

Oceanic anoxic events, subduction style and molybdenum mineralization

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Abstract

Nearly half of the world's Mo resources are hosted in Cenozoic porphyries along the east Pacific margin. In contrast, there are essentially no large Mo porphyry deposits along the west Pacific. We propose that this uneven distribution is mainly due to Oceanic Anoxic Events (OAEs) and the different subduction regimes in the eastern and western Pacific margins. Molybdenum is rare in the Earth, with an abundance of 50 ppb in the primitive mantle, and 0.8 ppm in the continental crust. Pre-enrichment is needed for such a moderately incompatible element to form porphyry Mo deposits. The oxidation–reduction cycle on the Earth's surface is the major process that concentrates Mo. Molybdenum was more intensively oxidized under high erosion rates during alternating high-atmospheric-CO₂ and high-oxygen periods immediately before OAEs, resulting in high Mo concentrations in surface water and subsequently higher Mo concentrations in organic-rich sediments during the OAEs. Large amounts of Mo-enriched sediments formed on the Pacific Ocean floor during at least 9 major OAEs since the Late Jurassic. Given that Mo comes from chemical weathering, far more Mo-enriched sediment was available in the east Pacific because of the erosion of the continental arc. In contrast, due to backarc extension, erosions in the Western Pacific margin was less extensive, resulting in less Mo in OAE sediments on the Pacific Ocean floor. Importantly, the Eastern Pacific plate has been mostly subducted, with only Cenozoic crust left. During plate subduction, large amount of the Mo-rich sediments in the Eastern Pacific have been taken down to the mantle wedge. Subsequently these sediments were metamorphosed and then Mo was transferred to porphyry deposits through partial melting. In contrast, only a small amount of the sediment in the Western Pacific has been subducted, with most of the Jurassic and Cretaceous oceanic crust well preserved.

Molybdenum deposits of the Eastern Pacific margin can be classified into three types: porphyry-Cu-Mo, high-F porphyry and low-F porphyry-Mo deposits. Large and superlarge porphyry-Cu-Mo deposits are usually associated with ridge subductions, and thus formed through partial melting of subducted oceanic crust and metamorphosed Mo-rich sedimentary material due to subduction erosion. The high-F porphyry-Mo deposits (e.g., Climax-type) were likely formed by partial melting of subducted and thus metamorphosed Mo-enriched sediments during slab rollback (usually associated with A-type granite). Low-F porphyry-Mo deposits were formed through direct partial melting of metamorphosed Mo-enriched sediments entrained into the mantle wedge through subduction erosion at slightly shallower depths (usually associated with arc granite). Porphyry-Cu (Au) deposits in the southwest Pacific margin are all associated with subduction of backarc basins younger than the last OAE (55.8 Ma). Therefore, porphyry Cu (Au) deposits in the southwest Pacific margin have no economic levels of Mo. The oxygen fugacity of northwest Pacific is lower than $\Delta\text{FMQ} + 2$, which inhibits the formation of porphyry deposits.

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Keywords: Porphyry Mo deposits; Oceanic anoxic events; Weathering; Pacific; Cretaceous; Jurassic; black shale; Subduction erosion

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1. Introduction

Molybdenum (Mo) is one of the most important elements for modern society because of its variable properties that allow it to make materials ranging from super-hard alloys to solid lubricants. There are three main types of Mo deposits, high-F porphyry Mo, low-F porphyry Mo, and porphyry Cu–Mo deposits. Remarkably, half of the world's Mo resources are hosted in Cenozoic porphyries along the east Pacific margin (Fig. 1). In contrast, there are hardly any large Mo deposits along the west Pacific margin, whereas more than one third of the world's Mo sources are hosted in Cretaceous porphyry Mo deposits in the Triassic Qinling–Dabie orogenic belt (Chen et al., 2000; Li et al., 2012, 2007; Zhang et al., 2014). The formation of Mo deposits along the west coast of the North and South American continents has been attributed to different mechanisms: melting of underplated mafic/ultramafic rocks or intermediate crustal/organic-poor sedimentary rocks (Stein et al., 2001); addition of ore-forming fluids from large Mo enriched magma chambers that crystallized and fractionated in the lower crust or at mid-crustal levels well below the porphyry Mo deposits (Klemm et al., 2008), or subduction-related magmatism (Ludington et al., 2009). However, the details of the mechanism that enriched Mo within a short period of time in such a limited space remain obscure. Here we show that subducted Mo-enriched sediments, which formed during Oceanic Anoxic Events (OAEs), were responsible for the large Mo deposit belt along the eastern Pacific margin.

Metamorphism of Mo-rich sediments during subduction is another key factor that controls porphyry Mo deposits.

