Slab-derived devolatilization fluids oxidized by subducted metasedimentary rocks

Jay J. Ague1,2✉, Santiago Tassara1, Megan E. Holycross3, Ji-Lei Li4,5, Elizabeth Cottrell6, Esther M. Schwarzenbach7, Charalampos Fassoulas8 and Timm John7

Metamorphic devolatilization of subducted slabs generates aqueous fluids that ascend into the mantle wedge, driving the partial melting that produces arc magmas. These magmas have oxygen fugacities some 10–1,000 times higher than magmas generated at mid-ocean ridges. Whether this oxidized magmatic character is imparted by slab fluids or is acquired during ascent and interaction with the surrounding mantle or crust is debated. Here we study the petrology of metasedimentary rocks from two Tertiary Aegean subduction complexes in combination with reactive transport modelling to investigate the oxidative potential of the sedimentary rocks that cover slabs. We find that the metasedimentary rocks preserve evidence for fluid-mediated redox reactions and could be highly oxidized. Furthermore, the modelling demonstrates that layers of these oxidized rocks less than about 200 m thick have the capacity to oxidize the ascending slab dehydration flux via redox reactions that remove H2 and/or H2S from the fluids. These fluids can then oxidize the overlying mantle wedge at rates comparable to arc magma generation rates, primarily via reactions involving sulfur species. Oxidized metasedimentary rocks need not generate large amounts of fluid themselves but could instead oxidize slab dehydration fluids ascending through them. Proposed Phanerozoic increases in arc magma oxygen fugacity may reflect the recycling of oxidative weathering products following Neoproterozoic–Palaeozoic marine and atmospheric oxygenation.

Metamorphic arcs above subduction zones produce most of the world’s explosive volcanism and host giant ore deposits of copper, molybdenum, gold and other valuable metals. Arc magmas are considerably more oxidized than mid-ocean ridge basalts and generate volcanic eruptions that can inject sulfur gases (mainly SO2) into the stratosphere, producing sulfate aerosols that trigger transient tropospheric cooling and stratospheric heating. The origins of the oxidized signature in arcs, as well as in the underlying lithospheric mantle, are vigorously debated. One family of hypotheses holds that the fluids released by subducting slabs are inherently oxidized relative to the pristine igneous rocks generated at mid-ocean ridges. The oxidation may take place during seafloor hydrothermal alteration of mafic crust and/or serpentization of ultramafic rocks at mid-ocean ridges before subduction. During subduction zone devolatilization, these rocks release fluids with a high oxidation potential to the mantle wedge and give rise to oxidized arc magmas via flux melting. In contrast, another set of hypotheses posits that the oxidized signature is acquired in the mantle or crust overlying the subduction zone. Some proposed oxidative pathways include the loss of reducing components (for example, H2) from ascending melts (or fluids) to the surrounding mantle or fractional crystallization of Fe3+-rich phases such as garnet in deep lithospheric magma chambers.

A corner-stone of this debate is determining whether subducting slabs can release oxidizing fluids. This has proved to be challenging, however, in part because many subducted lithologies lack mineral assemblages suitable for estimating oxygen fugacity. Moreover, field-based studies and theoretical modelling have produced strongly conflicting results for the oxidation state of mafic crust, underlying serpentinite and their respective fluids. For example, some exhumed slab rocks preserve evidence for relatively reducing geochemical fingerprints, whereas oxidizing fingerprints are preserved in others.

The veneer (~400 m thick) of sediments that covers subducted slabs worldwide provides another potential oxidative pathway but has received much less attention than other slab lithologies. Oxidized Fe3+-bearing sedimentary detritus containing goethite (FeO(OH)) and haematite (Fe2O3) from weathered continental sources can be transported to marine depositional settings thousands of kilometres from the shore (for example, the Bengal Fan). Aeolian fluxes of oxidized minerals to deep ocean basins can occur on similar scales (for example, Indian and Pacific Oceans). Furthermore, highly oxidized oceanic (meta)sediments (such as Fe- and Mn-rich cherts) are widely known from exhumed subduction complexes including those of California, Japan and New Zealand in the Circum-Pacific region, the Alps and other localities globally. Moreover, the substantial oxidation potential of sediment entering subduction zones, such as the Mariana subduction zone, has been clearly documented in extensive ocean floor drill cores. What is urgently needed now is a field-based evaluation of the redox states of subducted metasedimentary rocks and the extent to which they can regulate the fO2 of devolatilization fluids released from downgoing slabs.

To address this important gap in knowledge, we investigated metasedimentary rocks from two forearc subduction complexes in the Aegean region, Greece (Methods and Extended Data Fig. 1). The samples are from three islands (Andros, Naxos and Tinos) that form part of the Cycladic Blueschist Unit (CBU) and from Crete.
Both complexes reflect Tertiary subduction of the African plate beneath Eurasia, which continues today in the Hellenic subduction zone. The subduction complexes of the Aegean are among the most extensively studied and best-exposed on Earth.

Oxidized rock types and textures

The oxidized rock types we investigated are likely to be less familiar than the classic blueschists and eclogites of subduction complexes. Because of the high Fe$^{3+}$ contents of the rocks, Fe$^{2+}$-rich minerals including almandine-rich garnet porphyroblasts are uncommon or absent. Consequently, many of the rocks have an unremarkable appearance in outcrop. For this reason, we posit that oxidized metasediments have largely escaped attention in petrological studies and, thus, are probably much more common than is recognized at present. Moreover, they are not restricted to the islands we study; for example, oxidized metasedimentary (and metaigneous) rocks are known from the CBU on Evia and Sifnos.

A wide variety of oxidized rock types are exposed, including metabauxite, which is well known from Crete and Naxos (>90 localities on Naxos alone). The metabauxite protoliths were deep lateritic weathering horizons developed on carbonate sequences. Haematite and rutile are widespread, and relic soil pisolites were preserved in places (Fig. 1a).

