Modelling the electrical conductivity of iron-rich minerals for planetary applications

P. Vacher*, O. Verhoeven

Laboratoire de Planéétologie et Géodynamique, UMR-CNRS 6112, Université de Nantes, 2 rue de la Houssinière 44322 Nantes cedex3, France

Received 17 December 2004; received in revised form 26 September 2006; accepted 2 October 2006

Available online 4 December 2006

Abstract

In the framework of in situ exploration of planetary interiors, electromagnetic survey is one of the geophysical methods constraining the structure and composition of the mantle. One of the main parameters which governs the internal structure is the bulk iron content of the mantle. Unfortunately, the effect of iron on the electrical conductivity of mantle minerals is only known through a few high-pressure and high-temperature experiments. Reliable measurements on samples with different iron contents were reported for olivine, pyroxene, magnesiowustite and perovskite/magnesiowustite assemblage. In a first part, we parameterize the effect of iron on the electrical conductivity of these minerals. In a second part, we propose assumptions to extend this formulation to all minerals considered by the review of Xu et al. [2000b. Laboratory-based electrical conductivity in the Earth’s mantle. J. Geophys. Res. 105, 27865–27875], in order to extrapolate the conductivity of terrestrial samples (i.e. with iron fraction close to 10%) to the conductivity of iron-rich minerals (up to 40%). In a third part, we apply this formulation to the computation of a synthetic electrical conductivity profile of the Martian mantle. The computed conductivity profile is 1–1.5 order of magnitude higher than terrestrial profiles, because of the higher iron content of the Martian mantle. This result highlights the possible application of electrical conductivity for constraining the composition of planetary mantles.

Keywords: Electrical conductivity; Minerals; Planetary mantle; Mars

1. Introduction

A first order description of planetary interiors can be obtained using bulk observables of the planets, like total mass and moments of inertia. A more precise knowledge can be derived from in situ geophysical exploration, with measurements of geodetic anomalies, seismic waves travel times, or components of the magnetic field. On Earth, early seismic measurements revealed the size and physical state of its different internal layers. More recently, interpretations of mantle seismic profiles (see e.g. Duffy and Anderson, 1989; Cammarano et al., 2003), and of electrical conductivity profiles (see e.g. Dobson and Brodholdt, 2000a; Xu et al., 2000b) have proved to be successful for refining the thermal profile and composition of the mantle. Apart from the Earth, detailed geophysical surveys have been undertaken on the Moon. Seismic travel times measured in the seventies have recently been reinvestigated and lead to a smaller value of the crustal thickness (Khan and Mosegaard, 2002; Lognonné et al., 2003). Magnetometer data have been interpreted in terms of lunar thermal structure, using assumptions about its composition (e.g. Duba et al., 1976; Hood et al., 1982). Finally, Mars and Mercury are the future target planets for in situ and/or orbital geophysical explorations which are expected to provide a large amount of new data (Harri et al., 1999; Gold et al., 2001; Dehant et al., 2004).

Each kind of geophysical data requires specific methods to be inverted and interpreted in terms of planetary structure. But one can reasonably believe that a joint inversion of all data should be more powerful. For instance, the complementarity between seismic and electromagnetic data has been demonstrated by Mocquet and Menvielle (2000) in the framework of a network science mission deployed on
Mars. An interdisciplinary group of researchers has recently developed a global method to invert simultaneously various geophysical data sets, to get a better insight into the thermal structure and composition of any telluric planet (Verhoeven et al., 2005). The bulk iron content of the planet is one of the key parameters. It has been shown to be close to 10% for the Earth’s mantle, but is supposed to be around 25% for the Martian mantle, using the SNC composition as a guide (e.g. Dreibus and Wänke, 1985).

Therefore the inversion process proposed by Verhoeven et al. (2005) has been designed in order to recover this parameter from the data. The way density and seismic velocities (in fact elastic moduli) depend upon iron content has been experimentally investigated for many minerals (e.g. reviews in Duffy and Anderson, 1989; Cammarano et al., 2003; Stixrude and Lithgow-Bertelloni, 2005). Combinations of electrical conductivity of various minerals exist (e.g. Lastovickova, 1991; Tyburczy and Fisler, 1995; Xu et al., 2000b; Nover, 2005), but the effect of iron-content on these conductivities has never been investigated.

In the present paper we propose a simple empirical formulation of the electrical conductivity as a function of iron content. In a first part, we use the few experimental measurements of the electrical conductivity of iron-rich olivine, pyroxene, magnesiowüstite and a perovskite/magnesiowüstite assemblage to build a unique formulation of the effect of iron on the electrical conductivity. In a second part, we propose assumptions to extend this formulation to all minerals considered by the review of Xu et al. (2000b), in order to extrapolate the conductivity of terrestrial samples (i.e. with iron fraction close to 10%) to the conductivity of minerals in planetary mantles, i.e. with higher iron fractions (up to 40%). In a third part, an example of how to use this formulation is shown, based on the Martian mantle model of Bertka and Fei (1997).

