Geochemistry: An Introduction
The Exercises

FRANCIS ALBARÈDE

Ecole Normale Supérieure de Lyon

Introduction

These exercises are designed to illustrate my book *Geochemistry: An Introduction* published by Cambridge University Press in 2003. The reader will find a range of focus from low to high-temperature geochemistry and cosmochemistry, but with the constant drive to tease the reader with problems that are essential to the field. I emphasized exercises on the very same data used for major scientific breakthroughs (e.g., the age of the Earth). As the book is targeting a broad readership, the level of mathematical difficulty may occasionally exceed what a geology major is used to be confronted with, but never what he or she had been exposed to in classes of elementary calculus. The solutions have not been made available, so teachers can use this material for tests. They may eventually be posted at a later stage. I welcome requests for help on specific exercises at *albarede@ens-lyon.fr*. In principle, all the exercises have been fully worked out, but I will be grateful to anyone signaling errors and typos.

The reader should be aware of a number of typos in the first printing of the book itself. They will be corrected in a near future, but for the time being they are provided as an Appendix to this supplement.

Lyon August 25, 2004

Chapter 1: The Properties of the Elements

1. Give the first three quantum numbers of an electron in a $3p$ orbital

2. Find the electronic formula of the elements K, Hf, and F. Compare the orbital electronic configuration for K and Rb (s block), Hf and Zr (d block), F and Cl (p block). For each element, which ionic configuration should be the most stable?

3. Plot the ionic radius and the first ionization energy as a function of the number Z of protons

4. Which ion of Na^+, K^+, Rb^+, Mg^{2+}, Ca^{2+} has the smallest radius? Why?

5. Why is the ionic radius of Yb (0.99 Å) smaller than that of La (1.16 Å)?

6. Table 1 below gives the ionic radius of ions in angstroms for their most common charge and coordination number (CN). Plot (1) the ionic radius and (2) the coordination number vs charge. Comment on these two figures. The charge/radius ratio is a measure of the electrostatic field exerted on the environment of the ion: compare the field strength of Zr^{4+} and Nb^{5+} with that of Na^+ and Mg^{2+}.

Table 1: Ionic radius in Å for different ions with coordination number CN.

Ion	CN	radius	Ion	CN	radius	Ion	CN	radius
Al^{3+}	4	0.39	K^+	12	1.64	Si^{4+}	4	0.26
Al^{3+}	6	0.54	La^{3+}	6	1.03	Sr^{2+}	8	1.26
Ba^{2+}	12	1.61	Mg^{2+}	6	0.72	Th^{4+}	6	0.94
Ca^{2+}	6	1.00	Mn^{2+}	6	0.67	Ti^{4+}	6	0.61
Cr^{3+}	6	0.62	Na^+	6	1.02	U^{4+}	6	0.89
Fe^{2+}	6	0.61	Nb^{5+}	6	0.64	Yb^{3+}	6	0.87
Fe^{3+}	4	0.49	Ni^{2+}	6	0.69	Zn^{2+}	6	0.74
Fe^{3+}	6	0.55	P^{5+}	4	0.17	Zr^{4+}	6	0.84

7. What is the electronic formula of Fe^{2+}? Show that, depending on whether Δ, the energy gap between the e_g and t_{2g} orbitals, is large or small with respect to the electron-pairing energy, there are two ways of filling up the orbitals. Justify why one configuration is called low-spin and the other high-spin. For octahedra Fe^{2+}, calculate the Crystal Field Stabilization Energy (CFSE) in units of Δ for each case.

8. Calculate the Crystal Field Stabilization Energy (CFSE) in units of Δ for the common ions Sc^{3+} , Ti^{4+}, V^{5+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} in octahedral vs tetrahedral environments.

9. The platinum group elements (PGE) consist of the following transition elements: Ru (44), Rh (45), Pd (46), Os (76), Ir (77), and Pt (78) with their proton numbers given in parentheses. Discuss how to apply the crystal field theory to these elements and decide what you need to know to understand their crystal chemistry.

10. Let the length of a polyhedron edge be a and the radius of the circumscribed sphere be R. For a tetrahedron it can be shown that R = $(1/4)a/\sqrt{6}$ while for an octahedron R = $(1/2)a\sqrt{2}$. The ionic radius of O^{2-} is 1.4 Å. Calculate the radius of the cations that closely fit in a tetrahedral or octahedral site. Compare with the ionic radii of Table X.

11. Using the data listed in Table 2, draw a semi-logarithmic plot of the composition of:
    - ordinary chondrites normalized to CI carbonaceous chondrites for decreasing 50 percent condensation temperature
    - continental crust normalized to primitive mantle by decreasing values of the ratio
    - the primitive mantle normalized first to CI carbonaceous chondrites, then to ordinary chondrites using the same order
    - a Hawaiian basalt, a MORB, and an andesite normalized to primitive mantle using the same order

12. Using the first plot of the previous exercise, try to evaluate the condensation temperature of the elements for which this parameter is missing.

13. Using all the plots and a periodic table, find which group of elements is trivalent yttrium (Y) homologous to? Same question for thorium (Th) and uranium (U).

14. Equilibrium of silicate melts can be described by the reaction

    $$2\mathrm{O}^- \Leftrightarrow \mathrm{O}^{2-} + \mathrm{O}^0 \tag{1}$$

    in which O^0, O^-, and O^{2-} stand for bridging (Si-O-Si), singly bonded (Si-O) and free oxygen, respectively. Assuming that one mole of melt is produced from $X_{\mathrm{SiO_2}}$ moles of silica and (1- $X_{\mathrm{SiO_2}}$) mole of metal oxide MO, calculate the mole fractions of O^0, O^-, and O^{2-} with the assumption that the reaction above can be described by the equilibrium constant k.

Table 2: Concentration of various trace elements (in ppm) in different materials. CI = Orgueil-type chondrites, BSE = Bulk Silicate Earth. T_{cond} is the 50 percent condensation temperature.

	T_{cond}	Carbonaceous chondr. (CI)	Ordinary chondrites	Bulk Silicate Earth	Continental Crust	Basalt MORB	Basalt Hawaii
K	1000	558	798	240	15772	848	12200
Ti	1549	436	617	1205	4197	8513	1.7
Rb	1080	2.3	3.0	0.600	58	1.26	2.1
Sr	-	7.8	10.7	19.87	325	113.2	221
Y	1592	1.56	2.10	4.30	20	35.82	19.5
Zr	1780	3.94	6.03	10.47	123	104.24	108
Nb	1550	0.246	0.38	0.658	12	3.51	8.3
Ba	-	2.34	4.23	6.600	390	13.87	60.2
La	1520	0.2347	0.31	0.648	18	3.90	6.808
Ce	1500	0.6032	0.88	1.675	42	12.00	17.56
Pr	1532	0.0891	0.126	0.254	5	2.074	2.81
Nd	1510	0.4524	0.66	1.250	20	11.18	13.74
Sm	1515	0.1471	0.193	0.406	3.9	3.75	3.665
Eu	1450	0.056	0.076	0.154	1.2	1.335	1.246
Gd	1545	0.1966	0.304	0.544	3.6	5.077	3.93
Dy	1571	0.2427	0.353	0.674	3.5	6.304	3.61
Er	1590	0.1589	0.236	0.438	2.2	4.143	1.738
Yb	1455	0.1625	0.215	0.441	2.0	3.90	1.426
Lu	1597	0.0243	0.032	0.0675	0.33	0.589	0.203
Hf	1652	0.104	0.167	0.283	3.7	2.97	2.548
Ta	1550	0.0142	0.023	0.0372	1.1	0.192	0.679
Pb	-	2.47	0.305	0.150	12.6	0.489	0.633
Th	1545	0.0294	0.043	0.0795	5.6	0.187	0.527
U	1420	0.0081	0.013	0.0203	1.42	0.071	0.181

Chapter 2: Mass Conservation — Elemental and Isotopic Fractionation

Table 3: Concentration of major elements (in weight percent of oxide) in the different phases of a basaltic lava from the Reunion Island (Indian Ocean).

	glass	olivine	clinopyroxene	plagioclase
SiO_2	48.81	38.79	46.63	52.49
TiO_2	2.68	0.047	3.8	0.153
Al_2O_3	14.40	0.026	6.27	29.05
FeO	11.07	20.02	8.25	0.893
MnO	0.17	0.269	1.03	0.027
MgO	6.65	40.56	13.5	0.095
CaO	11.65	0.297	19.64	12.27
Na_2O	2.74	0.04	0.59	4.33
K_2O	0.79	0.024	0.05	0.372

1. Table 3 shows the major element compositions of the glass (= gl) and mineral phases (olivine = ol, clinopyroxene = cpx, and plagioclase = plag) in a basaltic lava from the Réunion Island hot spot (Indian Ocean). Calculate the composition of a lava with a similar interstitial glass with 15 wt% olivine and 10 wt% clinopyroxene phenocrysts.

2. Using the same data, calculate the major element composition of a wehrlite cumulate (80 wt% olivine and 20 wt% clinopyroxene), of a gabbroic cumulate (10 wt% olivine, 40 wt% clinopyroxene, 50 wt% plagioclase).

3. Using the same data, we consider how much cumulus olivine may change whole-rock compositions. Keeping the same interstitial glass and assuming variable proportions of olivine phenocryst from 0 to 40 percent, calculate the major element contents of the whole rock and turn the MgO and FeO oxide weight percents into moles per 100 grams of rock using the following atomic weights: 55.847 for Fe, 24.305 for Mg, and 16.00 for O. It is known that, at equilibrium, $(\mathrm{FeO/MgO})_{\mathrm{ol}}/(\mathrm{FeO/MgO})_{\mathrm{gl}}=0.3$ and this condition can be drawn as a line in the same diagram. Plot the molar FeO/MgO ratio of the olivine vs this ratio in the whole rock for olivine with different forsterite contents (e.g., different FeO/MgO ratios). Can you suggest a method to estimate whether olivine megacrysts present in a lava are phenocrysts in equilibrium with their host glass or xenocrysts? This method should not involve the analysis of the glass itself.

