Rheology

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Outline

fundamentals of defects
flow laws (constitutive equations)
extrinsic defects: water
seismic properties
cross-polarized light image of a peridotite

peridotite xenolith
Elastic behavior

Deformation: 
Force = spring const. x dist.

\[ F = k x \]  
(Hooke’s law)

strain: instantaneous - recoverable
Elastic behavior: Solids

Unique equilibrium position of atoms in crystal lattice
displacement from that position requires force: elastic moduli
e.g. $\sigma = E \varepsilon$

$E$ Young’s modulus (tensile deformation, linear strain)
$K$ bulk modulus (uniform compression)
$G$ shear modulus (rigidity, shear deformation)

Elastic moduli are of orders 10s of GPa
Deformation:

stress = modulus x strain

\[ \sigma = G \varepsilon \]

Ice:

\( G \approx 4 \text{ GPa} = 4 \times 10^9 \text{Pa}, \)
\[ \varepsilon \approx 1 \]

stress \approx \text{modulus}

driving flow of ice: gravity

Pressure (stress) = density x g x thickness
\[ = 1000 \text{ kg/m}^3 \times 10 \text{ m/s}^2 \times 1000 \text{ m} = 10^7 \text{ Pa} \]
moduli of rock-forming minerals of order of 100 GPa
convective stresses ~ 1 - 0.1 MPa

need to modify perfect elastic moduli: defects!
Why do we have defects?

**Thermodynamics** *(Fundamental state functions)*

**Internal energy** $U$: Energy content of a system, the sum of the potential energy stored in interatomic bonding (electrostatic energy) plus the kinetic energy of atomic vibrations.

In the Earth need to account for pressure:

**Enthalpy**: $H = U + PV$
Why do we have defects?

**Entropy** $S$: measure of the state of disorder in a system.

Example: Configurational entropy: Entropy is at a maximum for $XB = XA$
Thermodynamically why do we have defects?

Creation of point defect requires energy:
local distortion of lattice + imperfect satisfaction of bonding ➔ enthalpy $H$ increases.

But: point defect increases disorder in an otherwise perfect crystal: entropy $S$ increases.

Gibbs free energy: $G = H - TS$

For small defect concentrations entropy increase is greater than enthalpy increase, for larger defect concentrations enthalpy increase dominates:

Minimum of Gibbs free energy at some finite concentration of point defects!
Defects!
(point defects)
intrinsic defects
interstitial
Frenkel
Schottky
charge balance needs to be maintained
defects can also be impurity atoms: extrinsic defects
Dislocations - line defects

Transmission electron microscope image of screw dislocations in olivine
Grain boundaries

Why look at grain boundaries?
1. GB as crystalline defect present in all rocks.
2. GB affect
   • diffusion
   • deformation
   • seismic properties
   • electrical conductivity....

GB: 2-D lattice defect that introduces a change in lattice orientation

Lattice misorientation given by $\theta$

grain boundaries typically defined by $\theta > 10 - 15^\circ$
Visualization of types of grain boundaries

\[
\cos \frac{\theta}{2} = \frac{\gamma_{ss}}{2\gamma_{sl}}
\]

- \(\gamma_{ss}\) = solid - solid surface energy
- \(\gamma_{sl}\) = solid - liquid surface energy

subgrain boundary

olivine

high angle grain boundary

melt (glass)

0.5 \(\mu m\)
After atomic relaxation, the perfect edge dislocations of low-angle GBs (up to 22°/010) with Burgers vector [001] dissociate into an array of partial edge dislocations with Burgers vector $1/2[001]$ and a stacking fault between pairs, as illustrated in Fig. 5 for the (017)/[100] GB. This GB structure is similar to the one observed in low-angle tilt GBs in alumina (Ikuhara et al. 2003). At and around the GB, there are regions with high and regions with low particle densities. The partial dislocation cores are separated by regions of almost perfect lattice (perfect stacking for a distance $d_1$) and regions of distorted lattice (stacking fault for distance $d_2$), see Fig. 5. The structures of (017)/[100] GB with misorientation 9.58°/010 for intact SiO$_4$ tetrahedra and partly dimerized SiO$_4$ tetrahedra at the GB plane are presented in Fig. 5a, b, respectively. These structures have the same energy (1.46 J/m$^2$), which suggests that both partly dimerized SiO$_4$ tetrahedra and free oxygens may exist in low-angle Mg$_2$SiO$_4$ forsterite symmetric tilt GBs.

