Chapter 1A
An introduction to the Earth's composition

1.1 Introduction

The Earth can be subdivided into a number of reservoirs, i.e. large, coherent regions of mass characterized by a distinctive composition. The most obvious Earth reservoirs are the atmosphere, oceans, and the solid part of the Earth, which itself can be subdivided into continental crust, oceanic crust, mantle and metallic core (Fig. 1.1 and Table 1.1). That each of these reservoirs exists reflects the fact that the Earth has been unmixing (differentiating) ever since it was formed. We know that this is the case because each of these reservoirs is continually evolving in size and composition as each reservoir interacts with each other. For example, there is a flux of material from the mantle to the atmosphere, ocean, continental crust and oceanic crust:

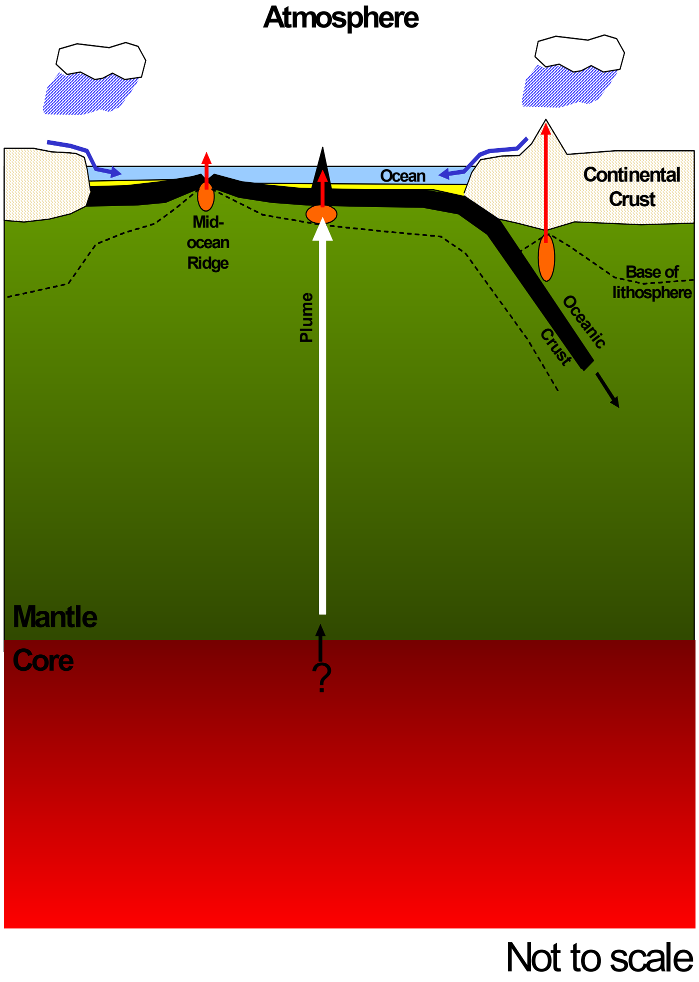

Figure 1.1. Schematic diagram showing some of the major reservoirs in the Earth (atmosphere, ocean, continental crust, oceanic crust, mantle, core) and how they may interact. Red ovals represent regions where solid mantle is being partially melted.

Table 1.1. Some physical properties of the Earth

Mean radius (km)	6371.01
Total surface area (km^2)	5.10×10^8
Oceanic surface area (km^2)	3.62×10^8
Volume (km^3)	1.08×10^{12}
Mass (kg)	5.97×10^{24}
Mean density (g/cm^3)	5.52
Core radius (km)	3485

	Mass (kg)	% of Whole Earth	% of Bulk Silicate Earth
Total atmosphere	5.14×10^{18}	8.65×10^{-5}	
Hydrosphere	1.66×10^{21}	0.0279	0.0413
Total Crust	2.37×10^{22}	0.3951	0.585
Continental crust	1.52×10^{22}	0.25	0.38
Oceanic crust	8.45×10^{21}	0.14	0.21
Mantle	4.01×10^{24}	67.08	99.37
Bulk Silicate Earth	4.03×10^{24}	67.51	
Core	1.94×10^{24}	32.5	

Data are from [*Lodders and Fegley*, 1998]

degassing at mid-ocean ridges or arcs releases magmatic gases to the atmosphere and oceans, hydrothermal fluxing at mid-ocean ridges results in the net flux of certain chemical components into the ocean, and magmatism at mid-ocean ridges and arc volcanoes result in the addition of new mass to oceanic and continental crust (Figs. 1.1 and 1.2). In addition, physical and chemical weathering of continental crust results in the transport of sediments to the seafloor, some of which are ultimately recycled along with oceanic crust back into the mantle at subduction zones. These examples represent only part of all the different ways in which these reservoirs can interact with each other (Figs. 1.1 and 1.2). As Earth scientists, we are interested in unraveling the history of the Earth, that is, how it formed and evolved to its present state. In this context, we are interested in understanding the physical and chemical processes responsible for Earth's origin and evolution, and just as importantly, we want to know the rates at which these processes proceed.

Studying the Earth is therefore analogous to the job of a historian, that is, Earth science is inherently a historical science. We study the present in order to understand the past, which in turn, ultimately helps us understand where we are right now. In order to do so, we need hard facts, just like a historian. Thus, if we want to understand how, for example, the continental crust formed, or how and when the Earth's core formed, we need to know, at the minimum, the chemical and physical characteristics of these reservoirs and some time constraints on when these unmixing events occurred. We can also use experimental analogs or present-day natural analogs to help us further our understanding of processes that may have happened in the past. We may even use these analogs to formulate hypotheses for ancient processes. Questions about the Earth's past therefore are answered by piecing together the data that have been collected in the context of answering a question or testing a hypothesis. However, in many cases the data are incomplete or inconclusive or even tenuous. The Earth scientist must therefore make use of what data have been obtained and attempt to test the hypothesis or construct a new working model that is internally consistent with the new observations. In turn, this new working model will be

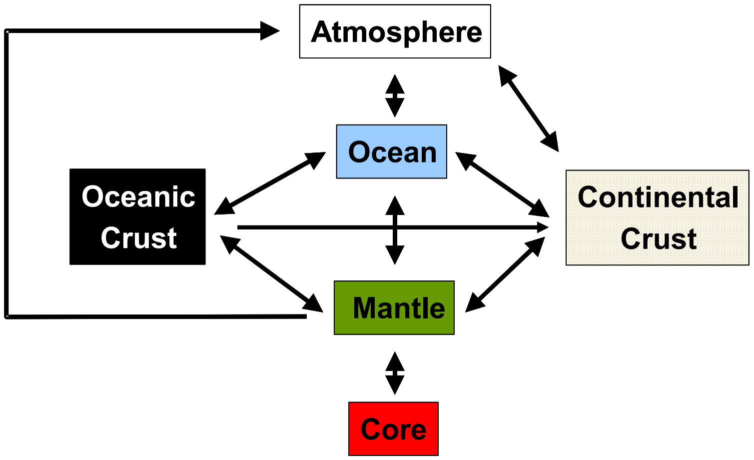

Figure 1.2. Earth systems cycles. A simplified subdivision of the Earth into its major reservoirs and how they interact with each other. Arrows reflect direction of mass transport.

subject to additional tests, i.e. additional gathering of data. Through an iterative process of data gathering, interpretation, and formulation of hypotheses, our understanding progresses.

