Tentamen: GEO3-1304, Structure and Properties of Earth Materials
Docenten: dr. C.J. Peach & dr. P.R.D. Mason
Datum: 4-11-2011, 13:30-16:30, Educatorium-µ (*mu*)

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, $N_A = 6.022 \times 10^{23}$ mol^{-1},
Planck's constant, $h = 6.626 \times 10^{-34}$ J s,
Rest mass of electron, $m_e = 9.10956 \times 10^{-31}$ kg,
Charge on electron, $e = 1.60219 \times 10^{-19}$ C,
1 electron volt (eV) $= 1.602 \times 10^{-19}$ J,
Universal Gas Constant, $R = 8.314$ J mol^{-1} K^{-1},
Boltzmann's constant, $k = 1.381 \times 10^{-23}$ 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 $\approx$ 100 MPa; 1 Ma $\approx 3.15576 \times 10^{13}$ s
(*Note:* "erf^{-1}" is the inverse error function not "1/erf")

Questions:
1.
- a) Which minerals could be used to indicate the depth of origin in a suite of mantle xenolith samples?
- b) Describe how you would identify the mineral Olivine under the optical microscope. In your answer explain as far as you can how the optical properties are related to the crystal structure of this mineral.
- c) Draw a phase diagram to show what would happen to the mineral Olivine $(Mg,Fe)_2SiO_4$ 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.

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 linear elastic modulus relate to the P-wave velocity in minerals and rocks? What can seismic P wave velocities and 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 heat capacity (3× most crystalline metals), despite being a fluid?
- d) Why do metals generally have higher heat capacities than non-metallic elements at low to moderate temperatures? (*continued*)

e) Current theory suggests that cyclic irradiation from solar heating and subsequent delayed radiative cooling of small rotating asteroids slowly forces these out of orbit (Yarkovsky effect). Calculation of this effect requires knowledge of heat capacity and thermal conductivity and is important because displaced asteroids (large or small) present a threat to our planet. Given that the asteroids (between Mars and Jupiter) are very cold (daily surface temperatures between 85K and 255K) and well below the Debye temperature for most of their constituent minerals (e.g. 460K for Fe, 2230K for carbon and ~700K for Fe,Mg-silicates) then comment on the use of "accepted" ~3R (25 $kJmol^{-1}K^{-1}$) values for heat capacity in these calculations What theory can help in this situation?

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 Perovskite change when it enters the D" layer?
   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?

4. Zircons [$(Zr_{1-y}, REE_y)(SiO_4)_{1-x}(OH)_{4x-y}$] are natural concentrators of Rare Earth Elements (REE) and importantly the radioactive elements Uranium (U) and Thorium (Th). These two unstable elements decay slowly by various nuclear processes to isotopes of Lead (Pb). Geoscientists assume that the system is chemically closed so that the variations, over geological time, in concentrations of U or Th relative to Pb can be used to estimate the age of rocks that contain the zircons. Knowledge of the mobility of these elements in zircon is therefore important to verify this assumption. The natural U, Th & Pb content of zircons has been used in simple diffusion experiments to measure these mobilities. Zircon crystals are placed in pure (U, Th & Pb free) solid sodium chloride (NaCl) to act as a sink with a sharp concentration gradient at the zircon crystal surface boundary to drive diffusion out of the crystals at high temperature. The NaCl becomes molten above 800°C and makes perfect contact with the zircon crystal surfaces. The initial concentration of the elements (U, Th or Pb) is C_0 within the crystal and is C_1 at the crystal surface boundary with the molten sodium chloride which surrounds the crystal. The NaCl is in excess and buffers this zero surface concentration throughout the experiment. The concentration profile inward from the surface of the crystal may be measured, using a sensitive high-resolution ion microprobe (SHRIMP; essentially, a secondary ion mass spectrometer), before and after a known period of diffusion under high temperature. The solution of Fick's second law for diffusion out of a semi-infinite medium and these boundary conditions is:

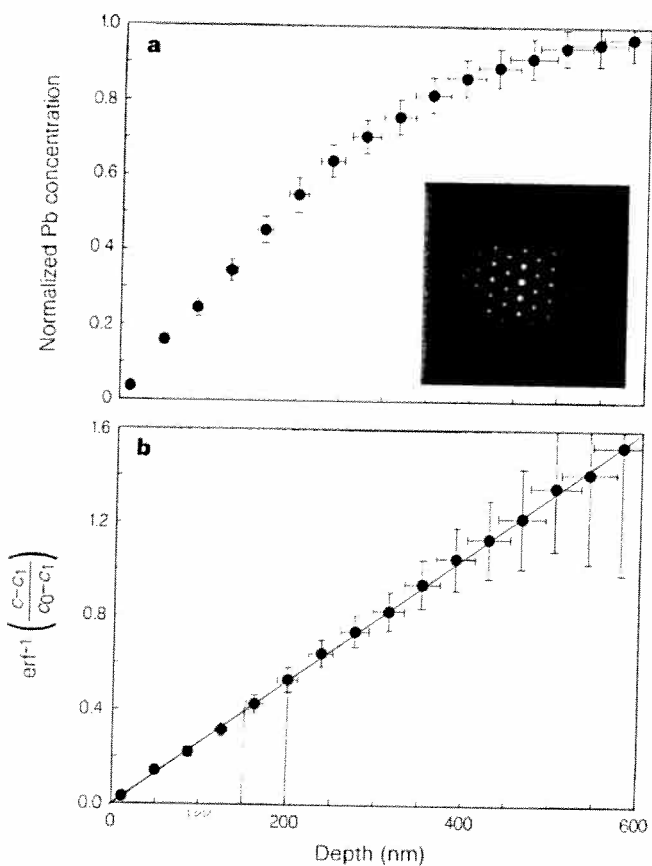$$\text{erf}^{-1}\left[\frac{C_{(x,t)} - C_1}{C_0 - C_1}\right] = \frac{x}{2\sqrt{Dt}}$$

