ARE PORE LINING CHLORITES A CAUSE OF LOW RESISTIVITY IN SANDSTONES?

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ABSTRACT

Low resistivity in argillaceous sandstone reservoirs may be attributed either to the effect of microporosity, or to specific effects due to clays and/or to conducting minerals. In the frame of a study on pore lining chlorite bearing sandstones, from different hydrocarbon reservoirs, measurements of cation exchange capacities and specific surface areas have been performed, on whole rocks as well as on size separated fractions. Both sets of values are low, in agreement with the structural and textural observations. The dielectric properties, including intrinsic conductivity, of these chlorites have been investigated, on size separated fractions, as a function of temperature, and compared to that of reference clays. The results show a large influence of the moisture, current frequency, and temperature on the electrical properties. The chemical composition and structure of the clays has an obvious influence as well. However, the range of conductivities is such that the intrinsic influence of clays on the conductivity of argillaceous sandstone is lower than that related to the presence of water by several orders of magnitude.

INTRODUCTION

In the frame of a Consortium study on pore lining chlorite bearing sandstones, formation resistivities have been found in the range 0.3 to 20 Ω.m, at depth, in the different hydrocarbon reservoirs made available by the partner companies. Laboratory experiments performed at room conditions on plugs selected from these reservoirs have shown that saturation exponents n drawn from resistivity index measurements are lower than the usual 2 value (Durand et al, 2000). The conclusions of the laboratory study were that the microporosity created by the texture of the chlorite pore lining had a major effect on the values of resistivity index, and that the cation exchange capacities (CEC) and specific surface area (SSA) effects were subordinated, due to the low values of these parameters. However, the question of the specific contribution of chlorite to low resistivity in sandstones was still open, due to poor documentation in literature. Moreover, the possible effect of temperature on these properties was not studied.

According to Worthington (2000), low resistivity in argillaceous sandstone reservoirs may be attributed either to the effect of microporosity, or to specific effects due to clays and/or to conducting minerals. Effect of CEC of usual clays, like smectite, illite and kaolinite, on resistivity measurements of sandstones has been widely studied in literature, and has contributed in the building of well known log interpretation models (Waxman and Smits,1968, Waxman and Thomas, 1974, Clavier et al, 1984, Raiga-Clemenceau et al., 1984, Revil et al., 1998 …). Even the models which do not deal explicitly with CEC (Poupon and Leveaux, 1984, Givens, 1991) assume a "clay conductivity". However these

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properties have not been studied widely on chlorites. On the other hand, iron-rich minerals, as pyrite (Clavier et al., 1976), and glauconite (Schultze, et al., 1985, Cook, et al., 1990) have been cited as causes of excess conductivity, but few data are available. Olhoeft (1979) gives values of conductivity at room temperature for a magnesian chlorite (6.3 10^{-10} S/m) higher than for muscovite (4.6 10^{-13} S/m), but lower than for glauconite or kaolinite (3.5 10^{-9} and 3.1 10^{-8} S/m). But chlorites have very large composition ranges, particularly concerning their iron content.
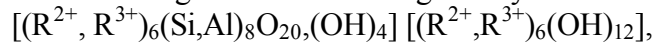
The purpose of the paper is
- to present experimental data of CEC, SSA and conductivity acquired on chlorites
- to compare them with reference clays of more widely studied minerals
  The final aim is to help using more appropriate values as input in log interpretation models. Meanwhile, the obtained data give insights on the fine structural properties of the chlorites coming from different origins.

THEORETICAL BACKGROUND
Structure of chlorite
The chlorite general formula is given by :
$[(R^{2+}, R^{3+})_6(Si,Al)_8O_{20},(OH)_4] [(R^{2+},R^{3+})_6(OH)_{12}]$,
where the first member is a talc-like sheet, the second member a brucite-like sheet, R^{2+} is the sum of the divalent cations (Mg, Fe), R^{3+} the sum of the trivalent cations (Al, Fe).

When Si is replaced by Al in tetrahedral sheet, as well as when R^{+2} is replaced by R^{+3} in octahedral sheet (either in the brucitic or in the talc-like sheet), charges are created. As substitution are of opposite sign in this case, the sum of these fixed charges can be low or null, and this explains a low charge, thus a low cation exchange capacity for chlorites. In addition to the fixed charge, variable charge is common to all mineral surfaces : it is due to broken bonds or defects at the surface, compensated by rearrangements with water molecules, creating OH groups, that may exchange for cations, but this CEC is usually very weak.

