



Separate zones of sulfate and sulfide release from subducted mafic oceanic crust



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ABSTRACT

Liberation of fluids during subduction of oceanic crust is thought to transfer sulfur into the overlying sub-arc mantle. However, despite the importance of sulfur cycling through magmatic arcs to climate change, magma oxidation and ore formation, there has been little investigation of the metamorphic reactions responsible for sulfur release from subducting slabs. Here, we investigate the relative stability of anhydrite (CaSO_4) and pyrite (FeS_2) in subducted basaltic oceanic crust, the largest contributor to the subducted sulfur budget, to place constraints on the processes controlling sulfur release. Our analysis of anhydrite stability at high pressures suggests that this mineral should dominantly dissolve into metamorphic fluids released across the transition from blueschist to eclogite facies (~ 450 – 650°C), disappearing at lower temperatures on colder geothermal trajectories. In contrast, we suggest that sulfur release via conversion of pyrite to pyrrhotite occurs at temperatures above 750°C . This higher temperature stability is indicated by the preservation of pyrite–bornite inclusions in coesite-bearing eclogites from the Sulu Belt in China, which reached temperatures of at least 750°C . Thus, sulfur may be released from subducting slabs in two separate pulses; (1) varying proportions of SO_2 , HSO_4^- and H_2S are released via anhydrite breakdown at the blueschist–eclogite transition, promoting oxidation of remaining silicates in some domains, and (2) H_2S is released via pyrite breakdown well into the eclogite facies, which may in some circumstances coincide with slab melting or supercritical liquid generation driven by influx of serpentinite-derived fluids. These results imply that the metallogenic potential in the sub-arc mantle above the subducting slab varies as a function of subduction depth, having the greatest potential above the blueschist–eclogite transition given the association between oxidised magmas and porphyry Cu(–Au–Mo) deposits. We speculate that this zoned sulfur liberation might be one of the factors that lead to the apparently redox-influenced zoned distribution of ore deposit types in the Andean arc. Furthermore, given the lack of sulfate-associated sea floor oxidation prior to the second great oxidation event, the pattern of sulfur transfer from the slab to the sub-arc mantle likely changed over time, becoming shallower and more oxidised from the Neoproterozoic onwards.

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1. Introduction

Sulfur is an abundant environment-influencing element that has played a key role in the evolution of life, and is a fundamental component of subduction-related ore-forming systems. Subduction of oceanic crust brings sulfur from the near-surface into the deep Earth, where metamorphism promotes further migration from the slab into the overlying sub-arc mantle (e.g., Richards, 2011), which is the ultimate source of metals for many of the world's largest ore deposits. However, there is little understanding of how the key

sulfur-bearing minerals, pyrite (FeS_2) and anhydrite (CaSO_4), behave during subduction zone metamorphism, so controls on the spatial and temporal distribution of sulfur liberation from the slab are poorly constrained.

Magmatic arcs contain numerous ore deposits, which collectively represent the main source of Cu and Mo, and a major source of Au (e.g., Richards, 2011). Some continental arcs have zoned metal distribution. In the Andes, in the vicinity of Chile, Bolivia and Argentina, the near-trench arc in the west contains gigantic porphyry Cu \pm Mo \pm Au and epithermal Au + Ag deposits, whereas to the east, further away from the trench, is a belt of pluton-related Sn-polymetallic and intrusion-related/orogenic gold deposits (Fig. 1). The oxidation state of felsic intrusions associated with these deposits also varies as a function of trench prox-

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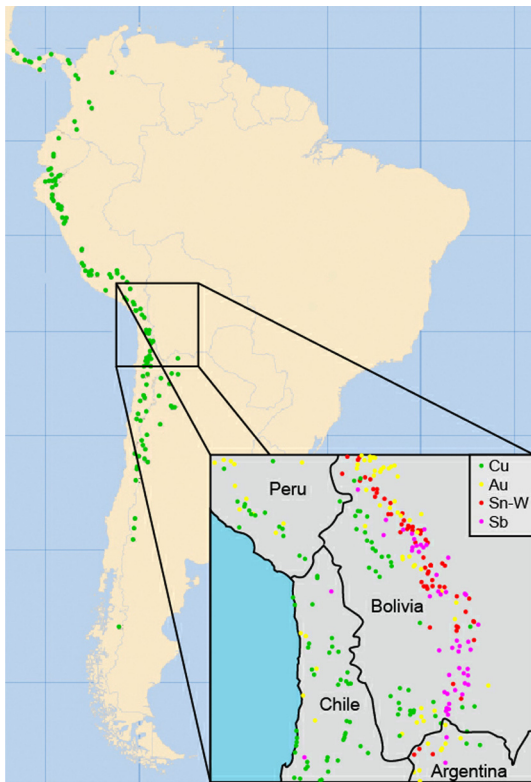


Fig. 1. Distribution of mineral deposit types in the central Andean arc, showing that trench-proximal deposits are dominated by porphyry Cu-(Au-Mo) and epithermal Au-Ag systems, whereas trench-distal deposits are dominated by intrusion-related Au and Sb systems. (For a colour version of this figure, the reader is referred to the web version of this article.)

imity; the near-trench porphyry Cu-associated intrusions tend to be oxidised (e.g., Richards, 2011), whereas those associated with the trench-distal deposit types tend to be reduced (Lang and Baker, 2001). It is generally accepted that magma oxidation state strongly influences the genesis of arc-related ore deposits (e.g., Richards, 2009, 2011). Although there is considerable discussion at present, some evidence favours the hypothesis that magma oxidation state is inherited from processes that occur in the mantle wedge above the subducting oceanic slab (e.g., Evans et al., 2012; McInnes et al., 2001, and references therein). A significant proportion of this mantle wedge oxidation may evolve through addition of slab-derived sulfate (Evans and Tomkins, 2011) via fluids that also carry other elements that are typically enriched in arc magmas.

