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Electrical conductivity and P-wave velocity in rock samples from high-temperature Icelandic geothermal fields

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Abstract

Measurements of electrical conductivity and P-wave velocity of seven rock samples were made in the laboratory under inferred in-situ conditions. The samples were collected from smectite and chlorite alteration zones in boreholes from the Krafla and Hengill, Iceland, geothermal areas. The measurements were done in the 25-250 °C range, with pore pressure and confining pressure equal to inferred in-situ hydrostatic and lithostatic pressures, respectively. Conductivity increases linearly with temperature over the 30-170 °C range; that rise is considerably smaller above 170 °C. Time-dependent effects on conductivity occur above approximately 100 °C. These effects may be related to ion exchange between the clay minerals or the Stern layer, and the pore fluid. The temperature coefficient of conductivity is found to be considerably higher than attributed to pore-fluid conduction alone, indicating interface conduction in an electrical double layer on the mineral-water interface in the pores. The results also show that there is no distinction in electrical conduction mechanism in the smectite and chlorite alteration zones; both are dominated by interface conductivity under in-situ conditions. The sharp decrease in conductivity at the top of the chlorite alteration zone, commonly observed in resistivity surveys in high-temperature geothermal systems, is most likely due to the lower cation exchange capacity of chlorite compared to that of smectite.

Keywords: Geothermal; Petrophysics; Electrical conductivity; Temperature; Hydrothermal alteration

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Nomenclature

\[ a = \text{Cementation factor} \]
\[ \text{CEC} = \text{Cation exchange capacity (meq/g)} \]
\[ F = \text{Formation factor} \]
\[ k = \text{Permeability (µD)} \]
\[ Q = \text{Flow rate of pore fluid (µl/min)} \]
\[ T = \text{Temperature (°C)} \]
\[ T_0 = \text{Reference temperature (°C)} \]
\[ T_1 = \text{Reference temperature (°C)} \]
\[ T_2 = \text{Reference temperature (°C)} \]

Greek symbols

\[ \alpha = \text{General temperature coefficient (1/°C)} \]
\[ \alpha_f = \text{Temperature coefficient for fluid conductivity (1/°C)} \]
\[ \alpha_s = \text{Temperature coefficient for surface conductivity (1/°C)} \]
\[ \alpha_{T_1} = \text{Temperature coefficient using reference temperature } T_1 (1/°C) \]
\[ \alpha_{T_2} = \text{Temperature coefficient using reference temperature } T_2 (1/°C) \]
\[ \varphi = \text{Porosity} \]
\[ \sigma = \text{Electrical conductivity (mS/cm)} \]
\[ \sigma_0 = \text{Bulk conductivity (mS/cm)} \]
\[ \sigma_f = \text{Pore fluid conductivity (mS/cm)} \]
\[ \sigma_i = \text{Interface conductivity (mS/cm)} \]

Conversion factors

\[ \mu l/\text{min} = 1.67 \times 10^{-11} \text{ m}^3/\text{s} \]
\[ \mu D \approx 10^{-18} \text{ m}^2 \]

1. Introduction

The heat source for most high-temperature geothermal resources suitable for electricity production is hot or even molten magma intrusions at shallow level in the Earth’s crust. These resources are typically located above or near to the intrusions, and consist of convecting fluid, usually water or brine, flowing mainly through a network of permeable fractures in hot, low-permeable rock bodies.

The lithology of geothermal reservoirs can be quite variable, with complex stratigraphic and structural relationships. Furthermore, associated igneous systems may be still active. Recent fracturing, faulting or magmatic intrusions can create new flow paths for hot or cold fluids, resulting in heating or cooling of the surrounding rock. Open fractures may also fill
over time, due to precipitation of secondary minerals, which reduce the overall permeability of the host rock mass.

Effective exploration methods are crucial for successful geothermal development due to the complexity of the subsurface systems. Not only the geological, but also the physical and geochemical characteristics of these systems vary greatly. In contrast to oil and gas where reflection seismic surveys are the main exploration method, none of such reliability has been found for locating and characterizing high-temperature geothermal systems, although electrical resistivity, magnetotelluric, seismic, magnetic and gravity techniques are all widely used. Experience has shown that the exploration strategy has to be tailor-made for each geothermal field.

A clear knowledge of the behaviour of parameters like resistivity and seismic wave velocity is necessary in order to reach reliable conclusions about geothermal properties based on geophysical survey data. Consequently, Iceland GeoSurvey (ISOR) and the GeoForschungsZentrum(GFZ) Potsdam established a co-operative research programme in 2003 to undertake controlled experiments on the behaviour of rock properties as a function of temperature, porosity and pore fluid properties. This co-operation was further strengthened by the EU-supported framework project I-GET with additional participation of other key players in the European geothermal exploration sector.

