Seismic Properties of Anita Bay Dunite: an Exploratory Study of the Influence of Water

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As a pilot study of the role of water in the attenuation of seismic waves in the Earth’s upper mantle, we have performed a series of seismic-frequency torsional forced-oscillation experiments on a natural (Anita Bay) dunite containing accessory hydrous phases, at high temperatures to 1300°C and confining pressure (Pc) of 200 MPa, within a gas-medium high-pressure apparatus. Both oven-dried and pre-fired specimens wrapped in Ni-Fe foil within the (poorly) vented assembly were recovered essentially dry after 50–100 h of annealing at 1300°C followed by slow staged cooling. The results for those specimens indicate broadly similar absorption-band viscoelastic behaviour, but with systematic differences in the frequency dependence of strain-energy dissipation Q−1, attributed to differences in the small volume fraction of silicate melt and its spatial distribution. In contrast, it has been demonstrated that a new assembly involving a welded Pt capsule retains aqueous fluid during prolonged exposure to high temperatures—allowing the first high-temperature torsional forced-oscillation measurements under high aqueous fluid pressure (Ph) at temperatures >1000°C, a marked reduction in shear modulus, without concomitant increase in Q−1, is attributed to the widespread wetting of grain boundaries resulting from grain-scale hydrofracturing and the maintenance of conditions of low differential pressure Ph = Pc – Pd. Staged cooling from 1000°C is accompanied by decreasing Ph and progressive restoration of significantly positive differential pressure resulting in a microstructural regime in which the fluid on grain boundaries is increasingly restricted to arrays of pores. The more pronounced viscoelastic behaviour observed within this regime for the Pt-encapsulated specimen compared with the essentially dry specimens may reflect both water-enhanced solid-state relaxation and the direct influence of the fluid phase. The scenario of overpressurized fluids and hydrofracturing in the Pt-encapsulated dunite specimen may have some relevance to the high Q−1 and low-velocity zones observed in subduction-zone environments. The outcomes of this exploratory study indicate that the presence of water can have a significant effect on the seismic wave attenuation in the upper mantle and provide the foundation for more detailed studies on the role of water.

KEY WORDS: seismic wave attenuation; water; dunite; hydrous mineral; shear modulus; viscoelasticity; olivine; grain-scale hydrofracturing

INTRODUCTION

Seismological observations have revealed that the propagation of seismic waves in the Earth’s mantle is significantly affected by viscoelastic processes, causing attenuation and frequency dependence (dispersion) of wave speeds (e.g. Kanamori & Anderson, 1977; Anderson & Hart, 1976). It is widely accepted that such viscoelastic processes are associated with the motion of crystal defects such as grain boundaries and dislocations in rocks at high temperatures and/or the stress-induced redistribution of fluids including melt (e.g. Nowick & Berry, 1972; Minster & Anderson, 1981; Karato & Spetzler, 1990; Jackson, 2007). However, further understanding of these processes has been limited by lack of direct measurements of viscoelasticity for mantle materials such as olivine at high temperature and seismic frequency.

In recent years the application of seismic-frequency torsional forced-oscillation methods to fine-grained polycrystalline olivine has become feasible and revealed that elastic behaviour breaks down at sufficiently high temperatures, even in melt-free material, resulting in stronger
temperature sensitivity of wave velocity and associated attenuation (Tan et al., 1997; Gribb & Cooper, 1998; Jackson et al., 2002). These viscoelastic effects vary systematically with grain size and have been attributed to elastically and/or diffusively accommodated grain-boundary sliding (Cooper, 2002; Jackson et al., 2002; Faul et al., 2004).

A pronounced effect of water on viscoelastic processes has been suggested (Karato & Jung, 1998; Karato, 2003) based on the analogy with its effect on creep, in which a trace amount of water significantly weakens olivine-rich rocks (Carter & Avé Lallemant, 1970; Chopra & Paterson, 1984; Karato et al., 1986; Mei & Kohlstedt, 2000). Water weakening of olivine aggregates in creep is currently interpreted in terms of increased concentrations of point defects, such as Si and/or Mg/Fe vacancies, resulting in enhanced rates of ionic diffusion and dislocation climb (e.g. Mei & Kohlstedt, 2000; Kohlstedt, 2006; Walker et al., 2007). However, the influence of water on the micro-strain viscoelasticity has not yet been investigated experimentally.

This exploratory study serves to test two hypotheses: (1) that water can be retained in the specimen at high temperatures (up to 1150°C) during the long duration (50–100 h) forced-oscillation experiments; (2) that the presence of water has an effect on the seismic wave attenuation in mantle materials. Here we report the first seismic-frequency measurements of the influence of water on seismic wave dispersion and attenuation in polycrystalline olivine. For these exploratory experiments we chose a naturally occurring material (see Jackson et al., 1992)—in this case a relatively fine-grained, hydrated but unserpentinitized, dominantly olivine rock from Anita Bay (New Zealand), previously used in the studies that first demonstrated the effect of water on creep behavior of olivine (Chopra & Paterson, 1981, 1984). We measured both pre-fired and initially untreated specimens (either wrapped in Ni–Fe foil or Pt-encapsulated) to isolate the effect of water.

