Interactive comment on "Effect of chemical composition on the electrical conductivity of gneiss at high temperatures and pressures" by Lidong Dai et al.

Anonymous Referee 2#:

Received and published: 23 October 2017

In their submitted manuscript the authors investigate the electrical properties of different gneiss samples at elevated temperatures and high hydrostatic pressures by means of state of the art experimental facilities. The paper focuses on the effect of the chemical composition to the measured conductivity and different conduction mechanisms are reported. Geophysical implication is also discussed. The work is interesting and worth publishing but additional aspects could also be revealed after further analysis of the experimental data. The authors should pay much effort to improve the quality of their work, in order to be suitable for publication. The following issues should be carefully addressed:

We thank the anonymous reviewer for very constructive and enlightened comments and suggestions in the reviewing process, which helped us greatly in improving the manuscript. In this revised paper, we conscientiously read through all comments from the valuable suggestions of the reviewer, and revised each one points by points, sentences by sentences. All of detailed revisions and responses are listed as follows.

1. In my opinion, the author should not just limited to the calculations of the dc-conductivity but also explore the advantages of the complex impedance spectroscopy. Otherwise, they could measure the dc-conductivity by varying linearly the temperature at different selected pressures. I suggest using also other formalisms of impedance data, such as ac-conductivity and complex impedance presentation of their data.

Thanks for your valuable and professional comments and suggestions. As a matter of fact, it is indeed one good idea that we can calculate the complex impedance presentation and ac-conductivity from the complex impedance spectroscopy. In the revised manuscript, we have already supplemented another one Figure 4: Real and imaginary parts of complex impedance as functions of the measured frequencies for run DS13 and DS14 gneiss under conditions of 1.5 GPa and 623–1073 K. (a) real and (b) imaginary parts for run DS13 gneiss; (c) real and (d) imaginary parts for run DS14 gneiss.

In order to explore the geophysical implication from the electrical conductivities of gneiss samples, we calculated the dc-conductivities of natural gneiss samples, and researched the influence of chemical compositions, temperatures and pressures. Indeed, most previous studies calculated dc-conductivities of minerals and rocks to compare with Magnetotelluric (MT) and geomagnetic depth sounding (GDS) results (Fuji-ta et al. 2007; Dai et al. 2016; Hu et al. 2017).

2. According to my previous comment, it would be also desirable to present the results of all the measured samples (or at least of 2 of them) in suitable figures, i.e. real and imaginary parts of ac-conductivity and impedance as a function of the measured frequency at different T and P, except of the Cole-Cole plots of complex impedance.

Thanks for your valuable and professional comments and suggestions. We added the diagram about the relationship between frequency and real and imaginary parts of impedance. From the real and imaginary parts of complex impedance as functions of the measured frequencies (Figure 4), the values of real parts almost keep unchanged in the frequency of 10^6-10^4 Hz, and sharply increased in the frequency of 10^4-10^2 Hz, and slowly then increased in the low frequency region; the values of imaginary slowly increased in the frequency of 10^6-10^5 Hz, and sharply increased and sharply decreased in the frequency of 10^5-10^2 Hz, and then slowly increased in the low frequency region.

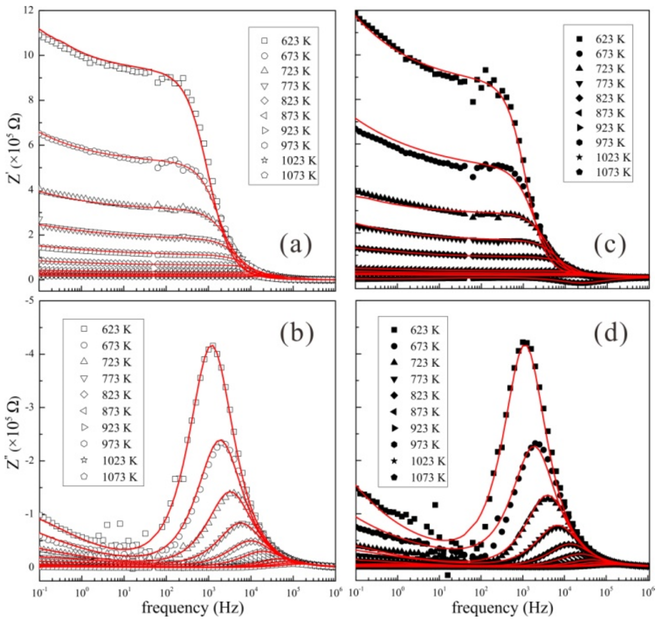

Figure 4. Real and imaginary parts of complex impedance as functions of the measured frequencies for run DS13 and DS14 gneiss under conditions of 1.5 GPa and 623–1073 K. (a) real and (b) imaginary parts for run DS13 gneiss; (c) real and (d) imaginary parts for run DS14 gneiss.