Laboratory measurements on core samples from Icelandic geothermal fields conducted as a part of the I-GET project and collaboration between ISOR and GFZ-Potsdam are discussed in four separate papers. Measurements of electrical conductivity and P-wave velocity vs. temperature are addressed here; measurements of conductivity vs. pore fluid conductivity (i.e. salinity) are covered in Flóvenz et al. (2005); discussion of sonic velocity vs. temperature is found in Jaya et al. (2010); and measurements of conductivity accompanying boiling of the pore fluid are treated in Milsch et al. (2010).
The main purpose of these laboratory studies was to acquire novel data on physical properties of the rock; the ultimate goal is to get information to assist with the interpretation of field survey data collected in volcanic environments as part of geothermal exploration programs.
2. Background

2.1. Importance of resistivity in geothermal exploration and development

High-temperature geothermal fields in Iceland and other volcanic areas of the world have a broadly similar electrical resistivity structure (Árnason and Flóvenz, 1992; Anderson et al., 2000; Ussher et al., 2000). A typical resistivity cross section, in this case for the Nesjavellir geothermal system (SW Iceland), is given in Fig. 1. It shows a broad resistivity anomaly consisting of an up-doming conductive cap overlying a resistive core. This type of resistivity structure has been discussed by several authors (Flóvenz et al., 1985; Árnason and Flóvenz, 1992; Árnason et al., 2000; Anderson et al., 2000; Ussher et al., 2000; Flóvenz et al., 2005; Kulenkampff et al., 2005). The conductive cap consists of rocks with considerable amount of conductive alteration minerals, like smectite, that have high cation exchange capacity (Árnason et al., 2000). The resistivity of the cap decreases with temperature until a core of high resistivity is reached. Well logging shows that the transition from the low-resistivity cap to the high-resistivity core coincides with a change in mineral alteration, i.e. from smectite to mixed-layer clays and chlorite.

The increase in resistivity from the smectite alteration zone over to the chlorite zone is likely due to the higher cation exchange capacity of smectite compared to chlorite (Árnason and Flóvenz, 1992). There has also been speculation about the influence of different electrical conduction mechanisms, e.g. that interface conduction is dominant in the smectite zone, whereas fluid conductivity dominates in the chlorite zone. However, Flóvenz et al. (2005) and Kulenkampff et al. (2005) indicate that interface conduction is dominant in both zones.

The change from a smectite to chlorite-type alteration assemblage is reported to occur at temperatures close to 230 °C in Icelandic geothermal systems (Kristmannsdóttir, 1979). Permeable geothermal reservoirs with temperatures above 230 °C are of great importance, since they are well suited for electricity generation. Hence, being able to detect the ca. 220-
240°C anomaly with resistivity measurements would help enormously the search for reservoirs suitable for power generation. However, the apparent change in resistivity appears to be fixed by the type of clay mineral alteration. The boundary between the low- and high-resistivity regions persists, even if the reservoir has cooled down and the measured temperatures no longer exceed 230°C. Consequently, whilst the top of the high resistivity zone represents a surface where the temperature may have been above ca. 230°C at some time in the past, present reservoir temperatures may be somewhat cooler.

For geothermal exploration it is important to be able to establish (prior to drilling) if the resistive core has cooled. Presently there are two methods to do that, one is to use chemical geothermometers, provided reliable fluid samples from hot springs or fumaroles are available; the other is to drill into the anomaly. The latter is very expensive, and therefore development of geophysical methods to resolve this problem is highly desirable, as it could significantly reduce the cost of geothermal energy development. A way forward is to learn more about changes in resistivity within the smectite and chlorite alteration zones as a function of temperature. Laboratory measurements at in-situ temperature-pressure-saturation (T-P-X) conditions on core samples from various mineral alteration zones may be helpful for distinguishing between reservoirs that may have cooled down and those that have not.

The most common in-situ conditions at a high-temperature geothermal field, where the pore fluid is liquid, are temperatures higher than 200 °C and pressures up to about 10 MPa. However, there is currently little published laboratory data for water-saturated rocks at these conditions. Some measurements of resistivity in dacite tuffs, sandstone, andesite, granite, and crystalline limestone at temperatures up to 250 °C were made by Llera et al. (1990); the measured resistivities did not most likely represent stable values due to the short heating cycles used. Resistivity hysteresis appeared in many samples which Llera et al. ascribed to opening of micro-cracks and some unspecified fluid-rock interaction and/or chemical process.
2.2. Electrical conduction mechanisms and their temperature dependence

The two main electrical conduction mechanisms in water-saturated rocks are pore fluid conduction and interface conduction (Rink and Schopper, 1976; Flóvenz et al., 1985; Revil and Glover, 1998); the possibility of conduction inside the rock grains is ruled out due to the low conductivity of dry samples. As a first approximation the two mechanisms act in parallel according to the (modified) Waxman-Smits equation, of Rink and Schopper (1976):

\[
\sigma_0 = \frac{\sigma_f}{F} + \sigma_s
\]  

where \(\sigma_0, \sigma_f, \sigma_s, \) and \(F\) are bulk conductivity, pore fluid conductivity, interface conductivity, and formation factor, respectively.

In their experiments on conductivity in clean and shaly sandstones and some artificial materials saturated with fluids of various salinities, Rink and Schopper (1976) noted that the bulk conductivity stayed almost unchanged for low-salinity solutions, but changed linearly with pore fluid conductivity for high-salinity brines, which they attributed to conduction on the fluid-matrix interface. The results of Flóvenz et al. (1985) for core samples from Icelandic geothermal wells, and of Pezard (1990) for basaltic cores from the Ocean Drilling Project support this conclusion. A thorough theoretical and experimental study on this subject has been undertaken by Revil et al. (1996, 1998, 2002) and Revil and Glover (1997).

