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Redox dynamics of subduction revealed by arsenic in serpentinite

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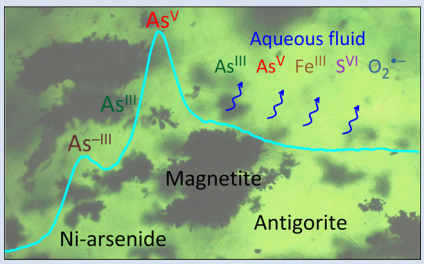
Abstract



Redox dynamics of subduction processes remain poorly constrained owing to the lack of direct geochemical tracers. We studied, using X-ray absorption spectroscopy, the chemical and redox state of arsenic in the Tso Morari serpentinites that are witnesses of the Himalayan subduction. Our measurements reveal remarkably contrasting redox speciation, from arsenide (As^{-III}) to arsenite (As^{III}) and arsenate (As^{V}). Combined with physical-chemical constraints, these data enable reconstruction of the 'redox travel' of arsenic in the subduction process. Upon early serpentinisation of mantle peridotite, arsenic was scavenged from the fluid and dragged down as insoluble nickel arsenide. Partial deserpentinisation close to the peak metamorphism (550–650 °C) resulted in oxidative dissolution of arsenide to aqueous As^{III} and As^{V} and their non-specific intake by antigorite. The As^{V}/As^{III} ratios (~0.1–10) analysed in the mineral are ~10^4 times higher on average than predicted assuming bulk system thermodynamic equilibrium. These findings reflect a transient out-of-equilibrium release of highly oxidised fluids, with f_{O_2} reaching ~10 log units above the fayalite-magnetite-quartz buffer (FMQ+10). Arsenic in serpentinite is thus a sensitive record of subduction redox dynamics inaccessible when using traditional equilibrium approaches applied to bulk fluid-mineral systems.

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Introduction

Serpentinite formation and breakdown are major phenomena occurring in subduction zones. Knowledge of the redox conditions (f_{O_2}) in these processes is necessary to interpret the transfers of many major and trace elements existing in multiple oxidation states. Most natural, experimental, and modelling studies have tackled redox evolution during subduction using major redox sensitive elements such as C, S, and Fe, but little attention has been devoted to trace elements. Among them, arsenic may be a promising redox indicator because it exhibits a wide range of formal oxidation states, from −III to +V, yielding a variety of minerals from (sulf)arsenides to arsenates, and oxyhydroxide As^{III} and As^{V} species in fluids that may be scavenged or released by major minerals and silicate melts depending on f_{O_2} (*e.g.*, Noll *et al.*, 1996; O'Day, 2006; Perfetti *et al.*, 2008; Borisova *et al.*, 2010; Testemale *et al.*, 2011; Scambelluri *et al.*, 2019).

The present study thus examines the potential of arsenic for tracing subduction zone redox conditions through measurement of arsenic oxidation state and speciation in the Tso Morari serpentinites (NW Himalaya). These rocks were formed by hydration of forearc mantle peridotites by slab-derived fluids and subducted to depth of ~100 km and temperatures of ~650 °C before having been exhumed during the Himalayan orogenesis (Hattori and Guillot, 2007 and references therein). The serpentinites, constituted mostly of antigorite and magnetite (Fig. 1), are highly enriched in As^{V} and As^{III} (up to ~100 ppm As, which is ~1000 times more than in mantle-derived rocks; Hattori *et al.*, 2005; Witt-Eickschen *et al.*, 2009). Combined with the well constrained geodynamic history of the Himalayan subduction (Supplementary Information), these serpentinites represent an excellent natural case to examine the redox cycle of arsenic in a palaeo-subduction zone across a wide range of temperatures (*T*) and pressures (*P*).

We used synchrotron X-ray absorption spectroscopy (XAS), which is the most direct method to probe a trace element redox state, chemical bonding and coordination at the atomic scale. Arsenic K-edge X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra were acquired on a thoroughly characterised set of serpentinite rock samples as well as their antigorite- and magnetite-enriched mineral fractions (Supplementary Information; Table S-1). Combined with simulations of

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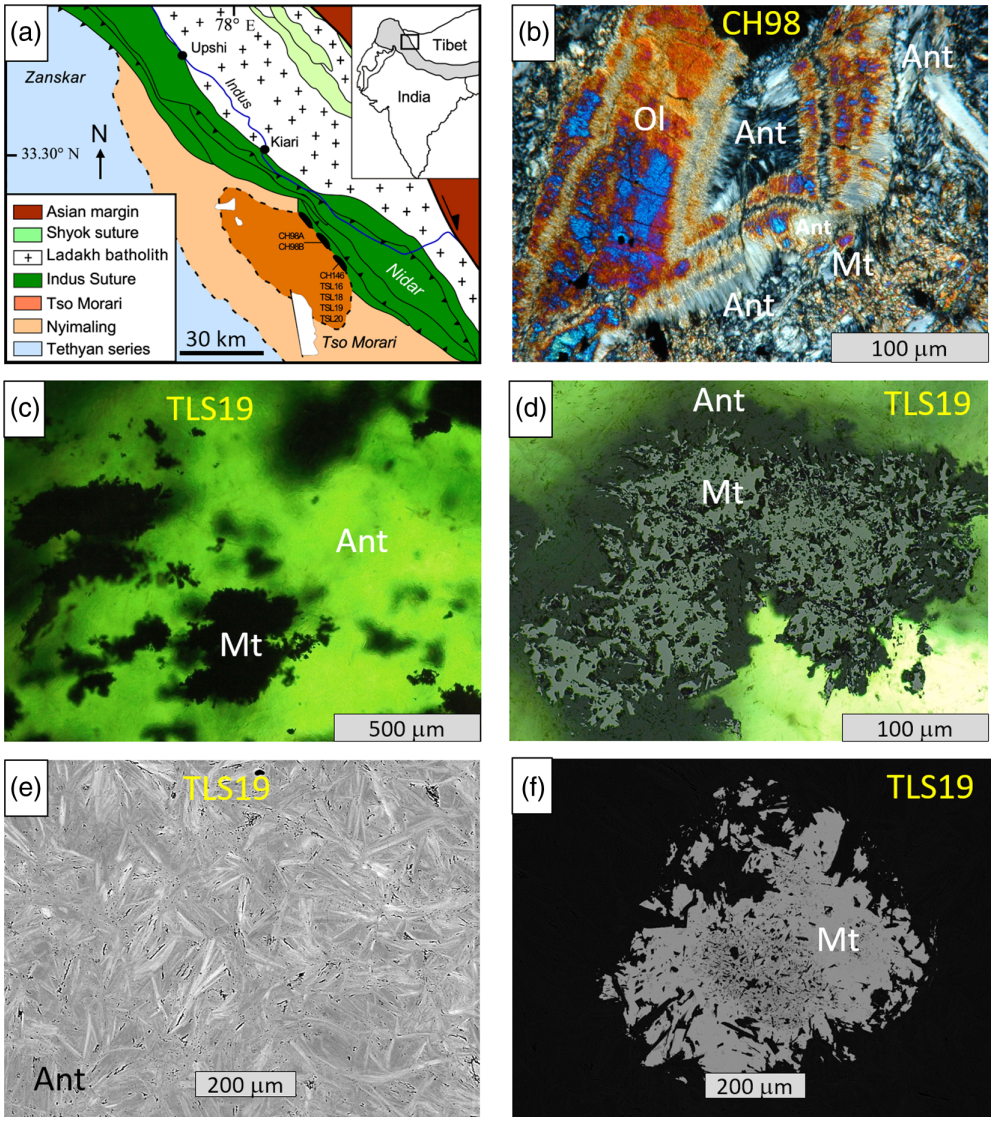

Figure 1 Geology and mineralogy of the Tso Morari serpentinite samples. **(a)** Geological map showing sampling locations. **(b)** Typical serpentinite sample (polarised light) showing dominant antigorite (Ant), metamorphic olivine (Ol) and subordinate magnetite (Mt). **(c)** and **(d)** Magnetite grains embedded in antigorite matrix. **(e)** and **(f)** Antigorite matrix with slight variations in Mg-Al-Si-Fe content and typical magnetite grain displaying Cr-rich core and resorption features (backscattered electron mode). See Supplementary Information for samples identity and characteristics.

fluid-rock interactions using robust thermodynamic data for As-bearing minerals and aqueous species, the results allow us to propose a novel redox model of arsenic behaviour enabling it to unveil f_{O_2} dynamics in subduction processes.

Arsenic Redox and Structural State in Serpentinites

XANES spectra reveal a large range of arsenic redox forms coexisting in serpentinite samples (Fig. 2). Arsenate ($As^{V}O_4$ tetrahedral coordination) is generally the dominant form both in serpentinite and its antigorite fraction (>95 % Ant) with an average of 55 ± 20 mol % (1 s.d.) of total As. The magnetite-enriched fraction (~90 % Mt + 10 % Ant) contains even more As^{V} (from 85 to >95 mol %; Table S-2); however, it accounts for a minor part of As^{V} in the total As budget in serpentinite (Supplementary Information). Arsenate in both minerals coexists with arsenite ($As^{III}O_3$ trigonal pyramidal coordination, from <5 to 55 mol % total As), as well as with arsenide (formal redox state As^{-III}, <5 to 47 mol % total As) in some antigorite samples. EXAFS analyses confirm these findings by showing a mixture of $As^{III}O_3$ and $As^{V}O_4$ first shell coordinations for arsenide-free antigorite and magnetite (*e.g.*, TSL16), and the simultaneous presence of Ni and O in the first atomic shell of As in antigorite samples containing both arsenide and arsenate, showing a mixture of $As^{-III}Ni_6$ and $As^{V}O_4$ coordination environments (*e.g.*, TLS19; Table S-3, Fig. S-1). Nickel arsenide nanoparticles were directly identified by transmission electron microscopy (TEM) in such samples whereas neither As^{III} nor As^{V} individual solid phases were detected (Fig. S-2). The very weak (if any) arsenic second shell EXAFS signals, along with the lack of correlations of As redox state and total contents with those of Fe or other subordinate elements (*e.g.*, Na, Al, V, Co, Ni) that commonly enter magnetite or antigorite structural sites, do not support substitution of As^{III} and As^{V} in $(Si,Fe^{III})O_4$ tetrahedral or $(Mg,Al,Fe^{II,III})O_6$ octahedral sites of both minerals (Supplementary Information). Indeed, the $[As^{III}O_3]$ geometry

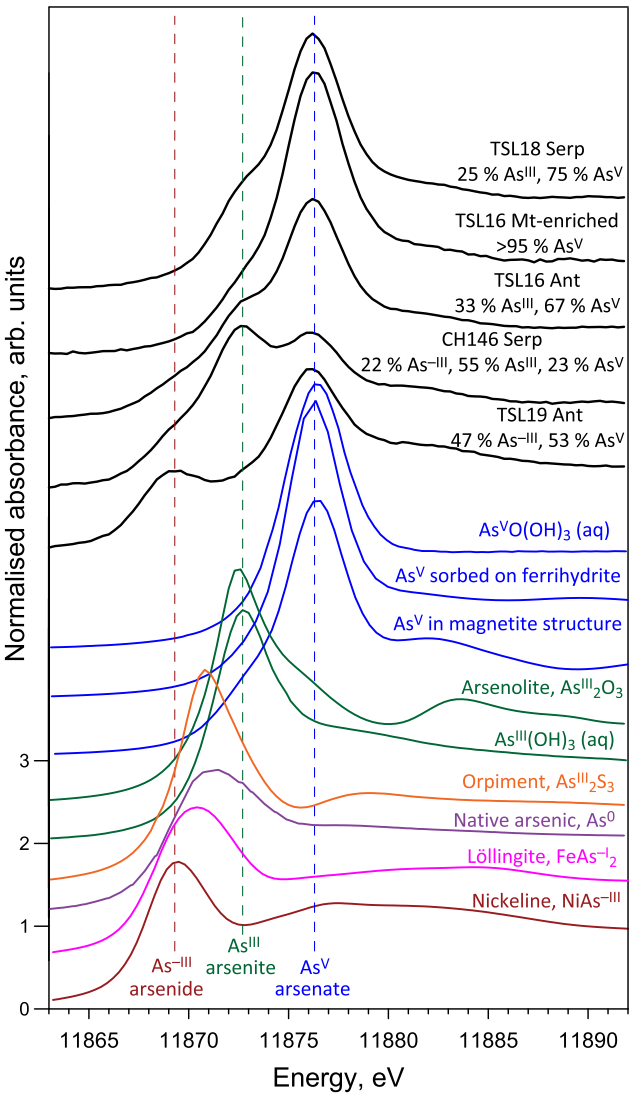

Figure 2 Representative As K-edge XANES spectra acquired on whole rock serpentinite (Serp) and its antigorite (Ant) and magnetite (Mt) enriched fractions, showing contributions of different arsenic formal redox states derived by linear combination fits using different sets of reference solid and aqueous (aq) compounds. Vertical dashed lines indicate the energy positions of the identified arsenic redox states. The best match of all serpentinite spectra was provided by a combination of the spectra of nickeline and aqueous arsenious and arsenic acid species or As^{III} and As^{V} adsorbed on Al/Fe-bearing mineral surfaces. In contrast, our spectra are poorly matched by that of arsenolite, displaying characteristic features arising from As^{III}-O-As^{III} bonds (at 11876 and 11884 eV), and that of As^{V} partially incorporated in magnetite and coordinated by multiple Fe atoms *via* As^{V}-O-Fe bonds (*e.g.*, feature at 11882 eV). See Table S-2 for full dataset and reference compounds, Figure S-1 for EXAFS spectra, and Supplementary Information text for more detailed comparisons.

