

## Porphyry deposits and oxidized magmas

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Porphyry deposits supply most of the world's Cu, Mo resources. Here we show that all the porphyry deposits are associated with oxidizing magmas. Oxidation promotes the destruction of sulfides in the magma source and thereby increases initial chalcophile element concentrations[1,2]. Sulfide remains undersaturated during the evolution of oxidized sulfur-enriched magmas where sulfate is the dominant sulfur species, leading to high chalcophile element concentrations in evolved magmas. The final porphyry mineralization is controlled by sulfate reduction, which starts with magnetite crystallization, accompanied by decreasing pH and correspondingly increasing  $fO_2$ . Hematite forms once sulfate reduction lowered the pH sufficiently and the  $fO_2$  reaches the hematite-magnetite oxygen fugacity buffer, which in turn increases the pH for a given  $fO_2$ . In addition to the oxidation of ferrous iron during the crystallization of magnetite and hematite, reducing wallrocks may also contribute to sulfate reduction and mineralization. For porphyry Cu deposits, slab melts (adakite) characterized by high Sr/Y is another controlling factor. Subduction of young ridge forms adakites with high fugacity, such that is the best geological process for porphyry Cu deposits[3,4]. Mo deposits are likely related to Mo-enriched metasediments.

[1] Sun W D *et al.* The link between reduced porphyry copper deposits and oxidized magmas. *GCA*, 2013, 103: 263-275. [2] Sun W D, *et al.* Geochemical constraints on adakites of different origins and copper mineralization. *J. Geology*, 2012, 120: 105-120. [3] Sun W D, *et al.* The genetic association of adakites and Cu-Au ore deposits. *International Geology Review*, 2011, 53: 691-703. [4] Sun W D, *et al.* Ridge subduction and porphyry copper-gold mineralization: An overview. *Science China-Earth Sciences*, 2010, 53: 475-484

## The global flux of calcium into and out of marine sediments

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Fundamental to understanding Earth's climate is an understanding of the removal of carbon from the surface into the rock reservoir. This removal of carbon is achieved through burial of carbon-bearing minerals, both carbonate and organic carbon, in marine sediments. Much of the organic carbon buried in marine sediments is oxidized back to inorganic carbon, which may react with subsurface calcium to precipitate authigenic carbonate, or may return via diffusion to the overlying ocean. The precipitation of authigenic carbonate has recently been invoked as a critical process in the long-term carbon cycle<sup>1</sup>.

We use a compilation of 674 pore fluid profiles acquired through the various drilling programs to calculate the flux of aqueous calcium across the sediment-water interface. In coastal regions and other areas of high organic-carbon supply to marine sediments, we calculate a flux of calcium into marine sediments; this calcium consumption is linked to the production of *in situ* authigenic carbonate. Parts of the ocean are dominated by a flux of calcium out of marine sediments, where calcium is produced in the subsurface through carbonate recrystallization, ion exchange, alteration of volcanic ash, or rarely subsurface gypsum dissolution. Our compilation suggests regional heterogeneity in the subsurface calcium (and carbon) cycle, as well as a global flux of calcium between the ocean and marine sediments that is significant in the global calcium cycle.

[1] Schrag *et al.*, (2013) *Science* **339**, 540-544.