**EXPERIMENTAL PROCEDURES**

**Specimen preparation**

**Starting material**

The natural dunite specimen from Anita Bay, New Zealand is a 30 cm diameter boulder that consists primarily of olivine (>90 vol. % of composition Fo89, Chopra & Paterson, 1981), orthopyroxene and chromite but also contains minor amounts of hydrous phases, in the form of chlorite, tremolite and thin sheets of talc. Cylindrical samples cored from the same boulder were used in the studies by Chopra & Paterson (1981, 1984) and Faul & Jackson (2007). It is compositionally banded with a strong mineral lineation but foliation is weak and no crystallographic preferred orientation is indicated, consistent with previous studies of Anita Bay material (Turner, 1942; Wood, 1972). A trimodal grain-size distribution is evident with an overall average grain size of 100 μm. The fine-grained fraction (20–30% of thin-section area) has a grain size around 20 μm and consists mainly of lineation-parallel domains of orthopyroxene mixed with olivine. The fine-grained material is crack free and has straight grain boundaries. The medium-grained fraction (50–60%) consists almost exclusively of ~100 μm sized olivine grains with no undulose extinction and minor intragranular fracturing. Olivine–olivine grain boundaries in these regions are distinctly serrated (Fig. 1). Large porphyroblasts of olivine and orthopyroxene (up to 8 mm in size and elongated parallel to the lineation) form 10–20% of the sample. They display undulose extinction and at least two generations of fractures.

Cylindrical specimens were cored parallel to the lineation and precision ground to 11.5 mm in diameter and 30 mm in length. All four samples were cored in close proximity to each other. The density of a representative oven-dried specimen was determined by the Archimedean method involving immersion in ethanol to be 3.296(2) × 10³ kg/m³. This is 99.7% of the theoretical density of olivine (Fo89) (Chopra & Paterson, 1984), in accordance with a dunite composition.

**Heat treatment prior to mechanical testing**

In preparation for mechanical testing the rock specimens were either simply oven-dried (at 110°C; runs 1066 and 1093) or fired at 1200°C for 20 h (runs 1055 and 1086) in a controlled oxygen fugacity furnace using a gas mixture comprising equal partial pressures of CO and CO₂ yielding log₁₀f(O₂)(Pa) ~ −6 (Muan & Osborn, 1965). Based on the weight loss on ignition, the initial volatile content of the as-received rock was estimated to be 0.20 wt %, which is within the range of previous estimates (0.18 ± 0.02 wt %) (Chopra & Paterson, 1981).

**Infrared spectroscopy for [H₂O] determination**

The water content [H₂O] was determined by unpolarized IR spectroscopy on doubly polished disks nominally of ~0.5 mm thickness cut from the cylindrical dunite specimens (Tan et al., 2001). For determination of the average concentration of water in the bulk specimens, an aperture of at least 4 mm diameter was employed, whereas for spot analyses, for example within olivine porphyroblasts, an aperture of 70 μm diameter was selected. The concentration of molecular water, contained mainly in fluid inclusions, and responsible for the broad absorption band at wavenumber ν of 3000–3700 cm⁻¹ (Fig. 2), was estimated from the absorbance measured at 3400 cm⁻¹ with an absorption coefficient of 8.1 cm⁻¹ (mol/l)⁻¹ (Rossman, 1988).

Hydroxyl chemically bound within the olivine structure is responsible for sharp IR absorption peaks within the
wavenumber ranges 3280–3380 and 3450–3510 cm\(^{-1}\), superimposed upon the broad-band absorption attributed to fluid inclusions (Fig. 2d). To facilitate comparison with the water concentrations reported by Zhao et al. (2004) for similar conditions, their procedure was adopted for the estimation of \([\text{H}_2\text{O}]\), notwithstanding emerging indications that it may systematically overestimate water concentrations estimated from unpolarized spectra (Kovács et al., 2008; Sambridge et al., 2008). First, we calculated the integrated absorbance associated with such peaks normalized to 1 cm thickness and appropriately averaged over similar spectra for multiple randomly oriented crystals (Fig. 2d). The molar absorption coefficient \(I(\text{cm}^2/\text{mol})\) of Paterson (1982) with an ‘orientation factor’ of 0.5 was used to calculate the concentration of water, which was then multiplied by 3.5 following the calibration of Bell et al. (2003).

The spectrum of the as-received specimen can be resolved into two components, a sharp peak at 3690 cm\(^{-1}\), reflecting the presence of hydrous phases, and a broader band around 3200–3600 cm\(^{-1}\). The sharp peak was eliminated and the broad-band absorption greatly diminished by firing under controlled atmosphere at 1200°C (Fig. 2a), consistent with breakdown of the hydrous phases and expulsion of most of the molecular water (Table 1).

**Mechanical testing**

The experimental conditions and specimen characteristics are presented in Table 1. The pre-fired specimens were wrapped in Ni\(_{30}\)Fe\(_{30}\) foil and the oven-dried specimens were either wrapped in Ni\(_{30}\)Fe\(_{30}\) foil or sealed within a welded Pt capsule for mechanical testing within an outer mild-steel jacket with torsional forced-oscillation methods (Jackson & Paterson, 1993; Jackson, 2000). At the outset of each experiment, the assembly was first annealed (for 45–100 h) at the highest temperature [1300°C for pre-fired and oven-dried Ni-Fe wrapped specimens and 1150°C for Pt-sealed specimen] and 200 MPa confining pressure. During this interval, forced-oscillation tests were repeatedly conducted to monitor time dependence in the mechanical behaviour associated with any microstructural evolution. After stabilization of the mechanical behaviour, mechanical data were collected during slow staged-cooling (1–2°C/min) from the annealing temperature to room temperature. The IR spectroscopy for the recovered oven-dried Ni-Fe wrapped specimen (1066) indicated that it retained no more water than the pre-fired specimen (1055; Table 1)—in contrast to previous experiments of shorter duration with similar assemblies (Chopra & Paterson, 1981). The alternative of a welded stainless steel capsule lined internally with sleeves of talc and Ni used in compressive tests by Mei & Kohlstedt (2000) was rejected as...
Unpolarized Fourier transform IR (FTIR) spectra for dunite specimens, as-received and recovered following pre-firing and/or pro-longed high-temperature mechanical testing [absorption coefficients plotted in (a)–(c) are normalized to 500 μm thickness]. (a) IR absorption spectra for the as-received and newly pre-fired bulk specimens; (b) IR absorption spectra for the oven-dried (1066) and pre-fired (1055) foil-wrapped bulk specimens and for the Pt-encapsulated bulk specimen (1093) recovered following high-temperature mechanical testing; (c) representative IR spectra (70 μm diameter spot analyses) for an olivine porphyroblast and the fine-grained matrix in Pt-encapsulated specimen (1093); (d) spectra for selected 70 μm diameter regions within randomly oriented olivine porphyroblasts in Pt-encapsulated specimen 1093 at a thickness of 460 μm; dashed lines highlight the regions occupied by the absorption peaks associated with structurally bound hydroxyl (see text for interpretation).