Conductivity measurements
Because of strong polarisation effects occurring at the blocking electrode/sample interface, dc conductivity of ionic materials has to be measured by means of complex impedance spectroscopy. Real and imaginary parts of the ac conductivity, $\sigma_{ac}^{*}(\omega)$, are then determined as a function of the electrical field pulsation ω. Assuming that ionic conductive samples can be represented by a RC parallel circuit, the real part of the conductivity, $\sigma_{ac}^{'}(\omega)$, is directly related to the conductivity or the dielectric losses $\varepsilon''(\omega)$ while the imaginary part, $\sigma_{ac}^{''}(\omega)$, corresponds to the real part of the permittivity, $\varepsilon'(\omega)$, which can allow us to assess the dielectric constant ε_r of the studied material.

Basically, dehydrated clays exhibit on the one hand poor dc conductivity σ_{dc} due to the low mobility of the cations trapped into the structure or due to the small amount of electron hopping between electronic defects – as for instance transition elements in substitution in the network- and on the other hand polarisation conductivity, $\sigma_{pol}^{'}(\omega)$ related to dipolar

relaxation. The later is frequency dependent. Consequently, these two contributions lead to express $\sigma'_{ac}(\omega)$ as (S.R. Elliott, 1994; F. Henn et al., 2000):

$$\boldsymbol{s}'_{ac}(\boldsymbol{w}) = \boldsymbol{s}_{dc} + \boldsymbol{s}'_{pol}(\boldsymbol{w}) \qquad [\text{eq. 1}]$$

When ω tends to zero, $\sigma_{pol}(\omega)$ becomes rapidly negligible and $\sigma'_{ac}(\omega)$ can tend to a frequency independent term σ_{dc} which is the inverse of the resistivity of the sample. However, σ_{dc} is not always detectable such as $\sigma'_{ac}(\omega)$ appears as resulting from the polarisation contribution only. It is well known, that, when ionic mobility is too high, interfacial polarisation effects due to the accumulation of ionic charges at the ionic sample/metallic electrode interface (S. Devautour et al., 1999-1), so called Maxwell Wagner polarisation, also occur at low frequency, making the exact determination of the dc conductivity quite difficult. (see fig. 4)

In this work, we attempted to measure σ_{dc} and the dielectric constant ε_r for a series of clays dehydrated at 105°C during 10 hours. We also measured the polarisation response of the sample, though for the sake of simplicity, no interpretation will be given in this article. When the determination of σ_{dc} was made possible, we measured its evolution upon temperature in order to estimate its activation energy $\Delta E_{\sigma_{dc}}$ accordingly to the Arrhenius law which derives from the Nernst-Einstein model (S.R. Elliott, 1998):

$$\sigma_{dc}(T) = \sigma_0 \exp(-\Delta E_{\sigma_{dc}} / kT) \qquad [\text{eq.2}]$$

The value of $\Delta E_{\sigma_{dc}}$ can shed some light on the mechanism responsible for σ_{dc}. Likewise, the value obtained for ε_r may lead to distinguish between conductivity due to ion or electron displacements. At a first sight, ionic conductor are expected to exhibit lower $\Delta E_{\sigma_{dc}}$ and higher ε_r because of the larger dipolar momentum associated to ionic bonds.

EXPERIMENTAL
Sampling
     Reference clays were chosen among the Clay Mineral Society repository:
- Kga-1 is a well crystallised kaolinite
- Imt-1 is a ferriferous illite,
- Cca-1 is a ferriferrous chlorite, as such it is the closest to the reservoir chlorites, despite differences in origin and polytype.

   The reservoirs samples come from six different localities. The water zones have low R_w (0.01 to 0.04 Ω.m, at temperatures ranging from 55 to 160°C), indicating salty brines (from 60,000 to 300,000 ppm equivalent NaCl) in the first five cases, the last being less salty. The resistivity of the formations is in the range 0.3 to 20 Ω.m.

