Carbonate Melts and Electrical Conductivity in the Asthenosphere

Fabrice Gaillard,1* Mohammed Malki,2,3 Giada Iacono-Marziano,1,4 Michel Pichavant,1 Bruno Scaillet1

Electrical conductively regions in Earth’s mantle have been interpreted to reflect the presence of either silicate melt or water dissolved in olivine. On the basis of laboratory measurements, we show that molten carbonates have electrical conductivities that are three orders of magnitude greater than either carbonate melt or water dissolved in olivine. On the basis of laboratory measurements, we show that molten carbonates can potentially explain high mantle conductivities.

Fig. 1. Electrical conductivity versus temperature for the most important mantle phases (dry and hydrous olivine, molten silicates, and molten carbonates). SO₃ refers to anhydrous olivine conductivity (2). For silicate melts, anhydrous results are shown in red and hydrous in blue. From the less to the more conductive, results for (a) a dry MORB at 2 GPa (7), (b) a dry MORB at 1 bar (7), (c) a dry alkali basalt at 1 bar (6, 10), (d) a hydrous silica-rich melt at 1 bar (9), and (e) a hydrous alkali basalt at 1 bar (10) are shown. In the upper part of the diagram, the conductivities of molten carbonates are presented, extrapolated from our experiments at 400 to 1000°C using Eq. 1 (see fig. S8). From the less to the more conductive, we show (KC₂O·½ CO₃)₂, (Na₂KCa·½ CO₃)₂, (Na₂K)·CO₃, and (LiNaK)·CO₃.

The carbon dioxide content of mantle-derived magmas is a few hundred parts per million by weight (ppmw) in mid-ocean ridge basalts (MORBs) and can reach a few thousand ppmw in specific settings (16, 17), which constrains the CO₂ content of the mantle source to a few tens to hundreds ppmw (16–18). Under most of the pressure-temperature-oxygen fugacity conditions prevailing in the upper mantle, carbon is likely to be present in the form of molten carbonates (19–22). Such carbonate melts have exceedingly large wetting properties (23); they form interconnected liquid networks at olivine grain boundaries even at very low-volume fractions (23, 24) and could therefore contribute to the electrical conductivity of the mantle. The available data on the electrical conductivity of molten carbonates cover Li-rich compositions of industrial interest (25). However, mantle carbonates are particularly Li-poor and Mg, Ca-rich and have variable K and Na (26). We measured the electrical conductivity of molten Li-free and Ca-rich carbonates.

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Laboratory measurements on anhydrous peridotite and olivine single crystals indicate that the electrical conductivity of the upper mantle, if dry, should be ~10⁻¹⁰ to 10⁻² S m⁻¹, with the higher values reflecting high mantle temperatures (1, 2) (Fig. 1). Deep magnetotelluric data, however, indicate that the electrical conductivity of some mantle regions exceeds these values (3–5). In the Pacific Ocean mantle, for example, conductivities of >10⁻¹ S m⁻¹ have been measured at depths of ~60 km (4, 5). Such zones require the presence of conductive phases; silicate melts or hydrated olivine crystals are commonly considered (3, 5–8). Silicate melts have electrical conductivities of 10⁻¹⁻¹ ≤ 10 S m⁻¹ (6, 7, 9, 10) (Fig. 1) but peridotite melting requires high temperatures or high water content (11). The high mantle conductivities have therefore usually been interpreted as indicating trace amounts of hydrogen in olivine (4, 5, 8, 12). Direct measurements in mantle xenoliths provide compelling evidence for hydrated mantle olivine (13). However, the magnitude of the effect of water on olivine conductivity remains under debate (14, 15) (Fig. 1). Furthermore, it is unclear how hydrated olivine can produce high electrical anisotropy measured in the asthenospheric mantle (15). We present here experimental data showing that molten carbonates (i.e., carbonates) can potentially explain high mantle conductivities.

