Tentamen: GEO3-1304, Structure and Properties of Earth Materials
Docenten: dr. C.J. Peach, dr. P.R.D. Mason
Datum: 05-11-2008, 13:00-16:00, C.008 & C.010

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) = 1.602×10^{-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 $\log_e 10 = 2.30258509$

Questions:

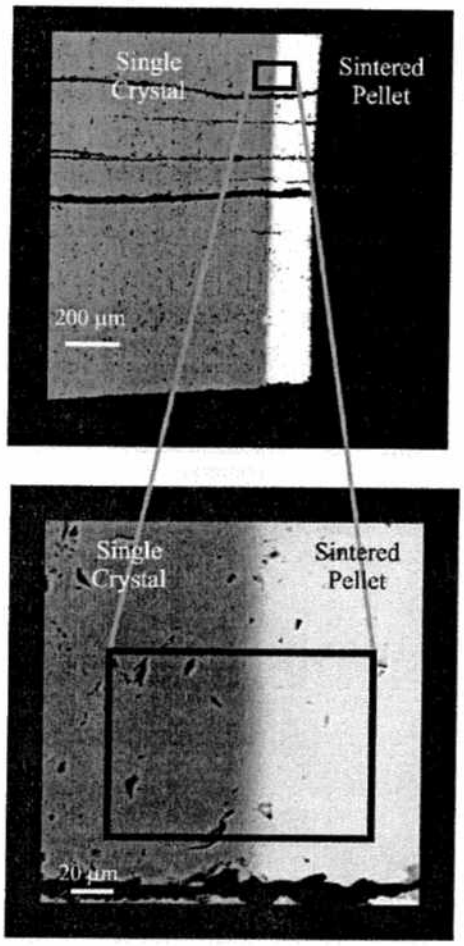
1.

a) Which minerals could be used to indicate the depth of origin in a suite of mantle xenolith samples?

b) Describe 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. Illustrate you answer with a sketch of a phase diagram with corresponding pressures of 0-150 kbar (upper mantle), 150-250 kbar (transition zone) and >250 kbar (lower mantle).

2.

In a study by Liermann and Ganguly, (2002), of high temperature diffusion of Fe^{2+} ions from a sintered pellet of iron bearing aluminous spinel $(Fe_{0.5}Mg_{0.5})Al_2O_4$ into a single crystal of pure magnesium aluminous spinel $MgAl_2O_4$, the inter-diffusion of iron and magnesium was experimentally determined. The data below was obtained from this simple diffusion couple type experiment at 1200°C and 2.16GPa for 48hr, in a piston-cylinder type high pressure apparatus. The electron backscattered image of the couple after the experimental run shows the diffusion of iron (white) into the darker magnesium rich single crystal as a gradational grey interface.



Above: *Electron backscattered images of the diffusion couple used to measure the concentration profile of Fe^{2+} in the spinel materials.*
Right: *Tabulated values of the error function and its compliment.*

η	erf η	erfc η
0	0	1.0
0.02	0.022565	0.977435
0.04	0.045111	0.954889
0.06	0.067622	0.932378
0.08	0.090078	0.909922
0.10	0.112463	0.887537
0.15	0.167996	0.832004
0.20	0.222703	0.777297
0.25	0.276326	0.723674
0.30	0.328627	0.671373
0.35	0.379382	0.620618
0.40	0.428392	0.571608
0.45	0.475482	0.524518
0.50	0.520500	0.479500
0.55	0.563323	0.436677
0.60	0.603856	0.396144
0.65	0.642029	0.357971
0.70	0.677801	0.322199
0.75	0.711156	0.288844
0.80	0.742101	0.257899
0.85	0.770668	0.229332
0.90	0.796908	0.203092
0.95	0.820891	0.179109
1.0	0.842701	0.157299
1.1	0.880205	0.119795
1.2	0.910314	0.089686
1.3	0.934008	0.065992
1.4	0.952285	0.047715
1.5	0.966105	0.033895
1.6	0.976348	0.023652
1.7	0.983790	0.016210
1.8	0.989091	0.010909
1.9	0.992790	0.007210
2.0	0.995322	0.004678
2.2	0.998137	0.001863
2.4	0.999311	0.000689
2.6	0.999764	0.000236
2.8	0.999925	0.000075
3.0	0.999978	0.000022