   a) Use the data from such an experiment performed at 1100°C for 51.5 days (4.4496×10^6 s) given in the figures a&b (below) to calculate the diffusion coefficient for Pb in zircon.

Figure a: Normalized Pb concentration vs Depth (nm)

Figure b: $\mathrm{erf}^{-1}\left(\frac{c - c_1}{c_0 - c_1}\right)$ vs Depth (nm)

b) If the diffusion coefficient of Pb in zircon at 1100°C is found to be a factor of 16130 faster than at 900°C then calculate the activation energy, in kJmol^{-1}, assuming there is no change in diffusive process between 900°C and 1100°C.

c) Use the $\langle x \rangle = \sqrt{Dt}$ expression for the characteristic length of a diffusive process to decide whether, for zircon grains of 0.1mm diameter and age of 100 Ma, the system may be regarded as closed for radiometric dating purposes at or below 900°C. Note, at 1100°C, $D_{(Pb)} : D_{(U\ or\ Th)} \approx 2 \times 10^4$.

Figures a&b, (left): Data from Lee et al., *Nature* Vol. 390, 13th Nov. 1997, pp159-162. The inset shows a diffraction pattern of the zircon crystal to verify its good crystallinity. Assume the initial normalized concentration of Pb at the crystal surface and in the surrounding molten NaCl to be zero ($C_1 = 0$). The initial normalized concentration of Pb, deep in the crystal, (C_0) is assumed to be 1.

5.

a) What are the three main types of *solid solution* observed in minerals? Give examples of specific minerals for each part of your answer.

b) How do the enthalpy and entropy of mixing in a solid solution interact to give *exsolution*? Sketch a diagram to show ΔH_{mix}, $-T\Delta S_{mix}$ and ΔG_{mix} vary in a binary system consisting of atoms A and B (*i.e.* over a composition from 100%A to 100%B).

c) Show how this information be used to construct a phase diagram with a solvus that gives two stable compositions at one temperature T?

d) There are two mechanisms for unmixing during exsolution. Explain what these are and under what conditions each mechanism might occur.

6.

a) What process produced the Widmanstätten lamellae in the iron meteorites and how may these be used to find cooling rates of planetary core material?

b) What physical processes compete in the exsolution 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 in typical crystals. Explain why considerable undercooling is often required before new phases appear and are accommodated in crystalline material despite thermodynamic prediction of their chemical phase stability.

7.

a) Why are mineral surfaces highly reactive? In your answer describe the different mechanisms by which new atoms may attach themselves to the surface of a mineral from a surrounding solution. *(continued)*

b) How does the presence of microorganisms on the mineral surface influence that surface? Illustrate your answer with an example of a mineral whose surface properties are changed by adhesion of bacteria.

8.

a) Explain why graphs of log(diffusion rate, D) versus $1/T_{abs.}$, for polycrystalline material 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. What sort of graphs are these? Draw one with labels to explain the underlying reasons for the changes in slope and give a general formula for the temperature dependence, in order to explain the significance of the magnitude of the slope in such graphs.

b) Explain how "clean" electricity may be generated from a fuel-cell using an ionic conductor like zirconia (ZrO_2) and hydrogen fuel? Describe the physical/chemical processes in operation, the transport of charge at each material interface and type of charge carriers transported in each material, including the connection wires. Why is this technology considered to be clean? Would such a fuel-cell operate at room temperature and if not why not?

9.

a) What kind of crystals would you observe growing from solution when the rate of crystallization slightly exceeds the rate of diffusion in the surrounding solution? Illustrate your answer with sketches.

b) What type of crystals would be formed if the crystallization rate increased? Give an example of a mineral or metal that could adopt this crystal form.

c) What effect might impurities (in the surrounding solution) have on crystal growth? Which crystallographic sites are most likely to be affected?

10.

a) 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 crystal viewed in this microscope has an atomic spacing of 564pm, then by what angle will such a beam of electrons be diffracted?

b) Scanning probe microscopy has many variants. Describe the basics of the atomic force microscope (AFM) and outline the principles at work in producing an atomic scale image. If the probe is raised and lowered near a crystal surface explain how the cantilever will respond and outline the forces involved? What effect of anisotropy in the crystal structure of lead zirconium titanate (*PZT*) is utilized in the actuator of these microscopes (the converse effect is used in gas ignition systems)?

c) Why do thermally equilibrated metamorphic rocks, like marbles and deep-crustal granulites, often have grain boundaries at 120°? Explain the role of surface/interface energetics.

d) Suggest reasons for the dendritic morphology of snow crystals grown in cold humid air and also for the basic characteristic hexagonal symmetry.

Good luck!