

## Electrical conductivity measurement of serpentine at high temperature and pressure

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**Abstract** The electrical conductivity of serpentine is measured at 1.0—3.0 GPa and 300—870°C. The effect of frequencies on electrical conductivity measurement is analyzed. The conduction mechanisms of serpentine before and after dehydration are discussed. Our experimental results show that the electrical conductivity of serpentine increases significantly after dehydration of serpentine, through which highly conductive layers (HCL) can be formed in the Earth's interior.

**Keywords:** high temperature and pressure, serpentine, electrical conductivity, dehydration.

LARGE amount of conduction information about the materials in the Earth's interior can be obtained from laboratory measurements of electrical conductivity at conditions relevant to the deep Earth. This information can provide not only important proof for explaining the magnetotelluric field data but also the important data for reconstructing temperature profile of the Earth. In addition, electrical conductivity measurements can also provide some evidence of phase transformation, formation and distribution of fluid and melt, and oxidation state in the Earth's interior<sup>[1]</sup>. There exist a series of highly conductive layers (HCL) in the Earth. Pursuit of the genesis mechanism of HCL is one of important aspects to refine the deep structure and compositions of the Earth by combining electrical conductivity measurements in laboratory with geochemical and geophysical observations. Serpentine is one of important hydrous minerals by volume in subduction zone, which has been studied in many aspects<sup>[2-4]</sup>. However, the electrical conductivity at high temperature and pressure is still unknown because of difficulties in laboratory measurements. Previous electrical conductivity measurements for serpentine were limited at relatively low pressure and temperature, and at single frequency<sup>[5, 6]</sup>. In this experiment, the electrical conductivity measurements for serpentine were performed at 1.0—3.0 GPa, 310—870°C, and in a frequency range of 12—10<sup>5</sup> Hz.

### 1 Sample preparation and experimental method

All samples were collected in the Ailaoshan orogenic belt, Yunnan Province. The main chemical compositions of the samples are: SiO<sub>2</sub> (33.06—41.30), Al<sub>2</sub>O<sub>3</sub> (0.44—0.86), Fe<sub>2</sub>O<sub>3</sub> (4.28—9.25), FeO (1.20—5.13), MgO (31.47—37.82), CaO (0.21—3.83), Na<sub>2</sub>O (0.01—0.08), K<sub>2</sub>O (0.01—0.12), H<sub>2</sub>O<sup>+</sup> (11.36—13.07). All the experimental samples were ground into discs with 8 mm in diameter, 2.7—3.34 mm in thickness, then cleaned in acetone and finally baked at 80—100°C for at least 6 h to eliminate absorbed water.

All the experiments were carried out in YJ-3000 Ton type press apparatus in Institute of Geochemistry, the Chinese Academy of Sciences. The details of the apparatus were described elsewhere<sup>[7]</sup>. The experimental setup is shown in fig. 1. Pyrophyllite cube (32 mm × 32 mm × 32 mm) used as pressure medium and pyrophyllite tube used as insulator medium were baked at 500 and 850°C respectively to eliminate absorbed and chemically bound water. Pyrophyllite tube is 32 mm long, 13.5 mm in outer diameter, and 8 mm in inner diameter. The electrode is copper column with 5 mm in diameter. The lead is copper wire. Pressure error is ± 0.01 GPa. Temperature is monitored by PtRh10-Pt thermocouple with an error of ± 5°C. The sensing junction of thermocouple is placed near the sample. The section area of

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the sample discs is bigger than that of the electrodes in order that surface electrical conductivity can be reduced. A two-layered stainless steel foil used as heating element is connected to the ground to shield surrounding electrical noise. Pressure is increased to a desired value at first, then temperature is increased at a rate of 15°C/min. A temperature remains constant long enough (15–30 min) at every measurement point to assure an equilibrium state before starting measurement. This state is assumed to reach when the relative error of the measured modulus  $|Z|$  is less than 5% within 5 min intervals, then modulus  $|Z|$  and phase angle  $\theta$  are recorded simultaneously at 45 different frequencies in a range of 12–10<sup>5</sup> Hz with a ZL5 type LCR meter. The real ( $Z_r$ ) and imaginary ( $Z_i$ ) parts are determined by  $Z_r = |Z| \cos\theta$  and  $Z_i = |Z| \sin\theta$ , respectively.

