

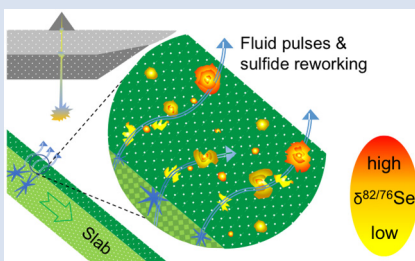
Selenium isotope evidence for pulsed flow of oxidative slab fluids

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Abstract



sulfide reworking within the subducted crust can be reconciled with episodes of oxidised fluid pulses from underlying slab mantle in modern subduction zones.

Isotope systematics of the redox sensitive and chalcophile element selenium (Se) were investigated on exhumed parts of subducted oceanic lithosphere to provide new constraints on slab dehydration conditions during subduction. The samples show increasing $\delta^{82/76}\text{Se}_{\text{NIST3149}}$ with higher abundances of fluid mobile elements, comprising a larger range (-1.89 to $+0.48$ ‰) than that of mantle (-0.13 ± 0.12 ‰) and altered ocean crust (-0.35 to -0.07 ‰). Our data point to pronounced, local scale redox variations within the subducting crust, wherein oxidative fluids dissolve sulfides and mobilise oxidised Se species. Subsequently recrystallising sulfides preferentially incorporate isotopically lighter, reduced Se, which shifts evolving fluids and late stage sulfides to higher $\delta^{82/76}\text{Se}_{\text{NIST3149}}$. Redistribution of Se by repeated cycles of

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Introduction

The development of a habitable Earth with its atmosphere–ocean system is closely linked to plate tectonics and the efficient exchange of elements between interior and exterior reservoirs. Key aspects are the subduction cycles of water, carbon and sulfur and the redox state of arc magmas. It is particularly debated if the oxidised nature of arc magmas is due to oxidised slab components or related to secondary processes during the evolution of arc melts (e.g., Lee *et al.*, 2012; Chen *et al.*, 2019; Tollan and Hermann, 2019). Likewise, different models for sulfate- and ³⁴S-enriched arc lavas involve either slab-derived sulfur flux into the overlying mantle wedge or crustal assimilation by ascending magma (e.g., Lee *et al.*, 2012; Pons *et al.*, 2016). Recent *in situ* S isotope investigations of sulfides from exhumed high pressure rocks reveal prograde subduction related mobilisation and re-entrapment of S during (partial) sulfide breakdown and recrystallisation, resulting in differences in $\delta^{34}\text{S}$ of almost 40 ‰ (Evans *et al.*, 2014; Su *et al.*, 2019; Li *et al.*, 2020; Walters *et al.*, 2020), with contrasting data for different localities suggesting either oxidised, SO₂- and CO₂-rich or reduced, H₂S-rich fluid involvement (see also Piccoli *et al.*, 2019).

To further elucidate the redox role of slab-derived components, we combine the novel tool of stable selenium isotopes with a suite of well characterised high pressure rocks of oceanic origin. In comparison to other redox sensitive elements like Mo, S and Fe, Se combines the characteristics of being chalcophile

and a trace element that does not act as a major constituent of sulfide. Selenium, therefore, participates in sulfide dissolution–recrystallisation processes within the slab as a witness without being biased as a major constituent of a mineral. Moreover, the transition to selenite (oxidised Se species; SeO₃²⁻; see S–Se species stability fields in Fig. 1) occurs at even higher *f*O₂ compared to the transition to sulfate (oxidised S species; SO₄²⁻). Thus, Se isotope fractionation reflects a strong reduction of at least selenite to selenide from originally higher *f*O₂ than the sulfate–sulfide transition (Fig. 1). Selenium isotopes may thus be useful in constraining the conditions during slab fluid-mediated sulfide redistribution, in particular, if more pronounced redox variations occur in fluids that so far remained beyond the scope of S isotope systematics (König *et al.*, 2019) and previously employed, lithophile (e.g., Mo–Li–N–Ti) stable isotopes in subduction related studies.