Pore fluid conductivity, \(\sigma_f\), at temperatures below 150 °C can be described by the linear model of Revil et al. (1998):

\[
\sigma_f(T) = \sigma_f(T_0)[1 + \alpha_f(T - T_0)]
\]  

where \(T_0\) is a reference temperature and \(\alpha_f\) is a temperature-independent coefficient. The value of \(\alpha_f\) was found to be 0.023/°C for \(T_0 = 25\) °C (Revil et al., 1998). Due to changes in density, viscosity and dielectric permittivity of water for temperatures above 150 °C, which affect the
mobility of free charges, conductivity diverges from linearity above this temperature and decreases with increasing temperature above 250 °C (Ucok et al., 1980).

Interface conductivity, \( \sigma_s \), is dependent on the surface area of pores, the surface charge density, the valence and mobility of surface ions, temperature, and acidity (pH) (Revil and Glover, 1998, and references therein). For temperatures below 200 °C, the interface conductivity can be approximated as being linear with temperature, i.e.,

\[
\sigma_s(T) = \sigma_s(T_0)[1 + \alpha_s(T - T_0)]
\]

where \( T_0 \) is the reference temperature and \( \alpha_s \) is the temperature-independent coefficient, as before. Revil et al. (1998) determined a value of \( \alpha_s = 0.040/°C \) for \( T_0 = 25 °C \). According to these authors, in general surface conductivity is more temperature-dependent than pore fluid conductivity.

Based on field measurements there is a difference in conductivity between rocks in the smectite and chlorite alteration zones (e.g. see Fig. 1). The cation exchange capacity (CEC), which is the quantity of exchangeable cations on a negatively charged mineral surface, is not the same for these two clay minerals: For smectite the CEC is 0.8-1.5 meq/g (Ellis, 1987); for chlorite, 0.01 meq/g (Thomas, 1976). This could explain the difference in conductivity between the smectite/zeolite and the chlorite/epidote alteration zones. The resistivity contrast at the top of the smectite zone is due to the onset of interface conduction in the rock (Flóvenz et al., 1985).

2.3. Further on interface conductivity

The zone between the surface of a solid clay mineral and the contiguous electrolyte is called the electrical double (or triple) layer (Fig. 2). It is divided into the Stern layer and the electrical diffuse layer. The Stern layer consists of adsorbed ions at the negatively charged mineral surface. According to the Grahame model, the Stern layer is bipartite (Gileadi et al.,
1975; p. 7), with specifically adsorbed anions, whose centres define the inner Helmholtz plane (Fig. 2), and non-specifically adsorbed and hydrated cations. The centres of the cations nearest to the mineral surface define the outer Helmholtz plane (Fig. 2). Outside the Stern layer a higher concentration of cations than in the remaining electrolyte form the diffusive part of the double layer. The plane of shear defines the boundary where the mobile part of the diffuse layer can move along the charged surface, i.e. all ions between the mineral surface and the plane of shear act as if attached to the mineral (Myers, 1991; p. 81).

According to Revil and Glover (1998), interface conduction is the sum of (a) conduction in the Stern layer; (b) conduction in the diffuse layer; and (c) a mechanism working directly on the mineral surface, possibly in connection with proton transfer. These authors showed that conduction in the diffuse layer is negligible in silica and alumino-silicates, and suggested that the main contribution to the interface conductivity may be due to counter-ions in the Stern layer.

3. Equipment and Procedures

An overview of the seven analyzed samples can be found in Table 1. The samples originate from Icelandic boreholes in the Krafla (samples K9, K58, 58, K40) and Hengill (samples NJ1, 2A and 3A) geothermal areas. They are right circular cylinders of height 50 mm and diameter 47.6 mm (samples NJ1, K9, and K58) or height 40 mm and diameter 30 mm (samples 2B, 3A, 58, and K40). A description of the cores including analysis of minerals and measurements of some physical properties are found in Steingrímsson et al. (1994) for well number NJ-17 (sample number NJ1), in Franzson and Tulinius (1999) for well ÖJ-1 (samples number 2A and 3A) and Gautason et al. (2007) for well number KH-5 (sample K40). Mineralogical data on wells KH-1 (samples 58 and K58) and K-2 (sample K9) are from Franzson (pers. com., January 2008). The details of the experimental setup can be
found in Kulenkampff et al. (2005) and Kristinsdottir et al. (2007). A schematic of the system is depicted in Fig. 3. The MuSPIS (Multiple Sample Production and Injection Simulator) measurement system is described in detail in Milsch et al. (2008). Each sample was submerged in pore fluid, wrapped around the sides by PTFE sleeves and connected to a pore fluid pump at either end, providing control of both pore fluid pressure and flow rate (see 1 and 5 in Fig. 3). Two silver rings were painted around each sample and potential electrodes applied to the ends of the sample, hence enabling a four-point resistivity measurement. Wave transducers were also attached to the ends. The assembly was immersed in an oil-filled chamber (3 in Fig. 3) that provided control of both temperature and confining pressure.