**Table 1: Experimental conditions and characteristics of Anita Bay dunite specimens**

<table>
<thead>
<tr>
<th>Run no.:</th>
<th>As-received</th>
<th>1055</th>
<th>6570</th>
<th>1066</th>
<th>6573</th>
<th>1086</th>
<th>1093</th>
<th>6579</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prior heat treatment, foil/capsule</td>
<td>Pre-fired, Ni–Fe</td>
<td>Recovered from 1055</td>
<td>Untreated, Ni–Fe</td>
<td>Recovered from 1066</td>
<td>Pre-fired, Ni–Fe</td>
<td>Untreated, Pt</td>
<td>Untreated, Pt</td>
<td></td>
</tr>
<tr>
<td>$T_{\text{max}}$ (°C)</td>
<td>1300</td>
<td>Re-equilibrated at 1300</td>
<td>1300</td>
<td>Re-equilibrated at 1300</td>
<td>1300</td>
<td>1150</td>
<td>1150</td>
<td></td>
</tr>
<tr>
<td>Recovery history</td>
<td>Stage-cooled</td>
<td>Quenched</td>
<td>Stage-cooled</td>
<td>Quenched</td>
<td>Stage-cooled</td>
<td>Stage-cooled</td>
<td>Quenched</td>
<td></td>
</tr>
<tr>
<td>Melt (fluid) fraction (vol. %)</td>
<td>0.01</td>
<td>0.02</td>
<td>0.1</td>
<td>0.1</td>
<td>0.05</td>
<td>0.2$^\dagger$</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Weight loss on ignition (%)</td>
<td>0.20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bulk [H$_2$O] (wt ppm)$^\ddagger$</td>
<td>162</td>
<td>38</td>
<td>36</td>
<td>34</td>
<td>187</td>
<td>156</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^*$Contains no detectable melt but 2% porosity.

$^\dagger$Based on the free-water absorption coefficient of Rossman (1988), excluding water in hydrous phases of as-received material.
impractical for quantitative torsional oscillation tests because of the difficulty of correcting the results for the unknown and potentially time-dependent complex modulus of the dehydrating talc sleeve. Instead, we conducted further measurements with the specimen enclosed within a welded Pt capsule of ~280 μm cylindrical wall thickness and 100 μm thick ends, to achieve H₂O-saturated conditions.

The data obtained from the forced-oscillation tests were processed to obtain the shear modulus G and strain-energy dissipation Q⁻¹ vs period T, for the interval 1–1000 s (Jackson et al., 2004). In a significant refinement of established procedures, the calibration factors for the displacement transducers were corrected for drift during the long intervals (typically 5–9 h) of pre-programmed data acquisition. The torsional compliance of the specimen assembly was compared with that for a foil-free reference assembly containing an alumina control specimen. Combined G and Q⁻¹ data for relatively high temperatures (800–1300 °C) for each specimen were parameterized in an internally consistent manner with a phenomenological model based on a Burgers-type creep function (Faul & Jackson, 2005; Jackson, 2005) briefly described in Table 2 (first footnote). Owing to the low strain amplitudes (~10⁻³) of torsional oscillation, the microstructures remained unchanged by mechanical testing.

RESULTS
Overview of shear modulus and dissipation data
The forced-oscillation data (both shear modulus G and dissipation Q⁻¹) at high temperatures, T > 1000 °C for pre-fired and oven-dried, T > 800 °C for Pt-encapsulated

Table 2: Parameters of Burgers-type model* fitted to the G and Q⁻¹ data for the various specimens of Anita Bay dunite

<table>
<thead>
<tr>
<th>Run no.:</th>
<th>1055</th>
<th>1066</th>
<th>1086</th>
<th>1093</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-fired (Ni–Fe)</td>
<td>Oven-dried (Ni–Fe)</td>
<td>Pre-fired (Ni–Fe)</td>
<td>Oven-dried, Pt-encapsulated</td>
<td></td>
</tr>
<tr>
<td>Background only</td>
<td>Background only</td>
<td>Background only</td>
<td>Background only</td>
<td></td>
</tr>
<tr>
<td>1000–1300 °C</td>
<td>1000–1300 °C</td>
<td>1000–1300 °C</td>
<td>800–1120 °C†</td>
<td></td>
</tr>
<tr>
<td>J₀</td>
<td>1.73(2)E–02</td>
<td>1.73(2)E–02</td>
<td>1.41(1)E–02</td>
<td>1.75(1)E–02</td>
</tr>
<tr>
<td>(δln J₀/δT)₀</td>
<td>2.75(1)E–04</td>
<td>5.98(6)E–04</td>
<td>6.6(6)E–04</td>
<td>4.25(5)E–04</td>
</tr>
<tr>
<td>Δ</td>
<td>1.88</td>
<td>1.41</td>
<td>2.00</td>
<td>4.00</td>
</tr>
<tr>
<td>log τ₁₀₀</td>
<td>–6.40E–01</td>
<td>1.29E–01</td>
<td>–5.00E–01</td>
<td>–4.00E–00</td>
</tr>
<tr>
<td>log τ₅₀₀</td>
<td>6.3(3)</td>
<td>7.26(12)</td>
<td>6.79(8)</td>
<td>6.34(13)</td>
</tr>
<tr>
<td>log τ₅₀₀₀</td>
<td>5.61(8)</td>
<td>6.85(12)</td>
<td>6.23(8)</td>
<td>4.34(13)</td>
</tr>
<tr>
<td>E</td>
<td>3.94(8)E+05</td>
<td>5.09(13)E+05</td>
<td>4.36(8)E+05</td>
<td>4.76(13)E+05</td>
</tr>
<tr>
<td>N</td>
<td>134</td>
<td>138</td>
<td>134</td>
<td>164</td>
</tr>
<tr>
<td>ρ₂ (G)⁰</td>
<td>111</td>
<td>74</td>
<td>57.6</td>
<td>71.3</td>
</tr>
<tr>
<td>ρ₂ (Q⁻¹)⁰</td>
<td>24.8</td>
<td>38.2</td>
<td>37.1</td>
<td>112.2</td>
</tr>
<tr>
<td>ρ₂ (total)</td>
<td>136.1</td>
<td>112.4</td>
<td>94.7</td>
<td>103.5</td>
</tr>
</tbody>
</table>