The Raspas Complex in SW Ecuador resembles a deeply subducted (~60 km) ophiolite complex that formed during the early Cretaceous at the South American margin. Trace element and radiogenic isotope data revealed that the ophiolite consists of depleted abyssal oceanic mantle, oceanic crust (MORB-type eclogites), associated seamounts (blueschists), and sedimentary cover (John *et al.*, 2010; Halama *et al.*, 2011). The entire complex was metamorphosed at HP/LT conditions (~600 °C and *ca.* 2.0 GPa) and most of the rocks experienced subduction related, prograde dehydration related intra-slab fluid flow during burial (John *et al.*, 2010; Halama *et al.*, 2011; Herms *et al.*, 2012;

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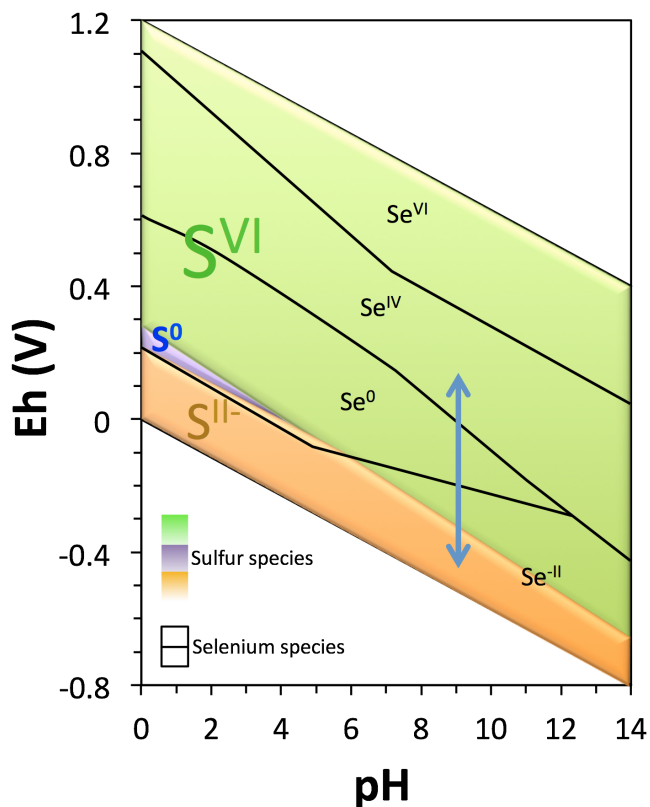


Figure 1 Combined S and Se Pourbaix diagrams for 25 °C and 1 bar pressure. Large arrow shows required minimum redox variation for selenite-selenide transition that requires higher redox variation than the sulfide-sulfate transition for slab fluids with pH of up to 9 in subduction zones (Galvez *et al.*, 2016).

Chen *et al.*, 2019; Urann *et al.*, 2020). The Raspas complex thus represents an exceptional example of a rather complete sequence of an oceanic lithosphere that has experienced long lived oceanic subduction and is not compromised by potential effects of subsequent continent-continent collision.

Samples

The samples analysed here comprise seven eclogites, one metapelite, and three high pressure serpentinites from the Raspas Complex (Supplementary Information Tables S-1 and S-2). They have been thoroughly investigated for their petrology and all samples record evidence for hydration prior to subduction, but have been mostly selected to avoid any detectable exhumation related overprint (John *et al.*, 2010; Halama *et al.*, 2011; Herms *et al.*, 2012). A comprehensive major, trace element, Rb-Sr, Sm-Nd, Lu-Hf geochronological and stable Mo-Li-N-Tl isotope dataset is also available (*e.g.*, Halama *et al.*, 2010; John *et al.*, 2010; Chen *et al.*, 2019; Su *et al.*, 2019). We also analysed four serpentinites and gabbros from the deepest Pacific drillcore available (IODP-1256D; Table S-1). We combine this sample set with an average composition of marine sediment from the literature to provide a reliable estimate of subduction input signatures.