4. The δ^{18}O value of modern seawater is 0‰ while the average value of the polar ice cap is -45‰. The ice cap holds 2 wt% of the oceanic water. Calculate the δ^{18}O value of an ice-free ocean. Other water reservoirs can be neglected.

---

5. Table 4 shows the partial analysis (wt% of oxide) of a deep-sea sediment composed of quartz, clay, and carbonates. Calculate the abundance of each mineral phase in this sample.

Table 4: Composition of a deep-sea sediment and its mineral phases

oxide	sediment	quartz	clay	carbonate
SiO_2	45.7	100	51.4	0
Al_2O_3	13.2	0	26.4	0
CaO	16.5	0	0	55

6. Let us evaluate the concentration of the siderophile elements Fe and Ni and the proportion of other elements in the Earth's core. We assume that the Earth is made of a silicate mantle (we neglect the crustal contribution), which is often referred to as the Bulk Silicate Earth, and a metallic core. The core makes 1/3 of the total mass of the Earth. We further assume that the Earth is made of ordinary chondrites and we will test two extreme compositions, those of the H chondrites and LL chondrites. Use data in Table 5. For each case, find the abundances of Fe, Ni, and the unaccounted elements.

Table 5: Concentration of Fe and Ni (wt%) in H and LL ordinary chondrites and for the Bulk Silicate Earth.

element	H	LL	mantle
Fe	27.5	18.5	6.3
Ni	1.6	1.0	0.020

7. Using the data of Appendix A and G and a spreadsheet, calculate the abundances of various elements in the mean mantle by removing the amounts held in the continental crust from the Bulk Silicate Earth inventory.

8. Table 6 gives the composition of water samples taken along an estuary. We assume that, because of its high solubility, Cl is a good mixing indicator between freshwater and seawater. Plot the concentration of each element vs [Cl] down the estuary. Elements Al, Si, and Fe are considered to be non-conservative. Explain why.

9. Explain why moderate contamination of a basalt by granitic rocks does not greatly change the FeO/MgO ratio of the hybrid magma with respect to the ratio of the original basalt.

10. Black smokers from mid-ocean ridges spout waters resulting from the mixing of hydrothermal solutions with seawater. Which of the following plots do you expect to produce binary mixing arrays that are straight-lines:

    (a) $^{87}Sr/^{86}Sr$ vs [Mg]

Table 6: Concentration of various cations in water samples taken from an estuary (μmol l^{-1}).

element	river	1	2	3	4	seawater
Cl	$2.20\ 10^{2}$	$1.07\ 10^{5}$	$2.13\ 10^{5}$	$3.20\ 10^{5}$	$4.26\ 10^{5}$	$5.33\ 10^{5}$
Mg	$1.69\ 10^{2}$	$1.05\ 10^{4}$	$2.08\ 10^{4}$	$3.11\ 10^{4}$	$4.15\ 10^{4}$	$5.18\ 10^{4}$
Al	1.85	0.493	0.134	0.040	0.0150	0.0083
Si	$2.32\ 10^{2}$	$1.49\ 10^{2}$	$1.18\ 10^{2}$	$1.07\ 10^{2}$	$1.02\ 10^{2}$	$1.01\ 10^{2}$
Ca	$3.75\ 10^{2}$	$2.36\ 10^{3}$	$4.35\ 10^{3}$	$6.34\ 10^{3}$	$8.33\ 10^{3}$	$1.03\ 10^{4}$
Fe	$7.14\ 10^{-1}$	$9.75\ 10^{-2}$	$1.41\ 10^{-2}$	$2.77\ 10^{-3}$	$1.24\ 10^{-3}$	$1.03\ 10^{-3}$

(b) ^{87}Sr/^{86}Sr vs [Sr]
(c) ^{87}Sr/^{86}Sr vs [Sr]/[Mg]
(d) ^{87}Sr/^{86}Sr vs [Mg]/[Sr]
(e) ^{87}Sr/^{86}Sr vs 1/[Sr]
(f) ^{87}Sr/^{86}Sr vs [Mg]/[Sr]
(g) ^{87}Sr/^{86}Sr vs [Mg]/([Mg]+[Sr])

11. Plot the Sr concentrations and ^{87}Sr/^{86}Sr ratios vs the Mg concentrations in mixtures of hydrothermal solutions and seawater (0-100 wt% mixing ratios) using the following data: ^{87}Sr/^{86}Sr = 0.709, [Sr] = 8 ppm, [Mg] = 1260 ppm in seawater; ^{87}Sr/^{86}Sr = 0.703, [Sr] = 16 ppm, [Mg] = 0 ppm in the hydrothermal end-member. The atomic weight of Sr is 87.62 and the atomic abundance of isotope 86 is 9.86 %.

12. Partial melting of a peridotite produces basaltic liquids. We assume that the mineral composition of the residue is invariable and made of 70 wt% olivine, 20 wt% orthopyroxene and 10 wt% clinopyroxene. Calculate the concentrations of the following elements: nickel (Ni), lanthanum (La), ytterbium (Yb), and the La/Yb ratio in the melt for melt fractions F equal to 0.002, 0.01, 0.02, and 0.1 Concentrations in the peridotitic source and mineral/melt partition coefficients are given in Table 7.

Table 7: Concentration C_0^i of Ni, La, and Yb in the peridotitic source and mineral/liquid partition coefficients $\mathrm{K}^i_{\mathrm{min/liq}}$.

element i	Ni	La	Yb
C_0^i	2500	0.5	0.4
$\mathrm{K}^i_{\mathrm{ol/liq}}$	10	0	0
$\mathrm{K}^i_{\mathrm{opx/liq}}$	1	0	0.05
$\mathrm{K}^i_{\mathrm{cpx/liq}}$	1	0.01	0.3

13. The melt calculated in the previous exercise for F = 0.1 rises and fractionates minerals in conduits before the residual liquids are erupted as differentiated lavas. The cumulates contain 70 wt% olivine and 30 wt% clinopyroxene. Calculate the Ni, La, and Yb

concentrations and the La/Yb ratios for a fraction crystallized X equal to 0.01, 0.1, and 0.2. Compare the relative evolution of these parameters resulting from partial melting and fractional crystallization.

14. Very low partition coefficients are particularly difficult to assess experimentally because their mineral concentrations are very low and prone to contamination by coexisting phases. This is the case for rare-earth elements between olivine and melt. Let us call r the ionic radius of the rare-earth elements in octahedral coordination in this mineral. Use the partition coefficients of Sm (r = 0.96 Å, $\mathrm{K}^{\mathrm{Sm}}_{\mathrm{ol/liq}}$ = 0.000424), Gd (r = 0.94 Å, $\mathrm{K}^{\mathrm{Gd}}_{\mathrm{ol/liq}}$ = 0.000973), and Yb (r = 0.87 Å, $\mathrm{K}^{\mathrm{Yb}}_{\mathrm{ol/liq}}$ = 0.0196) to evaluate the olivine/liquid partition coefficients of La (r = 1.03 Å), Ce (r = 1.01 Å), and Nd (r = 0.98 Å). (Hint: calculate the three coefficients of the parabola relating ln $\mathrm{K}^{\mathrm{i}}_{\mathrm{ol/liq}}$ with r).

15. The δ^{18}O values of benthic carbonates decreased from -1.2‰ to -2.5‰ between the Early Eocene and the Oligocene. Assume an ice-free ocean (no salinity variation) and determine the cooling of the deep ocean over the same period using the equation $\delta^{18}\mathrm{O}_{\mathrm{calcite}}$ - $\delta^{18}\mathrm{O}_{\mathrm{seawater}}$ = 2.78 $10^6 T^{-2}$ - 2.91 where T is the absolute temperature.

16. Explain why δD and δ^{18}O in ice cores can be used to trace local precipitation temperatures.

17. Oxygen isotope thermometry of a metamorphic rock. The oxygen isotope compositions of minerals from a gneiss sample have been measured and reported in Table 8. Let us call $\alpha^{\mathrm{O}}_{min}$ the value of the ^{18}O/^{16}O fractionation coefficients between minerals and water. The temperature dependence of this coefficient can be written as 1000 ln $\alpha^{\mathrm{O}}_{min}$ = $A_{min}T^{-2}$ + C_{min} in which A_{min} and C_{min} are mineral-dependent constant factors and T is the absolute temperature. The values of A and C are reported in Table 8 for the different minerals. What is the quartz-magnetite apparent equilibration temperature? Plot δ^{18}O - C for each mineral vs A: what is the slope of this alignment? What is the δ^{18}O value of the water in equilibrium with this mineral assemblage?

Table 8: Temperature coefficients of 1000 ln $\alpha^{\mathrm{O}}_{min}$ = $A_{min}T^{-2}$ + C_{min} for different minerals. Third column: values of δ^{18}O in minerals from the same gneiss samples.

mineral	$10^{-6}A_{min}$	C_{min}	δ^{18}O ‰
feldspar	3.38	-2.92	3.6
plagioclase	2.76	-3.49	3.0
magnetite	-1.47	-3.70	2.8
muscovite	2.38	-3.89	6.6

18. Explain why even subtle variations of δ^{18}O values in fresh basaltic glasses are said to indicate a source component processed at low temperature.