On Andros, Mn- and Fe-rich quartzites and schists are found within a volcano-sedimentary sequence that hosts synsedimentary Mn mineralization. Garnets are rich in the spessartine component (Mn$_3$Al$_2$Si$_3$O$_9$) and epidote can contain considerable piemontite (Ca$_2$Mn$^{3+}$Al$_2$Si$_3$O$_9$(OH)) (Fig. 1b). Similar rocks are found on neighbouring islands; over a dozen localities are known from Andros, Evia and Tinos. Seafloor metasediments that are less manganiferous and contain abundant haematite ± magnetite are not

---

**Fig. 1 | Examples of highly oxidized metasedimentary rocks.**

- **a,** A hand sample of metabauxite from Crete (jagcr10A). Note the deformed elliptical relic soil pisolite (an example is marked by the white arrow).
- **b–f,** Photomicrographs taken under plane-polarized light unless otherwise noted.  
  - **b,** Aggregate of piemontite (Pmt) and haematite (Haem) in manganiferous quartzitic schist from Andros (jagan01A). Note the strong orange–pinkish red pleochroism in the piemontite. Qz, quartz.  
  - **c,** Sodium amphibole-bearing quartzite from Tinos. Note the abundant small Mn-rich garnets (jagti90B). Amp, amphibole.  
  - **d,** Glauco-ferro-glaucophane–riebeckite Na amphibole (blue) in marble with magnetite (Mag) and haematite from Tinos (jagti68B). Amphibole Fe$^{3+}$/(Fe$^{2+}$ + Fe$^{3+}$) ≈ 0.53. Cal, calcite; Ep, epidote.  
  - **e,** Epidote- and phengite-rich schist from Tinos (jagti108D; crossed polarizers). Ph, phengite.  
  - **f,** Coarse haematite and rutile (Rt) in vein from Tinos (jagti23A). Note the haematite inclusions in the rutile (an example is marked by the white arrow).
uncommon; two quartzites from Tinos are studied herein (Figs. 1c and 2a,d). Their protoliths were probably cherts or sandstones.

Regionally widespread metapelitic phyllites and schists, as well as metacarbonate rocks, contain rhombohedral oxide ± rutile ± magnetite; we present examples from Tinos and Crete (Figs. 1d–f and 2c,e).

We also examined two rocks from Tinos that are intercalated with oxidized metasedimentary layers. One is an epidote- and Na amphibole-rich metabasaltic blueschist. The other is an Na-rich ‘albitite’ schist with complex mineralogy that includes Na amphibole, jadeite–aegirine (Na–Fe³⁺–Al) clinopyroxene, magnetite and haematite (Fig. 2b). This highly sodic rock is reminiscent of jadeitite and may have similar origins.

Multiple samples preserve textural evidence for reduction during metamorphism. For example, garnets whose cores contain only haematite inclusions can be found surrounded by matrix magnetite, indicating the reduction of haematite to magnetite some time after core growth (Fig. 2a). Garnet molar Fe³⁺ decreases ~70% from cores to rims (see Data availability). In another example, haematite-rich domains are cut by a network of Na amphibole-bearing veinlets in which haematite has been converted to coarse magnetite; these veinlets are inferred to be fluid infiltration pathways (Fig. 2b).

Fig. 2 | Evidence for synmetamorphic reduction. a–c. Plane-polarized light photomicrographs. a, Quartzite (jagti134N). Magnified inset shows haematite inclusions in a garnet (Grt) that is enclosed by magnetite. The rock initially contained only haematite, which was incorporated into growing garnets, but no magnetite. Subsequently, magnetite grew in the matrix and around garnets as a result of haematite reduction. Some haematite remains in the matrix. Garnet cores with haematite inclusions have high Fe³⁺/(Fe³⁺ + Fe²⁺) values of ~0.35, whereas the rims have much lower values (~0.05). b, Albite (jagt75A). Anastomosing ‘veinlets’ (light) containing magnetite formed by the reduction of fine-grained haematite are shown (haematite occurs in cloudy domains, which may also contain fine-grained albite, quartz, phengite, epidote, sodic clinopyroxene, and Na and Na–Ca amphiboles (Amp)). These anastomosing features are interpreted as infiltration channels for reducing fluids. c, Garnet containing inclusions of Na–Ca amphibole (green, right) that have ~25% greater Fe³⁺/(Fe³⁺ + Fe²⁺) values than matrix Na amphibole (blue, left) (jagt154F-1). The garnet core also contains small (tens of micrometres) inclusions of jadeite–aegerine clinopyroxene with ~0.4–0.6 Fe³⁺/(Fe³⁺ + Al) (not visible). d, Reflected light photomicrograph showing haematite and rutile inclusions in garnet (main image and inset) and matrix ilmenite (Ilm) (jagt90B). Note that matrix ilmenite surrounds and postdates the haematite-bearing garnets. e, Cut rock slab containing the alteration selvage (tan ‘bleached’ appearance) adjacent to a quartz vein cutting purple-red haematite-bearing phyllite. The haematite has been destroyed in the selvage by reducing fluids that infiltrated along the vein (jagcr00A). Siderite–magnesite in veins is the inferred sink for the reduced iron.
Fig. 3 | Metamorphic $f_{O_2}$. Values were calculated thermodynamically using coexisting mineral compositions measured with an electron probe microanalyser. HM, haematite–magnetite reaction; HIR, haematite–ilmenite–rutile reaction. The other reaction symbols are defined in the Methods. Red symbols are assemblages in garnet interiors and blue symbols are assemblages in matrix and/or garnet rims. The vertical red shaded band shows the approximate range of arc magma $\Delta FMQ$ values. The grey arrows denote $f_{O_2}$ decrease during metamorphism. Italic sample types on the left denote those preserving evidence for synmetamorphic reduction (Fig. 2). Mn denotes a minimum $f_{O_2}$ estimate. Calculations were done at Cycladic pressure–temperature conditions of 500 °C and 1.5 GPa, except for sample (2), for which 400 °C and 1.0 GPa were used. The $f_{O_2}$ corresponding to $h_{\text{H}2S} = f_{SO2}$ iso-fugacity is shown for 500 °C and 1.5 GPa and for subarc conditions of 700 °C and 3.0 GPa. Orange-to-yellow background shading represents an increase in oxygen fugacity from left to right. The ±1 σ standard deviation (SD) uncertainty on the oxygen fugacity estimates is shown in the legend. See Methods for calculation details and sample descriptions, and Supplementary Table 1 for $\Delta FMQ$ values.