(Fig. S-1) is structurally incompatible with those sites. The $[As^{V}O_4]^{3-}$ tetrahedron is also incompatible with octahedral sites in Mg/Fe layers and would induce strain and charge imbalance if substituted for smaller and higher charged $[Si^{IV}O_4]^{4-}$ in Si layers of antigorite. Therefore, our data collectively point to site unspecific intake of both As^{III} and As^{V}, likely in structural imperfections common in between Mg-Si layers of antigorite, as oxyhydroxide anions of arsenious and arsenic acid similar to those dominant in aqueous solution (*e.g.*, Perfetti *et al.*, 2008; Testemale *et al.*, 2011).

Arsenic Redox Cycle during Subduction

The presence of contrasting arsenic oxidation states revealed in this study strongly suggests that the serpentinites have undergone large redox changes in *T*-*P*-time space during subduction. Using equilibrium thermodynamics, we simulated arsenic speciation and solubility during interactions of hydrous sediments (pelite ± seawater) with the mantle wedge (harzburgite) in variable proportions, followed by subduction of the produced serpentinite either in closed or open (*i.e.* partial fluid loss) systems (Fig. 3, Tables S-5, S-6), along the geothermal path established for the Tso Morari metamorphic rocks (Guillot *et al.*, 2008).

We found that, independently of the initial redox state of arsenic, introduced with sediments or water either as sulfarsenide or arsenate, poorly soluble nickel arsenides such as orcelite (Ni_5As_2) and maucherite (Ni_8As_{11}) are the stable phases across a wide range of water/rock and sediment/harzburgite ratios (0.1–5 and 0.1–0.5), from early stages of serpentinisation (<200 °C) to at least 550 °C (Fig. 3). This *T* range corresponds to f_{O_2} of –7 to –3 log units relative to the conventional fayalite-magnetite-quartz buffer (FMQ–7 to –3), as imposed by reactions of Fe^{II}-bearing olivine and pyroxene with water producing Fe^{II}/Fe^{III}-bearing

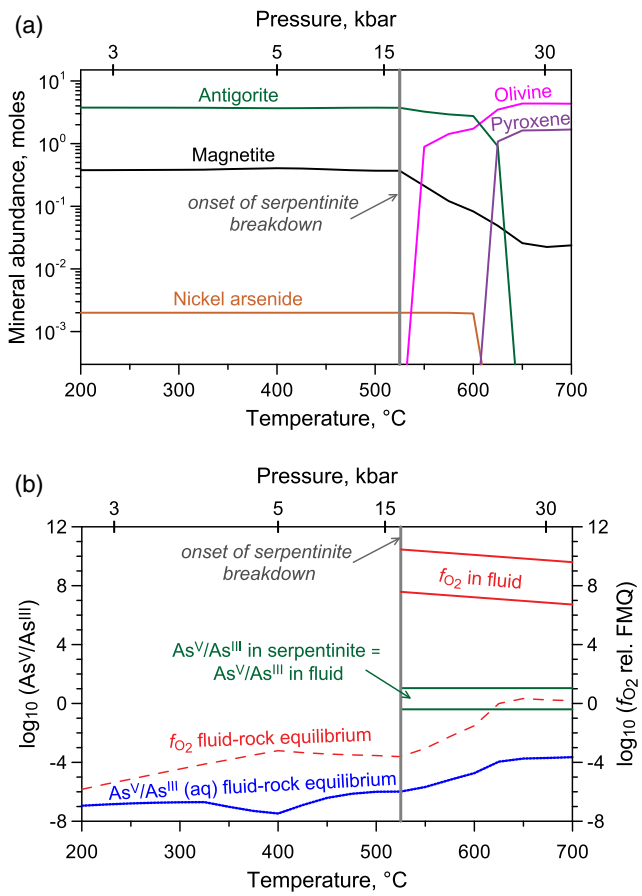

Figure 3 Thermodynamic simulations of serpentinisation in the system harzburgite-sediment-aqueous fluid (starting mass ratios 10:1:10, respectively), along the *T*-*P* subduction path from Guillot *et al.* (2008). **(a)** Equilibrium relative abundances of key minerals. **(b)** Predicted As^{V}/As^{III} species ratio in the aqueous fluid (dotted blue) and f_{O_2} (dashed red) assuming bulk system equilibrium, as compared to the range of f_{O_2} in the fluid (lower and higher bounds, solid red) corresponding to the range of As^{V}/As^{III} ratios measured in serpentinite (solid green).

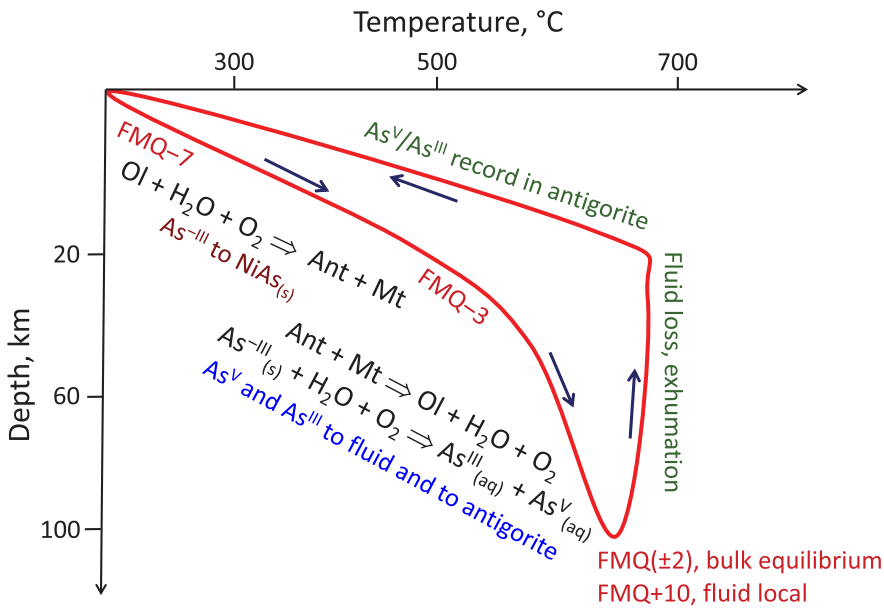

Figure 4 Arsenic redox transformation reactions along the *T vs.* depth subduction path of the Tso Morari metamorphic rocks. Arrows show the directions of the subduction and subsequent exhumation. Ant = antigorite, Mt = magnetite, Ol = olivine.

antigorite and magnetite while consuming oxygen (Fig. 4). The predicted aqueous arsenic concentrations are <1 ppb below 500 °C (Fig. S-5a), demonstrating that arsenic was not a fluid mobile element and was hosted by Ni arsenide phases, in full agreement with the XAS and TEM analyses (Figs. 2, S-2). Highly reducing conditions inherent to this subduction step are also supported by findings of methane-bearing inclusions in partly serpentinised olivine of the Nidar ophiolite complex adjacent to Tso Morari (Fig. 1a; Sachan *et al.*, 2007). Reducing environments at the serpentinisation step are equally common in other subduction settings, for instance as evidenced by Fe-Ni arsenides in Kamchatka peridotite xenoliths altered by slab-derived fluids (Ishimaru and Arai, 2008), and by graphite in the Alpine blueschist-to-eclogite facies (Malvoisin *et al.*, 2012). It is only above 550 °C, with onset of partial breakdown of antigorite and magnetite to olivine, that the solubility of the arsenide phases in the fluid as dominantly As^{III} oxyhydroxide species does significantly increase (Fig. S-5a). This simulated scenario is consistent with the textures and compositional variations of magnetite observed in our samples likely reflecting recrystallisation/replacement phenomena (Fig. 1f) as well as the lack of arsenide phases in some of our samples (Figs. 2, S-2).

Our modelling does not support the hypothesis of early intake of As^V by serpentinite (Hattori *et al.*, 2005), which is inconsistent with low f_{O_2} values at early serpentinisation steps (<FMQ–3; Figs. 3, S-5). Such highly reducing conditions are also supported by ubiquitous experimental evidence of H_2 production upon ultramafic rock hydration as well as the occurrence of reduced accessory minerals (sulfarsenides, Fe-Ni alloys) in serpentinisation reactions both in nature and laboratory (*e.g.*, Frost, 1985; McCollom and Bach, 2009; Marcaillou *et al.*, 2011; González-Jiménez *et al.*, 2021). Oxidation to As^V during exhumation is equally unlikely because it would have required either influx of extremely oxidising fluids (*i.e.* $f_{O_2} \approx$ FMQ+10) not evidenced during the inferred hydration events (Palin *et al.*, 2014), or direct near surface oxidation and weathering. Both phenomena would have produced hematite/goethite and clays not observed in the Tso Morari rocks (Hattori and Guillot, 2007; Deschamps *et al.*, 2010). Therefore, arsenic redox captured by serpentinite likely reflects subduction phenomena at depth.

Release of Highly Oxidised Fluids in Subduction Zones Revealed by Arsenic Redox

In light of our results demonstrating the absence of selective site specific As^V and As^{III} incorporation in serpentine, no significant As^V *vs.* As^{III} fractionation would be induced upon arsenic intake, thereby making the As^V/As^{III} ratio in the mineral to be representative of that in the coexisting aqueous fluid. The thermodynamically predicted As^V/As^{III} ratios (10^{-6} to 10^{-3}) in the fluid phase in the 550–650 °C range of the deserpentinisation step under redox conditions of bulk system equilibrium are, however, much lower than the ratios measured in our antigorite and magnetite-enriched samples (from 0.4 to >11; Fig. 3b, Table S-1). Assuming that all dissolved species including As^V and As^{III} rapidly re-equilibrate in aqueous solution at such elevated *T*, the measured As^V/As^{III} ratios in antigorite would correspond to f_{O_2} values of FMQ+8 to +12 in the fluid, which are ~10 log units higher than those calculated in the bulk fluid-mineral system at equilibrium (~FMQ; Fig. 4). This difference is beyond reasonable error margins of our f_{O_2} estimates (±2 log units; Supplementary Information), and therefore reflects out-of-equilibrium oxidised fluid release during partial serpentinite decomposition, according to the formal reactions shown in Figure 4. Note that even though our f_{O_2} estimates are close to mbar levels of partial P_{O_2}, the equivalent concentration of the aqueous molecular O_2^0 species at these *T-P* conditions is only ~10^{-10} molal. Therefore, the oxidation potential of the released fluid is mostly carried by more concentrated dissolved elements in their highest oxidation states, such as As^V, Fe^{III} and S^{VI} and, possibly, by reactive oxygen species like $O_2^{\bullet-}$ or H_2O_2. However, given the large predominance of both Fe^{II} and Fe^{III} in serpentinite rock, the amount of all dissolved redox sensitive elements (Fe, As, S, O) in the fluid (Fig. S-5) would be insufficient to significantly alter the Fe redox ratio of the major solid phases and, consequently, to leave clearly

detectable Fe redox imprint in the rock. Locally focused oxidised fluid release in the proximity of resorbing magnetite grains (Fig. 1) would also explain the more elevated As^{V}/As^{III} ratios (~10) found in magnetite-enriched fractions than in antigorite fractions (~1).