The reservoir samples were cleaned with fresh water and Soxhlet extraction with dichloromethane. Concentration of clay fraction was performed by sedimentation after cleaning, and resulted in "raw" fractions < 2 µm or 2-5 µm, some of them containing still some impurities, illite in major part. The quantity of chlorite was determined in these fractions by data reconciliation (Durand et al., 2001), and the results allowed to calculate the specific contribution of chlorite for the properties measured on these fractions. The structural formulae of the chlorites have been determined by Energy Dispersive

Spectrometry (EDS) in a Scanning Electron Microscope (SEM) (Durand et al., 2001) and are given in Table 1.

CEC and SSA determinations were performed on several grams of gently disaggregated whole rocks and fine fractions, and for checking purpose, on some reference clays. The SSA was determined by BET adsorption of N_2 after degassing at 60°C under a vacuum in a Micromeritics ASAP 2405 Kr. The CEC was determined by the cobaltihexamine method (Bardon et al., 1983).

	LS1 well	S1 well	D1-D2 wells	J1 well	T1 well	C1-C5 wells	Cca-1
Formation	Lower Silurian	Strunian (Upper Devonian)	Lower Devonian	Jurassic	Tertiary	Cretaceous	Reference CMS
Location	Libya	Algeria	Algeria	North Sea	North Sea	Argentina	
Si	**5.55**	**5.70**	**5.30**	**5.49**	**6.08**	**6.03**	**4.51**
Al IV	**2.45**	**2.30**	**2.70**	**2.51**	**1.92**	**1.97**	**3.49**
Al VI	3.43	3.36	3.18	3.45	3.12	3.80	0.6
Mg	**1.36**	**1.35**	**1.10**	**1.76**	**2.84**	**3.91**	**4.44**
Fe^{2+}	**6.71**	**6.76**	**7.46**	**6.18**	**5.43**	**3.35**	**3.02***
Ca	0.03	0.07	0.04	0.04	0.08	0.05	0.05
Ti	0.01	0.01	0.00	0.02	0.00	0.02	0.06
K	0.04	0.01	0.04	0.04	0.00	0.03	
Na	0.05	0.01	0.02	0.04	0.00	0.00	

Table 1. Structural formulae of the reservoir chlorites(*the Cca-1 formula holds 3.47 Fe^{3+} in addition)

The conductivity measurements were performed on fine fractions of reservoir rocks, and on reference clays. They were carried out on disc-shaped pellets (thickness˜1mm and diameter=13mm) made from clays powders pressed under about 5 tons. Gold electrodes were deposited by sputtering on both parallel faces. The pellets were placed in between the 2 parallel metallic electrodes of the dielectric spectrometer cell (Model Novocontrol BDS-4000) and their conductivity measured in air at room temperature from 10^{-2} to 10^6 Hz. Then, the sample were dehydrated, in-situ, under dry nitrogen at 105°C during 10 hours. Finally, the conductivity was recorded each 10 degree from 105°C to –55°C. The exact same procedure was applied to each clay.

RESULTS
CEC and SSA
Results obtained on whole rocks and fine fractions are shown in figures 1 and 2. In the whole rocks, the values are low and do not show a clear correlation between the two sets of data. The most obvious reasons may be the different amounts and nature of clays present in the whole rocks (between 3 and 11 wt-% chlorite, and 0 to 3 wt-% illite). In the "raw" fine fractions, including some impurities, correlations, slightly different, may be found for each field. The y ordinate at origin is about 10 m^2/g, that would correspond to the surface area of particles 2 μm diameter, 0.1 μm thick, without any CEC. The overall correlation, including all samples, is:

$$SSA\ (m^2/g)\ \#\ 200 * CEC\ (meq/g) + 10$$

To make comparisons clearer, values of CEC and SSA were calculated for "pure" minerals, chlorite and illite, taking into account the composition of the fine fractions, as

determined from data reconciliation (Durand et al., 2000). Results are given in Table 2 and Figure 3, together with values drawn from the literature. The CEC value found for the Cca-1 sample was 4.6 meq/100 g, for Kga-1, 3.4 meq/100 g, which are in the expected range. The correlation for chlorite is fairly good, and gives the following relationship:

$$SSA (m^2/meq) = 219 * CEC (meq/g) + 8 \text{ , with } R^2 = 1$$

Or $$SSA (m^2/meq) = 289 * CEC (meq/g), \text{ with } R^2 = 0.92$$

The one for illite is less good, and the correlation coefficient would be 400, with $R^2 = 0.41$.

