Atomistic insight into lithospheric conductivity revealed by phonon–electron excitations in hydrous iron-bearing silicates

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Amphiboles are essential components of the continental crust and subduction zones showing anomalous anisotropic conductivity. Rock properties depend on the physical properties of their constituent minerals, which in turn depend on the crystal phonon and electron density of states. Here, to address the atomic-scale mechanism of the peculiar rock conductivity, we applied in situ temperature-dependent Raman spectroscopy, sensitive to both phonon and electron states, to Fe2+–rich amphiboles. The observed anisotropic resonance Raman scattering at elevated temperatures, in combination with density-functional-theory modelling, reveals a direction-dependent formation of mobile polarons associated with coupled FeO6 phonons and electron transitions. Hence, temperature-activated electron-phonon excitations in hydrous iron-bearing chain and layered silicates are the atomistic source of anisotropic lithospheric conductivity. Furthermore, reversible delocalization of H+ occurs at similar temperatures even in a reducing atmosphere. The occurrence of either type of charge carriers does not require initial mixed-valence state of iron or high oxygen fugacity in the system.
Amphiboles, hydrous silicates with the general formula $AB_2C_2T_8O_{22}W_2$, are very important constituents of the Earth’s lithosphere, occurring in a diversity of rock types\(^5\). Being a structural bridge between pyroxenes and phyllosilicates, amphiboles are involved in a number of transformation processes at elevated temperatures and pressures during subduction. The ultimate effects of these processes include the oxidation of Fe and the release of water into the lower crust/mantle\(^3,4\). The strong structural anisotropy of the amphiboles results in heavily anisotropic elastic, thermoelastic, dielectric, and conductivity properties, which in turn contributes to the behavior of the host rock. The amphibole structure (see Fig. 1a) may accommodate a variety of chemical elements at the non-tetrahedrally coordinated crystallographic sites: $M(1)$, $M(2)$, and $M(3)$ occupied by C-type cations, as well as at the $M(4)$ site occupied by B-type cations, which strongly influences their properties and thermal stability\(^6\).

A particularly important issue in the crystal chemistry of these minerals is the stability of Fe-bearing species, because their oxidation processes have a paramount importance in a wide spectrum of fields, including geology and geophysics, but also materials science and toxicology\(^6,7\). Early ex situ work\(^8,9\) have revealed that oxidation of $^{56}$Fe is intrinsically coupled with a loss of hydrogen from the hydroxyl group, in the presence of external oxygen ($O_2$), according to the reaction:

$$2Fe^{2+} + 2W(OH)^- + 0.5O_2 \rightarrow 2Fe^{3+} + 2W^{2-} + \text{H}_2O \quad (1)$$

Further in situ studies have clarified the changes in the interatomic distances and site population associated with iron oxidation as well as the subsequent phase transformations\(^5,10,11\). Very recently, by combining diffraction and spectroscopic methods, thus probing the structure at different length and time scales, it has been shown that the above simple chemical reaction is preceded by multiple local-scale structural changes\(^12-15\). A particularly important issue, which has been achieved mainly via Raman spectroscopy, is the existence of a thermal state of reversible dynamic oxidation. This state consists of delocalization of electrons $e^-$ from the octahedrally coordinated iron cations as well as of $H^+$ from the W-type anions\(^13\). For temperatures within the range of dynamic oxidation, both $e^-$ and $H^+$ remain inside the crystal bulk but if the temperature decreases, they can be attached back to $^{56}$Fe$^{3+}$ and $W^{2-}$, respectively, to form again $^{56}$Fe$^{2+}$ and $W$(OH)$^-$. Only when the thermal energy is high enough, the atomic vibrations trigger a readjustment of the $TO_4$-ring geometry to match with smaller-size adjacent $MO_6$ octahedra (see Fig. 1a), which in turn allows for the irreversible $Fe^{2+}\rightarrow Fe^{3+}$ exchange and release of $H^+$ cations from the amphibole structure\(^13\).