The synthetic pore fluid was prepared according to an analysis of the water in the corresponding or some neighbouring borehole. All the major elements with the exception of silica were dissolved in the synthetic fluid. It should be noted here that the in situ fluid in both the geothermal fields is of meteoric origin and has low salinity; a typical chemical composition is given in Arnórsson et al. (2008). Sample 58 is an exception, though, since the pore fluid used was unintentionally prepared with slightly more than double the salt content of the in situ fluid. Measurements of bulk conductivity as a function of pore fluid conductivity performed in 2003 on a sample from the same core depth interval as sample 58 show that the higher salinity solution did not affect the results (cf. Figure 10 in Flóvenz et al., 2005).

All samples were kept dry at room conditions and placed in a drying cupboard at 60 °C prior to measurements, with the exception of sample K40 which was kept submerged in fluid and only dried slightly at the surface shortly before laboratory measurements and then again submerged in pore fluid. This was done in order to find out if drying the samples caused the unexpected experimental result of conductivity hysteresis, as will be explained in the next section.

The temperature- and pressure-dependent measurements were done in three stages, i.e. in
2003, 2006 and 2007. An overview of the experimental program (timetable) is given in Table 2. In this study the samples were heated in steps of mostly 25 ° or 50 °C (with the rare exception of 10 ° or 20°C steps) in the temperature range of 25-250°C, keeping confining and pore pressure constant (see Table 1). The heating and cooling rate was on the order of 10-30 °C/h. For a detailed temperature history, see Fig. 4.

Temperature, pore and confining pressure, and electrical conductivity (four-point measurement) were continuously recorded during the experiment. A measurement of impedance (at a frequency in the 0.01 Hz -1 kHz range for measurements made in 2003, or in the 0.1 Hz-100 kHz range for 2006 and 2007 measurements) and P-wave velocity was made once temperature and conductivity equilibrium had been reached in each step. In 2007, unfortunately the wave transducers were dysfunctional, and no sonic velocity measurements could be made. The frequency dependence of conductivity is not discussed in this paper but is covered by Flóvenz et al. (2005) for the 2003 measurements where only small dependence below 1 kHz is reported. Similar results were obtained in the 2006 and 2007 samples.

In 2007, permeability measurements were made three times at 150°C by letting the pore fluid flow through the sample at a constant rate \( Q \) (\( Q = 25 \mu l/min \) for sample K40; \( Q = 50 \mu l/min \) for sample 2B) and measuring the pressure gradient over the sample when the pressure had stabilized. Otherwise the pore fluid only flowed one-way through the sample on account of thermal expansion and contraction.

4. Results and Discussion

The temperature and conductivity histories for the seven core samples are given in Fig. 4; plots of conductivity vs. temperature are shown in Figs 5 and 6. Note the apparent change in conductivity above 100 °C (hysteresis effect), which seems to be completed when the sample is allowed to reach thermal equilibrium at 150 °C. Also, note the conductivity of sample K9
increases at 160 °C, presumably since it was not allowed to reach thermal equilibrium at 140 °C (which is possibly too cool to complete the physical-chemical changes). This might be the same effect as described by Llera et al. (1990).

There is a linear relationship between conductivity and temperature over the 50-170 °C range, both before and after the change in conductivity. At temperatures above 170-200 °C the conductivity becomes gradually less dependent on temperature; this is particularly clear for sample 3A (Figs 5 and 6).

Let us concentrate on the linear part of the $\sigma$-$T$ relation. According to Eqs (1) and (2), $\alpha_f$ should equal the slope $\alpha$ of the normalized conductivity curve, $\sigma(T)/\sigma(T_0)$, if fluid conductivity is dominant. On the other hand, if interface conduction dominates, according to Eqs (1) and (3), $\alpha = \alpha_s$. If both conduction mechanisms contribute, then the slope has a value between $\alpha_f$ and $\alpha_s$ and is given by:

$$\alpha = \frac{\alpha_s \sigma_s(T_0) + \alpha_f \sigma_f(T_0) / F}{\sigma(T_0)}$$

We assumed $T_0 = 50^\circ$C as the reference temperature, since if we choose $T_0 = 25^\circ$C, like Revil et al. (1998) did, we would have to extrapolate to calculate $\sigma(T_0)$.

