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Anomalous supply of bioessential molybdenum in mid-Proterozoic surface environments

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Highlights

We review widespread global occurrences of molybdenite in mid-Proterozoic granites

Mesoproterozoic sandstone provenance is dominated by mid-Proterozoic, and possibly Archean, sources

We conclude molybdenum availability to the Mesoproterozoic surface was high

Molybdenum needed for spread of multiceullar life at this time was readily available

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 to 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.

Key words: Molybdenum; Molybdenite; Proterozoic; provenance; evolution

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 de la 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 to 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 Paleoproterozoic 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 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 de la 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 & 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 to 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 to 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.

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 to 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 mineralization, particularly in the granite-greenstone belts of the Yilgarn and Superior cratons of West Australia and Canada (Laurentia), and in India (e.g. Jébrak & Doucet 2002, Stein et al. 2004, Duuring et al. 2007). These Archean sources might make a greater proportion to Mesoproterozoic sandstone and molybdenum provenance than in Baltica.

3. Granitoid provenance of Mesoproterozoic sedimentation

Evidence for the erosion of these granitoids into Mesoproterozoic surface environments comes from the detailed records of detrital zircons in Mesoproterozoic sandstone beds. Zircons are an ideal tracer of provenance as they are highly resilient, consistently produced by the erosion of granites, and can be dated by U-Pb analysis. The importance of the 1.9 to 1.5 Ga granitoids to crustal growth is evident in the high proportion of detrital zircons of that age which are encountered in modern river sediments (Voice et al. 2011). A similar dominance of these zircons in mid-Proterozoic sandstones would indicate that the granites had been unroofed and were being eroded into the sandstones. Zircon ages for mid-Proterozoic sandstones in three regions of Baltica, viz. southern Norway and Sweden, the Gulf of Bothnia, and the Gulf of Finland, are strongly dominated by 1.9 to 1.7 Ga sources (Fig. 3), equivalent to the peak in molybdenite ages. This pattern is repeated globally, so that sedimentation during the Mesoproterozoic became dominated by erosion and redeposition of the 1.9 Ga new crust (Hawkesworth and Kemp 2006). The equivalence of molybdenite ages and zircon ages confirms that molybdenum-bearing rocks were being eroded at the time required to confer a molybdenum enrichment to the surface environments where eukaryotes were developing. From that time onwards, the 1.9 to 1.5 Ga granitoids have supplied a consistently strong component to the zircons in siliciclastic sediments (Voice et al. 2011), and by implication have also been a consistent source of molybdenum.

The scale of this mid-Proterozoic concentration of molybdenum is further evident from models in which much younger molybdenum mineralization in both western North America and North China, each of which has been described as the biggest molybdenum province in the world, is inherited from reworking of molybdenum concentrations originally established at about 1.8 Ga (Pettke et al. 2010, Deng et al. 2013). We can further demonstrate the availability of molybdenum in the geological record in the composition of diagenetic ores precipitated from groundwaters. In the Mesoproterozoic, mineralization at the interface between groundwater sandstone aquifers and crystalline basement aquicludes (so-called 'unconformity' deposits) show us what metals were available for redox-controlled deposition. These Mesoproterozoic ores are exploited mainly for uranium, also derived largely from granite, but additionally they consistently contain molybdenum (Langford 1983), confirming its availability to Mesoproterozoic groundwaters.

4. Delivery of molybdenum to surface environments

The molybdenum in the oceans is largely delivered from weathered continents by rivers (McManus et al. 2006). Mid-Proterozoic oxygen levels were more than adequate to cause the weathering of sulphides in basement rocks, and thus for mobilization of molybdenum from molybdenite in the granites into surface environments (Sverjensky and Lee 2010, Greber et al. 2015). This is evident today as molybdenum anomalies in stream sediments and soil (e.g. Tauchid 1964) and lake sediments (Malinovsky et al. 2007) in the vicinity of granites. Databases for lakes in Canada and Sweden show concentrations of molybdenum 1 to 2 orders of magnitude greater than in the parent granites (Cook 2000, Malinovsky et al. 2007). Indeed, the molybdenum concentration in sediments is sufficiently marked to be valuable in mineral exploration (Cook 2000, Taylor et al. 2012). Lakes and other terrestrial environments are clearly important repositories for molybdenum in between continental weathering and delivery to the ocean. There is a growing recognition of the importance of terrestrial and shallow, marginal marine, environments to the mid-Proterozoic evolution of eukaryotic life (Strother et al. 2011, Blank 2013, Brasier 2013). There is also direct evidence of high concentrations of molybdenum in Mesoproterozoic lake sediments (Parnell et al. 2015). Current models suggest that molybdenum in the deep ocean became sequestered by euxinic conditions and was thus unavailable there, hindering the oceanic diversification of eukaryotes (Anbar and Knoll 2002, Scott et al. 2008). However the ready availability of molybdenum to continental and shallow marine environments in the mid-Proterozoic ensured that eukaryotes received the molybdenum required for their evolution.