Because the composite inter-diffusion coefficient $D_{(Fe\text{-}Mg)}$ has only a weak compositional dependence then a simple mathematical solution of the diffusion equation (Fick's second law) for the correct boundary conditions (Crank, 1983) could be applied (similar to the Grube method) to give:

$$C_{(x,t)} = \frac{C_1 - C_0}{2} \operatorname{erfc} \frac{x}{2\sqrt{Dt}}$$

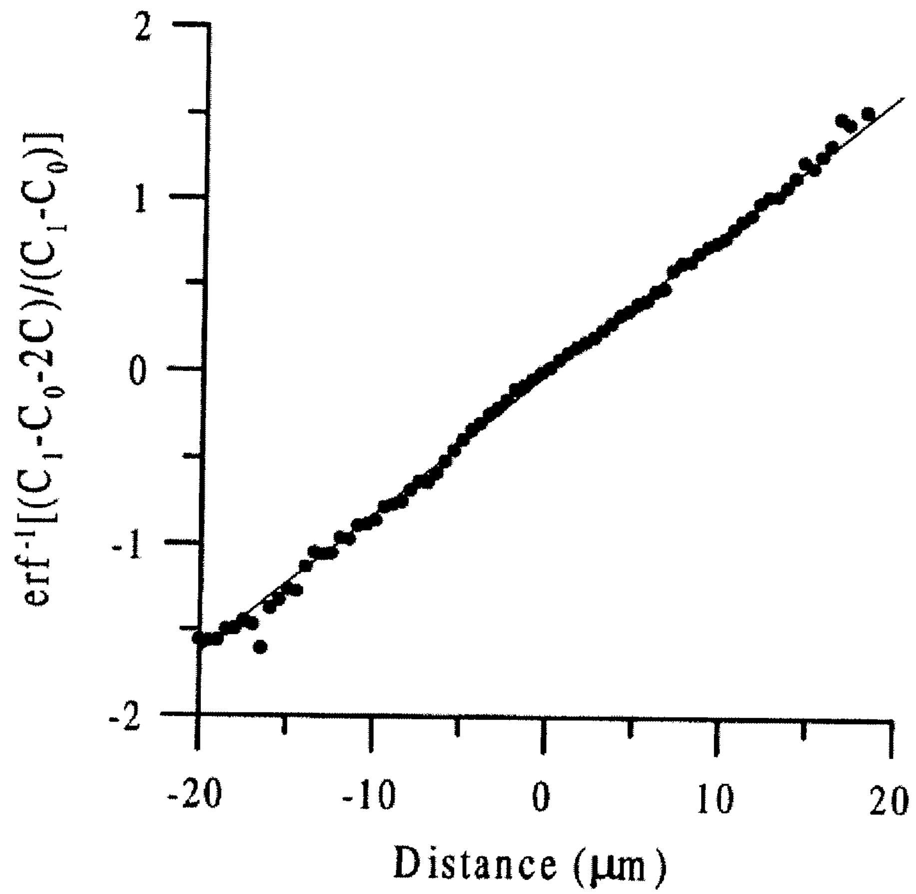
Where **erf** is the Gaussian error function and **erfc** is its compliment (tabulated above for reference).

Rearrangement gives:

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

Where, C_1 and C_0 are the initial concentrations of Fe^{2+} on the two sides of the interface with $C_1 > C_0$. $C_{(x,t)}$ is the concentration with position x after time t.

a) The data for the concentration profile for Fe^{2+} is given below, making use of the mathematical solution above. Use this to calculate the diffusion coefficient for Fe^{2+} ions into pure magnesium spinel and state your units.



b) If the inter-diffusion coefficient $D_{(Fe\text{-}Mg)}$ was concentration dependent then what method could be better applied to this problem?

c) What steps are required at the atomic scale for solid state diffusion to proceed?

3.

Three different widely-adopted crystal structures have been described in detail during the course. Choose one out of the Spinel (AB_2O_4), Perovskite (ABO_3) or Rutile (MO_2) types.

a) Sketch the unit cell of your chosen structure type.