*The dependence of G and Q⁻¹ upon oscillation period and temperature were fitted to the complex compliance expressed in terms of the Laplace transform of the generalized Burgers creep function:

\[ J(t) = J₀ \left\{ 1 + \delta \ln J₀(T) + \Delta \int_0^\infty D(\tau) \left[ 1 - \exp(-t/\tau) \right] d\tau + t/\tau_M \right\} \]

(Jackson, 2005). J₀ is the unrelaxed compliance, which is the reciprocal of the unrelaxed shear modulus, τₕ = η₁J₀ is the Maxwell relaxation time corresponding to viscosity η₁ and Δ is the relaxation strength associated with the distribution of anelastic relaxation times specified as D(τ) = τ²⁻¹/tₜ² (1/tₜ² – τ⁻²) for τₜ < τ < τₕ and zero elsewhere. The upper and lower limits to the distribution of anelastic relaxation times, respectively τₜ and τₜₖ, and the Maxwell relaxation time τ₉ₖ are each of the form τ = τ₉ₖ exp [(E/R)/(1/T – 1/T₉ₖ)], where τ₉ₖ is the value of τ at the reference temperature T₉ₖ (here 560 °C). δln J₀(T) = (δln J₀/δT)(T – T₉₆) accounts for the temperature dependence of J₀ including both anharmonic and relatively short-period viscoelastic effects (Jackson, 2005).

†Long-period data systematically excluded for T ≥ 1025 °C (open symbols of Fig. 5).

Based on a priori errors: σ(G)/G = 0.03 and σ[log₁₀(Q⁻¹)] = 0.05.
specimen) show strong viscoelastic behaviour and are generally well fitted by the Burgers model as illustrated in Figs 3–6. The parameters of the Burgers model for each of the four specimens are listed in Table 2. Monotonic variation of $Q^{-1}$ with oscillation period for each specimen is observed, which is similar to that obtained in previous studies for ‘melt-free’ olivine aggregates (e.g. Jackson et al., 2002), in spite of the presence in each specimen of a small silicate melt fraction, and in the Pt-encapsulated specimen, of ~2 vol. % of an aqueous fluid phase (see Microstructures section below). At lower temperatures, the specimen behaves nearly elastically, with relatively low levels of dissipation ($< 0.01$) and no measurable dispersion. The usual mildly monotonic increase of shear modulus with decreasing temperature is disrupted at low temperatures ($< 600^\circ$C, not plotted) by thermal micro-cracking attributed to the relatively large grain-size and multi-phase character of the dunite material under conditions of relatively low confining pressure (200 MPa).

Although the Pt-encapsulated specimen was mechanically tested at a substantially lower maximum temperature ($1150^\circ$C) than for the other specimens ($1300^\circ$C), the magnitudes of the dissipation $Q^{-1}$ for these different conditions are broadly comparable, indicating that the presence of H$_2$O has considerable influence on the mechanical behavior.

**Comparison of $G$ and $Q^{-1}$ data for the Ni–Fe-wrapped oven-dried (1066) and pre-fired (1055 and 1086) specimens**

As shown in Fig. 3, the pre-fired (1055) and oven-dried (1066) specimens display broadly similar levels of dissipation, but with a dependence on oscillation period $T_o$ that...
is markedly stronger for the pre-fired specimen (1055) 
\( \partial \log Q^{-1} / \partial \log T_c \sim \alpha = 0.45 \) compared with \( \alpha = 0.27 \) for the
oven-dried specimen, Table 2). The systematically lower
values of \( Q^{-1} \) at short periods for specimen 1055 are asso-
ciated with a narrower spread of the values of the modu-
lus at short period, which is reflected in a value
\( 2 \times 10^{-4} \) of \( \delta \ln J / \delta T \), the temperature sensitivity
of the unrelaxed compliance (Table 2, first footnote), that
is not much greater than the anharmonic value for Fo90 ol-
vine \( 2.4 \times 10^{-4} \), Anderson & Isaak, 1995). This indi-
cates that significant dissipation does not extend to
relaxation times much shorter than 1 s even for tempera-
tures as high as 1300°C. An experiment on another
pre-fired specimen (run 1086) of Anita Bay dunite (Fig. 4),
confirms the strong frequency dependence of \( Q^{-1} \) for the
pre-fired material but with consistently somewhat lower
\( Q^{-1} \) and significantly higher \( G \) for 1086 presumably
reflecting the heterogeneity in the Anita Bay dunite
boulder from which the specimens were cored.

Fig. 5. Results of forced-oscillation tests on the Pt-encapsulated speci-
men (1093). Data were obtained at \( \sim 25^\circ \) intervals between 1150 and
1000°C and at \( 50^\circ \) intervals for 1000–800°C. Data indicated by the
filled symbols were used to constrain the extended Burgers fit rep-
resented by continuous lines in the region where it is constrained by
data and by dashed lines elsewhere. The open symbols represent data
not used in constraining the model.

