Quantitative Questions: Supplement to Cosmochemistry by McSween and Huss

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Question 2.1. Calculate atomic weights.

a) Using the numbers from the Chart of the Nuclides, what is the atomic weight of calcium

Isotope	Percentage	atomic mass
⁴⁰ Ca	96.941	39.9625912
⁴² Ca	0.647	41.9586183
⁴³ Ca	0.135	42.958766
⁴⁴ Ca	2.086	43.955481
⁴⁶ Ca	0.004	45.953693
⁴⁸ Ca	0.187	47.952534

[Answer: 40.078]

B) The atomic weight of scandium is 44.955910. Why is the atomic weight of scandium known to higher precision than the atomic weight of calcium, a much-more-abundant element?

[Answer: There is only one stable isotope of scandium, so its mass can be determined by our most precise isotope techniques. Calcium has six stable isotopes, and its atomic weight depends on both the isotopic masses (each of which has a small uncertainty) and the abundances of the different isotopes, which aren't always the same.]

c) What is the atomic weight of tellurium.

Isotope	Percentage	atomic mass
¹²⁰ Te	0.09	119.90402
¹²² Te	2.55	121.903047
¹²³ Te	0.89	122.904273
¹²⁴ Te	4.74	123.902819
¹²⁵ Te	7.07	124.904425
¹²⁶ Te	18.84	125.903306
¹²⁸ Te	31.74	127.904461
¹³⁰ Te	34.08	129.906223
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[Answer: 127.060446]

d) What is unusual about the atomic weight of tellurium compared to other elements? [Answer: It is higher than that of iodine, which has a higher atomic number (A), by 2/3 of an amu.]

Question 2.2. Atomic Binding Energy calculations.

a) Using the information in the Chart of the Nuclides and the masses of a proton and a neutron, calculate the binding energy (mass defect) of these nuclides: ²⁸Si, ⁴⁰Ca, ⁵⁶Fe, ¹⁰⁷Ag, ¹⁹⁷Au, ²³⁸U. What is the binding energy/nucleon?

Particle Proton Neutron Electron	1.673 x 10^{-24} 1.675 x 10^{-24}		lass (Daltons) 1.00728 1.00866	Mass (MeV) 938.256 939.550 0.511
[Answer: in u	nits of Daltons (Da)]		
Nuclide	Atomic Mass	Mass of Part	s Binding End	ergy B. E./nucleon
²⁸ Si	27.976926533	28.22596	0.2490334	0.008894052
⁴⁰ Ca	39.9625912	40.3228	0.3602088	0.00900522
⁵⁶ Fe	55.934942	56.45508	0.520138	0.009288179
¹⁰⁷ Ag	106.90509	107.87376	0.96867	0.009052991
¹⁹⁷ Au	196.966552	198.6206	1.654048	0.008396183
²³⁸ U	238.050783	239.96332	1.912537	0.00803587

 b) Convert the results from Daltons to MeV (MeV/Dalton conversion factor = 931.3867093).

[Answer: in units of MeV]

Nuclide	Atomic Mass	Mass of Parts	Binding Energy	B. E./nucleon
²⁸ Si	26057.33754	26289.284	231.9464613	8.28380219
⁴⁰ Ca	37220.62631	37556.12	335.4936889	8.38734222
⁵⁶ Fe	5209706156	52581.156	484.0944382	8.64454354
¹⁰⁷ Ag	99569.97998	100471.032	901.0520222	8.42104694
¹⁹⁷ Au	183452.0287	184989.124	1537.095299	7.80251421
²³⁸ U	221717.3354	223493.852	1776.516586	7.4643554

c) What happens to the binding energy as the nuclide's atomic mass increases?

[Answer: the binding energy increases with atomic mass.

d) What happens to the binding energy per nucleon as the nuclide's atomic mass increases?

[Answer: the binding energy per nucleon increases with atomic mass until approximately ⁵⁶Fe, and then decreases slowly with further increase in atomic mass.

Question 4.1: Normalizing to the CI composition.

The relative abundances of the elements depend on fundamentally on the nucleosynthetic processes that produced the elements. Abundances in various objects also depend on the processes that produced the objects. We will discuss these processes in Chapter 7. Teasing out the unique signals of various processes from the compositions of their products is a critical part of cosmochemistry. In this exercise, we will look at Rare Earth Elements (REEs). These elements have similar, but not identical, electronic structures and behave as a group in some processes and behave very differently in others. But to interpret these compositions in terms of processes requires elimination of the large abundance variations that resulted from nucleosynthesis.

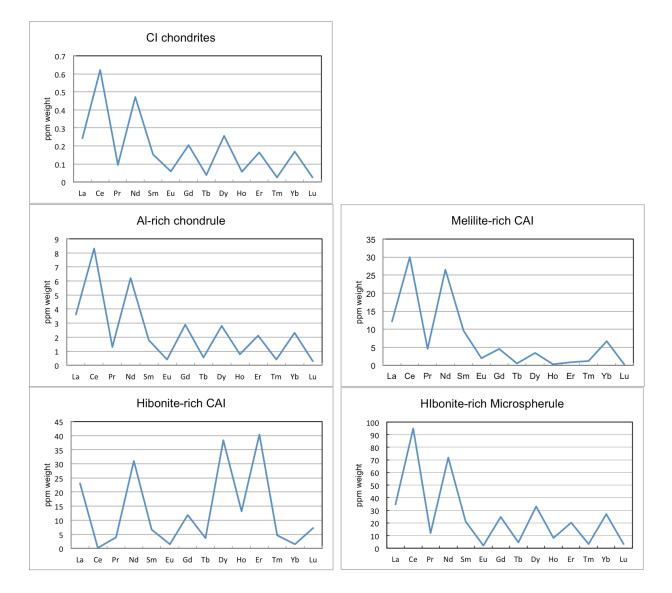
The solar system abundances of the REEs exhibit large differences (see column 2 of Table 4.1p below). A major cause of the abundance variation is the nuclear structure of the atoms (discussed in chapter 2). Table 4.1p also shows the REE abundances in four different constituents of chondritie meteorites, an Al-rich chondrule and three different CAIs. Before we manipulate the data, let's just look at it.