Below, we will discuss what we currently know about the composition of various reservoirs on Earth. To put it all into context, however, we will begin with a brief discussion of the elemental composition of the solar system. We will worry later about how and why these reservoirs exist and came to be. For the remainder of this course, we will look at how Earth scientists use elemental and isotopic geochemistry to put constraints on the extents and timescales of Earth differentiation processes.

1.2 The elemental composition of the solar system

The composition of the solar system is best illustrated by looking at the composition of the sun's photosphere using spectroscopic methods. The sun accounts for 99.999 % of the mass of the solar system and therefore its composition, for all intents and purposes, reflects that of the solar system. By convention, the composition of the solar photosphere is depicted by normalizing the composition to 10^6 Si atoms (Table 1.2 and Fig. 1.3). The elemental abundances of naturally occurring elements are shown in Figure 1.3. The main features of the solar composition are that H and He make up 99.9% of the mass of the solar system. H is the most elementary atom from which the solar system is built. He is abundant because it is the first fusion product of H in the sun. The other salient features to note are that elemental abundances decrease with increasing atomic weight and that elements with even atomic mass numbers (and even numbers of protons or neutrons) are more abundant than those with odd mass numbers. This can be seen from Figure 1.3, which shows that even atomic numbers (even number of protons) are more abundant than odd-numbered ones. We note also that there appears to be a local maximum in the abundance curve at Fe.

These first-order features can be explained by nucleosynthetic processes, which we will discuss in more detail later. For now, we provide only a brief explanation. Elements between mass number 1 and 56 are primarly formed by nuclear fusion plus or minus the addition of neutrons. These fusion reactions occur in the sun at different stages of its life, and because the basic building blocks are H and He, there is a systematic decrease in the abundance of elements with increasing mass. Mass 56 happens to be Fe (Z=26), and as we will learn later, it has the highest nuclear binding energy, which makes it the most stable nucleus in the periodic table. For

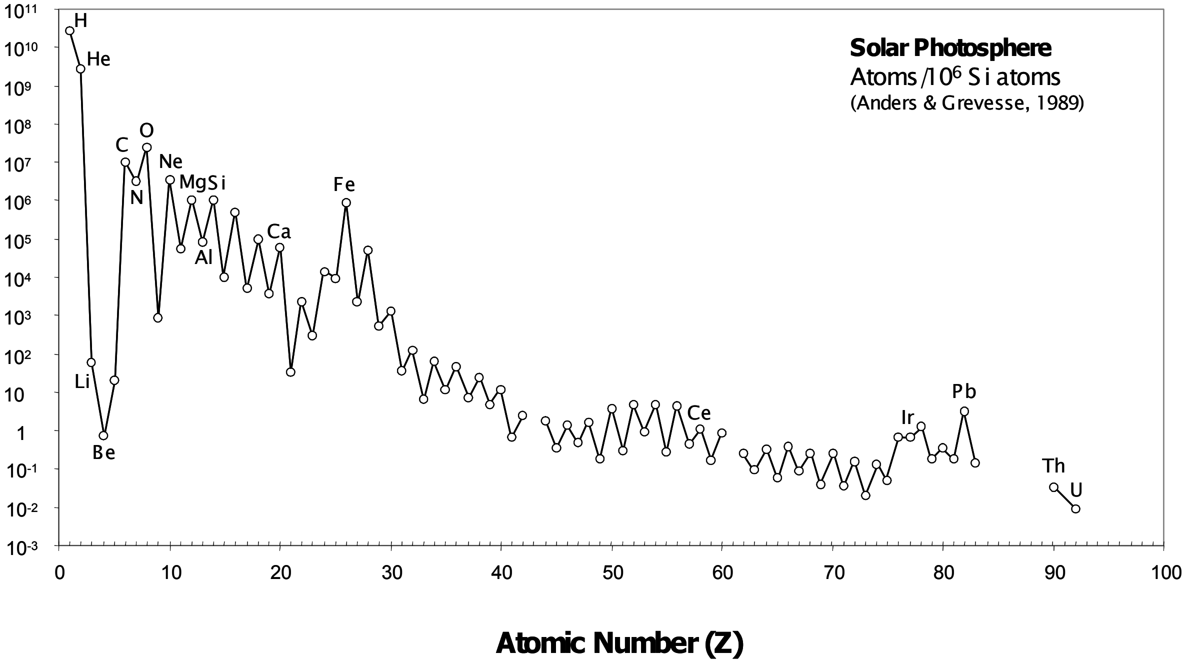

Figure 1.3. Solar photosphere elemental composition expressed in number of atoms per 10^6 atoms of Si. Data are from Anders and Grevesse (1989) and plotted versus atomic number Z.

this reason, there is a local maximum at mass 56 (Z=26), where elemental production essentially piles up. The formation of elements above mass 56 requires the rapid addition of neutrons (coupled with beta decays). High neutron fluxes occur only in supernova explosions, and therefore, the presence of these high mass elements indicates that our solar system inherited the integrated effects of previous supernovas that occurred before the solar system was born. The even-odd feature is due to the fact that nuclei with even numbers of protons and neutrons are more stable than those with odd numbers of protons and neutrons.

For geochemists, the most important feature to recognize from the solar photosphere composition is the inherent difference in abundance between even and odd atomic numbers. Thus, all materials in the solar system inherit this "sawtooth" signature to a certain extent. If we wish to compare elemental abundance patterns of various Earth materials, it would be convenient if we could remove this intrinsic sawtooth feature. Because all materials in the solar system inherit the solar signature, normalization to any material will remove the even-odd effect. The most common normalizations are to use CI-chondrites or "primitive mantle". As we will learn later, CI-chondrites are a class of primitive meteorites that have relative elemental abundances almost identical to the solar photosphere. We also learn later that "primitive mantle" is the theoretical composition of the bulk silicate part of the Earth. The *bulk silicate Earth* represents the solid Earth minus its metallic core. It represents what the mantle would look like if we mixed all the crust back into the mantle.

Table 1.2.
Composition of the Solar Photosphere, CI-chondrites and primitive mantle.

