

## Tentamen: GEO3-1304, Structure and Properties of Earth Materials

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### Instructions:

- Read all questions through, thoroughly, before answering.
- Answer **8** from the **10** questions and clearly label your answers with the question number.
- Use S.I. units, unless stated otherwise.
- Show any calculation steps clearly and use annotated diagrams where appropriate.
- Write your name clearly on each separate answer sheet.
- Duration of examination: 3 hours

### Use the following where needed:

Avogadro's Constant,  $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$ ,

Planck's constant,  $h = 6.626 \times 10^{-34} \text{ J s}$ ,

Rest mass of electron,  $m_e = 9.10956 \times 10^{-31} \text{ kg}$ ,

Charge on electron,  $e = 1.60219 \times 10^{-19} \text{ C}$ ,

1 electron volt (eV) =  $1.602 \times 10^{-19} \text{ J}$ ,

Universal Gas Constant,  $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ,

Boltzmann's constant,  $k = 1.381 \times 10^{-23} \text{ J K}^{-1}$

$\log_a x = \log_b x / \log_b a$  with  $\log_{10} e = 0.43429448$  and  $\log_e 10 = 2.30258509$

1 kbar = 100 MPa;

1 Ma  $\approx 3.15576 \times 10^{13} \text{ s}$

(Note: "erfc<sup>-1</sup>" is the inverse complimentary error function not "1/erfc")

### Reminder:

Do not use reference books, notes and information sources other than your wonderful brains!

Turn off all communications devices.

You may use a standard scientific calculator.

### Questions:

1.

- a) You are given a set of hand specimens of mantle rocks. How would you identify the depths of origin of the different samples? What clues would you look for to identify their mode of emplacement into the crust? Give as much information as you can about mineralogy, alteration and textures.
- b) Draw a phase diagram to show what would happen to the mineral Olivine ( $\text{Mg,Fe}_2\text{SiO}_4$ ) if it were to sink through the Earth's mantle from a depth of 100 km in the upper mantle, through the transition zone to a depth of 750 km in the lower mantle.
- c) Describe how you would distinguish olivine from clinopyroxene in a petrographic thin-section of a mantle rock. In your answer describe how the mineralogical properties (*e.g.* relief, colour, cleavage *etc.*) are linked to crystal structure.

2.

- a) Explain the forces that control the position of atoms in a crystal and, with the aid of force and energy diagrams, show the physical reasons behind linear elasticity and thermal expansion.
- b) How does the elastic shear modulus relate to the S-wave velocity in minerals and rocks? What can seismic S-wave detection tell us about the Earth's deep structure?

- c) Where is heat stored in a crystal and explain why liquid water has such a high  $\star$  heat capacity ( $3\times$  most crystalline metals), despite being a fluid?
- d) Why do metals generally have higher heat capacities, thermal conductivities and electrical conductivities than non-metallic elements, at low to moderate temperatures? *de-localized electrons*
- e) What is the Fermi level in electronic semiconductors and metallic- conductors?

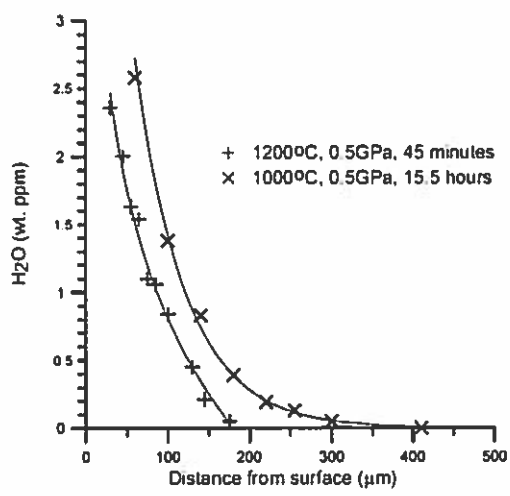
3.

Perovskite ( $MgSiO_3$ ) is the dominant mineral in the lower mantle.

- a) Sketch the unit cell of the structure of perovskite.
- b) What is the co-ordination number of Si in perovskite?
- c) How does the structure of Perovskite change when it enters the D'' layer at the base of the lower mantle? Give as much detail as you can.
- d) Why does your answer to (c) help explain the seismic properties of this region where the core and mantle interact and where mantle plumes may form?
- e) What other minerals are abundant in the lower mantle?