	CEC Chlorite meq/100g	SSA Chlorite m^2/g	CEC Illite meq/100g	SSA Illite m^2/g
LS1	2	6	69	
S1	5	20	54	50
D2	2	9		
J1		5		67
T1	12	35	26	62
C1-C5	14	39	20	134

Table 2: Values of CEC and SSA calculated for "pure" chlorite and illite from each field

Finally, we calculated the CEC and SSA that should be those of the whole rocks, if only chlorite and illite, having the CEC and SSA values determined from fine fractions for « pure » minerals, gave rise to these parameters, in the ratios present in the whole rock, as calculated from data reconciliation (Durand et al, 2000). If the calculated CEC values stay in the same range as the measured ones, the SSA are substantially higher in several cases.

Conductivity

Typical conductivity spectra before and after dehydration are shown in Figure 4. As expected, $\sigma'_{ac}(\omega)$ exhibits both a dc and polarisation contribution according to eq. 1.

It is clearly seen that the presence of water molecules strongly enhances the dc conductivity which turns out to be in the range 10^{-9} to 10^{-11} $\Omega^{-1}.m^{-1}$. It is difficult to draw conclusions from conductivity recorded in air since it depends much on the relative humidity. When dehydrated, the dc conductivity becomes much lower, about 10^{-14} $\Omega^{-1}.m^{-1}$, (case of Chlorite) or totally vanishes (cases of Illite and Kaolinite) in the explored frequency range. These results obviously indicate that water molecules are preferentially adsorbed on the cationic sites (H^+, Na^+….), making their mobility much higher. This effect is well known and has been already reported in clays and zeolites where Si substitution is compensated by cations (Chabanis et al., 1997). Further, it points out that conductivity is mainly ionic since water does not usually influence very much the bulk conductivity of electronic semi-conductors. Moreover, the non negligible Maxwell-Wagner polarisation contribution observed on the hydrated sample (see Fig. 4) is a clear evidence for an important ionic diffusion . They also confirm that the conductivity of clays measured in air can be considered as only due to the effect of the adsorbed water and not from their intrinsic properties. Likewise, these results show unambiguously that the low resistivity (in the order of 1 Ω.m) reported in argillaceous sandstone reservoirs is due to the important amount of absorbed water. In such case, it would be more appropriate to speak about the conductivity of the liquid phase trapped in the porosity of the sandstone rather than about the conductivity of the sandstone itself which is roughly 10^{14} lower. Apart from the porosity parameters of the sandstone, the change in conductivity would be directly linked to the nature of the trapped liquid and to the concentration of cations released into the brine which can be readily estimated from the CEC.

A comparison of the dehydrated samples conductivity, measured at 105°C is given in Figure 5. It can be seen that Chlorites have intrinsic conductivity higher than the Illite and Kaolinite reference samples which only show polarisation conductivity. It is noteworthy to report that two reservoir chlorites, namely T1 and LS1 exhibit exactly the same conductivity over the whole frequency range and that the reference chlorite is the most conductive material. At 25°C, dehydrated clays behave as insulating materials, the polarisation conductivity being, at low frequency, in the order of 10^{-14}-10^{-17} $\Omega^{-1}.m^{-1}$. This clearly emphasises that the charge mobility, whatever it is electrons or ions, is very low and cannot account for the conductivity measured in wetted sample. The evolution of the logarithm of $\sigma'_{pol}(\omega)$ which, as a function of frequency, is not strictly linear indicates that dielectric relaxation phenomena occur. These relaxations can be associated to local ion or water molecules re-orientational processes. This aspect will be analysed in a future article.