Atomic Number		Solar Photosphere			CI-chondrites		Primitive Mantle
		Anders and Grevasse, 1989			Anders and Grevasse, 1989	McDonough and Sun, 1994	McDonough and Sun, 1995
		atoms/10^6 Si					
1	H	2.79E+10	H	%	2.02		
2	He	2.72E+09	He				
3	Li	57.1	Li	ppm	1.5	1.5	1.6
4	Be	0.73	Be	ppm	0.0249	0.025	0.068
5	B	21.2	B	ppm	0.87	0.9	0.3
6	C	1.01E+07	C	ppm	34500	35000	120
7	N	3.13E+06	N	ppm	3180	3180	2
8	O	2.38E+07	O	%	46.4		
9	F	843	F	ppm	60.7	60	25
10	Ne	3.44E+06	Ne				
11	Na	5.74E+04	Na	ppm	5000	5100	2670
12	Mg	1.07E+06	Mg	%	9.89	9.65	22.8
13	Al	8.49E+04	Al	%	0.868	0.860	2.35
14	Si	1.00E+06	Si	%	10.64	10.65	21
15	P	1.04E+04	P	ppm	1220	1080	90
16	S	5.15E+05	S	ppm	62500	54000	250
17	Cl	5240	Cl	ppm	704	680	17
18	Ar	1.01E+05	Ar				
19	K	3770	K	ppm	558	550	240
20	Ca	6.11E+04	Ca	%	0.928	0.925	2.53
21	Sc	34.2	Sc	ppm	5.82	5.92	16.2
22	Ti	2400	Ti	ppm	436	440	1205
23	V	293	V	ppm	56.5	56	82
24	Cr	1.35E+04	Cr	ppm	2660	2650	2625
25	Mn	9550	Mn	ppm	1990	1920	1045
26	Fe	9.00E+05	Fe	%	19.04	18.1	6.26
27	Co	2250	Co	ppm	502	500	105
28	Ni	4.93E+04	Ni	ppm	11000	10500	1960
29	Cu	522	Cu	ppm	126	120	30
30	Zn	1260	Zn	ppm	312	310	55
31	Ga	37.8	Ga	ppm	10	9.2	4
32	Ge	119	Ge	ppm	32.7	31	1.1
33	As	6.56	As	ppm	1.86	1.85	0.05
34	Se	62.1	Se	ppm	18.6	21	0.075
35	Br	11.8	Br	ppm	3.57	3.57	0.05
36	Kr	45	Kr				
37	Rb	7.09	Rb	ppm	2.3	2.3	0.6
38	Sr	23.5	Sr	ppm	7.8	7.25	19.9
39	Y	4.64	Y	ppm	1.56	1.57	4.3
40	Zr	11.4	Zr	ppm	3.94	3.82	10.5
41	Nb	0.698	Nb	ppb	246	240	658
42	Mo	2.55	Mo	ppb	928	900	50
44	Ru	1.86	Ru	ppb	712	710	5
45	Rh	0.344	Rh	ppb	134	130	0.9
46	Pd	1.39	Pd	ppb	560	550	3.9
47	Ag	0.486	Ag	ppb	199	200	8
48	Cd	1.61	Cd	ppb	686	710	40
49	In	0.184	In	ppb	80	80	11
50	Sn	3.82	Sn	ppb	1720	1650	130
51	Sb	0.309	Sb	ppb	142	140	5.5
52	Te	4.81	Te	ppb	2320	2330	12
53	I	0.9	I	ppb	433	450	10
54	Xe	4.7	Xe				

Table 1.2. continued

55	Cs	0.372	Cs	ppb	187	190	21
56	Ba	4.49	Ba	ppb	2340	2410	6600
57	La	0.446	La	ppb	234.7	237	648
58	Ce	1.136	Ce	ppb	603.2	613	1675
59	Pr	0.1669	Pr	ppb	89.1	92.8	254
60	Nd	0.8279	Nd	ppb	452.4	457	1250
62	Sm	0.2582	Sm	ppb	147.1	148	406
63	Eu	0.0973	Eu	ppb	56	56.3	154
64	Gd	0.33	Gd	ppb	196.6	199	544
65	Tb	0.0603	Tb	ppb	36.3	36.1	99
66	Dy	0.3942	Dy	ppb	242.7	246	674
67	Ho	0.0889	Ho	ppb	55.6	54.6	149
68	Er	0.2508	Er	ppb	158.9	160	438
69	Tm	0.0378	Tm	ppb	24.2	24.7	68
70	Yb	0.2479	Yb	ppb	162.5	161	441
71	Lu	0.0367	Lu	ppb	24.3	24.6	67.5
72	Hf	0.154	Hf	ppb	104	103	283
73	Ta	0.0207	Ta	ppb	14.2	13.6	37
74	W	0.133	W	ppb	92.6	93	29
75	Re	0.0517	Re	ppb	36.5	40	0.28
76	Os	0.675	Os	ppb	486	490	3.4
77	Ir	0.661	Ir	ppb	481	455	3.2
78	Pt	1.34	Pt	ppb	990	1010	7.1
79	Au	0.187	Au	ppb	140	140	1
80	Hg	0.34	Hg	ppb	258	300	10
81	Tl	0.184	Tl	ppb	142	140	3.5
82	Pb	3.15	Pb	ppb	2470	2470	150
83	Bi	0.144	Bi	ppb	114	110	2.5
90	Th	0.0335	Th	ppb	29.4	29	79.5
92	U	0.009	U	ppb	8.1	7.4	20.3

1.3 The Earth minus the atmosphere and hydrosphere

The Earth minus the atmosphere and hydrosphere (e.g., the metallic core plus the silicate mantle and crusts) is predominantly made up of O (~30 wt. %), Fe (~32%), Mg (~14%), Si (~15%), Ca (1.5%), and Al (1.4%), as shown in Figure 1.4. Most of the Fe is in the core, which makes up ~32.5 wt. % of the entire Earth. This leaves the rocky outer part of the Earth (e.g., the mantle) with ~6% Fe, ~44% O, ~23% Mg, ~21% Si, 2.5% Ca and 2.4% Al. Thus, the outer part of the Earth is dominated by Si and O and is accordingly dominated by silicate minerals[1]. We will take these compositional estimates as given for now. In Chapter 2, we will discuss how the composition of the Earth was determined.

It is likely that the outer part of the Earth, the *bulk silicate Earth*, was more or less compositionally homogeneous during its earliest history because the oldest known rocks are only ~4.1 Ga old (the age of the Earth is 4.55 Ga), indicating that whatever rocks were created at the Earth's surface during the first ~0.5 Ga were efficiently rehomogenized in the bulk silicate Earth. It is clear now that the bulk silicate Earth has subsequently differentiated into various subreservoirs. The most striking subreservoirs are the continental crust and oceanic crust. Continental crust is on average ~35 km thick and makes up ~0.38 % by mass of the bulk silicate Earth. Oceanic crust averages ~7-10 km thick and makes up ~0.2 % by mass of the bulk silicate Earth. The remaining 99.4 % of the bulk silicate Earth is the mantle, which consists of that part of the mantle that is residual to the extraction of continental and oceanic crust, any primitive (e.g., undifferentiated) parts retaining bulk silicate Earth compositions, and any crustal components that may have been recycled back into the mantle by subduction or related processes.

Table 1.3 shows the average major element compositions of the bulk silicate Earth, oceanic crust, and continental crust. A striking difference is that continental crust is considerably enriched in Si and Al compared to the bulk silicate Earth. This difference is manifested in

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[1] Silicates are compounds based on the silica tetrahedron, in which a Si is surrounded by four O atoms.

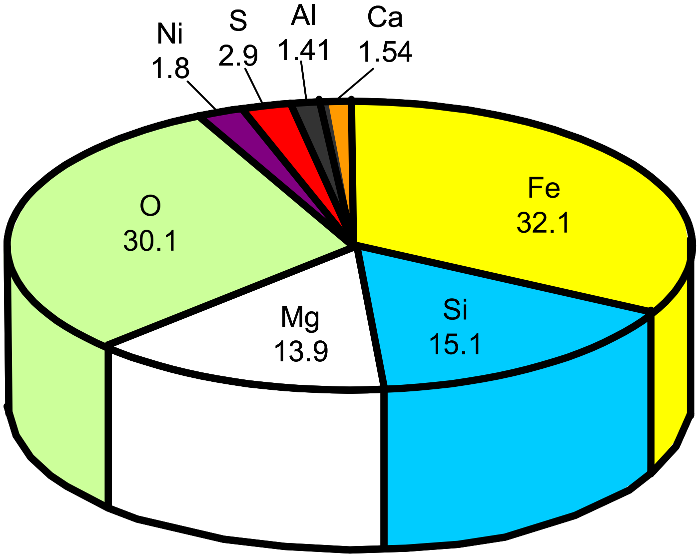

Figure 1.4. Relative atomic abundances of the eight most common elements that comprise 99% of the mass of the Earth minus the atmosphere and hydrosphere.

