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# **The electrical conductivity of liebermannite: Implications for water transport into the Earth's lower mantle**

Geeth Manthilake<sup>1\*</sup>, Federica Schiavi<sup>1</sup>, Chengcheng Zhao<sup>1</sup>, Mainak Mookherjee<sup>2</sup>, Mohamed Ali Bouhifd<sup>1</sup>, Laurent Jouffret<sup>3</sup>

<sup>1</sup> Laboratoire Magmas et Volcans, CNRS, IRD, OPGC, Université Clermont Auvergne, 63000 Clermont-Ferrand, France

<sup>2</sup> Earth Materials Laboratory, Department of Earth, Ocean and Atmospheric Sciences, Florida State University, Tallahassee, FL, 32306, USA

<sup>3</sup> Laboratoire des Matériaux et du Génie Physique, UMR 5628, 3 parvis Louis Néel - CS50257 - 38016 Grenoble, France

**\*Corresponding author:** Geeth Manthilake ([geeth.manthilake@uca.fr](mailto:geeth.manthilake@uca.fr))

## **Key Points:**

- The hopping of K<sup>+</sup> ions in liebermannite results in high electrical conductivity of more than 1 S/m.
- Water can be present as both molecular H<sub>2</sub>O and hydroxyl (OH<sup>-</sup>) groups in liebermannite
- High H<sub>2</sub>O contents of ocean island basalts can be related to deeply subducted hydrous liebermannite

**Abstract**

Liebermannite ( $\text{KAlSi}_3\text{O}_8$ ) is a principal mineral phase expected to be thermodynamically stable in deeply subducted continental and oceanic crusts. The crystal structure of liebermannite exhibits tunnels that are formed between the assemblies of double chains of edge-sharing (Si, Al)  $\text{O}_6$  octahedral units, which act as a repository for large incompatible alkali ions. In this study, we investigate the electrical conductivity of liebermannite at 12, 15, and 24 GPa and temperature of 1500 K to track subduction pathways of continental sediments into the Earth's lower mantle. Further, we looked at whether liebermannite could sequester incompatible  $\text{H}_2\text{O}$  at deep mantle conditions. We observe that the superionic conductivity of liebermannite due to the thermally activated hopping of  $\text{K}^+$  ions results in high electrical conductivity of more than 1 S/m. Infrared spectral features of hydrous liebermannite indicate the presence of both molecular  $\text{H}_2\text{O}$  and hydroxyl ( $\text{OH}^-$ ) groups in its crystal structure. The observed high electrical conductivity in the mantle transition zone beneath Northeastern China and the lower mantle beneath the Philippine Sea can be attributed to the subduction pathways of continental sediments deep into the Earth's mantle. While major mineral phases in pyrolitic compositions are almost devoid of  $\text{H}_2\text{O}$  under lower mantle conditions, our study demonstrates that liebermannite could be an important host of  $\text{H}_2\text{O}$  in these conditions. We propose that the relatively high  $\text{H}_2\text{O}$  contents of ocean island basalts derived from deep mantle plumes are primarily related to deeply subducted continental sediments, in which liebermannite is the principal  $\text{H}_2\text{O}$  carrier.

**Plain Language Summary**

Liebermannite ( $\text{KAlSi}_3\text{O}_8$ , formally K-hollandite) is an important mineral phase in deeply subducted continental and oceanic crusts. Liebermannite exhibits high ionic conductivity and could explain low resistivity in the Earth's mantle transition zone and the upper part of the lower mantle, hinting towards the subduction of hydrated crusts into the lower mantle. The liebermannite samples synthesized at these conditions indicate the presence of both molecular  $\text{H}_2\text{O}$  and hydroxyl ( $\text{OH}^-$ ) groups in its crystal structure, suggesting that liebermannite could be an important host of  $\text{H}_2\text{O}$  in the Earth's deep mantle. Compared to the basalts from mid-ocean ridges that exhibit trace quantities of water, ocean island basalts show higher water contents. It has been speculated that ocean basalts are derived from crustal components that were deeply subducted. It is also known that the lower mantle is relatively dry. Therefore, it is difficult to reconcile the higher water contents in OIBs that are derived from the deep mantle. Here, we demonstrate that the source crustal components for OIBs were likely to be hydrated. Liebermannite is a key mineral in deeply subducted crusts and can efficiently host water.

## 1. Introduction

Trace quantities of H<sub>2</sub>O stored in the Earth's mantle significantly influence the physical properties of mantle rocks (Smyth & Jacobsen, 2006). Although H<sub>2</sub>O plays an important role by affecting both mineral properties and mantle dynamics of the upper mantle, it is well known that the Earth's lower mantle is relatively dry, as indicated by the low (< 1000 ppm wt.) H<sub>2</sub>O solubility in major lower mantle mineral phases (Bolfan-Casanova et al., 2003; Fu et al., 2019; Hirschmann, 2006). Yet some oceanic island basalts (OIB), which are characterized by relatively high H<sub>2</sub>O contents up to ~ 2.0 wt. %, are fed by plumes rising from the lower mantle (Deschamps et al., 2011). These plumes are thought to originate from enriched reservoirs composed of recycled crustal materials that subducted into the deep mantle (Willbold & Stracke, 2006). Hydrous phases associated with subducting slabs descending into the lower mantle (van der Hilst et al., 1997) may provide a plausible mechanism for transporting H<sub>2</sub>O into the deep mantle. Dense hydrous magnesium silicates (DHMS), such as phase H and phase D, which are known to be stable in the depleted portion of the subducting slab at lower mantle conditions, are likely to transport H<sub>2</sub>O into the lower mantle and subsequently hydrate the subducted crustal components (Nishi et al., 2014; Pamato et al., 2014).

While the dominant component of all OIB is likely to be recycled basaltic oceanic crust, both chemical and isotopic signatures of OIB indicate the mixing of different source materials (Hart, 1988). Particularly the Enriched Mantle II (EMII)-type OIB, which have been found in the Society Islands, the Marquesas and Samoa, suggest a 5-10 % of continental and sedimentary components (Hart, 1988). Water contents up to 1.5 wt. % and low H<sub>2</sub>O/Ce (<150) have been reported in such EMI-type OIB (Cabral et al., 2014). The estimates based on geochemical analyses indicate that H<sub>2</sub>O concentrations in EMI sources are about 400 ppm wt. (Dixon et al.,

2002). The low H<sub>2</sub>O/Ce measured in EM-type magmas indicates up to 92 % H<sub>2</sub>O loss from the recycled continental components with progressive dehydration (Dixon et al., 2002). Despite intense dehydration, the deeply subducted slab appears to retain or rehydrate by the dehydration of dense hydrous phases such that a sufficient amount of H<sub>2</sub>O is available in the deep OIB sources (Dixon et al., 2002).

Liebermannite, formerly known as Liebermannite, is the high-pressure polymorph of KAlSi<sub>3</sub>O<sub>8</sub>-feldspar and is likely to be stable in deeply subducted (> 300 km) continental crust and mid-oceanic ridge basalt compositions enriched in potassium (Schmidt, 1996). The crystal structure of liebermannite exhibits tunnels that are formed between the assemblies of double chains of edge-sharing (Si, Al)O<sub>6</sub> octahedral units. At pressures  $\leq$  20-23 GPa, liebermannite (*lowP*) crystallizes in a tetragonal (*I4/m*) space group symmetry, whereas above these pressures, the tunnels are slightly squeezed, and the high-pressure polymorph of liebermannite (*hiP*) crystallizes in a monoclinic (*I2/m*) space group symmetry (Ferroir et al., 2006; Nishiyama et al., 2005). These tunnels accommodate incompatible cations such as Na, K, Sr, Ba, La, and Pb. A naturally occurring liebermannite containing Ba<sup>2+</sup> and K<sup>+</sup> is reported to contain up to 5 wt. % H<sub>2</sub>O in its crystal structure (Miura, 1986), indicating that liebermannite could be an important host for H<sub>2</sub>O. The *hiP* polymorph is observed to be stable down to the Earth's lowermost mantle conditions (Kawai & Tsuchiya, 2013; Sueda et al., 2004). At mantle transition zone conditions, phase equilibria studies indicate that average continental crust is composed of a mixture of liebermannite (~32 vol. %), stishovite (24 vol.%), majoritic garnet (30 vol. %) and minor amounts of calcium aluminosilicate (CAS) phases (Irifune et al., 1994).

