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$^{40}Ar/^{39}Ar$ dating of exceptional concentration of metals by weathering of Precambrian rocks at the Precambrian–Cambrian boundary

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ABSTRACT

The sub-Cambrian surface, including diverse metalliferous deposits, shows evidence of intense weathering of Precambrian rocks to form supergene-enriched ores and metalliferous placers, followed by widespread peneplanation. Much of the metal would have been flushed to the Cambrian ocean during peneplanation. An $^{40}Ar/^{39}Ar$ age of 542.62 ± 0.38 Ma (1 sigma, full external precision, Renne et al., 2011) for metalliferous alteration clays in Scotland shows that this event occurred immediately prior to the Precambrian–Cambrian boundary. A negative $\delta^{53}Cr$ isotopic signature for the clay is consistent with mobilization on land of redox sensitive metals by oxidative terrestrial weathering. This unprecedented flushing of metals from the weathered Precambrian surface would have contributed to the chemistry of the earliest Cambrian ocean at a time of marked faunal evolution.

1. Introduction

The Precambrian–Cambrian boundary marks one of the most dramatic episodes of change in Earth's history. The evolution and diversification of metazoans accelerated following a mass extinction, while ocean geochemistry was transformed globally. The temporal association has been interpreted to indicate a genetic link between geochemical change and faunal evolution (Amthor et al., 2003; Wille et al., 2008; Maloof et al., 2010; Peters and Gaines, 2012). Geochemical change at the boundary is evident as metal enrichment (Schrödinger and Grotzinger, 2007; Wille et al., 2008), and specifically Rare Earth Element (REE) enrichment (Xu et al., 1989), an iridium anomaly (Nazarov et al., 1983), increase in radiogenic marine strontium (Shields, 2007), and widespread phosphate deposition (Cook, 1992). Overall, the early Cambrian ocean is characterized as highly metalliferous (Lehmann et al., 2007). To understand the anomalous precipitation of metals in the oceans, we should examine the nature of the continental surface from which they would have been derived by erosion and run-off. The Precambrian–Cambrian boundary saw marine transgression across intensely weathered surfaces, which commonly show extensive alteration and related planation to a degree without parallel in the geological record (Fig. 1). Thus a sub-Cambrian altered surface can be traced over much of North America (Ambrose, 1964; Duffin, 1989), across the Pan-African Orogen for 6000 km from Morocco to Oman (Avigad et al., 2005), and over much of the Baltic region (Nielsen and Schovsbo, 2011). In each case, the surface is covered with clay alteration products where they are preserved from the accompanying planation, especially by a Lower Cambrian quartz-rich sandstone.

1.1. *Weathered and enriched ore deposits on the sub-Cambrian surface*

Investigation of the distribution of metalliferous ore deposits on the sub-Cambrian surface leads to two conclusions. Firstly, there was a relatively high abundance of such deposits, and secondly many of these deposits were demonstrably weathered and even enriched before the subsequent peneplanation and transgression. Unlike many unconformable surfaces, which are developed on older sedimentary rocks, the sub-Cambrian surface is extensively developed on deeply eroded crystalline basement, including a disproportionate volume of granites and pegmatites, and metasedimentary iron formations (Duffin, 1989; Avigad et al., 2005). These

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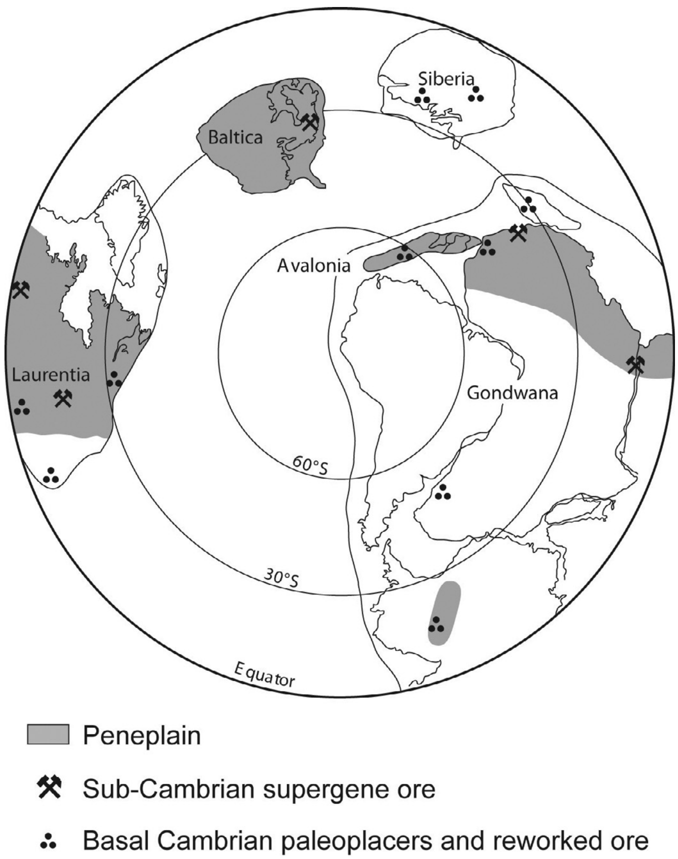

Fig. 1. Palaeogeography for end-Neoproterozoic (~550 Ma) (Torsvik et al., 1996), showing sites for supergene metal enrichment on the sub-Cambrian surface (data sources in text).