Table 1.3. Comparative chemistries of different Earth reservoirs

	Bulk Silicate Earth[1]	Continental Crust[2]	Oceanic crust	
			Most primitive basaltic glass[3]	Calculated primary composition[4]
MgO (wt. %)	36.33	4.4	10.1	17.81
Al_2O_3 (wt. %)	4.73	15.8	16.4	12.08
SiO_2 (wt. %)	45.56	59.1	49.7	47.85
CaO (wt. %)	3.75	6.4	13.0	11.22
FeO^T (wt. %)	8.17	6.6	7.9	8.98
Mg#	0.888	0.543	0.695	0.780

[1] [*O'Neill and Palme*, 1998]

[2] [*Rudnick*, 1995]

[3] [*Frey et al.*, 1974]

[4] [*Elthon*, 1979]

Mg# = molar Mg/(Mg+Fe); FeO^T is total Fe^{2+} and Fe^{3+}

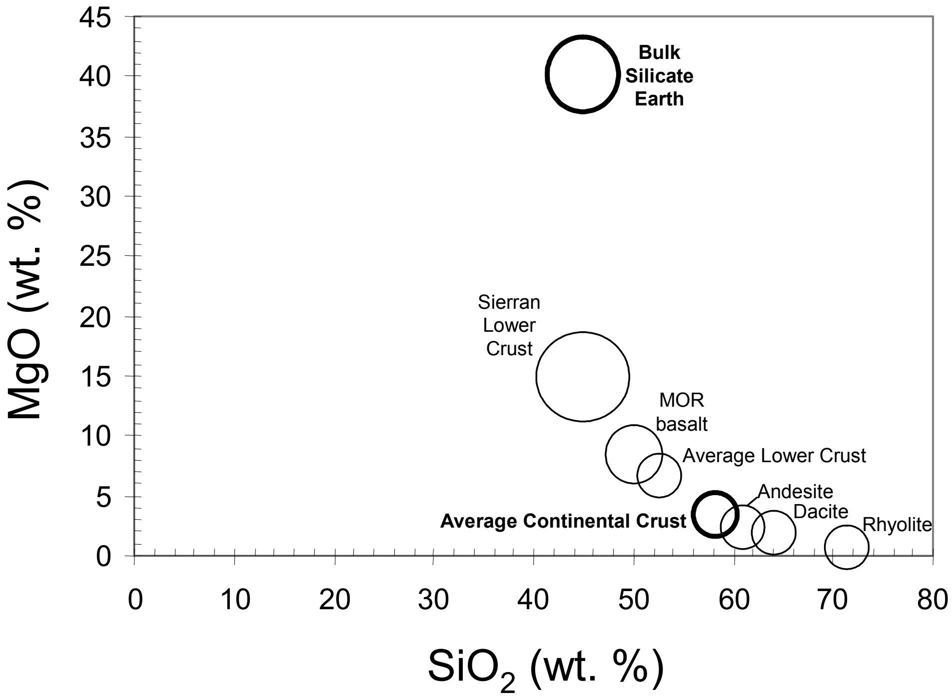

Figure 1.5. MgO versus SiO_2 content for Bulk Silicate Earth, Average Continental Crust, and other rock types.

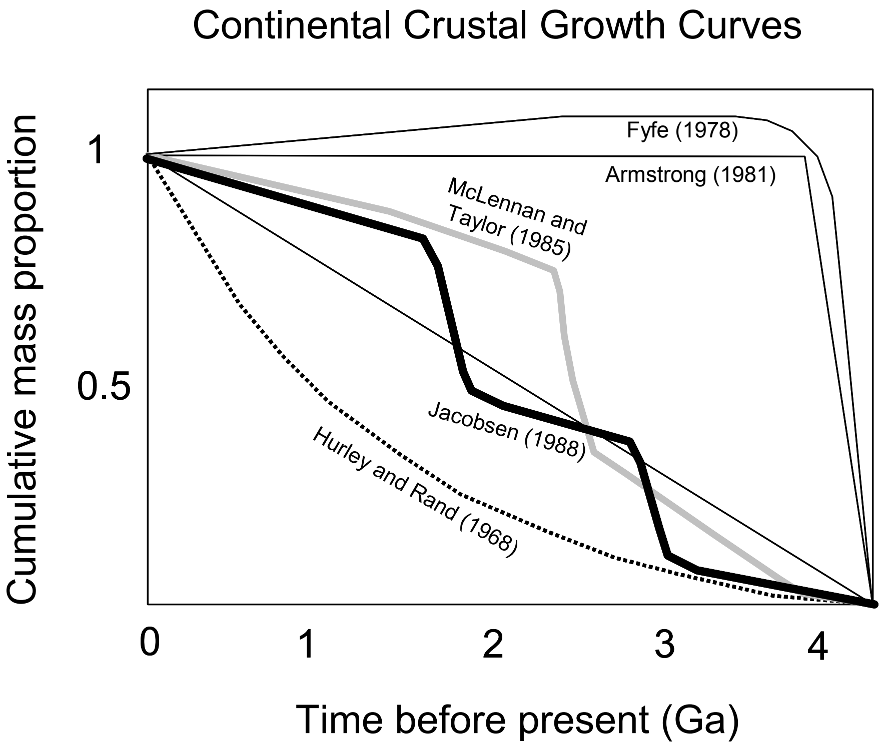

Figure 1.6. Various models for the continental crust growth curve (adapted from Bowring and Housh (1995) and Jacobsen (1988).

contrasting mineralogies: the continental crust is principally made up of quartz (SiO_2), feldspars ($KAlSi_3O_8$) and some mafic (mafic = Mg, Fe, and Ca-rich) minerals, such as hornblende and/or biotite. In contrast, the mantle is enriched in Mg and Fe relative to continental crust, and this is reflected in the fact that it is composed of mainly mafic minerals, such as olivine ($(Mg,Fe)_2SiO_4$) and pyroxene ($(Ca,Mg,Fe)_2Si_2O_6$), but no quartz. Differences in Mg and Si content are clearly shown in Figure 1.5. The continental crust appears to be very silicic and low in Mg content, having an approximately andesitic melt composition. Mid-ocean ridge basalts, one of the most ubiquitous lavas in the world, appear to have low Si contents and intermediate Mg contents. Why is the continental crust so silicic? The answer to this question may ultimately help us answer why continents exist because the silicic nature of the continental crust makes it intrinsically less dense than the mantle. This allows continents to "float" on the mantle rather than sink and disappear. It follows that perhaps if we can also understand the rates at which continents form, we can conversely shed light on the origin of the continental crust. Has the mass of continental crust been growing progressively through time, or is its present mass reflecting a long-term steady state situation? Constraining the rates of continental crust formation through time requires that we ultimately investigate the systematics of radiogenic isotope systems in continental crust rocks as this is really the only way we can obtain direct time constraints. Figure 1.6 shows various proposed models of continental crustal growth. Which model is correct?