19. Let us call α^{O} the value for ^{18}O/^{16}O vapor/liquid fractionation in water and α^{D} the ratio for D/H fractionation. Using the values listed in Table 9 calculate these coefficients at 5° C and 25° C. Calculate the δ^{18}O and the δD values of water vapor in equilibrium

with seawater at 25° C. This water vapor now condenses as rain at 5° C. Using the Rayleigh fractionation law, calculate the δ^{18}O and the δD values of of rainwater when 10, 20, 50, 80 wt% of the water vapor have condensed. Plot the corresponding δD vs δ^{18}O values and compare the slope of the alignment with the meteoritic water line.

Table 9: Coefficients of 1000 ln $\alpha^{\mathrm{O}}_{min}$ = AT^{-2} + BT^{-2} + C for the liquid water-vapor oxygen and hydrogen isotope exchange reactions.

	10^{-6}A	10^{-3}B	C
α^{O}	1.137	-0.4156	-2.0667
α^{D}	24.844	-76.248	52.612

Chapter 3: Geochronology and Radiogenic Tracers

1. What is the proportion of radiogenic ^{40}Ar* in the total ^{40}Ar of a sample with a ^{40}Ar/^{36}Ar ratio of (1) 50,000 (2) 2,000 (3) 300? If the total ^{40}Ar content is known to within 1 %, what do you expect for the precision on the concentration of radiogenic ^{40}Ar* in each case? Assume that atmospheric argon has a ^{40}Ar/^{36}Ar ratio of $\approx$296.

2. Calculate the age of a basalt containing 1.7 wt% K_2O and 6.0 10^{-11} mol g^{-1} ^{40}Ar. Assume that the atomic proportion of ^{40}K in natural potassium is 0.0117 %.

3. Two samples are irradiated with fast neutrons in the same vial. The K-Ar age of one of them (the monitor) is known. It is observed that some of the ^{39}K of the samples is transformed into ^{39}Ar. Using the monitor to assess the yield of the nuclear reaction, devise a method to infer the K-Ar age of the unknown sample from the age of the monitor and the ^{40}Ar*/^{39}Ar ratios of the sample and the monitor (* labels radiogenic argon).

4. A famous Rb-Sr isochron work: the Baltimore gneiss (Wetherill et al., 1968). Draw the whole-rock ^{87}Sr/^{86}Sr vs ^{87}Rb/^{86}Sr and the biotite-whole rock isochrons for the following samples (Table 10). Infer the emplacement age and the perturbation age of these rocks.

Table 10: Rb-Sr isotopic data for the Baltimore gneiss, Maryland (Wetherill et al., 1968).

sample		^{87}Rb/^{86}Sr	^{87}Sr/^{86}Sr
B105	W.R	2.244	0.738
B20C	W.R	3.642	0.7612
B20	W.R	3.628	0.7573
	biotite	116.4	1.2146
B41	W.R	6.59	0.7992
	biotite	289.7	1.969
B4	W.R	0.2313	0.7074

5. The Sm-Nd dating of Apollo 17 basalt 75075 (Lugmair et al., 1975). Plot the results of Table 11 in a ^{143}Sm/^{144}Nd vs ^{147}Sm/^{144}Nd isochron diagram, draw the internal (mineral isochron) and determine the eruption age of this basalt ($\lambda_{147\mathrm{Sm}}$ = 0.654 10^{-11} a^{-1}).

6. Write the master equation for the ^{187}Re-^{187}Os isochron using ^{188}Os as the stable reference isotope.

7. Introducing ^{40}K-^{40}Ca dating : the Pikes Peak granite (Wyoming). What are the respective probabilities that ^{40}K decays into ^{40}Ca and ^{40}Ar? What is the isochron equation of the ^{40}K-^{40}Ca system if one uses the stable isotope ^{42}Ca as the reference? Draw the internal (mineral) isochron for the PP 76-2 sample (Table 12). What is the age of the last homogenization of Ca in the Pikes Peak granite?

Table 11: Sm-Nd isotopic data for Apollo 17 basalt 75075 (Lugmair et al., 1975).

	^{147}Sm/^{144}Nd	^{143}Sm/^{144}Nd
plagioclase	0.1942	0.51300
ilmenite	0.2416	0.51417
whole-rock	0.2566	0.51454
pyroxene	0.2930	0.51542

Table 12: K-Ca isotopic data for Pikes Peak sample PP 76-2 (Marshall and DePaolo, 1982).

	^{40}K/^{42}Ca	^{40}Ca/^{42}Ca
whole-rock	0.1224	151.109
plagioclase	0.0123	151.040
K-feldspar	0.800	151.577
biotite	1.294	151.941

8. Minerals extracted from a basaltic andesite at the Soufrière St Vincent in the Antilles give the activity ratios listed in Table 13. Plot the Th-U isochron diagram and calculate the age of the last Th isotopic homogenization of these minerals. Beware that Eq. 3.19 (p.63) of the first edition has two typos: a minus sign should appear before the λ's in the exponentials.

Table 13: U-Th activity ratios of minerals in a basaltic andesite from the Soufrière St Vincent in the Antilles (Heath et al., 1998).

	$\left[^{238}\mathrm{U}\right] / \left[^{232}\mathrm{Th}\right]$	$\left[^{230}\mathrm{Th}\right] / \left[^{232}\mathrm{Th}\right]$
whole rock	1.253	1.496
olivine	1.089	1.183
clinopyroxene	1.145	1.259
plagioclase	1.136	1.244
groundmass	1.244	1.450
magnetic	1.230	1.458

9. Determination of the growth rate of a ferromanganese nodule from the excess of $^{230}\mathrm{Th}$ in different layers below the nodule surface. Plot the excesses liste in Table 14 in a semi-log diagram. Find the growth rate from the slope of the alignment. Beware that Eqn 3.14 (p. 56) is missing a minus in the exponential.

10. Dating the oldest terrestrial zircons (Wilde et al., 2001). Table 15 lists the ^{206}Pb/^{238}U and ^{207}Pb/^{235}U ratios of four zircons from the Jack Hills conglomerate (Australia). Plot

Table 14: $^{230}\mathrm{Th}_{\mathrm{ex}}$ (excess) at different depths in a ferromanganese nodule.

depth z (mm)	$^{230}\mathrm{Th}_{\mathrm{ex}}$
0	1242
0.2	788
0.4	488
0.6	285
0.8	180
1	119

the Concordia between 4.2 and 4.5 Gy and plot the Jack Hills data on the same diagram. What is the probable age of these zircons?

Table 15: U-Pb isotopic data for four old zircons from Jack Hills (Australia).

	^{206}Pb/^{238}U	^{207}Pb/^{235}U
1	0.928	69.5
2	0.919	68.2
3	0.965	71.9
4	0.968	74.6

11. A rather difficult one! In the mid-60s, it was proposed that an independent age of the Earth could be derived from the Pb isotope compositions of modern basalts, but this idea later proved to be incorrect. Plot x = ^{207}Pb*/^{235}U and y = ^{206}Pb*/^{238}U of basaltic samples from Mauna Kea, Hawaii in the Concordia diagram. The Pb isotope compositions and the U and Pb concentrations of the samples are provided in Table 16. In this context, the * superscript denotes the radiogenic isotopes accumulated since the Earth formed. Suppose that at that time, the Pb isotope composition of the Earth was that of the iron sulfide of the Canyon Diablo meteorite. We can safely assume a constant molar weight for Pb (207.2) and U (238.0) and the modern ^{238}U/^{235}U ratio is 137.8. What is the range of ^{207}Pb*/^{206}Pb* ratios of the mantle source of modern basalts (see p. 153)? Why is the age of the upper intercept of the Concordia close to the age of the Solar System? Discuss where the pitfall is. (Hint: from the Pb concentrations, calculate the moles of initial ^{204}Pb per mass unit present in each sample and use the Canyon Diablo values to derive the same parameter for the other isotopes).

12. Pat's invaluable legacy: the age of the Solar System (Patterson, 1956). Lead isotopes were analyzed in the five meteorites listed in Table 17. Plot the ^{207}Pb/^{204}Pb vs ^{206}Pb/^{204}Pb ratios. By trial and error, find Clair Patterson's estimate for the age of last Pb isotopic homogenization of the Solar System as a whole.

Table 16: U-Pb isotopic data for basaltic samples from Mauna Kea, Hawaii.

sample	Pb ppm	U ppm	$\frac{^{206}\mathrm{Pb}}{^{204}\mathrm{Pb}}$	$\frac{^{207}\mathrm{Pb}}{^{204}\mathrm{Pb}}$	$\frac{^{208}\mathrm{Pb}}{^{204}\mathrm{Pb}}$
SR0137-5.98	1.0	0.285	18.43	15.48	37.97
SR0157-6.25	0.593	0.192	18.44	15.48	38.00
SR0346-5.60	1.525	0.211	18.52	15.48	38.10
SR0664-5.10	0.765	0.415	18.55	15.49	38.14
SR0930-15.85	0.521	0.212	18.51	15.49	38.13
SR0967-2.75	0.695	0.319	18.49	15.48	38.11
Canyon Diablo			9.3066	10.293	29.475

Table 17: Pb isotopic data for five meteorites (Patterson, 1956).

	^{206}Pb/^{204}Pb	^{207}Pb/^{204}Pb
Nuevo Laredo	50.28	34.86
Forest City	19.27	15.95
Modoc	19.48	15.76
Henbury	9.55	10.38
Canyon Diablo	9.46	10.34

13. Isochrons improve with age. Table 18 lists the Sr isotopic data for six samples of modern shales. Using your favorite spreadsheet or any convenient software, calculate the ^{87}Sr/^{86}Sr ratios of each sample 100 My, 2700 My and 4560 My into the future. Plot the isochrons for today and for each of these future dates. Use your software to calculate the slope and the correlation coefficients and discuss the results.

