

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

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Datum: 09-11-2018, 13:30-16:00, Olympos, HAL-3

Instructions:

- Read all questions through, thoroughly, before answering.
- Answer any 6 from the 8 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: **2.5 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, $m_e = 9.10956 \times 10^{-31} \text{ kg}$;

Rest mass of a neutron, $m_n = 1.67493 \times 10^{-27} \text{ kg}$;

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, $k = 1.381 \times 10^{-23} \text{ J K}^{-1}$;

$\log_e x = \log_{10} x / \log_{10} e$ with $\log_{10} e = 0.43429448$ and $\log_e 10 = 2.30258509$;

10 kbar = 1GPa; 1Ma $\cong 3.15576 \times 10^{13} \text{ s}$

Reminder:

Do not use reference books, notes and information sources other than what is given on this paper!

Turn off all communications devices.

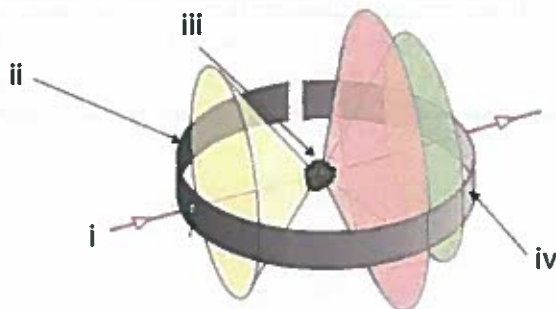
You may use a standard scientific calculator.

Questions:

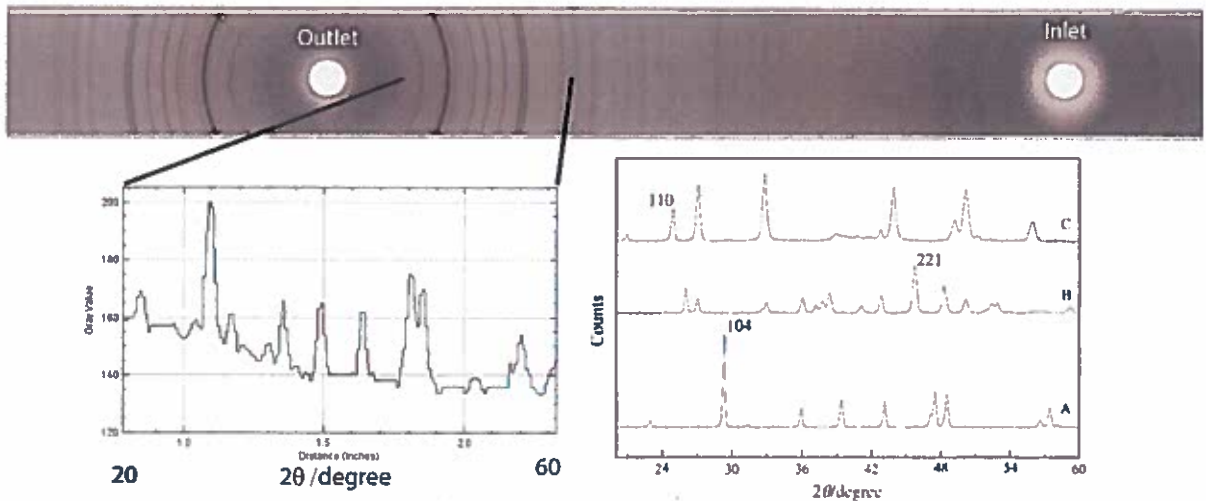
[n] indicates the marks allocated to each part question. All 8 questions carry equal weight.