The delocalization of $e^-$ and $H^+$ and consequent hopping within the amphibole structure results in an increase in mineral conductivity\(^14,16\), a feature that may have a tremendous impact on the physics of hydrous silicates with a quasi one-dimensional structure and on potential mineral-inspired technologies\(^6\). Moreover, the possible development of transport and magnetic properties in iron-bearing amphiboles at elevated temperatures is of extreme interest in geophysics\(^17-20\), especially when modeling lithospheric conductivity\(^16,21\). For the latter, dehydrogenation of amphiboles and other representative hydrous silicates is also considered to play an important role for the high-temperature anomalies in subduction zones\(^22\). Besides, the dehydrogenation of amphiboles and related layered silicates can contribute to the water cycling at depth or, depending on the local rock assemblages, to the formation of abiotic $H_2$ and $CH_4$\(^23\).

So far, studies on the stability of Fe-containing amphiboles have been mainly restricted to species from the sodium amphibole subgroup (e.g., ref. 13 and references therein), which are typical of high-pressure rocks. However, given the large compositional variety of amphiboles, it is important to study the high-temperature behavior of different amphibole subgroups, in order to understand whether the state of existing charge carriers in terms of delocalized $e^-$ and $H^+$ is a general property of all amphiboles. Hence, we have analyzed grunerite, ideally $\text{A}^{3+}\text{Fe}^{2+}$ $\text{Si}_8\text{O}_{22}$(OH)$_2$, a member of the magnesium-iron-manganese amphibole subgroup\(^24\). These species are particularly common in metamorphic rocks, where they may coexist with amphiboles of the tremolite-actinolite series or with serpentine-group minerals\(^2\). Amphiboles belonging to the Mg-Mg–Mn subgroup may crystallize in orthorhombic (Pnma or Pnmm) or monoclinic ($C2/m$ or $P2_1/m$) symmetry. The monoclinic structure is stabilized if $Fe^{2+}$ dominates both as B- and as C-type cation\(^25\). In Mg-dominant amphiboles, a reversible displacive $P2_1/m$-to-$C2/m$ phase transition may occur on heating\(^5\), with a critical temperature $T_c$ decreasing from ~600 to ~200 K, with the increase of $Fe^{2+}$ content\(^5,26\). Very recently, we have demonstrated the possibility of discriminating the crystal system of Mg-Fe-Mn and Li amphiboles by the position of a low-wavenumber Raman peak, which appears at ~75–85 cm$^{-1}$ and ~60–70 cm$^{-1}$ for monoclinic and orthorhombic amphiboles, respectively\(^27\). Similarly to pyroxenes\(^28\), this peak is assigned to an external $TO_4$
mode of the silicate double chain, and mirrors the relative geometry of the silicate anion with respect to small eight-coordinated (B-type) cations. For this reason, it is expected to be sensitive to temperature-driven phase transitions that are strongly controlled by the B-site size.

Here, we report the results of our temperature-dependent polarized Raman spectroscopic study of grunerite heated in air or in N₂ atmosphere, to follow the dynamics of multistep oxidation processes and the temperature-induced structural transformations. The most striking result is the existence of a strongly anisotropic reversible oxidation mechanism even under reducing atmosphere, which consists in direction-dependent coupled electron–phonon transition at elevated temperatures. Such temperature-induced conduction electrons associated with FeO₆ octahedra, in the presence of delocalized H⁺, should be a universal property of all one-dimensional or two-dimensional Fe-bearing hydrous silicates. This phenomenon provides insights into the atomistic driving force for the increasing conductivity observed in subducted rocks at convergent plate margins.

Results

Symmetry considerations, anomalous anisotropic Raman scattering, and selection rules. Two natural grunerite samples, designated as A85 and A86 and with chemical formulae given in Table 1, have been studied by in situ temperature-dependent Raman spectroscopy. At each temperature parallel polarized spectra (incident-light polarization $E_i$ parallel to the scattered-light polarization $E_s$) were collected in backscattering geometry (the direction of propagation of the incident light, $k_i$, is anti-parallel to the direction of propagation of the scattered light, $k_s$) from a natural crystal face in two different orientations of the crystal grain, i.e., with the crystallographic $c$ axis parallel to $E_i$ and the $a$ axis perpendicular to $E_i$. In Porto’s notation, $k_i(EE),k_s$, the former geometry corresponds to $y'(zz)y'$, whereas the latter to $y'(xx)y'$, where $z$ is along the $c$ axis and $x'$ and $y'$ are two mutually perpendicular directions within the ($a'$,$b'$) plane (see the sketch in Fig. 1b). In both geometries only $A_g$ modes are observed, whose Raman polarizability tensor in $2/m$ point symmetry is given by

$$\alpha(A_g) = \begin{pmatrix} \alpha_{xx} & \alpha_{xz} \\ \alpha_{xz} & \alpha_{zz} \end{pmatrix}$$