The presence of tunnels in the crystal structure of liebermannite facilitates the motion of K<sup>+</sup> ions along the channel, attaining superionic conduction at high temperatures (Furusawa et al.,

1988; Khanna et al., 1981; Yoshikado et al., 1982). More recently, the electrical conductivity of liebermannite, relevant for the deeply subducted crust, has been examined using molecular dynamics simulations. The predicted electrical conductivity for liebermannite with a 12.5 % vacancy in the tunnel is ~20 S/m at 10 GPa and 1600 K (He et al., 2016). The magnitude of the predicted electrical conductivity resulting from ionic conduction of  $K^+$  ions in the tunnels is significantly greater than that of the electrical conductivity due to extrinsic defects. Hence, owing to its high electrical conductivity, liebermannite potentially represents an ideal tracer mineral for tracking subducted pathways of continental crustal components into the Earth's lower mantle.

The unique crystal structure of liebermannite and the ability to accommodate large alkali ions and possibly  $H_2O$  in its tunnels highlight its importance as a possible  $H_2O$  repository in the subducted crustal components and a possible source for OIB. However, so far, studies on liebermannite have been restricted to the equation of state, elasticity (Caracas & Boffa Ballaran, 2010; Kawai & Tsuchiya, 2013; Mookherjee & Steinle-Neumann, 2009), and electrical conductivity (He et al., 2016) of the dry variety.

In this study, we first conducted high-pressure and temperature experiments to constrain the electrical conductivity of hydrous liebermannite at the upper mantle, transition zone, and lower mantle conditions, i.e., at pressures of 12, 15, and 24 GPa respectively. Then we examined the water incorporation mechanisms in liebermannite. Finally, we explore whether the high  $H_2O$  contents of OIB could have derived from hydrated crustal components of deeply subducted slabs penetrated down to the lower mantle.

## 2. Materials and Methods

The starting powder was prepared using high purity oxide mixtures of  $\text{K}_2\text{CO}_3$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{SiO}_2$ . The mixture was slowly heated to 1000 °C overnight in a platinum crucible for decarbonate  $\text{K}_2\text{CO}_3$ . The decarbonated powdered mixture was then heated to 1500 °C and kept 10 minutes to obtain homogeneous glass. The time was optimized to avoid possible K loss at high temperatures.

High pressure-high temperature experiments were conducted using a 1500-ton multi-anvil apparatus. The pre-synthesis of K-feldspar for electrical conductivity measurements were conducted at 2 GPa and 1200 K in a 14/8 assembly (Fig. 1a). To synthesize hydrous K-feldspar we add  $\text{Al}(\text{OH})_3$  to the glass mixture to obtain ~ 100 wt. ppm  $\text{H}_2\text{O}$ . The powdered mixture was packed into a capsule made of rhenium (Re), and kept at high-pressure and high-temperature for durations of 4 hours to obtain the cylindrical samples for electrical conductivity measurements. The water contents of K-feldspar is measured to be  $257 \pm 29$  wt. ppm.

The pressure and temperature conditions for the electrical conductivity measurements were carefully chosen based on the stability of liebermannite (Nishiyama et al., 2005) and represent the upper mantle (12 GPa), mantle transition zone (15 GPa), and the upper part of the lower mantle (24 GPa). Electrical conductivity measurements were performed using octahedral pressure medium composed of  $\text{MgO}$  and  $\text{Cr}_2\text{O}_3$  (5 wt. %) in a 14/8 assembly (octahedron edge length/anvil truncation edge length) at 12 GPa, in a 14/6 assembly at 15 GPa, and a 10/4 assembly at 24 GPa (Fig.1b).  $\text{MgO}$  ceramic sleeves insulated the electrode wires from the furnace. All ceramic assembly parts, including the pressure media, were baked at 1000 °C for more than 12 hours and then stored at 125 °C in high-vacuum furnaces ( $< 100$  mTorr) before assembling. This step reduces the exposure of assembly components to atmospheric moisture and other impurities. The sample temperature was measured using a type-C tungsten-rhenium (W95Re5-W74Re26)



thermocouple junction, placed at one end of the sample. One cable formed the thermocouple and a separate  $W_{95}Re_5$  cable placed at the opposite side of the sample connected to the impedance spectroscopy for the electrical conductivity measurements.

The electrical conductivity of liebermannite samples was determined using the impedance spectroscopy method using the Modulab MTS Impedance gain-phase analyzer. The frequency range for the analyses was  $10^6$ - $10^1$  Hz. After compressing the assembly to the desired pressure, samples were heated to 500 K and while maintaining a temperature of 500 K, the electrical resistance of the sample was measured regularly until the sample resistance reached a stable value. The decrease of electrical resistance observed at this step corresponds to the removal of the absorbed moisture in the sample capsule and the surrounding area, which could be incorporated into the sample at higher temperatures (Manthilake et al., 2015). During the measurements, sample resistance was determined in several heating and cooling cycles until the electrical resistance of heating and cooling paths become reproducible. For the discussion, we have used the data from the last cooling cycle, which minimizes the uncertainty in electrical conductivity. The sample resistance can be obtained by fitting the impedance spectra with an appropriate equivalent circuit. For polycrystalline samples, as we use in this study, the equivalent circuit can be illustrated by a combination of resistor-capacitor/constant phase element (R-C/CPE) components, connected in parallel, series, or a series-parallel combination. Once the electrical resistivity of the samples was determined from the fit of the impedance spectra, the electrical conductivity was determined using the radius and the axial length of the cylindrical sample measured after each experiment. The inherent assumption is that the sample geometry remained constant during the experiment.

The chemical compositions the experimental run products were investigated using a Cameca SxFiveTactis electron probe microanalyzer (EPMA) in wavelength dispersive (WDS)

mode operating at an accelerating voltage of 15 kV and 4 nA beam current. The low accelerating voltage was used to avoid the K loss in liebermannite.

Powder X-ray diffraction (PXRD) analyses of experimental run products were carried out to identify the crystal structures of liebermannite and the phases present in quenched samples at 15 and 24 GPa. The PXRD was obtained for  $\sim 1 \text{ mm}^3$  of crushed samples that were placed on zero-background Si sample holders. The PXRD was recorded using a Philipps X-Pert Pro diffractometer with  $\text{CuK}\alpha$  radiation source ( $\lambda = 0.15405 \text{ nm}$ ). The PXRD patterns were recorded over the  $10\text{--}90^\circ$  ( $2\theta$ ) range in steps of  $0.0167^\circ$  with a counting time of 700 s per step. Lattice parameters were obtained from LeBail fits using the FULLPROF program (Rodriguez-Carvajal, 1993). The background can be obtained by linear interpolation between twenty-six points, and the peak profiles were modeled using a pseudo-Voigt function.

Raman spectroscopy was used to identify liebermannite and the minor mineral phases present in the experimental run products. Raman spectra were collected in a back-scattered geometry using an InVia confocal Raman micro-spectrometer, equipped with a 532 nm diode laser, a Peltier-cooled CCD detector, a Rayleigh rejection edge filter (Schiavi et al., 2018). The laser power of 1-8 mW; the slit aperture of  $65 \mu\text{m}$ , and a grating of 2400 l/mm were used for the present analyses. These conditions result in lateral and axial spatial resolutions of  $\sim 1$  and  $3 \mu\text{m}$  and a spectral resolution of  $1 \text{ cm}^{-1}$ . Acquisition times were 30-60 s and 60-240 s for the low-wavenumber and high-wavenumber region, respectively.

The quantification of  $\text{H}_2\text{O}$  in liebermannite was performed using the Fourier Transform Infrared (FTIR) spectroscopy. Unpolarized FTIR spectra of liebermannite were acquired using a Vertex70 Bruker spectrometer equipped with a Globar light source, a KBr beamsplitter, and an MCT (Mercury-Cadmium-Tellurium alloy) detector. The beam size for the analyses was  $\sim 30 \mu\text{m}$ .