Figure 6 shows the stable atomic structure for a (012)/[100] symmetric tilt GB with a misorientation of 32.70°/010 which consists of an array of the structural units $a_1 b_1 c$. This structure obtained with rigid translation of one grain with respect to another with 0.64 nm along y direction and no translation in x direction showed the lowest GB energy (1.01 J/m$^2$) among all GBs considered here. This lowest energy can be related to the distribution...
High resolution transmission electron microscope images showing lattice planes

K. Marquardt, Bayerisches Geoinstitute
Grain boundaries are enriched in trace elements relative to the grain interiors.
Deformation - flow laws

‘first principles‘ derivations - physical model

constitutive equations relating strain rate to stress

Poirier, Creep of Crystals, 1985
Application of a differential stress:
Pure shear deformation of a single crystal (Nabarro- Herring creep)

Compressive stress at face B reduces the number of vacancies.
Tensile stress at face A increases the number of vacancies.
differential stress -> concentration gradients -> diffusion

concentration gradient face A - face B: length scale (grain size d)
diffusion ~ diffusivity (atomic species, crystal structure), temperature

flow law (constitutive equation, strain rate \( \dot{\varepsilon} \) as a function of stress \( \sigma \)):

\[
\frac{d\varepsilon}{dt} = \dot{\varepsilon} = A \sigma d^{-2} \exp[-(E+PV*)/RT] 
\]

A constant (experimentally determined), \( d \) grain size, 
\( E \) activation energy, \( V^* \) activation volume

\[
\frac{d\varepsilon}{dt} = A D_{SD} \Omega \sigma/kTd^2 
\]
Diffusion is rate controlling: slowest species along its fastest path

**Figure 15**

Comparison of grain boundary and lattice diffusion coefficients of Ca and O in calcite (all tracer diffusivities). The same conventions were used as in Figure 13 to illustrate and indicate the various data.

**Figure 16**

Farver et al. (1994) related their Mg diffusivity results at 0.1 MPa from experiments run in 0.1 MPa; Fo100

Condit et al. (1985)

Dohmen et al. (2002)

Chakraborty et al. (1994)

Shimojuku et al. (2009)

Farver and Yund (2000b)

Shimojuku et al. (2009)

Farver et al. (1994)

Shimojuku et al. (2009)

Farver et al. (1994)

Farver et al. (1994)

Farver & Milke, 2010
But: “Pure” diffusion creep would lead to shape change of grains:

Observation: Grains remain equiaxed after deformation.
Diffusionally accommodated grain boundary sliding (diffusion creep)

Macroscopic shape change without grain shape change
Hirth, 2003

![Graph showing strain rate vs. stress](image)

- Dry
- $T = 1250^\circ C$
- $P = 300$ MPa
- $d = 15$ μm

- Constitutive equation
- $n = 1.0$
- $n = 3.5$

- Open circles: MK (2000)
- Open squares: MK (2000)
- Filled circles: Dislocation creep component
Influence of water

\[ \dot{\varepsilon} = A \sigma^n d^{-p} f H_2O r \exp \left( \frac{-Q}{RT} \right) \]

viscosity \( \eta = \sigma / 2 \dot{\varepsilon} \) (Newtonian)
Hirth and Kohlstedt, 2003

Near linear relationship between water content and strain rate

Karato and Jung, 2003

S. Karato and H. Jung

olivine, "wet" condition

Near linear relationship between water content and strain rate
What does ‘water’ mean for a nominally anhydrous mineral?
Olivine ($\text{Mg}_2\text{SiO}_4$)

- Tetrahedrally coordinated Si, octahedrally coordinated M sites.
- Si-O bonds shortest and strongest.
- Large spacing of (010) planes and close spacing of (100) planes.
Back to defects

Dry ‘model’:

\[ [\text{Fe}_M^\bullet] = 2[V_M^{\prime\prime}] \]

dominant (most abundant) defects are M-site vacancies (charge: 2-), charge balanced by Fe\(^{3+}\) on M-sites

Nakamura and Schmalzried 1983, Kohlstedt, Karato and Co-workers
Water in olivine: a brief background

Water (hydrogen) is a trace element observable by Fourier Transform Infrared Spectroscopy (FTIR) (absorption of IR light) advantage: absorption depends on bonding environment

Most natural olivine has two dominant absorption bands in IR spectra, at 3525 and 3572 cm\(^{-1}\)

Bell et al., JGR, 2003
remarkable correlation with the trivalent ionic radius of the substituting element (Fig. 4). Additionally, the integrated intensity of the bands in this region varies with the concentration of the trivalent cation (Fig. 5).