1.

a) A schematic of an old powder XRD camera is shown below. Complete the missing labels. [4]



b) Inside of the camera there was still a photographic film of the last sample that was analysed. Look at the picture of the photographic film (below) and compare it to the different Ca-carbonate phases from Kontoyannis and Vagenas 1999. Which phase (A, B or C) is likely to be the last one measured in this X-ray diffractometer, explain how you came to your conclusion? [3]



c) A critical piece of information is missing if we want to calculate important parameters from the XRD pattern such as unit cell size and space between planes, called d , using the Bragg equation. What is it? How would increasing and decreasing this parameter affect the calculation of d spacing? [3]

d) Using the ΔH_f° for calcite and aragonite below and Hess' law calculate the ΔH associated with the transformation of calcite to aragonite. [4]



e) Name the type of reaction that describes this change in enthalpy. [1]

f) If we know the entropy changes during a reaction we can use Gibb's free energy to evaluate whether the reaction will occur or not, where the change in Gibb's free energy during a reaction is given by $\Delta G = \Delta H - T\Delta S$. Using the $\Delta S = -3.7 \text{ Jmol}^{-1}$ for the transformation of calcite to aragonite and your answer to d) for ΔH , calculate ΔG for the transformation of calcite to aragonite at standard conditions (1 atm and 298.15 K). Which phase do we expect to find at standard conditions and why? [5]

2.

a) The tip of a stylus used in an Atomic Force Microscope (AFM) is usually an atomically-sharp silicon nitride crystal under a thin flexible silicon cantilever. Extremely small contact forces (of the order of 10^{-12} N) are sensed using the flexure of the silicon cantilever. Explain the nature of the forces experienced by the stylus tip as it is lowered steadily towards the surface of a crystal under vacuum. Use a force versus displacement diagram to explain the response during approach and retreat of the stylus from the surface. [3]

b) What basic limitation does the scanning tunnelling microscope have that affects the choice of material which can be observed? [1]

c) Following on from part a), explain why the atoms in crystals have a regular structure, exhibit elasticity and thermal expansion. What is responsible for the forces between atoms in this case? Draw a force and potential energy diagram versus atomic separation to show that atoms in a crystal occupy potential wells, to illustrate your answer? [3]

d) What work is required to create two fresh crystal surfaces, each of unit area, by cleavage under a vacuum? [1]

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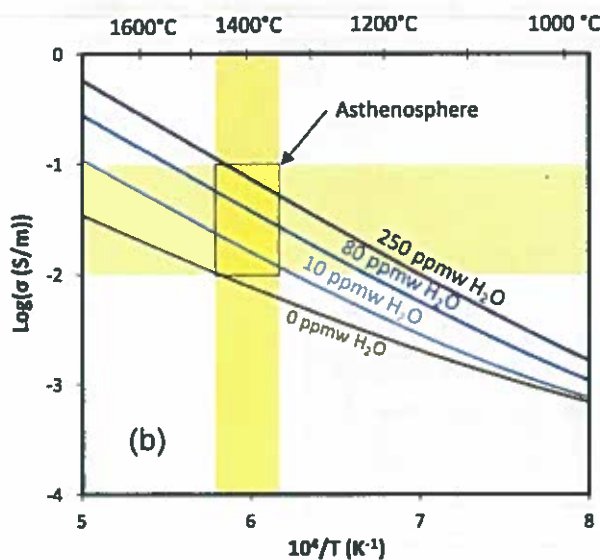
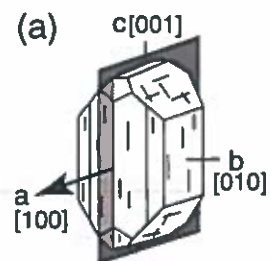
- e) Is the work required to cleave a quartz crystal in a vacuum the same as when this is done submerged under water? Explain your answer and what does this mean for the brittle strength of wet rocks. [4]
- f) How does electronic conduction vary with temperature in metals versus semiconductors? [2]
- g) Zirconia (ZrO_2) is an (O^{2-}) ionic conductor at high temperature. Explain with a diagram how it can be used to generate “environmentally friendly” electricity from hydrogen and air in a fuel cell. [3]
- h) Why does solid state ionic electrical conductivity often share the same activation energy to ionic diffusion? [2] What relation links the two transport processes? [1]

3.

