surface. So much iron was released that iron ore deposits were deposited and exploited within the Cambrian sandstone in Ontario (Ells, 1904) and occur in depressions on the unconformity surface in New York (Chamberlain et al., 2019).

In Sweden, two of the biggest REE prospects in Europe, at Kiruna (north Sweden) and in the Bergslagen ore field (south Sweden) are associated with Precambrian iron ores (Jonsson and Högdahl, 2013; Guthrie, 2023). Sporadic exposures of basal Cambrian sediments in these regions (Wickström and Stephens, 2020) suggest that the sub-Cambrian surface would have exposed them.

3.4. Exploration strategy

The examples of heavy mineral concentrations and iron formation cited above indicate that strategies for the exploration for REEs are applicable to Precambrian-Cambrian boundary sections where they are likely to be exposed. The rapid depletion of high-grade REE deposits means that future resources could eventually become dominated by low-grade ores and tailings, as cut-off grades fall. In this scenario, heavy mineral concentrations and iron ore tailings will become increasingly valuable.

Among the numerous instances of heavy mineral concentrations on the sub-Cambrian surface (Parnell et al., 2014) are several examples of 'black sands'. Deposits of black sands occur in the Cambrian of Namibia (Blanco et al., 2014), Quebec (Gauthier et al., 1994), Korea (Kim and Lee, 2006) and Antarctica (Laird, 1981). Modern black sands are regarded as potential sources of REEs (Bartlett et al., 1992; Saini, 2012; Abdel-Karim et al., 2016; Peristeridou et al., 2022), and fossil equivalents like those on the sub-Cambrian surface may be similarly REE-rich. The REEs in modern black sands reside particularly in monazite, which is attributed especially to the weathering and erosion of granites and pegmatites (Dawood and Abd El-Naby, 2007; Peristeridou et al., 2022; Khedr et al., 2023), as we propose here for mineral concentrations on the sub-Cambrian surface.

There is a substantial effort to find pegmatite deposits, by companies exploring for lithium, niobium, tantalum and other elements (Linnen et al., 2012; Steiner, 2019). The exploration for pegmatites could be supplemented by exploration for pegmatite weathering residues rich in REEs, which would reduce the economic and other resource costs.

Technology development for the exploitation of iron ore tailings for REEs is already at an advanced stage (Moran-Palacios et al., 2019; Abaka-Wood et al., 2022). World-class iron ore deposits, i.e., on a scale of billions tonnes of iron ore, with REE contents attracting prospectors, were exposed at the Precambrian-Cambrian boundary in Australia (Cook et al., 2022), USA (Grauch et al., 2010) and Sweden (Wanhainen et al., 2017). The sub-Cambrian surface is therefore a good target for further exploration.

3.5. Accompanying strontium

The petrographic evidence for alteration and denudation at the Precambrian-Cambrian boundary is matched by a global positive (heavy) strontium isotope excursion, recorded in marine carbonates, which is interpreted to be a result of enhanced continental weathering (Sawaki et al., 2008; Halverson et al., 2010; Li et al., 2013; Stammeier et al., 2019; Zhang et al., 2020). The weathering of granites and pegmatites releases strontium, especially from micas and feldspars (Bain and Bacon, 1994; Ma and Liu, 2001), so exposure of these rocks on the sub-Cambrian surface would have made strontium available, possibly at anomalous levels. Modern weathering of a Precambrian granite-greenstone terrane in North America, similar to what was exposed on the sub-Cambrian surface, yields water with a heavy strontium isotope composition (Stevenson et al., 2018). The strontium isotope composition of the alteration phyllosilicate (pinite) on the sub-Cambrian surface in Scotland is also markedly heavy, consistent with the weathering of continental crustal rocks (Parnell et al., 2014). The increased weathering is in turn linked to the delivery of nutrients to the ocean, which may have supported the Cambrian Explosion (Zhang et al., 2014; Stammeier et al., 2019). The weathering also delivered calcium, which could be used for biocalcification by the Cambrian biota (Brennan et al., 2004; Berner, 2004; Bengtson, 2004).

3.6. Global sub-Cambrian alteration

The altered surface in Scotland represents alteration and denudation recorded globally in the sub-Cambrian section. Even pinite is recorded elsewhere below the unconformity, in North America (Simpson et al., 2002) and Asia (Kim and Lee, 2003). The large number of exposures of the sub-Cambrian unconformity globally show alteration to a depth exceeding 10 m, and even 100 m in ore deposits (e.g., Di Prisco and Springer, 1991; May and Dinkowitz, 1996; Avigad et al., 2005). Previous calculations (Parnell et al., 2014) assuming a conservative mean denudation depth of 1 m suggest a yield of over 7×10^{16} kg rock. The crustal mean value for REEs in that rock would represent 100 times the current content dissolved in the world's oceans. However, considering the exceptional thicknesses of Lower Cambrian quartz sandstone derived by erosion of the sub-Cambrian surface (Avigad et al., 2005; Peters and Gaines, 2012; Poursoltani, 2020), the denudation could well have been an order of magnitude greater, and the REE release into the oceans would have been correspondingly greater. The early Cambrian oceans were highly metalliferous, notably in REEs (Schröder and Grotzinger, 2007, Pi et al. 2013, Abedini and Calagari, 2017), which implies a direct link between erosion and ocean chemistry.

4. Conclusions

The Precambrian-Cambrian boundary is marked, globally, by the intense weathering of Precambrian rocks followed by widespread peneplanation. This resulted in heavy mineral (placer) and authigenic ore deposits. The link between weathering and deposit formation at this particular time implies that the sub-Cambrian surface is a valuable vector in mineral exploration. Petrographic study of the Precambrian-Cambrian boundary section in Scotland shows that:

(i) Alteration conspicuously affected the Precambrian substrate, including pegmatite veins, below the boundary, indicating a mechanism for the availability of critical elements.
(ii) The alteration pinite extends down the pegmatites further than in other rocks, which therefore contributed disproportionately to the rock solute.

(iii) The alteration pinite layer can be traced for tens of kilometres, which together with records from other continents indicates a globally significant delivery of rock solute into the oceans.
(iv) The alteration pinite layer contains authigenic strontium/rare earth-bearing phosphates, indicating the mobility of strontium and REEs during the alteration event.
(v) The authigenic strontium-rich phases in the alteration pinite layer represent a signature of continental weathering.

CRediT authorship contribution statement

J.G.T. Armstrong: Formal analysis, Investigation, Writing – review & editing. **J. Parnell:** Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Supervision, Writing – original draft.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

All data is in the paper

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