Selenium Isotope Signatures of Prograde Metamorphic Rocks

Compared to the relatively small range for mantle samples including average MORB with $\delta^{82/76}\text{Se}$ ($\delta^{82/76}\text{Se} = [({}^{82}\text{Se}/{}^{76}\text{Se})_{\text{sample}} / ({}^{82}\text{Se}/{}^{76}\text{Se})_{\text{NIST3149}} - 1] \times 1000$) of -0.16 ± 0.12 ‰

(2 s.d.; Yierpan *et al.*, 2019), peridotites of -0.03 ± 0.07 ‰ (Varas-Reus *et al.*, 2019) and the limited variability observed in seawater overprinted altered ocean crust (AOC) with $\delta^{82/76}\text{Se}$ of -0.35 to -0.07 ‰ (Pacific drillcore samples; Table S-1), eclogites record a large variation in $\delta^{82/76}\text{Se}$ from -1.89 to $+0.48$ ‰ (Fig. 2; see Supplementary Information for analytical methods). High pressure serpentinites and metapelites show $\delta^{82/76}\text{Se}$ of $+0.07$ to $+0.39$ ‰, overlapping with the highest $\delta^{82/76}\text{Se}$ values of eclogites. $\delta^{82/76}\text{Se}$ values show no systematic variations with Se concentrations (6 to $106 \text{ ng}\cdot\text{g}^{-1}$) and samples with the highest Se contents span the entire Se isotope range of the dataset. High pressure serpentinites show highest relative abundances of fluid mobile elements like Pb, Rb, Cs (Fig. 2a–c) or Ba, Li (not shown) when plotted as ratios with fluid immobile Ce as the denominator (see also Fig. S-1). All eclogites show a trend towards lower $\delta^{82/76}\text{Se}$ with decreasing Pb/Ce, Rb/Ce and Cs/Ce (Fig. 2a). Eclogites with the lowest $\delta^{82/76}\text{Se}$ sample also display the lowest $\delta^{98/95}\text{Mo}$ (Fig. 2d; Mo data by Chen *et al.*, 2019) but two samples with only intermediate $\delta^{98/95}\text{Mo}$ show the most positive $\delta^{82/76}\text{Se}$. Additionally, eclogites with the lowest $\delta^{82/76}\text{Se}$ show the highest contents of Cu, Cl, Sc (Fig. 3) and N as well as the smallest $\delta^{15}\text{N}$ range (Fig. S-2; Halama *et al.*, 2010; Urann *et al.*, 2020). No correlations between $\delta^{82/76}\text{Se}$ and Li or Tl isotopes are observed (Fig. S-2).

Selenium Isotope Vestige of Slab Dehydration

Selenium isotopes do not fractionate significantly during melting, fractional crystallisation and metasomatism (Varas-Reus *et al.*, 2019; Yierpan *et al.*, 2019). The $\delta^{82/76}\text{Se}$ range of eclogites and clear positive covariations of $\delta^{82/76}\text{Se}$ with several fluid proxies (Fig. 2a–c) therefore suggest a non-magmatic origin of these signatures. Moreover, since the eclogite facies mineral assemblages show no evidence of subsequent retrograde greenschist facies overprint (except for one sample selected here; John *et al.*, 2010; Herms *et al.*, 2012), the $\delta^{82/76}\text{Se}$ and their preserved fluid related trends must be attributed to dehydration processes prior to exhumation. Analysed AOC extends to slightly lower $\delta^{82/76}\text{Se}$ and the high pressure serpentinites to slightly higher $\delta^{82/76}\text{Se}$ than mantle, while both assemblages maintain a much narrower range than the eclogites. Light S isotope compositions of pyrite in subducted rocks from SW Tianshan, China could be traced back to the alteration of oceanic crust and subsequent, fluid driven sulfide recrystallisation events with prograde metamorphism (Su *et al.*, 2019). Such abyssal seawater-rock interaction therefore also explains the low average $\delta^{82/76}\text{Se}$ in our AOC, due to scavenging related partial reduction of preferentially light Se isotopes in an entirely oxic water column (*e.g.*, Johnson, 2004). In conclusion, following subduction of AOC with moderately low $\delta^{82/76}\text{Se}$, higher $\delta^{82/76}\text{Se}$ of the high pressure serpentinites as well as the large $\delta^{82/76}\text{Se}$ range of the eclogites are best explained by slab dehydration during prograde metamorphism at the blueschist-eclogite transition.