Element	Solar System	Al-rich	Melilite-rich	Hibonite-rich	Hibonite-rich
	Abundances	Chondrule	CAI	CAI	Microspherule
La	0.242	3.60	12.12	23.14	34.71
Ce	0.622	8.30	30.01	0.12	94.94
Pr	0.0946	1.30	4.55	3.99	11.81
Nd	0.471	6.20	26.53	31.00	71.93
Sm	0.152	1.80	9.58	6.60	21.33
Eu	0.0578	0.42	1.99	1.53	2.04
Gd	0.205	2.90	4.54	11.89	24.58
Tb	0.384	0.55	0.58	3.65	4.68
Dy	0.255	2.80	3.48	38.37	33.13
Но	0.0572	0.78	0.28	13.15	7.94
Er	0.163	2.10	0.88	40.38	20.37
Tm	0.0261	0.40	1.17	4.59	3.24
Yb	0.169	2.30	6.70	1.48	26.96
Lu	0.0253	0.29	0.16	7.30	3.32

Table 4.1: Data for question 4.1 about normalization

 Plot each of the compositions above as a function of the element list in column 1 of Table 4.1. What stands out to you about these plots?

[Answer:



All plots are dominated by a zig-zag abundance pattern (remember the Oddo-Harkins rule) and the light REEs tend to be more abundant that the heavy REEs. What are the important differences between the various plots? Can you see through the zig-zag, pattern and the abundance differences across the REEs to understand what the true differences are?]

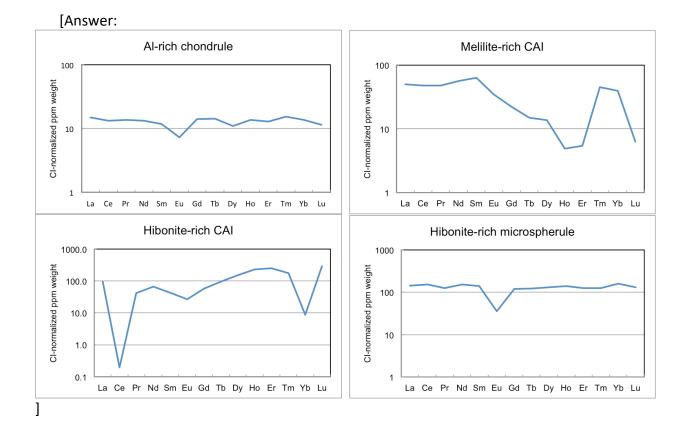
 Let's try plotting the data in a different way. Divide the abundances for columns 3-6 in Table 4.1 above by the corresponding abundance in column 2. You will be "normalizing" the data to the abundances in CI chondrites. [Answer: You should generate a Table that looks like this:

Element	Al-rich	Melilite-rich	Hibonite-rich	Hibonite-rich
	Chondrule	CAI	CAI	Microspherule
La	14.88	50.09	95.63	143.44
Ce	13.34	48.25	0.19	152.64
Pr	13.74	48.08	42.20	124.80
Nd	13.16	56.33	65.80	152.72
Sm	11.84	63.00	43.45	140.33
Eu	7.66	34.49	26.45	35.27
Gd	14.15	22.15	58.02	119.88
Tb	14.32	14.98	95.10	121.76
Dy	10.98	13.66	150.47	129.92
Но	13.64	4.86	229.98	138.81
Er	12.88	5.41	247.71	124.96
Tm	15.33	45.02	175.98	124.15
Yb	13.61	39.66	8.75	159.52
Lu	11.46	6.29	288.43	131.11

Table 4.2: CI normalized data for four objects from Table 4.1.

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3) Plot the CI-normalized abundances versus the elements listed in column 1. This time it will be helpful to make the vertical scale logarithmic.



4) What do you notice about these plots.

[Answer: The normalization has removed the zig-zag pattern and the general decrease in abundance from La to Lu. This leaves other features that can be interpreted.

For example, the Al-rich chondrule and the hibonite-rich microspherule have flat patterns except for a small depletion in europium. The Al-rich chondrule is enriched by a little more than a factor of 10 compared to CI chondrites. The hibonite-rich microspherule is enriched by a little more than a factor of 100. These enrichments are a signature of volatility-based fractionations—the more-volatile elements have been lost from these objects (we will discuss volatility-based fractionations in Chapter 7). The depletion in europium is because europium 2+ is slightly more volatile that its 3+ neighbors.

The melilite-rich CAI has what is known as a Group II REE pattern. This pattern is deficient in the most refractory elements, suggesting that the CAI condensed from a gas after the most refractory elements had already condensed and had been removed from the system.