The spectra were obtained through a CaF<sub>2</sub> window with a resolution of 4 cm<sup>-1</sup>. About 2000 scans were accumulated for a single spectrum. Thin slabs were cut perpendicular to the compression axis of the experimental run products using a high-precision diamond wire saw and polished using diamond mats without acetone or bond materials, such as crystal-bond or orthodontic adhesive paste to avoid IR signal contaminations. Being the samples polycrystalline, it was not possible to perform polarized measurements on single crystals; therefore, we estimated the H<sub>2</sub>O content of each sample based on several spectra that were taken over many randomly oriented crystals. The spectra were integrated between 2600 and 3800 cm<sup>-1</sup>, an average of several spectra was calculated for each sample and multiplied by a factor 3. The OH content was quantified using the Beer-Lambert law:

$$C_{H_2O} = 18.02 \times A \times 10^6 / \varepsilon \times t \times \rho$$

where C<sub>H<sub>2</sub>O</sub> is the concentration of hydrous species expressed in ppm H<sub>2</sub>O by weight, 18.02 is the molecular weight of H<sub>2</sub>O; A is the total integrated area of bands in the region of interest, *t* is the thickness of the sample in cm,  $\varepsilon$  is the molar absorption coefficient, and  $\rho$  is the density of the sample in g/L. For the estimation of H<sub>2</sub>O content in liebermannite, we used the theoretically predicted integral molar absorption coefficient of 250000 L/(mol.cm<sup>2</sup>) (Koch-Müller & Rhede, 2010).

### 3. Results

The electrical conductivity of liebermannite samples at 12, 15, and 24 GPa are summarized in **Fig. 2**. The discontinuous increase in electrical conductivity at a temperature above 660 K during the first heating cycle of the 12 GPa experiment coincides with the transformation of K-Feldspar to liebermannite with increasing temperature (**Fig. 2a**). This transformation accounts for more than

one order of magnitude increase of conductivity for liebermannite. After the complete transformation, the electrical conductivity of liebermannite increases with increasing temperature from 700 K to 1500 K and reached to about 1 S/m at 12 GPa and 1500 K. The increase of pressure appears to have an inverse effect on the electrical conduction in liebermannite (**Fig. 2b**). The impedance spectra of the sample undergoing K-feldspar to liebermannite transition with increasing temperature are shown (**Fig. 3**).

The activation enthalpy ( $\Delta H$ ) of each conduction mechanism can be calculated by fitting the data to equation,  $\sigma = \sigma_0 \exp(-\Delta H/RT)$ , where  $\sigma$  is the electrical conductivity (S/m),  $T$  is the absolute temperature (K),  $\sigma_0$  is the pre-exponential factor (S/m), and  $R$  is the gas constant (J/K mol). Here, we analyzed the activation enthalpy, first by manually fitting different temperature segments to the fitting equation and, second, by fitting the equation to the entire temperature range (Fei et al., 2020). The estimated activation enthalpies for different conduction mechanisms obtained using two fitting methods are listed in **Table 1**.

The EPMA, SEM, and Raman grid-analyses indicate that liebermannite is the principal phase present in samples synthesized at 12, 15, and 24 GPa (**Fig. 4**). However, minor amounts of wadeite, kyanite, and stishovite presence in our samples, an observation consistent with a previous study (Urakawa et al., 1994) (**Table. 2**) (**Fig.5**). The grid analyses with a step size of 5  $\mu\text{m}$  also confirmed the absence of melt in our samples. The minor phases mostly occur as isolated grains within the liebermannite matrix (**Fig 5a**) and the volume fraction of minor phases appeared to decrease with increasing pressure. Chemical analyses of minor phases at the 24 GPa sample were hampered by either absence of minor phases (e.g kyanite) at high-pressure samples or if present, their extremely small grain sizes ( $< 5\mu\text{m}$ ).

The FTIR analyses of liebermannite samples after the electrical conductivity measurements indicate water contents of  $1044 \pm 87$  wt. ppm at 12 GPa,  $885 \pm 78$  wt. ppm at 15 GPa and  $1104 \pm 18$  wt. ppm at 24 GPa (**Fig 6**). The high water contents compared to the K-feldspar starting material suggest that the absorbed moisture in the assembly parts may have been incorporated into the sample during the K-feldspar-liebermannite transformation at high-temperature, yielding high water contents in the liebermannite samples (i.e. higher than the amount of water produced by the decomposition of  $\text{Al}(\text{OH})_3$ ). We were not able to produce water-free liebermannite samples even with dry pressure materials.

The infrared spectra provide information on water incorporation in liebermannite (**Fig. 6**). Several O-H vibrational modes are observed: (1) the stretching vibrations of weakly hydrogen bound hydroxyl units produce intense bands between  $3700$  and  $3500 \text{ cm}^{-1}$ ; these modes are more pronounced in the 12 GPa sample. (2) The stretching vibrations of both  $\text{H}_2\text{O}$  molecules and more strongly hydrogen bound hydroxyl units occur in the  $3425$ - $3100 \text{ cm}^{-1}$  wavenumber range; they become dominant in the 15 and 24 GPa samples (**Fig. 6a**). (3) The O-H stretching and bending vibrations of the hydronium ( $\text{H}_3\text{O}^+$ ) ion are observed near  $2900 \text{ cm}^{-1}$  and  $1665 \text{ cm}^{-1}$ ; these modes disappear at the highest pressure. In the absence of organic contaminants, such as acetone or bond materials, the coexistence of these two modes confirms the presence of  $\text{H}_3\text{O}^+$  in *lowP* liebermannite. (4) The H-O-H bending vibration of the water molecule slightly shifts from  $1610$  to  $1630 \text{ cm}^{-1}$  with increasing pressure (**Fig. 6b**). (5) The combination (stretching/bending) modes of both  $\text{H}_2\text{O}$  molecules (near  $5200 \text{ cm}^{-1}$ ) and hydroxyl units (near  $4500 \text{ cm}^{-1}$ ) display continuous shift to lower frequencies with increasing pressure (**Fig. 6c**). This shift is compatible with the increase of the strength of hydrogen bonds with pressure, as usually observed in minerals (Cynn & Hofmeister, 1994). The observed spectral features suggest the presence of  $\text{H}_2\text{O}$  and  $\text{H}_3\text{O}^+$

substituting for  $K^+$  in the tunnel (Bethell & Sheppard, 1953) and the substitution of hydrogen ( $H^+$ ) in octahedral sites where it forms O-H bonds with one of the six possible oxygen ions in the vacant octahedral site.

The powder X-ray diffraction analyses were conducted on the samples synthesized at 15 GPa and 24 GPa. Both patterns can be refined with parameters consistent with the  $I4/m$  phase:  $a = 9.3304(4)\text{\AA}$ ,  $c = 2.7223(2)\text{\AA}$ . Obtaining the same lattice parameters for the samples out of the different pressures of annealing experiments implies that the liebermannite phase is elastic enough to regain its low-pressure parameters consistent with previous studies (Nishiyama et al., 2005; Sueda et al., 2004).

## 4. Discussion and conclusions

### 4. 1 Electrical conduction in liebermannite

The electrical conductivity of K-feldspar before transforming into liebermannite exhibit higher electrical conductivity compared to the previous electrical conductivity measurements of F-feldspar reported at 1 GPa (Hu et al., 2013). The high electrical conductivity of K-feldspar observed in our study can be explained by the 0.02 wt. %  $H_2O$  contents in our samples, compared to the dry verity reported by Hu et al. 2013 study. Similar electrical behavior has been observed in dry albite and water-bearing albite (Hu et al., 2013; Ni et al., 2011).

