



Insights into subduction zone sulfur recycling from isotopic analysis of eclogite-hosted sulfides

K.A. Evans^{a,*}, A.G. Tomkins^b, J. Cliff^c, M.L. Fiorentini^d

^a School of Applied Geology, Curtin University, GPO Box 1987, Perth, WA 6845, Australia

^b School of Geosciences, Monash University, Melbourne, Victoria 3800, Australia

^c Centre for Microscopy, Characterisation and Analysis, University of Western Australia, Crawley, Perth, WA 6009, Australia

^d Centre for Exploration Targeting, ARC Centre of Excellence for Core to Crust Fluid Systems (CCFS), The University of Western Australia, 35 Stirling Highway, Crawley 6009, Western Australia, Australia

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ABSTRACT

Subduction of sulfur in ocean crust makes a significant but poorly understood contribution to the global sulfur cycle. Part of the uncertainty arises from a lack of knowledge about the metamorphic changes that affect subducted sulfur-bearing minerals, and the ultimate source of sulfur that is subducted to depth. Sulfur $\delta^{34}\text{S}$ varies both as a function of the original sulfur source, and as a consequence of processes subsequent to sulfide crystallisation such as devolatilisation, redox reactions, and fluid loss. To investigate sulfur liberation during subduction, secondary ion mass spectroscopy (SIMS) was used to measure $\delta^{34}\text{S}$ in grains of pyrite, chalcopyrite and pyrrhotite in eclogites from the Zermatt–Saas zone in the Western Alps, and the Pouébo terrane of New Caledonia. Trace element mapping on selected sulfide grains was also performed.

Sulfides in these rocks are generally associated with greenschist retrogression assemblages, but also occur as inclusions in garnet, associated with glaucophane and omphacite, and as polysulfide grains with typical magmatic combinations of minerals. $\delta^{34}\text{S}$ varies significantly within individual pyrite grains, with striking correlations, in some cases, between Co zoning and changes in $\delta^{34}\text{S}_{\text{VCDT}}$. $\delta^{34}\text{S}_{\text{VCDT}}$ is, in many cases, greater than 13‰, consistent with derivation from seawater-derived sulfate. The dataset suggests that sulfur isotopes in pyrite experienced little or no post-crystallisation re-equilibration, that pyrite grew under open system conditions with heterogeneous fluid flow on a thin section scale, and that sulfide growth involved sulfur addition. Prograde subduction processes most likely involved sulfur loss. Sulfide growth occurred in some samples at the very earliest stages of exhumation. Therefore these sulfides provide useful information on the fluids present in slabs at great depths.

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1. Introduction

Approximately 2.4×10^{12} mol of sulfur is subducted every year (Evans, 2012), which is an order of magnitude higher than the $1.6\text{--}3.2 \times 10^{11}$ mol of sulfur released from arc volcanoes every year (Hilton et al., 2002). The combination of the eight electron difference between sulfate and sulfide, and the large subduction-related sulfur flux suggests that the global sulfur cycle may form a major component of the redox cycle that links the biosphere and the interior of the Earth (Canfield, 2004; Canfield et al., 2007).

Sulfur is also intimately associated with the formation of many important ore deposit types. Sulfide minerals are the major hosts of most metals of economic significance (e.g., Cu, Pb, Zn, Ni, Co, Mo, PGE, Au, Ag, Sb, Bi), some elements (e.g. Au, Ag, Cu) are transported to ore-forming locations by S-bearing ligands (Benning and Seward, 1996; Pokrovski et al., 2009; Jago et al., 2010), and exsolution of immiscible sulfide liquids in magmas promotes concentration of metals of

economic and environmental interest (Mungall et al., 2006; Wallace and Edmonds, 2011). It is, therefore, hardly surprising that studies of temporal variation in ore deposit style have recognised that changes in sulfur availability and speciation are a major control on global metallogeny (Barley et al., 1998; Farquhar et al., 2010; Leach et al., 2010; Evans and Tomkins, 2011; Evans et al., 2012; Tomkins, 2013).