Figure 2c shows a garnet core that contains Fe$^{3+}$-rich Na–Ca amphibole and clinopyroxene, whereas the matrix contains glaucophane with Fe$^{2+}$ > Fe$^{3+}$. In Fig. 2d, haematite is found in garnet interiors, but the matrix hosts Fe$^{3+}$-poor ilmenite. A redox profile is shown in phyllite from Crete, in which the rock distal to a cross-cutting quartz vein is rich in haematite, whereas the altered selvage rock proximal to the vein lacks haematite and is strongly depleted in iron (Fig. 2c).

$f_{O_2}$ estimates

We used various combinations of eight independent oxybarometers to estimate metamorphic $f_{O_2}$ (Methods), including the simple haematite–magnetite–haematite–ilmenite–rutile equilibria that are independent of the activity of $H_2O$. When possible, equilibria were applied to assemblages within garnet (preserved as inclusions) and in the rock matrix to evaluate $f_{O_2}$ changes during metamorphism.

Figure 3 shows that metasedimentary lithologies can preserve a highly oxidized signature during subduction. The estimates of $f_{O_2}$, relative to the fayalite–magnetite–quartz buffer (in log$_{10}$ units; $\Delta FMQ$) cover an extraordinary range exceeding seven orders of magnitude; all are at or above the typical $\Delta FMQ$ values of arc magmas. Rocks that lack magnetite can have $f_{O_2}$ values that extend far above the haematite–magnetite buffer, up to $\Delta FMQ$ ~9. These include Fe- and Mn-rich haematite–bearing schist, as well as haematite + rutile–bearing metabauxite, quartzite and metapelite phyllite, and epidote-rich schist (samples 1–5). The extreme $f_{O_2}$ of the maganiferous metasediments is consistent with comparable localities elsewhere. Another substantial fraction of the rock suite, which includes marble, quartzite, metabasalt intercalated with oxidizing metasediments and metapelitic schist, clusters between $\Delta FMQ$ ~2 and the haematite–magnetite buffer (samples 6–12).

Inclusion assemblages within garnet may record $f_{O_2}$ values that are ~1–4 log$_{10}$ units higher than matrix assemblages. This is consistent with textural evidence and indicates synmetamorphic reduction following initial garnet growth (Fig. 2a,c,d), as has also been documented in metabasalts. Furthermore, reduction need not cause a drop in $f_{O_2}$. For example, in Fig. 2b, the magnetite-rich veinlets formed at the expense of the intervening haematite-rich domains, but magnetite and haematite coexist. Thus, although the conversion of haematite to magnetite was proceeding, both phases were present so the $f_{O_2}$ was constrained to be near the haematite–magnetite buffer as the bulk-rock Fe$^{3+}$/Fe$^{2+}$ increased. We infer that reactive fluids ascending from deeper in the slab caused the reduction documented in Figs. 2 and 3 and were oxidized as a result.

Fluid fluxes and metasedimentary rock oxidizing capacity

The time-integrated fluid flux ($q_{TI} \cdot m_{\text{fluid}}^2 \cdot m_{\text{rock}}^{-2}$) must be used to evaluate changes in redox state due to the infiltration of externally derived reactive fluids (Methods). Consider a rock column with 1 m$^2$ cross-sectional area extending vertically through a slab. Devolatilization fluids are progressively released and flow up and out of this column into the mantle wedge as the slab (and column) descends. Thus, $q_{TI}$, as measured at the top of the column, increases with depth. For the subarc depth interval 80–150 km, we took $q_{TI} = 220 m_{\text{fluid}}^2 \cdot m_{\text{rock}}^{-2}$ (refs. 21,22). The fluid flux generated by
The reduction of one mole of FeO₂ by molecular H₂ in aqueous (O–H) fluids can be described by

\[ \text{H}_2 + \text{FeO}_3 = 2 \text{FeO} + \text{H}_2\text{O} \]  

The FeO and FeO₃ are considered to be generically present in oxides or silicates. The fluid composition can be determined if f₀₂ is known. Dehydration fluids released from relatively reducing sub-arc mafic crust and serpentinite are probably in the ΔFMQ range 1 to −2 (refs [20,21,23]); we took −1 as representative. The ΔFMQ of the haematite–magnetite buffer is representative of the oxidized metasediments and thus the fluids released from the top of the slab. With these bounding ΔFMQ values, we could quantify the capacity of the metasediments to oxidize the dehydration fluids passing through the slab cover into the mantle wedge at subarc conditions. The calculations were not particularly sensitive to the metasedimentary f₀₂ value as long as it was around or above that of haematite–magnetite. We note that some slabs may release more oxidized fluids[21,23]; these would be little modified by flow through the oxidized metasediments.

Figure 4b shows how thick metasedimentary layers would need to be to oxidize the slab dehydration flux. For O–H fluids, they are remarkably thin, ranging between ~20 cm (20 wt% FeO reduced) and ~2 m (2.5 wt% FeO reduced). This is because the amount of H₂ in the ascending dehydration fluids is small, and the redox buffer capacity of the metasediments is large[21,23].