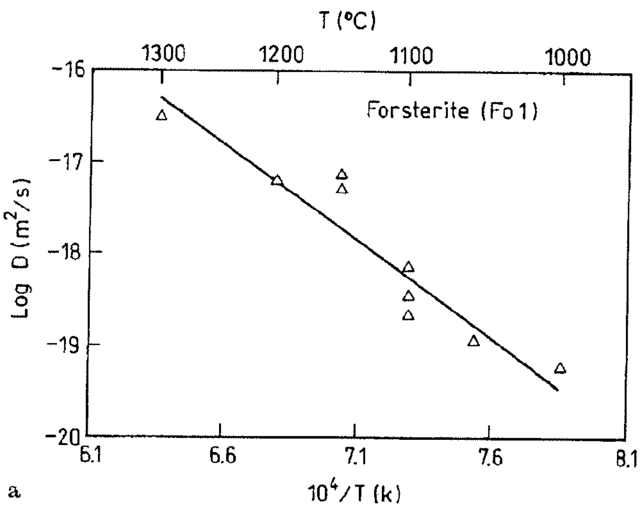
b) Give an example of a mineral that adopts this structure and describe where it could be found within the Earth.

c) **EITHER** - (*i*) How does this mineral reflect or respond to temperature and pressure conditions in the part of the Earth you just described in part (**b**) above?

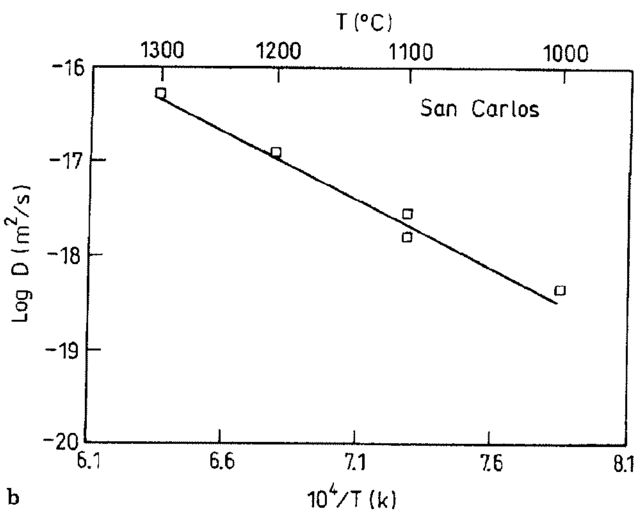
OR - (*ii*) How does your chosen mineral help to create or remediate environmental problems?

4.

The results of single crystal diffusion experiments for the diffusion of the tracer ^{26}Mg into two olivines are given, below, as a function of absolute temperature. Both experimental sets were carried out under similar low oxygen atmospheres to prevent oxidation of the iron from Fe2+ to Fe3+. Melt-grown crystals of pure forsterite (Mg_2SiO_4) and natural single crystals of olivine with composition $(Mg{:}92\%,Fe{:}8\%)_2SiO_4$ picked from San Carlos peridotite nodules (xenoliths in a basalt), are represented in the two plots (a) and (b) respectively, below:



a



b

a) What kind of diagrams are these?

b) Write an equation relating diffusion coefficient to absolute temperature, based on these diagrams.

c) What does the slope of these plots represent?

d) At 1100°C, in which type of olivine is the diffusion of ^{26}Mg easiest?

e) In both materials, what is the significance of only a single slope being visible over the temperature range?

f) Estimate the activation energy for diffusion of ^{26}Mg, in each olivine type, based on the presented data. *Note: $log_{10}D$ is plotted against 10000/T, (T in kelvin; i.e. 1000 celcius will plot as $(1/1273.15) \times 10000 = 7.854$ on the horizontal axis.*

g) Given that both crystals had similar crystallographic orientation for diffusion, then suggest what processes could be responsible for the difference in the measured slopes?

5.

a) Show how the enthalpy and entropy of mixing combine to control the Gibbs free energy of mixing in a regular solid solution. Demonstrate in your answer how phase separation can result from an overall free energy reduction and how this effect varies with temperature.

b) Under what conditions might unmixing occur through *spinoidal decomposition* instead of the phase separation mechanism that you described in part (a). In your answer show the compositional range over which this could take place.

6.

a) Most mineral surfaces are electrically charged, affecting their behaviour in aqueous solutions. Expand on this, using words and diagrams, to explain the Gouy-Chapman electrical double layer and its components?

b) Explain why mineral surfaces may change their net charge in different aqueous ionic solutions.

c) What is the point of zero charge (pzc)?

d) Referring to the diagram below (Figure 6.1) of a sessile water drop on a solid glass substrate, then the equilibrium contact angle θ, satisfies Young's equation: $\gamma_{Sl} = \gamma_{SW} + \gamma \cos\theta$. Here the water drop has a phase boundary either against water vapour or an organic liquid (alkane), such as heptane, octane or hexadecane. The effect of pH on the surface tension of the water against its vapour or against an alkane is negligible (see Figure 6.2).