Role of Oxidised Slab Fluids

In fluid-solid systems, isotopes of Se are significantly fractionated during partial reduction of oxidised Se^{6+} to Se^{4+} or further to Se^{2-} (Johnson, 2004). Sulfides thus preferentially incorporate isotopically light Se (*e.g.*, König *et al.*, 2019). Even at 25 °C and 1 atm, the transition from Se^{2-} to Se^0 and Se^{4+} starts at higher redox potential (Eh) and thus require higher $f\text{O}_2$ than the sulfide-sulfate transition (Fig. 1). This difference remains with slightly elevated slab fluid pH of up to 9 in subduction zones

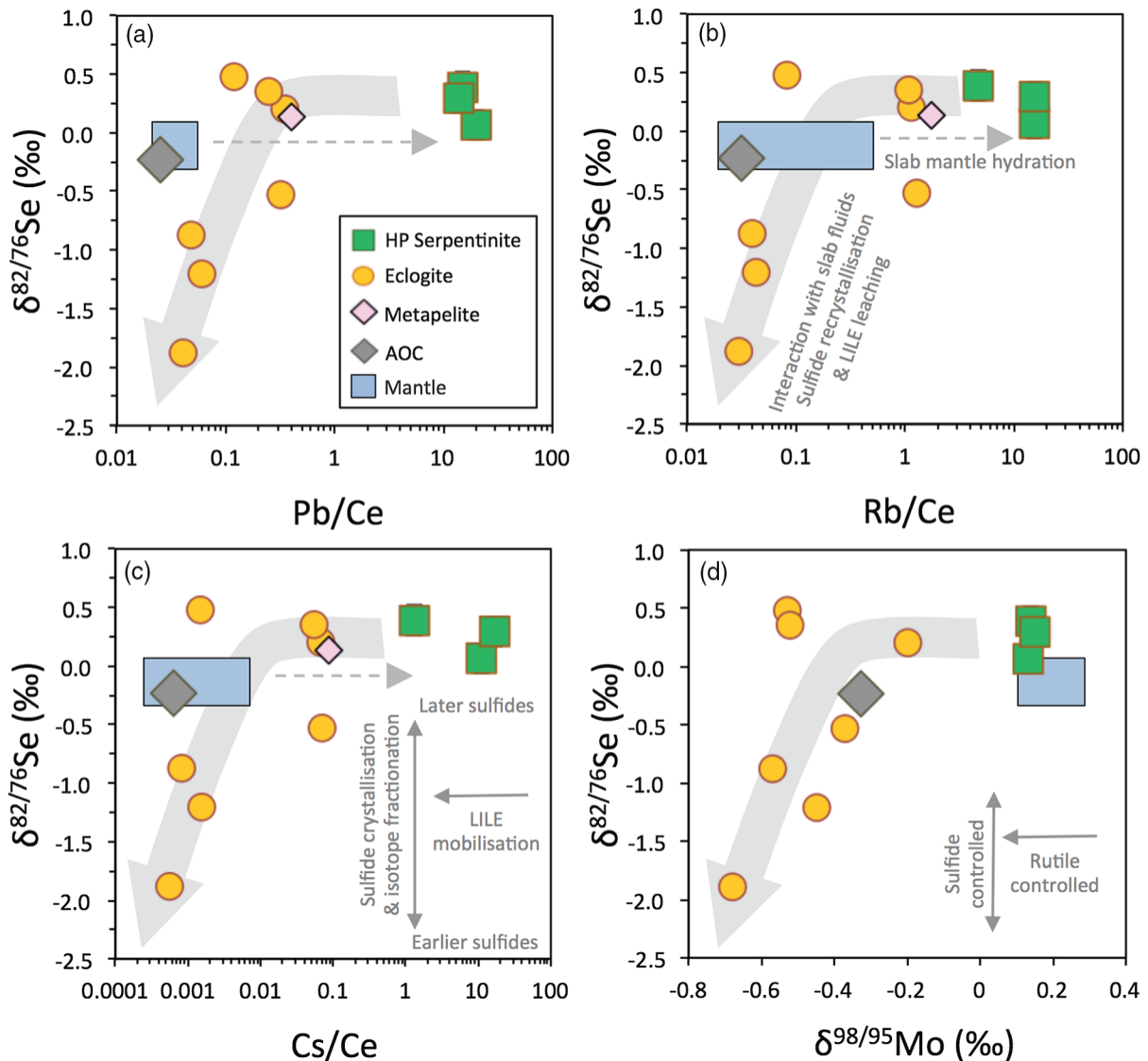


Figure 2 Selenium isotope composition of Raspas samples and AOC from 1256D vs. (a) Pb/Ce, (b) Rb/Ce, and (c) Cs/Ce (Halama *et al.*, 2010; John *et al.*, 2010), and (d) $\delta^{98/95}\text{Mo}$ variation. Mantle includes representative peridotites (Varas-Reus *et al.*, 2019) and MORB (Yierpan *et al.*, 2020). The large grey arrow (Figs. 2, 3) represents our interpretation of the effects of slab mantle dehydration and increasing interaction of subducted crust with slab fluids. The source of Mo is HP serpentinite (Chen *et al.*, 2019), whereas Se is derived mostly from the AOC. As HP serpentinites dehydrate and flush the overlying subducted AOC, rutiles in the subducted crust preferentially retain low $\delta^{98/95}\text{Mo}$ as the complementary, high $\delta^{98/95}\text{Mo}$ fluid is removed into the mantle wedge (Freymuth *et al.*, 2015; Chen *et al.*, 2019). Recrystallising, early sulfides preferentially incorporate light Se isotopes and later stage sulfides become isotopically heavier. Repeated sulfide dissolution-recrystallisation produces a spectrum of low and high $\delta^{82/76}\text{Se}$ in the flushed AOC.