The temperature dependence of $\sigma'_{ac}(\omega)$ of the reference Chlorite is reported in Fig.6, where a constant increase of the dc conductivity contribution with T is observed. The Arrhenius plot (Fig. 7) is linear and consequently allows us to determine the activation energy $\Delta E_{\sigma_{dc}}$ to be equal to 0.58 eV. This rather low value would attest that the dc conductivity arises from ionic displacement. Indeed, it is usually known that, in such insulating materials, electronic conductivity resulting from point charge defects would yield much higher $\Delta E_{\sigma_{dc}}$ values (>1eV). However, it is generally thought that activation energy as low as about 0.6 eV leads to much higher dc conductivity. The poor conductivity exhibited by Chlorites would then be due to an extremely low concentration of mobile cations. This assumption is confirmed i) by the very low CEC (Table 2), e.g. only a very few number of cations can migrate and be exchanged and ii) by the low value of the dielectric constants, ε_r, that we measured to be comprised between 2 and 7 (2.2 for the reference chlorite). To sum up, it can be concluded that intrinsic dc conductivity of Chlorites is mainly ionic, but very poor because of the extremely low concentration of mobile charge.

The last point we would like to underline is that depending on the dc conductivity level, on the nature of the charge carriers and finally on the sample/electrode interfaces, it can be clearly viewed that the overall behaviour of $\sigma'_{ac}(\omega)$ varies a lot as a function of the frequency. It is therefore very difficult to rely on single frequency impedance analysis to compare measurements carried out on different samples. For instance, at 1KHz, $\sigma'_{ac}(\omega)$ can be associated either to the dc conductivity or to the polarisation conductivity as well as to the interface polarisation effects. Solely, the determination of the conductivity over a broad frequency range can lead to select the "true" frequency which corresponds to the dc conductivity. This "true" frequency is not a constant but changes from sample to sample. It also varies with the experimental conditions, i.e. temperature and humidity.

DISCUSSION

CEC and SSA

The values found for CEC and SSA for "pure" chlorite and illite are rather low. The low values of CEC are in agreement with the structural data. It is interesting to notice that the most ferriferous chlorites have the lowest CEC, and even SSA, values. This might be related to the nature of their precursor, and to the degree of crystallinity (Durand et al, 2001). These values are in the range found in the literature for the kaolinites and the illites, respectively. The correlation coefficients found for the "raw" fine fractions and for the "pure" chlorite and illite in the studied reservoirs are lower than the 450 value recommended by Patchett (1975) and Clavier et al. (1984).

To investigate more thoroughly the comparison with reference data, two sets of data were plotted in the same manner (Figure 3) :
- the values of CEC and SSA found on API reference clays (smectites, illites, kaolinites) (Diamond and Kinter, 1958), SSA measured by glycerol adsorption, taking into account the total (external + internal) surface area, or only the external one,
- the values given by the CMS (van Olphen and Fripiat, 1979) for smectite and kaolinite reference clays, SSA obtained either by glycerol or by nitrogen adsorption

Obviously, the correlation closer to the popular 450 value is found with the API clays total glycerol surface area (477 m^2/meq, with R^2=0.89), while the values obtained on CMS clays by glycerol adsorption is 750, with R^2=0.99, and the CMS clays by N_2 adsorption 66, with R^2=0.72, no relationship being found for external surfaces for API clays. If the correlation is not forced to origin, the y ordinate is between 8 and 26 m^2/g. If the correlation is calculated for the same reference clays over only the kaolinite and illite samples, even with glycerol, the coefficient becomes 288, with a y ordinate 11m^2/g, quite the same as the one found for the reservoir chlorites.

Such results are related to the fact that the glycerol is one of the best swelling agent for smectites, and the reference clays selected by Diamond and Kinter (1958) were < 0.2 μm fractions. But such surface area values are accessible only for dilute suspensions of clay minerals in nearly pure water. It is known from the work of Norrish (1952) that smectite layers collapse with increasing concentration of clay and salt, so that the accessible surface turns to the external surface in most cases, e.g. when the brine is salted over about 20 g/l equivalent NaCl. For non smectite clays, there is no internal surface, use of correlation coefficient obtained for swelling clays surface areas obtained by glycerol leads to overestimation of the clays effect.

On the other hand, chlorite behaviour is quite comparable to that of reference kaolinite and illite, while the illite found in the chlorite reservoirs show a more dispersed behaviour, that may be related to a mixed layering including some swelling compound in the C1-C5 case.

A first conclusion is that when using log interpretation formulae, one should check what kind of clay is present, and in which brine it is. From the present results, and those of the non-smectite reference clays, a correlation coefficient about 200 m^2/meq seems a good choice, for non smectitic clays, with a constant value of 10 m^2/g for samples of clay size without CEC.