rocks are extensively mineralized. Cross-sections through ore deposits in North America in particular commonly show them truncated by the sub-Cambrian unconformity (Fig. 2), but not consistently by any other palaeosurface. This partly reflects the huge area transgressed by the Cambrian ocean. We draw attention to two types of ore on the surfaces that were especially significant to anomalous Cambrian chemistry. Iron deposits were exposed on the surface in many parts of the world, including USA, Canada, Sweden, Iran and West Africa. So much Precambrian iron ore was eroded during the transgression that the basal Cambrian rocks can be ores in their own right, for example, in Missouri and Wyoming (Murphy and Ohle, 1968; Hausel, 1989). Many of these iron deposits are gold-bearing, some are strongly phosphatic, and others contain associated REE deposits. Other types of gold deposit are exposed on the surface, especially in shear zones, for example, in Wyoming (Laurentia), Saskatchewan (Laurentia), Jordan (Gondwana) and Newfoundland (Avalonia) (Bayley et al., 1973; O'Brien, 2002; Saskatchewan Ministry of Energy & Resources, 2008; Al-Hwaiti et al., 2010). In Wyoming there are associated platinum group element ores at the surface, including iridium ore (Hausel, 1989). One of the most important sources of platinum group elements in the world, the Stillwater Complex in Montana, was eroded and exposed at the sub-Cambrian surface (Jackson, 1968). In each case, the ore deposits can be traced up to the sub-Cambrian unconformity (Fig. 3), and so were exposed at the time of peneplanation.

In addition to this evidence of widespread exposure of metalliferous ores on the sub-Cambrian surface, there is evidence for deep weathering and enrichment of the ores. The concentration of metals by weathering could be evident as either supergene enrichment, or the accumulation of palaeoplacers. Supergene alteration and enrichment due to oxidation upgraded the value of the ores before deposition of the Cambrian sediments. Most of the evidence is on the Laurentian continent (Fig. 4), as this has been intensively explored. Examples are supergene concentrations of copper in Wisconsin (May and Dinkowitz, 1996), Michigan (Bornhorst, 2002) and Quebec (Sinclair and Gasparrini, 1980), copper–silver–gold enrichment in Arizona (Schwartz, 1938), iron in Missouri (Emery, 1968), Michigan (James et al., 1968) and Saskatchewan (Cheesman, 1964), nickel enrichment in Manitoba (Cumming and Krstic, 1991), zinc–lead enrichment in New York (Brown, 1936), uranium enrichment in Michigan (Mancuso et al., 1985) and gold enrichment in Ontario (Di Prisco and Springer, 1991). The scale of enrichment is evident in Jerome County, Arizona, where a supergene sub-Cambrian copper ore earned $10 million in 1916 (Lindgren, 1926). In Scotland, which resides on the periphery of the Laurentian continent, supergene chromium minerals are concentrated on the surface, where the Archean gneiss-pegmatite bedrock includes basic layers rich in chromium (see below). Beyond Laurentia, supergene enrichments on the sub-Cambrian surface include copper ores in Morocco and Israel (Gondwana) and lead ores in Norway (Baltica) (Bjørlykke et al., 1990; Asael et al., 2007; Alvaro and Subias, 2011).

Where the weathered surface was eroded to yield an accumulation of resistant minerals, palaeoplacers rich in gold, monazite (rare earths, thorium) and other metalliferous phases became entrained in Cambrian sandstones. 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 Yenisey and Anabar regions of the Siberian Platform (Krendelev, 1966; Konstantinovskii, 2001) and Spain (Pérez-García et al., 2000). These concentrations occurred on a vast scale. The Cambrian gold palaeoplacers at the Homestake gold deposit, South Dakota, are estimated at up to a million ounces of gold, while in Wyoming 20 million tonnes of monazite palaeoplacer – rich rock were identified as prospective ore. Together with other Cambrian 'black sand' deposits (heavy mineral palaeoplacers) in Quebec (Gauthier et al., 1994), Namibia (Blanco et al., 2006), Antarctica (Laird, 1981) and Korea (Kim and Lee, 2006), there is global evidence for the concentration of metals on the sub-Cambrian surface that was incorporated into sandstones during the Cambrian transgression. Where the altered sub-Cambrian rock was completely stripped away, the denudation event would have also entrained fresh mineralized rocks. Thus, for example, gold-mineralized late Proterozoic rocks in Newfoundland (Avalonia), copper–silver–mineralized Proterozoic rocks in British Columbia, and Precambrian iron formation in Missouri, Michigan and Saskatchewan (Laurentia), Iran and Mauritania (Gondwana) were all exposed and eroded to supply clasts identified in basal Cambrian deposits (Awmack, 1994; Emery, 1968; O'Brien, 2002; Baldwin and Gross, 1967; Förster and Jafarzadeh, 1994). No comparable concentration and diversity of ore exists on post-Cambrian palaeosurfaces.

2. The sub-Cambrian surface in Scotland

The peneplained surface in NW Scotland is a 'remarkably flat' (Johnstone and Mykura, 1989) surface of Archean gneiss and mid-Proterozoic pegmatites. It is covered by alteration phyllosilicates beneath a protective cover of Lower Cambrian quartz sandstone which extends over a 40 km outcrop (Peach et al., 1907; Russell and Allison, 1985; Allison et al., 1992; Ferguson et al., 1998). X-ray diffraction data show that the cover mineralogy is dominated by pinite, a very fine-grained form of the potassium mica muscovite, which can form from meteoric fluids (Allison et al., 1992). The fine-grained mica (crystals up to 125 μm) has been interpreted as a weathering product because (i) it tops a profile of