2. Review of available experimental data

2.1. Theoretical considerations

Minerals and oxides are semi-conductors at conditions relevant to planetary interiors. Their electrical conductivity \( \sigma \) is due to the diffusion of charge-carrying species, and can be expressed through the Nerst–Einstein equation (e.g. Tyburczy and Fisler, 1995):

\[
\sigma = D z^2 e^2 n/kT ,
\]

where \( D \) is the diffusion coefficient, \( z \) is the valence of the conducting species, \( e \) is the charge of the electron, \( n \) is the concentration of the conducting species, \( k \) is Boltzmann constant and \( T \) is temperature. Since diffusion is a thermally activated process, the electrical conductivity of minerals is classically expressed as

\[
\sigma = \sigma_0 e^{-E/kT} ,
\]

where \( \sigma_0 \) is the preexponential constant and \( E \) is the activation energy. In principle, values of \( \sigma_0 \) and \( E \) could be derived from diffusion experiments, which are numerous for mantle minerals (e.g. Gautason and Muehlenbachs, 1993; Brady, 1995). Alternatively, electrical conductivity parameters can bring new constraints on conducting species diffusion, through the so-called compensation law (e.g. Wu and Zheng, 2003). In practice, the \( 1/T \) factor in the preexponential term is often omitted when direct measurements of electrical conductivities are performed. However, different behaviors in the electrical conductivity as a function of temperature are reported for some minerals, and Eq. (2) is then replaced by

\[
\sigma = \sum_{i=1}^{n} \sigma_{0,i} e^{-E_i/kT} ,
\]

where \( \sigma_{0,i} \) and \( E_i \) are the preexponential factor and activation energy of the \( i \)th conduction mechanism, respectively. If the temperature range under consideration is sufficiently large, this sum of different conduction mechanisms may result in a change of slope, or in a nonlinear curve, in Arrhenius diagrams (log(\( \sigma \)) versus \( 1/T \)).

In the present paper we propose to approximate the electrical conductivity of minerals with only one conduction mechanism. The reasons are detailed in the following, based on experiments performed on olivine, probably the most common mineral in planetary mantles, and on experiments made on phases of the Earth’s lower mantle, perovskite and magnesiowüstite. Consider first experiments on olivine samples. Many studies found a strong electrical anisotropy in olivine crystals, and log(\( \sigma \)) versus \( 1/T \) plots with changing slopes, depending on the crystallographic orientation (see e.g. Schock et al., 1989; Constable et al., 1992). The latter authors proposed a model for isotropic olivine between 720 and 1500°C, made of two different contributions (low and high temperature, dotted lines in Fig. 1), named SO2. The total conductivity (thin solid line in Fig. 1) has a very small, negligible, change in slope towards high temperatures. More recently, the same group of researchers reported new experiments also showing a linear trend between 1000 and 1400°C (Xu et al., 2000b). For comparison, experiments on olivine with various iron contents are also shown in Fig. 1 (thick solid lines, Hinze et al., 1981). Clearly, the effect of changing the iron content is much larger than the consideration of different temperature-dependent conduction mechanisms through a sum of Arrhenius expressions. The discrepancy between the experiments made by Hinze et al. (1981) and others can be due to a different oxygen fugacity control (solid \( f_O \) buffer mixture, versus CO/CO2 gas mix) or to different starting materials (synthetic versus natural crystals). The possibility to get rid of these discrepancies will be discussed in the following sections. Concerning phases of the Earth’s lower mantle, a pragmatic approach leads to consider only one conduction mechanism: magnesiowüstite has been
shown to have two very different electrical conductivities, below and above 1000 K (Dobson and Brodholdt, 2000b). Since it cannot be stable in any planetary mantle at temperatures below 1000 K (see e.g. Ito and Takahashi, 1989), only the high-temperature mechanism will be considered. The most recent experiments in perovskite conductivity have clearly identified two different mechanisms, electron hopping at low temperatures and ionic conduction at high temperatures (Xu and McCammon, 2002). However, the sum of the two mechanisms results in a linear trend in the log($\sigma$) versus $1/T$ plot identical to the former, unique, Arrhenius law (Xu et al., 2000b). Xu and McCammon (2002) therefore give a better understanding of the physical causes of electrical conductivity of perovskite as a function of temperature, but the single expression of Xu et al. (2000b) equally explains the data. Based on this review for olivine, perovskite and magnesiowüstite, we will therefore assume in the following a single Arrhenius law to explore the effects of iron content on electrical conductivity.