The results of the calculation of CEC and SSA of whole rocks from amount of clays and pure minerals values are widely spread. Some reasons have already been mentioned in former works (Patchett, 1975): representativity of the size separated fractions, and loss of material during the separation. These are actual problems: we have indeed checked that chlorite particles remain stuck on quartz grains, and that the balance of fractionation can only in limited cases be acceptable. That is also the reason why we used rather coarse fine fractions, having observed in the SEM that chlorite particles were larger than 1 μm, and sometimes up to 10 μm, while illite may be smaller, mainly in a fibrous habit. Other reasons for the poor agreement may be the poor precision of the data, but the fact that the SSA data are mostly higher is not only a statistical spreading. A bad estimation of the illite vs chlorite proportion, illite developing more SSA may be invoked, mainly in the C1-C5 case. In the other cases, another likely explanation is that even gentle disaggregation procedures create extra surfaces, so that "fine fractions" , either of reference clays, or from our size separations, overestimate the surfaces.

So care should be taken when using straightforward calculation of CEC and SSA for whole rocks from pure minerals data: such a procedure can lead to overestimated effects.

Conductivity measurements

We have discussed in the previous chapter the ionic nature of the intrinsic conductivity and the reasons of its fairly poor level. We have also clearly demonstrated the influence of the water molecules. Therefore, it seems more than reasonable to assume the clays investigated in this work as insulators and to exclude the influence of their conductivity on the resistivity measured in the water saturated rocks. The latter has to be associated with the CEC and with the porosity rather than with the intrinsic property of the materials. Of course, though the influence of water can be qualitatively pointed out, further investigations are needed to get more information. For instance, it would be relevant to study the variation of dc conductivity with the exact water pressure. Then, accurate comparison between the different samples could be achieved. Also, the influence of other adsorbed molecules, more or less polar, would help to shed some light on the conductivity mechanism (Abdoulaye et al., 2000).

We aim now at observing and understanding the variations observed between these different clays. It appears (Figure 8), by comparing the data in Figure 5 and in Tables 1 and 2, a clear correlation between the nature and the concentration of the substituting elements (Mg, Fe, Al) and the electrical behaviour. The higher the difference between the concentration of Al in tetrahedral sites and the concentration of $(Al^{3+} + Fe^{3+})$ in octahedral sites, the higher the dc conductivity and the lower the activation energy $\Delta E_{s_{dc}}$. A general qualitative interpretation can then be proposed. As far as we know, only theoretical calculations, as it has been done in zeolites (G. Maurin et al, 2001) could allow us to verify quantitatively the following assumptions. The ionic mobility, hence the dc conductivity, is directly associated to the strength of the interaction between cations in the clay network. At a first stage, we can conclude that the difference between the excess of negative charge due to tetrahedral Al and the excess of positive charge brought by trivalent elements, i.e. mainly Al or Fe^{3+}, in the octahedral layer, and the localisation of these charges among the two octahedral layers of the chlorite governs the mobility of the cations, thus the activation energy, thus the conductivity. A more accurate examination of these data could be done if the exact repartition Fe^{2+}/Fe^{3+} in octahedral sites was known.

The same trends have been observed in zeolites where it was reported that the activation energy associated to the ionic displacement depends on the Si/Al ratio (M. Pemba et al, 2000). Attempts to qualitatively and quantitatively interpret this trend can be done based on the Electronegativity Equalisation Method (W.J. Mortier, 1987; S. Devautour et al., 1999-2)

CONCLUSION

This study has provided SSA and CEC data for chlorite, that are consistent with the structural formula and texture of the chlorite. These data may be used for application of interpretation log formula that take into account their contribution.

Conductivity data have shown the influence of moisture, frequency and temperature on the conductivity of clay minerals. The conductivity appears to be related to the charge compensation arising from cations substitution within the cell of the clays.

However, the range of conductivities is such that the intrinsic influence of clays on the conductivity of argillaceous sandstone is lower than that related to the presence of water by several orders of magnitude, even in nearly pure water.

ACKNOWLEDGMENTS

NOMENCLATURE
σ'_{ac}, σ_{dc} and σ'_{pol} are defined as the ac , dc and polarisation conductivity respectively.
ω is the pulsation or the frequency of the ac electric field.
$\Delta E\sigma_{dc}$ is the activation energy for the dc conductivity.