Fig. 6. Comparison of selected data, at \( 50^\circ \) intervals between 1150 and
1000°C, for the oven-dried specimens 1066 (Ni-Fe-wrapped,
open symbols and dashed curves) and 1093 (Pt-encapsulated, filled
symbols and continuous curves).

Comparison of \( G \) and \( Q^{-1} \) data for the
oven-dried specimens 1066 (Ni–Fe-wrapped) and 1093 (Pt-encapsulated)
For the Pt-encapsulated specimen (1093), a satisfactory fit
to the Burgers model required exclusion of data pertaining
to the highest temperatures and longest periods (e.g.
214–1000 s at 1075°C, 22–1000 s at 1120°C and 1–1000 s at
1150°C; Fig. 5). The excluded \( Q^{-1} \) data are in fact broadly
compatible with the fit to the lower temperature data
but this is not valid for \( G \). Thus, there is a significant
reduction in modulus at relatively long periods and
temperatures >1000°C without any associated increase in
\( Q^{-1} \). The possibility that the modulus deficit reflects the
high pore pressure of H$_2$O will be addressed in the following section.

$Q^{-1}$ is consistently higher for the Pt-sealed specimen 1093 than for the Ni–Fe-wrapped specimen 1066 by $\sim 0.5$ log unit, but the frequency dependences are broadly consistent (with $\alpha \sim 0.26$; Fig 6). The offset is essentially independent of temperature. The shear modulus is substantially lower for 1093 than for 1066 in the regime where the extended Burgers fit applies. The systematically lower modulus and greater dissipation for the former specimen suggest that the presence of water might play an important role in the mechanical behaviour.

**Characteristics and microstructures of recovered specimens**

**Microstructures**

Representative microstructures for three types of recovered specimen are shown in Figs 1, 7 and 8. The melt fractions for the oven-dried and pre-fired specimens (Table 1) were estimated via light microscopy and scanning electron microscopy (SEM). Recovered specimens re-equilibrated and quenched from 1300°C at 300 MPa, expected to preserve the maximum melt fraction relevant to experimental conditions, show generally very small melt fractions averaging $<0.1\%$. Melt is distributed heterogeneously and is concentrated in areas where amphibole or chlorite was present or in adjacent olivine-rich regions of 100 μm grain size. Those hydrous phases have decomposed into olivine + orthopyroxene + melt ± clinopyroxene ± spinel. Melt fractions of up to 10 vol. % occur locally in those areas. Large gradients in melt fraction, particularly in pre-fired specimens, mean that melt fraction can drop to zero within as little as 50 μm distance from those former hydrous phases. On the sample scale, large areas with no melt present exist. In different parts of each sample, different melting paths are taken, in effective isolation, for different hydrous impurities. Consequently, the composition of glass formed by melt solidification is highly variable: for example, compositions in the pre-fired specimen (1055) show ranges of 53–58 wt % for SiO$_2$, 14–21 wt % Al$_2$O$_3$ and are very potassic, with $\sim 3$ wt % K$_2$O (Table 3). In the specimens that have been stage-cooled for attenuation measurements, the melts formed at high temperatures would have had the opportunity to partially crystallize.

For the oven-dried Ni–Fe-wrapped specimen (1066) subject to progressive dehydration during the course of the mechanical testing, the initial melting presumably occurred in the presence of an interconnected aqueous pore fluid with $P_f \sim P_c$ (see Discussion) explaining the more uniform glass composition (especially SiO$_2$, Al$_2$O$_3$, CaO, Na$_2$O and K$_2$O; Table 3), than for 1055. The much higher melt fraction in the recovered material than for
1055 presumably reflects a higher proportion of the non-olivine phases in that core.

For the specimen (6579) quenched from 1150°C under Pt-encapsulated conditions, the melt retained (~0.1 vol. %) is relatively homogeneously distributed and also reasonably uniform in chemical composition except for MgO and FeO, but is distinctively higher in SiO$_2$ and lower in Na$_2$O than the other melts. The melt pockets contain euhedral-subhedral orthopyroxene and subordinate clinopyroxene along with residual silicate melt. The melt composition (Table 3) is lower in Na$_2$O but otherwise closely comparable with the nano-crystalline plagioclase previously reported in melt-bearing olivines recovered from staged cooling (Faul et al., 2004).

In contrast, the Pt-encapsulated specimen 1093 recovered after staged cooling contains no detectable melt even at sites where the microstructure and mineral assemblage point to the prior existence of hydrous-phase grains. However, the average 2 vol. % porosity is distributed heterogeneously throughout the specimen with fractions locally up to 30% over regions of 300 µm$^2$ at prior hydrous-grain sites. Because 6579, quenched from 1150°C, showed a small amount of melt (~0.1 vol. %), it seems reasonable to assume that 1093 similarly contained a small amount of melt at the highest temperature. Apparently this melt had almost completely crystallized during staged cooling in the presence of 2 vol. % of an aqueous phase. Many olivine-olivine grain boundaries

**Fig. 8.** Scanning electron micrographs showing the ~2 vol. % porosity in Pt-encapsulated specimen 1093 created by the dehydration of the secondary hydrous phases, and modified to some degree by complete progressive crystallization (during staged cooling from 1150°C) of ~0.1 vol. % silicate melt. In panels (a)–(d), the epoxy-filled pores on the polished surface yield few back-scattered electrons and appear dark. In (e), plucking of a grain during polishing created a cavity whose walls display arrays of isolated pores on grain-boundary surfaces.
**Table 3: Chemical compositions of glasses (wt % oxides)**

<table>
<thead>
<tr>
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**DISCUSSION**