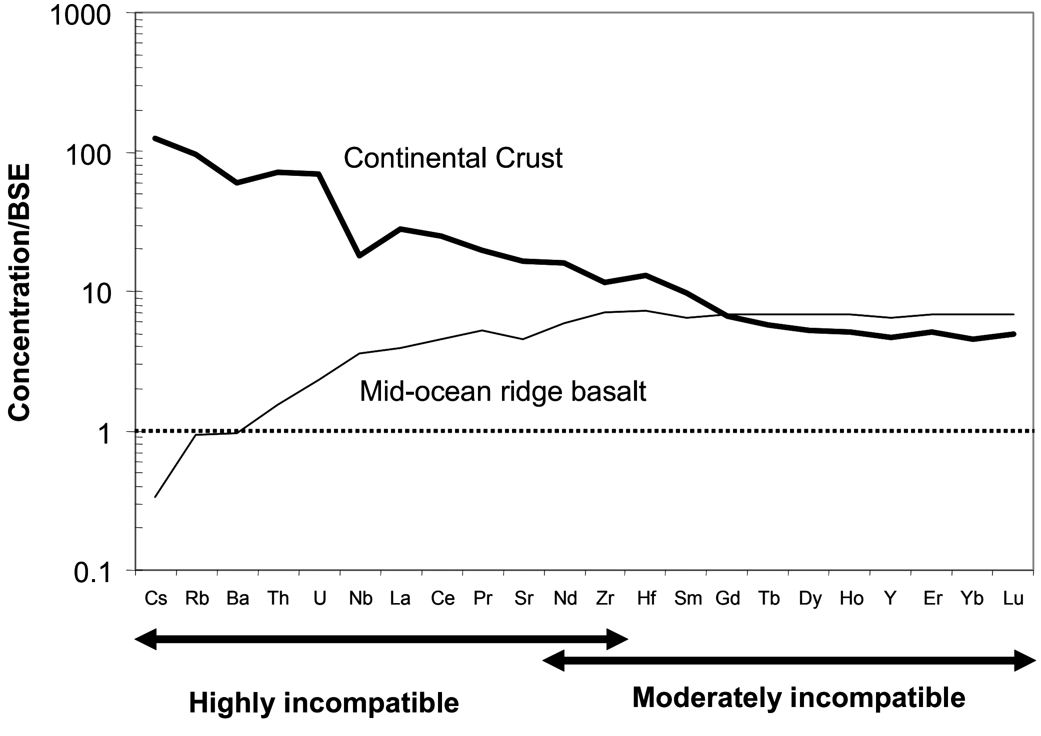

Figure 1.7. Trace-element abundances in continental crust and mid-ocean ridge basalt normalized to bulk-silicate Earth (primitive mantle). Elements are numbered in approximate order of increasing compatibility during silicate melting. Note the enrichment in incompatible elements in the continental crust. Mid-ocean ridge basalts have a negative slope.

Table 1.4. Composition of the Continental Crust

		Lower Continental crust Rudnick and Fountain, 1995	Upper Continental Crust Rudnick and Fountain, 1996	total Continental crust Rudnick and Fountain, 1997
Li	ppm	6	20	11
Na2O	%	2.6	3.9	3.2
MgO	%	7.1	2.2	4.4
Al2O3	%	16.6	15.2	15.8
SiO2	%	52.3	66	59.1
P2O5	%	0.1	0.4	0.2
K2O	%	0.6	3.4	1.88
CaO	%	9.4	4.2	6.4
Sc	ppm	31	11	22
V	ppm	196	60	131
Cr	ppm	215	35	119
MnO	%	0.1	0.08	0.11
FeO	%	8.4	4.5	6.6
Co	ppm	38	10	25
Ni	ppm	88	20	51
Cu	ppm	26	25	24
Zn	ppm	78	71	73
Ga	ppm	13	17	16
Rb	ppm	11	112	58
Sr	ppm	348	350	325
Y	ppm	16	22	20
Zr	ppm	68	190	123
Nb	ppm	5	25	12
Cs	ppm	0.3	5.6	2.6
Ba	ppm	259	550	390
La	ppm	8	30	18
Ce	ppm	20	64	42
Pr	ppm	2.6	7.1	5
Nd	ppm	11	26	20
Sm	ppm	2.8	4.5	3.9
Eu	ppm	1.1	0.9	1.2
Gd	ppm	3.1	3.8	3.6
Tb	ppm	0.48	0.64	0.56
Dy	ppm	3.1	3.5	3.5
Ho	ppm	0.68	0.8	0.76
Er	ppm	1.9	2.3	2.2
Yb	ppm	1.5	2.2	2
Lu	ppm	0.25	0.32	0.33
Hf	ppm	1.9	5.8	3.7
Ta	ppm	0.6	2.2	1.1
Pb	ppm	4.2	20	12.6
Th	ppm	1.2	10.7	5.6
U	ppm	0.2	2.8	1.42

Another striking observation is that the continental crust, despite its extremely small relative mass, contains most of the highly incompatible trace elements in the Earth, such as Cs, Rb, Ba, U, Th, and K (estimates range from 50 to 90% of the total budget in the bulk silicate Earth). Incompatible elements are those elements that are preferentially incorporated into the liquid phase during partial melting (compatible elements are those that are preferentially retained in the residual solid phase during partial melting). We will learn later how we actually know which elements are considered incompatible or compatible. Figure 1.7 shows the trace-element composition of average continental crust and average mid-ocean ridge basalt (MORB) normalized to Primitive Mantle (Bulk Silicate Earth)[2] (Table 1.4). We can see that continental crust is highly enriched in the highly incompatible elements. In contrast, MORB appears to have a somewhat complementary trace-element abundance pattern. If the Earth was originally homogeneous with a composition given by our estimate of the Bulk Silicate Earth, then the process of continental crust and oceanic crust formation clearly had profound consequences on the redistribution of trace-elements in the Earth. The question is whether trace-element systematics can tell us something about these differentiation processes? The astute reader may have noticed that the trace-element abundance pattern of MORB is paradoxical. Why are the more incompatible (or melt-loving) elements actually depleted relative to the less incompatible elements in MORB?

We are thus left with a myriad of questions. What processes dictate how the Earth unmixes, i.e. differentiates? In this context, we are concerned with not only the processes that control chemical mass transfer during differentiation, but also the physical processes of differentiation. How does the mantle melt? What conditions dictate the composition of the melt and how does the melt evolve in composition as it cools? How does tectonic environment control the nature of differentiation? How is melt transported from its source region to the crust? What processes allow for recycling of crustal material back into the mantle? What chemical changes occur during crustal recycling? Can we quantify how these differentiation processes and their rates have evolved through time?