Therefore, the $y'(zz)y'$ spectra are dominated by the $\alpha_{xz}$ component, whereas the $y'(xx)y'$ spectra are determined either by both $\alpha_{xx}$ and $\alpha_{zz}$ components or only by $\alpha_{xx}$ depending on whether the crystal-grain face is parallel to [110] or [010] cleavage plane.

Selected $y'(zz)y'$ in situ Raman spectra of near-end-member grunerite A85 in air are shown in Fig. 2a. The overall Raman scattering drastically changes above 650 K: new broad peaks appear at ~273, 470, 576, and 815 cm⁻¹, whereas all symmetry-allowed first-order Raman peaks are suppressed, and above 750 K they cannot be resolved any longer. The only exception is the Raman-active $M_0^+$ mode that at room temperature generates a doublet ~220 cm⁻¹. Note that in $y'(zz)y'$ geometry, the polarization of the incident light $E_i$ is parallel to the crystallographic $c$ axis. The temperature evolution of the Raman scattering is totally different when collected with $E_i \perp c$, i.e., in $y'(xx)y'$ geometry (Fig. 2b): on heating from 295 to 850 K all Raman-active phonon modes are well preserved, gradually decreasing in wavenumber and increasing in width, as it should be expected for crystals with a positive volume thermal expansion and no phase transitions. Only at 900 K the signal-to-noise ratio degrades and the Raman scattering generated by the $M_0^+$ vibrations ~220 cm⁻¹ is enhanced, but the overall Raman scattering characteristic of amphiboles is still retained. The $y'(xx)y'$ spectra thus show that the amphibole structure is stable at least up to 900 K and therefore, the change in the selection rules observed in $y'(zz)y'$ geometry at elevated temperatures cannot be related to a structural transformation. Here, we should recall that the Raman scattering of solids is a light-matter interaction process that depends not only on the equilibrium configuration of nuclei, but also on the electron density of states (DOS). In the case of non-metallic materials, if the photon energy of the excitation laser line $E_{\text{photon}}$ is smaller than the electron energy gap $E_g$, the selection rules are determined only by the phonon wave functions. However, when $E_{\text{photon}}$ is close to or larger than $E_g$, the incoming photon can excite simultaneously a phonon and an electron, and the selection rules under such resonance conditions depend on both the phonon and the electron wave functions. For insulating and semiconducting materials, the resonance Raman scattering (RRS) is achieved via the so-called Fröhlich interactions consisting in electrostatic interactions between electrons and longitudinal optical (LO) polar phonons. In the case of centrosymmetrical crystals as $C2/m$ amphiboles, under non-resonance conditions (i.e., no electron transitions) the phonon phonons at the Brillouin zone center are infrared-active but Raman inactive, and vice versa. Therefore, the optical phonon modes that are Raman-active under non-resonance conditions cannot participate in Fröhlich interactions because they do not carry polarity and can become forbidden under resonance conditions (i.e., when electron transitions are activated by a photon or another external stimulus). Moreover, the RRS owing to Fröhlich interactions is selective; a resonance enhancement is expected only for those LO polar phonons that are related to the local structural species in which the electron transition occurs and therefore can couple with the excited electron.

Assignment of the observed spectral features at elevated temperatures. In our experiment, we changed the temperature, maintaining constant the excitation wavelength ($\lambda = 514.532$ nm). Actually, the temperature at which we observe drastic changes in the spectra is ~700 K, which is equivalent to ~0.06 eV, well below the photon energy of 2.4 eV corresponding to $\lambda = 514.532$ nm. Hence, the puzzling picture observed for grunerite (Fig. 2) can only be explained by temperature-activated electron transitions across $E_g$ that interact with polar optical phonons, forming strongly anisotropic.