3. In the measured frequency range (0.1 Hz-1 MHz) the overall conductivity should usually include contributions from grains interior, grain boundaries and electrodes polarization. In their fitting procedure the authors included only two types of contributions, with the main one the bulk conductivity. It has to be clarified if this refers to both grains interior and grain boundaries or only to the conductivity of the grains interior. In the former case, the 2 contributions should be separated.

Thanks for your valuable comments. All the impedance spectra at the different temperatures contained almost ideal semicircles in the high-frequency domain and additional tails in the low-frequency domain. The ideal semicircles represent the bulk electrical properties of the sample, and the additional tails are the typical characteristic of the sample–electrode interface in diffusion processes (Roberts and Tyburczy 1991; Dai et al. 2014; Hu et al. 2015). Therefore, the bulk sample resistance can be determined by fitting the high-frequency semicircular arc. The equivalent circuit is composed of the series connection of R_S–CPE_S (R_S and CPE_S represent the resistance and constant-phase element of a sample, respectively) and R_E–CPE_E (R_E

and CPE_E represent the interaction of the charge carrier with the electrode).

4. An important finding which should be emphasized because it is rarely observed in minerals and rocks is the negative activation volumes that are observed, i.e. increase of conductivity with pressure. Their values should be calculated and compared with the activation volumes of the constituent minerals (biotite, feldspar and quartz) and/or other possible reported values of gneiss. Possible reasons for this finding should be also discussed. In fact, it is the effective activation volume that is found to have negative values and could be related to the influence of percolation effects in the grain boundaries.

According to the suggestion, we have already supplemented all of these results on the activation volume for Run DS12 gneiss. With increasing pressure, the electrical conductivity of gneiss increases, accordingly. The activation volumes for Run DS12 gneiss are -7.10 cm^3/mole and -2.69 cm^3/mole at low temperature region and high temperature region, respectively. Another one representative metamorphic rock for gneiss, we can compared it with the electrical conductivity of eclogite. Recently, Dai et al. (2016) measured the electrical conductivity of dry eclogite, and the obtained negative activation volume value for eclogite is -2.51 cm^3/mole under conditions of 1.0-3.0 GPa and 873-1173 K. It was proposed that the main conduction mechanism for dry eclogite is intrinsic conduction (Dai et al. 2016). The conduction mechanism for gneiss sample at high temperature region was also proposed to be intrinsic conduction, but the conduction mechanism at low temperature region was impurity conduction (possible charge carriers: K^+, Na^+, Ca^{2+}, H^+, et al.). In addition, it was suggested that the positive pressure effect on the electrical conductivities of gneiss samples may be due to the more complicated rock structure.

5. Lines 208-211,"... the gneiss samples were unstable in the first heating cycle." This could arise from the existence of bound water that is trapped in grain boundaries or in the rock structure in the form of hydroxyls and is desorbed at high temperatures. In this sense, the conduction mechanism of low activation energies at the low temperature region could be related to proton conduction. The corresponding

ac-conductivity spectra might give insights to these issues. This alternative explanation should be checked.

Thanks for your valuable comments and suggestions. According to previous studies, the electrical conductivities of most minerals and rocks with various conduction mechanisms were unstable at the first heating cycle (Fuji-ta et al. 2004, 2007; Dai et al. 2014). We determined the activation mechanism for gneiss samples by activation enthalpies. The activation enthalpies for the gneiss samples are 0.35–0.58 eV at lower temperature range, Dai et al. (2014) measured the electrical conductivities of granite which has the same mineralogical assemblage with gneiss samples. It was proposed that the conduction mechanism at low temperatures was impurity conduction owing to low activation enthalpy (0.5 eV). We suggested that H^+ may be also one kind of charge carriers of gneiss at low temperature region, other charge carriers were proposed to be K^+, Na^+, Ca^{2+}, et al.