5. Conclusions

The data assembled in this study combine to support a model of anomalous availability of molybdenum to the surface environment during the mid-Proterozoic, based on evidence for widespread mineralization of granites by molybdenum during the period 1.9 to 1.5 Ga, and evidence that sedimentation during the mid-Proterozoic was dominated by sand with a ~1.9 to 1.7 Ga provenance. This anomalous availability of molybdenum coincides with the timing of diversification of eukaryotic life, for which molybdenum is a bioessential element.

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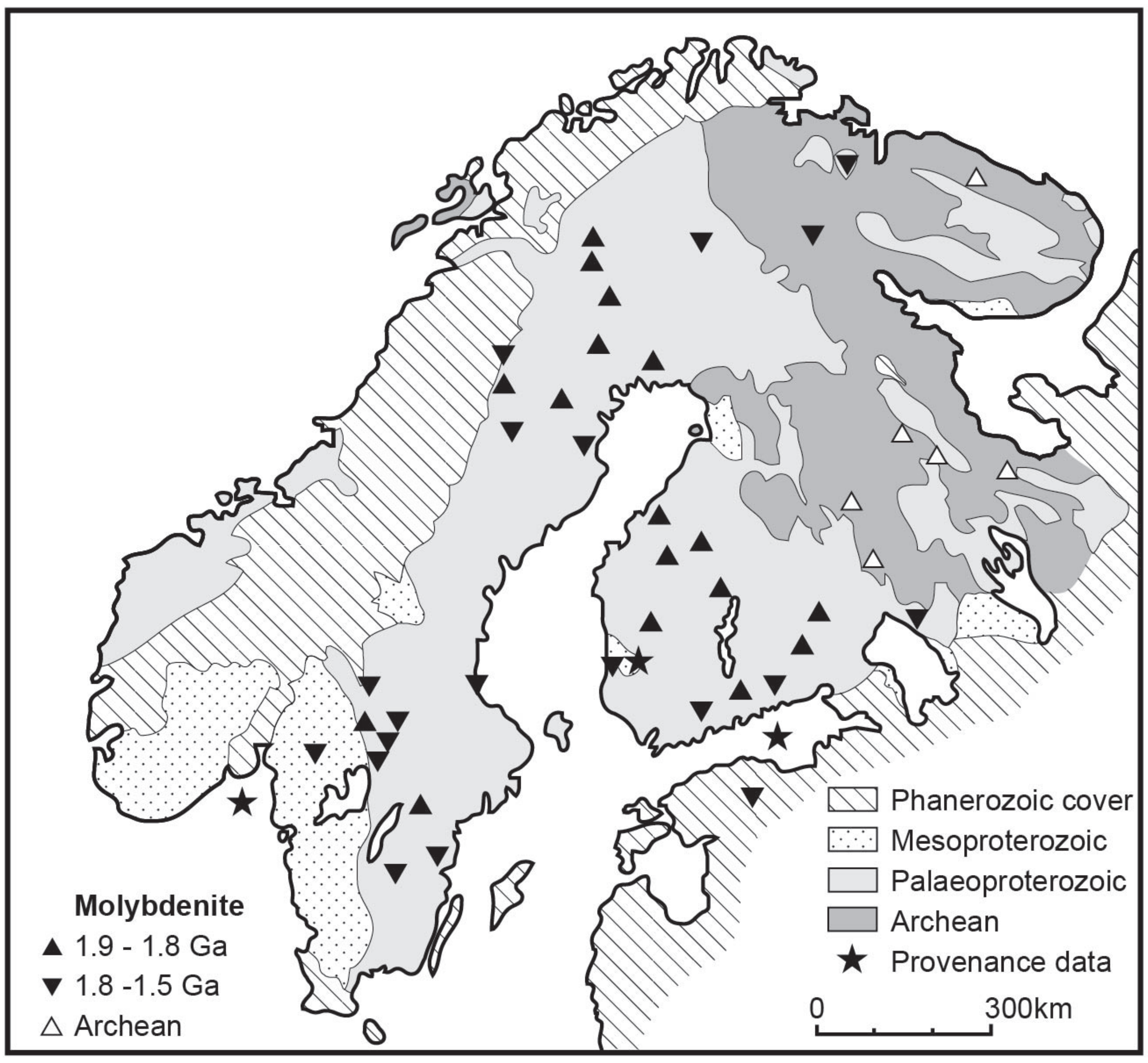
Figure captions