4.

In crystals of periclase ( $MgO$ ) the substitution of  $Mg^{2+}$  ions by  $H^+$  (protons) causes half-electrically-compensated cation vacancy defects ( $V_{OH}^-$ ) which effectively incorporate water in the crystal structure. These hydrous, colour-centre, defects absorb infrared radiation and their concentration may be measured using infrared spectroscopy. High pressure, high temperature diffusion experiments by Joachim *et al.*, 2012, *Phys. Chem. Minerals* 40:19-27, have recently measured the mobility of these protons in diffusion experiments and have shown that up to 3.5 ppm water, by weight, may be incorporated in the lattice of periclase at  $1200^\circ C$  and  $0.5 GPa$ . Initially dry, periclase crystals were surrounded by water in a capsule then heated under pressure and temperature to allow diffusion of water in through the crystal surface. Subsequent infrared spectroscopy measured the concentration profiles inwards from the surface as differences in infrared absorption. Data for two runs are given here in a graph:



Integrating Fick's 2<sup>nd</sup> law,  $\frac{\partial c}{\partial t} - D \frac{\partial^2 c}{\partial x^2} = 0$

gave the following solution for the boundary condition of a constant surface concentration,  $c_0$ , (assuming  $D$  is independent of concentration and position).

$$c_{(x,t)} = c_0 \left[ 1 - \operatorname{erf} \left( \frac{x}{\sqrt{4Dt}} \right) \right] = c_0 \left[ \operatorname{erfc} \left( \frac{x}{\sqrt{4Dt}} \right) \right]$$

So, by using the inverse complementary error function  $\operatorname{erfc}^{-1}$ , we obtain:

$$\operatorname{erfc}^{-1} \left[ \frac{c_{(x,t)}}{c_0} \right] = \frac{x}{\sqrt{4Dt}}$$

- a) Use the data from the following table to calculate the diffusion coefficients for protons in periclase at 1200°C and 1000°C.

1200°C, 0.5GPa for 45 minutes		1000°C, 0.5GPa for 15.5 hours	
$\text{erfc}^{-1}[c_{(x,t)}/c_0]$	$x$	$\text{erfc}^{-1}[c_{(x,t)}/c_0]$	$x$
0.1715	$20 \times 10^{-6} \text{m}$	0.3347	$50 \times 10^{-6} \text{m}$
0.3430	$40 \times 10^{-6} \text{m}$	0.6693	$100 \times 10^{-6} \text{m}$
0.5146	$60 \times 10^{-6} \text{m}$	1.0040	$150 \times 10^{-6} \text{m}$
0.6861	$80 \times 10^{-6} \text{m}$	1.3387	$200 \times 10^{-6} \text{m}$
0.8576	$100 \times 10^{-6} \text{m}$	1.6734	$250 \times 10^{-6} \text{m}$
1.0291	$120 \times 10^{-6} \text{m}$	2.0080	$300 \times 10^{-6} \text{m}$

- b) Give a general formula for the temperature dependence of diffusion which can be used graphically, to determine activation energy from the magnitude of the slope. What do we call such graphs?
- c) Use the two diffusivities you obtained, above, to calculate the activation energy for the diffusion of protons in periclase single crystals, in  $\text{kJmol}^{-1}$ .
- d) What are colour centres in ionic crystals and why do they cause colouration?
- e) Name an olivine-polymorph, from the deep mantle, which is known to accommodate water as defects in its structure and explain the possible significance of this for our planet's evolution.

5.

- a) Why do mineral transformations often not take place directly on the boundary between two stability fields on a phase diagram? How does this delayed response, beyond the equilibrium point, change with temperature?
- b) Why are some minerals metastable? Which thermodynamic parameter is this linked to?
- c) Exsolution can occur through two different mechanisms. Describe the different mechanisms and show how a phase diagram can be derived from the Gibbs free energy of mixing across a range of different temperatures and for a solid solution between two end-member compositions A and B. Show the position of the solvus and the spinodal curves on your phase diagram.
- d) Experiments were performed to measure the kinetics of coarsening exsolution lamellae. Two rate laws could be written, both of which fit within the range of experimental error:
- $$\lambda = \lambda_0 + kt^{1/3}$$
- $$\lambda = \lambda_0 + (kt)^{1/3}$$
- Which of the above equations could be used give the correct solution for activation energy  $E_a$  and why?