Furthermore, the manuscript should be carefully revised to improve the quality of the English language.

As for the issue of English language, we appreciated Dr Aaron Stallard in Stallard Scientific Editing Company for their helps in English improvements of the manuscript. The substantial corrections for English have been conducted sentences by sentences. After that, the revised paper becomes much more easily be read and understood.

Some less important issues that have to be addressed:

6. Line 73: for the sake of completeness it would be desirable to briefly refer to these different types of gneisses.

Thanks for your valuable comments and suggestions. We have already changed this sentence Line 73: “In light of mineralogical assembly of rock-bearing dominant mineral, it is general that gneiss can be divided into plagioclase gneiss, quartz gneiss, biotite, etc.” In the present studies, the rock-forming minerals of our three gneiss samples are feldspar, quartz and biotite, and the volume percentage for each correspondent rock-forming mineral in different gneiss samples were various (Table

1). It was indicated that three gneiss samples have the same mineralogical assemblage, and all of them belong to the biotite-bearing felsic gneiss.

7. Lines 96, 102, 106, 493: the measured specimens are 3, not 4, as stated incorrectly.

Thanks for your conscientious comments. We have already corrected them in the revised manuscript.

8. Lines 155-156: It would better to use the symbol CPE for the constant phase element, instead of Cs which corresponds to a capacitor.

Thanks for your important suggestion. The symbol CPE was used in our equivalent circuit to obtain the resistance, and the electrical conductivities of gneiss samples had little change. We have changed Cs into CPE in the revised manuscript.

9. Table 3: I suppose that the last column corresponds to the correlation coefficients of the fitting procedure. Please change the symbol (greek gamma) to the correct one, R.

Thanks for your valuable comments and suggestions. We have changed the symbol (greek gamma) to the correct one, γ.

In addition, taking into account the constructive comments of the 1st referee, I would suggest that the paper could focus not only to the effect of the chemical composition to the measured conductivity but also to the negative values of activation volumes, the geophysical implication that already exists in the manuscript and to the detailed investigation of the complex impedance spectra. In this sense, the title could be more general without focusing to the influence of chemical composition on the measured conductivity. For example "Complex impedance spectroscopy of gneiss samples at high temperatures and pressures".

Thanks for your valuable comments and suggestions. Indeed, it is more appropriate that the manuscript title "*Complex impedance spectroscopy of gneiss samples at high temperatures and pressures*". I am very appreciated that you put

forward such a large quantity of enlightened and precious comments and suggestions, which helped us greatly in improving the manuscript.

References

Dai, L.D., Hu, H.Y., Li, H.P., Wu, L., Hui, K.S., Jiang, J.J., and Sun, W.Q.: Influence of temperature, pressure, and oxygen fugacity on the electrical conductivity of dry eclogite, and geophysical implications. Geochem. Geophys. Geosyst., 17, 2394–2407, 2016.

Dai, L.D., Hu, H.Y., Li, H.P., Jiang, J.J., and Hui, K.S.: Influence of temperature, pressure, and chemical composition on the electrical conductivity of granite. Am. Mineral., 99, 1420–1428, 2014.

Fuji-ta, K., Katsura, T., Matsuzaki, T., Ichiki, M., and Kobayashi, T.: Electrical conductivity measurement of gneiss under mid- to lower crustal *P*-*T* conditions. Tectonophysics, 434, 93–101, 2007.

Fuji-ta, K., Katsura, T., and Tainosho, Y.: Electrical conductivity measurement of granulite under mid- to lower crustal pressure-temperature conditions. Geophys. J. Int., 157, 79–86, 2004.

Hu, H.Y., Dai, L.D., Li, H.P., Hui, K.S., and Sun, W.Q.: Influence of dehydration on the electrical conductivity of epidote and implications for high conductivity anomalies in subduction zones. J. Geophys. Res., 122, 2751–2762, 2017.

Hu, H.Y., Dai, L.D., Li, H.P., Hui, K.S., and Li, J.: Temperature and pressure dependence of electrical conductivity in synthetic anorthite. Solid State Ionics, 276, 136-141, 2015.

Roberts, J.J. and Tyburczy, J.A.: Frequency dependent electrical properties of polycrystalline olivine compacts. J. Geophys. Res., 96, 16205–16222, 1991.