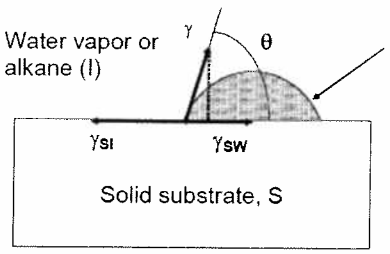


Figure 6.1

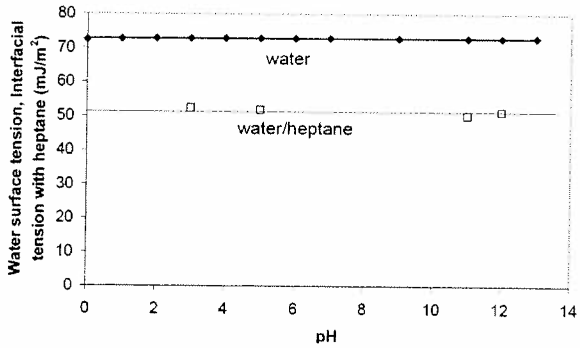


Figure 6.2

When the contact angle between water and an alkane on a silicate glass substrate is measured as a function of water pH then the following data is obtained see Figures 6.3 and 6.4. Explain why the contact angle is a function of water pH for these two sets of data.

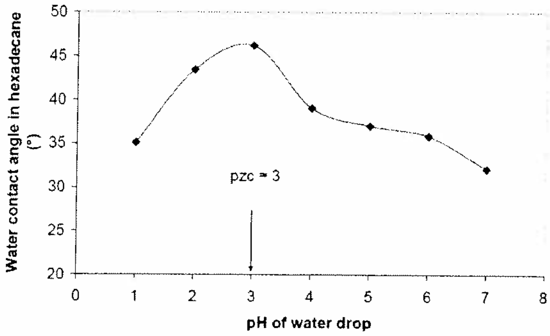


Figure 6.3

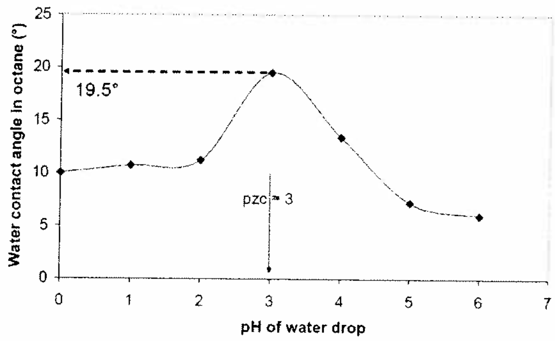


Figure 6.4

e) What are the consequences for light-crude oil production, by water flushing, from water-wet oil-filled pores in a low permeability siliciclastic reservoir rock with a similar composition to the silicate glass if the water pH is about 3? How can production be assisted through changes to the water pH?

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.

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 what is structurally responsible for the many extraordinary physical properties of water and indicate any significant effect these properties have on the present state of our planet.

b) Explain how the physical properties of water make it a good solvent for ionic solids such as sodium chloride. Why does the solubility fall dramatically as water becomes a super critical fluid near 375°C and 20 MPa?

c) Why does water absorb infrared radiation?

d) Why is this absorption property important for the Earth's climate?

e) Why does the sea look blue?

9.

a) Metallic silver can crystallize from a solution of silver nitrate in the following reaction

$$Zn + 2\,AgNO_3 = Zn(NO_3)_2 + 2\,Ag\downarrow$$

b) What are the mineralogical and chemical controls on the shape of the crystals and how do the diffusion and crystallization rates interact to give their distinctive shape?

c) What type of crystals would be formed if the diffusion rate increased but remained slightly lower than the crystal growth rate?

d) If acid was added to the solution the Ag would start to dissolve again. Which crystallographic sites would you expect to be most active during dissolution?

10.

a) What is Bragg's law and how may it be used to understand crystal structure?

b) What are the advantages of neutron diffraction over x-ray and electron diffraction in the characterization of atomic structures?

c) The energy of an electron is related to its wavelength via the De Broglie relation: $\lambda = h/p$, where the momentum $p = (2m_e\, e\, V)^{1/2}$, and h = Planck's constant. What is the wavelength of electrons produced in a transmission 1MeV electron microscope? If a crystal has an atomic spacing of 200pm, then by what angle will such a beam of electrons be diffracted?

Good luck!