The hibonite-rich CAI is enriched in REEs by a factor of ~100 compared to CI chondrites, with heavy REEs enriched somewhat more than light REEs. But is this CAI is highly depleted in cerium and ytterbium and somewhat depleted in europium. Cerium is volatile in an oxidizing gas and so could be preferentially lost if the environment was oxidizing. This does not explain the low ytterbium abundance, however, and europium is more volatile in a reducing environment.

None of the details of the REE patterns of the inclusions discussed above would be visible without normalizing the composition to CI chondrites, taken to be representative of the bulk solar system. The implicit assumption in the interpretation of the patterns is that they all formed from the bulk solar system pattern. So normalizing serves two purposes. It eliminates the abundance variations caused by the nuclear structure of the atoms, and it provides a framework for interpreting the observed compositions. For objects that did not form in the solar accretion disk, other compositions can be used for normalization (e.g., the bulk composition of a magma chamber can provide a framework for determining the partitioning of REEs among co-crystallizing minerals. Be aware of any normalizations that are done to sets of data—they can reveal processes not visible otherwise, but can also obscure processes if the wrong normalization is used.]

Question 6.1: Mineral compositions.

Mineral compositions are typically reported as weight percent oxides. This is a convention left over from the time when compositions were determined by wet chemical analysis. The products of the analysis were weighed and reported as weight percent; they were reported as oxides because that is their natural form in the analysis. But reporting data as weight percent oxides is really not very useful because this convention convolves the atomic weight of the element, its oxidation state, and its abundance together in a single number. We are typically interested in each of these three properties separately. So this exercise will start with an analysis in units of weight percent oxides, convert the analysis into weight percent elements, and then into atomic percentages.

Table 6.1 shows the chemical composition of a calcium-rich clinopyroxene. The data are presented in the standard weight percent oxides in column 2. We first convert the weight percent oxides to weight percent elements. To do this, we need the atomic weights of the elements (column 4 of Table 6.1). Use the atomic weights of the elements and oxygen to calculate the how much of the oxide compound is made of the element. For example, SiO₂ consists of two silicon atoms and one oxygen atom. The weight fraction of SiO₂ that is made up of silicon is (2*28.0855)/(2*28.0855+15.9994). Multiply this factor by the weight percent SiO₂ to get the weight percent Si. Follow this recipe to reproduce all of the values in column 5 of Table 6.1. In an analogous way, calculate the weight percent oxygen in each compound.

Next, we convert the weight percent elements into atom percent element and atom percent oxygen. This is done by dividing the element weight percent by the atomic weight of the element. This calculation gives the atom fraction of each cation and oxygen in the pyroxene. Reproduce the numbers in columns 7 and 8 of Table 6.1.

Compound	Wt %	Element	Element	Wt %	Wt. %	Atom	Atom %
	Oxide		Atomic	Element	Oxygen	Fraction	Fraction
			Weight			Element	Oxygen
SiO ₂	52.92	Si	28.0855	24.74	28.18	0.88076	1.76153
AI_2O_3	2.80	Al	26.981538	1.48	1.32	0.05492	0.08238
TiO ₂	0.50	Ti	47.867	0.30	0.20	0.00626	0.01252
Fe ₂ O ₃	0.85	Fe	55.845	0.59	0.26	0.01065	0.01597
Cr_2O_3	0.88	Cr	51.9961	0.60	0.28	0.01158	0.01737
FeO	5.57	Fe	55.845	4.33	1.24	0.07753	0.07753
MnO	0.15	Mn	54.938049	0.12	0.034	0.00211	0.00211
NiO	0.10	Ni	58.6934	0.08	0.021	0.00134	0.00134
MgO	16.40	Mg	24.3050	9.89	6.51	0.40690	0.40690
CaO	19.97	Са	40.078	14.27	5.70	0.35611	0.35611
Na ₂ O	0.35	Na	22.989770	0.26	0.090	0.01129	0.00565
K ₂ O	0.01	К	39.0983	0.0083	0.0017	0.00021	0.00011
		0	15.9994	43.84			2.73952

Table 6.1: Chemical composition of a calcium-rich clinopyroxene in three formats.

Table 6.2 gives the compositions of several different minerals as weight percent oxides. Convert these values into atom percent for each composition. You will have to renormalize the composition to convert from atom fraction to atom percent.

Compound	Subcalcic	Pigeonite	Albite	Anorthite	Fayalite	Forsterite
	Augite					
SiO ₂	49.68	49.72	67.41	44.17	30.56	41.07
TiO ₂	0.56	0.85			0.72	0.05
AI_2O_3	0.78	0.90	20.50	34.95	0.09	0.56
Fe_2O_3	3.29	1.72	0.07	0.56	0.10	0.65
FeO	18.15	27.77		0.08	60.81	3.78
MnO	0.59	0.98			3.43	0.23
MgO	16.19	12.69	0.10		3.47	54.06
CaO	9.90	3.80	0.81	18.63	1.13	
Na ₂ O	0.65	0.23	10.97	0.79		
K ₂ O	0.15	0.12	0.36	0.05		
Total	99.94	98.78	100.22	99.23	100.31	100.40

Table 6.2: Compositions of six minerals given in units of oxide weight percent.

[Answer:

Table 6.3: Compositions of minerals in Table 6.2 in units of atom percent (normalized to 100%).