The electrical conductivity of hydrous liebermannite increases discontinuously upon increasing temperature (**Fig. 2b**). At temperatures below 700 K, conductivity is likely to be dominated by molecular water that is loosely bound in the tunnel sites and the associated activation energy is less than 0.40 eV. In the temperature range between 700 K and 1100 K, the conductivity is likely largely due to extrinsic proton defects that are formed due to coupled substitutions of the

octahedral sites. The associated activation energy varies between 0.64 eV and 0.78 eV. At temperatures above 1200 K, the conductivity is likely to be dominated by fast motions of  $K^+$  or  $H^+$  ions (from  $H_3O^+$ ) ions in the channel. The associated activation energy is greater than 0.82 eV. Higher conductivity has also been observed in alkali bearing materials with the hollandite crystal structure (Khanna et al., 1981). Such higher conductivity is often referred to as super-ionic conductivity (He et al., 2016; Khanna et al., 1981). In our study, we are documenting such effects at extreme pressures of 12 to 24 GPa in liebermannite.

The electrical conductivity of minor phases, wadeite, stishovite, and kyanite should not interfere with the measured conductivity of liebermannite due to their low volume fractions (occur as isolated grains). Based on chemical analyses of individual liebermannite grains in our samples, we observe a maximum of 7 %  $K^+$  site vacancy in our liebermannite after electrical conductivity measurements at 12, 15, and 24 GPa. The intrinsic defects seem to dominate the conduction mechanism at high temperatures, whereas extrinsic defects may be responsible for the observed conductivity at lower temperatures.

## 4.2 Water incorporation in liebermannite

The occurrence of several OH stretching bands (Fig. 4a) suggests that different substitution mechanisms take place, including  $H^+$  substitution in octahedral sites and  $H_2O/H_3O^+$  in tunnels, resulting in distinct hydrogen bonding strengths. Protons attachment to both bridging and non-bridging oxygen can also help to explain such a wide range of OH stretching vibrations. Strong pleochroism in the 3500-3600  $cm^{-1}$  range of the polycrystalline sample at 12 GPa indicates the random orientation of the crystals, in contrast to higher pressure samples. Water/hydrogen could be incorporated in liebermannite structure in a variety of sites including the substitution of  $H^+$  in

the silicon octahedral sites, i.e.,  $\text{Si}_{\text{Si}}^{4+} = \text{Al}_{\text{Si}}^{3+} + \text{H}_{\text{Si}}^{1+}$  or  $\text{Si}_{\text{Si}}^{4+} = 4\text{H}_{\text{Si}}^{1+}$ , the substitution of  $\text{H}^+$  in the aluminum octahedral site  $\text{Al}_{\text{Al}}^{3+} = 3\text{H}_{\text{Al}}^{1+}$ , the substitution of  $\text{H}^+$  and  $\text{H}_3\text{O}^+$  in the potassium site ( $\text{K}_{\text{K}}^{1+} = \text{H}_{\text{K}}^{1+}$ , or  $\text{K}_{\text{K}}^{1+} = (\text{H}_3\text{O})_{\text{K}}^{1+}$ ) and accommodation of molecular  $\text{H}_2\text{O}$  in the tunnel as in  $\text{KAlSi}_3\text{O}_8 + \text{H}_2\text{O} = \text{KAlSi}_3\text{O}_8 \cdot \text{H}_2\text{O}$ . The chemical analyses provide crucial information on possible coupled substitution mechanisms for hydrogen incorporation in liebermannite. The slight deficiency in silicon and increase in aluminum observed in some liebermannite grains ( $\text{K}_{0.957 \pm 0.044} \text{Al}_{1.090 \pm 0.057} \text{Si}_{2.931 \pm 0.032} \text{O}_8$ ) is consistent with a reaction involving a substitution in the distorted octahedral with the direct replacement of  $\text{Si}^{4+}$  by  $\text{Al}^{3+}$  and  $\text{H}^+$  or by  $4\text{H}^+$ . The chemical analyses also indicate a slight aluminum deficiency in some crystals ( $\text{K}_{1.00} \text{Al}_{0.983} \text{Si}_{3.01} \text{O}_8$ ). This may suggest possible proton substitution in the octahedral site, replacing  $\text{Al}^{3+}$  with  $3\text{H}^+$ .

As the *hiP* liebermannite is considered the dominant polymorph throughout the Earth's lower mantle, knowledge on water solubility in the *hiP* structure becomes crucial to assess the transport of  $\text{H}_2\text{O}$  to the deepest lower mantle regions through deep extending slabs. Given the positive clapeyron slope of  $P$  (GPa) =  $16.6 + 0.007 K$  (T) between the *lowP* and *hiP* liebermannite and assuming that trace quantity of water is unlikely to affect the slope, the hydrous liebermannite sample synthesized at 24 GPa and 1500 K is expected to be the *lowP* polymorph with tetragonal symmetry (Nishiyama et al., 2005). However, upon a decrease of temperature to 1000 K, at constant pressure, the sample is likely to transform to *hiP* liebermannite with monoclinic symmetry (Nishiyama et al., 2005). Upon structural transformation from *lowP* to *hiP* liebermannite, the electrical resistivity measurements of the sample do not indicate a discontinuous decrease of the electrical resistance, which indicates the release of free fluid phase or hydrous melting in the sample (Freitas & Manthilake, 2019). Assuming that the water incorporation into the liebermannite structure occurs at the highest temperature, this crucial observation suggests that the *hiP*



liebermannite structure is capable of sequestering  $H^+$  into octahedral sites as molecular  $H_2O$  or ionic  $H_3O^+$  in its structure similar to the *lowP* liebermannite. The incorporation of  $H_2O$  has been observed in both naturally occurring tetragonal and monoclinic hollandite crystal structures with different stoichiometry (Miura, 1986), thus confirming our observations on liebermannite. The micro Raman grid-analyses of our samples after electrical conductivity measurements indicate the absence of melt phases, confirming that the water expulsion may not occur in our samples at high temperatures.

Due to the small grain sizes ( $< 5 \mu m$ ), infrared analyses in these minor phases were not possible; nevertheless, absence of peaks in the high-wavenumber region of the Raman spectra of wadeite and Al-free stishovite indicates that water is not present within their crystal structure (**Fig. 7**). However,  $H_2O$  contents up to 3 wt. % have been observed in stishovite containing aluminum (Litasov et al., 2007; Yoshino et al., 2014). IR spectral features of Al-free stishovite exhibit some similarities with those of liebermannite in the spectral range from 3111 to 3261 (Litasov et al., 2007). Particularly peak position of  $3117 \text{ cm}^{-1}$  in the sample synthesized at 15 GPa (**Fig. 7a**) overlaps the main peak position of stishovite at  $3117 \text{ cm}^{-1}$  observed for Al-free and Al-bearing stishovite (Yoshino et al., 2014). In order to confirm that the spectral feature at  $3117 \text{ cm}^{-1}$  in liebermannite, we have analyzed the O-H region of the Raman spectra of stishovite in the 15 GPa sample. The observed water-free conditions (**Fig 7a**) strongly suggests the spectral feature at  $3117 \text{ cm}^{-1}$  observed in liebermannite could be unrelated to stishovite, rather a spectral feature characteristic of liebermannite. We conclude that the similarities between liebermannite and stishovite may be related to similar substitution mechanisms of hydrogen in octahedral sites  $SiO_6$  or  $AlO_6$ . The preferential partitioning of water into the liebermannite phase over stishovite observed in our samples may be partly due to the low Al content in stishovite that is in equilibrium with

liebermannite (**Table 2**). Therefore, the presence of Al-free stishovite in the studied samples should not influence the IR spectra of liebermannite. Even in the case of very low water contents of about 16-30 wt. ppm observed in Al-free stishovite (Litasov et al., 2007), these should not affect water quantification of liebermannite in this study.

