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THE EFFECT OF REDOX CONDITIONS ON SEISMIC WAVES IN IRON-BEARING OLIVINE: IMPLICATIONS FOR UNDERSTANDING PLANETARY INTERIROS THROUGH SEISMILOGY.

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Introduction: Seismic data, inclusive of velocities and attenuation, can be utilized to elucidate the physical state of planetary interiors [1-3]. However, numerous micromechanical factors have been either experimentally demonstrated, or theoretically considered, to affect the propagation and dissipation of seismic energy within crystalline solids - including, but not limited to, changes in grain size, temperature, melt fraction, pressure and dislocation density [4,5]. Thus, observed variations in seismic wave speeds and attenuation may be used to ultimately 'map' variations in physical properties, such as those listed above, within planetary bodies [6]. But, in order to complete a successful inversion of seismic data into representations of physical properties, a first requirement is to obtain a fundamental laboratory-based understanding of how each of these possible factors individually influences seismic waves.

Here we conduct an experimental study with the initial objective to further understand one of the most commonly invoked, yet least studied, mechanisms that could alter intrinsic seismic wave attenuation: water content (occurring as chemically-bound hydroxyl). The historical basis for determining the effect of water on seismic properties was established predominantly through analogy with large-strain creep experiments conducted on olivine under water-saturated conditions [7]. While these deformation experiments routinely demonstrate a weakening of olivine in the presence of water [8], they represent a fundamentally different deformation regime in comparison to the micro-strains experienced due to a passing seismic wave [4]. Thus, in order to directly assess the effects of water on seismic properties, small-strain experiments are required. Substantially modified seismic properties in the presence of water have been observed previously at low strains and low frequencies, but only in a single exploratory study conducted under water-saturated conditions [9]. Thus, to properly test the theoretical predictions we conducted a systematic study of the seismic properties of olivine using low-frequency torsional oscillation on aggregates containing varying concentrations of bound hydroxyl, for the first time at undersaturated conditions [10].

Methods: *Specimens* - We fabricated eight experimental specimens by hot-pressing a variety of olivine starting powders at 300 MPa and 1200°C for 24 hours within sealed Pt capsules. The specimen compositions included a natural San Carlos derived powder and seven synthetic sol-gel derived powders (six Fo_{90} and one Fo_{100}) with varying concentrations of Ti-dopant between 0 and 800 ppm Ti/Si. Ti was added to create controlled concentrations of the hydrous defect referred to as the 'Ti-clinohumite-like' defect [11], which involves the substitution of Ti on an M-site in olivine, charged balanced by a doubly protonated Si-vacancy [12]. For mechanical testing, the hot-pressed precursor specimens were sleeved in either Pt, Ni, or $Ni_{70}Fe_{30}$ ('NiFe') foil to influence the oxygen fugacity (fO_2) during the experimental run. The creation of the Ti-OH defect requires relatively oxidizing conditions, and can thus be suppressed by sleeving the specimen in the more reducing NiFe foil [10,13].

Experimental – All samples were tested in forced-torsional oscillation at 200 MPa confining pressure using a modified internally-heated Paterson gas-medium apparatus [14]. Experimental protocol involved first annealing the samples in-situ at 1200°C, then an oscillatory torque was applied at 10 different periods between 1 and 1000 s. Once the test was complete, the temperature was lowered by 50°C, and the test repeated, continuing until the sample was ultimately tested at room temperature.

Analytical – After mechanical testing, all samples were longitudinally sectioned and mapped via Fourier-transform infrared spectroscopy (FTIR) to determine the spatial distribution and speciation of any hydrated defects. In addition, electron backscatter diffraction (EBSD) was utilized to determine the average grain size and grain size distribution.

Results: *Water content* – Representative FTIR spectra collected after the mechanical test are shown in Fig. 1c, and demonstrate that within the experimental suite, we were successful in creating different concentrations and species of hydrated defects. This includes a systematic variation in the concentration of the Ti-OH defect, different molecular water (H_2O) concentrations, and hydrated defects associated with trivalent ions (Fe^{3+}).

Seismic properties – All specimens tested display the 'high-temperature background' behavior, a monotonic increase in dissipation and decrease in shear modulus with increasing oscillation period [15], see Fig. 1a and b.