The f_{O_2} values derived from arsenic redox are significantly higher than those estimated based on Fe oxy-thermobarometry of metamorphic minerals associated with deep subduction (*e.g.*, garnet, spinel, pyroxene, amphibole; Cannaò and Malaspina, 2018; Gerrits *et al.*, 2019), equilibrium thermodynamic simulations of fluid-rock interactions in this and previous work (*e.g.*, Debret and Sverjensky, 2017; Piccoli *et al.*, 2019; Evans and Frost, 2021), and antigorite dehydration experiments (Maurice *et al.*, 2020). Their f_{O_2} estimations commonly range from FMQ to FMQ+5, with an upper limit being close to the hematite-magnetite equilibrium. Our arsenic-derived f_{O_2} values of FMQ+8 to +12 in the absence of hematite thus clearly indicate out-of-equilibrium release of highly oxidised fluids that is not captured by iron as the overwhelmingly dominant redox sensitive element in serpentinite. Interestingly, comparably high f_{O_2} values were inferred from manganese-bearing metacherts in subduction mélanges (Tumiati *et al.*, 2015), pointing to potentially wide occurrence of phenomena of oxidised fluid generation.

Our findings thus provide novel insight into the redox dynamics and geochemical cycles in subduction zones. Like for arsenic, the transfer of other metalloids (*e.g.*, P, Sb, Se, Te) in subduction zones may be fundamentally controlled by f_{O_2}, spanning over >15 orders of magnitude relative to FMQ across subduction, from early reducing conditions stabilising poorly soluble Fe/Ni phases of these elements, to highly oxidising conditions promoting their soluble oxyanions. More generally, our results highlight an important divide between the redox potential of a bulk serpentine rock (Tumiati *et al.*, 2015; Evans and Frost, 2021; Galvez and Jaccard, 2021) and that of the out-of-equilibrium aqueous fluid phase generated therefrom. Such highly oxidised fluids may selectively carry major redox sensitive elements in their highest valence states (Fe^{III}, Mn^{IV}, sulfate, carbonate), in contrast to equilibrium thermodynamic predictions in rock buffered systems that suggest reduced valence states of these elements to be equally (or more) abundant in the fluid. Our findings may thus provide new constrains on the speciation and transfer of metals and volatiles and their associated stable isotope signatures (*e.g.*, Debret *et al.*, 2016; Walters *et al.*, 2019) and, more globally, on the dynamics of redox reactions at depth.

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Additional Information

Supplementary Information accompanies this letter at https://www.geochemicalperspectivesletters.org/article2225.

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Redox dynamics of subduction revealed by arsenic in serpentinite

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Supplementary Information

The Supplementary Information includes:

- Materials and Methods
- Tables S-1 to S-6
- Figures S-1 to S-5
- Supplementary Information References

Materials and Methods

Serpentinite samples and geodynamic setting

The geodynamic setting, *T*-*P*-time evolution, and geochemical and petrological features of the Tso Morari serpentinites have thoroughly been described elsewhere (Guillot *et al*., 2000, 2001, 2008; Hattori and Guillot, 2003, 2007; Deschamps *et al*., 2010 and references therein). Briefly, these rocks originate from the forearc mantle overlying the northward subducting Neo-Tethys lithosphere and the margin of the Indian continent. They are associated with the eclogites of the Tso-Morari ultra high-pressure metamorphic unit that was once a shallow-water sedimentary sequence prior to being subducted beneath Eurasia at ~55 Ma. The unit reached ~100 km depth and ~650 °C before being exhumed together with serpentinites at ~50 Ma. The *T*-*P*-time trajectory of the rocks has been thoroughly reconstructed using a range of petrological, geochronological and thermobarometric indicators (*e.g.*, Guillot *et al*., 2008; Soret *et al*., 2021 and references therein). They suggest rapid cooling and fast exhumation after the peak metamorphism. The serpentinite rocks are dominated by antigorite with subordinate magnetite, secondary olivine, occasional chromite, and minor later chrysotile, lizardite, calcite, and talc. The distinguishing feature of these serpentinites is their strong enrichment in As, Sb, B, Li, Pb, and U compared to mantle peridotites; this enrichment was likely due to sediment-derived aqueous fluids and/or seawater at early stages of subduction (see Deschamps *et al*., 2010 for detailed petrological and geochemical description). Another key feature of these rocks is their pristine deep imprint and the absence of any indication of (near)surface oxidation (*e.g.*, complete absence of hematite, goethite, or clay minerals). The major chemical and mineralogical characteristics of the investigated samples, relevant to the present study, are summarised in Table S-1.

Samples of the CH series are from Deschamps *et al.* (2010). Samples of the TSL series were collected in a later campaign from the same locality, and selectively characterised in the present work using a range of laboratory techniques such as optical microscopy (OM), powder X-ray diffraction (XRD), scanning electron microscopy (SEM), bulk-rock chemical analyses (BR), electron probe micro analyser (EPMA), and laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS), following established protocols (*e.g.*, Borisova *et al*., 2021; Pokrovski *et al*., 2021). Antigorite mineral fractions of samples TSL16 and TSL19 with strongly contrasting As redox state (Tables S-1, S-2) were additionally examined by transmission electron microscopy (TEM) following conventional methods described in Auzende *et al*. (2006).

X-ray absorption spectroscopy data collection

X-ray absorption spectroscopy (XAS) measurements at the Fe (7112 eV) and As (11867 eV) K-edges (including the X-ray absorption near-edge structure region - XANES, and the extended X-ray absorption fine structure region - EXAFS) were performed both on bulk serpentinite rocks and their antigorite-enriched and magnetite-enriched mineral fractions at BM30-FAME beamline at the European Synchrotron Radiation Facility, ESRF, Grenoble, France (Proux *et al*., 2005). Energy was selected using a liquid-nitrogen cooled Si(220) double-crystal monochromator with dynamic sagittal focusing. Unwanted high-energy photons (harmonics) were removed using two Rh-covered mirrors surrounding the monochromator; mirrors being also used to collimate the beam in the vertical direction (1st mirror) and to focus the beam in the same direction (2nd mirror). These optical elements yield a beam spot on the sample of 300 µm horizontal × 200 µm vertical (full width half maximum), an X-ray flux of 5×10^{11} (Fe K-edge) and 10^{12} (As K-edge) photons/s and an energy resolution close to the intrinsic resolution of the monochromator crystals (i.e. ~0.4 eV at Fe K-edge, ~0.6 eV at As K-edge). This setup allows acquisition of very good quality XANES and EXAFS spectra at concentrations as low as a few 10s of ppm As. Fluorescence spectra were collected in the right-angle geometry using a 30-element solid-state germanium detector (Canberra). Energy calibration of each scan was checked using the As_2O_3 (cubic, arsenolite)

and Fe metal references whose K-edge energies were set, respectively, to 11871.5 and 7112.0 eV as the maximum of the spectrum first derivative. The uncertainty of the energy position is <0.3 eV.

To prepare mineral-enriched fractions, antigorite crystals were hand-picked under a stereo microscope from mildly ground fresh pieces of serpentinite rocks, whereas magnetite grains were separated using a magnet. The magnetite-enriched fraction, however, inevitably contained some part of the antigorite matrix (up to ~10%) in which the magnetite grains were solidly embedded. Arsenic associated with magnetite-enriched fractions makes, however, a rather small contribution to total arsenic inventory in serpentinite (<5 % As_{tot}), both because of the low abundance of magnetite itself (average content in our samples is 1.8 ± 1.0 mol. %, 1 s.d. error) and associated relatively small As concentrations as determined by LA-ICPMS (Table S-1) and from X-ray fluorescence amplitude (Table S-2). These data show that magnetite would account for only ~0.02 (CH98B) to <10 % (TSL19) of total arsenic in our samples. To ensure homogeneity necessary for good quality spectra, fresh pieces of bulk rock and its mineral fractions were thoroughly ground under ethanol thereby avoiding any potential oxidation. The powders were dried under an N_2-atmosphere and pressed into 5-mm diameter pellets, which were placed in a liquid He cryostat (~10–15 K). The low temperature and inert atmosphere of the spectra acquisition setup were essential both to avoid potential X-ray beam-induced damage to redox-sensitive elements like As and Fe (Testemale *et al*., 2009, 2011; Borisova *et al*., 2010), and to significantly increase the signal-to-noise ratio of the EXAFS spectra by dampening thermal disorder. In addition, the beam position at the sample was slightly changed at each following scan to further reduce potential beam-redox artefacts. Before summing up, multiple scans were carefully examined and were found to be identical independently of beam-exposure time, thereby demonstrating that beam-induced changes were insignificant.

A large number of As reference compounds (Table S-2) was recorded, using the same protocol at liquid He temperature, to enable accurate and straightforward determination of As redox state using linear combination fit (LCF) analyses of As K-edge XANES spectra. Reference As aqueous solutions were also measured in cryostat in a frozen state with addition of small amounts of glycerine to avoid formation of ice crystals that may generate diffraction peaks in the EXAFS spectra. The iron redox ratio Fe^{III}/Fe^{II} (±0.05, 1 s.d. error) and Fe coordination in antigorite fractions were determined from the Fe K pre-edge and main-edge XANES features, using calibrations and numerical algorithms developed in Muñoz *et al*. (2013). Arsenic K-edge EXAFS spectra were analysed using the Horae software (Ravel and Newville, 2005) and following established protocols (Kelly *et al*., 2008; Borisova *et al*., 2010).

Our approach, combining macro-XAS measurements with micro-analytical laboratory techniques, is believed to be well-suited for the samples context of this study. The use of macroscopic mineral fractions and homogenised samples for XAS both allows the best representability of measurements at the rock-sample scale and enables the best quality XANES, and in particular, EXAFS spectra that are very sensitive to sample inhomogeneity. Note that these two critical aspects could not have been fulfilled using the X-ray micro-beam approach. It can be seen in Fig. 1 that our mineral grains are big enough (100–1000 µm in size) both to allow us to use physical mineral separation procedures and to enable *in situ* microanalytical elemental analyses (SEM, EPMA, LA-ICPMS) to ensure the grain homogeneity and representativeness across the given sample scale, and provide the necessary analytical sensitivity (*e.g.*, detection limits of <0.1 ppm for As by LA-ICPMS), unachievable at present using micro-beam XRF/XAS. Combined with other whole-rock and mineralogical analyses (Table S-1), our approach therefore allows us to place robust constraints on As and Fe mass and redox balance across the whole sample scale.

X-ray absorption spectroscopy results

The obtained structural data are reported in Tables S-2, S-3 and S-4, and representative XANES and EXAFS spectra of samples and reference compounds are shown in Figures 2 and S-1, respectively. As K-edge XANES LCF fits were performed using different structural and redox reference compounds listed in Table S-2. Best fits of the whole set

of samples were achieved using a combination of arsenide, nominally As^{-III} (NiAs, nickeline), arsenite, As^{III} (aqueous arsenious acid solutions), and arsenate, As^{V} (aqueous arsenic acid solutions or arsenate adsorbed on ferrihydrite or gibbsite, which exhibit very similar XANES spectra, but see below for EXAFS). Neither native arsenic nor arsenic sulfides (As_2S_3, FeAsS) were detected (detection limit <3 at. % As). Similarly, fits using As^{III} and As^{V} references compounds, in which the As absorber has closely spaced second-shell heavy atoms such as As or Fe (*e.g.*, arsenolite, As_2O_3, Testemale *et al.*, 2004; As^{V} partially incorporated into magnetite structure, van Genuchten *et al.*, 2019, 2020), could not match the post white-line XANES spectral part of our antigorite and magnetite samples (see also Fig. 2, main text). This result suggests that oxidised As is unlikely to be hosted in the structural sites of both minerals, nor does forms arsenic own oxide or metal arsenate phases.