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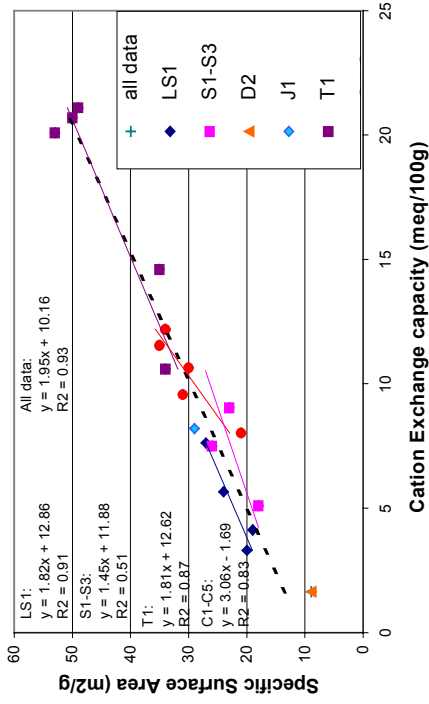
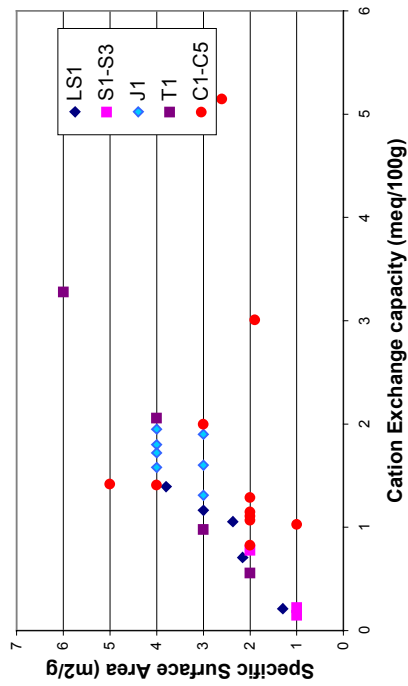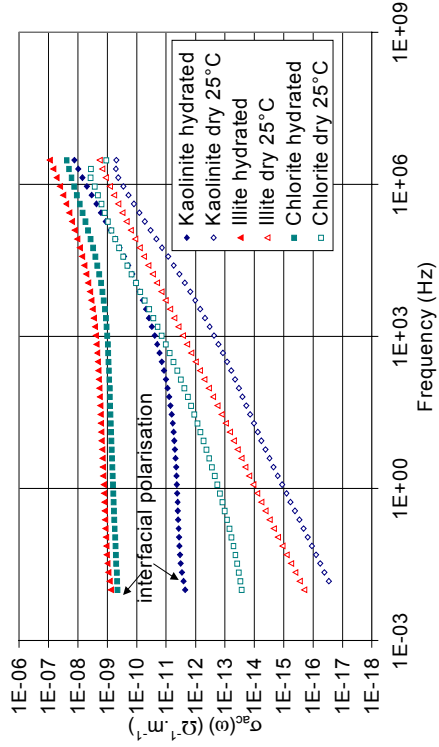Figure 2: Measured CEC and SSA values on Fine fractions

Figure 4: Comparison of the ac conductivity values of the reference clays, hydrated and dehydrated.