**Solid-state viscoelastic relaxation in dry dunite**

The results of the present study that are most closely comparable with previous seismic-frequency data for the oven-dried Ni–Fe-wrapped specimen 1066, recovered essentially dry. A useful comparison can be made with the Andrade–Gaussian pseudo-period model for $Q^{-1}$ for a suite of synthetic melt-bearing olivine polycrystals (Jackson et al., 2004, table 4). For comparison with the data from the present study for specimen 1066, this model has been evaluated at 100 μm grain size and at the representative melt fractions of 0.01 and 0.1 vol. %. A good match to the data for 1066 is obtained for $\phi = 0.01\%$ (Fig. 9a). However, for $\phi = 0.1\%$, the estimated melt fraction for specimen 1066 (Table 1), the model deviates systematically from the data at short periods where a subtle $Q^{-1}$ plateau at temperatures of 1150–1250°C predicted by the model is not strongly expressed in the data (Fig. 9b). Thus there is no compelling evidence for a melt-related dissipation peak despite the fact that the olivine grain edges are perhaps sufficiently rounded at grain-edge triple junctions (Fig. 7c) to facilitate elastically accommodated grain-boundary sliding as envisaged by Faul et al. (2004). However, the milder dependence of $Q^{-1}$ upon oscillation period for the oven-dried Ni–Fe-wrapped specimen 1066 might in fact mask the presence of a dissipation peak of low amplitude associated with a silicate melt fraction somewhat greater and more uniformly distributed than for the pre-fired specimens.

Despite the microstructural complexities of Anita Bay dunite, the Andrade–Gaussian pseudo-period model of simple synthetic melt-bearing olivine (Jackson et al., 2004)
The volume $\phi$ and mass $m_i$ fractions of the H$_2$O pore fluid are related by

$$\phi = \left(1 + \left(p_i / p_r \right)(1/m_i - 1)\right)^{-1}$$

where $p_r$ and $p_i$ are the densities of the rock matrix and fluid, respectively.

For $m_i = 0.0028$ (for 1093, Table 1) and $p_i = 3.3$ g/cm$^3$ and pore fluid pressure $P_i$ of 200 MPa (equal to confining pressure $P_c$), $\phi$ is predicted to decrease linearly with temperature from 3.1% at 1150°C to 2.0% at 750°C—compared with our estimate of 2% porosity in the recovered specimen. At the highest temperatures of runs 1093 and 6579, the condition $P_i = P_c$ is thus expected to be realized. Any tendency for $P_i$ to exceed $P_c$ will be countered by swelling of the Pt capsule and enclosing steel jacket to increase the volume available for the pore fluid. On cooling, restoration of a significant differential pressure $P_i = P_c - P_l$ (sometimes called effective pressure) is expected for temperatures <750°C.

Considering the low initial porosity in the as-received dunite, the 2 vol. % porosity must have been created by dehydration accompanied by the development of a small silicate melt fraction, leading to high pore-fluid pressure and pervasive grain-boundary hydrofracturing. This microstructural evidence, along with the IR evidence of molecular water in fluid inclusions within the olivine phryroblasts and the substantial weight loss of 0.28% on oven drying of the recovered specimen (Table 1), suggests that the specimen remained H$_2$O-saturated during the experiment (see Grant et al., 2007). In these circumstances, the available H$_2$O would have been partitioned among a substantial volume fraction (~2%) of an aqueous fluid phase, a subordinate amount (~0.1% at the maximum temperature) of an immiscible silicate melt phase (e.g., Hirschmann et al., 2005) subject to essentially complete progressive crystallization during staged cooling, and hydroxyl chemically bound in the crystal structure of the nominally anhydrous minerals.

Using the recent results of Zhao et al. (2004), we estimate the equilibrium solubility in the olivine of specimen 1093 to be 26 wt ppm H$_2$O at $P_i = P_c = 200$ MPa and $1150^\circ$C, for the relatively oxidizing conditions expected to prevail within the Pt capsule (Grant et al., 2007). However, Mackwell & Kohlstedt (1990) reported re-equilibration of dissolved water on timescales of hours in millimetre-sized crystals during cooling to ~1000°C, suggesting that equilibrium in this study would have been maintained to lower temperatures of perhaps ~800°C during staged cooling involving 25°C steps and 6–10 h at each stage. This scenario is consistent with more recent data concerning H diffusivity reviewed by Ingrin & Blanchard (2006). At 800°C, a substantially lower solubility of about 8 wt ppm H$_2$O is expected (Zhao et al., 2004). This estimate is to be compared with the concentrations of 2–3 wt ppm

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**Fig. 9.** Comparison of data (filled and open symbols for alternate temperatures between 1300 and 1000°C in intervals of 50°C) for oven-dried Ni-Fe-wrapped Anita Bay dunite specimen 1066 with the results of a previous study. (a) Comparison with an a priori model (dashed lines) for melt-bearing olivine polycrystals (Faul et al., 2004) evaluated for a mean grain size of 100 μm and melt fraction $\phi = 0.01%$. (b) As for (a) but with $\phi = 0.1%$.

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**H$_2$O in the Pt-encapsulated specimen 1093**

The results obtained for the Pt-encapsulated specimen (1093) display consistently lower shear modulus and higher dissipation than the foil-wrapped specimen 1066. To interpret this contrast in seismic properties, we first estimate the pore fluid pressure using the equation of state for pure H$_2$O given by Holland & Powell (1991, Fig. 2a).
H$_2$O for the olivine porphyroblasts in the Pt-encapsulated specimen from the sharp IR absorption peaks. Significant variability amongst the various porphyroblasts (Fig. 2d) probably reflects a combination of two factors: variation of absorbance with lattice orientation, and diffusion profiles associated with incomplete re-equilibration to lower [H$_2$O] during staged cooling (see Peslier & Luhr, 2006). The observed concentration of structurally bound hydroxyl in the olivine porphyroblasts of the Pt-encapsulated specimen, along with the presence of fluid inclusions, is therefore broadly consistent with expectations based on equilibrium partitioning with the pore fluid during staged cooling.

