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Comment on 'Electrical conductivity of albite–(quartz)–water and albite–water–NaCl systems and its implication to the high conductivity anomalies in the continental crust' by Guo, X., Yoshino, T. & Shimojuku, A.

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In their otherwise excellent study of the electrical conductivity of mineral systems including albite and aqueous fluids in the continental crust, Guo et al. (2015) note that when Archie's Law (Archie, 1942) is fitted to the data for bulk conductivity as a function of fluid fraction, the exponent values are negative for all measurements made between 500 K and 900 K. They note that the negative values indicate that the bulk conductivity decreases with increasing fluid fraction and that this is opposite to the accepted behaviour (e.g., Glover, 2015). Guo et al. (2015) attempt to explain the behaviour by noting that the melting point of the Ab–Qtz–H₂O system varies with increasing water content. However, there is an underlying problem with their use of the simple Archie's law.

Archie's Law is given by the equation

$$\sigma_b = \sigma_f \phi^n,\tag{1}$$

where, σ_f is the conductivity of the aqueous fluid (S/m), ϕ is the fluid fraction, σ_b is the bulk conductivity (S/m), and n is the exponent, which when expressed in terms of resistivity is termed the cementation exponent. Note that there is no preceding non-unity constant C in Eq. (1) compared to the Guo et al. (2015) implementation. This constant was introduced by Winsauer et al. (1952) and has no physical basis because it forces the contradiction $\sigma_b = \sigma_f = C\sigma_f$ when $\phi \rightarrow 1$. Nevertheless, it is often included as an empirical fitting parameter when Archie's Law is used in the oil industry (Glover, 2015), where it allows reasonable fits to data that contain systematic errors. However, it is not this constant that is causing the problem for Guo et al. (2015). In fact, the inclusion

of the constant C taking a non-unity value has probably allowed the fitting to take place as well as it has.

The reason for the negative exponents is simply that Archie's Law is only valid if the matrix material in which the fluid is embedded has zero electrical conductivity. That assumption is generally valid at the low temperatures one would find in reservoirs in the upper crust, but is not valid at middle and lower crustal temperatures. This was recognised by Glover et al. (2000a), who generated a Modified Archie's Law (MAL) that is valid when the matrix of a rock has non-zero conductivity. The Modified Archie's Law has two exponents, each of which is related to the connectedness (Glover, 2009) of each conductive phase in the rock (i.e., the fluid and the matrix phase in this case). The modified Archie's Law, appropriately modified for use in the Guo et al. application, is given by

$$\sigma_b = \sigma_s (1 - \phi)^p + \sigma_f \phi^n \quad \text{where } p = \frac{\log(1 - \phi^n)}{(1 - \phi)}, \tag{2}$$

and where σ_s (S/m) is the conductivity of the solid phase.

The Modified Archie's Law was developed to model conductive magma at middle to lower crustal depths under the Pyrenees. At these depths the host rock also had a significant conductivity (Glover et al., 2000b). When applied to this problem, the Modified Archie's Law was able to predict the bulk conductivity of the rock in an ancient subducting slab. Furthermore, inverting the Modified Archie's Law and using magnetotelluric (MT) measurements of bulk conductance at depth allowed the melt fraction in the subducting slab to be determined, and was found to be significant, at no less than 4.7%. Indeed, volcanoes are not present in the Pyrenees only because this region is in a compressional regime rather than an extensional one.

Returning to the Guo et al. (2015) paper, at surface conditions albite has an electrical conductivity which is so much lower than

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Fig. 1. The Electrical conductivity of Ab–(Qtz)–H₂O system as a function of fluid fraction at different temperatures showing the Guo et al. (2015) data. The solid lines are fits using the Modified Archie's Law (Glover et al., 2000a). Input parameters are: 500 K ($\sigma_s = 0.14$ S/m, $\sigma_f = 0.005$ S/m, n = 0.5), 600 K ($\sigma_s = 0.11$ S/m, $\sigma_f = 0.005$ S/m, n = 0.4), 700 K ($\sigma_s = 0.055$ S/m, $\sigma_f = 0.005$ S/m, n = 0.25), 800 K ($\sigma_s = 0.055$ S/m, $\sigma_f = 0.005$ S/m, n = 0.25), $\sigma_f = 0.005$ S/m, n = 0.005 S/m, n = 0.005 S/m, $\sigma_f = 0.005$ S/m, $\sigma_$

that of most crustal fluids that the conventional Archie's law can be used. However, as we descend into the continental crust, the electrical conductivity of the albite increases and the presence of surface conduction occurring within the interface between the albite and the pore fluids also become significant. The combination of these two effects ensures that the electrical conductivity of the matrix is significant compared to that of the pore fluids. This problem becomes larger as temperature increases and it is possible that matrix may present a larger contribution to the overall conductivity than the pore fluids in the lower continental crust (Glover and Vine, 1994; Glover, 1996). Under these conditions the conventional Archie's law will not work and it is important to use either the modified Archie's law or some other mixing model that takes into account the conductivity of the matrix material.

The two exponents in the Modified Archie's Law are interrelated. This fact implies that in any three-dimensional porous medium there is a finite amount of connectedness that is possible. This hypothesis allowed Glover (2010) to produce a version of Archie's Law that is valid for any number of conducting phases. While the version of Archie's Law for *n*-phases is not required to model Guo et al.'s (2015) data, the application of the Modified Archie's Law should provide exponents that make more sense, as well as producing better fits to their experimental data.

We have applied the Modified Archie's Law to the Guo et al. (2015) data, and the results are shown in Fig. 1. It is clear that the data is described by the Modified Archie's Law, and provides positive values of the *n*-exponent. The values of σ_s , σ_f and *n* that each of these models uses are given in the figure caption. In the absence of specific data, we have assumed that $\sigma_f = 0.005$ S/m for all temperatures, although this is unlikely to be the case in reality. Fits are possible for a matrix conductivity varying between 0.14 S/m and 0.055 S/m, decreasing with temperature. The exponent *n* varies between 0.5 and 0.08 becoming smaller at temperature increases, indicating that the electrical connectedness of the fluid fraction is increasing as temperature increases.

Recent information from the authors of the original paper has furnished experimentally measured values of the electrical conductivity of the polycrystalline albite which was used in Guo et al. (2015) as 2.57×10^{-4} , 6.58×10^{-5} , 1.14×10^{-5} , 1.10×10^{-6} and 4.16×10^{-8} S/m for temperatures of 900, 800, 700, 600 and 500 K, respectively. However, these values cannot be used in modelling the data incorporated in Fig. 6 of Guo et al. (2015) because they are many orders too small. The reason for the apparent inconsistency between these values and the tendency in Fig. 6 of the original paper is not at present known and may be related to the conditions under which the measurements were made.

Earlier in the paper Guo et al. (2015) mention that Yoshino and Noritake (2011) concluded that graphite films are unstable and cannot exist for geologic timescales. Hence, the proposal that graphite might be the cause of high conductivities in the crust (Frost et al., 1989; Glover and Vine, 1992, 1995) seems not to be the case. However, in 2008 Glover and Adám (2008) combined MT and laboratory triaxial testing to show that it was possible for conductivity due to graphite to increase as a result of shearing leading to high crustal conductivities and an increase in seismicity.

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