In C–O–H fluids, one mole of methane (CH₄) will reduce four moles of FeO₃.

\[ \text{CH}_4 + 4 \text{FeO}_3 = 8 \text{FeO} + \text{CO}_2 + 2 \text{H}_2\text{O} \]  

We calculated the input CH₄ mole fraction (XCH₄) assuming graphite saturation, which yielded the maximum possible XCH₄, and is thus the most conservative value. Thicker sequences of metasediment are required to oxidize this fluid relative to the O–H case (Fig. 4b). This is because the CH₄ concentrations are higher than those of H₂ and the CH₄:FeO₃ ratio is 1:4. Nonetheless, the thicknesses are still only ~10–30 m. As XCH₄ in the input fluid is still relatively small, the evolved CO₂ is also small and will, in general, not precipitate carbonate phases unless they were already stable in the rock.

S²⁻ species will be dominant in S–O–H fluids at low f₀₂ (refs. [21,27]). The oxidation of H₂S to produce SO₂ can be represented using SO₂ (ref. [22]), the most abundant S species in volcanic gases.

\[ \text{H}_2\text{S} + 3 \text{Fe}_2\text{O}_3 = 6 \text{FeO} + \text{SO}_2 + \text{H}_2\text{O} \]  

Fluid and/or minerals can host the product Fe and S. For such reactions to go strongly to the right, f₀₂ must be above that for f_{H₂S} = f_{SO₂} (isosufugacity; Methods). As shown in Fig. 3, this would be the case for the highest f₀₂ rocks at forearc conditions; the f₀₂ for isosufugacity drops sharply with increasing pressure (P) and temperature (T) and would be below haematite–magnetite at T > ~650 °C for typical subduction geotherms. Thus, SO₂ will be important in fluids equilibrated with oxidized subarc metasediments.

For O–H and C–O–H fluids we used molecular H₂, CH₄ and CO₂ as their thermodynamic and mixing properties are reasonably well established (Methods). For S–O–H fluids, calculations based on aqueous species[21] including HS⁻ (the DEW model[22]) tend to give higher total S concentrations than those based on molecular H₂S. We calculated the input mole fraction X_{H₂S} at ΔFMQ = −1 using the molecular approach for typical mid-ocean ridge basalt[22] at pyrite saturation to represent fluids exiting the top of the metageneous portion of the slabs. The H₂S:FeO₃ ratio will vary depending on the valence of S in SO₂; the maximum ratio is 1:4 (for sulfate). Taking H₂S:FeO₃ = 0.25, the metasediment thickness needed to oxidize the
The metasedimentary oxidative filter

Our results show that oxidized metasedimentary rocks have the capacity to oxidize the dehydration flux of fluids ascending from slabs at subarc depths. In general, metasedimentary rocks will be at the top of a slab and, thus, will be the last rock type encountered by the fluids before they enter the mantle wedge. Consequently, oxidized metasediments will act as an ‘oxidative filter’ that imposes a high-oxidation fingerprint on the slab fluids that ultimately drive fluid melting and arc magmatism (Fig. 5). This model can reconcile evidence for the release of relatively reducing (for example, H,S-bearing) fluids from subducted metabasalts and serpentinites in the subarc4,10,12,36 with the presence of an oxidized (for example, sulfate-bearing) slab fluid component in arc lavas4,12,14. In addition, any high-oxidation fluids generated in underlying hydrothermally altered metabasalt or serpentinite13,14 would pass through the filter with their oxidizing character preserved. Moreover, the filter does not preclude oxidation processes operating in the overlying mantle wedge or lithosphere. Such metasediments could also undergo dehydration or partial melting themselves, contributing to the oxidized flux.

The O–H and C–O–H fluid models require reduction of <10% of an average subducted sedimentary sequence (400 m thick25) to oxidize the slab flux. The S–O–H models require a higher, but still reasonable, proportion of <15–50%. Consequently, the oxidizing potential of the metasedimentary sequence could be realized even if the rocks experienced thinning by offscraping in an accretionary prism or by compaction, if flow was channeled or if the sequence was not composed entirely of oxidized metasediments. On the other hand, thrust faulting or folding in the subduction channel would lead to greater thicknesses. A further implication is that considerable amounts of surface-derived oxid component in slabs could be subducted past the subarc deep into the mantle, consistent with geochemical modelling6 and an oxygen mass balance of the Marianas subduction zone.

A rough assessment suggests that fluids ascending from metasediments could oxidize the mantle at a rate of ~4 km yr−1, comparable to the global arc magma generation rate of ~2.5 km yr−1 (ref. 49; Supplementary Information). The majority of this oxidation would be accomplished by sulfur species, highlighting their much greater efficacy as redox agents relative to O–H and C–O–H species4,8,23,47. Nonetheless, O–H and C–O–H species could still contribute to the total.

The fO2 of arc magmas ranges over two to three orders of magnitude4. At least some of this variability could be related to the oxidative capacity of subducted metasedimentary sequences. Some sequences of oceanic affinity, such as the Palaeozoic Tianshan high-pressure/ultrahigh-pressure metamorphic belt9, are relatively poor in oxic components8. By contrast, oxidative weathering-derived detritus would be expected to be important in depositional basins more proximal to continents. The Aegean setting represents a hybrid case that contains both oxidized oceanic (for example, Mn-rich) and weathering-related sedimentary source components. Whether flow is pervasive or channelized to some degree2,13,19–21 will increase the variability of the redox signal delivered to arcs. Postulated increases in the fO2 of Phanerozoic island arc lavas relative to Precambrian equivalents51 may be related to the global emergence of oxidative weathering driven by Neoproterozoic–Palaeozoic marine and atmospheric oxygenation4–6, and thus reflect the ultimate recycling of weathering products in subduction zones.

Online content
Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/s41561-022-00904-7.

Received: 17 August 2021; Accepted: 16 January 2022; Published online: 17 March 2022

References
1. Wood, B. J., Bryndzia, T. & Johnson, K. E. Mantle oxidation state and its relationship to tectonic environment and fluid speciation. Science 248, 337–345 (1990).
2. Carmichael, I. S. E. The redox states of basic and silicic magmas: a reflection of their source regions? Contrib. Mineral. Petrol. 106, 129–141 (1991).
22. Li, J.-L., Klemd, R., Huang, G.-F., Ague, J. J. & Gao, J. Unravelling slab dehydration. Geology 40, 783–786 (2012).

