Tentamen: GEO3-1304, Structure and Properties of Earth Materials
Docenten: dr. C.J. Peach, dr. P. Mason
Datum: 09-11-05, 14:00-17:00, C.108 & C.110

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 $^{-1}$,
1 electron volt (eV) = 1.602×10^{-19} J,
Universal Gas Constant, R = 8.314 J mol $^{-1}$ K $^{-1}$,
Boltzmann's constant, k = 1.381×10^{-23} J K $^{-1}$
$\log_a x = \log_b x / \log_b a$, $\log_{10} e = 0.43429448$

Questions:

1.

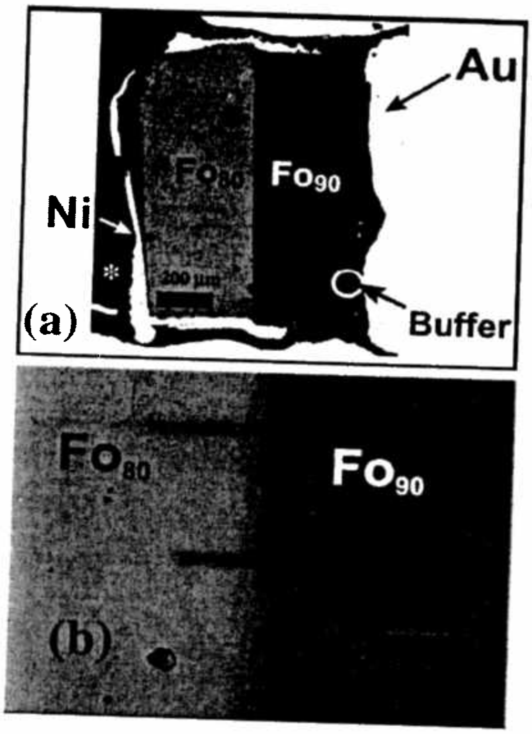
Describe what would happen to the mineral Olivine $(Mg,Fe)_2SiO_4$ if it were to sink through the Earth's mantle from a depth of 100 km in the upper mantle, through the transition zone to a depth of 750 km in the lower mantle. Illustrate you answer with a sketch of a phase diagram with corresponding pressures of 0-150 kbar (upper mantle), 150-250 kbar (transition zone) and >250 kbar (lower mantle).

2.

a) Solid-state diffusion requires a number of steps at the atomic scale. Describe these steps and explain why diffusion is faster at elevated temperature.
b) Show how the slope of a graphical plot of $\log_e$(diffusion coefficient) against 1/(absolute temperature), can give insight into the energetics of such steps.
c) What generic name is given to such a graph?
d) If such a graph shows a shallow slope at lower temperatures and a steeper slope at high temperatures then what possible physical processes could explain that behaviour, if seen in (*i*) polycrystalline and (*ii*) monocrystalline material?
e) The slope of a graph of $\log_{10}$[conductivity, (S m^{-1})] versus 1/[absolute temperature, (K)], gave a slope of –2000K, what was the activation energy for conduction in electron volts per atom?

3. Perovskite $(MgSiO_3)$ is the dominant mineral in the lower mantle consisting of a corner sharing array of SiO_6 octahedra.
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. A recent paper by Hier-Majunder *et al.*, 2005, documents diffusion experiments based on bi-crystals of olivine with two different iron (Fe) contents, Fo_{80} and Fo_{90}. Using a multi-anvil apparatus, to apply high pressure and temperature to the encapsulated bi-crystal (Figure 1a), the two crystals were allowed to inter-diffuse for 6 hours.



Figures 1a&b (left): a) encapsulated bi-crystal of olivine, surrounded by buffer material including nickel to control the oxidation conditions, within a gold jacket; b) electron backscatter image in atomic-number contrast to show diffusion of iron between the two crystals as a grey-scale.

The resulting diffusion profiles of iron content, after 6 hours at the experimental conditions, are visible in Figure 1b as grey-scale variations in the backscattered electron image. The profiles were measured, along the lines crossing the bi-crystal interface, using energy dispersive spectral analysis (EDS) of the backscattered electrons and also by wavelength dispersive spectral analysis (WDS), which gave smoother results (see Figure 2a, squares are WDS measurements compared with the noisier EDS background).