Analyses of EXAFS spectra show that in arsenide-free antigorite (ant) and magnetite-enriched (mt) samples (*e.g.*, CH98A, TSL16), the EXAFS signal is largely dominated by the first atomic shell of oxygen atoms corresponding to [AsO_3] and [AsO_4] moieties. Quantitative EXAFS analysis for As^{III}/As^{V}-dominated samples yields 3 to 4 oxygen atoms at mean As-O distances between 1.69 and 1.75 Å (±0.02 Å), demonstrating a mixture of $As^{III}O_3$ and $As^{V}O_4$ types of species. In arsenide-bearing samples, part of As is directly bound to Ni (*e.g.*, sample TSL19, As-Ni distance = 2.45 ± 0.02 Å, As-Ni coordination number = 3 ± 0.5; Table S-3), indicating the presence of nickel arsenide phases (NiAs-like). The remaining As atoms are bound to O (or OH groups, H atoms being too light to be detected by XAS) as arsenate ($As^{V}O_4$), in quantitative agreement with the XANES results (see Fig. 1). The very weak (if any) EXAFS signal arising from outer-shell atomic neighbours in As^{III}/As^{V}-bearing antigorite (and magnetite, see below) fractions indicates disordered second shell coordination environments, likely composed of relatively light cations (Al, Mg, $R_{As\text{-}Mg} \approx 2.7$–2.9 Å) and weak multiple scattering contributions within the AsO_4 tetrahedron (MS), similar to those from As surface-sorbed complexes on gibbsite (Fig. S-1). Neither 2nd shell Fe (or another heavy metal, *e.g.*, Ni, Cr, As), nor Si or Mg contributions from adjacent structural Si or Mg atoms ($R_{As\text{-}Si} \approx 3.2$–3.3 Å; $R_{As\text{-}Mg} \approx 3.4$–3.5 Å), which would arise in case of As entering the anionic (Si,As)O_4 structural sites, could be detected. This result suggests that As is unlikely to substitute for Si in antigorite. Furthermore, a lack of correlation of different As redox fractions or total As contents with the Fe^{III} fraction or Al^{III} content in antigorite (Figs. S-3 and S-4), along with the absence of As-O-As bond contributions in the EXAFS spectra, does not support charge-compensated substitution mechanisms such as $As^{V} + As^{III} = 2Si^{IV}$ or $As^{V} + Fe^{III}/Al^{III} = 2Si^{IV}$. In addition, the absence of correlations of total As contents with those of other trace/minor elements of comparable concentrations (*e.g.*, Al, V, Ni, Na, B; *e.g.*, Fig. S-3) that commonly enter the antigorite structural sites further points to a different, likely site-unspecific, As^{III} and As^{V} position in the mineral. Our XANES and EXAFS analysis is thus more consistent with both [$As^{V}O_4H_n^{n-3}$] and [$As^{III}O_3H_n^{n-3}$] oxyanions being incorporated in-between antigorite structural layers or in structural defects and imperfections and loosely bound to [MgO_6] cationic sheets, rather than with direct isomorphic substitution of As for Si in SiO_4 tetrahedrons or for Mg in MgO_6 octahedra.

Like for antigorite, our EXAFS data clearly rule out incorporation of As^{III} and As^{V} into the magnetite structural sites or adsorption as stable inner-sphere complexes on the mineral surface. It can be seen in Figure S-1 that the As K-edge EXAFS spectra of magnetite-enriched fractions are completely devoid of the pronounced second-shell signals typical of arsenate absorbed onto Fe^{III} oxyhydroxide minerals (strong As-O-Fe bonds, *e.g.*, Cancès *et al.*, 2005) and of arsenate incorporated into tetrahedral (Fe,As)O_4 structural sites of low-temperature magnetite in which the AsO_4 tetrahedron was shown to be surrounded by 6 to 12 second-shell Fe atoms at 3.4–3.6 Å, giving rise to an intense 2nd-shell contribution in the EXAFS spectrum (*e.g.*, van Genuchten *et al.*, 2019, 2020); see the "TSL16 mt" sample compared to the "As^{V} on ferrihydrite" and "As^{V} in magnetite" standards in Figure S-1.

Notes on the available data on arsenic incorporation in serpentine-like minerals and magnetite

Our findings of non-specific incorporation of oxidised arsenic in antigorite and magnetite allow us to explore the concept that the As^{III}/As^{V} ratio in the mineral may directly reflect that in the coexisting aqueous fluid. The few direct available data of arsenic incorporation into silicate minerals seem to support this concept as discussed below.

Our structural data are in agreement with direct laboratory experiments of olivine serpentinisation in aqueous alkaline solutions at 200 °C suggesting As^{V} sorption on the formed serpentinite, rather than its incorporation into SiO_4 structural sites (Lafay *et al*., 2016). However, another experimental study by Ryan *et al*. (2019), devoted to the synthesis of serpentinite from alkaline Mg-, Si-, Al- and As-bearing aqueous solutions at 200 °C, reported formation of As^{III}- and As^{V}-bearing serpentinites with up to 1 wt. % As. These authors postulated that both As^{III} and As^{V} substitute for SiO_4 in the tetrahedral sheets of the mineral, but direct evidence for such a mechanism remained elusive. The lack of stoichiometric (*i.e*. the presence of talc interlayers) and charge balance in the synthesised As-substituted serpentinite compositions, the absence of correlation with Al content, and the very weak 2nd shell signal in their reported single EXAFS spectrum, which is similar to our spectra (Fig. S-1), all these features do not support As substitution in Si structural sites. In addition, based on general isomorphic substitution rules, the tetrahedral $As^{V}O_4$ moiety should have a much greater ability than its trigonal pyramidal $As^{III}O_3$ counterpart to substitute for tetrahedral SiO_4. Therefore, it should normally be expected that As^{V} would strongly enrich the synthetic serpentines compared to As^{III}, if arsenic were to substitute for Si. This was not, however, observed in Ryan *et al.*'s (2019) study, with equally significant fractions of As^{III} present in the synthetic products. The largest As^{V}/As^{III} ratio was 4:1, as reported in a single sample investigated using XAS in their study, which was synthesised from a solution containing equal amounts of As^{V} and As^{III}. Such fractionation seems to be too weak to support an isomorphic substitution mechanism for As^{V}. More likely, such modest fractionations would be due to sorption processes, with slightly preferential sorption on the mineral surface of the stronger charged arsenate ion ($As^{V}O_4^{3-}$) *vs*. the arsenite ion ($As^{III}O(OH)_2^{-}$) that are expected to be the dominant As^{V} and As^{III} species, respectively, in the highly alkaline solution used in Ryan *et al.*'s (2019) synthesis. In contrast to their study, the predominance of uncharged or weakly charged As^{III} and As^{V} oxyhydroxide complexes, as shown by fluid speciation calculations at the serpentinisation conditions of our study (see below and Fig. S-5), would further hamper both arsenite and arsenate substitution for SiO_4^{4-} tetrahedrons in the antigorite structure. Other literature data on As intake by aluminosilicate minerals, such as kaolinite, montmorillonite and micas at near-ambient conditions obtained by XAS (Foster and Kim, 2014 and references therein), collectively point to rather minor differences in As^{III} *vs*. As^{V} affinities for their sorption on the mineral surfaces, with dominant formation of outer-sphere arsenate and arsenite complexes.

Although no direct experimental data are available, to the best of our knowledge, on As incorporation into magnetite at hydrothermal conditions, our XAS analysis above clearly rules out As^{V} preferential incorporation in magnetite. This finding apparently contrasts to available reports on partial As^{V} incorporation into the $Fe^{III}O_4$ tetrahedral sites of nano-crystalline magnetite synthesised at ambient laboratory conditions by bacteria-mediated or chemical reduction of Fe^{III} oxyhydroxides, As^{V}-Fe^{III} co-precipitation or electrochemical Fe^{0} oxidation (*e.g.*, Coker *et al*., 2006; Huhmann *et al*., 2017; van Genuchten *et al*., 2019, 2020). However, the conditions of those low-temperature experiments are very different from those of subduction-zone contexts. Multiple instances of direct and complementary evidence provided in this study rule out a significant role of magnetite as the As^{V} host both in the context of our study and, more generally, for hydrothermal-metamorphic environments. This evidence includes *i)* the lack of 2nd shell Fe contribution in our As EXAFS spectra of magnetite-enriched fractions and their great spectral similarity with antigorite (Fig. S-1); *ii*) the absence of any specific correlations of As concentrations with those of elements entering the magnetite structure (*e.g*., Al, V, Co; Fig. S-4); *iii*) the absence of any significant relationship between the As^{V} fraction and magnetite abundance in the serpentinite rock or Fe^{III} fraction in serpentinite (Fig. S-4); *iv*) mass balance estimations showing the major part of As^{III} and As^{V} to be hosted by antigorite, and *v)* the extensive data sets from a variety of high-temperature

hydrothermal and metamorphic environments showing that magnetite is a poor host of arsenic, often displaying concentrations below typical detection limits of few ppm As for LA-ICPMS (*e.g.*, Nadoll *et al.*, 2014), despite the ubiquity of As in hydrothermal fluids (up to 100–1000 ppm As, *e.g.*, Kouzmanov and Pokrovski, 2012).

Thus, our spectroscopic and analytical data, coupled with a critical analysis of literature data, collectively suggest that both As^{III} and As^{V}, as oxyhydroxide anions of arsenious and arsenic acids in aqueous solution (*e.g.*, Perfetti *et al.*, 2008; Testemale *et al.*, 2011), are likely to be adsorbed from the aqueous fluid and incorporated with minimal fractionation into antigorite (and magnetite), *e.g.*, in structural defects and vacancies or in-between Mg-Si cation-anion layers, during the mineral (re)growth, (re)crystallisation or partial (re)dissolution during subduction. In light of these results, pointing to fairly comparable incorporation degrees of As^{III} and As^{V} in serpentinite from aqueous fluid, it would be plausible to assume that the As^{V}/As^{III} ratio in the fluid should reflect that in serpentinite. Therefore, this ratio in both minerals may be used as an indicator of redox conditions in the fluid. This concept is placed in a more quantitative physical-chemical framework in the following sections.

Thermodynamic modelling

Thermodynamic simulations of arsenic solubility and speciation in serpentinisation processes, along the subduction *T-P* path in the geodynamic and geochemical context of the Tso Morari rocks (Guillot *et al.*, 2008 and references therein), were performed in a model harzburgite-sediment-fluid system in a wide range of initial rock/fluid ratios (Table S-6). Calculations were carried out using the HCh package (Shvarov, 2008) enabling extension of the HKF model of aqueous species to the high pressures of the subduction context (up to ~60 kbar; Sverjensky *et al.*, 2014), and employing up-to-date revised thermodynamic datasets for arsenic- and nickel-bearing species and solid phases, major fluid components, rock-forming minerals and their solid solutions, and well-established activity coefficient models (Table S-5).