| Sample | $A^*(M(4))_2E^*(M(0))_2(M(2))_2(M(3))_2T_0O_2W_2$ | Symmetry |
|--------|-------------------------------------------------|-----------|
| A85    | \[Fe^{2+}_{1.96}Mg_{0.02}Ca_{0.00}Na_{0.00}\] \(M(0)(Fe^{2+}_{1.86}Mg_{0.14})M(2)(Fe^{2+}_{1.76}Mg_{0.17}Al_{0.03})M(3)(Fe^{2+}_{1.76}Mg_{0.02})\) \(\{Si_{7.97}Al_{0.03}\}O_2W_2\) |
|        | \[[OH]_2\]                                     | $C2/m$    |
| A86    | \[Fe^{2+}_{1.87}Ca_{0.13}Mg_{0.00}Na_{0.00}\] \(M(0)(Fe^{2+}_{1.86}Mg_{0.14})M(2)(Fe^{2+}_{1.77}Mg_{0.00}Al_{0.03})M(3)(Fe^{2+}_{1.76}Mg_{0.02})\) \(\{Si_{7.97}Al_{0.03}\}O_2W_2\) |
|        | \[[OH]_2\]                                     | $C2/m$    |

No traces of Fe³⁺ were detected by Mössbauer spectroscopy in either sample.
intrinsic local polarizations $P_{\text{loc}}$, i.e., mobile polarons with aligned dipole moments. These temperature-activated coupled electron–phonon excitations will change the Raman selection rules from non-resonant to resonant only when $P_{\text{loc}}$ is parallel to the photon polarization $E_0$, to fulfill the requirement for three-particle interaction among the excited electron, the phonon, and the incoming photon. When $P_{\text{loc}}$ is perpendicular to $E_0$, the temperature-induced polaron dipole moments do not interact with the photon polarization and hence the inelastic light scattering is realized only via photon–phonon interaction. This causes the appearance of RRS only in $y'(zz)|y'$ scattering geometry, while the $y'(x'x')|y'$ spectra still correspond to non-resonant selection rules. All phonons related to the silicate anion, including the $\text{SiO}_4$-stretching modes ~900–1100 cm$^{-1}$, the $\text{SiO}_4$-ring mode ~658 cm$^{-1}$, the $\text{SiO}_4$-chain mode ~78 cm$^{-1}$, as well as the OH-stretching modes are suppressed under resonance conditions (see Fig. 2a). In contrast, phonons involving vibrations of $\text{MO}_6$ octahedra, e.g., ~220 cm$^{-1}$, are resonantly enhanced. Moreover, the most pronounced resonantly activated phonon mode appears ~570 cm$^{-1}$, a wavenumber that is typical of Fe$^{2+}$-$\text{O}_6$ stretching in $^{56}$Fe-bearing amphiboles$^{27,34}$. Therefore, the electron transition responsible for the anisotropic RRS occurs between electron levels related to the FeO$_6$ octahedra and has an induced dipole moment parallel to the $c$ axis. Because of such a transition, conduction electrons form in the crystal and locally, the oxidation state of the corresponding $^{56}$Fe$^{3+}$ ions changes from divalent to trivalent. This being the case, the direction-preferred formation of conduction electrons at elevated temperatures is expected to be an intrinsic feature of all amphiboles containing octahedrally coordinated Fe, allowing for polaron mobility associated with the strips of octahedra. Note that the temperature above which we observe this phenomenon is consistent with the requirement that the threshold temperature of small polaron hopping is about half the Debye temperature of the system$^{35–37}$.