Table 18: Sr isotopic data for six samples of modern shales.

sample	^{87}Rb/^{86}Sr	^{87}Sr/^{86}Sr
a	6.2	0.7121
b	2.7	0.7102
c	0.5	0.7083
d	52.5	0.7111
e	13.1	0.7081
f	21.4	0.7096

14. Isochron or mixing line? A series of modern lavas are speculated to form by mixing (hybridization) of mingling basaltic and rhyolitic magmas. Table 19 lists the Nd isotopic

---

data of two end-member magmas. Calculate the ^{147}Sm/^{144}Nd and ^{143}Nd/^{144}Nd ratios of hybrid rocks formed by 20-80, 40-60, 60-40, and 80-20 % of basalt-rhyolite mixtures. Plot the mixing line with its end-members in the isochron diagram and 'age' the samples by 1 Gy and 2 Gy. Calculate the apparent ages of the alignment for 0, 2, and 3 Gy into the future. Devise a strategy to decide whether an alignment in the isochron diagram is a mixing line or a true isochron.

Table 19: Nd isotopic data of the basaltic and granitic end-members.

	[Nd] (ppm)	^{147}Sm/^{144}Nd	^{143}Nd/^{144}Nd
rhyolite	40	0.11	0.5115
basalt	15	0.17	0.5128

15. Sketch the evolution of the Bulk Silicate Earth (^{147}Sm/^{144}Nd = 0.1967 and ^{143}Nd/^{144}Nd = 0.512638 today) in a ^{143}Nd/^{144}Nd vs t evolution diagram between 2 Ga and the present and the evolution of a crustal rock formed at 2 Ga from the primitive mantle with a ^{147}Sm/^{144}Nd ratio of 0.11. What is the modern $\varepsilon_{\mathrm{Nd}}$ of this rock?

16. Compare the evolution diagram ^{143}Nd/^{144}Nd vs t and the isochron diagram ^{143}Nd/^{144}Nd vs ^{147}Sm/^{144}Nd. Plot the points representing the modern depleted mantle (^{147}Sm/^{144}Nd =0.222 and ^{143}Nd/^{144}Nd = 0.51312) and a crustal sample with ^{147}Sm/^{144}Nd =0.12 and ^{143}Nd/^{144}Nd = 0.5111. First, find graphically in each diagram the model age at which the protolith of this crustal sample was extracted from the depleted mantle. Second, derive a common expression that will let you calculate this model age with precision.

Chapter 4: Element Transport

1. Which of these properties are conservative: total energy, kinetic energy, temperature, velocity, moles of iron content, moles of ferric iron, concentration of iron, pH, alkalinity?

2. At a given locality at the bottom of the ocean, the rate of sedimentation is 10 mm ky^{-1}. The density of the surface sediment is 2.0 g cm^{-3} and its phosphorus content is 0.65 wt%. What is the sedimentary (advection) flux of phosphorus in kg P m^{-2} My^{-1}?

3. Explain why, during exhumation of mountain ranges, minerals should be treated as Lagrangian bodies.

4. During crystal growth from their melt, elements partition across the interface with, for element i, C^i_{min}= $K^i_{\mathrm{min/liq}}$ C^i_{liq}. The position of the mineral-melt interface is set at x = 0, growth rate V is constant, and the density change during crystallization is neglected. We will assume that diffusion in the solid ($x < 0$) is slow enough to be neglected and that the diffusion coefficient of i in the melt ($x > 0$) is D^i_{liq}. Write the advection fluxes on each side of the interface, the diffusion flux in the liquid, and the overall transport balance of element i during crystallization. This situation is reminiscent of sedimentation. What is the major difference?

5. Experiments by van Orman et al. (2001) determined the parameters for Nd diffusion in pyrope crystals. The pre-exponential term D^{Nd}_0 = 10$^{-9.2}$ m^2 s^{-1} and the activation energy E^{Nd} = 300 kJ mol^{-1}. It is determined that the core of a spherical garnet of 1 cm radius contains about 1 ppm Nd. Concentration decreases in the depleted rim to a zero value at the surface and this is thought to be the result of a metamorphic pulse with a steady temperature of 800°C. The thickness of the depleted rim (diffusion boundary layer) is 0.1 micron and we assume that concentration decreases linearly between the core and the surface. The specific weight of garnet is 3.5 g cm^{-3}. Calculate the total flux of Nd in kg s^{-1} out of the garnet during the metamorphic pulse.

6. Helium is lost by diffusion from an apatite crystal assumed to be spherical with a radius a of 100 microns (μm) during a short episode of reheating (Δt = 200,000 years at 100°C). The parameters for He diffusion in apatite are D^{He}_0 = 0.064 m^2 s^{-1} and the activation energy E^{He} = 148 kJ mol^{-1}. Calculate the parameter τ = D^{He} $\Delta t/a^2$ and the fraction of He lost at the end of the thermal disturbance.

7. Using the parameters given in the previous exercise, what is the closure temperature of He diffusion in apatite for a cooling rate of 10 K per My ? Hint: use a guess for the temperature to calculate θ then T_c, and proceed by successive refinements.

8. Cygan and Lasaga (1985) determined that the parameters for Mg diffusion in pyrope garnet are D^{Mg}_0 = 9.8 × 10^{-9} m^2 s^{-1} and the activation energy E^{Mg} = 239 kJ mol^{-1}. If the cooling rate is 10 K per My, what is the closure temperature of Mg exchange between a spherical garnet of 1 cm radius and its neighbors?

9. A very large number of different ^{39}Ar-^{40}Ar analyses of K-feldspar in granites and gneisses showed that the Ar diffusion parameters are E^{Ar} = 380 kJ mol^{-1} and D^{Ar}_0/a^2 = 5 s^{-1}, where a is the ‘effective’ diffusion radius (Harrison and McDougall, 1991).

Calculate the closure temperature for Ar diffusion in feldspar for a cooling rate of 20 K per My. The value of D_0^{Mg} was also determined on homogeneous gem-quality material and by comparison with the previous data, it was shown that the 'effective' diffusion radius a is only 6 μm. Discuss the implications of these observations for chronology.

10. Discuss the significance of the apparent temperatures given by (a) fractionation of oxygen isotopes between minerals (b) Fe-Mg fractionation between coexisting clinopyroxene and orthopyroxene.

11. Ground water percolates through the sedimentary basement at a velocity of 10 meters per year. Rock volumic porosity is one percent and we neglect the difference in density between water and sediment. Let D^i be the partition coefficient of element i between the matrix and ground water. How far will ground water movement take a contamination in 10,000 years for the following elements: Cl (D^{Cl} = 0), I (D^{I} = 0.01), Sr (D^{Sr} = 0.2), U (D^{U} = 100), Th (D^{Th} = 10^8)?

12. Basaltic melt percolates through a matrix of molten peridotite. Let us assume that the degree of melting (F = 2 percent) does not change significantly over the distance of interest. Discuss the relative velocity of Ni ((D^{Ni} = 10), Yb (D^{U} = 1), and Ba (D^{Ba} = 0.0001). Discuss the behavior of major elements (e.g., Si, Al) and explain which assumption of the chromatography theory breaks down for these elements.

Chapter 5: Geochemical Systems

1. What is the average time spent (1) by water in the ocean before being renewed by the rivers (2) by material in the mantle before being extracted into the oceanic lithosphere? Use the data of Appendix G and neglect density differences.

2. Using the data of Appendix A and G and assuming steady-state, calculate the residence times of the following elements in the ocean: Br, Rb, Mg, Fe, Sr, Pb. Which elements do you expect to be homogeneously distributed across the ocean? Which elements should show regional or vertical variations? Do you expect the fluctuations of the seawater ^{87}Sr/^{86}Sr ratio to be modulated by glacial-interglacial cycles? Why?

3. The composition of the mean mantle can be calculated by removing the amount of elements hosted in continental crust (see exercise on Chapter 1). Using the data of Table 2 on the composition of MORB and the appropriate massic data from Appendix G, calculate the mean residence times of K, Sr, Zr, La, Yb, Th, and U in the mantle before they are extracted into the oceanic crust. Discuss mantle homogeneity for these elements.

4. The diameter of a nearly circular lagoon on a Pacific atoll is 3.5 km and its mean depth 500 meter. The water flow through the inlet at a rate Q = 10^8 m^3 y $^{-1}$.

   - What is the residence time of water in the lagoon?
   - The lagoon is accidentally contaminated by strontium 90, which has a half-life of 29.1 y. If sedimentation could be ignored, what would be the residence time of this nuclide in the water of the lagoon?
   - Reef growth leaves carbonated sediment on the floor of the lagoon. We assume a sediment density of 2000 kg m^{-3} and a sedimentation rate v of 1 mm y^{-1}. Calculate the sediment flux P in kg y^{-1}. Strontium is scavenged by the sediment with a carbonate-seawater partition coefficient D of 25 m^3 kg^{-1}.
   - What is the residence time of ^{90}Sr in the lagoon in the presence of sedimentation?
   - Give an alternative theory in which you replace the residence times by probabilities.

5. Using an equation similar to Eq. 5.5, show that, if Sr concentrations do not change very significantly through a sequence of volcanic eruptions, the resorption of a pulse in the ^{87}Sr/^{86}Sr ratio can be used to estimate the residence of Sr in the magma chamber (discuss the potential importance of plagioclase on the liquidus). Show that, if the eruption rate is known, the volume of the magma chamber can be calculated. In 1880, an unusual change of ^{87}Sr/^{86}Sr of a Hawaiian volcano was resorbed in about 30 years. What was the approximate volume of the magma chamber if the eruption rate was 0.05 km^3 y^{-1}?

6. Strontium has a residence time in the ocean of about 4 My. What is the proportion of Sr atoms that have been in the ocean for more than 20 My? for less than 100 ky?

7. If the mean residence time of Nd in the mantle is 6 Gy, what is the proportion of Nd atoms in the mantle that have never been extracted into the ridges?