Compound	Subcalcic	Pigeonite	Albite	Anorthite	Fayalite	Forsterite
	Augite					
Si	18.98	19.73	22.67	15.83	14.28	13.97
Ti	0.16	0.25			0.25	0.01
Al	0.35	0.42	8.12	14.76	0.05	0.22
Fe ³⁺	0.95	0.51	0.02	0.15	0.04	0.17
Fe ²⁺	5.80	9.22		0.02	23.76	1.07
Mn	0.19	0.33			1.36	0.07
Mg	9.22	7.51	0.05		2.42	27.40
Са	4.05	1.62	0.29	7.15	0.57	
Na	0.48	0.18	7.15	0.55		
К	0.07	0.06	0.15	0.02		
0	59.75	60.17	61.54	61.50	57.29	57.09
Total	100.00	100.00	100.00	100.00	100.00	100.00

Question 6.2: Structural formulas.

Atom fractions or atom percentages can be used to calculate structural formulas of minerals. This information can be used to validate the chemical composition of a mineral. An accurate chemical composition for a mineral can be converted into valid structural formula. The structural formula can give information about the oxidation state of elements such as iron. If the composition does not give a valid structural formula, the composition is probably not accurate.

Table 6.4 gives the atom fractions and structural information of the clinopyroxene from Table 6.1. Minerals have fixed proportions of cations to oxygen, but the proportion is different from mineral to mineral. To calculate a structural formula it is necessary to know what that proportion is. The calculation can be done using that proportion or an integral multiple of that proportion (this is useful when calculating structural formulae for a group of minerals). Clinopyroxene has a chemical formula in the form of $X_{1-p}Y_{1+p}Z_2O_6$. The Z site is occupied by silicon and perhaps Al, while X and Y are occupied by divalent and trivalent cations, respectively. The letter "p" describes the partitioning of charge. The structural formula of pyroxene is typically calculated based on 6 oxygen atoms.

In order to calculate the structural formula, the atom fractions must be normalized to 6 oxygen atoms (our clinopyroxene in Table 6.4 has 2.73952 oxygen atoms). We must calculate a factor that normalizes the composition of 6 oxygens (in this case 6/2.73952). Column 4 in Table 6.4 given the normalized atom fractions.

Element	Atom	Atom	Atoms per	Cations	Cations per
	Fraction	Fraction	6 oxygen	Partitioned	cite
	Element	Oxygen			
Si	0.88076	1.76153	1.9290	1.9290	
Al	0.05492	0.08238	0.1203	0.0710	2.00000
Al				0.0493	
Ti	0.00626	0.01252	0.01371	0.01371	
Fe ³⁺	0.01065	0.01597	0.02332	0.02332	
Cr	0.01158	0.01737	0.02536	0.02536	
Fe ²⁺	0.07753	0.07753	0.16980	0.16980	1.98539
Mn	0.00211	0.00211	0.00463	0.00463	
Ni	0.00134	0.00134	0.00293	0.00293	
Mg	0.40690	0.40690	0.89118	0.89118	
Ca	0.35611	0.35611	0.77995	0.77995	
Na	0.01129	0.00565	0.02474	0.02474	
К	0.00021	0.00011	0.00047	0.00047	
0		2.73952			3.98539

Table 6.4: Structural Formula for clinopyroxene from Table 6.1 based on 6 oxygens.

To calculate the structural formula, we assign all of the silicon to the Z site. For every six oxygens, there should be two silicon atoms. We have slightly less than that (1.9290). Aluminum can substitute for silicon, so we assign enough aluminum to the Z site to make it equal to 2.000 (cf., Table 6.4, column 5). The rest of the aluminum and all of the other elements are assigned to the X and Y sites. For this exercise, we will not distinguish between the two sites and simply total all of the remaining cations. Our expectation from the formula for a pyroxene is that these elements should add up to 2.000 (one X and one Y for every two Z and six oxygens). For this analysis, the total is 1.98537. This is about 0.7% lower than the expected value, but this is within the analytical uncertainty of most electron microprobe data.

Calculate the structural formulae for the minerals in Table 6.3. You will need to know the number of oxygens for each of the minerals. Augite and pigeonite are pyroxenes and so will have six oxygens per formula unit. There are always two silicon atoms per six oxygens in pyroxene.

Element	Atom	Atom	Atoms per	Cations	Cations per
	Fraction	Fraction	6 oxygen	Partitioned	cite
	Element	Oxygen			
Si	0.82684	1.65368	1.9054	1.9290	
Al	0.01530	0.02295	0.0353	0.0710	2.0000
Al				0.0493	
Ті	0.00701	0.01402	0.0162	0.0137	
Fe ³⁺	0.04121	0.06181	0.0950	0.0233	
Fe ²⁺	0.25263	0.25263	0.5822	0.1698	1.9854
Mn	0.00832	0.00832	0.0192	0.0046	
Mg	0.40169	0.40169	0.9256	0.8912	
Са	0.17654	0.17654	0.4068	0.7800	
Na	0.02097	0.02097	0.0483	0.0247	
К	0.00318	0.00159	0.0073	0.0005	
0		2.60372			

Table 6.5: Structural Formula for subcalcic augite from Table 6.3 based on 6 oxygens.

[Answer for pigeonite

Table 6.6: Structural formula for pigeonite from Table 6.3 based on 6 oxygens.