To verify our conclusions, density-functional theory (DFT) calculations were performed on three model systems with the same structure, using that of A85, but having different occupancy at the $M$(1), $M$(2), $M$(3), and $M$(4) sites: (i) all sites occupied by Fe$^{2+}$, (ii) octahedrally coordinated $M$(1–3) sites occupied by Fe$^{2+}$, and $M$(4) by Mg, and (iii) octahedrally coordinated $M$(1–3) sites occupied by Mg, and $M$(4) by Fe$^{2+}$. The projected electron DOS for Fe, O, Si, and Mg in different models is shown in Fig. 3. The calculated energy gap for end-member grunerite (where $M$(1) = Fe, $M$(3) = Mg, $M$(4) = Fe) is $E_g$ = 0.05 eV (see Supplementary Figure 5 and Supplementary Table 5), close to the value of 0.06 eV suggested from the experiment, although one should keep in mind that in general only semi-quantitative conclusions can be gained from DFT calculations. The projected DOS for the two imaginary compounds ($M$(1)$M$(2)$M$(3)$M$(4) = FeMgFeMg and = MgMgMgFe) clearly show that Fe at $M$(1–3) contributes to the conduction band between ~0.01 and 0.02 eV, whereas Fe at $M$(4) to that ~0.6 eV $\approx$ ~6900 K. Therefore, we can safely state that the experimentally observed phenomena ~700 K are exclusively related to octahedrally coordinated Fe. Moreover, the orbital DOSs of Fe as well as of O atoms from the $\text{MO}_6$-strip (see Supplementary Figures 2–7) suggest that the top of the valence band results from the hybridization between O 2$p_x$ orbitals and Fe 3$d_y$ orbitals, whereas the bottom of the conduction band from the hybridization between O 2$p_x$ and Fe 3$d_{x^2–y^2}$ orbitals. Therefore, the dipole moment related to electron transitions across $E_g$ is along $z$ (parallel to the crystallographic $c$ axis), in full agreement with the conclusions derived from the experimentally observed anisotropic appearance of RRS.

**Quantitative trends from heating experiments on near-end-member grunerite (A85) in air.** The Raman spectra of A85 measured in air at room temperature after annealing the sample at different temperatures (Fig. 4) show an almost total recovery of the $y'(zz)|y'$ scattering after heating up to 700 K. The non-RRS peaks, however, are gradually suppressed after heating up to 750 K and 800 K, and completely disappear after heating at 850 and 900 K. This trend can be quantified by the intensity ratio $I_{\text{RRS}}/I_{\text{RS6}}$, i.e., the relative intensity between the strongest RRS peak ~586 cm$^{-1}$ and the strongest non-RRS peak generated by framework vibrations, namely the ring mode ~658 cm$^{-1}$. Figure 4a demonstrates that the experimental data plotted versus the heating temperature follow a Boltzmann growth function with an inflection at $T_{\text{heat}}$ = 720 K. This value matches exactly the transition temperature obtained by X-ray diffraction (XRD) and X-ray absorption spectroscopy for the closely related
In situ high-temperature experiments of near-end-member grunerite (A85) in N₂. In order to determine whether the presence of α₂O₂ is a necessary precondition for the anisotropic development of conduction (delocalized) electrons, we performed in situ Raman experiments purging the sample chamber with N₂. Figure 6 shows that reversible anisotropic RRS appears also under reducing atmosphere, but at higher temperatures than in air. Therefore, the presence of α₂O₂ favors the direction-preferred electron transition between the hybridized O 2p and Fe 3d levels, but it is not required for this process to occur. Hence, anisotropic conductivity due to mobile electrons can exist in amphiboles at elevated temperatures, independently of the external environment. Another interesting observation is that above 700 K the OH-stretching peaks can hardly be resolved in either scattering geometry, but they fully recover on cooling back to room temperature, emphasizing that the reversible delocalization of WH⁺ at high temperatures is also unaffected by the absence of α₂O₂. The diffusion of these delocalized H⁺ cations through the crystal bulk should also contribute to the overall electrical conductivity of amphiboles. The room-temperature y'(x'x')y' spectra before and after heating in N₂ are identical, whereas there are weak extra peaks ~583 and 464 cm⁻¹ in the y'(zz)y' spectrum measured at room temperature after heating in N₂ up to 800 K. The same is observed in the y'(zz)y' spectrum measured at room temperature after heating up to 700 K in air (see Fig. 4a). Note that in both cases the ratio between the total integrated intensity generated by OH-stretching vibrations and by the framework vibrations (below 1200 cm⁻¹) remains unchanged within uncertainties, confirming negligible loss of H⁺ upon heating to 800 K in N₂ or 700 K in air. Therefore, for charge-balance reasons, there should be no ejection of electrons from the crystal bulk. On the other hand, the extra peaks are indicative of presence of CFe³⁺. This suggests that on cooling a small amount of temperature-activated conduction electrons have been trapped in deep defect levels and hence, some octahedrally coordinated iron ions could not recover their initial divalent oxidation state.