2.2. Experimental data with various iron contents

In order to get a mineral data set consistent with density and elastic parameters, the dependence of electrical conductivity upon iron content is expressed through the variable $X$

$$X = \frac{\text{Fe}}{\text{Mg} + \text{Fe}},$$  

where Mg and Fe are atomic concentrations of magnesium and iron in the sample, respectively. Eq. (3) with one single conduction mechanism can be expressed as a function of $X$ as

$$\sigma(T, P, X) = \sigma_0(X)e^{-\Delta U(X)/kT},$$

where $\Delta U$ and $\Delta V$ are activation energy at atmospheric pressure and activation volume, respectively (see, e.g., Xu et al., 2000b). For low-pressure phases (low pressure phases include here phases stable at pressure smaller than 23 GPa, corresponding to the upper mantle in the Earth), reported values of $\Delta V$ (see Xu et al., 2000a for olivine and Lacam, 1985 for ringwoodite) lead to a negligible effect of pressure compared to the effects of temperature and iron content. Therefore values of $\Delta V$ will be given only for high-pressure phases, for which pressure leads to a noticeable effect.

Reliable measurements on mineral samples with different iron contents were reported for olivine (e.g. Hinze et al., 1981), pyroxene (e.g. Seifert et al., 1982), magnesiowüstite (e.g. Dobson and Brodholdt, 2000b), perovskite (Peyronneau and Poirier, 1989) and for a perovskite/magnesiowüstite assemblage (e.g. Shankland et al., 1993). Paying attention to use measurements relevant for each mineral to the same buffering technique, we have investigated the effect of iron on the three parameters of Eq. (5) which can possibly be iron-dependent: $\sigma_0(X)$, $\Delta U(X)$ and $\Delta V(X)$.

In Fig. 2 are shown fits of the experimental values of log($\sigma_0(X)$) as a function of log($X$) (left), and of the values of the activation energy $\Delta U(X)$ as a function of $X$ (right). Each line deals with a different phase, namely olivine, pyroxene, high-temperature magnesiowüstite and a magnesiowüstite/perovskite assemblage. Several general observations can be made before studying phases independently.

- The choice of the logarithmic scale for the iron dependence of $\sigma_0$ is based on theoretical considerations: the electrical conductivity is proportional to point defect concentration, which is itself proportional to given power $z$ (different for each mineral) of $X$ for iron-bearing phases (e.g. Tyburczy and Fisler, 1995). Corresponding linear trends appear clearly in Fig. 2 (left). For all phases except pyroxene, log($\sigma_0$) increases linearly with log($X$) whereas it decreases linearly for pyroxene of Seifert et al. (1982).

- To our best knowledge, the iron content dependence of the activation energy has not been modelled yet at the atomic scale. Therefore, we merely estimate empirical trend by a linear fit $\Delta U(X)$ (right column of Fig. 2). For all phases except magnesiowüstite, $\Delta U$ decreases with iron content.

- Regarding the lack of any reported experiment demonstrating a noticeable effect of iron on $\Delta V$, this dependence will be ignored.

We now focus on the details of the computation, for each phase, of $z = \frac{d\log(\sigma_0)}{d\log(X)}$ and $\beta = \frac{d\Delta U}{dX}$ from the linear fit of log($\sigma_0$) with respect to log($X$) and $\Delta U$ with respect to $X$, respectively. Experimental uncertainties
were taken into account in the least square fitting (Press et al., 1992). They are typically of the order of a few percent (e.g. Dobson and Brodholdt, 2000b). When the authors did not report any uncertainty, we supplied an estimated error of 10% on both $\log(\sigma_0(X))$ and $\Delta U(X)$.

A systematic study of the electrical conduction of Fe-bearing synthetic olivine under defined thermodynamic activities has been performed by Hinze et al. (1981) at temperatures between 600 and 1373 K. Their measurements of $\sigma_0(X)$ and $\Delta U(X)$ for samples with $X = 10\%$, 20\% and 40\% (Fa/Q/M buffer) can be fitted with $a = 2.42 \pm 0.18$ and $b = -0.48 \pm 0.25$. These values are different from the values of $a = 1.81 \pm 0.02$ and $b = 0$ reported more recently by Hirsch et al. (1993). The origin of this different is probably twofold: first, the latter authors fit their data with a $1/T$ factor in the preexponential term (Eq. (2)) and second, their measurements were performed in the temperature range 1423–1573 K, which is probably too narrow to discriminate the effect of iron on both $\sigma_0$ and $\Delta U$. A more detailed comparison of our formulation with the results of Hirsch et al. (1993) is provided in the next section.

Electrical conductivity of synthetic pyroxenes under defined thermodynamic conditions were measured by Seifert et al. (1982) at 1 and 2 GPa and between 773 and 1273 K. Studying the effect of iron on $\sigma_0(X)$ and $\Delta U(X)$ on samples with $X = 10\%$, 20\% and 50\%, we find that $x = -1.28 \pm 0.51$ and $\beta = -1.41 \pm 0.35$. To our best knowledge, this study on synthetic pyroxene is the only experiment on samples with an iron fraction significantly different from 0.1.