Element	Atom	Atom	Atoms per	Cations	Cations
	Fraction	Fraction	6 oxygen	Partitioned	per cite
	Element	Oxygen			
Si	0.82750	1.65501	1.9679	1.9679	
Al	0.01765	0.02648	0.0419	0.0321	2.0000
Al				0.0099	
Ti	0.01064	0.02129	0.0253	0.0253	

Fe ³⁺	0.02154	0.03231	0.0512	0.0512		
Fe ²⁺	0.38653	0.38653	0.9192	0.9192	1.9720	
Mn	0.01381	0.01381	0.0328	0.0328		
Mg	0.31485	0.31485	0.7488	0.7488		
Ca	0.06776	0.06776	0.1611	0.1611		
Na	0.00742	0.00742	0.0176	0.0176		
К	0.00255	0.00255	0.0061	0.0061		
0		2.52303			3.9720	
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Plagioclase is a solid solution between albite, the sodium-rich end member, and anorthite, thee calcium-rich end member. The chemical formula is $Na[AlSi_3O_8] - Ca[Al_2Si_2O_8]$ and the structural formula of plagioclase can be calculated with respect to eight oxygens. Aluminum and silicon occupy one site with four atoms per eight oxygens. Calcium, sodium, and trace elements occupy the other, totaling one atom per eight oxygens. Calculate the structural formulae for albite and anorthite from Table 6.3.

[Answer for albite

Element	Atom	Atom	Atoms per	Cations	Cations	
	Fraction	Fraction	8 oxygen	Partitioned	per cite	
	Element	Oxygen				
Si	1.1219	2.2439	2.9465	2.9465		
Al	0.4021	0.6032	1.0561		4.0026	
Fe ³⁺	0.0009	0.0013	0.0023	0.0023		
Mg	0.0025	0.0025	0.0065	0.0065	0.9965	
Ca	0.0144	0.0144	0.0379	0.0379		
Na	0.3540	0.1770	0.9297	0.9297		
К	0.0076	0.0038	0.0201	0.0201		
0		3.0461			4.9991	

Table 6.7: Structural formula for albite from Table 6.3 based on 8 oxygens.

[Answer for anorthite

Table 6.8: Structural fo	rmula for anorthite fr	om Table 6 3 based	on 8 ovugens
Table 0.0. Structural 10	initia for anorthite fr	UIII Table 0.5 based	UII o Uxygelis.

Element	Atom	Atom	Atoms per	Cations	Cations			
	Fraction	Fraction	8 oxygen	Partitioned	per cite			
	Element	Oxygen						
Si	0.7351	1.4703	2.0594	2.0594				
Al	0.6855	1.0283	1.9205	1.9205	3.9799			
Fe ³⁺	0.0070	0.0105	0.0196	0.0196				
Fe ²⁺	0.0011	0.0011	0.0031	0.0031	1.0278			

Ca	0.3322	0.3322	0.9307	0.9307	
Na	0.0255	0.0128	0.0714	0.0714	
К	0.0011	0.0005	0.0030	0.0030	
0		2.8557			5.0057

Olivine is also a solid solution between iron-rich fayalite and magnesium-rich forsterite $[Fe_2SiO_4 - Mg_2SiO_4]$. The structural formula can be calculated with respect to four oxygens, with one silicon atom and two magnesium or iron atoms (and trace elements) per four oxygens.

[Answer for fayalite

Element	Atom	Atom	Atoms per	Cations	Cations	
	Fraction	Fraction	6 oxygen	Partitioned	per cite	
	Element	Oxygen				
Si	0.5086	1.0172	0.9969	0.9969		
Al	0.0018	0.0027	0.0035	0.0035	1.0004	
Ті	0.0090	0.0180	0.0177	0.0177		
Fe ³⁺	0.0013	0.0019	0.0025	0.0025		
Fe ²⁺	0.8464	0.8464	1.6590	1.6590	1.9821	
Mn	0.0484	0.0484	0.0948	0.0948		
Mg	0.0861	0.0861	0.1687	0.1687		
Са	0.0202	0.0202	0.0394	0.0394		
0		2.0408			2.9825	

Table 6.9: Structural formula for fayalite from Table 6.3 based on 4 oxygens.

[Answer for forsterite

Table 6.9: Structural formula for forsterite from Table 6.3 based on 4 oxygens.

					- 70	
Element	Atom	Atom	Atoms per	Cations	Cations	
	Fraction	Fraction	6 oxygen	Partitioned	per cite	
	Element	Oxygen				
Si	0.6835	1.3671	0.9785	0.9785		
Al	0.0110	0.0165	0.0157	0.0157	0.9942	
Ti	0.0006	0.0013	0.0009	0.0009		
Fe ³⁺	0.0081	0.0122	0.0117	0.0117		
Fe ²⁺	0.0526	0.0526	0.0753	0.0753	2.0126	
Mn	0.0032	0.0032	0.0046	0.0046		
Mg	1.3413	1.3413	1.9201	1.9201		
0		2.7942			3.0068	
1						

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Question 7.1: Volatility Fractionation.

The purpose of this exercise is to show how volatility of elements controls elemental fractionation in the nebula. The Table below lists a number of elements along with their solar system abundances on a scale of atoms/10⁶ silicon atoms (see Table 4.1 in Chapter 4). Also listed are their 50% condensation temperatures from (from Table 7.1).