1.4 The oceans

The mass of the ocean is 1.4×10^{21} kg and makes up ~0.03% of the Earth's mass. The composition of seawater is given in Table 1.5. A selection of trace-element concentrations in seawater are shown in Figure 1.8. In Figure 1.8a, we have normalized the data to bulk silicate Earth and we have also plotted the elements in the same order as in Figure 1.7. We can see that the trace-element abundance pattern of seawater is roughly similar to that of continental crust, but there appear to be extreme depletions in Th and extreme enrichments in Sr. There also appears to be a subtle difference in the relative abundances of the rare-earth elements. La, Ce, Pr, and Nd do not appear to be as enriched over the heavy rare-earth elements (e.g, Dy, Ho, Er, Yb, Lu) as continental crust is. In fact, if we normalize the seawater composition to continental crust, we can see how seawater differs distinctly from continental crust. If we also compare Tables 1.5

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[2] Trace element < 1000 ppm
Minor element <1 wt. %
Major element >1 wt. %
% = 1 g/100 g
ppm = parts per million = 1 μg/g
ppb = parts per billion = 1 ng/g
ppt = parts per trillion = 1 pg/g
1 wt. % = 10^4 ppm

Table 1.5
Seawater Composition from GERM database

H	%	11	Sr	ppb	8100
O	%	88.3	Zr	ppt	26
Na	%	1.08	Y	ppt	13
Cl	%	1.94	Nb	ppt	15
Mg	ppm	1290	Mo	ppb	10
S	ppm	904	Ru	ppt	0.7
K	ppm	392	Ag	ppt	280
Ca	ppm	411	Cd	ppt	110
Br	ppm	67.3	Sn	ppt	810
Li	ppm	0.17	Sb	ppt	330
Be	ppb	0.0006	I	ppb	64
B	ppm	4.45	Cs	ppt	300
C	ppm	28	Ba	ppb	21
Na	ppm	15.5	La	ppt	2.9
F	ppm	13	Ce	ppt	1.2
Al	ppb	1	Pr	ppt	0.64
Si	ppb	2900	Nd	ppt	2.8
P	ppb	88	Sm	ppt	0.45
Sc	ppb	0.004	Eu	ppt	1.3
Ti	ppb	1	Gd	ppt	0.7
V	ppb	1.9	Tb	ppt	0.14
Cr	ppb	0.2	Dy	ppt	0.91
Mn	ppb	0.4	Ho	ppt	0.22
Fe	ppb	3.4	Er	ppt	0.87
Co	ppb	0.39	Tm	ppt	0.17
Ni	ppb	6.6	Yb	ppt	0.82
Cu	ppb	0.9	Lu	ppt	0.15
Zn	ppb	5	Re	ppt	8.4
Ga	ppb	0.03	Au	ppt	11
Ge	ppb	0.06	Hg	ppt	150
As	ppb	2.6	Pb	ppt	30
Se	ppb	0.9	Bi	ppt	20
Rb	ppb	120	Th	ppt	0.4
			U	ppt	3300

and 1.4, we see that seawater is also considerably more enriched in Na, Cl, and K than the continental crust.

What controls the concentration of an element in seawater? An obvious explanation is that the elemental budget of seawater reflects what goes into the oceans (Fig. 1.9). Inputs into the ocean include riverine and groundwater flow, Aeolian deposition, rain, hydrothermal circulation, extraterrestrial infall, and sediment diagenesis. Each of these inputs have different compositions and chemistries, and therefore seawater represents a mixture of all these sources. The relative contribution of these sources is different for each element. For example, the inputs of Na, Sr, Rb, and K are likely to be dominated by riverine inputs carrying dissolved components from the continental crust. Some heavy metals like Co, Mn, Fe, Pt, Os, and Ir may have relatively larger hydrothermal and/or extraterrestrial input fractions.

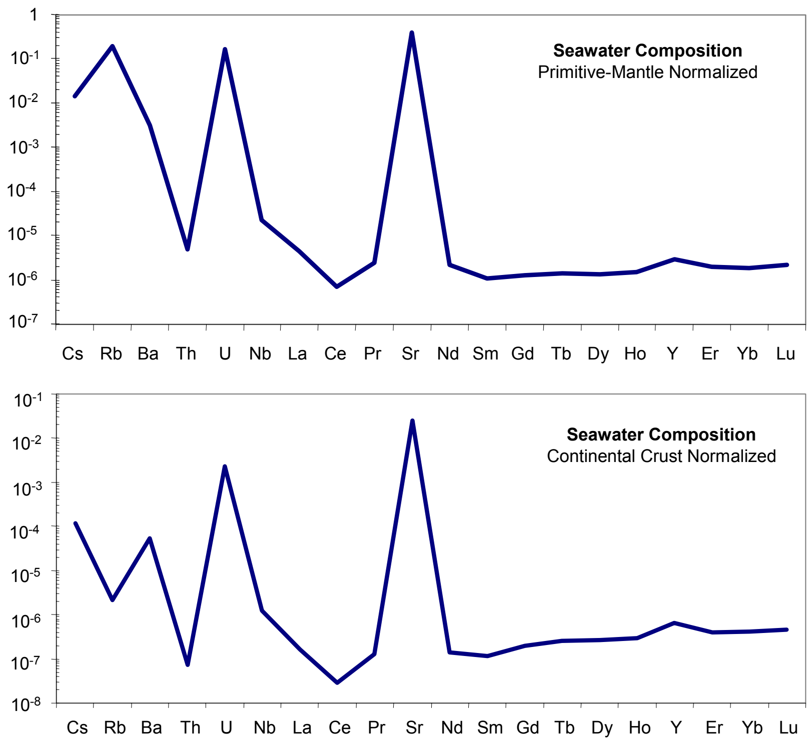

Figure 1.8. Seawater Composition. A) primitive-mantle normalized. B) Continental-Crust Normalized.

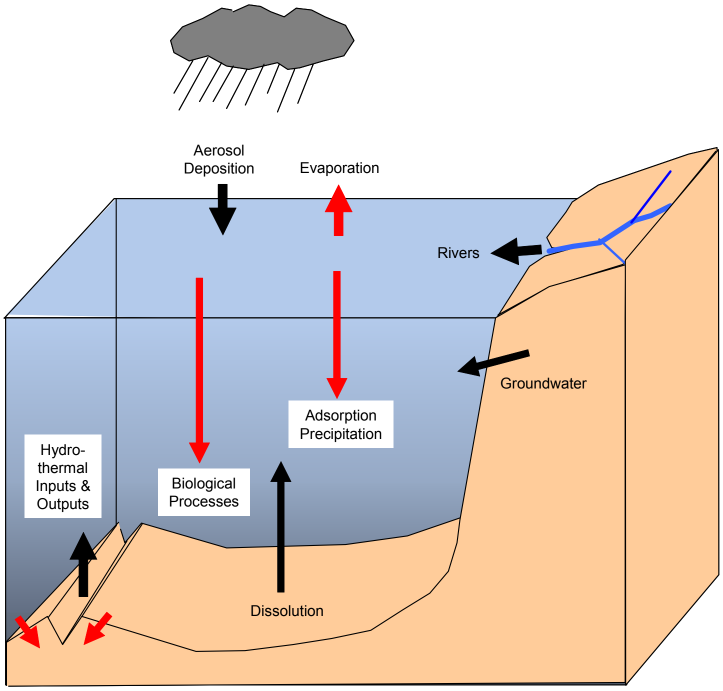

Figure 1.9. Schematic diagram showing various input and output fluxes of elements into and out of the ocean.

Looking at only the inputs, however, is an over simplification. We know that there are many possible elemental sinks in the ocean, such as hydrothermal circulation, evaporation, formation of sea spray, and sediment burial (dead organisms, chemical precipitates, adsorption onto particulates, etc.). Some elements are efficiently pulled out of the ocean, while others are not. Na, Sr, Rb and K are highly soluble and therefore only a tiny fraction of the entire oceanic budget is lost by one of the above output mechanisms. In contrast, some elements like Co and Ir are extremely particle reactive, that is, they adsorb readily onto sinking particulates. Their concentrations in the ocean are therefore low.