In a recent paper, Dobson and Brodholdt (2000b) investigated the conductivity of magnesiowüstite up to 10 GPa and 2000 K. They isolated two dominant conduction mechanisms, depending on temperature. For temperatures higher than 1000 K, which corresponds to the stability domain of magnesiowüstite in planetary mantles, the dominant mechanism is a large-polaron process. Among the various samples used in their study, an homogeneous set is found with iron content varying between 4\% and 20\% and a constant ferric iron concentration around 4\%. Dobson and Brodholdt (2000b) fitted their data on a modified Arrhenius law, with a power law temperature dependence in the preexponential term. We have therefore recomputed their data for sampled temperatures within the experimental range of (1000, 2000 K) to get the values of $\sigma_0(X)$ and $\Delta U(X)$ for Eq. (5). The power dependence of $\sigma_0(X)$ is clearly visible in Fig. 2 and we calculated that $a = 3.14 \pm 0.07$. The effect of iron on the activation energy cannot reasonably be
constrained by the available data as can be seen on the linear fit of $\Delta U(X)$. Therefore we assume that there is no clear effect of the iron content on the activation energy of magnesiowüstite at high temperature, i.e. $\beta = 0$.

In a series of papers (Peyronneau and Poirier, 1989; Poirier and Peyronneau, 1992; Shankland et al., 1993; Poirier et al., 1996; Goddatt et al., 1999), Poirier and collaborators studied the electrical conductivity of perovskite and a perovskite–magnesiowüstite assemblage between room temperature and 673 K at 40 GPa. The assemblage was prepared from natural olivines with iron fractions between 11% and 20%. Among all their results for the assemblage, we have chosen to study their conductivity between 11% and 20%. Among all their results for the room temperature and 673 K at 40 GPa. The assemblage collaborators studied the electrical conductivity of perovskite–magnesiowüstite with different oxygen fugacity dependences, reported two different conduction mechanisms in San Carlos olivine with different oxygen fugacity dependences, but no effect along [0 0 1]. Wanamaker and Duba (1993) found a one order of magnitude change in conductivity which is more than one order of magnitude greater than the prediction of Hirsch et al. (1993). The two formulations agree very well for temperatures below 1500 K and for iron contents below 30%. At higher iron content, our formulation predicts a conductivity which is more than one order of magnitude greater than the prediction of Hirsch et al.

Concerning olivine, we can now compare our formulation of the conductivity of olivine to the formulation of Hirsch et al. (1993). The two formulations agree very well for temperatures below 1500 K and for iron contents below 30%. At higher iron content, our formulation predicts a conductivity which is more than one order of magnitude greater than the prediction of Hirsch et al.

To our best knowledge, the electrical conductivity of wadsleyite ($\beta$-phase) has never been measured for various iron contents. We therefore use the values of $\sigma_0$ and $\Delta U$ of Xu et al. (2000b), to which we apply the same iron content dependence as for olivine. This approximation is probably not correct: indeed, the polaron hopping conduction mechanism depends on many parameters, e.g. jump distance of the charge carriers, ferric Fe fraction (e.g. Hirsch et al., 1993), which take different values for olivine and its high-pressure phases. However, for the purpose of simulating planetary conductivity profiles, this approximation will do a better work than ignoring the effect of iron on wadsleyite conductivity. For ringwoodite ($\gamma$-phase), Lacam (1985) did some measurements on synthetic samples.
with iron content between 0.5 and 1, at room temperature and pressures up to 20 GPa. Extrapolating the derived iron dependence to Fe-poor samples (X in the range 0–0.5) and to high temperatures seems too hazardous, and we have decided to use for ringwoodite the \( \log(\sigma_0) \) and \( \Delta U \) values of Xu et al. (2000b), and the values of \( x \) and \( \beta \) derived for olivine.

Xu et al. (2000b) also give the electrical properties of the high pressure phases of the starting orthopyroxene: clinopyroxene at 13 GPa and the assemblage garnet + akimotoite (ilmenite phase) at 21 GPa. In the lack of any other experimental result, we use their values of \( \log(\sigma_0) \) and \( \Delta U \), with corrections for the iron content dependence using the values of \( x \) and \( \beta \) found for orthopyroxene. Apart from the garnet + akimotoite assemblage investigated by Xu et al. (2000b), the only experiment made on a garnet sample is by Kavner et al. (1995). They reported measurements on a meteoritic majorite \( \text{Mg}_9\text{Fe}_{0.75}\text{Fe}_{0.25}\text{Si}_3 \) and on almandine garnet \( \text{Mg}_0.475\text{Fe}_{0.525}\text{Si}_3 \), at ambient pressure and in the temperature range 290–370 K. These experimental conditions are too far from the expected \( P-T \) values in planetary mantles to allow any extrapolation to be done, and garnet is therefore not included in Table 1.