As might be expected, no peak is observed for the Co-bearing sample, since the anomalously high concentration and colour indicate substitution as Co$^{2+}$. Similarly, only weak peaks were found for the Mn-doped sample, where substitution predominantly as Mn$^{2+}$ seems to have occurred. Bands in this region were observed for the unbuffered Ti sample, synthesised under the mildly reducing conditions intrinsic to the apparatus, but are absent under the strongly oxidising conditions of the experiment with PtO$_2$, where only Ti$^{4+}$ is expected.

Peaks were also not observed for the B-bearing sample, where due to the small size of the cation substitution is expected on the tetrahedral site; the absence of any additional hydroxyl bands indicates that the substitution B$_{3+}$+$\text{H}^+$+$\text{Si}^{4+}$ is not important (Kent and Rossman, 2002). Taken together these results provide unambiguous evidence that the peaks between 3300 and 3400 cm$^{-1}$ are due to water associated with a trivalent cation. Peaks in this region attributed to water associated with Al$_{3+}$ have also been reported by Grant et al. (in press). The spectral range over which these "trivalent peaks" occur will hereafter be referred to as the "trivalent region".

The correlation between the peak energy and ionic radius exhibits some scatter (Fig. 4). This is not unexpected since in addition to the size of the trivalent cation, the nature of its bonding (e.g. degree of Fig. 2. Concentration (ppm by weight) of dopant elements in forsterite as a function of the trivalent (M$^{3+}$) ionic radius. (M$^{3+}$–Mg$^{2+}$) is the difference between the size of the trivalent cation and Mg$^{2+}$. Error bars are one standard deviation of the analytical precision.

Fig. 3. OH stretching region of infrared absorption spectra of forsterite doped with the elements indicated. The dashed lines at 3612 and 3165 cm$^{-1}$ indicate the low and high silica activity bands, while those at 3400 and 3300 cm$^{-1}$ indicate the spectral region characterised by bands attributable to the trivalent dopant element. Spectra were recorded from unoriented single crystals using unpolarised light and were normalised to the integrated intensity of the Si–O stretching overtone bands. Spectra are offset for clarity.

Berry et al., 2007
Where is the water?

Titanium clinohumite “Point Defect”: Coupled substitution of 6-fold coordinated Ti on M1 site with 2 H on Si vacancy. Energetically the most stable. Supported by synchrotron observations.

calculated OH - vibrational frequencies: 3572 and 3525 cm⁻¹

Berry et al., 2005, Walker et al., 2007
Experiments in Paterson (gas medium) apparatus, 300 MPa confining pressure, 1200 - 1350°C. Water not buffered, samples encapsulated in Pt.

Fo$_{90}$ olivine doped with 0.04 wt% TiO$_2$
Absorption of infrared light reveals structural location of hydrogen in olivine crystal lattice.
- Rheology controlled by structurally bound water (hydroxyl)
- Water incorporation linked to titanium:

Extrinsic defects control water incorporation and rheology

Faul et al., 2016

Disloc. creep, $\sigma = 150$ MPa,
$T = 1200^\circ$C, $P = 0.3$ GPa

$r = 1 - 1.2$

dry rheology

Faul et al., 2016
Deformation at a range of time scales

\[ \epsilon < 10^{-4} \]

\[ \epsilon >> 1 \]

Yuen & Peltier, 1982
Experiments: Measurement of shear modulus (G) and attenuation (1/Q)

Experiments at:
- temperatures to 1300°C
- periods 1 - 1000s
- 200 MPa confining pressure

Measure shear modulus G and dissipation/attenuation

Attenuation (1/Q): energy loss per cycle
Microcreep experiments (time domain)

\[ \varepsilon < 10^{-4} \]
Maxwell body: viscoelastic

instantaneous, reversible + time-dependent permanent
Anelastic behavior (transient creep)

\[ \sigma = \eta \dot{\varepsilon} + G \varepsilon \]

Stress vs. Time:
- \( t_1 \) to \( t_2 \)

Strain vs. Time:
- \( t_1 \) to \( t_2 \)

time-dependent, unique equilibrium, recoverable
Microcreep experiments

\( \varepsilon < 10^{-4} \)
Viscoelastic behavior: Burgers Model

\[ \varepsilon(t) = \varepsilon_e + \varepsilon_t(t) + \dot{\varepsilon}t \]
Timescales of deformation in the Earth

- Transient creep
- Steady-state creep
- Anelastic
- Viscous
- Elastic

- Earthquakes
- Seismic waves
- Post-glacial rebound
- Mantle convection

- Strain
- Time

- Recoverable
- Irrecoverable
Attenuation/dissipation (frequency domain)

amplitude decreases with each cycle

\[ Q^{-1} = \delta \frac{E}{E} \times \frac{1}{2\pi} \]
Forced torsional oscillation (frequency domain): Temperature, grain size and frequency dependence of dry, melt-free polycrystalline olivine

Sol–gel specimens 6381, 6585, 6365 and San Carlos specimens 6261 and 6328 (also controls the grainsize sensitivity of Herring) creep controlled by grain-boundary (lattice) diffusion.