By performing a linear regression ($R = 0.99$) on the conductivity (Fig. 6) using only stable conductivity data from the LCR-meter in the 50-150°C range, we obtain the values of $\frac{d\sigma}{dT}$ shown in Table 3, both before and after the conductivity change. The slope $\alpha$ of the normalized conductivity curve $\sigma(T)/\sigma(T_0)$ is calculated by the formula $\alpha = \frac{d\sigma}{dT} / \sigma(T_0)$; the results are shown in Table 3. Note that we used different values of $\sigma (50^\circ$C) for measurements before and after the conductivity change, as there clearly is no common reference value $\sigma(50^\circ$C) for these two cases.
We obtain the temperature coefficients $\alpha$ corresponding to $T_0 = 25^\circ C$ (Table 3) based on the relation,

$$\alpha_{T_2} = \frac{\alpha_{T_1}}{1 + (T_2 - T_1)\alpha_{T_1}}$$  \hspace{1cm} (5)

where $\alpha_{T_1}$ ($\alpha_{T_2}$) is the temperature coefficient using reference temperature $T_1$ ($T_2$). The values obtained are in the range $\alpha = 0.027$-0.28 $/^\circ C$, i.e. all are higher than $\alpha_f = 0.023 /^\circ C$. This could indicate that pore fluid conduction is less important than interface conduction both in the smectite and chlorite zones, although samples 2B and 3A from well ÖJ-1 likely reflect a mix of interface and pore fluid conduction after the conductivity change at $150^\circ C$ [$\alpha = (0.027 \pm 0.003) /^\circ C$]. We conclude that there is no difference in conduction mechanisms in the smectite and mixed-layer clays/chlorite zones, and therefore that the lower CEC of chlorite compared to smectite is the most likely cause of the conductivity decrease between the smectite and chlorite zones in high-temperature geothermal systems.

The temperature coefficient $\alpha$ decreases for all analysed samples at the conductivity change occurring at $150^\circ C$, i.e. the conductivity becomes less temperature dependent, whereas the conductivity increases. Since fluid conductivity is less temperature dependent than surface conductivity ($\alpha_f < \alpha_s$), we reason that the contribution of fluid conductivity increases during the change in the sample's intrinsic properties. The possibility of an experimental artefact causing the change in conductivity is excluded, since the measurements were performed using two experimental setups; i.e. the MuSPIS and the Field Laboratory Experimental Core Analysis System (FLECAS) (Kulenkampff et al., 2005). Furthermore, the conductivity of a Fontainebleau sandstone sample (clean quartz sandstone) measured at 25-150 $^\circ C$ using the MuSPIS gave the same linear relationship between conductivity and temperature, but without the hysteresis (Fig. 7).

It is interesting to compare the results for samples 2B and 3A, and for samples 58 and
K58, since the sample pairs are from the same respective core (Table 1). Pore fluid prepared according to the same procedure was used for samples 2B and 3A, but as mentioned in Section 3, the pore fluid used in the measurements of sample 58 had more than double the salt content used in sample K58. Measurements of conductivity vs. pore fluid conductivity made by Flóvenz et al. (2005), however, indicate that this extra pore fluid salinity (conductivity 1970 µS/cm instead of about 900 µS/cm) should not affect the normalized conductivity, and hence the temperature coefficient should not be affected.

We note that the conductivity of sample 3A is more than double that of sample 2B and that the conductivity of sample 58 is nearly twice that of sample K58 (Fig. 6). The higher conductivity may be due to the porosity of 3A and 58 being higher than that of 2B and K58, respectively (Table 1), although the additional pore fluid salinity might add to the conductivity of sample 58. Note, however, that the temperature coefficient $\alpha$ for 3A and 2B is the same after the conductivity change at 150°C (Table 3), and that the same is true for 58 and K58.

Permeability measurements for samples K40 and 2B are shown in Table 4. The permeability decreases as the samples are heated from 40° to 150°C (i.e. before conductivity hysteresis) from 9.3 to 5.5 µD for sample K40 and from 25.4 to 21.8 µD for sample 2B, respectively. The reason for this drop in permeability remains unresolved, but could be due to a combination of compaction and crack healing, thermo-elastic mismatch between mineral grains, clay swelling and/or fines migration. At constant temperature (i.e. 150 °C) after the conductivity hysteresis the permeability of samples 2B and K40 is approximately stable within experimental resolution; i.e. \( k = (5.3 \pm 0.2) \mu \text{D} \) for K40, and \( k = (18.7 \pm 0.6) \mu \text{D} \) for 2B.

After the change in conductivity at 150°C, during each permeability test (i.e. as pore fluid flowed through the sample at a rate of \( Q = 25 \mu \text{l/min} \) or \( Q = 50 \mu \text{l/min} \)) conductivity...
decreased monotonically, with the exception of sample K40 where the conductivity increased at first, but overall decreased during the test (Table 4). The rate at which the conductivity decreased was 5-10 μS/cm·h for sample K40, and 8-12 μS/cm·h for sample 2B, except in the last two measurements when it was as high as 72 μS/cm·h. This last conductivity decrease in sample 2B is shown in red in Fig. 5. The final conductivity value after this large decrease falls onto the curve $\sigma_1$ in Fig. 6, i.e. the conductivity seems to be back to the initial state as before the initial conductivity increase (hysteresis) at 150°C. After this conductivity reduction, the temperature was lowered and increased to achieve the $\sigma$-$T$ relation (Fig. 5). Thereafter the conductivity at 150 °C slightly increased, but this change is negligible when compared to the rise in conductivity observed during the first heating cycle.

The conductivity change around 150°C is yet to be satisfactorily explained. Possible clues to what causes it include:

1. the decrease in temperature coefficient $\alpha$ that was observed in every sample after the conductivity change indicating that conductance is more closely associated with fluid conductivity than before the change;

2. the overall decrease in conductivity when the pore fluid flows through the samples. There is one example (2B) when pore fluid flowed long enough that conductivity decreases until it stabilized at a value matching the conductivity before the initial conductivity change.