Put the data into a spreadsheet. To make the calculations easier, renormalize the data to 100% (add up the abundances, then divide each abundance by the sum of the abundances and multiply by 100).

Element	CI	Cond T.
Li	55.59	1225
Ве	0.6116	1490
В	18.816	964
Na	55,300	970
Mg	1,045,000	1340
Al	82,730	1650
Si	1,000,000	1340
К	3,607	1000
Са	61,670	1518
Ti	2,574	1549
V	276.7	1455
Cr	13,340	1301
Mn	9,107	1190
Fe	872,700	1337
Со	2,270	1356
Ni	48,350	1354
Zn	1,212	684
Sb	0.3126	912
La	0.4424	1544
Sm	0.2672	1560
Eu	0.1003	1338
Yb	0.2564	1493
Lu	0.0380	1598
Os	0.7046	1812
lr	0.6404	1603
Au	0.1946	1284
Pb	3.332	520
U	0.00893	1580

Now we want to compare the compositions of solar system material that has been processed to different temperatures. Sort the data according to condensation temperature, from lowest temperature to highest. Starting with the CI abundances in atom percent, generate three new

compositions: 1) all elements with condensation temperatures above 700 K, 2) all elements with condensation temperatures above 1200 K, and 3) all elements with condensation temperatures above 1400 K. Normalize each of these new compositions to 100 % (divide each abundance by the total for that composition and multiply by 100).

Element	CI abundances	Cond	CI abundances	700 K	1200 K	1400 K
	(/10 ⁶ Si)	Temp. (K)	(atom percent)			
In	0.1779	470	0.0000049			
S	426,660	648	11.77			
Pb	3.332	520	0.000092			
Zn	1,212	684	0.0334			
Sb	0.3126	912	0.0000086	0.0000086		
В	18.816	964	0.000519	0.000519		
Na	55,300	970	1.526	1.526		
К	3,607	1000	0.100	0.100		
Mn	9,107	1190	0.251	0.251		
Li	55.59	1225	0.00153	0.00153	0.00153	
Au	0.1946	1284	0.0000054	0.0000054	0.0000054	
Cr	13,340	1301	0.3680	0.3680	0.3680	
Fe	872,700	1337	24.075	24.075	24.075	
Eu	0.1003	1338	0.0000028	0.0000028	0.0000028	
Mg	1,045,000	1340	28.829	28.829	28.829	
Si	1,000,000	1340	27.587	27.587	27.587	
Ni	48,350	1354	1.334	1.334	1.334	
Со	2,270	1356	0.0626	0.0626	0.0626	
V	276.7	1455	0.0076	0.0076	0.0076	0.0076
Ве	0.6116	1490	0.000017	0.000017	0.000017	0.000017
Yb	0.2564	1493	0.0000071	0.0000071	0.0000071	0.0000071
Ca	61,670	1518	1.701	1.701	1.701	1.701
La	0.4424	1544	0.0000122	0.0000122	0.0000122	0.0000122
Ti	2,574	1549	0.0710	0.0710	0.0710	0.0710
Sm	0.2672	1560	0.0000074	0.0000074	0.0000074	0.0000074
U	0.00893	1580	0.0000025	0.0000025	0.0000025	0.0000025
Lu	0.0380	1598	0.0000010	0.0000010	0.0000010	0.0000010
lr	0.6404	1603	0.000018	0.000018	0.000018	0.000018
Al	82,730	1650	2.282	2.282	2.282	2.282
Os	0.7046	1812	0.000019	0.000019	0.000019	0.000019

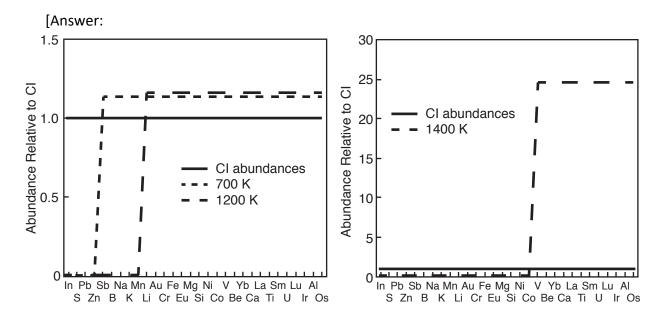
[Answer:

Now normalize the three new compositions to CI abundances in atom percent (divide the compositions by that of CI chondrites, column 4 in the Table above).

[Answer:

