



# Sulphide–sulphate stability and melting in subducted sediment and its role in arc mantle redox and chalcophile cycling in space and time



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## ABSTRACT

The redox budget during subduction is tied to the evolution of oxygen and biogeochemical cycles on Earth's surface over time. The sulphide–sulphate couple in subducted crust has significant potential for redox and control on extraction of chalcophile metals from the arc mantle. We derive oxygen buffers for sulphide–sulphate stability ('SSO buffers') using mineral assemblages in subducted crust within the eclogite facies, and examine their disposition relative to the  $fO_2$  in the arc mantle along various P–T trajectories for subduction. The  $fO_2$  required for sulphide stability in subducted crust passing beneath an arc is shifted by variations in the bulk Ca/(Ca + Mg + Fe) of the subducting crust alone. Hotter slabs and more Fe-rich sediments stabilize sulphide and favour chalcophile sequestration deep into the mantle, whereas colder slabs and calcic sediment will stabilize anhydrite, in some cases at depths of melt generation in the arc mantle (<130 km). The released sulphate on melting potentially increases the  $fO_2$  of the arc mantle. We performed melting experiments on three subducted sediment compositions varying in bulk Ca/(Ca + Mg + Fe) from 0.3 to 0.6 at 2.5 GPa and 900–1100 °C to confirm how anhydrite stability can change by orders of magnitude the S, Cu, As, Zn, Mo, Pb, and Sb contents of sediment melts, and their subsequent liberation to the arc mantle. Using Cu/Sc as a proxy for the behaviour of S, the effect of variable subducted sediment composition on sulphide–sulphate stability and release of chalcophiles to the arc mantle is recognizable in volcanic suites from several subduction zones in space and time. The  $fO_2$  of the SSO buffers in subducted sediment relative to the arc mantle may have changed with time by shifts in the nature of pelagic sedimentation in the oceans over earth history. Oxidation of arc mantle and the proliferation of porphyry Cu deposits may be latter-day advents in earth history partly due to the rise of planktic calcifiers in the oceans in only the past 250 million years.

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## 1. Introduction

The upper oceanic crust is overlain by a thin veneer of sediments, the bulk compositions of which are an integration of weathering, hydrothermal alteration, and biochemical processes in the oceans. Some chemical components of oceanic sediment are recycled by subduction into the mantle source region for arc magmas which rise, form new crust that weathers and erodes, completing the cycle (Tera et al., 1986; Plank, 2005). The long-term impact of subducted sediment is recognizable in the geochemistry of mantle-derived magmas over time (Collerson and Kamber, 1999; Andersen et al., 2015) and is an important facet of the geochemical cycles for S, H, and C (Canfield, 2004; Hirschmann and Dasgupta, 2009).

The recycling of S by subduction is particularly important for biogeochemical cycles, the history of degassing of magmas, and the transfer of ore metals to the crust. Oceanic sediment contains significant levels of S (Alt and Burdett, 1992) and its release or sequestration during subduction may play a role in the redox of arc mantle and magmas (Evans, 2012), or control the deep earth S cycle over long time scales (Canfield, 2004). Sulphur isotopes in arc magmas suggest that subducted oceanic sediment is a likely and significant source for the S enrichment observed in arc magmas (Alt et al., 1993; De Hoog et al., 2001). Fluids or melt liberated from the subducted crust are efficient vectors for transport of S into the arc mantle (Evans, 2012; Jago and Dasgupta, 2013, 2014; Tomkins and Evans, 2015). What is not known, however, is if the recycling and release of S and other chalcophile elements into the sub-arc mantle is controlled by the parameters of subduction, or the wide range of possible bulk compositions of oceanic sediments, both of which vary in modern settings and over geologic time.