However, the temperature coefficient $\alpha$ does not change back to the initial value, i.e. it does
not increase again. In fact it continues to decrease\(^1\) and attains a final value matching the
temperature coefficient for fluid conductivity;

(3) the change in pore fluid conductivity when fluid flows through the core sample. Before the
laboratory measurements were made on sample 2B the fluid in the system had a conductivity
of \( \sigma = 970 \, \mu S/cm \), both in the sample and in the upstream and downstream pumps. After the
measurements, the conductivity of the fluid in the upstream pump (which had not flown
through the sample) was \( \sigma = 1125 \, \mu S/cm \) and that in the downstream pump (some of which
had flown through the sample) was \( \sigma = 1280 \, \mu S/cm \). This conductivity increase may be
explained by diffusion of ions and charged particles against the fluid flow, or some unknown
effects in the pumps and capillaries;

(4) the lack of mineralogical changes in the samples. Thin-section examination of the core
samples before and after the conductivity measurements showed no visible change in the
rock, clay minerals and other minerals in the pores (Hjalti Franzson, pers. com., January
2008). In particular, there are no signs of micro-cracking, consistent with the observations of
Llera et al. (1990). The large clay content in our samples might explain this difference since
clays are more yielding than solid rock; and

(5) the slight decrease in P-wave velocity during the conductivity change, the difference,
however, is insignificant (Fig. 8).

Bearing in mind that the measured conductivity increased during heating and decreased
during percolation of pore fluid, and that the temperature coefficient \( \alpha \) decreased during
heating, we suggest that the conductivity change is likely related to a flow of ions across the
boundary between the clay mineral, or the Stern layer, and the pore fluid. More precisely, that
there is (a) some ion exchange, such that the ions which the pore fluid receives contribute

\(^1\) The temperature coefficient \( \alpha \) has the value \( \alpha = (0.040 \pm 0.004) /\, ^\circ C \) during warm-up, \( \alpha =
(0.027 \pm 0.003) /\, ^\circ C \) after the conductivity increase, and \( \alpha = (0.023 \pm 0.003) /\, ^\circ C \) after the final
conductivity decrease. The final temperature coefficient has exactly the same value as the
temperature coefficient for pore fluid conductivity.
more to the conductivity than the ions it looses; (b) that the pore fluid captures some ions from the clay minerals, or from the Stern layer, without giving back any ions; or (c) that both mechanisms are true. Hence, when the pore fluid flows through the sample those extra ions (or better conducting ions) in the pore fluid are flushed out of the sample, and thus conductivity decreases.

Finally, we have a few suggestions regarding the experimental procedure when carrying similar laboratory measurements in the future. Apart from letting the pore fluid flow through the sample only in one direction, and taking care to ensure that the conductivity stabilises after the hysteresis and after each successive temperature step, it would be advisable to measure sample porosities both before and after the measurements, in order to detect any openings of micro-cracks, or swelling of clays. The same goes for repeat measurement of conductivity and chemical analysis of the pore fluid, to see if its chemical composition has changed during the experiments. Finally, permeability tests should be made at the end of measurements to test the effect of percolation on the conductivity, i.e. to see if the conductivity always returns to the same values as before the initial conductivity hysteresis (for example, to determine if the results of the measurements made on sample 2B were only a coincidence).

5. Conclusions

Our study found no strong distinction between electrical conduction mechanisms in the smectite and chlorite alteration zones, though interface conduction is apparently dominant in the majority of cases. The most likely explanation of the much higher resistivity in the mixed-layer and chlorite zone is that the cation exchange capacity (CEC) of chlorite is considerably lower than that of smectite.

The relationship between conductivity and temperature is linear over the 50-170 °C range,
apart from a sharp rise in the conductivity of the samples as the temperature reaches 100-150 °C for the first time. This increase appears as a single hysteresis on a $\sigma$-$T$ plot and seems to reflect a change in the sample's intrinsic properties. The reason for this behaviour is unknown. It may be that the phenomenon is related to an ion exchange between the clay minerals, or the Stern layer, and the pore fluid. However, to date no measurements have been made that confirm or reject this hypothesis. On the other hand, the fact that conductivity is less temperature dependent after the hysteresis and that the conductivity decreases considerably when pore fluid is allowed to flow through the sample, as observed in samples K40 and 2B, could provide important clues.

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Figure captions

Fig. 1. Typical resistivity structure of a high-temperature geothermal reservoir showing a high resistivity core under a low-resistivity cap. The isotherms are derived from the estimated true formation temperature in each well based on numerous temperature logs obtained during and after drilling. The section is from the Nesjavellir geothermal field, Iceland. (Modified from Árnason and Flóvenz, 1992).

Fig. 2. Schematic diagram of the double layer according to the Gouy-Chapman-Stern-Grahame model (not to scale) (Gileadi et al., 1975); see text for further details.