Despite the undoubted importance of sulfur cycling, parts of the global sulfur cycle are poorly understood. Some sulfur is recycled from oceanic crust to magmatic arcs. The S content of arc basalts is higher than that of mid-ocean ridge basalt (MORB) (Wallace and Edmonds, 2011) and $\delta^{34}\text{S}$ of sulfide and sulfate minerals in subduction zone-related porphyry copper deposits, which sample supra-arc crust is elevated over magmatic values, consistent with a contribution from seawater-derived sulfur (Marini et al., 2011). These data suggest that sulfur is transported into porphyry deposits via fluids that are released from the slab and propagate upwards through the mantle (Kelley and Cottrell, 2009; Richards, 2011). This inference is supported by sulfur isotope data from arc and back arc magmatic and gaseous products with elevated $\delta^{34}\text{S}$, consistent with recycling of modern seawater sulfate, which has a $\delta^{34}\text{S}$ of around 20‰ (Ueda and Sakai, 1984; Woodhead

* Corresponding author. Tel.: +61 8 92664682; fax: +61 8 92663153.
E-mail address: k.evans@curtin.edu.au (K.A. Evans).

et al., 1987; Marini et al., 2011). Some sulfate is released in fore-arc environments; observations of fluids released from the Mariana trench suggest that sulfate is released at shallow depths from sediments and altered basalt in the subducting plate into aqueous fluids that migrate up the subduction interface (Mottl et al., 2004). Some sulfur is also transported into the mantle; sulfides are common inclusions in eclogitic diamonds found in mantle xenoliths (Aulbach et al., 2010; Aulbach et al., 2012). The notion of deep recycling over at least the last 2.45 Ga is supported by mass independent sulfur fractionation signatures in sulfide inclusions in eclogitic diamonds (Thomassot et al., 2009), and in 20 Ma basaltic lavas thought to sample ancient recycled oceanic crust (Cabral et al., 2013).

Processes on the input side of the sulfur subduction cycle are less well understood. Surprisingly little is known about the reactions that release or retain sulfur within the subducting slab, or the nature and relative importance of mechanisms that release sulfur into the sub-arc environment.

Sulfides are common in blueschists and eclogites, although only a small fraction of papers describe sulfur-bearing phases in detail (Itaya et al., 1985; Reinecke, 1998; Spandler et al., 2004; Brown, 2007; Dale et al., 2009). Sulfide textures can be ambiguous, so that it is difficult to distinguish, for example, between pre-subduction hydrothermal, and retrograde pyrite. However, a combination of careful textural and trace element analysis with sulfur isotope measurements may provide a means to distinguish between the different sulfur sources and to recognise processes that modify sulfur distribution and speciation. Over the last 100 Ma, magmatic sulfides have entered subduction zones with a $\delta^{34}\text{S}$ value of around 0‰ (Ohmoto and Rye, 1979), seawater-derived sulfates with much higher $\delta^{34}\text{S}$ values, around 20‰ (Alt, 2003; Canfield, 2004), and sulfides related to sea-floor hydrothermal alteration cover a range of $\delta^{34}\text{S}$ values, between -10% and 10% (Alt, 2003; Alt et al., 2007). Bacterial sulfate reduction (BSR) imparts a wider range of $\delta^{34}\text{S}$ with fractionation values of up to 50‰ (Canfield, 2001). Metamorphic loss of sulfur-bearing volatiles, such as H_2S , changes the sulfur isotope value of the residue. These changes can be estimated, given information on fractionation factors between solid and fluid-hosted phases, and the extent to which the fluid–rock system operates as open or closed system (e.g. Ohmoto and Rye, 1979). It may, therefore, be possible to use the sulfur isotope composition of sulfides in subducted and exhumed rocks to constrain the sources of sulfur and the processes experienced by these sulfides during subduction.

In this work, we present the results of high spatial resolution sulfur isotope, trace element, and textural analyses for sulfides hosted by blueschists, eclogites and retrogressed eclogites. The data are used to derive preliminary constraints on the subduction-related component of the sulfur cycle.

2. Geological setting

Samples for this study were taken from three well known blueschist/eclogite localities: Pfulwe pass and Lago di Cignana in the Zermatt–Saas zone in the European Alps (Rubatto et al., 1998), and the Pouébo eclogite melange of New Caledonia (Aitchison et al., 1995). These localities were chosen because they are well studied and characterised, and because they provide examples of different geothermal gradients and subduction environments. Details of these localities are summarised briefly below.