(Galvez *et al.*, 2016). At present, $\text{Se}^{6+}/\Sigma\text{Se}$ equilibrium values for substantially higher temperatures and pressures are unavailable and therefore the quantification of $f\text{O}_2$ from the inferred presence of oxidised Se in slab fluids requires further experimental work. However, such experimentally derived constants exist for $\text{S}^{6+}/\Sigma\text{S}$ and were previously used to infer a range of slab fluid FMQ of +1.0 to +1.4 at 1.5 GPa from observed sulfate as well as anhydrite saturation in sub-arc mantle peridotites and melt inclusions (Bénard *et al.*, 2018). The sulfate-sulfide transition at conditions relevant to the Raspas eclogite suite at 2 GPa and 600 °C requires *ca.* FMQ +2.5. If significant ΔEh between lower sulfate and selenite stabilities persist at 600 °C and 2 GPa, the occurrence of oxidised Se points to above FMQ +2 for slab fluids involved here. This would agree with previous estimates for slab fluid $f\text{O}_2$ above FMQ +2 based on Mo isotope data of Raspas eclogites (Chen *et al.*, 2019). More accurate constraints require experimental work, yet Se isotope data can already be

attributed to more pronounced minimum redox variations than those required for stability of oxidised S and even Mo in the subducting slab, as supported by other studies arguing for variably pronounced oxidation potentials of fluids in subduction zones (*e.g.*, Bénard *et al.*, 2018; Chen *et al.*, 2019; Piccoli *et al.*, 2019; Li *et al.*, 2020; Walters *et al.*, 2020).

Sulfide Dissolution-Recrystallisation

High pressure, intra-slab fluid flow occurs as channelised and in pulses, variably affecting slab mineralogy (*e.g.*, Herms *et al.*, 2012; John *et al.*, 2012; Chen *et al.*, 2019). The lack of systematic covariations between $\delta^{82/76}\text{Se}$ and other stable isotope signatures of Li, N, and Tl in Raspas eclogites points to different controls on each isotope signature. Kinetically controlled Li isotope fractionation is related to diffusion during fluid-rock interaction