IHP: Inner Helmholtz Plane; OHP: Outer Helmholtz Plane. The figure is a reproduction of diagrams by Gileadi et al. (1975, p. 11) and Revil et al. (2002).

Fig. 3. A schematic diagram of the Multiple Sample Production and Injection Simulator (MuSPIS) (from Milsch et al., 2008). The equipment includes two pairs of pore fluid syringe pumps (maximum pressure: 52 MPa); two downstream pumps (1) acting as a pore pressure stabiliser and two upstream pumps (5) that provide a constant fluid flow of up to 107 ml/min; reservoirs for chemical fluid analysis (2) (maximum pressure: 10 MPa; maximum temperature: 100 °C); pressure vessel with heater (3) (maximum pressure: 140 MPa; maximum temperature: 200 °C, although 250 °C were reached during the measurements); a confining pressure pump (4); and a 10 l fluid reservoir (6) (maximum Pressure: 10 MPa; maximum temperature: 100°C. The FLECAS (Field Laboratory Experimental Core Analysis System) is similar in design, although without the reservoirs for chemical fluid analysis and providing up to 70 MPa confining pressure and 50 MPa pore fluid pressure.
Fig. 4. Measured conductivity and temperature histories for the seven Icelandic samples.

Fig. 5. Measured conductivity versus temperature plots (continuous scans) for the seven Icelandic samples.

Fig. 6. Measured conductivity versus temperature plots corresponding to continuous scans and those obtained using a LCR-meter. The change (hysteresis) in the $\sigma$-$T$ relation around 150 °C is evident for all samples, except sample K58 which had been heated above 150 °C previously. See also Fig. 5 for a clearer view of the progress of measurements.

Fig. 7. Measured conductivity and temperature histories (top panel), and conductivity versus temperature (bottom panel) for a Fontainebleau sandstone sample (clean quartz sandstone). The conductivity increases linearly with temperature, and there is no hysteresis over the 100-150 °C range.

Fig. 8. Measured P-wave velocity versus temperature plots for the seven Icelandic samples, before (in black) and after (in red) the change in conductivity behaviour.
Figures

Figure 1

Figure 2
Figure 3
Figure 4
Figure 5
Figure 6
Figure 8
Tables:

Table 1. Data on the seven Icelandic samples used in the experiments. The porosity of samples NJ1 and K58 was not measured, but an estimate was made based on Archie's law ($\sigma \propto \varphi^a$; where $\varphi$ and $a$ are porosity and cementation factor, respectively). MLC: Mixed Layer Clays.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Location</th>
<th>Well no.</th>
<th>Year of sampling (well drilling)</th>
<th>Lithology</th>
<th>Alteration zone</th>
<th>Sample depth (m)</th>
<th>In-situ temperature (°C)</th>
<th>Estimated in-situ fluid conductivity at 25°C (µS/cm)</th>
<th>Porosity (%)</th>
<th>Density (g/cm³)</th>
<th>Year of measurement</th>
<th>Year of measurement</th>
<th>Year of measurement</th>
<th>Year of measurement</th>
<th>Year of measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>2B</td>
<td>Hengill</td>
<td>ÖJ-1</td>
<td>1994</td>
<td>Hyaloclastite</td>
<td>Chlorite / Epidote</td>
<td>794.5</td>
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<tr>
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<td>Hengill</td>
<td>ÖJ-1</td>
<td>1994</td>
<td>Hyaloclastite</td>
<td>Chlorite / Epidote</td>
<td>795.0</td>
<td>200</td>
<td>808</td>
<td>20.7</td>
<td>2.46</td>
<td>2006</td>
<td>15.0</td>
<td>8.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NJ1</td>
<td>Nesjavellir</td>
<td>NJ-17</td>
<td>1986</td>
<td>Hyaloclastite</td>
<td>Chlorite</td>
<td>1003</td>
<td>~230</td>
<td>751</td>
<td>~12</td>
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</tr>
<tr>
<td>K9</td>
<td>Krafla</td>
<td>K-2</td>
<td>1974</td>
<td>Basalt</td>
<td>MLC</td>
<td>540</td>
<td>200</td>
<td>909</td>
<td>6.8</td>
<td>2.71</td>
<td>2003</td>
<td>15.0</td>
<td>5.4</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>Krafla</td>
<td>KH-5</td>
<td>2006</td>
<td>Basalt</td>
<td>MLC / Chlorite</td>
<td>537.5</td>
<td>120</td>
<td>-</td>
<td>13.2</td>
<td>2.29</td>
<td>2007</td>
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<td>Basalt</td>
<td>Smectite / MLC</td>
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<td>780</td>
<td>~16</td>
<td>2.7</td>
<td>2003</td>
<td>4.7</td>
<td>1.9</td>
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<tr>
<td>58</td>
<td>Krafla</td>
<td>KH-1</td>
<td>1991</td>
<td>Basalt</td>
<td>Smectite / MLC</td>
<td>187.5</td>
<td>~160</td>
<td>780</td>
<td>20.0</td>
<td>2.37</td>
<td>2006</td>
<td>5.0</td>
<td>1.9</td>
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</table>
Table 2. An overview of the measurement timetable, detailing which system was used and what parameters and samples were measured during each laboratory program.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Year of measurements</th>
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<td>2003</td>
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<tr>
<td>Measurement unit</td>
<td>FLECAS</td>
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<tr>
<td>Conductivity as a function of temperature</td>
<td>X</td>
</tr>
<tr>
<td>P-wave velocity as a function of temperature</td>
<td>X</td>
</tr>
<tr>
<td>Conductivity during boiling of pore fluid</td>
<td>X</td>
</tr>
<tr>
<td>P-wave velocity during boiling of pore fluid</td>
<td></td>
</tr>
<tr>
<td>Number of samples</td>
<td>3</td>
</tr>
<tr>
<td>Samples tested</td>
<td>K9, K58, NJ1</td>
</tr>
</tbody>
</table>