- a) Olivine undergoes several phase transitions as it descends to deeper depths, thus higher pressures and temperatures in the Earth’s mantle. Draw a phase diagram to show what would happen to the mineral olivine 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. What phases does olivine transform into along this path? [10]
- b) When the mantle rocks are sampled at the Earth’s surface we no longer see the higher pressure phases that olivine transforms into unless they are contained within high pressure minerals such as diamond. Explain why this is in terms of the structures of these minerals and how they transform. [5]
- c) Although we rarely find direct evidence for these minerals in mantle rock specimens, we clearly observe the phase transformations during experiments. What other, indirect measurement do we have that indicates that these transformations occur in the mantle? [1]
- d) At higher pressures, perovskite is formed. Describe the structure of perovskite and explain how the structure of the Mg silicate minerals has adapted to the high pressure environment. [4]

4.

- a) Olivine ($(Mg,Fe)_2SiO_4$) is an abundant and therefore important mantle material. To what crystal system does it belong? [1]
- b) Olivine is anisotropic and exhibits different solid state diffusivities parallel to a [100], b [010] and c [001], see figure (a).



Experiments were recently performed to investigate the self-diffusion of hydrogen in olivine by Novella *et al.*, 2017, *Nature: Scientific Reports* 7:5344. Hydrogen (associated with water) is an important, small and mobile charged defect which affects solid state ionic electrical conductivity (via proton diffusion) and may explain high conductivities in the deep mantle measured by geophysical magneto-telluric methods, see their diagram (figure b, left) of conductivity (S/m) versus reciprocal temperature ($1/T$). What do we call such a diagram? [1]

Continued

- c) What is the significance of the slopes in such a diagram? [2]
 d) What relation allowed these scientists to use high temperature solid state diffusivity to predict high temperature ionic electrical conductivity of the same material? [2]
 e) In these experiments, Olivine single crystals were first sliced perpendicular to 3 principal directions a, b & c and the slices then annealed dry under reducing (low pO₂) conditions using a Ni-NiO buffer at 1300°C for at least 16 hours. Next these were hydrated in closed capsules using normal water (¹H₂O) at 2GPa for 18-48 hours dependent on the chosen temperature and finally these crystals were put in contact with heavy water ²H₂O where ²H is Deuterium, the stable heavy isotope of hydrogen. Just 1 hour was enough to produce a self-diffusion profile of exchanged deuterium with hydrogen defects within the crystals, for three different crystallographic directions, see figure (c) below, for 2GPa at 750°C. Analysis of the background deuterium content was performed by infrared absorption and the diffusion profiles were measured using secondary ion mass spectrometry (Nano-SIMS) as a function of depth from the crystal surface. The concentration profiles allow the diffusion coefficients to be determined. A solution of Fick's second law was used for a constant concentration of deuterium at the crystal surface C₁ and a zero concentration C₀ of deuterium, deep inside the crystal.

$$(C_{(x,t)} - C_0)/(C_1 - C_0) = \text{erfc}(x/(2\sqrt{(D_H t)}))$$

Rearrangement yields a formula for a straight line:

$$\text{erfc}^{-1}((C_{(x,t)} - C_0)/(C_1 - C_0)) = (1/(2\sqrt{(D_H t)})) \cdot x$$

where erfc^{-1} is the inverse complementary error function (not 1/erfc)