The same procedure is applied for the higher pressure phases. As these phases are stable under much higher pressure that the minerals of the upper mantle, values of the activation volume \( \Delta V \) have to be supplied. Dobson and Brodholt (2000b) measured that \( \Delta V = -0.26 \pm 0.69 \text{ cm}^3/\text{mol} \) for magnesio-wüstite. Studying the pressure dependence of Al-free perovskite, Shankland et al. (1993) measured a value \( \Delta V = -0.26 \pm 0.03 \text{ cm}^3/\text{mol} \). Recasting the results of Xu et al. (2000b) for magnesio-wüstite in Eq. (6) with the above values of \( x \), \( \beta \), and \( \Delta V \), finally gives \( \log(\sigma_{\text{ref}}) = 2.56 \pm 0.10 \text{ and } \Delta U_{\text{ref}} = 0.88 \pm 0.03 \text{ eV} \). The same method is applied for Al-free perovskite for which the values of \( x \) and \( \beta \) are identical to those of the magnesio-wüstite/perovskite assemblage. Two main reasons motivated this approximation. First, perovskite is the main phase in the assemblage (70 wt%), whatever temperature and iron content. Second, Peyronneau and Poirier (1989) noted that, for an iron content equal to 11%, the electrical conductivity of perovskite is not significantly different from that of the mixture of perovskite and magnesio-wüstite. The comparison with \( x \) and \( \beta \) values for magnesio-wüstite (Table 1) suggests that this approximation underestimates the \( x \) value and overestimates the \( \beta \) value of perovskite. As Xu et al. (2000b) did, we also consider an Al-bearing perovskite. The combined effects of Al-O and a high iron content have never been investigated, and we apply the value of \( x \), \( \beta \), and \( \Delta V \) derived for Al-free perovskite to the electrical parameters of Al-bearing perovskite given by Xu et al. (2000b).

Fig. 3a shows an Arrhenius diagram of electrical conductivity as a function of \( 10000/T \) (lower axis) and \( T \) (upper axis), for low pressure phases with \( X = 0.1 \). Two kinds of temperature dependences can be seen in Fig. 3a. On one hand, olivine, pyroxenes and the assemblage akimotoite + garnet all show an electrical conductivity in the order of \( 10^{-5} - 10^{-8} \text{ S/m} \) at a temperature of 1000 K. These values increase by 4 orders of magnitude when temperature increases to 2000 K. On the other hand, wadsleyite and ringwoodite have higher electrical conductivities, with values around \( 10^{-3} \text{ S/m} \) at a temperature of 1000 K. When temperature is increased to 2000 K, electrical conductivity increases by 3 orders of magnitude for wadsleyite and ringwoodite. Fig. 3b shows the electrical conductivity as a function of temperature for high-pressure phases with \( X = 0.1 \). Dashed and solid lines are computed electrical conductivity at ambient pressure and 30 GPa, respectively. At a pressure of 30 GPa, Al-free and Al-bearing

### Table 1

<table>
<thead>
<tr>
<th>Mineral Name</th>
<th>( \log(\sigma_{\text{ref}}) )</th>
<th>( \Delta U_{\text{ref}} ) (eV)</th>
<th>( \Delta V ) (cm(^3)/mol)</th>
<th>( x )</th>
<th>( \beta ) (eV)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olivine</td>
<td>2.69 ± 0.12</td>
<td>1.62 ± 0.04</td>
<td>–</td>
<td>2.42 ± 0.18</td>
<td>–0.48 ± 0.25</td>
<td>Xu et al. (2000b)</td>
</tr>
<tr>
<td>Wadsleyite</td>
<td>3.29 ± 0.20</td>
<td>1.29 ± 0.06</td>
<td>–</td>
<td>2.42 ± 0.18</td>
<td>–0.48 ± 0.25</td>
<td>Hinze et al. (1981)</td>
</tr>
<tr>
<td>Ringwoodite</td>
<td>2.92 ± 0.04</td>
<td>1.16 ± 0.01</td>
<td>–</td>
<td>2.42 ± 0.18</td>
<td>–0.48 ± 0.25</td>
<td>Seifert et al. (1982)</td>
</tr>
<tr>
<td>Orthopyroxene</td>
<td>3.66 ± 0.12</td>
<td>1.79 ± 0.02</td>
<td>–</td>
<td>–1.28 ± 0.51</td>
<td>–1.41 ± 0.35</td>
<td>Xu et al. (2000b)</td>
</tr>
<tr>
<td>Clinopyroxene</td>
<td>3.19 ± 0.13</td>
<td>1.86 ± 0.02</td>
<td>–</td>
<td>–1.28 ± 0.51</td>
<td>–1.41 ± 0.35</td>
<td>Xu et al. (2000b)</td>
</tr>
<tr>
<td>Akimotoite + garnet</td>
<td>3.29 ± 0.20</td>
<td>1.65 ± 0.03</td>
<td>–</td>
<td>–1.28 ± 0.51</td>
<td>–1.41 ± 0.35</td>
<td>Xu et al. (2000b)</td>
</tr>
<tr>
<td>Al-free Perovskite</td>
<td>1.28 ± 0.18</td>
<td>0.68 ± 0.04</td>
<td>–0.26 ± 0.03</td>
<td>3.56 ± 1.32</td>
<td>–1.72 ± 0.38</td>
<td>Dobson and Brodholt (2000b)</td>
</tr>
<tr>
<td>Al-Pero skite</td>
<td>2.03 ± 0.17</td>
<td>0.76 ± 0.04</td>
<td>–0.26 ± 0.03</td>
<td>3.56 ± 1.32</td>
<td>–1.72 ± 0.38</td>
<td>Dobson and Brodholt (2000b)</td>
</tr>
<tr>
<td>Magnesio-wüstite</td>
<td>2.56 ± 0.10</td>
<td>0.88 ± 0.03</td>
<td>–0.26 ± 0.69</td>
<td>3.14 ± 0.07</td>
<td>0</td>
<td>Dobson and Brodholt (2000b)</td>
</tr>
</tbody>
</table>