Finally, as an alternative, consistent with the notion of a single pseudoelastic modulus peak model.

Jackson and Faul, 2010
Here $J_U$ is the unrelaxed (high frequency) compliance of the Maxwell element, equated with the anharmonic shear modulus of olivine at a reference temperature [Jackson and Faul, 2010]. The compliance of the Voigt element has been replaced with a relaxation strength $P_B$ for the peak (P) and background (B), respectively. The relaxation strength relates to $J_V$ as

$$J_R = \frac{J_R + J_V}{J_R},$$

with $J_R = J_M + J_V$, and characterizes the increase in compliance (drop in modulus) due to an anelastic process (see Figure ??).

Temperature ($T$), pressure ($P$) and grain size ($d$) dependence are incorporated in the relaxation times for the peak ($\tau_P$), the cut-off times ($\tau_L,H$) and the Maxwell time ($\tau_M$):

$$\tau_i(T,P,d) = \tau_{i0}d^m \exp\left(\frac{E}{RT}\right) \left[\ln(\tau/\tau_M)/\sigma\right]^2 d\tau$$

where $\tau_{i0}$ are reference values, $m$ is a grain size exponent, $E$ the activation energy, $V$ activation volume and $R$ the gas constant. The grain size exponent for the Maxwell time, $m_v$, is fixed at a value of 3, corresponding to diffusion creep limited by grain boundary diffusion, the exponent for anelastic processes $m_a$ is determined from the data.
1. Elastically accommodated sliding

viscous sliding of grain boundaries leads to elastic stress concentrations at grain corners

time scale: $\tau_E = \eta_{gb} d/G \delta$

recoverable strain, anelastic process, dissipation peak

After Raj and Ashby, 1971; Raj, 1975
2. Diffusionally assisted sliding

- stress concentrations cause diffusion away from corners
- transient phase is characterised by diffusion over increasing length scales

distribution of relaxation times, transient, recoverable
3. Diffusionally accommodated sliding (steady state)

1. end of elastically accommodated sliding

2. diffusionaly assisted sliding

3. steady state creep

**time scale:** \( \tau_D \sim \frac{T d^3}{G \delta D_{gb}} \)

gb normal stresses are highest in center between grain corners (steady state diffusion creep)

Raj 1975, Gribb and Cooper, 1998
Microphysical model: Continuum of relaxation times (absorption band) is required. Diffusionally assisted grain boundary sliding occurs at frequencies outside the seismic frequency band. However, relaxation at higher frequencies will result in a reduced modulus at seismic frequencies.

The relaxation timescale for process $b$ is sensitive to the geometry of the melt:

$$\tau_f \propto \frac{\eta_f}{K \xi^n},$$

(25)

where $K$ is the bulk modulus of the solid, $\eta_f$ is the viscosity of the melt, and $\xi$ is the parameter that describes the aspect ratio of disk-shaped inclusions (with $n = 3$) (O'Connell & Budiansky 1977) or the ratio of length to diameter for tubules (with $n = 2$) (Mavko 1980). For tubules and the viscosity of basaltic melt ($\eta_f = 1–10$ Pas), $\tau_f$ is calculated to be at frequencies above the seismic band. This means that a partially molten region would have the same $Q$ as a subsolidus region at the same temperature, but that velocities would be lower. For disk-shaped inclusions, the aspect ratios have to be of order $10^{-3}–10^{-4}$ for relaxation (dissipation) to occur at seismic frequencies (Schmeling 1985, Faul et al. 2004), implying that both $Q$ and velocity will be affected by melt. Processes $a$ and $b$ affect only the shear modulus, whereas process $c$ affects the bulk modulus and hence is one of a few mechanisms that can cause bulk attenuation and reduction of the bulk modulus.

### 3.3. Dislocations

Dislocations are line defects that can give rise to both anelastic and viscoelastic dissipation. Detailed reviews of dislocation processes are provided, for example, by Karato & Spetzler (1990) and Jackson (2014); therefore, they are only discussed briefly here. Dislocations can be modeled as having a seamless transition from transient creep to steady-state deformation.

Morris and Jackson, 2009, Lee et al., 2011 Faul & Jackson, AREPS, 2015
Defects

Point defects, affect diffusion

diffusion affects:
  deformation
  grain growth
  seismic properties

Factors affecting diffusion rates: temperature, ‘water’?, melt, oxygen fugacity