Table 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

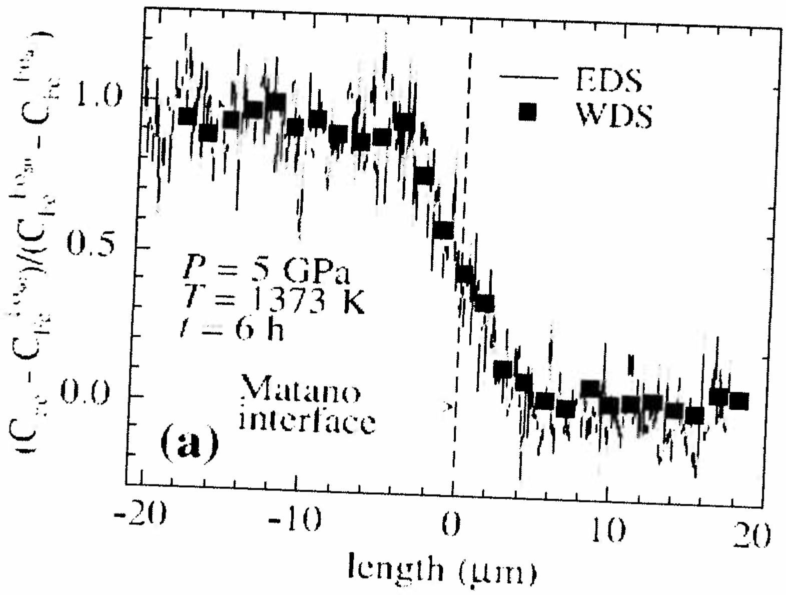


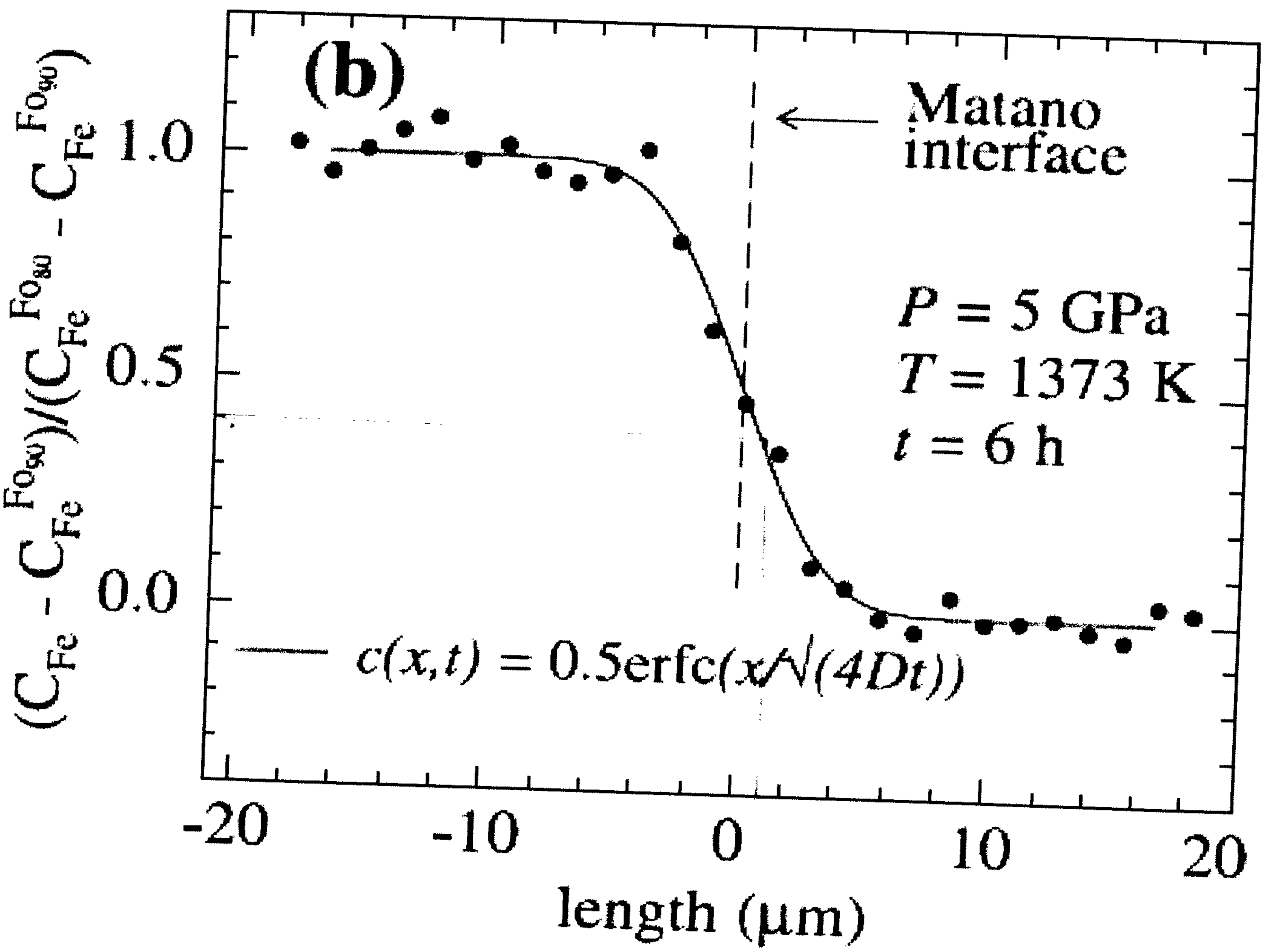
Figure 2a: (left) Diffusion profiles across the olivine bi-crystal measured by EDS and WDS, after a 6hour run.