\( \Delta V \) is the activation volume. \( x \) and \( \beta \) give the iron dependence of \( \sigma(X) \) and \( \Delta U(X) \), respectively.

\( a \) Xu et al. (2000b).

\( b \) Hinze et al. (1981).

\( c \) \( x \) and \( \beta \) identical to olivine values.

\( d \) Seifert et al. (1982).

\( e \) \( x \) and \( \beta \) identical to orthopyroxene values.

\( f \) Shankland et al. (1993).

\( g \) \( x \) and \( \beta \) identical to py/mw assemblage values.

\( h \) Peyronneau and Poirier (1989).

\( i \) Dobson and Brodholt (2000b).
perovskites show a similar behavior, with an electrical conductivity around \(10^{-1.5}\) S/m for a temperature of 1000 K, rising to values of around 1 S/m for a temperature of 2000 K. Mg-wüstite electrical conductivity has a similar temperature dependence, with values increasing from \(10^{-1.5}\) to \(10^{0.5}\) S/m when temperature increases from 1000 to 2000 K. For the three phases, increasing the pressure from ambient to 30 GPa increases electrical conductivity by an order of 0.3 log unit (value slightly depending on temperature). This identical pressure dependence comes from the values of \(\Delta V\), equal for the three phases (see Table 1).

Fig. 4a shows the electrical conductivity of low pressure minerals and phases as a function of iron content \(X\) between 8% and 40%, for a temperature of 1500 K and ambient pressure. Increasing the iron content from 10% to 40% leads to the following results: (1) electrical conductivity of olivine, wadsleyite and ringwoodite, supposed to have the same iron content dependence, increases by 2 orders of magnitude; (2) for orthopyroxene, clinopyroxene, and the akimotoite + garnet assemblage, no significant iron content dependence of electrical conductivity is observed in the explored range for \(X\). Fig. 4b gives the iron content dependence of electrical conductivity of high-pressure phases, at a temperature of 1800 K and a pressure of 30 GPa. For an iron content increase of 10–40%, electrical conductivity increases by 2 orders of magnitude for Mg-wüstite, and 4 orders of magnitude for perovskite. Among all the conductivities studied, the conductivity of the perovskite has the stronger iron dependence.

These results are to be considered with caution. All of the samples discussed here have iron content smaller than 50% for low pressure phases and smaller than 20% for high-pressure phases. Extrapolation of electrical conductivities of samples with iron content well above these upper bound values is therefore not relevant. The major drawback of this work is that it relies on very few experimental results, with some of them performed on synthetic samples. Assuming the same iron dependence as the closest mineral phase may also be questionable. Nevertheless, our choice to ground the extrapolation of the conductivity of all
phases on the measurements of Xu et al. (2000b) guarantees some confidence in our results. These measurements were indeed performed on natural terrestrial samples, and the same experimental setup was used to measure the conductivity of all minerals.

Note that the same modelling can be used to study the effect of aluminium on the conductivity of minerals. Apart for the Al-bearing perovskite, the pyroxenes and its high-pressure phases (orthopyroxene, clinopyroxene, akimotoite + garnet) are the sole mineral phases of Table 1 that can bear some aluminium. Among these phases, the orthopyroxene is, to our best knowledge, the only mineral for which measurements of the conductivity have been reported for different Al$_2$O$_3$ content. This may be of great interest to evaluate the effect of aluminium on the conductivity of orthopyroxene and further constrain the lunar temperature profile. The conductivities of the different samples have been reviewed by Hood (1986) and are shown on Fig. 5. This figure shows an increase of the electrical conductivity of the orthopyroxene with the Al$_2$O$_3$ content, as was originally suggested by Huebner et al. (1979). Unfortunately, the three samples studied did not bear the same iron content. The later was 14–15% for Duba et al. (1976) and Huebner et al. (1979) and 23% for Duba et al. (1979). From Fig. 4, we do not expect however a large effect of the iron for such iron contents. The electrical conductivity of orthopyroxene computed from formula (6) is drawn on Fig. 5 for comparison. At high temperatures, the effect of iron becomes negligible for such iron contents. Fig. 5 shows that the effect of aluminium is independent of the temperature for temperatures higher than 1500 K. Following the same procedure as for the effect of iron in Section 2, we suppose a power law dependence of $\sigma_0$ in terms of Al$_2$O$_3$ weight percent. Fig. 6 shows a linear fit of the log($\sigma_0$) for the three samples. The slope $\alpha_{Al}$ = 0.53 ± 0.18 measures the effect of Al$_2$O$_3$ content (in weight%, logarithmic scale) on the log($\sigma_0$) of aluminous orthopyroxene which is now written as