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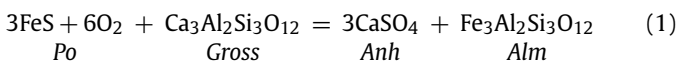
The redox budget of subducted sediment and its potential for oxidation of the arc mantle is dictated by the abundance and the interplay of S, H, C and/or Fe (Evans, 2012). Sulphur is the smallest in abundance of these elements in subducting crust, but has a large oxidation power: one mole of  $S^{6+}$  can oxidize eight moles of  $Fe^{2+}$  to  $Fe^{3+}$ . Constraints on the subduction and release of S inform the debate of how the arc mantle can become oxidized (Parkinson and Arculus, 1999), or whether the redox state of arc magmas is imprinted in their source, or a product of their ascent and differentiation (Kelley and Cottrell, 2012; Lee et al., 2005, 2010). Reducing conditions in oceanic sediment would stabilize sulphide and sequester S for limited oxidation potential, whereas oxidizing conditions will stabilize sulphate, possibly causing greater release of S during subduction and mantle oxidation (Prouteau and Scaillet, 2013). The budget for other ore metals in the arc setting (Cu, Pb, Zn) would also be controlled by the stability of sulphide, their primary host (McInnes et al., 1999; Mungall, 2002).

To this end, we first investigate how the bulk composition of oceanic sediments may control the stability of sulphide and sulphate during subduction. We then performed melting experiments on different oceanic sediment compositions at slab interface conditions to examine how the release of S or other chalcophiles is affected by redox state and sulphide stability, in scenarios where subducted sediments melt. Possible proxy signals on the cycling of S and chalcophile elements into the arc mantle are made evident using data from modern arcs in which the history of volcanism and incoming subducted sediment composition are known. We speculate how the mechanism for S recycling or arc mantle oxidation may have changed over earth history, due to shifts in the mode of carbonate sedimentation in the oceans over geologic time.

## 2. Sulphide–sulphate (SSO) oxygen buffers during subduction

The total bulk composition of a given sedimentary column on the ocean floor varies broadly between Si–Al-rich or ‘pelitic’ and Ca–Mg carbonate-rich end members (Fig. 1) depending on sedimentation rate, proximity to continental sources, biological productivity in the ocean, and the preservation of carbonate or opal (Plank and Langmuir, 1998). The hosts for S in oceanic sediments are sulphate (anhydrite) precipitated from oxic ocean water and sulphide (pyrite or pyrrhotite) formed hydrothermally or by biogenic reduction of seawater sulphate (Alt et al., 1993; Canfield, 2004). The concentration of sulphide or sulphate in oceanic sediments varies regionally, or even within the same sedimentary column (Alt and Burdett, 1992). Possible return pathways of S in these hosts to the mantle during subduction will be controlled by oxidation state (Prouteau and Scaillet, 2013).

Experiments show that all oceanic sediment compositions, regardless of whether pelitic or carbonate-rich (Fig. 1), produce an eclogitic assemblage (clinopyroxene + garnet + quartz/coesite ± phengite ± kyanite) when subducted (Mann and Schmidt, 2015). To examine and quantify the effect of  $fO_2$  on sulphide–sulphate stability in deeply subducted oceanic crust, we consider buffer reactions involving sulphides, anhydrite and the eclogite assemblage (clinopyroxene + garnet ± kyanite ± quartz/coesite). The first two are named ‘GAP’ (garnet–anhydrite–pyrrhotite):



and ‘CAP’ (clinopyroxene–anhydrite–pyrrhotite):