In particular, we included a variety of As/Ni-bearing minerals with robust thermodynamic data (Gamsjäger et *al.*, 2005) and a complete set of aqueous As^{III} and As^{V} oxyhydroxide species with well-constrained thermodynamic properties, which have been omitted in previous thermodynamic modelling studies of serpentinisation processes. Figure S-5 shows the distribution of these species in the fluid from the simulation exemplified in Fig. 3 in the main text. Note that robust HKF-model parameters for the $As(OH)_3^0$ and $AsO(OH)_3^0$ species, which are needed for reliable extrapolations to the *T-P* conditions of the present study, were derived from direct colorimetric and densimetric measurements of the partial heat capacity and volume of arsenious and arsenic acid solutions to 350 °C and 300 bar (Perfetti *et al.*, 2008). Likewise, the HKF-model parameters of arsenate and arsenite anions were derived from the measurements of $As(OH)_3^0$ and $AsO(OH)_3^0$ dissociation constants available to at least 100–200 °C and extrapolated to high *T-P* conditions using the well-constrained correlations of the HKF coefficients for anionic species (Shock *et al.*, 1997; Perfetti *et al.*, 2008). Arsenate and arsenite ion pairs with mono- and divalent alkali and alkali-earth cations (Na, K, Ca, Mg, and Fe) with recently published HKF-parameter estimations (Marini and Accornero, 2010) were also tested. Note that these estimations are exclusively based on rare ambient *T-P* data and/or inter-species correlations. These ion pairs were found to be negligible compared to the oxyhydroxide species in our low-salinity solutions. The single exception was the $KAsO_4^{2-}$ ion pair whose predicted association constants were more than 4 log units higher at $T > 400$ °C than that for analogous, and far better constrained, $NaAsO_4^{2-}$. In light of such inconsistencies and the lack of direct experimental data on the $KAsO_4^{2-}$ species, its available HKF thermodynamic parameters are likely unreliable and thus were ignored in the present modelling. Arsenic sulfide complexes, known in low-temperature geothermal springs and anoxic H_2S-rich (near)surface waters (*e.g.*, Keller *et al.*, 2014 and references therein), were not included in the modelling because there are currently no thermodynamic data allowing quantitative calculations of their abundances above ~150 °C. Tentative extrapolations of these data to moderate-temperature fluids (~300 °C), along with rare direct experiments

(*e.g.*, Pokrovski *et al.*, 1996, 2002 and references therein), indicate that such complexes would be negligible under most hydrothermal conditions above 200–300 °C. These data are also in line with the fundamental tendency of weakening covalent metal-sulfur bonds (As-S) while strengthening more ionic As-O bonds with increasing temperature (*e.g.*, Crerar *et al.*, 1985), thereby making As-O oxy-hydroxide complexes far more stable in aqueous solution at elevated temperatures of our subduction zone contexts. Our modelling predicts that nickel arsenides, orcelite (Ni_5As_2) and maucherite (Ni_8As_{11}), are the only As-bearing phases to form in our subduction context. No As-bearing pyrite, arsenopyrite or other arsenic sulfide phases (*e.g.*, AsS, As_2S_3) were predicted to precipitate. These predictions are in agreement with the absence of such phases in the serpentinite samples of this study and the very low total sulfur concentrations (<0.01 wt. %) in the bulk rock (Table S-1).

Aqueous Fe species for which reliable high *T-P* thermodynamic data are available (Table S-5) were also included in the modelling. Among them, the dominant Fe species were predicted to be Fe^{II} chlorides and hydroxides ($FeCl_2$ and $HFeO_2^-$) and Fe^{III} hydroxides ($Fe(OH)_4^-$). Ferrous sulfate and carbonate complexes were hypothesised in subduction zone fluids to explain Fe isotope ratios (*e.g.*, Debret *et al.*, 2016, 2020). However, there are no thermodynamic data for aqueous Fe^{II} and Fe^{III} carbonate and sulfate complexes that may actually allow their abundance to be predicted at the subduction zone conditions of the present study. Considering the relative stabilities of Cl-CO_3-SO_4 complexes known at near-ambient conditions, combined with generally lower abundances of sulfate and carbonate ligands than chlorides in hydrothermal-metamorphic fluids, it is expected that the abundances of Fe sulfate and carbonate complexes may be comparable with those of chlorides and hydroxides. However, the amount of total dissolved Fe in the fluid would always be largely inferior to that of Fe in the rock (*e.g.*, Fig. S-5).

Magnesium antigorite endmember was found to be the thermodynamically stable polymorph amongst the other Mg-serpentine polymorphs such as chrysotile and lizardite that are more common in lower *T-P* serpentinisation settings. Although the transformation of those phases to antigorite upon subduction may release small amounts of water, silica and some trace elements, and slightly modify the Fe^{II}/Fe^{III} ratio in the mineral and proportions of accompanying minerals such as magnetite (*e.g.*, Kodolányi and Pettke, 2011; Vils *et al.*, 2011; Evans *et al.*, 2012; Schwartz *et al.*, 2013), this transition has a minor effect on the redox state of the bulk system considered in this study. We also included estimations of the properties of Fe^{III}-bearing antigorite and chrysotile, based on mineral exchange reactions and polyhedral contribution approaches (see Table S-5 for details and references). Our data are in agreement with the rare early estimations (*e.g.*, Klein *et al.*, 2009). Even though such estimations are subjected to potentially large uncertainties, the inclusion in the model of Fe^{III}, which represents the dominant Fe fraction in the studied natural serpentinites, enables far better constraints on Fe^{III} mass balance of the system dominated by antigorite. Our thermodynamic predictions (Fe^{III} = 20–80 % of total Fe in antigorite at T > 550 °C) account well for the directly measured Fe^{III} fractions in antigorite from Fe K-edge XANES spectra (Fe^{III} = 40–70 %, Table S-4). Furthermore, the calculated antigorite Fe^{III} contents display similar temperature trends as those known in natural serpentinites from different subduction environments (Debret *et al.*, 2014), thereby independently confirming the temperature range of our serpentinite samples (~550–650 °C). Moreover, the thermodynamically predicted Mg# number of olivine formed by breakdown of serpentine above 600 °C (Mg# = 92–96) is in excellent agreement with the analysed values for secondary (*i.e.* metamorphic) olivine from Tso-Morari serpentinite rocks and other localities (Mg# = 92–98; *e.g.*, Hattori and Guillot, 2007; Deschamps *et al.*, 2010) while being distinctly different from that of mantle olivine (Mg# = 90, Table S-6). This result further supports the plausibleness of our thermodynamic model, and provides independent confirmation to the process of partial deserpentinisation evidenced by published geochemical and geodynamic data.

Assessment of oxygen fugacity in the fluid using arsenic redox state

Our calculations are in general agreement with previous experimental and thermodynamic modelling studies focused on major elements (*e.g.*, McCollom and Bach, 2009; Merkulova *et al*., 2016, 2017; Piccoli *et al*., 2019; Maurice *et al*., 2020; Evans and Frost, 2021 and references therein), predicting similar equilibrium mineral phases and compositions, and oxygen fugacity evolving roughly from FMQ–10 to FMQ–5 at relatively low-temperature serpentinisation step (<300 °C) to FMQ±2 at higher temperatures closer to the onset of serpentinite breakdown, depending on the harzburgite/pelite/fluid ratios and open (*i.e.* partial fluid escape) *vs.* closed system behaviour. However, equilibrium arsenic redox state and exact speciation were found to be very little dependent on the given scenario, with Ni(Fe) arsenide phases being systematically stable and weakly soluble below ~500 °C, and progressively dissolving with further temperature increase by releasing dominantly As^{III} oxyhydroxide species ($As(OH)_3$ and $AsO(OH)_2^-$) in the fluid phase (Fig. S-5a), with very little As^V corresponding to an equilibrium As^V/As^{III} ratio of 10^{-6} to 10^{-3} at *T-P* peak metamorphism of 600–700 °C and ~30 kbar (Fig. 3). These equilibrium thermodynamics predictions in the bulk system strongly differ from the XAS-measured As^V/As^{III} ratios in serpentinites (~0.4 to ~11, Tables S-1, S-2).

Assuming that the As^V/As^{III} ratio in serpentinite records that of the aqueous fluid, such differences between predictions and analyses are well beyond the potential uncertainties related to the thermodynamic properties of arsenic aqueous species. Their extrapolations to the investigated *T-P* conditions of the serpentinite peak metamorphism (~650 °C) would yield a plausible error of less than ±1 log unit for the As^V/As^{III} ratio. Additional uncertainties may arise from the relatively small differences in As^V *vs*. As^{III} fluid/mineral partition coefficients based on rare available experiments (*e.g.*, Ryan *et al.*, 2019; see discussion above), which are unlikely to exceed ±0.5 $\log(As^V/As^{III})$. These combined errors, which would plausibly amount ±2 $\log f_{O_2}$ units, cannot account for the high As^V/As^{III} ratios analysed in the mineral. We therefore suggest that these ratios rather record strongly oxidising conditions in the fluid phase, out of equilibrium with the dominant serpentinite rock. Such a fluid was temporarily created via focused release due to antigorite and magnetite partial breakdown occurred close to the peak metamorphism.

Given that redox equilibria between As aqueous species in the fluid phase are rapidly attained, oxygen fugacity values in the fluid in the 550–700 °C range may be estimated from redox reactions between the dominant aqueous As species (Fig. S-5) to match the measured As^{III}/As^V ratios preserved in serpentinite:

$$As^{III}O(OH)_2^- + ½\ O_2 = As^VO_2(OH)_2^- \qquad \text{(Eq. S-1)}$$

$$As^{III}\ (OH)_3^0 + ½\ O_2 = As^VO_3(OH)^{2-} + 2\ H^+ \qquad \text{(Eq. S-2)}$$

At constant fluid pH, which is buffered by fast reactions of proton exchange between the fluid and the Mg-Si minerals and therefore is not affected by local O_2 changes, these reactions may be collectively expressed in a general form such as

$$As^{III}(aq) + ½\ O_2 \rightarrow As^V(aq) \qquad \text{(Eq. S-3)},$$

and thus

$$\log(f_{O_2})_{local} = 2\times[\log(As^V/As^{III})_{measured} - \log(As^V/As^{III})_{bulk\ equil}] + \log(f_{O_2})_{bulk\ equil} \qquad \text{(Eq. S-4)},$$

where 'bulk equil' stands for equilibrium values calculated in the fluid assuming thermodynamic equilibrium within the bulk system. The derived local f_{O_2} values in the fluid range from FMQ+8 to FMQ+12, depending on the exact scenario of subduction and fluid/rock ratio.

Supplementary Tables

Table S-1 Key characteristics of serpentinite samples from the Tso-Morari massif investigated in this study.

Sample number[a]	Method	CH98A	CH98B	CH146	TSL16	TSL18	TSL19	TSL20
Coordinates		78.22E, 33.13N	78.22E, 33.13N	78.25E, 33.10N	78.25E, 33.10N	78.25E, 33.10N	78.25E, 33.10N	78.25E, 33.10N
Major minerals	OM, SEM	antigorite						
Subordinate minerals	OM, SEM	magnetite						
Occasional minerals (if any)	OM, SEM	metamorphic olivine, later chrysotile, chromite, calcite, talc						
SiO_2, wt. %	BR	35.1	40.2	40.6	39.8	–	40.7	–
MgO, wt. %	BR	40.0	41.8	36.7	37.6	–	38.2	–
Al_2O_3, wt. %	BR	0.54	0.37	0.77	1.39	–	0.88	–
Fe_2O_3 (total), wt. %	BR	6.83	7.54	7.59	8.31	–	7.53	–
Mt in bulk rock, mol. %	XRD	1.0	0.5	<0.3	2.2	2.4	1.4	3.7
Fe^{III} in antigorite, at. %	XANES	66	61	70	59	72	38	61
Ni in antigorite, ppm	EPMA	2255	2825	2260	2050	–	1820	–
Ni in mt embedded in ant, ppm	LA-ICPMS	–	60–260	–	–	–	5834	–
Si in mt embedded in ant, wt. %	LA-ICPMS	–	–	–	–	–	0.22–0.81	–
Mg in mt embedded in ant, wt. %	LA-ICPMS	–	–	–	–	–	0.25–1.5	–
As in serpentinite rock, ppm, mean	BR	80 [b]	65	6.7	28	–	127	–
As in antigorite, ppm, mean (range)	LA-ICPMS	25 (18–33)	34 (4–76)	7.5 (4–12)	–	–	15 (4–56)	–
As in mt embedded in ant, ppm (range)	LA-ICPMS	–	0.3-0.6	–	–	–	129 (2–470)	–
Ant in mt-rich fraction, wt. %	OM, SEM	<10	<10	<10	<10	<10	<10	<10
As^{V} relative to total As in serp, %	XANES	60	60	23	72	75	54	45
As^{V}/As^{III} in serp	XANES	1.6	1.5	0.4	2.6	3.0	>11	0.8
As^{-III} relative to total As in serp, %	XANES	<5	<3	22	<3	<3	43	<3

[a] Elemental composition for the CH series is adopted from Hattori and Guillot (2007) and Deschamps *et al*. (2010), and for the TLS-series from this study. [b] A value of 275 ppm As was reported for bulk-rock by Hattori *et al*. (2005) obtained by As extraction followed by atomic absorption spectroscopy. This value might be overestimated due to intrinsic limitations of the AAS analysis; alternatively, their sample might have contained traces of nickeline/pentlandite, (Fe,Ni)(S,As), with high As tenors (*cf*. Table 2 in Hattori *et al*., 2005). Total sulfur content in bulk-rock samples is <0.01 wt. %. Mineral abbreviations: serp = serpentinite rock, mt = magnetite, ant = antigorite. Method abbreviations: OM = optical microscopy; BR = bulk-rock chemical analyses; XRD = powder X-ray diffraction; SEM = scanning electron microscopy; EPMA = electron probe micro analyser; LA-ICPMS = laser ablation inductively coupled plasma mass spectrometry; XANES = X-ray absorption spectroscopy at As or Fe K-edges.