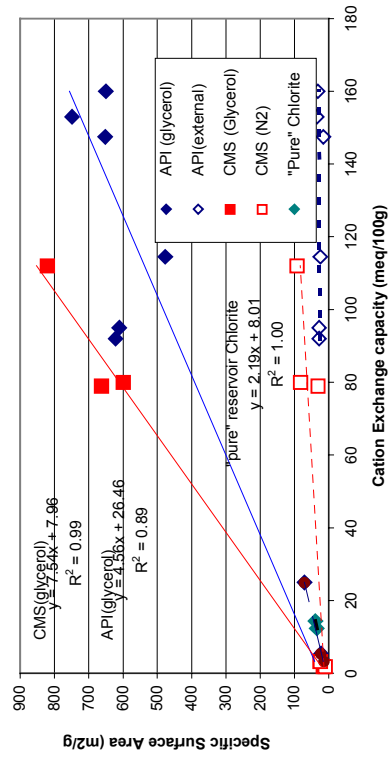

Figure 1: Measured CEC and SSA values on Whole rocks

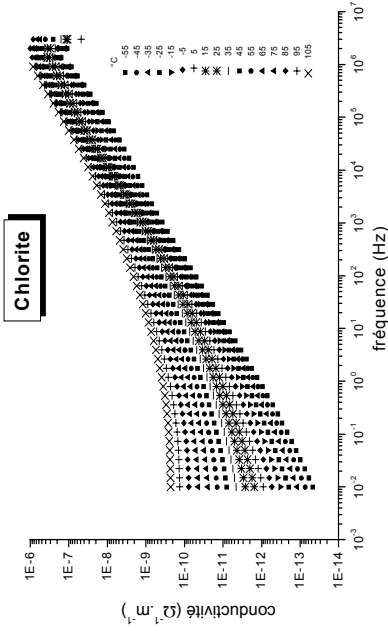Figure 3: Calculated values of CEC and SSA for « pure » reservoir chlorites, compared with values of reference clays in literature

Figure 6: ac conductivity of the reference Cca-1 chlorite as a function of temperature
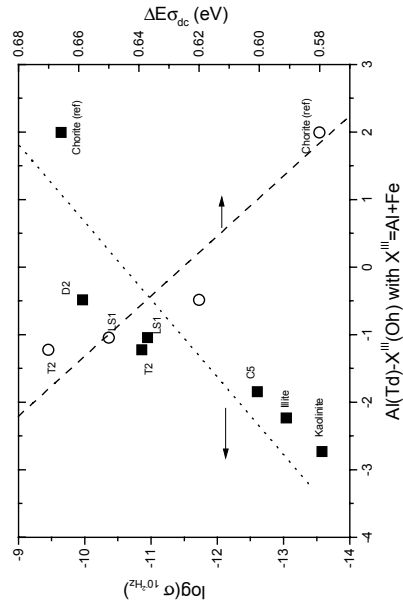
Figure 8: Correlation between the conductivity at 10^{-2} Hz or the dc conductivity activation energy and the X^{3+} cations distribution between tetrahedral and octahedral sites
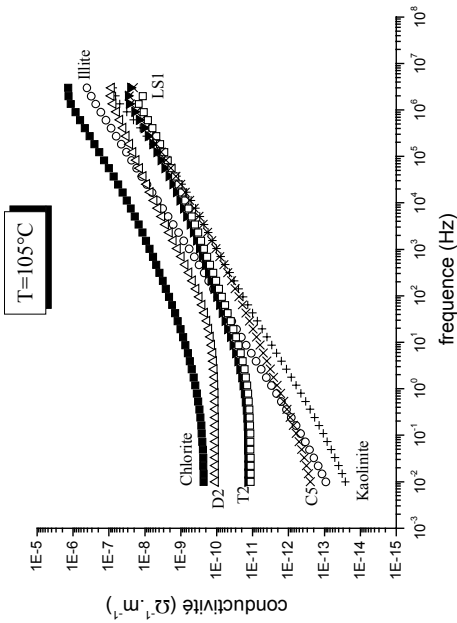
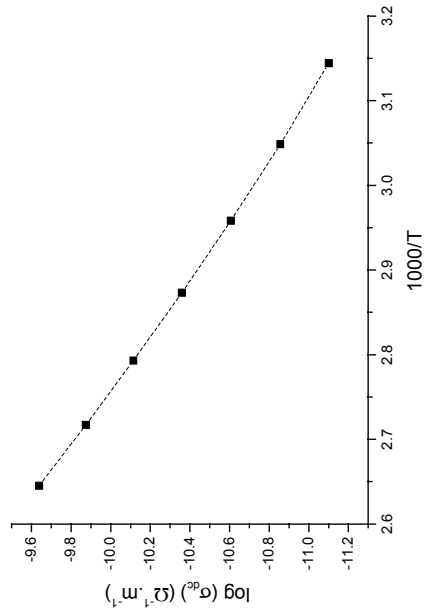Figure 5: ac conductivity measured at 105°C under dry N_2

Figure 7: Evolution of the dc conductivity as a function of temperature. (Cca-1 chlorite)