8. The two-box ocean model of Broecker (see Fig. 6.13). The ocean is divided into two boxes, the surface ocean and the deep ocean, separated by the thermocline. Modify equations 5.12 and 5.13 to take into account (1) the input from river flux (2) the sedimentation of particles formed in the surface ocean: a fraction of these particles are redissolved below the thermocline, the rest is rapidly exported into the sediments with no re-equilibration with deep water.

9. Another two-box ocean model. Again, the ocean is separated into two boxes, but this time horizontally, an Atlantic basin and a Pacific basin. Modify equations 5.12 and 5.13 to take into account (1) the input from river flux into the Atlantic only (a good approximation!) (2) sedimentation in each basin.

10. Discuss the oceanic cycle of Sr and its isotopic variations. Include a river flux with radiogenic Sr, carbonate precipitation, and exchange of seawater with unradiogenic basalt in ridge-crest hydrothermal systems.

11. Write the equations that were used to draw Fig. 5.5.

12. Let us define a series of one-dimensional ‘cells’ or bins between 0 and 1 (e.g., 0-0.05, 0.05-0.0.10, 0.10-0.15, etc). Use a generator of random deviates from a uniform distribution (e.g., the function RAND in Excel) to produce n pairs (e.g., start with n = 100) of values. Each sample in a pair can be labelled ‘Rb’ and ‘Sr’. Sort the pairs, then bin them. The number of values in each bin is the ‘concentration’ of Rb and Sr in each particular cell, and the ratio of these numbers is Rb/Sr. Build the histograms of Rb, Sr, and Rb/Sr. Redo the exercise with a different value of n (e.g., n = 500). How do you think the histograms will look when $n \to \infty$? Discuss different applications to the mantle and the ocean.

13. Nothing to be afraid of: let us consider a section of the ocean or the mantle as a two-dimensional enclosure x=[0-1], y=[0-1] and the position-dependent velocity field (v_x,v_y) at steady-state:

$$v_x\left(x,y\right)=\frac{dx}{dt}=\cos\left(\pi y\left[t\right]\right)\sin\left(\pi x\left[t\right]\right)$$
$$v_y\left(x,y\right)=\frac{dy}{dt}=\sin\left(\pi y\left[t\right]\right)\cos\left(\pi x\left[t\right]\right)$$

so that the x-velocity is zero along the upper and lower edge and the y-velocity is zero along the left and right boundaries. Let us take two points initially positioned at x_1 = 0.1, y_1= 0.1 and x_2 = 0.1, y_2= 0.2, respectively. How does the distance between these two points change through time (t = 0.1, 0.2, etc)? (Hint: remember that x and y are time-independent to infer the position at t + Δt from the position at t and proceed by small increments, e.g., Δt = 0.01; use a spreadsheet or any other software).

Chapter 6: Waters Present and Past

1. Discuss how the variables $\Sigma\mathrm{CO}_2$, pH, Alk, and P_{CO_2} are controlled in the following cases: (1) a parcel of surface water in equilibrium with the atmosphere at constant P_{CO_2} (2) a parcel of surface water saturated in calcium carbonate (3) a parcel of water in the deep ocean. Assume that Ca^{2+} is the only metallic cation present in solution and find, as in Section 6.2, the breakdown of the system into its components, species, and their relating equations.

2. Discuss what happens to a glass of sparkling mineral water when HCl (or a lemon twist) is added to it. Show that a plot of $[\mathrm{H}^+] = 10^{-\mathrm{pH}}$ vs the concentration of the HCl added is a way of titrating the alkalinity (Gran titration).

3. What is wrong with the following statement: in an atmosphere of increasing P_{CO_2}, more carbonates are added to seawater, so more calcium carbonate is precipitated? Why are some springs with CO_2-rich waters turning into petrifying fountains?

4. Demonstrate Eq. 6.25 for the fractions $\alpha_{\mathrm{CO}_3^{2-}}$, $\alpha_{\mathrm{HCO}_3^-}$, and $\alpha_{\mathrm{H}_2\mathrm{CO}_3}$.

5. Use concentrations of Na, K, Mg, Ca, Cl, and SO_4^{2-} from Appendix A to calculate the alkalinity of the rivers and the ocean. Use Appendix G to calculate the residence time of alkalinity in the ocean.

6. A measurement on a surface ocean sample gives $[Alk]$= 2.35 meq kg^{-1} and $\Sigma\mathrm{CO}_2$ = 2.15 mmol kg^{-1}. A similar measurement on a deep water sample gives $[Alk]$= 2.45 meq kg^{-1} and $\Sigma\mathrm{CO}_2$ = 2.40 mmol kg^{-1}. Calculate $\left[\mathrm{CO}_3^{2-}\right]$, $\left[\mathrm{HCO}_3^-\right]$, and pH in each seawater sample. Explain the differences.

7. The major component of olivine is forsterite ($\mathrm{Mg}_2\mathrm{SiO}_4$). Write a weathering reaction of forsterite by water to serpentine $\mathrm{Mg}_3\mathrm{Si}_2\mathrm{O}_5(\mathrm{OH})_4$.

8. Aqueous silica is present in freshwater as $\mathrm{H}_2\mathrm{SiO}_3$ and HSiO_3^-. Silicic acid $\mathrm{H}_2\mathrm{SiO}_3$ precipitates as amorphous silica following the reaction SiO_2 (solid) + $\mathrm{H}_2\mathrm{O}$ = $\mathrm{H}_2\mathrm{SiO}_3$ (log K = -2.7) and dissociates following the reaction $\mathrm{H}_2\mathrm{SiO}_3$ = HSiO_3^- + H^+ (log K = -9.6). Calculate the abundance of each soluble species in equilibrium with amorphous silica as a function of pH.

9. Complexation of Zn^{2+} in seawater. We define a complexation constant β_n of a metal ion M in solution as:

   $$\beta_n = \frac{[ML_n]}{[M][L]^n}$$

   For Zn^{2+}, the decimal logarithm of complexation constants are (1) for OH^-: 5.0 (n = 1), 11.1 (n = 2), 13.6 (n = 3), 14.8 (n = 4) (2) for CO_3^{2-}, 10.0 (n = 1). What are the relative proportions of the main species of Zn in seawater for a water sample in which $[Alk]$= 2.35 meq kg^{-1} and $\Sigma\mathrm{CO}_2$ = 2.15 mmol kg^{-1} (assume that the second dissociation constant of carbonic acid is 9.0). Hint: write the sum of all the Zn species and factor $[\mathrm{Zn}^{2+}]$, calculate $[\mathrm{Zn}^{2+}]/\Sigma\mathrm{Zn}$, then the other species.

10. What are the sources of alkalinity in river water?

11. Show how Eq. 6.37 giving the slope of the meteoritic δD–δ^{18}O correlation in meteoritic waters can be derived from Eq. 2.32.

12. From the definition of the isotopic fractionation factor $\alpha^{18\mathrm{O}}$ between liquid water and vapor, show that $D^{16\mathrm{O}} \approx 1$, and $D^{18\mathrm{O}} \approx \alpha^{18\mathrm{O}}$. For fractionation of oxygen isotopes during water vapor condensation, use Eq. 2.29 to show that $\left({}^{18}\mathrm{O}/{}^{16}\mathrm{O}\right)_{\mathrm{res}} \approx \left({}^{18}\mathrm{O}/{}^{16}\mathrm{O}\right)_{0} f^{\alpha^{18\mathrm{O}}-1}$, where f is the fraction of original ^{16}O (and therefore of original water vapor) left in the atmosphere. What is the corresponding relationship in δ units? Establish similar relationships for the D/H ratio. Remember that liquid water is enriched in the heavier isotope.

13. In the range [0-20]°C, the vapor pressure of water at saturation $P^{\mathrm{sat}}_{\mathrm{H_2O}}$ changes with temperature T as ln $P^{\mathrm{sat}}_{\mathrm{H_2O}}$ = -5365.37 T^{-1} + 26.06, where pressure is in Pa and temperature in K. Assume that atmospheric water vapor forms above the ocean at low latitudes at 15°C and calculate a relationship between the residual fraction f of water vapor as given by the previous exercise and temperatures at low temperature. Assuming that 1000 ln $\alpha^{18\mathrm{O}}$ = 1.0779 10^6 T^{-2} - 2.796, infer a relationship between the δ^{18}O values of rainwater and their precipitation temperature. Find appropriate linear approximations to all these equations.

14. The west coast of the Americas is fringed by elevated coastal mountain ranges. Explain how, in a regime of west winds, the isotopic composition of oxygen and hydrogen in precipitations changes with elevation.

15. A core of salty seawater depleted in nutrients and relatively oxygenated is observed in the South Atlantic at a depth of 2200 m about 200 km east off the Brasilian continental slope. What is the origin of the core water?

16. Discuss the properties of the water column in the Pacific at 26°N and 160°E (Table 20) by plotting temperature, salt, O_2, and the nutrients vs depth. Identify the thermocline, the oxygen minimum. What is the halocline? Compare the profile of the soft (N,P) and hard (Si) nutrients.

17. Silicon and erbium (Er) concentrations have been analyzed in samples taken at different depths of the water column at a South Atlantic station (Table 21). Plot Si vs depth and explain the observations. Plot Er vs Si and explain why an element of no biological interest can be correlated to Si.

18. What thickness of $CaCO_3$ sediment spread over the entire surface of the ocean would it take to remove 100 ppmv of CO_2 from the atmosphere? Use data from Appendix G and a specific gravity of 2700 kg m^3 for $CaCO_3$.

19. Explain why upwelling of deep water, such as under equatorial latitudes, reintroduces CO_2 into the atmosphere.

20. What is the potential paleoceanographic use of the following records: (1) δ^{18}O in pelagic forams? (2) δ^{18}O in benthic forams? (3) the δ^{13}O difference between benthic and pelagic forams of the same age?