23. Evans, K. A. & Frost, B. R. Deserpentinization in subduction zones as a control on oxygen and strontium decoupling in the Trois Seigneurs Massif—a consequence of kinetic dispersion? J. Geol. Soc. 157, 73–86 (2000).

24. van Keken, P. E., Hacker, B. R., Syracuse, E. M. & Abers, G. A. Subduction zone fluid flow from underlying slab serpentine dehydration. Contrib. Mineral. Petrol. 162, 1035–1051 (2011).

25. Johnson, C. A. & Harlow, G. E. Guatemalan jadettes and albitites were formed by deuterium-rich serpentinizing fluids deep within a subduction zone. Geology 27, 629–632 (1999).

26. Brounce, M., Cottrell, E. & Kelley, K. A. The redox budget of the Mariana subduction zone. Earth Planet. Sci. Lett. 528, 115839 (2020).

27. Tollan, P. & Hermann, J. Arc magmas oxidized by water dissociation in subduction zones. J. Petrol. 47, 1755–1780 (2017).

28. Coombs, D. S., Dowse, M., Grapes, R., Kawachi, Y. & Roser, B. Geochemistry of subduction zone fluids derived from serpentinite breakdown in subduction zones. J. Petrol. 46, 2531–2536 (2005).

29. Trott, P., Kusky, T. M. & Green, J. M. A. High-temperature fluids in subduction zones: implications for the chemical composition of the mantle and the crust. Contrib. Mineral. Petrol. 155, 109–129 (2008).

30. Feenstra, A. Coulombic versus solvophobic surfactant systems in subduction zone environments. Rev. Geophys. 48, 10.1029/2009RG000307 (2010).
Methods

Mineral abbreviations follow Whitney and Evans\(^{3}\), except Haematite. Amphibolite nomenclature follows Hawthorne et al.\(^{4}\).

Metamorphism. The CBU underwent high-pressure/low-temperature metamorphism during the Eocene. Metamorphic P–T conditions reached 500–550 °C and 1.5–2.0 GPa (refs. 10, 11). The samples from Crete are from the Phyllite-Quartzite unit and the Plattenkalk nappe, which comprise the high-pressure/low-temperature rocks collectively known as the lower nappes\(^{12}\). Metamorphism occurred in the late Miocene and reached ~400 °C and ~1.0 GPa (refs. 5, 6).

Thermodynamic data. The thermodynamic calculations were done using the database of Holland and Powell\(^{7}\), incorporating the standard-state properties of \(\text{H}_2\text{O}, \text{CO}_2, \text{H}_2, \text{CH}_4, \text{CO}, \text{H}_2\text{S}\), and \(\text{S}_2\), together with the equations of state of ref. 8 for \(\text{H}_2\text{O}\) and \(\text{CO}_2\), and ref. 9 for \(\text{H}_2\). We computed the isofugacities of relevant reactions using the above thermodynamic models of refs. 8, 9. Thermodynamic data for \(\text{SO}_2\) were also included\(^{10}\); the critical pressure was adjusted slightly from 7.87 MPa to 9.87 MPa to better fit available volume relations at elevated P–T conditions\(^{11}\) using the state equation of ref. 12. \(\text{SO}_2\) was assumed to mix ideally; this assumption had no impact on the \(f_{\text{O}_2} = f_{\text{O}_2}\) isofugacity calculations. Equilibria involving the above C–O–H–S species were calculated using Theriak-Domino\(^{72}\) version 11.03.2020 (Supplementary Table 2). The 'fluid' standard state was adopted, which specifies unit activity of the pure substance at the P–T conditions of interest. \(f_{\text{O}_2}\) was not considered as a fluid constituent because its concentrations are so low that there is effectively no free \(\text{O}_2\) in the fluid\(^{13}\).

We estimated fluid \(S\) concentrations in two ways. First, we considered the average mid-ocean-ridge basalt composition of ref. 14 at \(\text{FMQ} = 1\) with enough added \(S\) to stabilize pyrite at subarc conditions of 700 °C and 3 GPa (1.895 \(10^{-3}\) molar \(S/\text{Si}\) ratio; Supplementary Information). Such fluids need not be generated in the metamass; they could also be derived from underlying reduced serpentinite that achieved redox equilibrium with metamass. Using the fluid standard-state model above and pseudequilibrium calculations following ref. 15, this yields a total \(S\) mole fraction of 5.6 \(10^{-4}\) (almost entirely \(\text{H}_2\text{S}\)).

Second, we considered the aqueous species treatment used in the DEW model\(^{16}\) computed in ref. 17. The standard state is: unit activity for a hypothetical 1 molal \(\text{O}_2\) buffer. Using the fluid standard-state model above and pseudequilibrium calculations following ref. 15, this yields a total \(S\) mole fraction of 5.6 \(10^{-4}\) (almost entirely \(\text{H}_2\text{S}\)).

We estimated \(f_{\text{O}_2}\) for \(\text{H}_2\text{S}\) from the choice of model. \(f_{\text{O}_2}\) was not considered as a fluid constituent because its concentrations are so low that there is effectively no free \(\text{O}_2\) in the fluid\(^{13}\).

The last of these was used to compute the \(f_{\text{O}_2}\) for \(\text{H}_2\text{S}–\text{SO}_2\) isofugacity (\(f_{\text{O}_2} = f_{\text{O}_2}\) assuming unit activity of \(\text{H}_2\text{O}\) \(a_{\text{H}_2\text{O}} = 1\)). Decreasing \(f_{\text{O}_2}\) decreases the \(f_{\text{O}_2}\) for \(\text{H}_2\text{S}–\text{SO}_2\) isofugacity, but low \(a_{\text{H}_2\text{O}}\) fluids are unlikely\(^{18}\). Donnole and Essene\(^{19}\) determined \(f_{\text{H}_2\text{O}}\) in the range of 3.5–4 for the calcilicate. This rock is from a continental subduction zone and was subjected to Neoproterozoic granulite facies metamorphism and potential metamorphism before the Paleozoic high-pressure event. Thus, it is from a very different setting than that studied herein.