2. Molybdenum enrichment

Molybdenum is a very rare element with an abundance of only ~50 parts per billion (ppb) in the silicate Earth (McDonough and Sun, 1995), which is only ~0.1% of that of Cu. As a moderately incompatible chalcophile element, Mo is enriched in the continental crust during mantle magmatic processes (McDonough and Sun, 1995; Sun and McDonough, 1989; Sun et al., 2003b), but only by a factor of ~15 compared to the primitive mantle (Rudnick and Gao, 2003) to a level of ~0.8 parts per million (ppm). Nonetheless, Mo forms independent porphyry-Mo deposits with grades up to 0.3% of Mo metal, which is more than 3500 times higher than its abundance in the continental crust. Considering the similarities of Mo and Cu during magmatism and hydrothermal processes, it is surprising that the Mo concentration can be increased by more than 3 orders of magnitude during magmatic and/or hydrothermal processes without concomitant enrichment of Cu.

One of the most important ways that Mo can be concentrated and fractionated from Cu is through the oxidation–reduction cycle during chemical weathering on the surface of the Earth. During weathering, molybdenum is readily oxidized to form water-soluble MoO_4^{2-} in surface environments (Sun et al., 2015b), after the second major elevation of atmospheric oxygen in the Earth's history that occurred

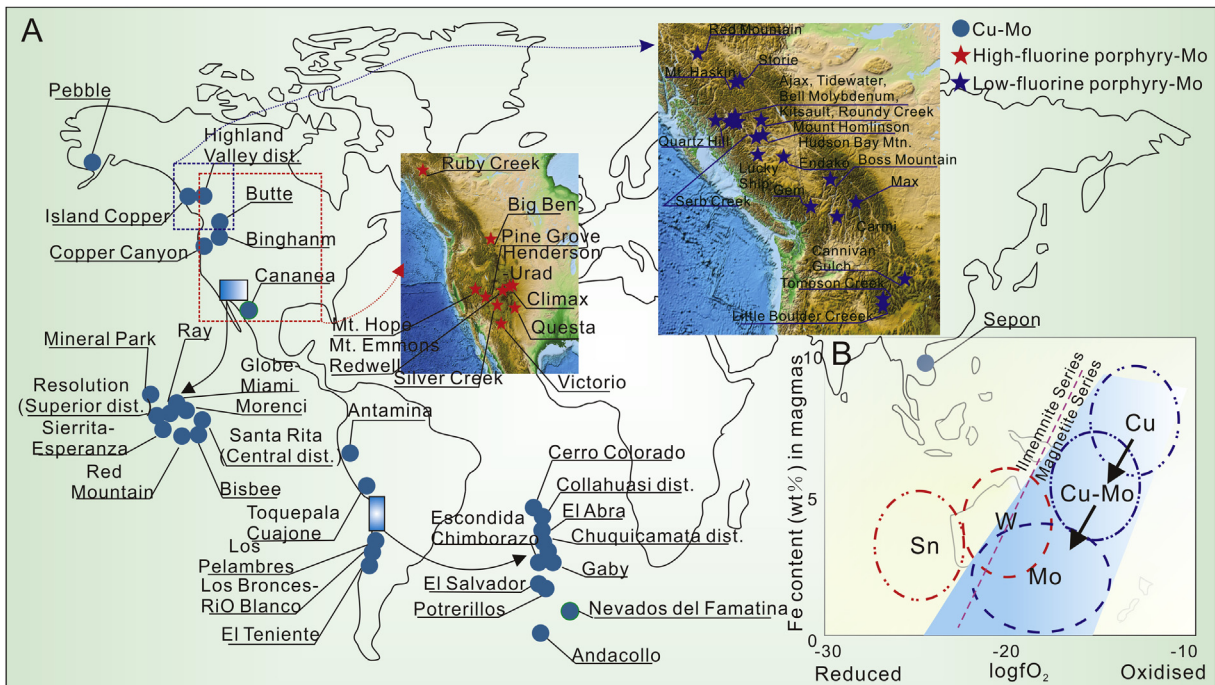


Fig. 1. A. The distribution of porphyry Mo deposits along the Pacific margins. Most of the porphyry-Cu-Mo deposits are closely associated with ridge subductions (Sillitoe, 2010; Sun et al., 2010). High-F porphyry-Mo deposits are found mainly in the Colorado mineral belt (COMB), which was a backarc basin in the Cretaceous and thus collected abundant Mo enriched sediments especially during the oceanic anoxic events (OAEs) (Ludington and Plumlee, 2009). Low-F porphyry-Mo deposits are closely related to porphyry-Cu deposits, but with low Cu contents (Ludington et al., 2009). B. Diagram of Fe versus oxygen fugacity, illustrating that porphyry-Cu-Mo deposits are systematically more oxidizing with higher Fe than porphyry-Mo deposits.

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