The concentration of an element in seawater therefore represents a complex balance between inputs and outputs. If inputs and outputs are identical and unchanging, then the concentration in the ocean is constant, i.e. at steady-state. If inputs or outputs suddenly change, then the ocean is said to be in a transient state, and the ocean progresses to a new steady-state. The rate at which it progresses to the new steady-state depends on the chemical behavior of the element of interest. Changes in the input of a given element can be caused by many factors, such as a change in climate or tectonic activity. Changes in output of a given element can be caused by climate change or changes in the chemistry of seawater. It is thus clear that the evolution of an element's concentration in seawater reflects the interplay between the atmosphere, oceans, continents, seafloor, and mantle.

REFERENCES AND USEFUL READINGS

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Bowring, S. A., and T. Housh, The Earth's early evolution, *Science, 269*, 1535-1540, 1995.

McDonough, W. F., and S.-S. Sun, The composition of the Earth, *Chem. Geol., 120*, 223-253, 1995.

USEFUL WEBSITES

- *Geochemical Earth Reference Model (GERM)* - http://earthref.org/GERM/main.htm. This website represents a community effort to build a geochemical database for all the major Earth reservoirs.
- *GEOROC* - http://georoc.mpch-mainz.gwdg.de/. A large geochemical database of igneous rocks around the world.

EXERCISES

1. The TiO_2 concentration in the mantle is estimated to be approximately 0.2 % by weight. Calculate the concentration of elemental Ti in parts per million (ppm)? The atomic weight of Ti is 47.867 g/mole and that of oxygen is 15.9994 g/mol.

2. The Fe content of silicate rocks is often expressed as FeO or Fe_2O_3. What is the difference between these two expressions? The FeO content in the mantle is 8.2 wt. %. Calculate the wt. % of Fe_2O_3 in the mantle if all of the Fe is assumed to be in the form of Fe_2O_3 instead of FeO. The atomic weight of Fe is 55.845 g/mole and that of oxygen is 15.9994 g/mol.

3. Write out a mass balance equation equating the total amount of K in the Earth to the sum of the K in the major Earth reservoirs (core, mantle, crust, atmosphere, ocean). The mass balance equation should be of the form $C_{Earth}M_{Earth} = \sum C_i M_i$, where C_i is the concentration (by weight) of K in the whole Earth or a given reservoir, and M_i is the mass of each reservoir. Use the data from the tables in this chapter. Assuming that there is no K in the atmosphere, what proportion of the Earth's total K budget resides in the continental crust and oceans? How much K must reside in the interior of the Earth (e.g., the mantle and possibly the core)?

4. **Continental growth**. The origin of the continental crust is a fundamental question that has still not been fully answered. By "origin", we are interested in the petrogenetic processes that govern its formation. We are also interested in the rates of continental crust formation as this may tell us something about the geodynamic environment in which continental crust is formed. As a working hypothesis, let's assume that the continental crust is created by amalgamation of island arcs, manifestations of arc magmatism. Let's also assume that some amount of the continental crust is recycled (or remixed) back into the convecting mantle at subduction zones. This could be in the form of subducting continentally-derived sediments or it could be in the form of physical removal of the continents' underbellies during subduction. Let us attempt to track how the cumulative mass M_{CC} of the continental crust changes with time by writing a mass balance equation. This is constructed by assuming that the rate of change in mass of the continental crust $\frac{dM_{CC}}{dt}$ at any given time is equal to the amount of continental crust being generated at subduction zones $\frac{dM_{in}}{dt}$ minus the amount being recycled at subduction zones $\frac{dM_{out}}{dt}$:

$$\frac{dM_{cc}}{dt} = \frac{dM_{in}}{dt} - \frac{dM_{out}}{dt} \qquad \text{(Eq. 1)}$$

Let us further assume that the amount of continental crust recycled at subduction zones is proportional to that being generated, that is,

$$k\frac{dM_{in}}{dt} = \frac{dM_{out}}{dt} \qquad \text{(Eq. 2)}$$

We can also assume as a working hypothesis that the rate of continental crust generation has decreased exponentially with time so that we may be able to account for the gradual decrease in the vigor of convection (note this is a largely unsupported assumption)

$$\frac{dM_{in}}{dt} = \left(\frac{dM_{in}}{dt}\right)_o e^{-\lambda t} \qquad \text{(Eq. 3)}$$

where $\left(\frac{dM_{in}}{dt}\right)_o$ was the rate of crust generation at the beginning of Earth's history and λ is the exponential decay constant for crustal growth.

a) Plug Eqs. 2 and 3 into Eq. 1. Write down this equation and explain what each of the terms mean. Assume that $\left(\frac{dM_{in}}{dt}\right)_o$, k, and λ are constant and that $M(0)=0$, integrate the equation you have on hand with respect to time in order to obtain an expression for the cumulative growth of continental crust. Do the integration from time $t=0$ to an arbitrary time t. Show that the answer is

$$M_{cc}(t)=\left(\frac{dM_{in}}{dt}\right)_o\frac{1-k}{\lambda}\left(1-e^{-\lambda t}\right) \qquad \text{Eq. 4}$$

b) Express Eq. 4 for the case in which λ approaches zero. Hint: you can derive this by assuming λ is zero to begin with and re-deriving Eq. 4 in part a). Alternatively, you can make use of the approximation $e^{-\lambda t}\approx 1-\lambda t$ for very small λ[3].

c) Express Eq. 4 for the case in which $k = 0$.

d) Express Eq. 4 for the case in which $k = \lambda = 0$.

e) On Figure 1.6, schematically plot the form of the equations you derived in parts b, c, and d. Comment on the results of your model and how they compare to inferred crustal growth models.

f) The Hurley and Rand (1968) growth curve exhibits an exponential increase in the mass of continental crust with time (Figure 1.6). One way to generate such a curve is to have an exponentially *increasing* function for growth of continental crust and a *decreasing* function for recycling. If we let k in Eq. 2 represent an exponentially decaying function with a decay constant of λ_{out}, then we can re-derive Eq. 4 to yield

$$M_{cc}(t)=\left(\frac{dM_{in}}{dt}\right)_o\left[\frac{k_o}{\lambda_{in}-\lambda_{out}}\left(1-e^{(\lambda_{in}-\lambda_{out})t}\right)+\frac{1}{\lambda_{in}}\left(e^{\lambda_{in}t}-1\right)\right] \qquad \text{Eq. 5}$$

where λ_{in} represents the growth constant of continental crust generation (identical to the λ in Eq. 4). Re-express Eq. 5 for the case in which $\lambda_{out} = 0$ (hint: see part c). Show on Figure 1.6 that this is an exponential growth curve.