**Water-enhanced solid-state viscoelastic relaxation**

The Pt-encapsulated specimen 1093 has a similarly low value of $\alpha$ (0·25(1)°) to 1066 (recovered essentially dry following *in situ* dehydration) but generally much higher $Q^{-1}$ and lower $G$ (Fig. 6). A modulus deficit, essentially independent of oscillation period, is attributed to the direct influence of the fluid phase as discussed in the next section. However, the water-saturated conditions maintained in specimen 1093 are also expected to promote solid-state viscoelastic relaxation—through a combination of grain-boundary and intragranular mechanisms. Increased grain-boundary mobility has already been inferred microstructurally. The effective grain-boundary viscosity $\eta$ should be markedly reduced by the presence of the aqueous fluid phase, so that the characteristic timescale (is proportional to $\eta$) for relaxation associated with grain-boundary sliding might be significantly less than for essentially anhydrous conditions (e.g. for specimen 1066). The mild period dependence of $Q^{-1}$ would then be explained as for 1066 by the superposition upon the dissipation background of a broad peak, having its impact at lower temperatures than for 1066 because of the influence of water in reducing the grain-boundary viscosity. The elevated water fugacity may also enhance intragranular viscoelastic relaxation by increasing the mobility of dislocations as suggested by Karato (2003).

**The direct influence of the fluid phase**

Both wetted grain boundaries and their tendency to evolve into arrays of isolated grain-boundary pores are evident in the Pt-encapsulated (1093) specimen (Fig. 8). However, the presence of pores at most olivine triple junctions indicates the preservation of high fluid connectivity. Presumably the hydrofracturing and high $P_t$ created and maintained a high degree of boundary wetting at the highest temperatures. During subsequent staged cooling, $P_t$ eventually became significantly less than $P_s$ and the arrays of isolated grain-boundary pores began to form. In specimen 1093, the small silicate melt fraction evidently crystallized very effectively, and presumably early, during the staged cooling from 1150°C. In this scenario, it is the $\sim$2 vol. % aqueous fluid phase, present throughout staged cooling but with progressively lower $P_h$ that is relevant to the observed viscoelastic relaxation.

It is widely recognized that elastic moduli and wave speeds will be influenced by the presence of a bulk pore fluid to a degree determined mainly by the properties of the porous or cracked rock matrix and the saturating fluid, notably the volume fraction $\phi$ of pore fluid, the aspect ratio of the fluid-filled ‘inclusions’ (defined as minimum/maximum dimension), and the bulk modulus of the fluid. The effective elastic properties are also predicted to vary with the timescale or frequency of the measurement. For the saturated isolated regime, probed at the MHz frequencies of ultrasonic techniques, experimentally determined elastic properties can be related to those of the dense matrix via the ‘soft-fluid’ saturation theory of O’Connell & Budiansky (1974). Ultrasonic methods have been used by Kono *et al* (2007) to measure the reduction of compressional wave speed ($V_p$) resulting from the *in situ* dehydration of hydrous minerals in altered ultramafic rocks of low initial porosity encapsulated, like those of the present study, within welded metal containers. Observed reductions in $V_p$, reaching only 15% for $\phi = 0·12$ at 1 GPa and 100°C and interpreted as representative of the saturated isolated regime, suggest an average aspect ratio of $\sim$0·15 indicative of sub-equant fluid inclusions rather than extensively wetted grain boundaries with aspect ratios $<0·01$.

For conditions representative of the present study of specimen 1093 ($\phi = 0·02$ and water saturation with $P_t = P_s = 200$ MPa at 1150°C), and the average aspect ratio of 0·15 inferred from the preceding analysis, a shear modulus reduction of $\sim$5% would be predicted within the saturated isolated regime. A further $\sim$2% shear modulus relaxation would be expected under these conditions from local fluid flow (O’Connell & Budiansky, 1977, equation (25)) yielding an essentially frequency-independent modulus deficit of perhaps 7% for the saturated isobaric regime presumably probed by the present low-frequency forced-oscillation measurements.

At the highest temperatures of the present study, the pressurized fluid phase may exert additional influence by compromising the mechanical coupling between torsion rods and specimen that depends upon maintenance of significant differential pressure $P_d$ (Jackson *et al*., 1984). Low $P_d$ provides a plausible explanation for the anomalous reduction of modulus without associated dissipation evident at progressively longer periods for temperatures above 1000°C.

The direct influence of the fluid phase on the measured modulus is expected to diminish during staged cooling on account of the previously mentioned microstructural changes. As grain boundaries that were at least transiently
wetted at \( P_f \sim P_c \) evolve to form the arrays of isolated grain-boundary pores and the connected grain-edge tubules at lower \( T \) and \( P_c \), the average aspect ratio of the fluid inclusions will increase substantially, resulting in a progressively smaller modulus deficit.

In summary, these first forced-oscillation data provide compelling evidence of markedly lower shear moduli and higher attenuation under water-saturated conditions. These effects are attributable in part to the presence of a bulk pore fluid and partly to the enhancement of solid-state relaxation processes by the high water fugacity. However, the heterogeneity and microstructural complexity of the Anita Bay dunite tested in this exploratory study preclude a definitive quantitative interpretation. It is intended that a further study on the role of water on seismic wave attenuation will use simpler synthetic polycrystalline olivine specimens. Such a study will provide more conclusive answers concerning the effect of water on seismic wave attenuation in the upper mantle.