21. Discuss the potential climatic changes and the depth of CCD upon (1) a nearly instantaneous surge in atmospheric CO_2 triggered by a massive subaerial volcanic eruption

Table 20: Water column properties in the Pacific at 26°N and 160°E.

depth m	temp °C	salt psu	O_2 ml l^{-1}	PO_4 μmol l^{-1}	SiO_3 μmol l^{-1}	NO_3 μmol l^{-1}
0	25.62	35.05	4.84	0.16	4.8	0.1
10	25.49	35.07	4.81	0.11	4.4	0.2
20	25.30	35.07	4.82	0.11	4.3	0.2
30	24.92	35.08	4.90	0.12	4.1	0.2
50	23.70	35.10	5.01	0.10	4.3	0.2
75	22.03	35.07	5.06	0.11	4.8	0.4
100	20.55	35.01	5.00	0.15	5.4	0.8
125	19.31	34.94	4.86	0.16	4.7	1.3
151	18.35	34.89	4.79	0.24	5.4	2.1
201	17.04	34.79	4.73	0.36	7.8	4.0
252	16.15	34.71	4.74	0.42	8.2	6.7
302	15.38	34.64	4.66	0.47	10.3	7.0
403	13.15	34.46	4.46	0.78	16.1	13.1
504	10.59	34.25	4.26	1.29	27.6	18.8
605	7.97	34.12	3.31	1.89	44.1	26.1
706	6.07	34.13	2.35	2.38	65.3	33.8
807	4.95	34.18	1.55	2.81	87.8	38.8
908	4.26	34.25	1.28	2.91	107.6	41.5
1009	3.86	34.34	1.03	3.06	118.6	42.4
1111	3.44	34.40	1.05	3.06	126.1	42.9
1212	3.16	34.46	1.09	3.06	131.7	42.5
1313	2.96	34.49	1.23	3.05	139.1	42.3
1415	2.76	34.51	1.43	2.97	141.7	42.5
1516	2.60	34.53	1.57	3.03	146.4	41.8
1770	2.23	34.58	1.90	2.87	151.4	41.5
2024	2.00	34.62	2.21	2.89	157.1	38.9
2533	1.72	34.65	2.65	2.74	157.7	37.9
3043	1.58	34.67	2.90	2.67	155.4	37.3
3554	1.51	34.68	3.31	2.61	155.6	36.4
4067	1.47	34.69	3.50	2.57	152.5	35.7
4580	1.47	34.69	3.78	2.56	148.2	35.0
5095	1.46	34.70	3.83	2.51	142.9	35.3
5610	1.52	34.69	3.99	2.48	138.6	35.4

(2) the ensuing surge in riverine alkalinity flux resulting from the weathering of the lava flows (3) an increase in primary productivity (4) a strong decrease in oceanic thermohaline convection.

Table 21: Silica and erbium concentrations at different depths of the water column at a South Atlantic station (Bertram et al., 1993).

depth (m) m	SiO_3 mmol kg^{-1}	Er pmol kg^{-1}	depth (m) m	SiO_3 mmol kg^{-1}	Er pmol kg^{-1}
241	3.6	3.49	2332	57.8	6.09
331	6.3	3.66	2581	57.4	5.6
418	10.1	3.74	2832	58.8	5.18
495	13.8	3.87	3082	61.2	5.75
565	16.7	3.97	3330	65.6	5.89
741	25.6	4.14	3532	74.1	6.81
839	31.3	4.31	3737	84.7	6.71
1082	47	4.67	3945	95.9	6.53
1273	59.6	4.92	4202	104.7	7.44
1466	61.5	5.64	4458	108.4	8.1
1657	66.2	5.35	4700	110.5	7.3
1841	63.2	5.24	4995	111.3	7.99
2088	60.3	5.58			

22. The solubility of calcite varies in the ocean with depth. Since $[Ca^{2+}]$ is essentially constant over the residence time of this element (≈ 1 My), this variation is expressed as $\left[CO_3^{2-}\right]$ = 90 $e^{0.16(z-4)}$, where z is the depth in kilometers and solubility is expressed in μmol kg^{-1}. Using the assumption that a change in the depth of the CCD is nearly equivalent to a change in the depth of the lysocline (saturation level) and that the relative change of $\left[HCO_3^-\right]$ can be neglected with respect to the relative change of $\left[CO_3^{2-}\right]$, estimate the relative change of P_{CO_2} associated with a shallowing of the CCD by 1 km. (Hint: consider using Eq. 6.2 and 6.31).

Chapter 7: Mineral reactions

1. Show that if the changes of enthalpy $\Delta H\left(T,P\right)$, entropy $\Delta S\left(T,P\right)$, and volume $\Delta V\left(T,P\right)$ of a reaction are approximately constant, Eq. 5 of Appendix C can be integrated into
$$\Delta G\left(T,P\right) \approx \Delta H_0 - T\Delta S_0 + \Delta V_0\left(P-1\right) \tag{2}$$
where $\Delta G\left(T,P\right)$ is the free enthalpy of the reaction at T and P and the subscript 0 denotes a reference state (usually 298 K and 1 bar). Show that at equilibrium, this relation provides an equation for the reaction curve. Use the previous result to draw the reaction curve defining the onset of the 'eclogite' facies
$$\begin{array}{ccccc} \mathrm{NaAlSi_3O_8} & \Leftrightarrow & \mathrm{NaAl_2SiO_6} & + & \mathrm{SiO_2} \\ \mathrm{(albite)} & & \mathrm{(jadeite)} & & \mathrm{(quartz)} \end{array}$$
in which the sodic plagioclase breaks down into a sodic pyroxene, which dissolves into ambient clinopyroxene, and quartz. Use the following values: ΔH_0 =-2115 J mol^{-1}, ΔS_0 =-32.25 J mol^{-1} K^{-1}, and ΔV_0 =-17.0 10^{-6} m^3.
2. Aragonite is a denser polymorph of calcite $CaCO_3$ and is therefore more stable at high pressure than calcite. Using the following values ΔH_0 =+1132 J mol^{-1}, ΔS_0 =-0.146 J mol^{-1} K^{-1}, and ΔV_0 =-2.78 10^{-6} m^3 for the calcite ⇔ aragonite reaction, calculate the pressure of the transition at 500°C.
3. Show that the constant in Eq. 7.2 is equal to $\Delta S_0\left(T,P\right)/R$, the entropy of the reaction in standard conditions (hint: refer to Appendix C and use the definition of the free enthalpy to show that $\Delta G_0\left(T,P\right)$=$\Delta H_0\left(T,P\right)$-$T\Delta S_0\left(T,P\right)$). When the solids are maintained at a pressure $>$ 1 bar, in particular when solid and gaseous phases are identical, a small correction for mineral expansivity is necessary but is normally very small.
4. The reaction described by Eq. 7.1 has a $\Delta H_0\left(298,1\right)$ of 111,090 J mol^{-1} and a $\Delta S_0\left(298,1\right)$ of 188.9 J mol^{-1} K^{-1}. Assume that these two values remain constant, use the result of the previous exercise, and calculate $P_{\mathrm{H_2O}}$ for a range of temperature of 450-650°C.
5. The reaction described by Eq. 7.7 has a $\Delta H_0\left(298,1\right)$ of 528,600 J mol^{-1} and a $\Delta S_0\left(298,1\right)$ of 235.8 J mol^{-1} K^{-1}. Assume that these two values remain constant and calculate P_{0_2} for a range of temperature of 800-1200°C.
6. Magnesite ($MgCO_3$) reacts with quartz to produce forsterite according to the reaction:
$$\begin{array}{ccccccc} \mathrm{2MgCO_3} & + & \mathrm{SiO_2} & \Leftrightarrow & \mathrm{Mg_2SiO_4} & + & \mathrm{2CO_2} \\ \mathrm{(magnesite)} & & \mathrm{(quartz)} & & \mathrm{(forsterite)} & & \end{array}$$
The $\Delta H_0\left(298,1\right)$ of this reaction is 173,000 J mol^{-1} and the $\Delta S_0\left(298,1\right)$ 350.2 J mol^{-1} K^{-1}. Assume that these two values remain constant and calculate $P_{\mathrm{CO_2}}$ for a range of temperature of 350-550°C.

7. Calculate the P_{CO_2} as in the previous exercise for a carbonate with equal molar proportions of calcite ($CaCO_3$) and magnesite ($MgCO_3$).

8. Use Eq. 7.15 to retrieve the ΔH_0 and ΔS_0 values for quartz dissolution in water at atmospheric pressure. From thermodynamic data tables, we find that ΔV_0 between the molar volume of dissolved silica and quartz is -9.1 10^{-6} m^3. Calculate the solubility of silica at 300°C at the surface and 0.1 GPa (1 kb). Discuss the potential implications for the interpretation of the chemistry of hydrothermal solutions.

9. A difficult but important exercise. Let us assume that the only elements constituting the upper mantle are Si, Mg, Al, and O. Potential mineral phases are the magnesian olivine, or forsterite (fo = Mg_2SiO_4), the magnesian orthopyroxene or enstatite (en = $Mg_2Si_2O_6$), Al-Mg oxide or spinel (sp = $MgAl_2O_4$), and the magnesian garnet or pyrope (py = $Mg_3Al_2Si_3O_{12}$).

   (a) Make a 3×4 table with the minerals as column entries (e.g., spinel) and oxide mole fractions (e.g., [MgO]) as row entries. Convert the mineral compositions into oxide mole fractions (spinel will have, for example 0.5 for both [MgO] and [Al_2O_3] and 0 for [SiO_2]).

   (b) Make a tri-dimensional plot with oxide proportions as x = [SiO_2], y = [MgO], and z (a mock projection will do) and report the mineral compositions in this plot. Plot the following mantle composition (x = 0.4 y = 0.55, z=0.05).