5. **Oceanic Residence Times**. Let M_{SW} represent the total mass of an element in seawater (e.g., its concentration multiplied by the mass of the oceans). The rate of change in mass of an element in seawater dM_{SW}/dt is given by

$$\frac{dM_{SW}}{dt}=\frac{dM_{in}}{dt}-\frac{dM_{out}}{dt} \qquad \text{Eq. 6}$$

where dM_{in}/dt and dM_{out}/dt represent the total input and output rates to and from the ocean (units = mass/time). At steady state,

$$0=\frac{dM_{in}}{dt}-\frac{dM_{out}}{dt} \qquad \text{Eq. 7}$$

that is, total inputs and total outputs are balanced. Under these conditions, the average time an element resides in the ocean is called the **residence time**, which is defined as

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[3] This approximation is derived using the Taylor expansion $f(x)=\sum_{n=0}^{\infty}\frac{f^{(n)}(0)}{n!}x^n$ where $f^{(n)}$ represents the *nth* derivative of the function *f*.

$$\tau_{res} = \frac{M_{SW}}{dM_{in}/dt} = \frac{M_{SW}}{dM_{out}/dt} \qquad \text{Eq. 8}$$

a) Calculate the residence time (in years) of Ir and Os in the ocean given the following information. The concentration of Ir and Os in rivers are 1.75 and 9 pg/kg, and in seawater are 0.1 and 10 pg/kg. The mass of the ocean is 1.4×10^{21} kg and the total river flow into the oceans is 3.6×10^{16} kg/yr. What is the basic assumption in this calculation (hint: see part c)?

b) If 80% of the Os in rivers is extracted in estuaries, just before the rivers enter the ocean, how does your calculation of the Os residence time change?

c) In order to calculate the oceanic residence time, the **total** input or output rates must be known. In the case of Os, there may be other inputs into the ocean, such as hydrothermal or extraterrestrial inputs. If only one input is considered, then the calculated residence time is over-estimated. If we have *n* number of inputs, then we can define a **fractional** residence time for each input, τ_n. Using equations 7 and 8, show that the total residence time can be expressed in terms of the fractional residence times as follows

$$\frac{1}{\tau_{res}} = \frac{1}{\tau_1} + \frac{1}{\tau_2} + \cdots \frac{1}{\tau_n} \qquad \text{Eq. 9}$$

d) Let us now take a look at what the residence time means physically. Let's look at the case in which the concentration of an element in the ocean suddenly changes due to an instantaneous increase of that element's concentration in the ocean. For example, immediately after the large meteorite hit the Earth at the K-T boundary, the concentration of Os and Ir may have abruptly increased. The question then is how long would it take for the elevated Os and Ir contents to decay back to steady-state conditions. Returning to Eq. 6, let us assume that the rate at which an element is pulled out of the ocean is proportional to its abundance in the ocean. Therefore,

$$\frac{dM_{out}}{dt} = kM_{SW} \qquad \text{Eq. 10}$$

where the proportionality constant, *k*, has units of 1/[time]. Let us also assume that the inputs are independent of the element's concentration in seawater and that the input is constant. If we define the constant input as

$$\frac{dM_{out}}{dt} = A \qquad \text{Eq. 11}$$

we find that Eq. 6 can be expressed as

$$\frac{dM_{SW}}{dt} = A - kM_{SW} \qquad \text{Eq. 12}$$

This equation can be integrated with the boundary conditions that at t = 0, $M_{SW}(0) = M^o_{SW}$. Verify that the solution to this equation is

$$M_{SW} = \frac{A}{k} - \left[\frac{A}{k} - M^o_{SW}\right]e^{-kt} \qquad \text{Eq. 13}$$

This equation essentially shows the response curve of an element's mass in the ocean due to a sudden change in input, *A*.

- Show that at steady-state (t = ∞), the steady-state content of the element of interest is *A/k*.
- Show that at steady-state, the residence time (defined above) is equal to 1/*k*. It can be seen from Eq. 13, that the rate at which the system returns to steady-state decreases exponentially and is controlled by the time constant *k*. Thus, for this simple case, the residence time is a measure of the response time of the system to an instantaneous perturbation.

6. Helium (He) has two isotopes, having mass numbers of 3 and 4. How may protons, neutrons and electrons are associated with each of these isotopes?

7. The following represents the major and minor element composition in terms of weight percent oxide of a dioritic rock from the Sierra Nevada pluton in California.

SiO_2	58.2
TiO_2	0.74
Al_2O_3	17.1
FeO	6.51
MgO	3.79
MnO	0.12
CaO	7.01
Na_2O	2.83
K_2O	1.4
P_2O_5	0.1

   a. Convert MgO, FeO and Al2O3 wt. % to wt. % and ppm Mg, Fe, and Al.
   b. Calculate the number of corresponding moles of Mg, Fe, and Al.
   c. Calculate the Mg# or the rock, which is the molar ratio Mg/(Mg+Fe).

8. The mineral olivine is represented by the following chemical formula $(Mg_{0.9}Fe_{0.1})_2SiO_4$. Calculate the composition of this olivine in terms of wt. % MgO, FeO and SiO_2. What is its Mg# (see above)?

9. ^{87}Rb decays to ^{87}Sr with a decay constant of 1.42 x 10^{-11}/yr. What is the half-life of ^{87}Rb in Gy units? Show how you arrived at this answer (you can refer to Section 3.1 in Faure for help).

10. The dissolved cobalt (Co) concentration of seawater is controlled by the inputs and outputs of Co into the ocean. In an idealized system, let's assume that the only input of Co into the ocean is via river waters and the dominant output of Co is in oxidized pelagic clays.

    a. The present-day Co concentration in river waters is ~0.1 microg/kg and in seawater is 0.002 microg/kg. The global riverine flow of water into oceans is 3.6 x 10^{16} kg/yr. Calculate the rate (microg/year) at which Co enters the ocean via rivers. The mass of the oceans is 1.4 x 10^{21} kg; calculate the present day total amount of Co in the oceans.

b. Assume that the Co concentration of seawater is at steady-state. What does steady-state mean? What is the rate at which Co must precipitate from the oceans in pelagic sediments in order to maintain steady-state.

c. At steady state, the average residence time (yr) of a Co atom in the ocean is equal to

$$t_{res} = m_{sw} / J_{in} = m_{sw} / J_{out} \qquad \text{Eq. 1}$$

where m_{sw} is the total mass of Co in the oceans, J_{in} is the total input of Co into oceans via river waters, and J_{out} is the total output of Co from the oceans via sedimentation. Using parts a) or b), calculate the residence time of Co in seawater today.

d. Assume that the output (microg/yr) of Co from seawater via authigenic sedimentation is proportional to the total amount of Co in seawater, $M_{Co,sw}$, that is,

$$J_{out} = kM_{Co,sw} \qquad \text{Eq. 2}$$

where k is the proportionality constant. Calculate k. Hint (assume steady state).

e. Show that the change in total mass of Co in seawater can be expressed as

$$\frac{dM_{Co,sw}}{dt} = J_{in} - J_{out} = J_{in} - kM_{Co,sw} \qquad \text{Eq. 3}$$

This equation can be integrated to yield $M_{Co,sw}$ as a function of time given specific initial conditions. Show that the solution to the above equation is

$$M_{Co,sw} = \frac{J_{in}}{k}\left(1 - e^{-kt}\right) + M^{o}_{Co,sw} e^{-kt} \qquad \text{Eq. 4}$$

where t is time, $M^{o}_{Co,sw}$ is the initial amount of Co in the oceans at time $t=0$. Make a graph of this equation for the case in which $M^{o}_{Co,sw}$ is zero and $M^{o}_{Co,sw}$ is twice as high as the present-day steady-state amount of Co in the ocean.

f. Explain the meaning of each of the terms on the left-hand side of Eq. 4. What happens when there is no input of Co into the oceans, that is, $J_{in} = 0$? What happens if Co never precipitates, that is, there is no output from the ocean? What happens when t approaches infinite (hint: recall the concept of steady-state)?

g. Examination of your graph from part e) will reveal that the amount of time it takes for the system to roughly reach steady state will be $1/k$. This quantity is called the response time of the system. Show that under steady-state conditions, the residence time of Co is also equal to $1/k$.