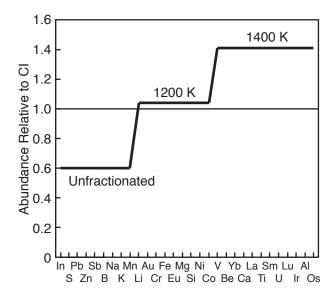
Element	CI abundances	s Cond	CI abundances	700 K / CI	1200 K / CI	1400 K / CI
	(atom	Temp. (K)	(atom percent)			
	percent)					
In	0.0000049	470	0.0000049			
S	11.77	648	11.77			
Pb	0.000092	520	0.000092			
Zn	0.0334	684	0.0334			
Sb	0.0000086	912	0.000086	1.1338		
В	0.000519	964	0.000519	1.1338		
Na	1.526	970	1.526	1.1338		
К	0.100	1000	0.100	1.1338		
Mn	0.251	1190	0.251	1.1338		
Li	0.00153	1225	0.00153	1.1338	1.1585	
Au	0.0000054	1284	0.0000054	1.1338	1.1585	
Cr	0.3680	1301	0.3680	1.1338	1.1585	
Fe	24.075	1337	24.075	1.1338	1.1585	
Eu	0.0000028	1338	0.0000028	1.1338	1.1585	
Mg	28.829	1340	28.829	1.1338	1.1585	
Si	27.587	1340	27.587	1.1338	1.1585	
Ni	1.334	1354	1.334	1.1338	1.1585	
Со	0.0626	1356	0.0626	1.1338	1.1585	
V	0.0076	1455	0.0076	1.1338	1.1585	24.617
Ве	0.000017	1490	0.000017	1.1338	1.1585	24.617
Yb	0.0000071	1493	0.0000071	1.1338	1.1585	24.617
Са	1.701	1518	1.701	1.1338	1.1585	24.617
La	0.0000122	1544	0.0000122	1.1338	1.1585	24.617
Ti	0.0710	1549	0.0710	1.1338	1.1585	24.617
Sm	0.0000074	1560	0.0000074	1.1338	1.1585	24.617
U	0.0000025	1580	0.0000025	1.1338	1.1585	24.617
Lu	0.0000010	1598	0.0000010	1.1338	1.1585	24.617
lr	0.000018	1603	0.000018	1.1338	1.1585	24.617
Al	2.282	1650	2.282	1.1338	1.1585	24.617
Os	0.000019	1812	0.000019	1.1338	1.1585	24.617

Plot the three compositions as a function of element, ordered by condensation temperature.



Note that as the volatile elements are removed, the abundances of the remaining elements increase. This is because the compositions always total ~100%, so when you remove one component, the others become more abundant in what remains. If you were to add elements to the mixture, the relative abundances of the original elements would go down because some of the 100% is taken up by the new elements. "Some of it plus the rest of it equals all of it."

Mixtures of components: Plots of the elements making up an object arranged in the order of their relative volatility can provide a lot of information. Using the CI composition and the three compositions you calculated above, construct the composition of an object composed of 60% unfractionated material, 38.5% of the 1200K component and 1.5% of the 1400K component. Plot the resulting composition on plots like those you made above.



Compare the plot you just made with Figure 7.10 in the Cosmochemistry textbook. It should now be obvious how one can interpret CM chondrites to consist of `60% fine-grained matrix material rich in volatile elements, ~38..5% chondrules and related material that has lost its volatile elements but retains elements more refractory than Mn, and ~1.5% high-temperature materials, mostly CAIs, that retains only the most refractory elements.,

Question 7.2 Trace element partitioning.

Trace-element partitioning among minerals and between minerals and melt provides lets us probe of igneous processes. When minerals crystallize from a melt at equilibrium, partitioning of trace elements between liquid and crystals is given by the Distribution Coefficient:

$$D = C_S/C_L$$

Where C_S is the concentration of an element in the solid, and C_L is the concentration of an element in the accompanying liquid. Table 7.1 shows a set of distribution coefficients for some rare-earth elements in minerals crystallizing from basaltic liquid.

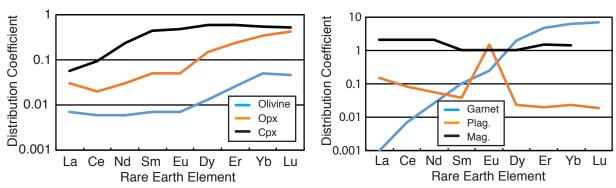
Element	Olivine	OPX	Срх	Garnet	Plagioclase	Amphibole	Magnetite
La	0.0067	0.030	0.056	0.001	0.1477	0.544	2
Ce	0.0060	0.020	0.092	0.007	0.0815	0.843	2
Nd	0.0059	0.030	0.230	0.026	0.0551	1.340	2
Sm	0.0070	0.050	0.445	0.102	0.0394	1.804	1.6
Eu	0.0074	0.050	0.474	0.243	1.1255	1.557	1
Dy	0.0130	0.150	0.582	1.940	0.0228	2.024	1
Er	0.0256	0.230	0.583	4.700	0.0202	1.740	1.5
Yb	0.0491	0.340	0.542	6.167	0.0232	1.642	1.4
Lu	0.0454	0.420	0.506	6.950	0.0187	1.563	

Table 7.1: Distribution Coefficients (C_S/C_L) for some REEs in minerals crystallizing from basalt.

Data table based on Rollinson (1993).

[Answer to #1:

1) Plot the distribution coefficients as a function of element for each mineral in the Table. These plots show the patterns of rare-earth element enrichments or depletions for the minerals relative to the melt. What do these plots tell you about REEs in basaltic melts?



The plot on the right shows that garnet also prefers heavy REEs, and in this case the distribution coefficients for Dy, Er, Yb, and Lu are >1. This means that these elements

will be depleted from the melt by crystallization of garnet. The light REEs are very incompatible in garnet and so would increase significantly through the crystallization of garnet. Magnetite has distribution coefficients for REEs of ≥ 1 . Plagioclase excludes REEs as it crystallizes from basaltic melt, except for Eu, which is much more compatible than the other REEs. Large excesses of Eu are observed in many plagioclase-rich rocks.]