## 2 Experimental results

Previous experiments showed that the electrical conductivity measurement was strongly dependent on frequency<sup>[8–10]</sup>. This phenomenon is caused by polarization and dielectric loss in the sample system and surroundings, and can be identified efficiently with impedance spectroscopy<sup>[10]</sup>. 1–3 semicircular arcs, according to the equivalent circuit principle of impedance spectroscopy<sup>[11]</sup>, can be presented in the Zr-Zi plane in a wide range of frequencies. The arcs stand for grain interior at high frequencies (left) side, grain boundary at middle frequencies (middle), and sample-electrode at low frequencies (right) processes, respectively. The bulk electrical conductivity of the samples is controlled dominantly by grain interior conduction. Our experimental results show that  $|Z|$  and  $\theta$  are pronouncedly dependent on frequencies, and that there are one semicircular arcs at 1.0 GPa, and 2–3 at 2.0–3.0 GPa in the Zr-Zi plane. Fig. 2 shows the dependence of  $\theta$  on frequencies and fig. 3 is a typical impedance spectroscopy at 2.0 GPa. The dependence of phase angles on frequencies is much evident before dehydration of serpentine, however, this dependence becomes weak, even disappears at high temperature, particularly after dehydration of serpentine (fig. 2). The minima of the imaginary parts shift toward left with increasing temperature (fig. 3). The bulk electrical conductivity  $\sigma$  of samples is determined at a given temperature by

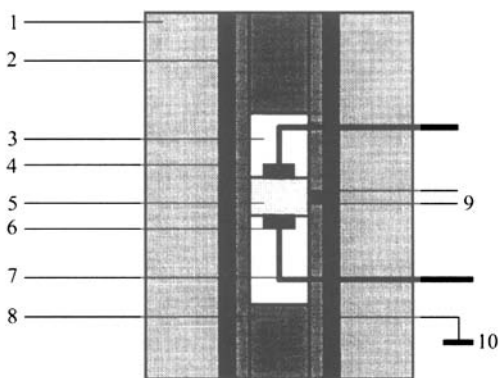


Fig. 1. The experimental setup. 1, Pressure medium; 2, heating element; 3, boron nitride (BN) powder; 4, pyrophyllite insulator medium baked up to 850°C; 5, sample; 6, electrode; 7, lead; 8, pyrophyllite spacer baked up to 850°C; 9, thermocouple; 10, to the ground.

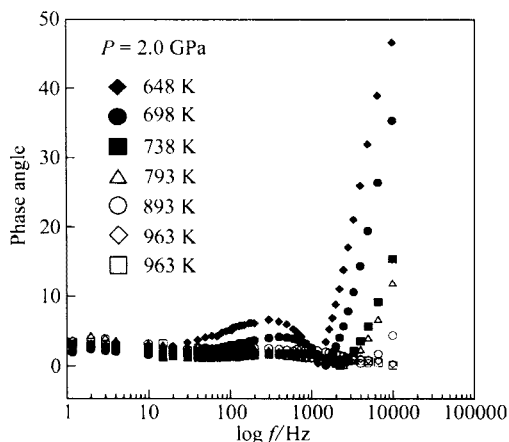


Fig. 2. The relationship between phase and frequencies for serpentine at 2.0 GPa and 648–963 K (two measurements at 963 K, interval is about 1 h).