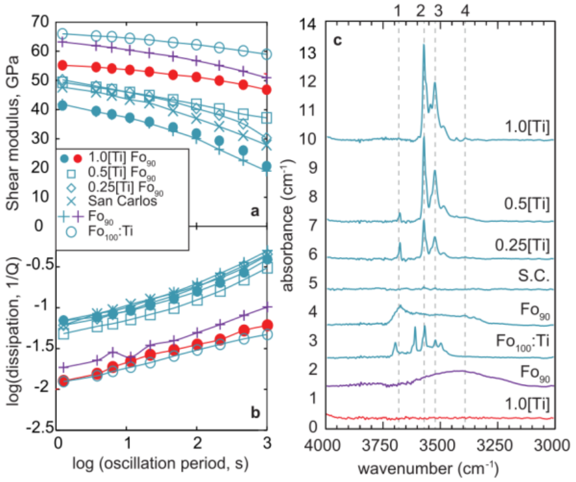

Figure 1 (modified from [10]). Shear modulus (a) and dissipation data (b) for a representative temperature of 1,100°C, along with FTIR spectra for all specimens after mechanical testing (c). Pt-sleeved specimens are displayed in blue, Ni-sleeved in purple and NiFe-sleeved in red. Ti-doped samples are denoted by the nomenclature *x*[Ti] where *x* is the approximate amount of Ti normalized to the sample with the highest Ti-dopant concentration, that is, 800 atom parts per million Ti/Si. In panel (c), labelled peak (1) is a secondary hydrous phase, (2) and (3) are indicative of the Ti-OH defect, and (4) is OH associated with trivalent ions.

Discussion: *The insensitivity to water content* – Comparison of the forced-oscillation data for all specimens at a common temperature is given in Fig.1a & b. Despite the large variation in water content amongst the Pt-sleeved specimens (plotted in blue), there is no substantial corresponding change in the dissipation characteristics. Further, the Fo_{100} specimen, containing an appreciable concentration of Ti-OH defects, displays the lowest levels of dissipation amongst the suite. These results together suggest that the seismic properties of olivine are in fact insensitive to water content, contrary to theoretical considerations. Rather, for Fo_{90} olivine, we observe an ordering of the dissipation trends according to the fO_2 conditions imposed during the mechanical test, influenced by the choice of metal sleeving. The highest levels of dissipation are observed for the most oxidizing conditions (Pt), followed by Ni (purple), and then the most reducing conditions provided by the NiFe foil (red) have the lowest dissipation [13].

Moving towards a quantified seismological model to include the effects of redox conditions on seismic properties – In order to produce a quantifiable seismological model for use in planetary systems, which will incorporate this sensitivity to prevailing redox conditions, we first fit each individual experimental run to a rheological (Burgers type) model that describes both the measured moduli dispersion and dissipation, see Fig. 2 [16].

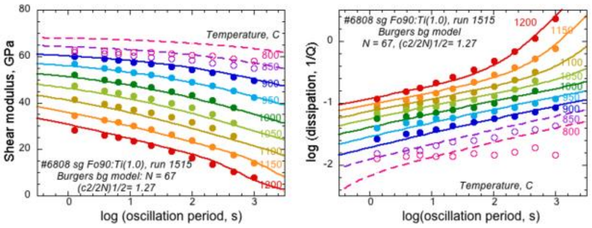

Figure 2. Shear modulus (a) and dissipation (b) data for the Pt-sleeved, 1.0[Ti] Fo_{90} specimen (~800 ppm Ti) plotted at different temperatures (colors) as a function of oscillation period. Solid lines represent the optimal Burgers model fit to the 67 individual (G,Q^{-1}) data pairs. Hollow circles indicate data pairs excluded from constraining the Burgers model fit. A priori errors are ±3% in G and ±0.05 in $\log Q^{-1}$, and model was fit with a reduced χ^2 of 1.27.

During the initial fitting of Burgers-type creep function models to (G,Q^{-1}) data for individual specimens, the unrelaxed shear modulus at a reference temperature of 900°C (G_{UR}) and the temperature derivative of the unrelaxed shear modulus (dG_U/dT), were treated as adjustable parameters. For all Fe-bearing olivine samples (but not the hydrous and oxidized Fo_{100} sample) we observe deficits of G_{UR}, and increased values of dG_U/dT, relative to the expected elastic (anharmonic) behavior of Fo_{90} olivine (e.g. observe low values of modulus at 1 s oscillation period in Fig.2). This behavior is indicative of additional anelastic relaxation occurring at shorter periods than those used during the mechanical test - However, the creation of a seismologically applicable model requires a seamless link between our experimental data and truly elastic behavior. We will report our progress towards reconciling the truly anharmonic and elastic behavior of Fo_{90} olivine with our observed forced-oscillation data. Once this seismological model is constructed, it will provide a much better understanding of the physical state of planetary interiors through the use of seismic or tidal strain-energy dissipation data [1-3].

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