The mineral Fe\(^{3+}\) contents were calculated by stoichiometry from the DEW analyses. Haematite–illite: 2 cations per 3 oxygens. Magnetite: 3 cations per 4 oxygens. Epidote: Fe\(^{3+}\) + Mn\(^{2+}\) + Al + Cr + Ti = 3 per 12.5 oxygens. We assumed all Mn\(^{2+}\) for manganiferous epidote in sample jagan1A from Andros, and Mn\(^{2+}\) for epidote in the other samples. Garnet: two octahedral sites per 12 oxygens (Fe\(^{2+}\) + Al\(^{3+}\) + Cr + Ti = 2). Very low garnet Fe\(^{3+}\)/Fe\(^{2+} + \text{Fe}^{3+}\) estimates were deemed unreliable. This is mainly a concern for reaction GH, above, which involves an andradite component. Furthermore, the activity–composition relations for Fe\(^{3+}\)-bearing epidote at low Fe\(^{3+}/\text{Fe}^{2+} + \text{Fe}^{3+}\) are probably subject to large uncertainties. Consequently, we only used \(f_{\text{O}_2}\) for several rocks, including high-pressure calcilicates from the Bergen Arcs, Norway. They obtained high \(f_{\text{O}_2}\) in the range of 3.5–4 for the calcilicate. This rock is from a continental subduction zone and was subjected to Neoproterozoic granulite facies metamorphism and potential metamorphism before the Paleozoic high-pressure event.

NATURE GEOSCIENCE | www.nature.com/naturegeoscience

| \(f_{\text{O}_2}\) calculations. | Mineral compositions (Data availability) for \(f_{\text{O}_2}\) estimates were obtained using the JEOI JX-85030 field-emission electron-probe microanalyzer (EPMA) at Yale University. Analyses used natural and synthetic standards, off-peak background corrections, a 15 kV accelerating voltage and a 10 nA beam current. The beam diameter ranged from focused to 5 μm, depending on the grain size and mineral type (5 μm was used for all hydrous phases). Rhombohedral oxides in three of the four lowest- \(f_{\text{O}_2}\) samples (DEWFMQ = 2–3; jagi909A, jagi1068b, jagi1545F) contain exsolution lamellae that were integrated with the host grain using multiple (up to 12) EPMA analysis spots per sample\(^{19}\).

We utilized the following equilibria \(10 \text{Fe}_2\text{O}_3 + 8 \text{CaAl}_2\text{Si}_2\text{O}_8 (\text{OH}) + 12 \text{SO}_2 (\text{H}_2\text{O}) (\text{Fe}) = 8 \text{CaFe}_2\text{Al}_2\text{Si}_3\text{O}_8 (\text{OH}) + 4 \text{Fe}_3\text{Al}_2\text{Si}_2\text{O}_12 + 3 \text{O}_2 (\text{H}_2\text{O}) (\text{Alm}) (\text{Ep}2)\) 2 \text{Fe}_2\text{O}_3 + 4 \text{CaTi}_2\text{O}_5 + 4 \text{CO}_2 (\text{H}_2\text{O}) (\text{Fe}) = 4 \text{Si}_2\text{O}_3 + 4 \text{Fe}_2\text{Ti}_2\text{O}_7 + 4 \text{CaCO}_3 + 2 \text{O}_2 (\text{H}_2\text{O}) (\text{Ap}) (\text{IHAS})\)

8 \text{Na}_2\text{Si}_2\text{O}_5 + 6 \text{Fe}_2\text{O}_3 + 16 \text{SO}_2 + 4 \text{H}_2\text{O} (\text{Jd}) (\text{H}) = 4 \text{Na}_2\text{Fe}_2\text{Al}_2\text{Si}_2\text{O}_8 (\text{OH}) + 3 \text{O}_2 (\text{Fe–Gl}) (\text{JHGI})\)

8 \text{Na}_2\text{Si}_2\text{O}_5 + 12 \text{SiO}_2 + 10 \text{Fe}_2\text{O}_3 (\text{H}) = 4 \text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_8 (\text{H}_2\text{O}) (\text{Alm}) (\text{JAH})\)

4 \text{Ca}_3\text{Al}_2\text{Si}_2\text{O}_12 + 10 \text{Fe}_2\text{O}_3 + 12 \text{SiO}_2 (\text{H}) = 4 \text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_8 (\text{H}_2\text{O}) (\text{Ad}) (\text{GH})\)

\(\text{H}_2\text{O} + \text{SO}_2 = \text{H}_2\text{S} + 1.5 \text{O}_2 (\text{SO}_2–\text{H}_2\text{S})\)
smaller ΔFMQ uncertainty of ±0.12. To evaluate the effects of uncertainties on mineral analyses, thermodynamic data and the extent and timing of equilibration, we calculated the standard deviation on ΔFMQ with respect to the mean for four samples with ΔFMQ estimates made using different reactions (jagi75A, jagt09A, jagt106B and jagt154F: 17 total estimates). This yielded a standard deviation of ±0.21. Summing this and the haematite–magnetite uncertainty in quadrature (√(0.22² + 0.21²)) yielded ±0.30, our preferred value for the standard deviation of an individual ΔFMQ estimate. This is far smaller than the observed range of log (ΔFMQ) (Fig. 3). The uncertainties for the Mn-rich sample from Andros (jagan1A-1) are deemed larger due to uncertainties in the thermodynamic properties of clinozoisite– epidote–piemontite solid solutions. Nonetheless, the extremely high fO2 of such rocks is clear (ΔFMQ ~9) and is comparable to estimates made on similar rocks elsewhere.