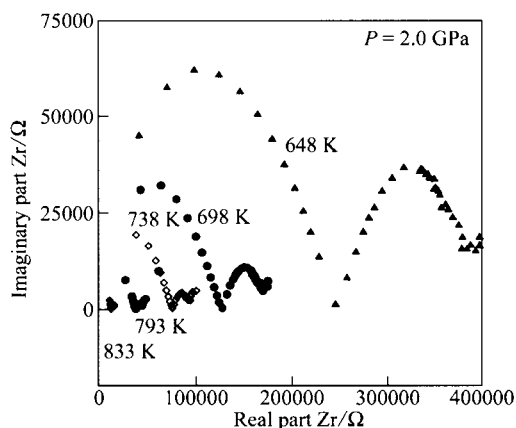


Fig. 3. The Zr-Zi impedance spectroscopy for serpentine at 2.0 GPa and 648–833 K.

$$\sigma = (d/s)(\cos\theta/|Z|), \tag{1}$$

where  $d/s$  is geometrical factor,  $d$  thickness of the samples, and  $s$  section area of the electrodes.  $|Z|$  and  $\theta$  in eq. (1) are chosen at a frequency where the phase angle, and therefore the magnitude of the imaginary part is near 0 because the capacitance is minimized at this frequency. Recovered assemblies show that geometrical distortions of samples and electrodes are small before dehydration of serpentine, and introduce errors of less than 10%. This small error can introduce conductivities errors of about 0.1 natural logarithm units, and therefore are negligible<sup>[9]</sup>. The geometrical distortions of sample assemblies after sample dehydration are bigger than 15%, and geometrical factors are determined after experiments. The bulk conductivities are fit to the Arrhenius equation:

$$\sigma = \sigma_0 \exp[-\Delta E/(kT)], \tag{2}$$

where  $\sigma_0$  is a preexponential factor,  $T$  absolute temperature,  $k$  the Boltzmann constant, and  $\Delta E$  activation energy. Conductivities are fit to eq. (2) before and after dehydration of serpentine because of different conduction mechanisms. Fig. 4 shows the changes in the electrical conductivity of serpentine with increasing temperature. The fit parameters are shown in table 1. At the low temperature region, the electrical conductivity of serpentine at 1.0 GPa is smaller than that at 2.0 and 3.0 GPa at a given temperature (fig. 4). This is because a little amount of fluid in partially interconnected pores plays a significant role in the bulk conduction below 1.0 GPa<sup>[6]</sup>. Above this pressure, partially interconnected pores are almost closed and porous fluid become tiny isolated pockets<sup>[12, 13]</sup>, and therefore plays a relatively small role in the bulk conduction. Consequently, the electrical conductivity is lower above 1.0

GPa than below 1.0 GPa at a given temperature. Small  $\Delta E$  at all experimental pressures before dehydration of serpentine infers that extrinsic electrons are dominant conduction species (table 1). Above 2.0 GPa, the electrical conductivity increases with increasing pressures at a given temperature before dehydration of serpentine (fig. 4). Theoretically, the decrease of lattice constants with increasing pressures is profitable for electron conduction (but not for ion), consequently,  $\Delta E$  decreases and electrical conductivity increases. Our experimental results are in agreement with theoretical analysis above. After dehydration, the effect of pressure on the bulk electrical conductivity of serpentine is negligibly small (fig. 4); and  $\Delta E$  increases with increasing pressures, which hints extrinsic ions as dominant conduction species. Based on the analysis above, the conduction mechanisms, and thereby  $\Delta E$  is different before and after dehydration. Therefore, the electrical conductivity is fit to  $1/T$  separately by eq. (2) in figure 4.

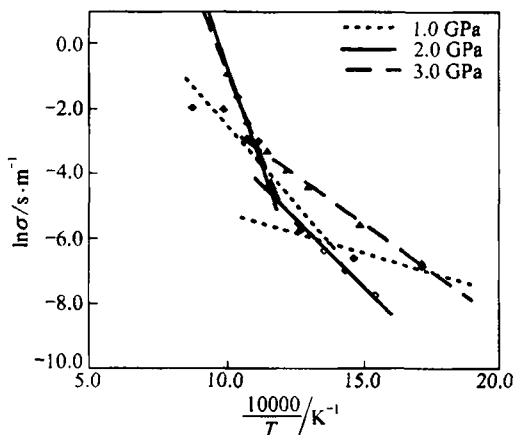


Fig. 4. The relationship between  $\ln\sigma - 1/T$  for serpentine at 1.0–3.0 GPa.