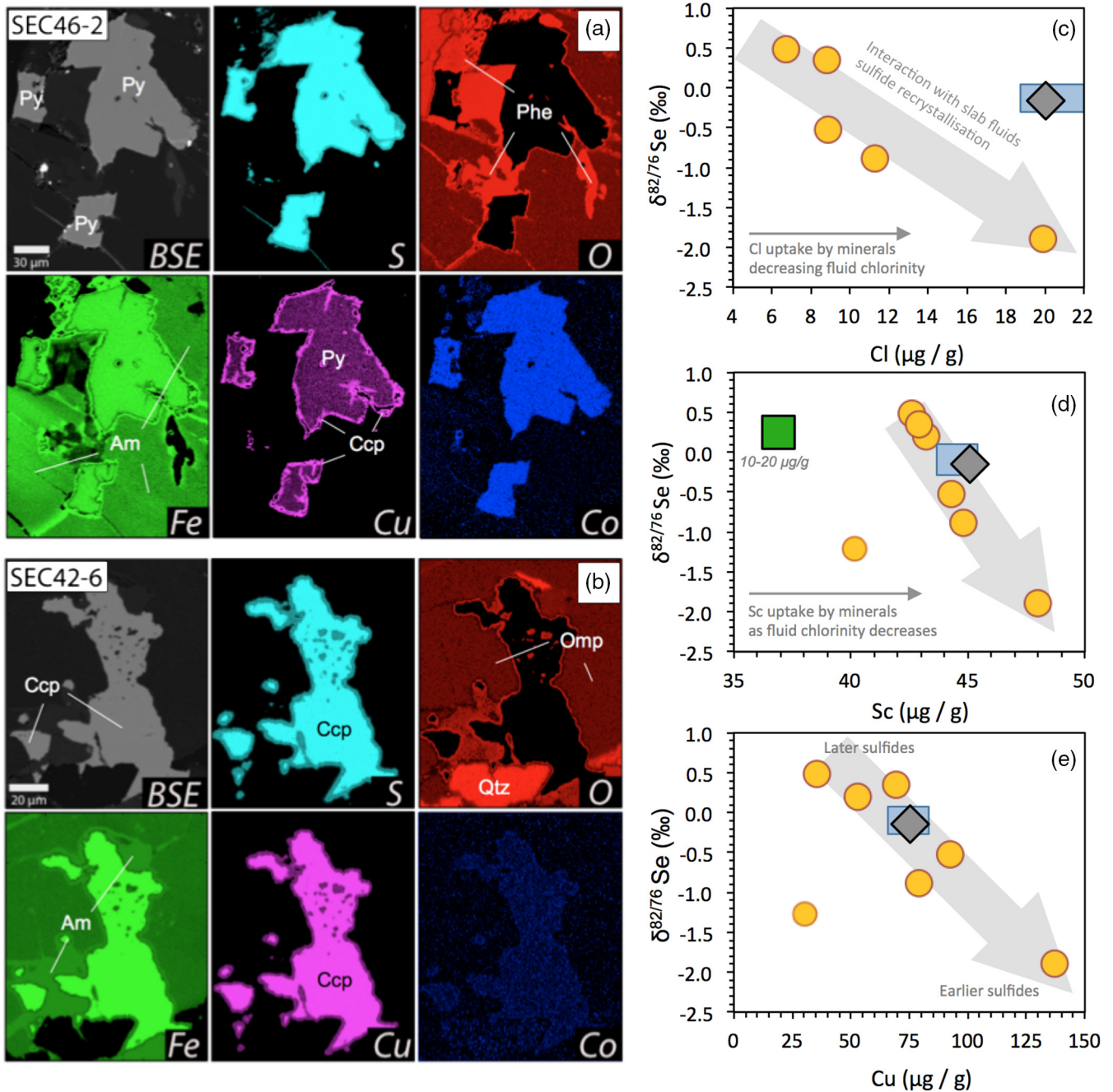


Figure 3 BSE images and semi-quantitative element mapping of sulfides in Raspas eclogites: (a) a partially resorbed Co-bearing pyrite, showing high Cu and Fe contents at the recrystallised chalcopyrite rim and (b) an example of a chalcopyrite with a narrow and oxidised rim, indicated by the lower S and Cu contents. Trends of $\delta^{82/76}\text{Se}$ vs. concentrations of (c) Cl, (d) Sc and (e) Cu in prograde eclogites are interpreted to result from this changing fluid-mineral chemistry. Symbols are the same as those used in Figure 2.