### Time-integrated fluid flux calculations and the fluid:rock ratio

The fluid:rock ratio (FRR) is a measure of the amount of fluid infiltration needed to drive a given reaction in a rock, but in general it will underestimate the fluid flux required to propagate a reaction front. Consider a volumetric FRR of 1 mmol m⁻³, this seems like a modest number, but it only considers a rock volume in isolation and does not account for the spatial extent of flow. Imagine a 1-km-long vertical column of rock with a 1 m² cross-section through which this fluid flows vertically. To react the entire column, 1 m³ of fluid is required for every 1 m³ of rock (the FRR). Thus, 1,000 m³ of fluid is required to react 1,000 m³ of rock, far greater than the FRR implies. In other words, the FRR must be multiplied by the length scale of flow to obtain the time-integrated fluid flux (q), yielding 1,000 m³ m⁻¹, for our example.

The one-dimensional conservation of mass expression describing fluid advection (flow) with chemical reaction for a chemical species, i, in the fluid is

\[
\frac{\partial(c_i)}{\partial t} = -\frac{\partial(c_i v_i)}{\partial x} + \sum R_{ij}
\]

where \(c_i\) is the concentration of species \(i\) (mol m⁻³) and \(v_i\) is the average fluid velocity in the \(x\) direction (m s⁻¹). \(R_{ij}\) is the rate of production or consumption of species \(i\) by reaction \(j\) (mol m⁻³ s⁻¹) and \(t\) is time. Assuming local fluid–rock chemical equilibrium, one simple overall redox reaction \((R = 1)\) and constant porosity, this expression can be integrated and recast to give \(q_f\) at the fluid inlet

\[
q_f = \left(\frac{M_{\text{Fe}}}{\Delta X_{\text{Fe}} v_X L}\right) L + L\Phi
\]

Here, \(L\) is the length of a unit column of rock that has been reacted. A reaction front, which moves in the direction of flow, separates the reacted and unreacted regions (Fig. 4a). The \(V_r\) term is the molar volume of the fluid, \(M_i\) is the molar mass of \(i\) produced or consumed per unit volume rock and \(\Delta X_i\) is the difference between the mole fraction of \(i\) in the fluid upstream and downstream of the front. The term in parentheses on the right-hand side of the equation is the volumetric redox reaction rate \(q_f\) in m³ m⁻¹ s⁻¹ for this reaction.

If diffusion and mechanical dispersion operated in addition to advection and/or if there were kinetic departures from local fluid–rock equilibrium, reaction fronts would be smeared out to a large extent. However, if the reaction progress and reaction rates at the redox front are constant, we could solve equation (5) for \(q_f\). Diffusive mass transfer will occur adjacent to conduits such as veins (Fig. 2c). These features are too small to resolve individually with our methods but are incorporated in a general way by the continuum approach of equation (4). Fluid channelization at larger scales in subduction complexes is well documented, e.g., for metagraywacke rocks below the metasedimentary cover\((52,83,84)\), but reaction progress and oxygen isotope evidence indicate that fluxes within the metasedimentary units of the CBU were largely pervasive.

### Rock descriptions

White micas refer to undifferentiated K-rich and/or Na-rich micas. The samples are listed in the approximate order of decreasing fO2. Extended Data Fig. 1 shows the sample locations and general geologic relations for Tinos. 4.3 (a, b).

1. Sample jagan1A. Mn- and Fe-rich quartzitic schist, Andros (Fig. 1b).

2. Sample jagt00A. Phylite cut by 3.5-mm-wide metamorphic quartz vein, Crete, Greece.

3. Sample jagt00B. Phylite cut by 2.5-mm-wide metamorphic quartz vein, Crete, Greece.

4. Sample jagt01. Phylite cut by 3-mm-wide metamorphic quartz vein, Crete, Greece.
vein and selvage, but the destruction of haematite and the production of carbonate indicate a metamorphic fO2 decrease. Location: Kerames village area, 35°09.805′ N, 24°30.777′ E.

3. Sample 57. Metabasalt from Naxos described by Feenstra containing diaspore and haematite together with rutile, calcite, white mica and margarite. This rock is from the low-grade regional zone I and thus was not strongly overprinted by the later Barrovian metamorphism that affected other parts of the island. Location: 35°57.667′ N, 25°33.083′ E. A comparable rock from Crete (sample jagt10A) is shown in Fig. 1a; its location is: 35°23.153′ N, 24°53.672′ E.

4. Sample jagt108FC. Micaceous schist, Tinos, which contains white mica, Na amphibole, epidote, quartz, calcite (infused former aragonite), dolomite–ankerite solid solution, sphene and haematite. The assemblage haematite + sphene + calcite is widespread in the metasediments of Tinos. Given constraints on the activity of CO2 in the fluid17, the fO2 can be estimated for these rocks via equilibrium IHAS. Location: 37°35.834′ N, 25°04.664′ E.

5. Sample jagt108C. Micaceous schist, Tinos (Fig. 1c). This is representative of a very common rock type on Tinos, composed predominantly of phengite + chlorite + quartz + chloritoid + rutile or sphenite ± albite ± carbonates + Na-bearing amphibole/clinoxyroxene. The high-pressure/low-temperature origin of such rocks is clear, as phengite is very Sr rich and can attain 3.52 Sr per formula unit (see Data availability). Veins and adjacent selvages in such rocks can contain coarse haematite and calcite and sometimes biotite. Location: 37°32.693′ N, 25°36.281′ E.

6. Sample jagt134AN. Magnetite + haematite + garnet quartzite, Tinos (Fig. 2a). Garnet cores contain only haematite inclusions, whereas the matrix contains magnetite and haematite. Matrix magnetite grew around garnet with haematite inclusions, demonstrating a decrease in fO2 associated with reduction (Fig. 3). Location: 37°33.221′ N, 25°12.742′ E.

7. Sample jagt175A. Alumomite, Tinos. That contains substantial Na amphibole and Mn-rich garnet (Fig. 1c). Garnet has inclusions of haematite-rich rhombohedral oxide whereas the matrix contains Mn-bearing ilmenite that grew around garnet (Fig. 2d). These textures document a metamorphic decrease in fO2 (Fig. 3). Location: 37°37.454′ N, 25°02.833′ E.