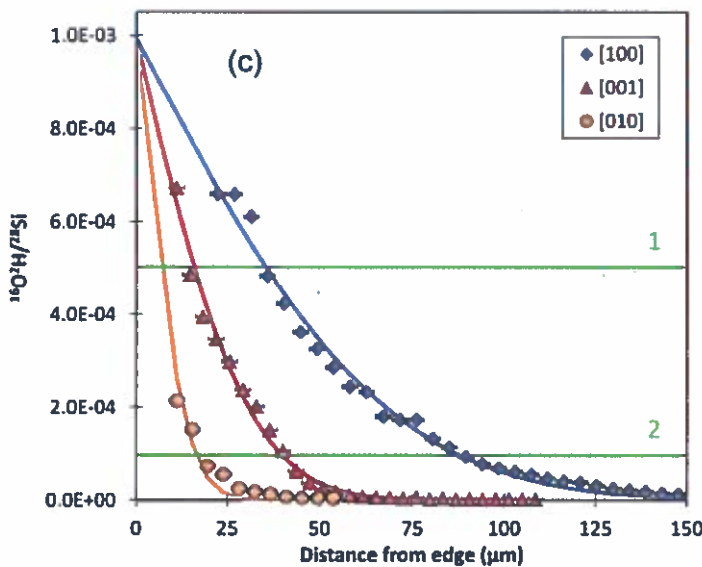


Figure (c) (left). Self-diffusion of hydrogen (as deuterium ²H by exchange with ¹H) profiles for three principal orthogonal crystal directions in olivine (from Novella *et al.*, 2017). All for 1 hour at 750°C, 2GPa. Green lines of constant concentration are drawn for the analysis.

Use the following data (below) taken from figure (c) to determine the 3 orthogonal diffusion coefficients. [4]

Tip: The inverse complimentary error functions are calculated for you!

Deuterium concentration at crystal edge (C₁) 1.00E-03
 Deuterium concentration deep in crystal (C₀) 0
 Diffusion time = 1 hour at 750°C, 2GPa (t = 3600 seconds)

| Profile crossing points at 2 concentrations: | 1 | 2 |
|---|----------|----------|
| Deuterium Concentration | 5.00E-04 | 1.00E-04 |
| [100] Blue: distance from crystal edge (m) | 3.69E-05 | 9.00E-05 |
| [001] Red: distance from crystal edge(m) | 1.69E-05 | 4.06E-05 |
| [010] Orange: distance from crystal edge (m) | 8.38E-06 | 1.75E-05 |
| $(C_{(x,t)} - C_0)/(C_1 - C_0)$ | 5.00E-01 | 1.00E-01 |
| $\text{erfc}^{-1}((C_{(x,t)} - C_0)/(C_1 - C_0))$ | 0.476936 | 1.163087 |

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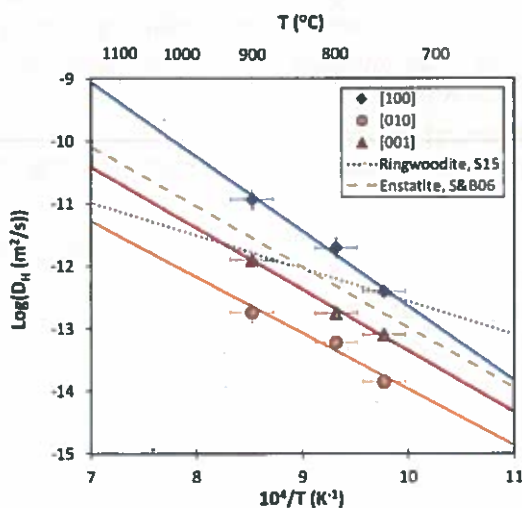
- d) Give a 3×3 matrix tensor representation of the anisotropy of these diffusion coefficients for olivine. [1]
 e) What deep mantle polymorph of olivine could hold more water in its crystal structure than olivine and where would you expect to find it? [2]

5.

- a) When we are looking for evidence of depth in mantle minerals we rely on so called depth marker minerals. Name the depth marker minerals in the order of low to high pressure, therefore depth. [4]
 b) What type of transformation do these minerals undergo and how is this related to their preservation in mantle rock samples? [3]
 c) To form the depth marker minerals you need to nucleate a new phase and diffuse the different chemical constituents to this newly growing phase. We also see this happening during unmixing of feldspars to create exsolutions. Draw a binary phase diagram of the Gibb's energy of mixing and use the change in this parameter with temperature to explain why you get unmixing. [8]
 d) Kinetics plays a big role in the number of exsolutions formed and their size. What would you expect to see for (i) very fast cooling and (ii) very slow cooling? Explain how this is related to the diffusion and nucleation processes required to make exsolutions. [5]

6.