Fig. 3 Electron density of states. The total and projected electron densities of states are calculated for M(1)M(2)M(3)M(4) = Fe²⁺Fe²⁺Fe²⁺Fe²⁺ (Model 1), M(1)M(2)M(3)M(4) = Fe²⁺Fe²⁻Fe²⁺Fe²⁺ (Model 2), and M(1)M(2)M(3)M(4) = MgMgMgFe²⁺ (Model 3); the red dashed lines mark the Fermi energy set at 0 eV.
The complete recovery of the Fe oxidation due to its higher Fe oxidation reported so far for grunerite.

This further emphasizes the importance of our results for potential technological applications based on materials comprising quasi one-dimensional octahedral systems.

At last, we have considered the temperature evolution of the SiO2-ring mode ωring ~660 cm⁻¹ as well as of the SiO2-chain mode ωchain ~78 cm⁻¹ in the range 100–950 K (Fig. 8). Both modes appear at slightly lower wavenumbers for A85 than for A86 due to its higher CFe²⁺ content. A minimum in ωring(T) marks the temperature of SiO2-ring modification to adopt the smaller Fe₃+O₆ volume, triggering the release of e⁻ and H⁺ from the crystal, that is, the irreversible CFe oxidation. The threshold temperature of irreversible oxidation T_{irr.ox} is not reached for A86 in the studied T range (Fig. 8a), whereas T_{irr.ox} is 850 K for A85, in excellent agreement with the value derived from the temperature dependencies of ωring(T)/ωring + ωring mode) and I_r(152) (Fig. 5). At low temperatures, ωring(T) reaches a saturation, indicating no further change within the silicate double chains; however ωchain(T) exhibits a broad minimum ~170 K (Fig. 8b), suggesting a rearrangement of the double chain with respect to the (M4) site. A minimum in the wavenumber of a low-energy phonon points to a phase transition, especially when we know that this particular phonon mode is sensitive to the symmetry of the crystal structure. Following the concepts of hard-mode spectroscopy, we attribute the minimum in ω(T) chain(T) to a P2₁/m ↔ C2/m phase transition of mixed displacive and order/disorder character, which has been already observed for cummingtonite. The phase transition temperature T_c depends on the total content of Fe²⁺ and for x = Fe/(Fe + Mg) ranging between 0 and 0.45, T_c varies between ~600 and 200 K. A linear extrapolation to T_c(x) suggests that grunerite with x above 0.7 should not undergo a phase transition to P2₁/m in agreement with the data provided by infrared spectroscopy or XRD. Our Raman data however clearly indicate a structural instability in the silicate chain, which commonly leads to a P2₁/m ↔ C2/m symmetry change in both amphiboles and pyroxenes suggesting that T_c(x) follows a more complex trend. The small depth in ωchain(T) around the minimum suggests only subtle structural alteration, which could explain why such a phase transition has not been reported so far for grunerite.
Discussion

Seismic and electromagnetic anomalies in subduction zones have triggered continuously growing interest on amphiboles and layer silicates, as well as of hydrogen-bearing nominally anhydrous minerals, as responsible for the electrical conductivity of the mid-crust and subduction zones. Metasomatic processes leading to the formation of hydrous fluids may considerably contribute to the anomalies in lithospheric conductivity. However, recent studies have indicated that conductive aqueous fluids alone cannot explain the anisotropic conductivity observed in some locations. Moreover, although the geophysical anomalies generally depend on both temperate and pressure as thermodynamical parameters, temperature rather than pressure is the major factor influencing the electrical conductivity of rock-forming minerals. Two main temperature-activated solid-state processes have been considered to cause the rock conductivity: (i) hopping of electrons/electron holes between ferrous and ferric iron and (ii) diffusion of $H^+$. The former process presumes the presence of minerals with mixed-valent Fe state, that is, with coexisting Fe$^{2+}$ and Fe$^{3+}$ in the nominal formula, like riebeckite or arfvedsonite, leading to polaron conductivity. An additional process, postulated for Fe-free minerals, involves...
Fig. 8 Temperature dependence of the wavenumber of selected modes for A85 and A86. a Trends for the ring mode; b trends for the chain mode. Data points derived from the $y'(zx'y')$ spectra measured in situ in N$_2$ atmosphere are given with circles; data points derived from $y'(x'y')$ spectra measured in situ in air are given with squares. Blue symbols refer to A85, red symbols to A86.

