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Short communication

Anomalous supply of bioessential molybdenum in mid-Proterozoic surface environments

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ABSTRACT

Granites aged 1.9 Ga to 1.5 Ga exhibit molybdenite mineralization globally. Sandstones deposited during the mid-Proterozoic have a provenance dominated by 1.9–1.7 Ga basement. The mid-Proterozoic surface environment was, consequently, receiving detritus from the molybdenum-rich granites. Thus there was a supply of molybdenum available in terrestrial or shallow marine environments at a time when molybdenum was required to support the evolution of multicellular life.

1. Introduction

Research in genomics, biochemistry and geochemistry is converging on an understanding of the importance of metal availability to the emergence of eukaryotic life during the Proterozoic (Anbar and Knoll, 2002; Williams and da Silva, 2006; Dupont et al., 2010). Thus the availability of copper, zinc and molybdenum has been identified as critical to the evolution of multicellular life in the mid-Proterozoic (~1.8 to 1.0 Ga). In particular, molybdenum is believed to be essential to biological nitrogen fixation and a range of other metabolic processes (Schwarz et al., 2009; Wang, 2012). This model implies an increased occurrence of rock that could be eroded to supply molybdenum to surface environments in the mid-Proterozoic, but the geological record of molybdenum-rich rocks is largely limited to the last 200 million years (Goldfarb et al., 2010; Golden et al., 2013; Richards and Mumin, 2013). However, recent models for the origin of these young deposits suggest that they are derived from reworking of a molybdenum-rich Proterozoic protolith (Pettke et al., 2010; Deng et al., 2013), inviting a careful appraisal of the extent of Proterozoic molybdenum mineralization. Our review shows that a unique combination of three global-scale settings for granitoids all hosted molybdenum sulphide (molybdenite) mineralization over the period 1.9–1.5 Ga on at least eight palaeocontinents. Age data for detrital zircons in Mesoproterozoic sediments show that they have a provenance dominated by these late Palaeoproterozoic granitoids. These observations confirm that the newly molybdenum-rich crust was releasing molybdenum and other metals to surface environments where they were available to an evolving biota.

1.1. The record of granites and sediment provenance

The delivery of metals to continental depositional environments, and ultimately to the ocean, depends on what rocks are available in the hinterland to be eroded and transported. A major proportion of sediment provenance, globally, lies in granite. Quartz is predominantly derived from granite, and is the most abundant component of clastic (i.e. non-chemical) sediment, demonstrating how granites control sediment composition. Granites are buoyant, and form topographic highs including mountain chains, so are readily susceptible to erosion. The erosion products include not only resistant minerals such as quartz, but solutes in the run-off that drains the exposed and weathered portions of the granites. Many granites are strongly metalliferous, or at least more so than most other components of continental crust. These metals are naturally included in the erosion products, and are thereby available to derived sediments in terrestrial environments, either in detrital form or as new precipitates from groundwaters. Granites form

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continental crust, so are not lost by subduction. We therefore have a geological record of granite abundance, metalliferous mineralization of granites, and the contribution of granites to sediment provenance.

The geological record of molybdenum in granites is especially helpful. It has very low crustal abundance (1–2 ppm) and is normally a trace element incorporated in other minerals, but when present in anomalously high concentrations it forms the molybdenum sulphide molybdenite. Molybdenite is amenable to Re–Os dating, so its occurrence provides both an age and an indication of relative abundance. Molybdenite mineralization is taken as a proxy for molybdenum enrichment in the crust. Molybdenite does occur more widely as a trace component (e.g. Audetat et al., 2011), but molybdenite-mineralized terrains have a conspicuous signature of molybdenum enrichment in river waters (e.g. Salminen et al., 2005), which drain to the ocean. Furthermore, molybdenum is one of the metals whose availability is believed to be most critical to the evolution of eukaryotes (Zerkle et al., 2005; Williams and da Silva, 2006; Dupont et al., 2010; Parnell et al., 2012), which diversified particularly in the mid-Proterozoic (Porter, 2004; Knoll et al., 2006; Parfrey et al., 2011; Butterfield, 2015). We may therefore use the record of molybdenite occurrences in granites, dated by molybdenite Re–Os ages or by other methods, as a broad measure of molybdenum availability to continental environments, and test whether anomalous availability coincided with the main period of expansion of eukaryotic life. The rock record is sufficiently complete to allow the assessment of variations in mineralization throughout the Proterozoic and Phanerozoic (Barley and Groves, 1992; Groves et al., 2005). Our approach was based on literature searches for coupled references to molybdenite and granite, followed by detailed searches using syntheses of regional metallogeny.