   (c) Refer to Eq. 2.5 and 2.6 (the = 1 on the RHS of Eq. 2.6 of the first edition should be disregarded) and to your table to highlight the following mineral assemblages: fo-en-sp and fo-en-ga.

   (d) Which relationship does a fo-en-ga-sp mineral assemblage require from the columns of your table? Discuss the transition between the fo-en-sp and fo-en-ga assemblages.

   (e) Now add FeO to the composition knowing that Fe makes a solid solution with Mg in each phase (no need to replot anything): which constrain does this addition relieve on the existence of the olivine-orthopyroxene-oxide-garnet mineral assemblage? Discuss the transition between the spinel-peridotite and garnet-peridotite assemblages.

   (f) Instead of FeO, let us add CaO, which is not soluble enough in the existing minerals and therefore forms a new mineral phase, diopside (di = $CaMgSi_2O_6$). What is the difference with respect to the case of FeO?

   (g) Use this example to discuss the geochemical controls of elements which remain below their saturation level in each mineral (Ni, Rb) and of those which quickly exceed their solubility limit (Au, Th, P). Where does H_2O stand and what does the concept of 'nominally anhydrous mineral' refer to?

10. Olivine is a solid solution of forsterite (Mg_2SiO_4) and fayalite (Fe_2SiO_4). Write the simultaneous equations of weathering by pure water (hydrolysis) reactions of fayalite to magnetite (Fe_3O_4) and of forsterite to serpentine $Mg_3Si_2O_5(OH)_4$ and explain why low-temperature alteration of peridotites is a source of hydrogen. How many moles of mantle olivine fo_{90} (with 90 mole percent forsterite and 10 percent fayalite) does it take to produce one mole of H_2? Assuming that a mass equivalent to 10 percent ($\approx$ 2 km^3

y^{-1}) of the annual production of oceanic crust is serpentinized, what is the annual flux of hydrogen from the mid-ocean ridges to the ocean and the atmosphere? What do you think its fate is?

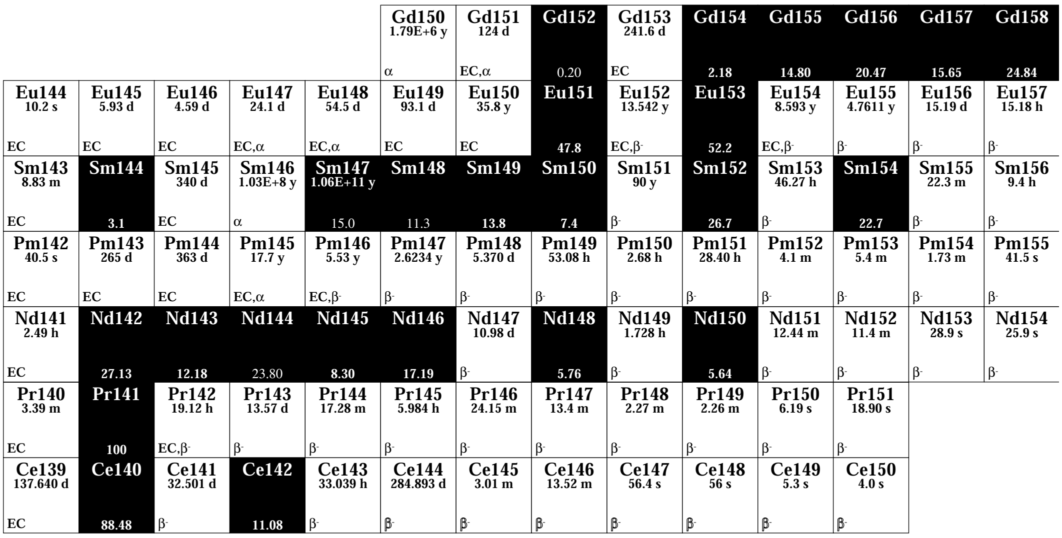
11. Fresh MORB contain about 10 wt% FeO. Upon reaction with sulfate from seawater infiltrated into the young oceanic crust, some of the Fe^{2+} is oxidized to Fe^{3+}. How many grams of seawater with a concentration $[SO_4^{2-}]$ = 28.9 mmol kg^{-1} of sulfate would it take to oxidize all the Fe^{2+} contained in one hundred grams of MORB?

12. Hydrothermal solutions spouted by black smokers at mid-ocean ridges result from interaction between seawater and fresh basalts at temperatures of 300-400°C. The $^{87}Sr/^{86}Sr$ ratios of the hydrothermal solutions are 0.7040 and contrast with the value of 0.7091 observed for seawater and 0.7025 for fresh MORB. The Sr content of the solution does not seem to be greatly affected by the hydrothermal process (8 ppm for both seawater and hydrothermal solutions). Fresh MORB contains about 120 ppm Sr. Assuming isotopic equilibrium between hydrothermal solutions and the host basalt, calculate the water/rock ratio controlling the hydrothermal process. Many ophiolites show $^{87}Sr/^{86}Sr$ ratios of about 0.708. What is the apparent water/rock ratio of the hydrothermal processes leading to the formation of these rocks?

13. List potential electron acceptors (oxidizing substances), both ions dissolved in interstitial solutions and sedimentary minerals, that will eventually be used by organisms to oxidize organic carbon in sediments. Discuss how they affect the mineral composition and oxidation state of common sediments at the surface of the Earth.

Chapter 9: The Earth in the Solar System

1. Figure 1 shows the portion of the chart of the nuclides in the Ce-Gd range.
   (a) Draw the path of the s process in that range.
   (b) Assign each stable nuclide to the most probable process (s, r, p or a mixture of these).
   (c) Use pure s Sm nuclides and the data of Table 22 to calculate the relative contributions of the s and r processes to ^{147}Sm and ^{149}Sm (neglect the p contributions).



					Gd150 1.79E+6 y α	Gd151 124 d EC,α	Gd152 0.20	Gd153 241.6 d EC	Gd154 2.18	Gd155 14.80	Gd156 20.47	Gd157 15.65	Gd158 24.84
Eu144 10.2 s EC	Eu145 5.93 d EC	Eu146 4.59 d EC	Eu147 24.1 d EC,α	Eu148 54.5 d EC,α	Eu149 93.1 d EC	Eu150 35.8 y EC	Eu151 47.8	Eu152 13.542 y EC,β-	Eu153 52.2	Eu154 8.593 y EC,β-	Eu155 4.7611 y β-	Eu156 15.19 d β-	Eu157 15.18 h β-
Sm143 8.83 m EC	Sm144 3.1	Sm145 340 d EC	Sm146 1.03E+8 y α	Sm147 1.06E+11 y 15.0	Sm148 11.3	Sm149 13.8	Sm150 7.4	Sm151 90 y β-	Sm152 26.7	Sm153 46.27 h β-	Sm154 22.7	Sm155 22.3 m β-	Sm156 9.4 h β-
Pm142 40.5 s EC	Pm143 265 d EC	Pm144 363 d EC	Pm145 17.7 y EC,α	Pm146 5.53 y EC,β-	Pm147 2.6234 y β-	Pm148 5.370 d β-	Pm149 53.08 h β-	Pm150 2.68 h β-	Pm151 28.40 h β-	Pm152 4.1 m β-	Pm153 5.4 m β-	Pm154 1.73 m β-	Pm155 41.5 s β-
Nd141 2.49 h EC	Nd142 27.13	Nd143 12.18	Nd144 23.80	Nd145 8.30	Nd146 17.19	Nd147 10.98 d β-	Nd148 5.76	Nd149 1.728 h β-	Nd150 5.64	Nd151 12.44 m β-	Nd152 11.4 m β-	Nd153 28.9 s β-	Nd154 25.9 s β-
Pr140 3.39 m EC	Pr141 100	Pr142 19.12 h EC,β-	Pr143 13.57 d β-	Pr144 17.28 m β-	Pr145 5.984 h β-	Pr146 24.15 m β-	Pr147 13.4 m β-	Pr148 2.27 m β-	Pr149 2.26 m β-	Pr150 6.19 s β-	Pr151 18.90 s β-		
Ce139 137.640 d EC	Ce140 88.48	Ce141 32.501 d β-	Ce142 11.08	Ce143 33.039 h β-	Ce144 284.893 d β-	Ce145 3.01 m β-	Ce146 13.52 m β-	Ce147 56.4 s β-	Ce148 56 s β-	Ce149 5.3 s β-	Ce150 4.0 s β-		

Figure 1: The chart of the nuclides in the Ce-Gd range. The solid squares represent stables nuclides or nuclides with a long half-life.

2. Show that for the ^{182}Hf-^{182}W chronometer ($T_{1/2}$ = 9 My) the 'isochron' diagram x = (^{180}Hf/^{183}W)$_\infty$, y = (^{182}W/^{183}W)$_\infty$ (where $_\infty$ stands for now) has a slope s = (^{182}Hf/^{180}Hf)$_t$ and an intercept i = (^{182}W/^{183}W)$_t$, where t is the time at which the last equilibration of W isotopes took place while ^{182}Hf was still alive. ^{183}W and ^{180}Hf are stable non-radiogenic nuclides used for normalization.

3. The data listed in Table 23 give the ^{180}Hf/^{183}W and ^{182}W/^{183}W ratios measured in two whole-rock chondrites (Dhurmsala and Dalgety Downs) and their silicate and metal phases. Examination of the ^{180}Hf/^{183}W ratios shows that Hf is lithophile and W siderophile.
   (a) From the slope of the isochron formed by the six points, calculate the (^{182}Hf/^{180}Hf)$_t$ ratio of the chondritic material at the time its constitutive phases last equilibrated with each other.
   (b) Calculate the (^{182}W/^{183}W)$_t$ ratio of the mean chondritic reservoir (CHUR) at that time, given its mean ^{180}Hf/^{183}W listed in the table.
   (c) Using these values as those of the parent reservoir, calculate the (^{182}Hf/^{180}Hf)$_t$ ratio of the Earth at the time the core and silicate material last equilibrated.