### **4.3 Geophysical implications**

The upper mantle underneath the Philippine Sea (Tarits & Mandéa, 2010) and Northeastern China (Kelbert et al., 2009) is characterized by unusual electrical and seismic wave velocity structures, in particular, electrical conductivities as high as 1 S/m and high-velocity anomalies of up to  $+\delta V_P$  1.5 % and  $\delta V_S$  2.0 % have been observed in these regions. The observed anomalies cannot be readily explained by normal mantle consisting of major mantle phases such as olivine and wadsleyite (Manthilake et al., 2009). If the observed positive velocity anomalies were assumed to be caused by temperature variations alone, the temperature in the uppermost region of the mantle transition zone estimated to be about 800 K below the normal mantle geotherm (Manthilake et al., 2009). The corresponding electrical conductivity of hydrous olivine and wadsleyite for such low temperatures would be significantly lower; as a consequence, the proton conduction in olivine and wadsleyite cannot be responsible for the electrical conductivity observed at the upper mantle and in the mantle transition zone (Manthilake et al., 2009). Similarly, the presence of melt cannot explain the observed anomalies, because even a minor fraction of melt would significantly decrease both the primary ( $V_P$ ) and secondary ( $V_S$ ) wave velocities (Chantel et al., 2016; Freitas et al., 2017; Weidner et al., 2018).

Due to superionic conduction properties and high modal abundance (> 30 vol. %) of liebermannite in deeply subducted crustal components, the electrical conduction in slabs is likely

to dominate by the liebermannite. This would make such slab components highly conductive compared to slabs consisting of mafic and ultramafic lithologies (Huang et al., 2005; Yoshino et al., 2008, 2008, 2014). However, the presence of liebermannite alone cannot account for the positive velocity anomaly observed in the upper mantle beneath the Philippine Sea (Tarits & Mandéa, 2010) and northeastern China (Kelbert et al., 2009) because the elastic wave velocities measured in liebermannite are comparable with those of common mantle mineral phases (Caracas & Boffa Ballaran, 2010; Mookherjee & Steinle-Neumann, 2009). Instead, the seismic wave velocities of Al-poor stishovite, another principal mineral phase stable in subducting continental sediments, are notably faster than those of mantle mineral phases (Gréaux et al., 2016). The stishovite co-existing with liebermannite in our samples is noticeably devoid of aluminum (**Table 2**). Here we propose that Al-poor stishovite coexisting with liebermannite in the subducted continental sediments may be responsible for the positive velocity anomaly observed at the mantle transition zone beneath the Philippine Sea (Tarits & Mandéa, 2010) and northeastern China (Kelbert et al., 2009).

Continental crustal portion of the subducted slab, consisting of liebermannite, majoritic garnet, and stishovite, are expected to have a higher  $0.2 \text{ g cm}^{-3}$  density than the ambient mantle, but this density relation is overturned at the 660 km discontinuity (Irifune et al., 1994; Nishiyama et al., 2005). This implies that subducting crustal components of the slabs may penetrate into the mantle transition zone, but are prevented from entering the lower mantle (Nishiyama et al., 2005), such as those observed in the Northeastern China subduction system (Ichiki et al., 2006). However, the lower mantle origin of some of the plumes (French & Romanowicz, 2015; Hart et al., 1992) carrying the EM-type components in OIB magmas (Hart et al., 1992) provides strong evidence supporting the presence of recycled continental materials in the lower mantle. We propose that

421 mixing of continental with oceanic sediments may increase the density of sedimentary components  
422 facilitating the sinking of slabs towards the core-mantle boundary. The high electrical conductivity  
423 observed at a 1200 km depths in the Earth's lower mantle beneath the Philippine sea subduction  
424 system (Kelbert et al., 2009; Tarits & Mandéa, 2010) may be linked to such continuous subduction  
425 of continental sediments across the mantle transition zone into the Earth's lower mantle (**Fig. 7**).

426 Owing to hotter temperatures relative to the ambient mantle, the rising plume is unlikely  
427 to exchange incompatible elements, including water, with the surrounding mantle, including the  
428 hydrated MTZ and the upper mantle (Bercovici & Karato, 2003). Thus, it is likely that the H<sub>2</sub>O  
429 present in plume-derived rocks is primarily linked to the deep lower mantle source. The relatively  
430 high H<sub>2</sub>O contents of OIB derived from deep mantle plumes hint towards the presence of hydrated  
431 crustal components present in the deeper part of the lower mantle (**Fig. 8**). While major mineral  
432 phases in pyrolitic compositions are almost devoid of H<sub>2</sub>O under lower mantle conditions, our  
433 study demonstrates that liebermannite could be an important host of H<sub>2</sub>O in the Earth's lower  
434 mantle. In this scenario, H<sub>2</sub>O in the EMII-source OIB is primarily related to deeply subducted  
435 continental materials, in which liebermannite is the principal H<sub>2</sub>O carrier. On the other hand, the  
436 subducted continental materials that may reach the core-mantle boundary would hydrate the HIMU  
437 type plume sources together with a possible contribution from *dense hydrous magnesium silicates*  
438 (DHMS) (Nishi et al., 2014; Pamato et al., 2014) and primordial H<sub>2</sub>O (Dixon et al., 2002).

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([https://figshare.com/articles/Water\\_content\\_calculations/12179067](https://figshare.com/articles/Water_content_calculations/12179067))

and ([https://figshare.com/articles/Experimental\\_data\\_xlsx/12179046](https://figshare.com/articles/Experimental_data_xlsx/12179046)).

The authors declare no competing financial interests.

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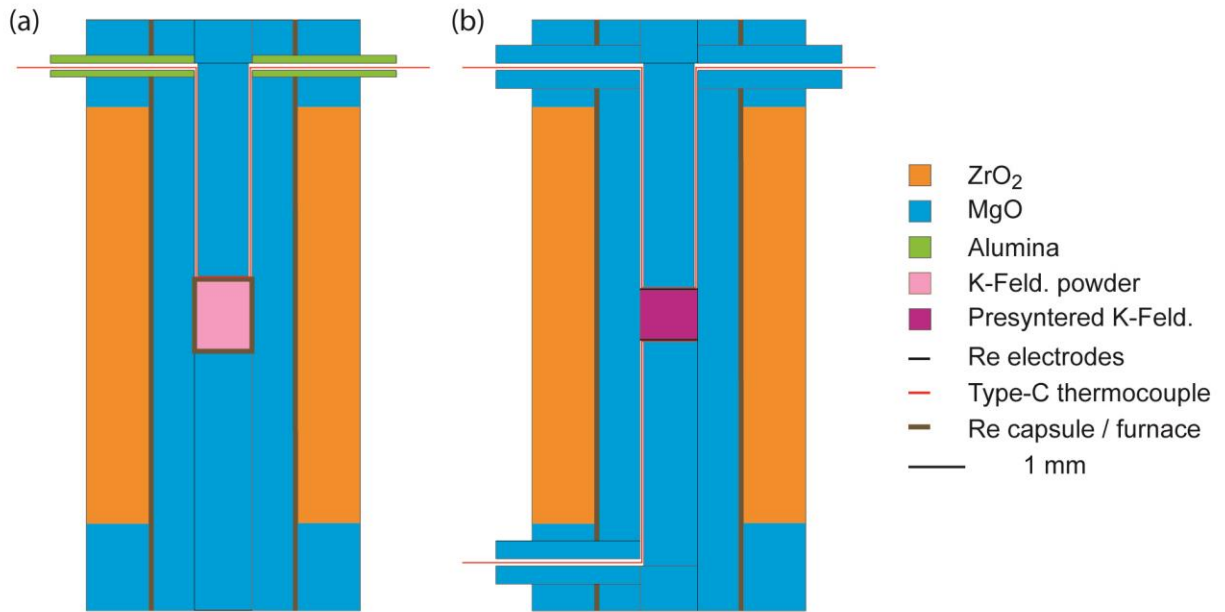
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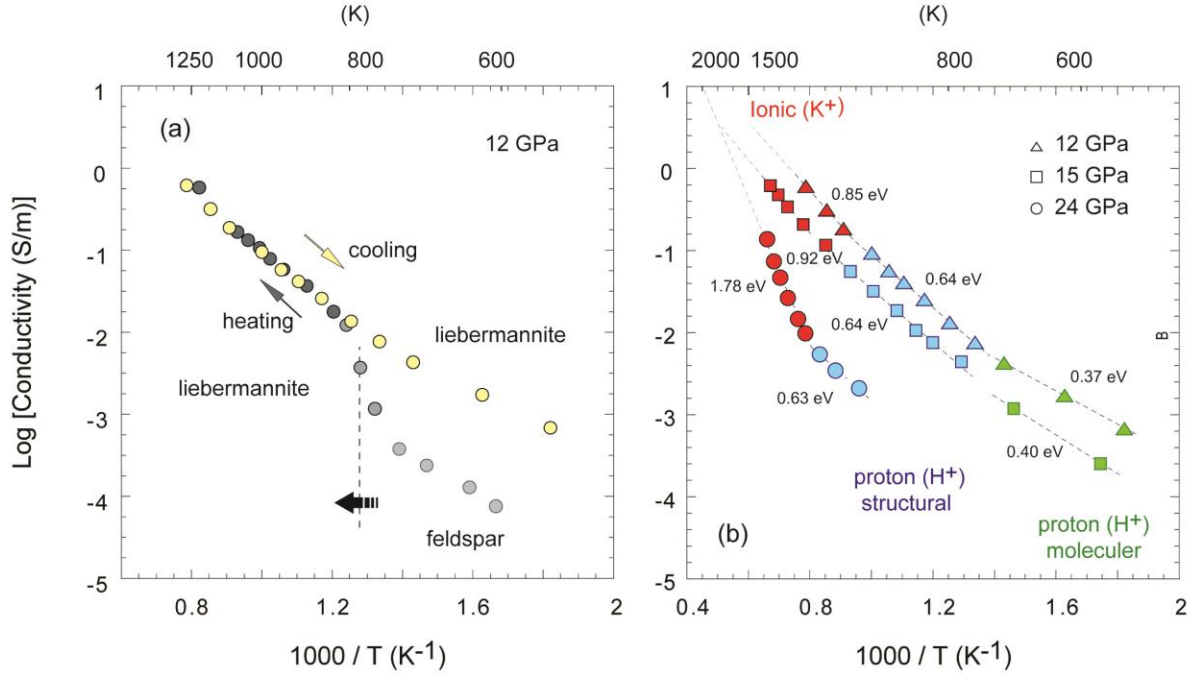
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## Figures