(Halama *et al.*, 2011). Lighter N and Tl isotope signatures of Raspas eclogites compared to MORB indicate preservation of low temperature AOC signatures during subduction (Halama *et al.*, 2010; Shu *et al.*, 2019). In contrast to these lithophile element based isotope systems, chalcophile Se substitutes for S in sulfides and witnesses repeated sulfide dissolution-recrystallisation events as fluids pulse through the slab (Evans *et al.*, 2014; Su *et al.*, 2019; Li *et al.*, 2020). This is supported by the mineral assemblages of the eclogites that show sulfides in different stages of dissolution and recrystallisation (Fig. 3a,b) and covariations between $\delta^{82/76}\text{Se}$ and trace elements (Fig. 3c–e). Eclogite 46-2, for which a partially recrystallised pyrite with highest Co contents and high Cu (chalcopyrite) rims is shown

(Fig. 3a), has the lowest bulk $\delta^{82/76}\text{Se}$ and highest Cl contents (Fig. 3c). This sample also contains abundant apatite, with up to $300 \mu\text{g}\cdot\text{g}^{-1}$ Cl (Urann *et al.*, 2020), suggesting that breakdown of hydrous Cl complexes, possibly cause co-precipitation of cations like Sc that partition into matrix minerals (e.g., Sc into omphacite and garnet, Fig. 3d). This coincides with recrystallisation of sulfides that increase Cu contents in eclogites (Fig. 3a,e). Whereas Mo isotopes in the bulk eclogites record the integrated and unidirectional signature of interaction between fluid and rutile-bearing rocks (Fig. 2d; Chen *et al.*, 2019), $\delta^{82/76}\text{Se}$ signatures in subducted rocks seem to capture snapshots of repeated and localised sulfide dissolution-recrystallisation effects during highly oxidised, channelised intra-slab fluid flow.

We compared our data to closed system equilibrium and Rayleigh-type fractionation models, which express Se isotope behaviour during partial reduction of Se incorporated into (re)-crystallising sulfides from migrating slab fluids. Sulfides that partly dissolve, recrystallise and dissolve again are neither entirely removed nor fully remixed into the system and hence neither closed nor open system Rayleigh fractionation alone, but a combination of the two can adequately express the entire natural process. This was also previously inferred for such prograde metamorphic conditions for S isotopes (Evans *et al.*, 2014; Supplementary Information and Fig. S-3). As such, the result of repeated sulfide dissolution-recrystallisation cycles during continuous and pulsed fluid flow is the most plausible scenario that generates the $\delta^{82/76}\text{Se}$ spectrum of eclogites. This encompasses low $\delta^{82/76}\text{Se}$ for early stage, only partially re-dissolved sulfides and high values for late stage and/or significantly reworked, i.e. re-dissolved sulfides (Figs. 2, 3, S-3).

Implications for the Se Subduction Cycle

Our Se data can be reconciled with a repetitive cycle of sulfide dissolution and recrystallisation during oxidising fluid flow through the subducted AOC as previously suggested for S (e.g., Evans *et al.*, 2014; Su *et al.*, 2019). Small scale Se isotope heterogeneities are however likely re-homogenised at the slab scale with continuous sulfide reworking (see Graphical Abstract). We therefore speculate that any significant volume of Se, and by analogy also S, that ultimately crosses the slab-mantle wedge zone into the sub-arc mantle might not be isotopically distinct from an initial subduction input. In other words, considering the big picture mass balance, slab dehydration may affect the mass fraction of Se without necessarily affecting its isotope signature. Preservation of the overall isotope signature of the slab, which is further subducted into the deeper mantle, is able to explain high $\delta^{82/76}\text{Se}$ of plume-related lavas that trace recycled sedimentary components subducted from a redox stratified Proterozoic ocean (Yierpan *et al.*, 2020), as well as low $\delta^{82/76}\text{Se}$ of Mariana arc lavas that include recycled materials subducted from a fully oxygenated modern ocean (Kurzawa *et al.*, 2019).

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Additional Information

Supplementary Information accompanies this letter at <https://www.geochemicalperspectivesletters.org/article2110>.



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