6.

- a) Explain why graphs of  $\log$  (diffusion rate coefficient,  $D$ ) versus  $1/T_{\text{abs}}$ , for polycrystalline materials often show a kinked plot, with the low temperature negative slope steepening rapidly above a certain temperature to a, well defined, steeper slope at high temperatures. Draw a typical graph with labels to explain the underlying reasons for the changes in slope in terms of diffusive processes that occur in the polycrystalline material. What sort of graphs are these?

- b) What probability distribution underlies the thermal behaviour seen in these graphs?
- c) What is the role of defects in assisting solid state diffusion?
- d) Why do solid state diffusion couples produce concentration profiles which are often displaced from the original material junction?
- e) Why does solid state ionic electrical conductivity share similar activation energies to solid state diffusion in ionic crystals?

same transport process

X 7.

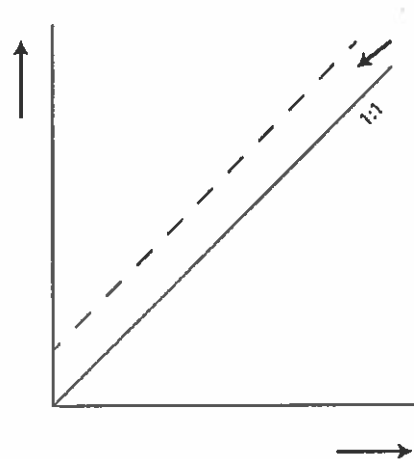
- a) The human body is full of biominerals. What type of biomineralization, that is also observed to occur with bacteria, is present in the human body?
- b) What is the name of the most important biomineral in the human body? How is it different from the same type of mineral that we can also find in geological settings?
- c) The chemical and structural characteristics of this mineral are beneficial and specific for its use within the human body. What are the benefits of these differences for its use in bone?
- d) How does the mineral present in tooth apatite differ? How does this reflect its use in the body?

X 8.

- a) Is the work required to cleave a quartz crystal in a vacuum the same as when this is done submerged under water? Explain your answer.
- b) Explain the interfacial contact angle formed by liquid droplets on a solid surface.
- c) What is disjoining pressure and what minerals are likely to show its effect when wet?
- d) In a glass of carbonated drink, why do small gas bubbles form on dirty spots on the glass wall or hairs and dust floating in the liquid?
- e) What are chondrules in chondritic meteorites? Why are they *i*) spherical, *ii*) often show glassy rims and *iii*) may have fine crystals radiating inward from their outer surfaces?

8 9.

- a) The morphology of crystals is controlled by a number of different factors. Fill in the missing pieces of information in the diagram, including the names of the morphologies adopted by crystals above the dotted line, between the dotted line and 1:1 line and below the 1:1 line.
- b) Draw a diagram of the three different types of crystals.
- c) Explain how and why crystals display the morphology expected under fast growth but slow diffusion conditions.
- d) What happens to NaCl crystals grown in a solution containing Pb (lead), draw a diagram and describe?
- e) Explain why this happens in terms of a Kossel crystal.



10.

- a) What is Bragg's law of diffraction and how may it be used to determine the lattice spacing of crystals?
- b) What advantage does neutron diffraction have over electron and x-ray diffraction, in measurement of crystal unit cell dimensions?
- c) The energy of an electron is related to its wavelength via the De Broglie relation:  $\lambda = h/p$ , where the momentum  $p = (2m_e eV)^{1/2}$ , and  $h =$  Planck's constant. What is the wavelength of electrons produced in a 1MeV transmission electron microscope? If a cubic magnetite crystal viewed in this microscope has a unit cell lattice parameter of 840pm, then by what angle will such a beam of electrons be diffracted?
- d) How may line defects (dislocations) in deformed crystals be imaged and what instrument achieves this?

*Good luck!*