Most mineral deposits found in magmatic arcs could not form without sulfur because it is a complexing ligand for aqueous transport of some metals, and a necessary co-precipitant for others. Oxidation state controls the nature of the chemical compounds that sulfur can form, and thus redox processes regulate sulfur-associated metal mobilisation, transport and deposition. For example, sulfide is an order of magnitude less soluble in basaltic melt than sulfate (Jugo et al., 2010), which thus influences the uptake of metals into basaltic magma during partial melting of the mantle wedge and during upward migration of arc magmas through the crust (Jenner et al., 2010; Tomkins et al., 2012). It is therefore important to understand the metamorphic reactions that release sulfur from the subducting oceanic slab, and the controls on sulfur redox state.

As metasomatised oceanic crust is subducted into the mantle at convergent margins, it is subjected to high pressure – low temperature metamorphism. As metamorphism progresses, pore water and exchangeable water are driven off at relatively shallow depths,

and then structurally bound water is liberated by a series of progressive metamorphic reactions as the slab pressure–temperature conditions increase from prehnite–pumpellyite to blueschist to eclogite facies. In this process hydrated silicates such as chlorite, glaucophane and lawsonite (in blueschists) are converted to anhydrous garnet and omphacite (in eclogites). The metamorphic reactions between silicate minerals are well understood, but there has been minimal research on the metamorphic controls on sulfur liberation from the slab prior to melting.

Here, we investigate the metamorphic processes that control sulfur liberation from subducting oceanic crust, in order to place constraints on the global sulfur cycle and on ore genesis. Basaltic oceanic crust provides the biggest contribution to the subduction zone sulfur cycle (Evans et al., 2012; Evans and Tomkins, 2011), so this paper focuses on sulfur-bearing mineral stability during subduction zone metamorphism of oceanic basalts. We firstly review the current understanding of the distribution of sulfur within the basaltic oceanic crust prior to subduction, before examining the metamorphic stability of two key minerals, anhydrite and pyrite. For anhydrite there are good experimental data, so we use thermodynamic modelling to investigate anhydrite dissolution in fluids produced by progressive slab metamorphism. However, there are few experimental data for pyrite above 0.5 GPa, so we use observations of natural samples of pyrite-bearing eclogites to place some constraints on pyrite stability. Our results suggest that sulfur may be released from subduction zones initially as sulfate at shallower levels, and then as sulfide at deeper levels. Because oxidation of the oceanic crust prior to subduction is driven by infiltration of sulfate in seawater, which has changed in abundance over time, our results have implications for understanding changes in the oxidation state of arc magmatic systems over billions of years.

2. Pre-metamorphic sulfur addition to the oceanic crust

In the modern Earth, sulfur is mainly dissolved in seawater as sulfate, which is the second most abundant anion after Cl^- . Unaltered mid-ocean ridge basalt (MORB) typically has a primary sulfur content of 950 to 1450 ppm (Jenner et al., 2010), mainly in the form of reduced magmatic sulfide (pyrrhotite – Fe_{1-x}S , chalcopyrite – CuFeS_2 , pentlandite – $(\text{FeNi})_9\text{S}_8$, and bornite – Cu_5FeS_4 in some cases). Prior to subduction, mafic oceanic crust becomes metasomatised at two main localities: (1) at mid-ocean ridges and ridge flanks, active rifting and high heat flow combine to promote downward seawater circulation into the upper oceanic crust, some of which is later expelled at black smoker chimneys close to the ridge axis (Fig. 2; e.g., Hannington et al., 2005); (2) at the pre-trench bend in the oceanic crust, normal faulting allows draw down of seawater into the oceanic crust (Faccenda et al., 2009). During this metasomatic alteration the upper oceanic crust initially reacts with oxidised sulfate-bearing seawater to transform the primary sulfides into a secondary sulfide assemblage, which varies as a function of oxidation state (Alt et al., 2010; Alt and Shanks, 2011; Barker et al., 2010; Staudigel, 2003). Pyrrhotite may be transformed into pyrite, and chalcopyrite, although typically retained, can be converted to bornite (Alt, 1989). Pentlandite is common in the secondary sulfide assemblage, and millerite (NiS) has also been observed (Alt, 1989). These authors also observed sphalerite and galena (PbS) in the secondary sulfide assemblage.

This sulfate reduction drives iron oxidation, and seawater infiltration is commonly associated with increased $\text{Fe}^{3+}/\Sigma\text{Fe}$ and hematite formation (Barker et al., 2010). More extensive infiltration and reaction precipitates anhydrite (CaSO_4) at temperatures up to $\sim 408^\circ\text{C}$ (Alt et al., 2010; Hannington et al., 2005). The oceanic crust is somewhat vertically zoned in its sulfur-bearing mineral distribution, varying as a function of extent of seawater infiltration and temperature, with lateral variation controlled by extent of

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