2. The mid-Proterozoic record of molybdenum mineralization

The geological record of molybdenum mineralization is strongly dominated by the Mesozoic and Cenozoic, as the majority of dated occurrences are in the interval back to 150 Ma (Golden et al., 2013). Porphyry style mineralization, which accounts for many of the known economic molybdenum deposits, is usually emplaced between 1 and 4 km below the surface in active orogenic belts (Sillitoe, 2010). These deposits are frequently eroded as the result of continued uplift. However, the cupolas of the large underlying parent batholiths, containing anomalous but usually uneconomic mineralization at depths of >5 to 15 km, often survive to be subsequently exposed (Goldfarb et al., 2010; Sillitoe, 2010). Mineral exploration in Precambrian terranes is uncovering increasing evidence for mineralization of Proterozoic granitoids in several continents, including Australia, Eurasia, North America and South America. There are records of molybdenite-mineralized granites of Archean and early Palaeoproterozoic age, but most of the record relates to the period 2.0–1.5 Ga. Over this mid-Proterozoic time, a succession of three distinct global-scale settings for granitoids combined to bring widespread molybdenite mineralization to the upper crust. Firstly, the Nuna supercontinent (also known as Columbia) was assembled (1.9–1.8 Ga) from several smaller continents, with each suture resulting in orogenic activity including granite emplacement. Following that continental collision, a laterally extensive accretionary orogen along an external margin of Nuna hosted further granite emplacement from 1.8 to 1.65 Ga. Thirdly, an unprecedented period of within-plate anorogenic magmatism, including the global formation of so-called Rapakivi granites, continued from 1.8 to 1.3 Ga (Larin, 2009; Parnell et al., 2012). Each of these three environments engendered molybdenite mineralization.

Fig. 1. Global palaeogeography in the mid-Proterozoic (1500 Ma), showing palaeocontinents with mid-Proterozoic molybdenite mineralization (star symbols). Map based on Pisarevsky et al. (2014). Continents: Am, Amazonia; Ba, Baltica; Con, Congo; G, Greenland; Kal, Kalahari; La, Laurentia; NA, North Australia; NC, North China; Sib, Siberia; SF, São Francisco; WA, West Australia.

Molybdenite mineralization related to these granites is recorded in at least eight Mid-Proterozoic paleocontinents (palaeogeography of Pisarevsky et al., 2014) of Laurentia, Baltica, South Australia, North Australia, North China, Kalahari, Amazon and Sao Francisco (Fig. 1). The data base for mid-Proterozoic mineralization is most detailed in Baltica (Sweden, Finland, adjacent Russia, Estonia) and South Australia, and both have yielded numerous records of molybdenite including economic molybdenum ore deposits. Occurrences in Baltica exemplify all three sets of mineralized granitoids, including plutons formed during the Svecofennian/Svecokarelian Orogeny, porphyry-style mineralization related to arc accretion, and anorogenic granites in southern Fennoscandia (Lundmark et al., 2005). The molybdenite deposits include skarns associated with granites, and other products of metamorphism. A detailed study of Baltica (Fig. 2; Supplementary Table 1) shows over 30 occurrences of molybdenite mineralization of age 1.9–1.5 Ga, including major ore fields in Bergslagen (south Sweden), Norrbotten (north Sweden) and southern Finland. In the east of the region there are additionally several molybdenite deposits of late Archean age (Fig. 2). Deposits in both north and south Australia, which include the recently discovered high-grade Merlin Mo–Re prospect, are mostly of age 1.6–1.5 Ga (Skirrow et al., 2007; Duncan et al., 2011; Reid et al., 2013). Molybdenite of mid-Proterozoic age is also recorded in at least three deposits in North China (Zhao et al., 2009; Li et al., 2011; Deng et al., 2013), two in Namibia, Kalahari (Minnitt, 1986; Viljoen et al., 1986), eight in Brazil, Amazon and Sao Francisco continents (Giuliani et al., 1990; Botelho and Moura, 1998; Dall'Agnol et al., 1999; Santos et al., 2001; Teixeira et al., 2001; Pimentel et al., 2003; Tallarico et al., 2004), and in Arizona, Colorado and Wyoming, USA, Laurentia (McCallum et al., 1976; Lehmann, 1987; Schmitz and Burt, 1990) and Greenland, Laurentia (Luck and Allègre, 1982). The individual deposits are listed in Supplementary Table 2. In summary, taking account of the age of the rocks, there is a marked global distribution of molybdenite occurrences of mid-Proterozoic age. In addition to the eastern part of Baltica (Fig. 2), other Archean terrains also host significant molybdenite