Table S-2 Redox state of arsenic in the serpentinite samples investigated in this study (in mol. % of total As), as obtained from linear combination fits (LCF) of As K-edge XANES spectra using As-bearing reference compounds [a].

Sample number	Mineral fraction	Number of scans	Absorption edge step $\Delta\mu_{fluo}$ [c]	% arsenide $As^{-III\ to\ -I}$	% arsenite $As^{III}O_3$	% arsenate $As^{V}O_4$
CH98A	bulk	8	0.042	<5	40 ± 5	60 ± 3
CH98B	bulk	8	0.022	ND[b]	40 ± 5	60 ± 5
CH146	bulk	15	0.007	22 ± 5	55 ± 5	23 ± 5
TSL16	bulk	4	0.023	ND	28 ± 5	72 ± 5
TSL16	antigorite	5	0.022	<5	33 ± 3	67 ± 5
TSL16	magnetite	2	0.011	ND	<5	95 ± 5
TSL18	bulk	5	0.012	ND	25 ± 3	75 ± 3
TSL19	bulk	5	0.039	43 ± 5	<5	54 ± 5
TSL19	antigorite	1	0.043	47 ± 5	<5	53 ± 5
TSL20	bulk	8	0.022	ND	55 ± 3	45 ± 3
TSL20	magnetite	12	0.006	ND	15 ± 3	85 ± 3
TSL20	magnetite-bis	3	0.006	ND	10 ± 5	90 ± 5

[a] As-bearing reference compound standards used in LCF: As^{V} = arsenate sorbed on ferrihydrite (As5Fh), $NiAsO_4$, $Na_2HAsO_4{\times}7H_2O$, $FeAsO_4{\times}2H_2O$ (scorodite), As_2O_5, arsenic acid aqueous solutions (pH = 2, 10 and 13); As^{III} = As_2O_3 (arsenolite and glass), $NaAsO_2$, arsenious acid aqueous solutions (pH = 5 and 11); As-sulfides: As_2S_3 (orpiment), Cu_3AsS_4 (enargite); As^0 = amorphous native arsenic; $As^{-III\ to\ -I}$: FeAsS (arsenopyrite), $FeAs_2$ (löllingite), NiAsS (gersdorffite), NiAs (nickeline)[1].
[b] ND = not detected (<3% of total As, unless indicated).
[c] Absorption-edge amplitude is a rough indication of total relative As concentration in the studied samples.

[1] As K-edge XAS spectra of reference compounds and serpentinite samples are available upon request to the corresponding author.

Table S-3 Structural parameters of arsenic in serpentinite samples obtained by fitting EXAFS spectra.

Sample number	Mineral fraction	Atom	*N*, atoms	*R*, Å	σ^2, Å^2	$\mathcal{R}$-factor	*k*-range	*R*-range
CH98A	bulk	O	3.6 ± 0.5	1.73 ± 0.03	0.0030	0.025	2.7–12.0	1.1–3.4
		Mg	*1.5 ± 1*	*2.73 ± 0.05*	*0.007f*			
CH98B	bulk	O	3.9 ± 0.5	1.73 ± 0.03	0.0040	0.033	2.7–12.0	1.1–3.4
		Mg	*1.5 ± 1.0*	*2.7 ± 0.1*	*0.007f*			
CH146_RE	bulk	–	–	–	–	–	–	–
TSL16	bulk	O	3.9 ± 1.0	1.72 ± 0.03	0.0025	0.022	2.7–11.2	1.1–3.5
TSL16	magnetite	O	3.9 ± 0.9	1.70 ± 0.02	0.0015	0.040	2.7–10.0	1.1–3.5
TSL16	antigorite	O	3.4 ± 0.5	1.74 ± 0.03	0.0033	0.030	2.7–10.0	1.1–3.5
		±Mg	*1 ± 1*	*2.6 ± 0.1*	*0.007f*			
TSL18	bulk	O	3.6 ± 0.6	1.73 ± 0.02	0.0026	0.028	2.7–10.0	1.1–2.2
TSL19	bulk	O	2.3 ± 0.2	1.70 ± 0.01	0.0020	0.021	2.7–12.8	1.1–3.6
		Ni	3.0 ± 0.5	2.45 ± 0.02	0.0050			
		±S	*<0.4*	*2.20*	*0.005f*			
		±As/Ni	*2 ± 1*	*3.4 ± 0.1*	*0.01f*			
TSL19	antigorite	O	2.0 ± 0.5	1.70 ± 0.01	0.005	0.018	2.7–11.0	1.1–3.6
		Ni	3.0 ± 0.3	2.43 ± 0.02	0.003			
		±As/Ni	*2 ± 1*	*3.4 ± 0.1*	*0.005*			
TSL20	bulk	O	3.3 ± 1.4	1.73 ± 0.03	0.003	0.030	2.7–10.0	1.1–2.2
TSL20	magnetite	O	4.1 ± 1.4	1.70 ± 0.05	0.0015	0.046	2.7–10.0	1.1–2.2
TSL20	magnetite-bis	O	4.0 ± 1.0	1.69 ± 0.02	0.001	0.030	2.7–10.0	1.1–3.5

R = As-neighbour mean distance, *N* = number of neighbours, σ^2 = mean squared displacement of the bond length (relative to σ^2 = 0 adopted in the calculation of reference amplitude and phase functions by FEFF), its typical error is 30–50% of the value; $\mathcal{R}$-factor defines goodness of the total fit in *R*-space. The value of Δe, which is a non-structural parameter accounting for phase shift between experimental spectrum and FEFF calculation, is 9 ± 2 eV for all spectra. Amplitude reduction factor, S_0^2 = 0.9 ± 0.1, as determined from fits of a large number of As-bearing reference compounds recorded in the same experiment. "–" = not fitted due to insufficient EXAFS signal quality; *f* = parameter was fixed in the fit. Values is italic for As outer shells are tentative.

Table S-4 Iron redox and coordination in antigorite fractions from analysis of Fe K-edge XANES spectra [a].

Sample	Pre-edge centroid energy, eV [b]	Fe^{III} (octahedral and tetrahedral) of total Fe, at. %	Fe^{III} tetrahedral of total Fe^{III}, at. %
CH98A	7114.09	66	10
CH98B	7113.90	61	<5
CH146	7.114.14	70	10
TLS16	7113.89	59	<5
TLS18	7114.05	72	<5
TSL19	7113.60	38	<5
TSL20	7113.91	61	<5
Error	±0.1	±5	±5

[a] Numerical algorithms of pre-edge calibration and fitting are from Muñoz *et al.* (2013) and Wilke *et al.* (2001)

[b] Centroid position = intensity-weighted average of the pre-edge components energy positions.

Table S-5 Sources of thermodynamic data for key aqueous species and minerals used in this study.

Chemical species and phases[a]	Data source
Aqueous species	
H_2O, H^+, OH^-, Cl^-, Na^+, $NaCl^0$, $NaOH^0$, KCl^0, K^+, KOH^0, KSO_4^-, $KHSO_4^0$, $NaHSO_4^0$, HS^-, HSO_3^-, SO_3^{2-}, HSO_4^-, SO_4^{2-}, H_2S^0, SO_2^0, H_2^0, O_2^0, Mg^{2+}, $Mg(OH)^+$, Ca^{2+}, $CaOH^+$, $CaCl^+$, $CaCl_2^0$, $CaSO_4$, Fe^{2+}, $FeOH^+$, FeO^0, $HFeO_2^-$, $FeCl^+$, $FeCl_2^0$, Fe^{3+}, $FeOH^{2+}$, FeO^+, $HFeO_2^0$, Ni^{2+}, $NiOH^+$, $Ni(OH)_2^0$, $Ni(OH)_3^-$	Johnson *et al*. (1992 (updated Supcrt database)
HCl^0, $NaSO_4^-$, $NaHS^0$, KHS^0, $NaHSO_4^0$, $S_3^{\bullet-}$	Pokrovski and Dubessy (2015)
$NiCl^+$, $NiCl_2^0$, $NiCl_3^-$	Liu *et al*. (2012)
$Fe(OH)_4^-$	Diakonov *et al*. (1999)
Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_4^-$, $NaAl(OH)_4^0$	Tagirov and Schott (2001)
$As^{III}(OH)_3^0$, $As^{III}O(OH)_2^-$, $As^{V}O(OH)_3^0$	Perfetti *et al*. (2008)
$H_2As^{V}O_4^-$, $HAs^{V}O_4^{2-}$, $As^{V}O_4^{3-}$	Shock *et al*. (1997)
Solid phases	
native elements S, As, Fe, Ni; most Fe-Mg-Ca-Al-Na-K oxide and silicate minerals	Holland and Powell (2011)
pyrite, pyrrhotite, fayalite, α,β-quartz, magnetite, O_2 ideal gas	Robie and Hemingway (1995)[e]
arsenolite, orpiment, realgar	Pokrovski *et al*. (1996)
Fe sulfarsenides: FeAsS, $FeAs_2$, FeAs	Perfetti *et al*. (2008)
Ni arsenides/arsenates/sulfides: NiAs, Ni_5As_2, $Ni_{11}As_8$, $Ni_3(AsO_4)_2(H_2O)_8$, NiS, Ni_3S_2	Gamsjäger *et al*. (2005)
oxides and arsenates: As_2O_5, AlAs, $AlAsO_4$, $Ca_3(AsO_4)_2$, $Mg_3(AsO_4)_2$	Barin *et al*. (1995)
scorodite $FeAsO_4(H_2O)_2$	Majzlan (2012)
Mg-antigorite $Mg_3Si_{2.125}O_{5.3125}(OH)_{3.875}$	Holland and Powell (2011)
Fe^{II}-antigorite $Fe_3Si_{2.125}O_{5.3125}(OH)_{3.875}$	Merkulova *et al*. (2016)
Fe^{III}-antigorite $Fe_2Si_{2.125}O_{5.3125}(OH)_{3.875}$	This study [c]
Fe^{III}-chrysotile $Fe_2Si_2O_5(OH)_4$	This study [d]
Aqueous species activity coefficient models [b]	
$\log \gamma_i = -A z_i^2 \sqrt{I}/(1 + B \mathring{a}_i \sqrt{I}) + b I + \Gamma_\gamma$, for charged species $\log \gamma_i = \Gamma_\gamma + b_i I$, for uncharged species	Helgeson *et al*. (1981)
Solid solution models	
olivine: subregular; brucite, orthopyroxene, clinopyroxene, plagioclase, talc, actinolite, chlorite, and garnet: multisite; serpentine: molecular (local charge balance)	Powell (1977)
arsenic in pyrite, $Fe(As,S)_2$	Xing *et al*. (2019)

[a] Thermodynamic properties of H^+ are equal to 0 at all *T* and *P*; the reference states for the solid phases and H_2O are unit activity for the pure phase at all *T* and *P*; for gases the reference state is ideal gas at 1 bar pressure; for aqueous species, the reference state corresponds to unit activity coefficient for a hypothetical one molal solution whose behaviour is ideal.

[b] *A* and *B* are the Debye-Hückel (DH) electrostatic parameters; *I* is the effective molal ionic strength ($I = 0.5 \sum z_i^2 m_i$); z_i and $\mathring{a}_i$ are the ionic charge and the distance of the closest approach for KCl or NaCl electrolyte solutions, respectively; *b* is the extended DH parameter for KCl or NaCl electrolyte solutions; Γ_γ is the mole fraction to molality conversion factor, $\Gamma_\gamma = \log(1 + 0.018m^*)$, where m^* is the sum of the molalities of all solute species. For uncharged aqueous species, b_i is the empirical Setchenov coefficient, which was taken as zero for all neutral species; this yields activity coefficients close to one.