8. Sample jagt1008B. Marble composed mostly of calcite (infused former aragonite), glaucophane–riebeckite Na amphibole, Na–Ca amphibole, magnetite and haematite, together with minor chlorite, epidote and quartz. Tinos (Fig. 1d). Location: 37°33.697′ N, 25°13.405′ E.

9. Sample jagt175A. Alumomite, Tinos. A complex rock consisting of albite, quartz, phengite, magnetite, haematite, garnet, Na and Na–Ca amphiboles, and sphene. Rare Fe3+–bearing sodic clinopyroxene (jadeite–aegerine) can be found as inclusions in Na amphibole and in the matrix. The rock is cut by anastomosing veins in which haematite has been converted to magnetite (Fig. 2b). We interpret these anastomosing features to be the fossil flow paths of infiltrating reducing fluids that reduced haematite to magnetite. The fO2 must have been near haematite–magnetite values during this process. Location: 37°35.764′ N, 25°04.483′ E.

10. Sample jagt106B. Schist, Tinos. A garnetiferous rich schist in epidote which also contains phengite, chlorite, albite and magnetite. The garnets include haematite, rutile, magnetite, Na amphibole and probable lawsonite pseudomorphs. Some of the Mn–Fe related exsolution is haematite. Sodium amphibole in the matrix is largely or completely replaced by aggregates of chlorite and albite. The rock contains appreciable dark bluish-green tourmaline throughout. Location: 37°32.821′ N, 25°13.643′ E.

11. Sample jagt154F. Micaceous Na amphibole schist, Tinos, characterized by Na amphibole, phengite, epidote and porphyroblasts of garnet. Rutile and rhombohedral oxides are found as inclusions in garnet, whereas the matrix, garnet rims and Na amphibole contain sphene. Garnets have inclusions of Fe3+–bearing Na–Ca amphibole in their interiors which have a ~25% greater Fe3+/Fe2+ (Fe3+/Fe2+) ratio than matrix Na amphibole (Fig. 2c). Garnet also contains inclusions of clinopyroxene dominated by jadeite–aegerine with ~0.4–0.6 Fe3+/Fe2+ (Fe3+/Fe2+), as well as epidote. Magnetite (now maritite) is found in the matrix and in contact with garnet rims. The rhombohedral oxides contain complex exsolution lamellae and replacement textures; we infer that two rhombohedral oxides coexisted during high-pressure/low-temperature metamorphism. Location: 37°33.358′ N, 25°06.430′ E.

12. Sample jagt90A. Metabasaltic blueschist dominated by Na amphibole, epidote and garnet, with lesser amounts of quartz, rhombohedral oxides, rutile and magnetite. Titanium-bearing haematite and Fe3+–bearing ilmenite are present, both of which contain exsolution lamellae. This indicates crystallization on the haematite–ilmenite solidus, followed by exsolution during cooling. The sample is intercalated with oxidized metasediments (for example, sample jagt90B) raising the possibility that metabasalt becomes oxidized due to redox exchange with metasediments, in addition to other processes such as seawater hydrothermal alteration. Location: 37°37.454′ N, 25°02.833′ E.

13. Sample jagt935E. Micaceous phengite, Na amphibole, garnet, quartz, chloritoid schist that contains finely disseminated graphitic carbon.
Acknowledgements

We thank C. M. Breeding, M. Bröcker, E. L. Donald, D. S. Keller, D. Levy, S. A. Menemenlis, E. M. Stewart, M. Tian and D. E. Wilbur for discussions and fieldwork, and J. O. Eckert Jr for assistance with electron-probe microanalysis. We gratefully acknowledge funding provided by the US National Science Foundation Directorate of Geosciences (grant numbers EAR-0105927, EAR-0744154 and EAR-1650329 to J.J.A.; grant number EAR-1855208 to M.E.H.), Yale University and the Yale Peabody Museum of Natural History (J.J.A.), a Bateman Postdoctoral Fellowship, Department of Earth and Planetary Sciences, Yale University (S.T.), the National Natural Science Foundation of China (grant number 42122011 to J.-L.L.) and the Deutsche Forschungsgemeinschaft (DFG) through grant number CRC 1114 ‘Scaling Cascades in Complex Systems’, Project Number 235221301, Project (C09) – ‘Dynamics of Rock Dehydration on Multiple Scales’ (T.J.).

Author contributions

J.J.A. designed the study, coordinated the fieldwork and collected samples, performed the electron probe microanalysis, prepared the petrographic thin sections and did the pseudosection and time-integrated fluid flux calculations. S.T., M.E.H., E.C. and J.-L.L. provided perspectives and conceptual advice and guidance on model development and the oxygen fugacity of arc lavas in relation to subducted oceanic lithosphere. J.J.A., J.-L.L. and M.E.H. performed oxygen fugacity calculations and uncertainty analysis. J.-L.L., E.M.S., T.J., S.T. and J.J.A. constrained the sulfur mass balance, and C.F. provided guidance in the field, including the location of key outcrops. All authors contributed extensively to the interpretation of the data, discussions and preparation of the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

Extended data is available for this paper at https://doi.org/10.1038/s41561-022-00904-7.

Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s41561-022-00904-7.

Correspondence and requests for materials should be addressed to Jay J. Ague.

Peer review information Nature Geoscience thanks Dimitri Sverjensky and Sarah Penniston-Dorland for their contribution to the peer review of this work. Primary Handling Editor: Rebecca Neely, in collaboration with the Nature Geoscience team.

Reprints and permissions information is available at www.nature.com/reprints.
Extended Data Fig. 1 | Location maps. Location maps. a, Aegean region showing Crete and the extent of the Cycladic high-pressure/low-temperature (HP/LT) metamorphic belt (Cycladic Blueschist Unit; CBU). Sample locations are shown with red symbols. b, Generalized geologic map of Tinos showing sample locations. Map adapted from ref. 43, Springer Nature Limited; field relations from refs. 43, 85, 86.