$$\log(\sigma_0(\text{Al}_2\text{O}_3\%)) = \log(\sigma_{0,\text{ref}}) + \alpha_{\text{Al}} \log(\frac{\text{Al}_2\text{O}_3\%}{\text{Al}_2\text{O}_3\%_{\text{ref}}}),$$

where log($\sigma_{0,\text{ref}}$) and Al$_2$O$_3$%$_{\text{ref}}$ are, as before, the reference values provided by the sample of Xu et al. (2000b), namely log($\sigma_{0,\text{ref}}$) = 3.66 (see Table 1) and Al$_2$O$_3$%$_{\text{ref}}$ = 2.9%. Again the data are too scarce to claim that the empirical relation (7) is perfectly true. Nevertheless, this relation models an increase of one log unit in the conductivity of orthopyroxene when the Al$_2$O$_3$ content increases from 0.14% (Duba et al., 1976) to 6.8% (Duba et al., 1979). Considering this effect of aluminium, Huebner et al. (1979) has interpreted the electrical conductivity of the lunar mantle in terms of temperature. As the lunar mantle is rich in Al$_2$O$_3$, the temperature profile is therefore lower than expected, which is more in accord with independent constraints (see Hood, 1986 for a review). In the lack of any measurement of the effect of the Al$_2$O$_3$ on the conductivity of the high-pressure phases of orthopyroxenes, we assume that the relation (7) can be applied also to the clinopyroxene and the akimotoite + garnet assemblage. Again the reference values are those provided by Xu et al. (2000b) (see Table 1).
4. Synthetic conductivity profile of the Martian mantle

In this section, we use our modelling of the effect of iron on the electrical conductivity to compute a conductivity profile of the Martian mantle. The Martian mantle model of Bertka and Fei (1997) has been chosen here. Starting from high-pressure, high-temperature experiments, they computed the modal mineralogy associated to the Dreibus and Wänke (1985) composition along a selected areotherm (see their Fig. 1). This composition was derived from the study of SNC meteorites which suggested an iron fraction around 25%. The selected areotherm may represent a hot end-member for the Martian thermal structure, but we consider this model as an example because it gives self consistent mineralogy, temperature and pressure profiles. Discussions about other compositions and areotherms can be found in Verhoeven et al. (2005).

The question of the oxidation state of the Martian mantle must be investigated before computing its electrical conductivity. It can be estimated through the geochemical study of SNC meteorites. Consistent estimations have been proposed: Wadhwa (2001), Herd et al. (2002) and McCanta et al. (2004) proposed a reduced Martian mantle, with an oxidation state near the Iron-wüstit buffer, i.e. three orders of magnitude below the Quartz-Fayalite-Magnetite buffer. This is similar to what can be expected in the Earth’s upper mantle (e.g. Arculus, 1985; Hirsch, 1991). Therefore, the difference between oxygen fugacity in the mantle of the Earth and of Mars is of the same order of magnitude, probably smaller, than typical discrepancies among laboratory experiments conditions on mineral conductivity. Besides, the log($f_{O2}$) effect on electrical conductivity is relatively small (about 0.5 order of magnitude, see above). We can therefore use the present formulation of iron content dependence of conductivity for an application to the Martian mantle.

At a given depth, we compute the conductivity of each phase using formula (6) with iron and Al$_2$O$_3$ fraction computed from the microprobe analysis of Bertka and Fei (1997). For garnet, we use the same electrical parameters as the akimotoite + garnet assemblage. Concerning perovskite, we use the values of the Al-bearing phase in agreement with the reported experimental composition. The electrical conductivity profile of the aggregate is then computed as the average of the Hashin–Shtrikman (1962) upper and lower bounds of the individual conductivities weighted by the volume fractions reported by Bertka and Fei (1997) (Fig. 7). Xu et al. (2000b) discussed all the possible averaging procedures for electrical conductivities, and selected the effective medium and Hashin–Shtrikman bounds as best methods. The average of the two Hashin–Shtrikman bounds being very close to the effective medium mean, we use this method. Using one or the other method implies an error of less than 0.2 log unit for the Earth’s upper mantle (Xu et al., 2000b).