- a) Experiments were recently performed to investigate the self-diffusion of hydrogen in olivine single crystals by Novella *et al.*, 2017, *Nature: Scientific Reports* 7:5344. Some of this data was used in question 2. Self-diffusion data for three orthogonal directions in olivine are plotted in the figure below as function of temperature. Determine the activation energy for solid state self-diffusion of hydrogen, from the three coloured lines plotted for the [100], [010] and [001] directions in olivine in figure below. This graph shows Log_{10} (Diffusivity of hydrogen) plotted versus reciprocal temperature ($\times 10^4$). [4]
Tip: The slopes are already measured as:
 Blue [100]: -27.544×10^3 K, Red [001]: -22.612×10^3 K & Orange [010]: -20.688×10^3 K.



- b) Also shown in the diagram is data for hydrogen diffusion in Ringwoodite and Enstatite. For which of these two minerals is hydrogen diffusion easiest? [1]
 c) Give an equation giving diffusion as a function of absolute temperature. What thermo-statistical distribution forms a part of this equation? [3]
 d) Show how this equation may be transformed to produce the kind of plot in the figure (left). [2]
 e) Infrared (IR) spectroscopy is used to determine the concentration of hydrogen defects as OH groups or as water molecules. What is being measured in such analysis? [3]
 f) Is heavy hydrogen (^2H , deuterium), contained in heavy water, going to shift the IR spectrum from normal $^1\text{H}_2\text{O}$ to higher or lower wave numbers? [1]
 g) How can pressure be measured in a Diamond Anvil Cell using small ruby crystals? [2]

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- h)** How can changes in chemical phase and reaction kinetics be monitored in very high pressure experiments? [2]
- i)** In tomographic experiments, using the synchrotron x-ray source at ESRF - Grenoble, crystals of halite (NaCl) become defective and coloured blue after exposure to the intense x-ray beam. Explain the source of this colour within the crystal structure? [2]

7.

- a)** Growing crystals have different sites, which show different reactivities. These can be described using the Kossel crystal model. Name the three different types of sites on the Kossel crystal and explain why their reactivities differ during dissolution. [5]
- b)** The shape of a crystal changes depending on the rate of crystal growth in comparison to the diffusion of the crystal building blocks. Silver dendrites are a good example of this. Explain how the dendrites form and how this is controlled by diffusion rate. Why do the dendrites show a characteristic 60° angle? [5]
- c)** Adsorption of impurities to different surfaces can change the overall shape of a crystal. Explain how the adsorption of Pb to halite changes the morphology of the crystal. Relate this to the halite crystal structure to explain why one surface is preferred over another by Pb. [5]
- d)** Biological organisms use impurities to force minerals to grow into specific shapes. Changing mineral chemistry can also assist with biological functions. Describe how apatite in bone is different from its geological counterpart and how this helps to fulfil its biological function. [5]

8.

- a)** Explain the interfacial contact angle formed by liquid droplets on a solid surface by a balance of interfacial tensions. How is this contact angle modified when the solid can deform easily? [4]
- b)** Why do some high temperature metamorphic rocks like marble have grain boundary triple junctions that meet at near 120° ? [2]
- c)** What physical processes compete in the nucleation and growth of new crystalline phases in the solid state? Illustrate your answer with energy diagrams of the main processes relating to solid state nucleation and growth of new phases within typical crystals. Explain why considerable undercooling is often required before new phases appear and become accommodated within crystalline material despite favourable thermodynamic prediction of their chemical phase stability. [5]
- d)** Explain the electrical structure near to mineral surfaces submerged in water. What is meant by the point of zero charge? [4]
- e)** How can ionic solutions flowing close to charged mineral surfaces generate a “streaming potential”? [3]
- f)** Explain why fine particles of minerals can be suspended in fresh water but may become quickly flocculated and sedimented by mixing with sea water. [2]

Good luck!