[c] Estimated using the polyhedral contributions approach of Chermak and Rimsdidt (1989) for $\Delta_f G^0_{298K,1bar}$ and assuming that $\Delta_r S$ and $\Delta_r C_p$ equal to 0 at all *T* and *P* for the exchange reaction: $Mg_3Si_{2.125}O_{5.3125}(OH)_{3.875}$ (Mg-antigorite) + Fe_2O_3 (hematite) = $Fe^{III}{}_2Si_{2.125}O_{5.3125}(OH)_{3.875}$ (Fe^{III}-antigorite) + 3 MgO (periclase), yielding the following standard thermodynamic properties for Fe^{III}-antigorite: $\Delta_f G^0_{298K,1bar} = -3055.54$ kJ/mol, $S^0_{298K,1bar} = 228.11$ J/(mol K), $C_p^0(T \text{ in K}) = 287.73 + 0.188 \times T - 6.9831e6 \times T^{-2}$ J/(mol K), $V^0_{298K,1bar} = 105.03$ cm^3/mol.

[d] Estimated using the polyhedral contributions approach of Chermak and Rimsdidt (1989) and Klein *et al*. (2009), assuming that $\Delta_r G_{298K,1bar}$, and $\Delta_r S$, $\Delta_r C_p$ and $\Delta_r V$ equal to 0 at all *T* and *P* for the exchange reaction: $Al_2Si_2O_5(OH)_4$ (kaolinite) + Fe_2O_3 (hematite) = $Fe^{III}{}_2Si_2O_5(OH)_4$ (Fe^{III}-chrysotile) + Al_2O_3 (corundum), yielding the following standard thermodynamic properties for Fe^{III}-antigorite: $\Delta_f G^0_{298K,1bar} = -2959.60$ kJ/mol, $S^0_{298K,1bar} = 236.90$ J/(mol K), $C_p^0(T \text{ in K}) = 289.32 + 0.141 \times T - 5.5913e6 \times T^{-2}$ J/(mol K), $V^0_{298K,1bar} = 105.03$ cm^3/mol. Plausible uncertainties on $\Delta_f G^0_{298K,1bar}$ values for both Fe^{III}-antigorite and Fe^{III}-chrysotile are ±40 kJ/mol.

[e] FMQ-scale f_{O_2} values used here are according to the Robie and Hemingway (1995) thermodynamic database, which is in excellent agreement (within 0.2 log unit) with high-temperature calibrations (>575 °C) of Myers and Eugster (1983) with pressure correction of Chou (1987). Values of f_{O_2} in water-rock equilibrium simulations of this study are calculated using the equilibrium activity of O_2^0(aq) and the formal Henry constant O_2(aq) = O_2(gas) from the cited reference sources.

Table S-6 Compositions of the model fluids and rocks used in thermodynamic simulations of this study.

Component	mol/kg	reacted mass, kg
Harzburgite mantle rock [a]		1.0
Olivine, $Mg_{1.8}Fe_{0.2}SiO_4$	5.42	
Orthopyroxene, $Mg_{0.8}Fe_{0.2}SiO_2$	1.43	
Clinopyroxene, $CaMg_{0.9}Fe_{0.1}Si_2O_6$	0.22	
Ni_2SiO_4	0.017	
Pelite-type sediment rock [b]		0.1–0.5
SiO_2	11.24	
Al_2O_3	13.39	
FeO	0.95	
$FeO_{1.5}$	0.09	
K_2O	0.43	
Na_2O	0.085	
CaO	0.042	
MgO	0.545	
H_2O	1.81	
FeS_2	0.083	
FeAsS	0.02	
Seawater		0.1–1.0
H_2O	55.5	
NaCl	0.5	
$MgSO_4$	0.03	

[a] McCollom and Bach (2009); [b] Zhong *et al*. (2015)

Supplementary Figures

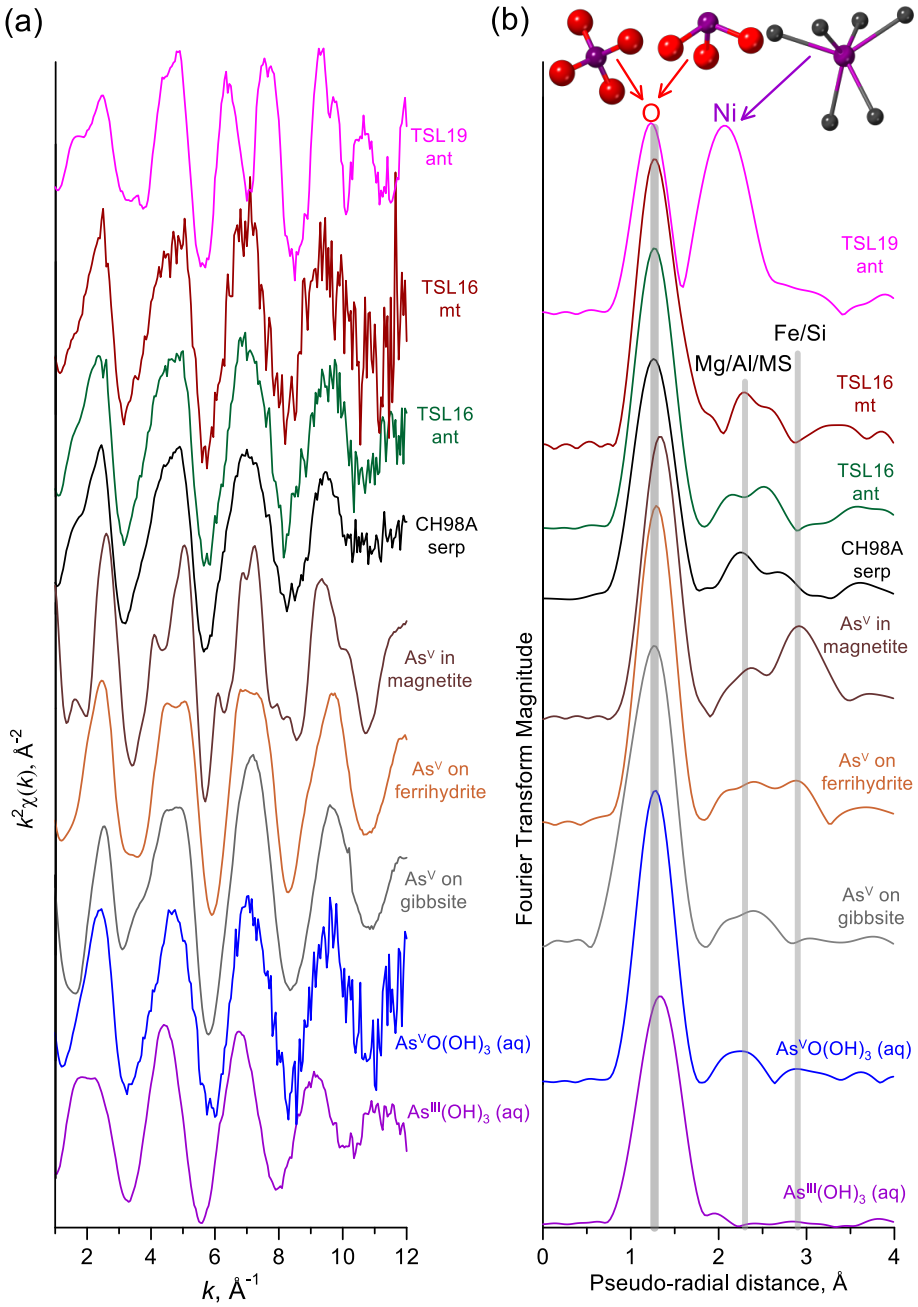

Figure S-1 **(a)** EXAFS spectra (k^2-weighted) at As K-edge, and **(b)** their corresponding Fourier Transform magnitudes of representative serpentinite samples and key reference compounds: arsenious acid $As^{III}(OH)_3$ and arsenic acid $As^{V}O(OH)_3$ aqueous solutions, arsenate incorporated in the magnetite structure (van Genuchten *et al.*, 2019), and arsenate sorbed on ferrihydrite (Cancès *et al.*, 2005) and on gibbsite (Foster and Kim, 2014). Mean positions in *R*-space of major atomic shells around As are indicated by vertical lines in **(b)** (not corrected for phase shift, see Table S-3 and supplementary text for true interatomic distances). Arsenide, arsenide and arsenate first-shell coordination structures are shown by ball-and-stick clusters (As = violet, O = red, Ni = dark grey).

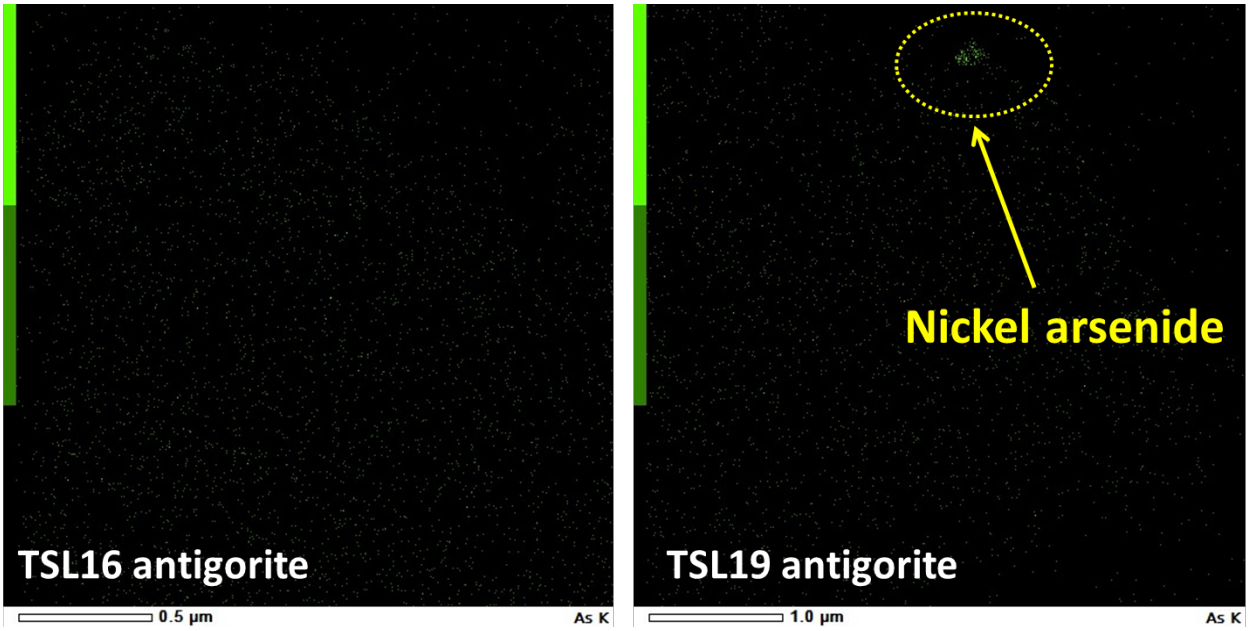

Figure S-2 Transmission electron microscopy (TEM) fluorescence maps at As K-edge of representative antigorite samples (TSL16 and TSL19). Note the absence of detected As-bearing nanoparticles in TSL16 (small single dots are individual illuminated pixels due to background signal), whereas a NiAs-bearing nanoparticle is visible in TSL19 as a group of multiple illuminated pixels (encircled). These findings are in excellent agreement with the bulk antigorite XAS data demonstrating As^{III} and As^{V} to be disseminated in the antigorite structure in TSL16, and the presence of As-Ni bearing phase contributions in TSL19 (Tables S-2 and S-3).