**GEOPHYSICAL IMPLICATIONS**

As discussed in the previous section, the homogeneous distribution of fluids along grain boundaries, presumably resulting from hydrofracturing, is consistent with our semi-quantitative estimate of \( P_f \sim P_c \) at high temperature. Broadly analogous conditions may be realized, at least transiently, during dehydration of subducting oceanic lithosphere, where pore pressures comparable with the prevailing lithostatic pressure might induce hydrofracturing, thereby facilitating fluid transport into the overlying mantle wedge triggering partial melting (Davies, 1999). The development and persistence of such conditions of high pore-fluid pressure will depend strongly on the grain-scale permeability, which is a function of the instantaneous wetting behaviour and the temporal evolution of the fluid–solid microstructure (e.g. Faul, 1997). Increasing pressure with depth in the upper mantle increases the silica content of the aqueous fluid resulting in lower dihedral angles, connectivity of the fluid phase distributed in grain-edge tubules, and hence higher permeability (e.g. Mibe et al., 1998). The presence of a few per cent of a fluid phase thus accommodated mainly in grain-edge tubules would have limited impact upon the seismic wave speeds. However, the complete wetting of grain boundaries, inferred for the highest temperatures of the present study and recently reported by Yoshino et al. (2007) for pressures corresponding to the deepest part of the upper mantle, results in much larger reductions in wave speeds that are likely to be seismologically observable. Thus the reduced wave speeds and pronounced dissipation observed in the fluid-pressurized specimens of the present study and that of Kono et al. (2007) may be relevant particularly to the deepest zones of low velocity and high attenuation in mantle-wedge environments (e.g. Zhao et al., 1992; Takanami et al., 2000; Nakajima & Hasegawa, 2003). However, the very different timescales for grain-scale hydrofracturing, textural re-equilibration and fluid migration in the laboratory and subduction-zone settings, along with the markedly different fluid compositions, preclude any immediate quantitative seismological application of these experimental data.

**SUMMARY**

An exploratory study of the role of water in upper-mantle seismic-wave attenuation and dispersion has been undertaken on a natural dunite, of 100 \( \mu \)m average olivine grain size, containing \( \sim 0.3 \) wt % \( \text{H}_2\text{O} \) mainly in accessory hydrous silicate minerals. Cylindrical samples, either oven-dried or thoroughly dehydrated by pre-firing at 1200°C under controlled atmosphere, and either wrapped in Ni–Fe foil or sealed within a welded Pt capsule, have been tested in torsional forced oscillation at seismic periods of \( 1–1000 \) s and low strain amplitudes, under conditions of simultaneous high pressure (200 MPa) and temperature (to 1300°C).

Both oven-dried and pre-fired specimens, wrapped in Ni–Fe foil in the standard vented experimental assembly, were recovered after staged cooling following annealing for tens of hours at 1300°C and 200 MPa, containing no more than 40 wt ppm bulk molecular \( \text{H}_2\text{O} \). On the other hand, Pt encapsulation of dunite allows retention of essentially the entire inventory of water, including 150 wt ppm bulk molecular water trapped as fluid inclusions in the recovered specimens, for the duration of similar experiments at peak temperatures of 1150°C. *In situ* dehydration of the hydrous minerals liberates water at a pore pressure \( P_f \) locally and transiently greater than the confining pressure, resulting in pervasive hydrofracturing and redistribution of the dominant aqueous fluid and coexisting minor silicate melt phases. During staged cooling from 1150°C the \( \sim 2 \) vol. % porosity thus created is occupied mainly by the aqueous pore fluid. The decrease of \( P_f \) with decreasing temperature leads eventually to the restoration of a significantly positive differential pressure \( P_d = P_c - P_f \) and a consequent transition from grain-boundary wetting for \( P_d \sim 0 \) towards arrays of isolated grain-boundary pores for \( P_d > 0 \).

Each specimen displays intense viscoelastic relaxation at sufficiently high temperatures; both pronounced dissipation \( Q^{-1} \) and associated inverse dependence of the shear modulus upon oscillation period are measured. The behaviour is of the ‘high-temperature background’ type, whereby \( Q^{-1} \) varies monotonically with period and temperature without any well-resolved dissipation peak. For each of the pre-fired specimens, the absence of a melt-related dissipation peak is attributed to the highly localized distribution of a small melt fraction (\( \leq 0.05 \) vol. %); the bulk of the specimen is simply melt-free. For the Ni–Fe-wrapped oven-dried specimen (066), the somewhat more abundant
melt (0.1 vol. %) is more uniformly distributed on an account of the hydrofracturing associated with transiently high $P_T$ early in the experiment. A poorly resolved broad melt-related peak of low amplitude superimposed on the background dissipation may explain the milder period dependence of $Q^{-1}$ for this specimen.

Where $\sim$2 vol. % of an aqueous fluid phase is retained (in the Pt-encapsulated specimen) the lowest shear moduli and highest levels of attenuation were measured. The mild period dependence of $Q^{-1}$, like that for 1066, may be attributable to the superposition on the background of a poorly resolved dissipation peak associated with grain-boundary sliding. The higher dissipation and lower modulus for a given temperature (Fig. 6) than for specimen 1066 may reflect both water-enhanced solid-state relaxation (grain-boundary and intragranular mechanisms) and the direct influence of the fluid phase. The anomalously low moduli measured at the highest temperatures are attributed to conditions of low differential pressure resulting in extensive wetting of grain boundaries by aqueous fluid and compromised mechanical coupling between the specimen and torsion rods. It has been shown in this exploratory study that water may have a significant effect on seismic wave attenuation in mantle material, thereby giving incentive for more detailed studies.

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REFERENCES


Holland, T. J. R. & Powell, R. (1999). A Compensated-Redlich-Kwong (CORK) equation for volumes and fugacities of CO$_2$ and H$_2O$ in the range 1bar to 50kbar and 100–1600°C. Contributions to Mineralogy and Petrology 160, 170–182.