Table 22: Element abundances (normalized to Si=10^6), cross-sections σ (in mb = millibarn or 10^{-28} m^2), and isotopic abundances (in percent) of the nuclides in the Ce-Gd range.

	abund. Si=10^6	σ (mb)	isotopic abund.		abund. Si=10^6	σ (mb)	isotopic abund.
Ce	1.14			Sm	0.258		
^{140}Ce		11	88.48	^{144}Sm		92	3.1
^{141}Ce		76		^{147}Sm		973	17.5
^{142}Ce		28	11.08	^{148}Sm		241	11.3
Pr	0.167			^{149}Sm		1820	13.8
^{141}Pr		111.4	100	^{150}Sm		422	7.4
^{142}Pr		415		^{151}Sm		2710	
^{143}Pr		350		^{152}Sm		473	26.7
Nd	0.828			^{153}Sm		1095	
^{142}Nd		35	27.13	^{154}Sm		206	22.7
^{143}Nd		245	12.18	Eu	0.0973		
^{144}Nd		81.3	23.8	^{151}Eu		3775	47.8
^{145}Nd		425	8.3	^{152}Eu		7600	
^{146}Nd		91.2	17.19	^{153}Eu		2780	52.2
^{147}Nd		544		^{154}Eu		4420	
^{148}Nd		147	5.76	^{155}Eu		1320	
^{150}Nd		159	5.64	Gd	0.33		
Pm				^{152}Gd		1049	0.2
^{147}Pm		1290		^{153}Gd		4550	
^{148}Pm		2970		^{154}Gd		1028	21.8
^{149}Pm		2510					

(d) Calculate the apparent age of core segregation from the Bulk Silicate Earth.

(e) Redo the same calculation for the Moon.

4. Define similar isochron diagrams for other extinct radioactivities: ^{26}Al-^{26}Mg (normalize to ^{24}Mg and ^{27}Al), ^{53}Mn-^{53}Cr (normalize to ^{52}Cr and ^{55}Mn), ^{60}Fe-^{60}Ni (normalize to ^{58}Ni and ^{56}Fe), ^{146}Sm-^{142}Nd (normalize to ^{144}Nd and ^{144}Sm). Refer to Table 3.1 for the decay constants. From your knowledge of the geochemical properties of the elements of the parent and daughter isotopes and from the half-life of the radioactive nuclide, discuss some potential geochronological applications of each system.

5. Dating the Universe I.

   (a) Explain why the radioactive nuclides ^{238}U and ^{232}Th must have been produced by the r process.

   (b) The present-day ^{232}Th/^{238}U of the Solar System is 3.7. Calculate the value of this ratio 4.56 Gy ago. Refer to Table 3.1 for the decay constants.

Table 23: ^{182}Hf-^{182}W results for two whole-rock chondrites and their silicate and metal phases (Yin et al., 2002).

		^{180}Hf/^{183}W	^{182}W/^{183}W
CHUR		2.84	
Bulk Silicate Earth		36.87	1.8513
Moon		53.88	1.8515
Dhurmsala,	silicate	16.96	1.8524
Dhurmsala,	metal	0.10	1.8507
Dhurmsala,	whole rock	3.52	1.8511
Dalgety Downs	silicate	6.30	1.8513
Dalgety Downs	metal	0.02	1.8507
Dalgety Downs	whole rock	2.84	1.8510

(c) Let us assume that these two nuclides have been created at a constant rate since the formation of the Universe and call p_i their production rates (i = ^{238}U or ^{232}Th). Show that the number of nuclides at time t after the Big Bang, the number N_i of nuclides in the Universe is given by:

$$N_i = \frac{p_i}{\lambda_i}\left(1 - e^{\lambda_i t}\right)$$

(d) From the ratio $p_{^{232}\mathrm{Th}}/p_{^{238}\mathrm{U}}$ = 1.65, calculate the age of the Universe.

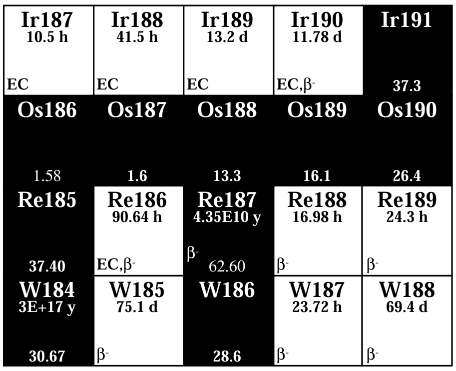
6. Dating the Universe II. We now use the slowly decaying ^{187}Re-^{187}Os chronometer. Figure 2 shows the portion of the chart of nuclides in the W-Ir range.

   (a) We neglect the contribution of the p process to nucleosynthesis in that range. Explain why the ^{186}Os and ^{187}Os nuclides are pure s nuclides. Draw the s process pathway on Figure 2.

   (b) Using the abundances shown on the figure and cross-sections of 422 (^{186}Os) and 896 (^{187}Os) millibarns (1 mb = 10^{-28} m^2), find the abundance of radiogenic ^{187}Os which is due to the decay of ^{187}Re since the beginning of the Universe.

   (c) Using the solar abundances of Re and Os (0.0517 and 0.675 atoms per 10^6 Si), calculate the age of the universe. Refer to Table 3.1 for the decay constants. You will need to consider that ^{187}Re decays so slowly that its abundances are not affected by radioactivity. Although other solutions are easily worked out (e.g., continuous production, see previous exercise), it is easier to assume that all the ^{187}Re was created in one single event just after the Big Bang.

7. We assume that core formation completely eliminated the very siderophile elements, in particular Ir and Os, from the terrestrial mantle. The modern mantle nevertheless contains 3.43 ppb of Os and 3.19 ppb of Ir. What is the proportion of late veneer in the form of chondrites with 520 ppb Os and 490 ppb Ir which has contributed to the modern mantle? Neglect the contribution of the continental crust. Assuming that the



Ir187 **10.5 h** EC	**Ir188** **41.5 h** EC	**Ir189** **13.2 d** EC	**Ir190** **11.78 d** EC,β^-	**Ir191** 37.3
Os186 1.58	**Os187** **1.6**	**Os188** **13.3**	**Os189** **16.1**	**Os190** **26.4**
Re185 **37.40**	**Re186** **90.64 h** EC,β^-	**Re187** **4.35E10 y** β^- 62.60	**Re188** **16.98 h** β^-	**Re189** **24.3 h** β^-
W184 **3E+17 y** **30.67**	**W185** **75.1 d** β^-	**W186** **28.6**	**W187** **23.72 h** β^-	**W188** **69.4 d** β^-

Figure 2: The chart of the nuclides in the W-Ir range. The solid squares represent stables nuclides or nuclides with a long half-life.

mantle is dry and that ocean was added by the late veneer, what is the water content of the incoming projectiles? Refer to Appendix G for the appropriate constants.

8. The acceleration of gravity g at the surface of a planet varies as $g = GM/r^2$ where G = 6.67 10^{-11} m^3 kg^{-1} s^{-2} is the universal gravitational constant, and M and r the mass and radius of the planet, respectively. Calculate g at the surface of the planets listed in Table 24. Let us consider a basaltic magma formed in the shallow mantle of these planets and assume a constant mantle density.
    (a) If the cross-over between plagioclase and clinopyroxene (i.e., the pressure at which the order of saturation is reversed) is at 0.5 GPa, at which depth will this cross-over be located? Discuss the implications in terms of the evolution of a molten planet.
    (b) In the terrestrial mantle, garnet is stable at pressures in excess of 2GPa. What is the equivalent depth for the other planets? Discuss the presence of garnet in the mantle of each planet.

Table 24: Radius r and density ρ of different planets in the inner Solar System.

	Venus	Earth	Moon	Mars	Vesta
r (km)	6052	6371	1737	3390	520
ρ (g cm^{-3})	5.24	5.52	3.34	3.93	3.16

Errata to the first printing of *Geochemistry: An Introduction*

Page 5: update http://www.ens-lyon.fr to http://perso.ens-lyon.fr/francis.albarede/Exercises.pdf

Page 13: (item 4) replace ”the difference being the number of sheets in their basic pattern” by ”the difference being the proportions of 2+ and 3+ cations and therefore site occupancy”.

Page 26: equation (2.6) should not have =1 on right hand side

Page 56: (eq 3.14): add a minus sign in the exponential before $\lambda_{230\mathrm{Th}}t$

Page 63: (eq 3.19): add a minus sign in both exponentials before $\lambda_{230\mathrm{Th}}t$

Page 63: (eqs 3.20, 3.21, 3.22): in the exponentials, the λ’s should be at the same level as t but the nuclide (e.g., 235U) should appear as a superscript. See 3.19 as a reference.

Page 57: (4th line of 2nd para): Should say ”Potassium-40 also decays by and ordinary...” not Argon

Page 66: first equation should have 6.54 on denominator, not 0.654

Page 86: before equation, mean modifying (5.2) not (4.2)

Page 88: replace both (n_1/Q)’s by (n_1/M)’s in eq. 5.11

Page 142: (7th line of 2nd para): CO2 instead of Co2

Page 144: (line 9 from bottom): Replace ”Fig. ??” by ”Fig. 8.4”

Page 233: (eq. H.9) has an unnecessary dt on the first term of the right-hand side

Page 9: Figure 1.2 will be replaced

Page 173: Figure 9.6 will be replaced

Thanks to Peter Kolesar, Ran Qin, and John Rudge.