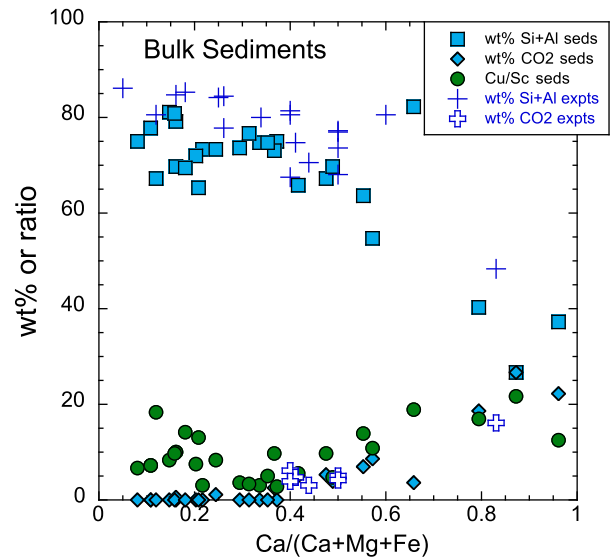
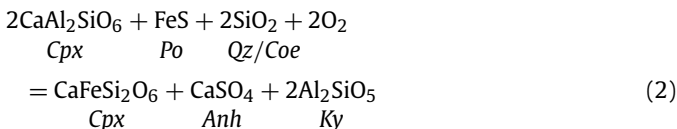
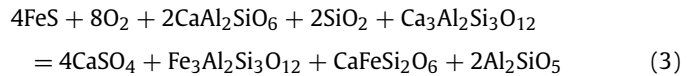
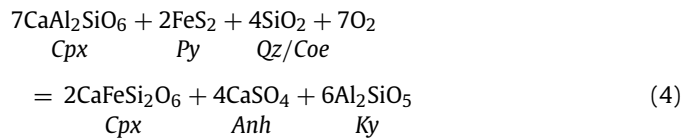


Fig. 1. Bulk compositions (wt%  $SiO_2 + Al_2O_3$ , Cu/Sc, wt%  $CO_2$  and  $X_{Ca}$  = molar  $Ca/(Ca + Mg + Fe)$ ) derived for composite marine sediment columns at trenches of various convergent margins (Plank and Langmuir, 1998). Note the spectrum of convergent margin sediments varies from pelitic to carbonate-rich, with no change on bulk Cu/Sc. These data are compared with those for starting materials in experiments on melting of sediments at subduction zone P–T conditions (Spandler et al., 2010; Hermann and Spandler, 2008; Thomsen and Schmidt, 2008; Skora and Blundy, 2010; Skora et al., 2015; Tsuno and Dasgupta, 2011; Prouteau and Scaillet, 2013; Mann and Schmidt, 2015).

These can be combined for clinopyroxene + garnet assemblages as ‘GCAP’:



Evidence from blueschists and eclogite terrains suggests the identity of the sulphide phase can be either pyrrhotite or pyrite during subduction at various metamorphic grades, though pyrrhotite is more common in metasediments at higher grades (Brown et al., 2014). Substitution of pyrite for pyrrhotite in (2) leads to the ‘CAPY’ reaction (clinopyroxene–anhydrite–pyrite):



Hereafter, we refer collectively to any of GCAP, GAP, CAP or CAPY (1)–(4) as the ‘SSO buffers’ in sediments at eclogite facies conditions.

Experimental data also show that the Ca and Fe components in garnet at eclogite facies conditions change with the bulk  $X_{Ca}$  (= molar  $Ca/(Ca + Fe)$ ) of subducted sediment compositions (Fig. 2). For this reason, the  $fO_2$  of the GAP or GCAP buffer (1), (3) at a given P and T is expected to shift in oceanic sediments as a function of their bulk composition, due to changing the activities of Fe- and Ca-bearing components in the garnet phases with bulk composition. A similar shift in the CAP or CAPY (2), (4) buffers is less obvious, however, because experimental data on sedimentary protoliths at eclogite facies conditions show that in clinopyroxene, the Tschermak ( $CaAl_2SiO_6 - X_{CaTs}$ ) component is typically low and varies little (<0.05), and the hedenbergite ( $CaFeSi_2O_6$ ) component is as strongly affected by T as by bulk composition (Fig. 2).

At a given P and T, the  $fO_2$  of the SSO buffers in equations (1) to (4) can be calculated using an internally consistent ther-

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