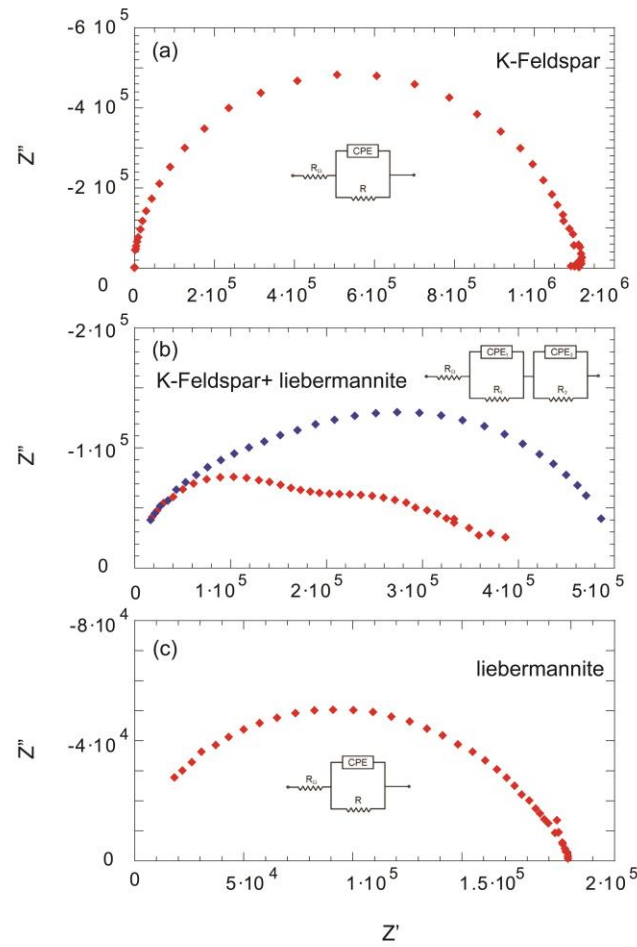


**Fig.1. A schematic cross-section of the assembly. (a) Used for the synthesis of K-feldspar. (b) For electrical conductivity measurements at high-pressure and high-temperature.** The three-electrode configuration for electrical conductivity, which designed to avoid electrode leads sharing the same tungsten carbide anvil in the KAWAI-cell, is expected to improve the insulation resistance of the assembly.



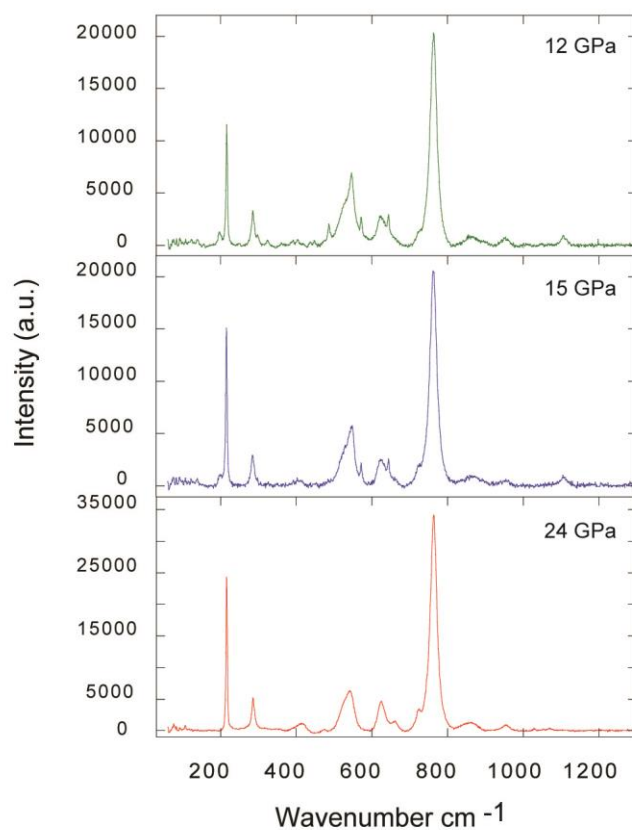
**Fig. 2. The electrical conductivity of liebermannite as a function of inverse temperature. (a)**

A plot of the logarithm of electrical conductivity as a function of inverse temperature. The transformation of K-feldspar to liebermannite occurred above 600 K resulting in more than one order of magnitude increase of conductivity. (b) Liebermannite at pressures 12, 15, and 24 GPa. Different conduction mechanisms are labeled in different colors. The activation enthalpies are shown next to individual fitting lines. The error bars associated with the electrical conductivity data measurements are less than the symbol size at high temperatures.

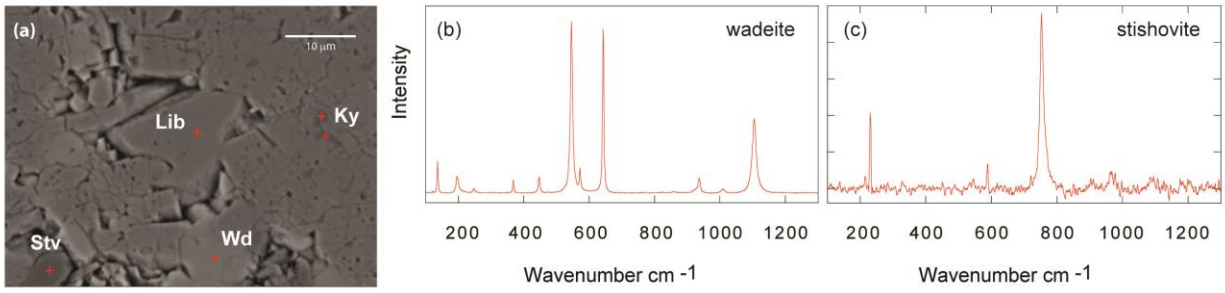


**Fig. 3.** Impedance spectra of the sample at different stages of heating at 12 GPa. (a) at 500 K electrical conductivity of K-feldspar before transforming into liebermannite, (b) at 718 K and 750 K, on the onset of the phase transformation, the second arc in the spectra develops. These additional arcs correspond to the formation of liebermannite. (c) At 850 K, after the complete transformation into liebermannite, there is a significant increase in the sample resistance. The sample resistance is due to the single conductive liebermannite phase. The corresponding equivalent circuit.