The carbon dioxide content of mantle-derived magmas is a few hundred parts per million by weight (ppmw) in mid-ocean ridge basalts (MORBs) and can reach a few thousand ppmw in specific settings (16, 17), which constrains the CO₂ content of the mantle source to a few tens to hundreds ppmw (16–18). Under most of the pressure-temperature-oxygen fugacity conditions prevailing in the upper mantle, carbon is likely to be present in the form of molten carbonates (19–22). Such carbonate melts have exceedingly large wetting properties (23); they form interconnected liquid networks at olivine grain boundaries even at very low-volume fractions (23, 24) and could therefore contribute to the electrical conductivity of the mantle. The available data on the electrical conductivity of molten carbonates cover Li-rich compositions of industrial interest (25). However, mantle carbonates are particularly Li-poor and Mg, Ca-rich and have variable K and Na (26). We measured the electrical conductivity of molten Li-free and Ca-rich carbonates.

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References

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Such conductivity values are comparable to those reported on Li-rich molten carbonates (25, 28). Molten carbonates at 1000°C are 1000 times as conductive as molten silicates (6, 7, 9, 10) at the same temperature and at least 100,000 times as conductive as hydrous and dry olivine single crystals (2, 14, 15). In our measurements, the electrical conductivity of molten carbonates varied slightly with chemical composition. Calcium-free carbonates containing 30 mole % Li2CO3 were about two to three times as conductive as a Li-free melt containing 50 mole % CaCO3 (Fig. 1, fig. S8, and Table 1). Another feature of molten carbonate conductivities is their small temperature dependence. The temperature dependence of molten carbonate electrical conductivities (σ) can be adequately fitted using an Arrhenius law

\[ \sigma = \sigma_0 \times \exp \left[ -\frac{E_a}{(RT)} \right] \]  

where R is the universal gas constant, 8.314 J K⁻¹ mol⁻¹, and T is the temperature in kelvin.

The derived pre-exponential terms (σ₀) and the activation energies (Ea) for each investigated composition are in Table 1. Activation energies are 30 to 35 kJ/mol, which is about one-third of the average Ea for natural molten silicates (70 to 150 kJ/mol (6, 7, 9, 10)) and one-tenth of those for dry olivine (200 to 300 kJ/mol (2)). Such low activation energies are similar to those (38 kJ/mol) reported for the viscosity of synthetic molten carbonates of composition (K₂Ca)(CO₃)₂ (29). Furthermore, we calculated (table S1) that the diffusing process responsible for the electrical conductivity and the viscosity of molten (K₂Ca)(CO₃)₂ are similar (~10⁻⁹ m² s⁻¹ at 1000°C). This suggests that, unlike silicate melts (9, 10), both viscosity and electrical conductivity of carbonate melts entail similar transport mechanisms. Extrapolation to mantle conditions requires an evaluation of the effect of MgCO₃ on the conductivity of molten carbonates, because mantle carbonatites should contain 5 to 15 weight % MgO at equilibrium with mantle minerals (26), and of the effect of pressure. In view of the similarities between conductivity and viscosity, both effects can be deduced from the effect of MgCO₃ and pressure on the viscosity of molten carbonates. Magnesium-bearing molten carbonates are slightly less viscous than those that are Mg free (29). We therefore expect that the conductivities of Mg-bearing carbonatites are slightly higher than those of Mg-free molten carbonates. Experimental data (29) and molecular dynamics calculations (30) indicate that pressure has little effect on the viscosity of molten carbonates up to mantle pressures. We thus conclude that mantle carbonatites should preserve the high conductivity we determined at 1 bar (28). The electrical conductivity of mantle carbonatites can therefore reasonably be described by the Arrhenius equation given in Table 1.