FLECAS: Field Laboratory Experimental Core Analysis System; MuSPIS: Multiple Sample Production and Injection Simulator.
Table 3. Data and parameters derived from the laboratory measurements made on the seven Icelandic samples. ‘Change’ refers to the change in the intrinsic properties of the sample. MLC: Mixed Layer Clays.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Lithology</th>
<th>Type of alteration</th>
<th>Year of measurements</th>
<th>$d\sigma/dT$ before change (µS/cm°C)</th>
<th>Estim. conductivity at 50°C before change (µS/cm)</th>
<th>Temperature coefficient $\alpha$ using $T_0=50°C$ before change (1/°C)</th>
<th>Estim. conductivity at 50°C after change (µS/cm)</th>
<th>Temperature coefficient $\alpha$ using $T_0=50°C$ after change (1/°C)</th>
<th>$d\sigma/dT$ after change (µS/cm°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2B</td>
<td>Hyalo-</td>
<td>Chlorite /</td>
<td>2007</td>
<td>1.2</td>
<td>0.020 ± 0.002</td>
<td>0.040 ± 0.004</td>
<td>1.9</td>
<td>120/125</td>
<td>0.016 ± 0.001</td>
</tr>
<tr>
<td></td>
<td>clastite</td>
<td>Epidote</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3A</td>
<td>Hyalo-</td>
<td>Chlorite /</td>
<td>2006</td>
<td>3.4</td>
<td>0.027 ± 0.003</td>
<td>0.083 ± 0.012</td>
<td>4.8</td>
<td>300/320</td>
<td>0.016 ± 0.001</td>
</tr>
<tr>
<td></td>
<td>clastite</td>
<td>Epidote</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>NJ1</td>
<td>Hyalo-</td>
<td>Chlorite</td>
<td>2003</td>
<td>5.0</td>
<td>0.024 ± 0.002</td>
<td>0.060 ± 0.008</td>
<td>6.7</td>
<td>310</td>
<td>0.021 ± 0.002</td>
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<td>clastite</td>
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</tr>
<tr>
<td>K9</td>
<td>Basalt</td>
<td>MLC</td>
<td>2003</td>
<td>2.9</td>
<td>0.035 ± 0.003</td>
<td>0.28 ± 0.010</td>
<td>6.2</td>
<td>200</td>
<td>0.032 ± 0.003</td>
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<tr>
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<td>MLC / Chlorite</td>
<td>2007</td>
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<td>0.019 ± 0.002</td>
<td>0.036 ± 0.006</td>
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<td>110</td>
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<tr>
<td>K58</td>
<td>Basalt</td>
<td>Smectite /</td>
<td>2003</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>170</td>
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<tr>
<td></td>
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<td>MLC</td>
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</tr>
<tr>
<td>58</td>
<td>Basalt</td>
<td>Smectite /</td>
<td>2006</td>
<td>1.7</td>
<td>0.032 ± 0.003</td>
<td>0.16 ± 0.06</td>
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<td>230/260</td>
<td>0.025 ± 0.002</td>
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<tr>
<td></td>
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</table>
Table 4. Data and results of measurements made on samples K40 and 2B. Water viscosity for the corresponding pore fluid pressure (see Table 1) and temperature was taken from Lemmon et al. (2005).

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Time (h)</th>
<th>Flow rate (ml/min)</th>
<th>Pressure difference (MPa)</th>
<th>Temperature (°C)</th>
<th>Viscosity of water (Pa·s)</th>
<th>Length (cm)</th>
<th>Cross sectional area (cm²)</th>
<th>Permeability (µD)</th>
<th>Electrical conductivity before test (mS/cm)</th>
<th>Electrical conductivity after test (mS/cm)</th>
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<tbody>
<tr>
<td><strong>K40</strong></td>
<td>0.0</td>
<td>0.025</td>
<td>1.68</td>
<td>40</td>
<td>6.53 x 10⁻⁴</td>
<td>4.0</td>
<td>7.07</td>
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<tr>
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<td>41.8</td>
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<td>4.0</td>
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<td>5.5</td>
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<tr>
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<td>162.2</td>
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<td>5.3</td>
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<tr>
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<td>0.292</td>
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<td>40</td>
<td>6.54 x 10⁻⁴</td>
<td>4.0</td>
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<td>7.07</td>
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<td>7.07</td>
<td>18.6</td>
<td>0.242</td>
<td>0.181</td>
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NA: data not available