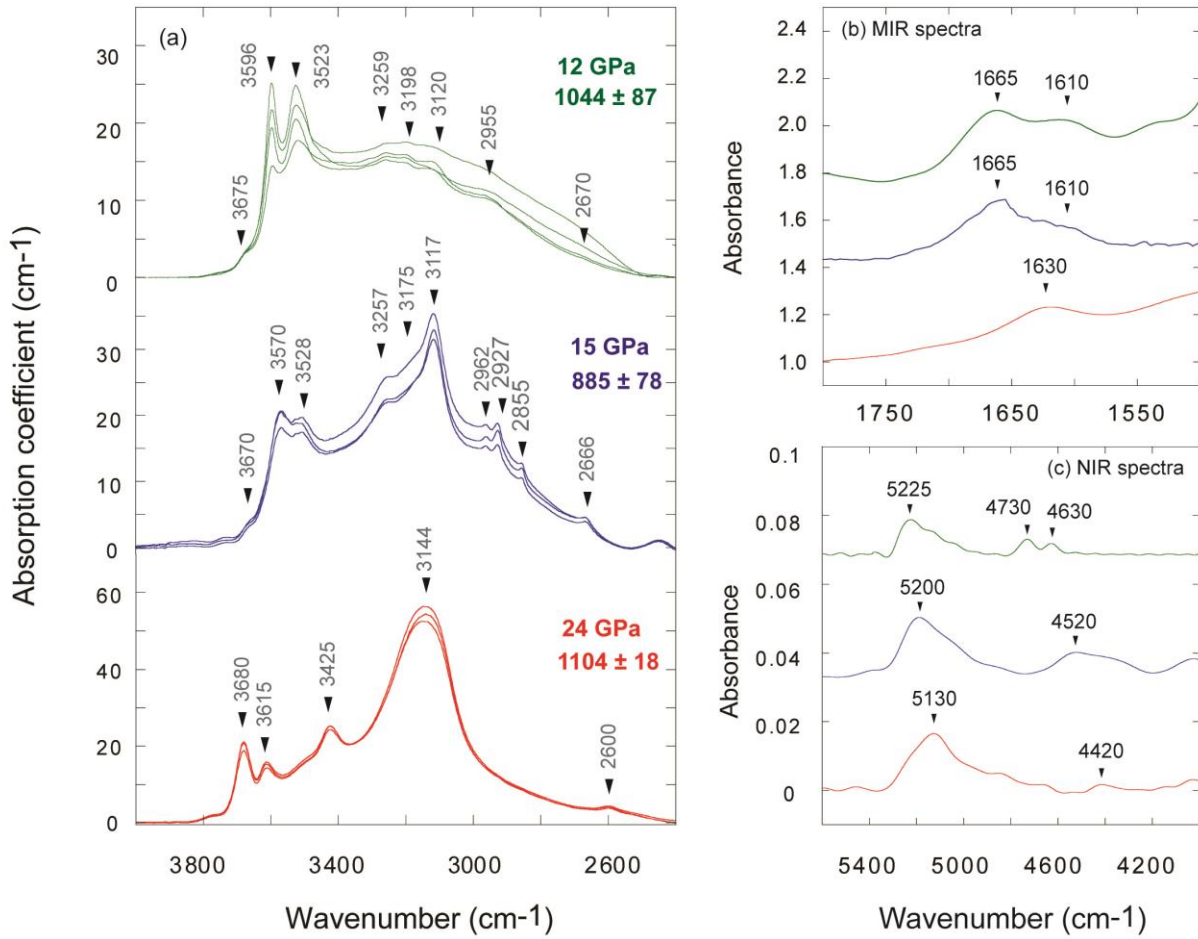




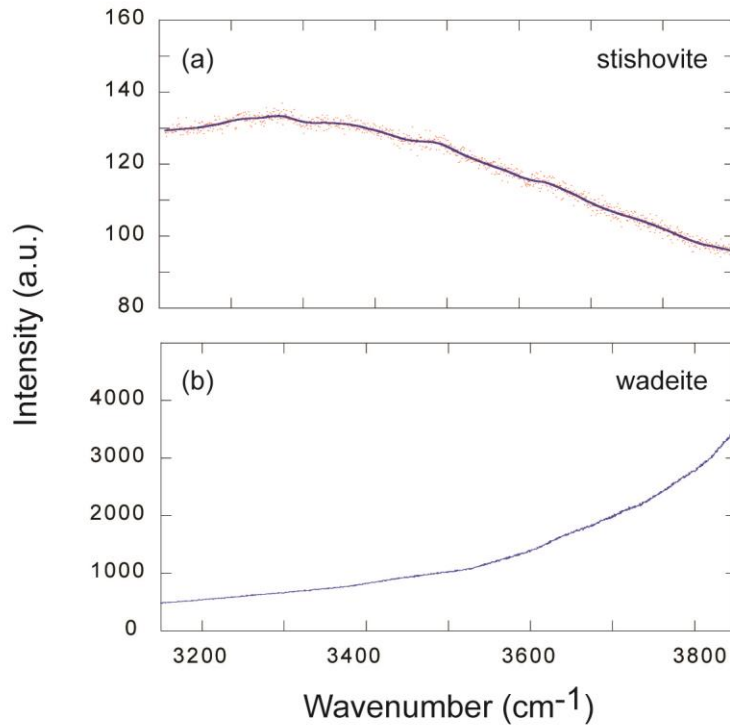
**Fig. 4.** Raman spectra of liebermannite at 12, 15, and 24 GPa.



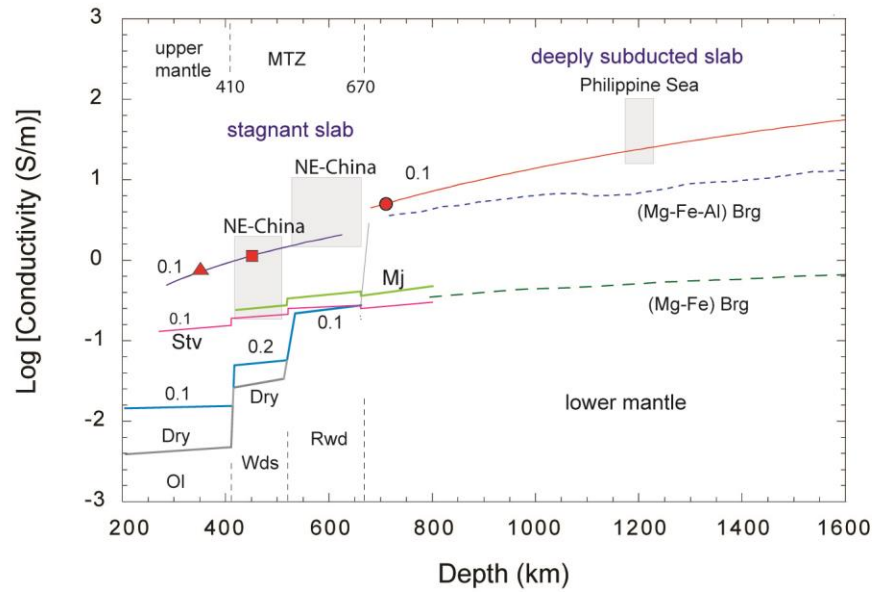
**Fig. 5. Mineral assemblages of the recovered sample.** (a) A back-scattered electron image showing the mineral assemblage at 15 GPa. (b, c) Low-wavenumber bands corresponding to vibrations of the alumino-silicate network; (b) wadeite, (c) stishovite.