The analysis of the diffusion profiles showed that a simple application of the diffusion equation was adequate and that the diffusion coefficient was not dependent upon concentration. A solution of the diffusion equation, for normalized concentrations of iron, as a function of position x, and time t, yielded:

$$c_{(x,t)} = \frac{C_{(x,t)} - C_{(\min)}}{C_{(\max)} - C_{(\min)}} = \frac{C_{Fe} - C_{Fe}^{Fo_{90}}}{C_{Fe}^{Fo_{80}} - C_{Fe}^{Fo_{90}}} = \frac{1}{2}\left[1 - \operatorname{erf}\frac{x}{\sqrt{4Dt}}\right]$$

Use this equation to calculate the diffusion coefficient for iron in the olivine. Use the smoothed function line that has been fitted to the data of Figure 2b, to make your calculation. The error function and its compliment are plotted in the attached table.

Figure 2b: Enlarged graph showing smoothed data from the 6hr run, to be used for your estimate of the diffusion coefficient for Fe in olivine.



Reference: Hier-Majunder, S., Anderson, I.M., and Kohlstedt, D.L., (2005), Influence of protons on FeMg interdiffusion in olivine, *J. Geophys. Res.*, V110, B022202, doi:10.1029/2004JB003292.

5.

a) How does the Gibbs free energy of a mineral vary with temperature?
b) Consider two phases α and β. Phase α is stable at low temperature and phase β is stable at high temperature. Describe what happens to the Gibbs free energy as the mineral transforms from α to β, on heating.
c) If the transformation is reversed, would you expect to see the same magnitude of change in Gibbs free energy and if not why not?

6.

a) Explain the energy changes in bringing, i) two similar and ii) two dissimilar material surfaces, into permanent contact.
b) What are these two processes called?
c) What is the consequence of two material phases having a negative interfacial energy when in contact with each other, in the fluid state?
d) In a thermally equilibrated rock, what can one conclude about the interfacial energy between a pore-fluid and a solid phase if the pore/grain interfacial angles are i) less than 60° and ii) greater than 60°?
e) A narrow tubular pore connects two fluid-filled inclusions, in a quartz crystal. One inclusion is 10x larger than the other. What will happen to the inclusions if the rock is subjected to prolonged high temperatures leading to textural equilibrium whilst the trapped fluid in the inclusions remains connected?
f) What role does surface energy play in the determination of crystal form?

7.

a) What are the three main types of *solid solution* observed in minerals? Give examples of specific minerals in your answer.
b) How do the enthalpy and entropy of mixing in a solid solution interact to give *exsolution*?
c) 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).
d) How can this information be used to construct a phase diagram with a solvus that gives two stable compositions at one temperature T?

8.

a) Most mineral surfaces are electrically charged, affecting their behaviour in aqueous solutions. Expand on this 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 known as the "point of zero charge", for a surface submersed in an aqueous ionic solution?
d) Why do suspensions of clay minerals and certain hydroxides increase their sedimentation rate when transported from fresh to salty water?
e) Explain how aqueous brine flowing through porous sandstone can generate a measurable electrical potential.

9.

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

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

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?

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

c) During dissolution of NaCl crystals in water which crystallographic sites would you expect to be most active?

10.

a) What is Bragg's law of diffraction?

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

c) How is pressure determined in a diamond anvil cell, when operating at conditions typical of the Earth's lower mantle?

d) What are the differences between the Atomic Force Microscope and Scanning Tunneling Microscope, in terms of their physics of operation at the microscopic level?

Good luck!