Molten carbonates are therefore by far the most conductive phase of Earth’s upper mantle. High electrical conductivity globally observed in the asthenosphere (3) could therefore reveal small amounts of carbonate melts hosted in the mantle. As an example of application of these data, we focus on the asthenosphere below the Pacific Oceanic ridge. This region of the mantle has been relatively well studied by geophysical imaging (4, 5), and petrological evidence suggests that small quantities of carbonate liquids are formed in such asthenospheric mantle at depths of up to ~300 km (19, 20). The geophysical surveys imaged a resistive body (σ ~ 10⁻⁻ to 10⁻² S m⁻¹) consistent with anhydrous peridotite in the upper 60 km of the mantle (4, 5), which corresponds to the oceanic lithosphere. A conductive structure (σ ~ 10⁻¹ to 10⁻² S m⁻¹) extends down to 200 km below the ridge axis (5). A structure of nearly comparable conductivity (σ ~ 10⁻¹ to 10⁻² S m⁻¹) extends

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**Table 1. Summary of experimentally defined parameter values for electrical conductivity of molten carbonates (Eq. 1).**

<table>
<thead>
<tr>
<th>Compositions</th>
<th>(\sigma^a) S m⁻¹ (±800)</th>
<th>(E_a) J mol⁻¹ (±350)</th>
<th>(\sigma) at 1000°C S m⁻¹ (±15)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(LiNa₂)₂(CO₃)₃</td>
<td>6590</td>
<td>32,500</td>
<td>305</td>
</tr>
<tr>
<td>(Na₂K₂)₂(CO₃)₃</td>
<td>4177</td>
<td>31,427</td>
<td>214</td>
</tr>
<tr>
<td>(Na₂KCa₂)₂(CO₃)₃</td>
<td>4314</td>
<td>32,500</td>
<td>192</td>
</tr>
<tr>
<td>(Na₂KCa)₂(CO₃)₂</td>
<td>2504</td>
<td>30,307</td>
<td>143</td>
</tr>
<tr>
<td>(K₂Ca)₂(CO₃)₂</td>
<td>3149</td>
<td>34,489</td>
<td>121</td>
</tr>
<tr>
<td>Mantle carbonatites</td>
<td>3440</td>
<td>31,900</td>
<td>169</td>
</tr>
</tbody>
</table>

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**Fig. 2.** Electrical conductivity (and resistivity in brackets) versus depth calculated assuming adiabatic temperature changes (19) (i.e., \(T_{300\text{ km}} \sim 1420°C\)) for dry olivine (gray line), hydrous olivine (blue line), dry olivine with 5 and 30 volume % of basalt (green lines), and dry olivine with 0.005, 0.035, and 0.35 volume % of carbonate melt (red lines). For the calculation of electrical conductivity of mixtures, we assume a Hashin-Shtrikman upper bound that implies an interconnected melt between olivine grains (6). Dry olivine conductivity is calculated from (2), and the hydrous olivine is calculated after (15) for crystals containing ~150 ppmw water (average between fast and slow crystallographic orientation). The olivine + 5 volume % basalt is calculated by taking the conductivity of dry basalt at 1 bar (7); increasing pressure would decrease the conductivty of such a mixture, but the magnitude of the pressure effect differs between different laboratory studies (7, 9, 10). The olivine-carbonatite mixtures are calculated after the conductivity of mantle carbonatite given in Table 1. The asthenosphere conductivity below the Pacific ridge (5) (red box) is best explained by olivine with 0.035 to 0.35 volume % of carbonate melts. The top of the asthenosphere extending 350 km east of the ridge (4, 5) (orange box) is best explained by the presence of 0.005 to 0.035 volume % of carbonate. The resistive lithosphere (4, 5) (blue box) matches the conductivity of dry olivine, whereas the lithosphere below the ridge axis is characterized by a broad range of conductivities, with the highest range probably reflecting the contributions of the rising MORB. The expected depth of carbonate melting (19, 20) and the one of silicate melting (11, 19) are shown by the arrows on the left of the figure.
in the direction perpendicular to the ridge axis on the east side of the ridge at depths between 70 and 120 km (4, 5). Such structure was not observed on the west side of the axis (4, 5). Both conductive structures show strong anisotropy that cannot be accounted for by hydrated olivine crystals (15). An additional conductive component is therefore needed, and the presence of silicate melt has been suggested (15).