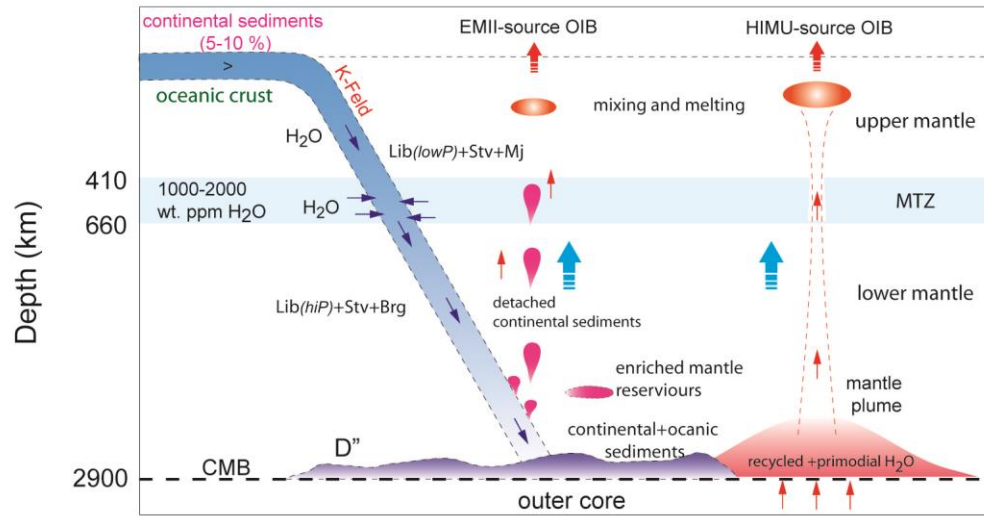
**Fig. 6. FTIR spectra of liebermannite.** (a) Near IR spectra of samples synthesized at 12 (green lines), 15 (blue lines), and 24 (red lines) GPa. The calculated H<sub>2</sub>O contents (ppm wt.) are indicated next to spectra. (b) Middle IR spectra of the three samples showing bending modes of H<sub>2</sub>O molecules and H<sub>3</sub>O<sup>+</sup> ions. (c) High-wavenumber IR region displaying bands at ~5200 (stretching vibrations of H<sub>2</sub>O) and 4500-4700 cm<sup>-1</sup> (O-H stretching vibrations). The peak at 4170 cm<sup>-1</sup> could be related to H-H vibrations.



**Fig. 7. Raman spectra of minor phases observed at the sample synthesized at 15 GPa.** The background uncorrected Raman spectra in the O-H region of stishovite (a) and wadeite (b), co-existing with liebermannite. The background noise of the Raman spectrum of stishovite was smoothed using the loess regression method shown in the blue line. Both indicate water absent conditions in their crystal structure. Raman analyses of kyanite were not possible due to their small grain sizes.



**Fig. 8. Comparison of electrical conductivities of liebermannite with global and regional electrical conductivity profiles.** The blue and red lines correspond to the extrapolation of electrical conductivity along the relevant subduction geotherms (Syracuse et al., 2010), and along the adiabatic geotherm in the lower mantle (Katsura et al., 2010), respectively. The red shaded triangle, square, and the circle indicate the electrical conductivity of liebermannite at 12, 15, and 24 GPa, respectively. The gray shaded boxes indicate the conductivity profiles of NE-China (Kelbert et al., 2009) and the Philippine Sea (Tarits & Mandéa, 2010). The electrical conductivity profiles of dry (black lines) and wet (blue lines) olivine, wadsleyite, ringwoodite (Yoshino et al., 2008), stishovite with 0.1 wt% of H<sub>2</sub>O (Yoshino et al., 2014) (pink lines) and majorite garnet (Yoshino et al., 2008) (light green lines) are shown for comparison. The electrical conductivity of (Mg, Fe) bridgmanite (Katsura et al., 1998) (green dashed line) and (Mg, Fe, Al) bridgmanite (Ohta et al., 2010; Sinmyo et al., 2014; Yoshino et al., 2016) (blue dashed line), extrapolated along the adiabatic geotherm in the lower mantle (Katsura et al., 2010), are shown for comparison. The numbers next to conductivity lines are the water contents in wt. %.



**Fig. 9. The potential mechanism explaining the elevated H<sub>2</sub>O content in ocean island basalts.**

K-feldspar in subducting continental sediments transforms to libermannite above 8 GPa and continues to be stable down to the core-mantle boundary conditions. Most of the H<sub>2</sub>O carried to the lower mantle by deep penetrating slabs may have been incorporated into the slab at the surface. However, due to the imbalance of the mass of H<sub>2</sub>O transported to the Mantle Transition Zone (MTZ) via subduction (Hacker, 2008) and the estimated mass of H<sub>2</sub>O stored in MTZ based on H<sub>2</sub>O contents of constituent phases (Freitas & Manthilake, 2019), extraction of H<sub>2</sub>O from MTZ to the lower mantle can be expected. Because of the ability of libermannite to accommodate several wt. % of the water in its structure (both in lattice defects and the tunnel structures), we argue that libermannite could be a possible carrier of water from the MTZ to the lower mantle. In this two-step, H<sub>2</sub>O conveyor process, the extraction of H<sub>2</sub>O by rehydration of deep penetrating slabs at the MTZ would be a likely scenario. Depending on gravitational stability, the subducting continental sediment component may detach from deep-extending slabs, rise through the mantle forming EMII-source OIB, in which libermannite is the principal water carrier. Some continental sediments may reach the CMB and provide H<sub>2</sub>O for HIMU-source lower mantle-derived plumes. (Lib: libermannite, Sa: K-feldspar, Mj: majorite garnet, Brg: bridgmanite, Stv; stishovite).

## List of tables

**Table 1.** The reference pre-exponential factor  $\text{Log } \sigma_0$  and the activation enthalpy in eV for liebermannite at 12, 15, and 24 GPa and their respective water contents.

Pressure (GPa)	Temperature (K)	$\text{Log } \sigma_0^*$ (S/m)	$\text{Log } \sigma_0^{**}$ (S/m)	$\Delta H^*$ (eV)	$\Delta H^{**}$ (eV)	H <sub>2</sub> O contents ppm wt.
12	550 - 750	0.57	n.a	0.37	n.a.	1044 ± 87
	750 - 1100	2.19	2.32	0.64	0.78	
	>1100	3.14	3.88	0.85	0.82	
15	573 - 683	0.58	n.a	0.4	n.a.	885 ± 78
	773 - 1173	1.76	1.61	0.64	0.76	
	> 1173	2.78	3.96	0.92	0.83	
24	1040 - 1200	0.38	0.24	0.63	0.76	1104 ± 18
	> 1270	5	8.26	1.78	0.89	

\* parameters from individual fitting

\*\* parameters from single fit

n.a: not nalyzed

**Table 2.** Chemical composition of the constituent mineral phases.

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**Table 2.** Chemical composition of the constituent mineral phases.

	Liebermannite			Wadeite		Stishovite		Kyanite	
	12 GPa	15 GPa	24 GPa	12 GPa	15 GPa	12 GPa	15 GPa	12 GPa	15 GPa
<b>SiO<sub>2</sub></b>	64.44 (0.7)	63.91 (2.5)	66.70 (0.2)	73.00 (0.9)	71.82 (0.5)	100.50 (0.8)	101.13 (0.5)	38.23 (0.9)	39.11 (0.9)
<b>K<sub>2</sub>O</b>	16.47 (0.4)	16.18 (1.2)	16.42 (1.8)	27.16 (0.8)	28.22 (0.6)	0.06 (0.3)	0.13 (0.07)	0.15 (0.06)	0.61 (0.4)
<b>Al<sub>2</sub>O<sub>3</sub></b>	18.98 (0.3)	20.4 (2.9)	17.21 (2.0)	0.15 (0.1)	0.6 (0.5)	0.05 (0.2)	0.07 (0.03)	62.6 (1.2)	61.35 (1.2)
<b>Total</b>	<b>99.89</b>	<b>100.49</b>	<b>100.33</b>	<b>100.31</b>	<b>100.64</b>	<b>100.62</b>	<b>101.33</b>	<b>100.98</b>	<b>101.07</b>

The standard deviation indicated in parenthesis.

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