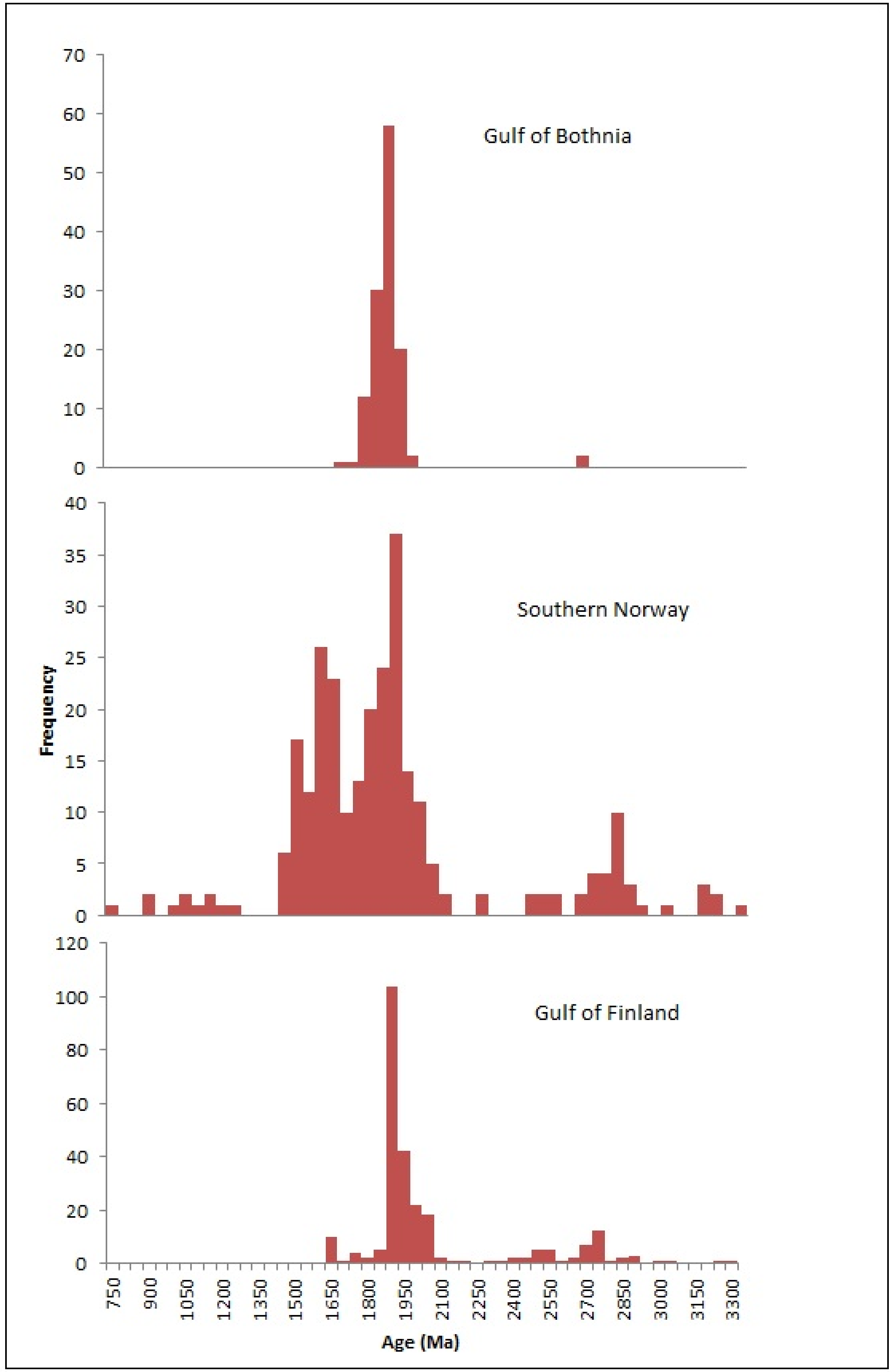
Fig. 1. Global palaeogeography in the mid-Proterozoic (1500 Ma), showing palaeocontinents with mid-Proterozoic molybdenite mineralization (star symbols). Map based on Pisarevsky et al. (2014). Continents: Am, Amazonia; Ba, Baltica; Con, Congo; G, Greenland; , Kal, Kalahari; La, Laurentia; NA, North Australia;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

Fig. 2. Mid-Proterozoic molybdenite occurrences in Baltica (Sweden, Finland, Russia, Estonia). Occurrences classified by age range. Stars indicate three regions of Mesoproterozoic zircon provenance data. Data sources in Supplementary Figure 1 and Supplementary Table 1.

Fig. 3. Zircon ages for mid-Proterozoic sandstones from three regions of Baltica. Data indicate sandstones are dominated by late Palaeoproterozoic sources, coincident with period of widespread molybdenite mineralization in Baltica (Fig. 2). Zircon data from Åhäll et al. (1998), de Haas et al. (1999), Bingen et al. (2001), Pokki et al. (2010, 2013).


SA
WA
Am
La
NA
NC
G
Sib
Ba
SF
Con
Kal


Phanerozoic cover
Mesoproterozoic
Palaeoproterozoic
Archean
Provenance data
0
300km
Molybdenite
1.9 - 1.8 Ga
1.8 -1.5 Ga
Archean


Gulf of Bothnia
Southern Norway
Gulf of Finland
Frequency
Age (Ma)
0
10
20
30
40
50
60
70
5
15
25
35
80
100
120
750
900
1050
1200
1350
1500
1650
1800
1950
2100
2250
2400
2550
2700
2850
3000
3150
3300