Figure 2 shows in a conductivity-depth plot the different electrical structures of the Pacific Ocean mantle described above. We also show electrical conductivities calculated for different model mantles consisting of dry and hydrous olivine, dry olivine with 5 to 30 volume % of MORB and dry olivine with variable amounts of carbonatite melt. All calculated conductivities vary with depth following an adiabatic path (19, 20). The deep conductive asthenosphere (70 to 200 km) under the ridge axis can be explained considering olivine mixed with between 0.035 and 0.35 volume % of carbonatite. Olivine with more than 5 volume % of basalt could alternatively account for the high conductivity of this region, but an elevated degree of peridotite melting is precluded at such depth (11, 19). Hydrous olivine is unable to account for such a high conductivity domain (14, 15). The presence of a small amount of carbonatite is therefore the best explanation for the high conductivity of this region. Furthermore, the range 0.035 to 0.35 volume % of carbonatite corresponds (31) on average to ~300 ppmw of CO2 stored in the asthenosphere, in reasonable agreement with the variable estimates of CO2 concentrations in the source region of MORBs (16–18, 32). The off-axis conductive asthenospheric zone joins the deep asthenosphere under the ridge (70 to 200 km) with a conductivity of ~1 S m−1. Such value, however, designates the conductivity in the cross direction to the ridge axis, whereas the conductivity in the perpendicular direction is lower by a factor of 10 (20). We do not incorporate such anisotropies in our interpretation, which implies that on average 0.1 volume % of carbonatite melts (300 ± 200 ppmw CO2) would be needed to explain such mantle conductivities.

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Materials and Methods
Figs. S1 to S8
Table S1
References
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Tight Regulation of Unstructured Proteins: From Transcript Synthesis to Protein Degradation

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Altered abundance of several intrinsically unstructured proteins (IUPs) has been associated with perturbed cellular signaling that may lead to pathological conditions such as cancer. Therefore, it is important to understand how cells precisely regulate the availability of IUPs. We observed that regulation of transcript clearance, proteolytic degradation, and translational rate contribute to controlling the abundance of IUPs, some of which are present in low amounts and for short periods of time. Abundant phosphorylation and low stochasticity in transcription and translation indicate that the availability of IUPs can be finely tuned. Fidelity in signaling may require that most IUPs be available in appropriate amounts and not present longer than needed.

Up to one third of all eukaryotic proteins have large segments that are unstructured and are commonly referred to as intrinsically IUPs. These proteins lack a unique structure, either entirely or in parts, when alone in solution (1). The lack of structure is thought to provide several advantages, such as (i) an increased interaction surface area, (ii) conformational flexibility to interact with several targets, (iii) the presence of molecular recognition elements that fold upon binding, (iv) accessible posttranslational modification sites, and (v) the availability of short linear interaction motifs (2–5). These and other properties are ideal for proteins that mediate signaling and coordinate regulatory events, and indeed proteins that participate in regulatory and signaling functions are enriched in unstructured segments (6–9) [supporting online material (SOM) text S1]. Because of their unusual structural and important functional properties, the presence of IUPs in a cell may need to be carefully monitored. In fact, altered abundance of IUPs is associated with several disease conditions. For instance, overexpression of thyroid cancer 1 (TC-1) (9) or underexpression of adenine

References and Notes

28. Materials and methods are available as supporting material on Science Online.
32. A mantle peridotite with 0.35 volume % of carbonatite melts yields a conductivity of 1 mS m−1, which matches the highest value detected by geophysicists at a depth of 150 km (5). Such value, however, designates the conductivity in the direction parallel to the ridge axis, whereas the conductivity in the perpendicular direction is lower by a factor of 10 (5). We do not incorporate such anisotropic effects in our interpretation, which implies that on average 0.1 volume % of carbonatite melts (300 ± 200 ppmw CO2) would be needed to explain such mantle conductivities.

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