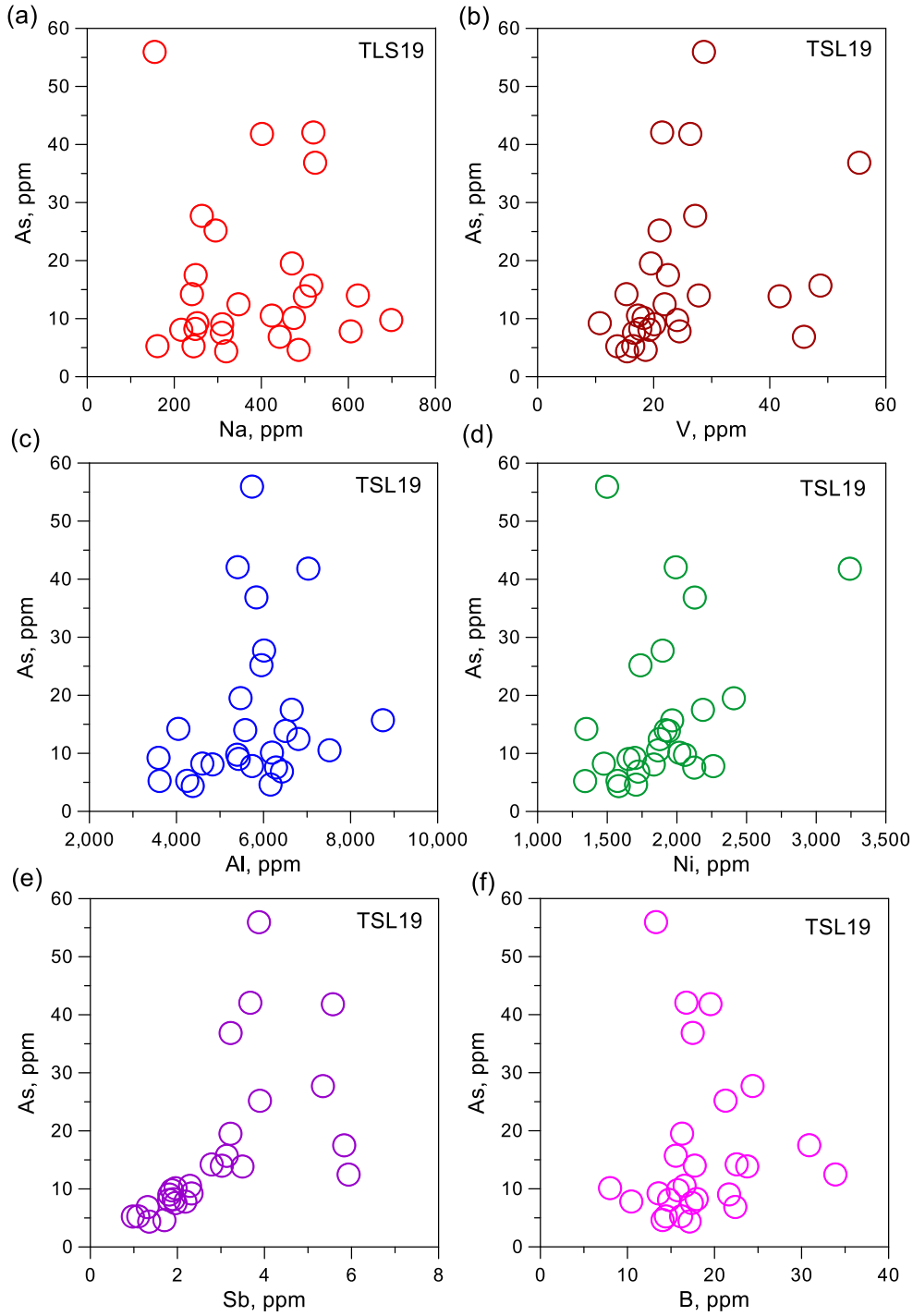

Figure S-3 Scatter plots of arsenic *vs.* the indicated minor and trace elements contents in TSL19 antigorite sample from individual laser spots as probed by LA-ICPMS. Errors are comparable with the symbol size. The lack of apparent correlations of arsenic content with any of those elements (except probably Sb) indicates that arsenic is "decoupled" from these elements that exert no structural/chemical control on As incorporation into antigorite.

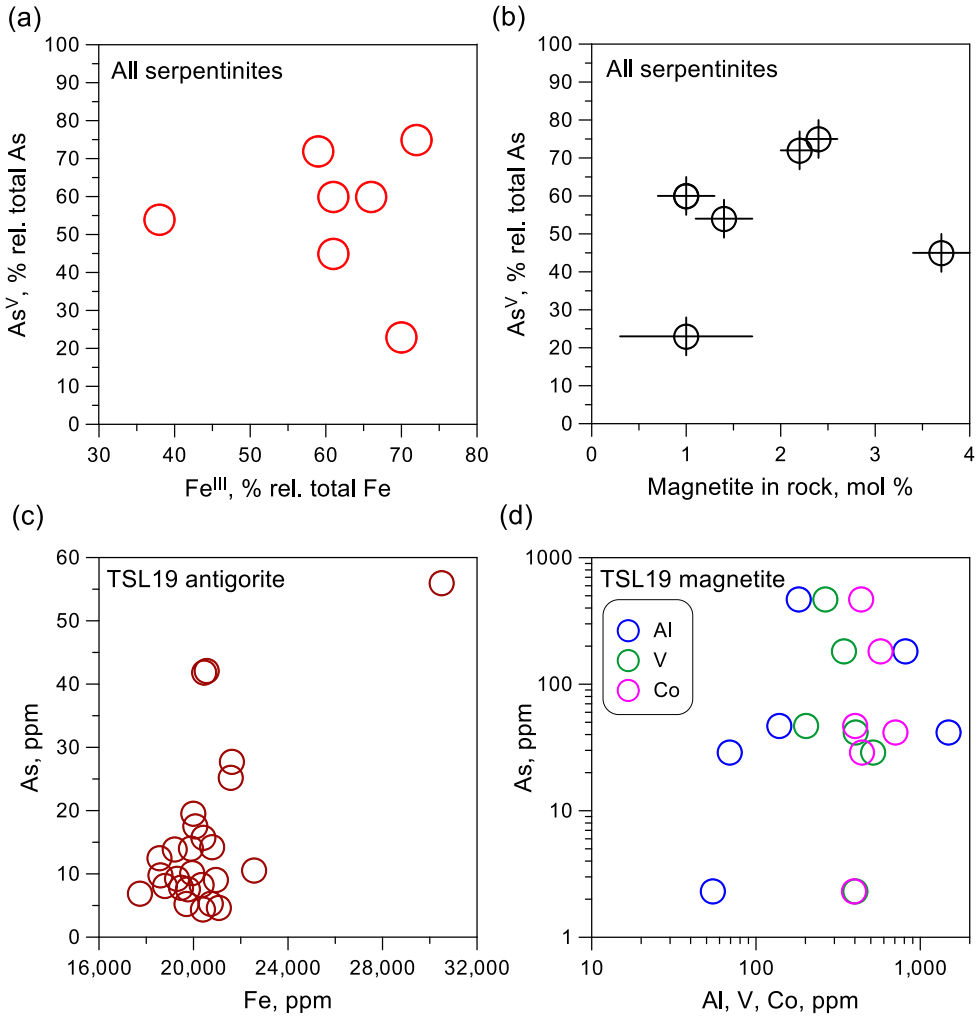

Figure S-4 Arsenic-iron relationships in serpentinite. **(a)** As^V *vs*. Fe^{III} fraction relative to total As and Fe in all antigorite samples as determined by XANES spectroscopy. **(b)** As^V fraction of total As (XANES) *vs*. magnetite mineral fraction in serpentinite rock samples (XRD). **(c)** and **(d)** Total arsenic *vs.* indicated element concentrations in TSL19 antigorite sample from individual laser spots as probed by LA-ICPMS. Errors (unless indicated) are comparable with the symbol size. The lack of any significant correlation of arsenic redox and concentration with Fe and associated elements demonstrates that both As total concentration and redox state are uncorrelated from iron in serpentinite and are not controlled by magnetite.

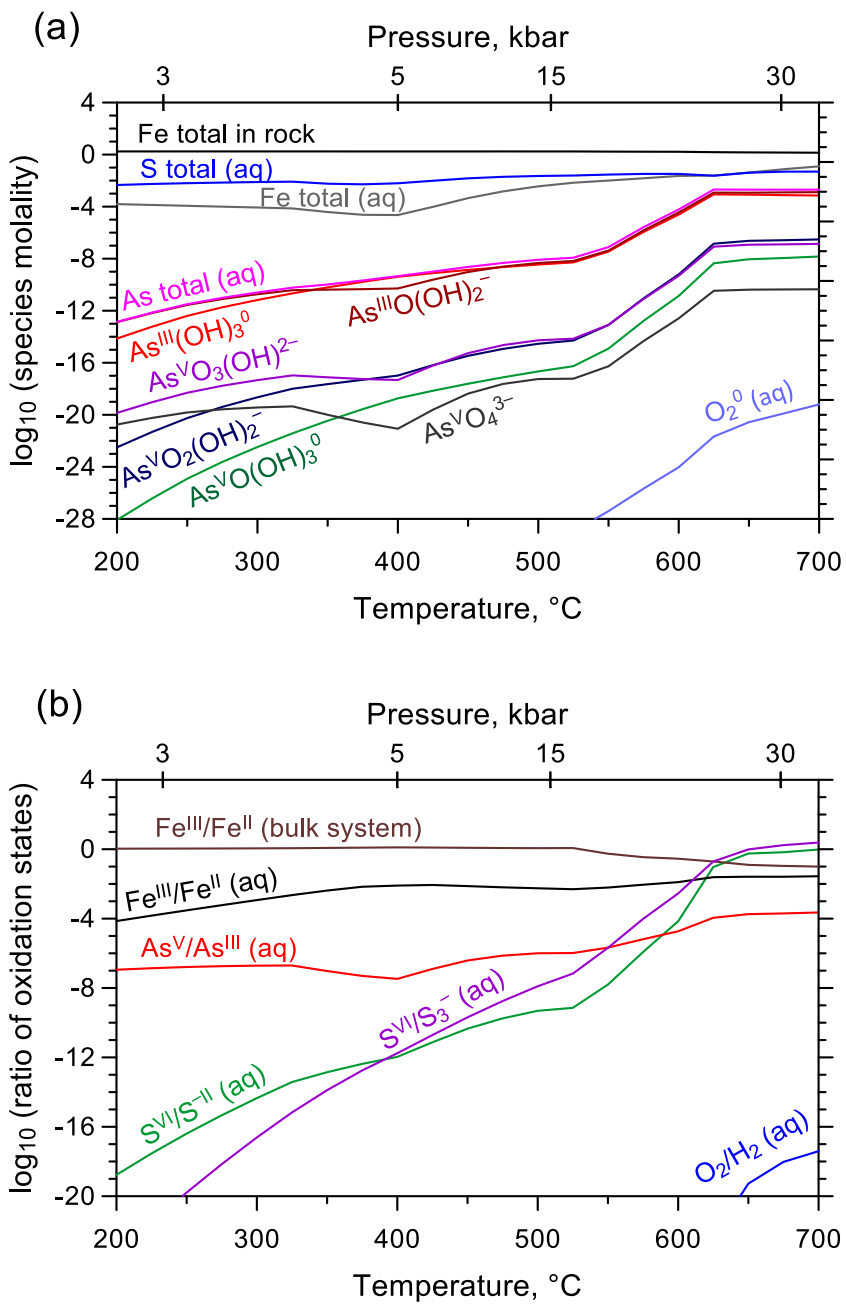

Figure S-5 **(a)** Concentrations of arsenic oxyhydroxide species, total dissolved arsenic, sulfur and iron in the aqueous fluid and total iron in the serpentinite rock (moles per 1 kg of water). **(b)** Ratios of aqueous As^V/As^{III}, sulfate/sulfide, trisulfur ion/sulfide and ferric/ferrous iron and molecular oxygen/hydrogen in the fluid, and Fe^{III}/Fe^{II} in the bulk system at equilibrium as a function of temperature, in the example of thermodynamic simulation of serpentinisation in the harzburgite-sediment-water system, along the *T-P* path of Himalayan subduction considered in Fig. 3 of the main text. Note that at the f_{O_2} values of the oxidised fluid generated by out-of-equilibrium serpentinite breakdown, as derived from the As^V/As^{III} ratios captured by serpentinite (As^V/As^{III}≈1, FMQ+8 to +10, Fig. 3b, main text), the corresponding ratios of aqueous Fe and S redox forms would be proportionally higher that those shown in the figure, largely in favour of the oxidised species. Note, however, that the amount of major redox-sensitive elements in such highly oxidised fluid is too small compared to that of the dominant rock (*e.g.*, there is >10 to 1000 times more Fe^{II} and Fe^{III} in the rock than in the fluid) to leave any significant imprint to the rock in terms of the Fe^{III}/Fe^{II} ratios.

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