2.1. Zermatt–Saas zone

The Zermatt–Saas zone in the Penninic domain of the Western Alps provides spectacular km-scale ophiolites, which have been interpreted as Tethyan oceanic lithosphere formed in the late Jurassic (Rubatto et al., 1998) although more recent work suggests that the ultramafic units may, instead, be continental mantle lithosphere associated with the ocean-continent transition (Beltrando et al., 2010). The Zermatt–

Saas zone has been proposed to be a continuous slice of lithosphere (Angiboust et al., 2009), based on relatively homogeneous pressures and temperatures, of around 2 GPa and 540–600 °C, across the block, although this interpretation is not universally held (Martin et al., 2008). The lithosphere represented by the Zermatt–Saas zone was subducted and exhumed to form part of a nappe stack between 50 and 40 Ma (Bocquet et al., 1974; Barnicoat and Fry, 1986; Rubatto et al., 1998). The ophiolite contains serpentinites (Li et al., 2004), gabbros, metabasalts, hydrothermally altered mafic rocks (Martin et al., 2008) and Jurassic metasediments (Reinecke, 1991; Rubatto et al., 1998).

2.1.1. Lago di Cignana

Lago di Cignana provides undisputed evidence of subducted oceanic crust that has reached ultra-high pressure metamorphic (UHPM) conditions (Reinecke, 1991, 1998; Frezzotti et al., 2011). Coesite-bearing rocks at Cignana occur within an area of around 2 km², which is bounded by masses of serpentinitised peridotites, and comprise a sequence of relict coesite-glaucophane eclogites and retrogressed greenschists, plus metasediments that overlie the eclogites. The fresh eclogites consist of garnet + omphacite + phengite + glaucophane ± rutile. Overprinting blueschist and greenschist retrograde assemblages are common.

A Mn-rich layer lies at the base of the metasediments (Reinecke, 1991). This layer is overlain by interlayered garnet + phengite + quartz schists, phengite-bearing quartzites, garnet + phengite mica schists, and dolomite-bearing calc-schists (Reinecke, 1998). Inclusions of chalcopyrite and pyrite have been recorded in sediment-hosted garnets at Cignana (Reinecke, 1998).

2.1.2. Pfulwe

Pfulwe pass lies about 10 km east of Zermatt (Fig. 1A). Rocks in the vicinity of the pass include metagabbros of the Allalin Gabbro, and eclogite metabasalts, some of which locally preserve pillow lava structures (Barnicoat and Fry, 1986). Samples used in this study were collected from the basaltic units. Zircon dates from the gabbro adjacent to the basalts gives a Jurassic age of around 164 Ma (Rubatto et al., 1998). Peak metamorphic pressures and temperatures for the Pfulwe area were estimated to be >2 GPa and 550–600 °C (Barnicoat and Fry, 1986); it has been suggested that peak pressures for the Allalin gabbro were as high as 3.5 GPa (Barnicoat, 1985). Some of the basalts are partially retrogressed, but most preserve eclogitic assemblages with minor evidence of modification during exhumation. Minerals present are omphacite + garnet + paragonite ± glaucophane ± quartz ± epidote ± chloritoid ± talc (Widmer and Thompson, 2001). High-pressure vein assemblages in the area include quartz + glaucophane + ankerite, quartz + omphacite, and omphacite veins. Dale et al. (2009) provide a detailed description of sulfide mineral assemblages in rocks of the Allalin gabbro. Relatively unaltered gabbro contains pyrrhotite, pentlandite and chalcopyrite, which are inferred to have had an igneous origin. More altered gabbros, and the basalts, contain large pyrite grains, which are attributed to a metamorphic-hydrothermal origin. Further evidence for pre-metamorphic sulfides in these rocks is provided by Barnicoat and Fry (1986) who note that chalcopyrite is distributed throughout the basaltic rocks in this area, and in pre-metamorphic veins.

2.2. Pouébo eclogite melange, New Caledonia

Blueschists and eclogites crop out in the north-east of New Caledonia. These high pressure, low temperature rocks are inferred to have formed during subduction of oceanic crust in the Eocene (Black, 1977; Spandler et al., 2005). The region of interest for this study are the highest pressure rocks, which lie at the north-eastern corner of the island (Fig. 1B), and have been named the Pouébo terrane (Cluzel et al., 1995; Clarke et al., 1997; Carson et al., 1999; Fitzherbert et al., 2003), the Pouébo eclogitic melange (Spandler and Hermann, 2006), or the omphacite zone (Itaya et al., 1985). These eclogites and transitional eclogites are mostly mafic, with subordinate ultramafic and pelitic lithologies. The protoliths to

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