To quantify the effect of the uncertainties affecting the electromagnetic constants of Table 1 on our results, we perform Monte Carlo simulations of the conductivity by considering each constant as a random variable. The probability distribution of each electromagnetic constant is considered as gaussian with mean and standard deviation given by the value and its uncertainty reported in Table 1. We sample 10 000 times these distributions and compute, for each set of samples, the electrical conductivity profile. The empirical means and standard deviations over the 10000 computed data sets are shown in Fig. 7. Concerning the mean electrical conductivity profile, we observe first a monotonous increase of log($\sigma$) from $-2.2$ at 200 km depth to $-0.8$ at 1000 km depth. This is mostly due to the temperature increase, since the transition from orthopyroxene to clinopyroxene is very smooth and has a small electrical signature (see Figs. 3 and 4). Then the conductivity increases by 1.7 order of magnitude between depths of 1000 and 1200 km. Two successive jumps can be identified and correspond to phase transitions of olivine to ringwoodite and olivine to wadsleyite, respectively. The first of these transitions is characterized by a small amount of ringwoodite (less than 15%), but it is very iron-rich (up to 38%). This last feature explains the sharp increase of conductivity. These jumps are followed by a slight decrease of conductivity (0.2 order of magnitude) between depths of 1250 and 1390 km. This is due to the decrease of iron
content in all phases during the wadsleyite-ringwoodite and clinopyroxene-majorite transitions. A final conductivity jump of 1 order of magnitude is observed at a depth of 1800 km, due to the breakdown of ringwoodite into perovskite + Mg-wüstite.

Most of the profile of Fig. 7 is characterized by an uncertainty of the order of 0.15 log unit, except for two regions where the uncertainty is much higher. The first of these regions is from 1130 to 1190 km depth. At this depth, the uncertainty is of 0.25 log unit. This increase is due to the transition to wadsleyite and garnet which possess higher uncertainty on their log($\sigma_{\text{ref}}$) and $\Delta U_{\text{ref}}$ values than their lower pressure phases (see Table 1). The second region is the lower part of the mantle (below 1800 km depth). The uncertainty affecting the electrical conductivity is by far the most important in this region as it reaches 0.35 log unit. As it can be seen from Fig. 7, the composition of the Martian mantle at such depth is a binary mixture of perovskite and magnesiowüstite. The very high uncertainty is related to both the high uncertainty on the $z$ value of perovskite and on the activation volume $\Delta V$ of the magnesiowüstite.

The effect of the Al$_2$O$_3$ content of the pyroxenes on the electrical conductivity of the Martian mantle is comparatively small compared to the effect of iron content and temperature. Indeed, the results of Bertka and Fei (1997) show that the Al$_2$O$_3$ content of pyroxenes is very different from the terrestrial reference value (2.9%) only for the garnet and only in the first 1100 km of the mantle. At such depths, the Al$_2$O$_3$ content in garnet reaches values of the order of 20%. From Eq. (7), we compute that the related increase in the conductivity of the garnet due to the high Al$_2$O$_3$ will be of the order of 0.5 log unit. Nevertheless, at such depths, the garnet fraction is only 10% of the composition in the mantle (see Fig. 7) which leads through the Hashin–Shtrikman mean to an average increase of the conductivity of olivine, pyroxene, magnesiowüstite and perovskite/magnesiowüstite assemblage with different iron contents have been reviewed. In all studies, a systematic variation of both the preexponential factor and the activation energy have been reported. But these studies are performed with different experimental set up, and/or in different oxygen buffer conditions.

A synthetic conductivity profile of the Martian mantle is computed, based on the Bertka and Fei (1997) Martian mantle model. The computed profile is more conductive than terrestrial estimations, by 1–1.5 order of magnitude. This is partly due to the higher iron content of the martian model with respect to the earth’s mantle.

Many extrapolations are made during this modelling study. Definitely, more experiments are needed to avoid these extrapolations, but they allow us to estimate more realistic electromagnetic signatures of iron-rich planetary mantles. The main interest of the new formulation of electrical conductivity is to get a similar description of elastic and electrical parameters as a function of iron content. This is a first step towards fully joint interpretations of results from seismic and electromagnetic surveys.

Acknowledgments

O.V. acknowledges the financial support provided through European Community’s Improving Human Potential Programme under contract RTN2-2001-00414.
MAGE. We thank Antoine Mocquet and Michel Menvielle for valuable discussions. We also thank two anonymous reviewers for very useful comments.

References

Seifert, K.F., Will, G., Voigt, R., 1982. Electrical conductivity measurements on synthetic pyroxenes MgSiO3–FeSiO3 at high pressures and temperatures under defined thermodynamic conditions. In: Schreyer,
W. (Ed.), High Pressure Researches in Geoscience, E. Scheier-
bart’sche Verlagsbuchhandlung, Stuttgart, pp. 419–432.