Table 1 Perexponential terms and activation energies from fitting eq. (2)

$P/\text{GPa}$	$T/^\circ\text{C}$	$\ln\sigma_0$	$\Delta E/\text{eV}$
1.0	before dehydration (310–515)	-2.81	0.208
	after dehydration (625–870)	7.08	0.828
2.0	before dehydration (375–600)	5.01	0.718
	after dehydration (600–690)	23.70	2.103
3.0	before dehydration (310–600)	3.29	0.506
	after dehydration (600–725)	20.33	1.826

The dehydration temperature of serpentine is different due to the difference of chemical compositions<sup>[3]</sup>. The precise dehydration temperature of serpentine is not determined in this study. The dehydration temperature of our experimental samples is between 500–600°C from estimation of abrupt changes in

the electrical conductivity with increasing temperature in figure 4.

The slopes of the fit lines in fig. 4 are substantially different before and after dehydration of serpentine. It is most likely that dehydration changes charges' conduction paths and mechanisms.

### 3 Discussion and conclusion

Some studies in recent years showed that dependence of electrical conductivity measurement on frequencies is very common for most silicate minerals of geological interest<sup>[8-10]</sup>. However, some researchers reported independence of electrical conductivity measurement on frequencies or negligible effect of frequencies on electrical conductivity measurement<sup>[14]</sup>. It was most likely that the range of frequencies used was not wide enough or there existed serious leakage current in their sample assemblies. Our experimental results confirm the dependence of electrical conductivity measurement on frequencies and the validity of impedance spectroscopy to determine sample conductance and to distinguish different conductance in the sample environment. Based on the fact above, it is suggested that the effect of frequency on electrical conductivity must be taken into account with caution when laboratory electrical conductivity data are used to interpret field geophysical observations, otherwise wrong conclusions may be drawn. In addition, the range of frequencies used in previous experiments must be checked when their laboratory data are evaluated.

At low temperature, the main charge carriers pass through grain interior and grain boundaries of serpentine sample. The two conductance paths, according to the equivalent circuit principle<sup>[11]</sup>, are both equivalent to a parallel circuit composed of a resistor ( $R$ ) and a capacitor ( $C$ ). Hence the bulk conductivity has intimate relationship with used frequencies. After dehydration of serpentine, free water forms highly conductive network in the sample system, through which other charge carriers, for example ions, can easily move. In addition, free water as such is at the supercritical state and thereby has high conduction<sup>[15]</sup>. These factors govern the bulk conductance of the sample system and shadow grain interior and grain boundary conductance. Consequently, the dependence of the electrical conductivity on frequencies becomes weak, even disappears. Abrupt increase in the electrical conductivity after dehydration of serpentine at 1.0—3.0 GPa in our experiments confirms that it is likely to form HCL (0.01—0.1 S/m) through dehydration of some minerals in the Earth. Therefore, dehydration can form HCL when some hydrous minerals are brought into the lower crust and/or upper mantle at the subduction zone. Field observations showed that HCL would occur at about 20—60 km beneath the Earth at different tectonic units, different crustal thickness and thermal flow areas<sup>[16, 17]</sup>. Serpentine, according to two typical geotherms at Phanerozoic (20.37 °C/km) and stable Precambrian (12.7 °C/km) crust, could dehydrate at the depths of about 24—47 km beneath the surface. The depth range is in agreement with that of HCL. Similarly, HCL can also be formed in other high temperature and/or high pressure metamorphic areas, for example, continental orogenic belts and regional thermal metamorphic belts, through dehydration of some minerals, for example, amphibole, mica, etc.<sup>[18]</sup>.

In conclusion, electrical conductivity measurement is strongly dependent on used frequencies; this dependence becomes weak even disappears after dehydration of serpentine. The conduction mechanisms of serpentine are different before and after dehydration; and dehydration is probably the main reason responsible for the changes of the conduction mechanisms. The electrical conductivity increases abruptly after dehydration of serpentine, through which HCL can be formed in the Earth's interior.

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