Conclusions

The appearance of anisotropic RRS at elevated temperatures directly evidences the formation of temperature-activated polarons involving an electron transition between hybridized O 2p and Fe 3d levels with a dipole moment along the octahedral strips in the amphibole structure. These anisotropically coupled electron and phonon excitations in hydrous Fe-bearing chain/layered silicates are the atomistic source of anisotropic lithospheric conductivity, rather than phenomena limited to solid-fluid interfaces.

The presence of mobile electronic polarons and H$^+$ cations at temperatures above 700 K, which are typical of the lithosphere and forearc regions of slab-mantle wedge interfaces in subduction zones, indicate that both types of charge carriers can contribute to the overall lithospheric conductivity.

The occurrence of either type of charge carriers does not require the initial coexistence of ferrous and ferric iron in the mineral and does not depend on the oxygen fugacity of the system. The presence of external oxygen is however required to trigger H$^+$ expulsion as H$_2$O molecules, thus making the amphibole an efficient carrier of water into the crust/mantle.

Methods

Sample characterization. The chemical composition was analyzed by wavelength-dispersive electron–microprobe (Supplementary Note 1, Supplementary Table 1). The oxidation state of iron and the site populations were further checked by Mössbauer spectroscopy (Supplementary Note 2, Supplementary Figure 1 and Supplementary Table 2). The room-temperature structure was refined to single-crystal XRD data (Supplementary Note 3, Supplementary Table 3, Supplementary Data 1, and Supplementary Data 2). The chemical formulae were calculated using the Excel sheet developed by Locock49, taking into account the Fe$^{2+}$–Fe$^{3+}$ site population from the structure refinements and Mössbauer data. Euhedral crystal grains of size ~0.1 × 0.1 × 0.5 mm$^3$ with the prism axis along the crystallographic [001] direction and natural crystal faces parallel to the common cleavage planes ([110] or [010]) were used in the Raman spectroscopic experiments. Pristine grains of similar size have been used for each temperature run.
Raman spectroscopy. The Raman spectra were collected with a Horiba Jobin-Yvon T64000 triple-monochromator spectrometer equipped with an Olympus BX41 microscope and a liquid-N$_2$-cooled charge-coupled-device detector, using the 514.522-
nm line of a Coherent Innova 90 C FreD Ar$^+$ laser. The spectrometer was calibrated to the Si Raman peak at 5205.1 cm$^{-1}$. The spectral resolution was ~1.9 cm$^{-1}$, whereas the instrumental precision in determining the peak positions was ~0.35 cm$^{-1}$. Prior and after the temperature runs, spectra were also collected with the 488-nm laser line, to verify the reproducibility of the peaks observed. In situ temperature-dependent experiments in N$_2$ atmosphere were performed with a LINKAM THMS-6000, whereas in air with a LINKAM TS1200 EV-1015. Detailed information about the temperature ramps is given in Supplementary Table 4. The as-measured spectra were baseline-corrected, temperature-reduced for the Bose-Einstein population factor, and fitted with pseudo-Voigt functions (see Supplementary Note 4).

DFT calculations. The electron band structure and DOS were calculated using the DFT based on the generalized gradient approximation of Perdew-Burke-Ernzerhof as implemented in the Vienna Ab-initio Simulation Package[20]. The electron and core interactions are included using the frozen-core projector augmented wave method, with the plane-wave cutoff energy chosen as 360 eV for model structures (see also Supplementary Note 5). The lattice constants and the atom coordinates are optimized until the convergence of the force on each atom is <0.01 eV/Å. The Monkhorst-Pack scheme is used to sample the Brillouin zone. The structures are optimized using the plane-wave pseudopotential calculations with the plane-wave cutoff energy chosen as 360 eV for model structures.

Data availability. The data sets generated during and/or analyzed during the current study are available.

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Author contributions
B.M., G.D.V., J.S., and R.O. planned and developed the original project. B.M. analyzed the Raman data. G.D.V. provided the samples and performed electron–microprobe analysis. N.W. collected the Raman data. W.X. performed the DFT calculations. J.S. helped with the spectroscopic analyses. FG helped with the sample characterization. A.M. helped with the DFT analysis. G.J.R. performed the Mössbauer analysis. M.B. collected the XRD data. R.O. interpreted the structure-refinement data. B.M. and G.D.V. wrote the manuscript. All authors reviewed the manuscript.

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