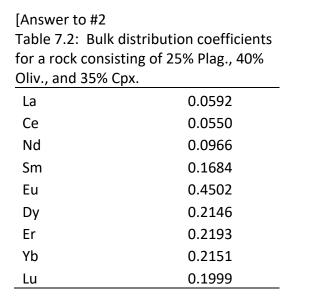
Olivine and pyroxene have distribution coefficients of <1 relative to basaltic melts. This means that the REEs are concentrated in the melt as these minerals crystallize. The left plot shows that olivine and pyroxene preferentially accept the heavy REEs. As these minerals crystallize, the light REEs are enriched more than the heavy REEs in the basaltic melt

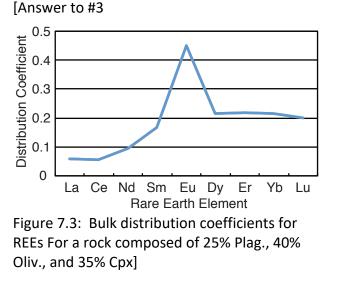
What would you expect the rare-earth element pattern for a rock composed of plagioclase, olivine, and clinopyroxene to look like? The bulk distribution coefficients for a rock can be calculated from the individual distribution coefficients weighted by the proportion of each mineral in the rock.

$$D_{Bi} = x_1 D_1 + x_2 D_2 + x_3 D_3 \dots$$

where D_{Bi} is the bulk distribution coefficient for element *i*, and x_1 and D_1 etc. are the percentage of mineral 1 in the rock and the distribution coefficient of element *i* in mineral 1, respectively.

- Calculate the REE pattern for a bulk rock (Rock #1) consisting of 25% plagioclase, 40% olivine, and 35% clinopyroxene that crystallized from a basaltic melt. Use the distribution coefficients from Table 7.1 above.
- 3) Plot the resulting bulk distribution coefficients versus the REEs. Would you expect a rock composed of these three minerals to be enriched or depleted in REEs. Why?]





[Because all of the individual distribution coefficients are less than unity, the rock will be depleted in REEs compared to the parent melt.]

Question 7.3 Modeling trace-element distributions in melts and crystals.

<u>Equilibrium melting and crystallization</u>: One can model the trace elements distributions in melts and associated crystal using the distribution coefficients. One such model assumes equilibrium crystallization, where the melt and the crystals remain in equilibrium during the crystallization process. The behavior of the melt in this model can be describe by:

$$\frac{C_L}{C_0} = \frac{1}{D + F(1 - D)}$$

where C_L is the concentration in the liquid, C_0 is the initial concentration in the liquid, D is the distribution coefficient, and F is the fraction of liquid remaining (for F = 1, the system is entirely liquid). The behavior of the solid is describe by:

$$\frac{C_S}{C_0} = \frac{D}{D + F(1 - D)}$$

Where C_S is the concentration in the solid and C_0 , D, and F are the same as before.

1) Calculate the value of C_L/C_0 for various degrees of melting (F) and for different values of D ranging from 0.1 to 10. Plot the results on a C_L/C_0 vs F diagram.

What happens to the concentration of the trace element in the liquid as F changes for values of D > 1? What about for D < 1?

2) Calculate the value of C_S/C_0 for various degrees of melting (F) and for different values of D ranging for 0.1 to 10. Plot the results on a C_S/C_0 vs F diagram.

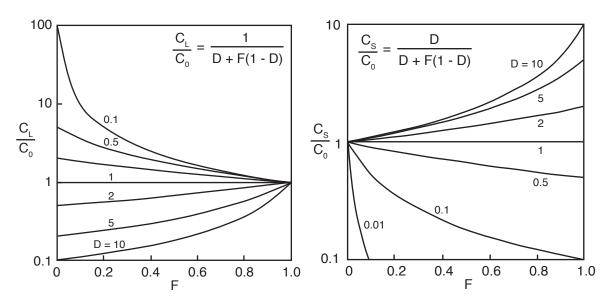
What happens to the concentration of the trace element in the solid as a F changes for a given value of D?

What happens to the concentrations of the trace element in the liquid and solid when D < 1? Which case describes an "incompatible" element?

[Answers: See plots at the top of the next page.

On the C_L/C_0 diagram, when D > 1, the trace elements are preferentially extract into the crystals from the melt. As crystallization proceeds, the amount of trace elements left in the liquid declines. For D < 1, the trace elements preferentially remain in the melt and as crystallization proceeds the trace-element concentrations in the melt increase.

On the CS/CO, we see that when D > 1, the concentration of trace elements in the crystal starts out high, but as crystallization proceeds, the liquid becomes depleted in trace elements and the degree of enrichment in the melt declines. When the system is completely crystallized, the solid has the same C_s as the bulk system.



For D > 1, the concentration of the trace element in the liquid decreases in the fraction of melt remaining decreases. The concentration in the solid increases. D >1 describes a "compatible" element, and the more crystals form, the greater the fraction of the compatible element is sequestered in the solid. For D < 1, and "incompatible" element, the concentration of the trace element in the liquid increases as the crystals grow and exclude the trace element from their structure.]

<u>Fractional crystallization</u>: The equilibrium melting model does not describe natural systems very well. In most systems, either the melt is removed as it is produced, or crystals form from the melt that separate from the bulk of the liquid by crystal settling or by flotation. In its pure form, where the crystals and liquid are separated from each other as they form, this type of fractionation is known as Rayleigh fractionation. The equation that describes the composition of the liquid as it crystallizes and the crystals are immediately removed from the system is:

$$\frac{C_L}{C_0} = F^{(D-1)}$$

where C_L in the concentration of the trace element in the liquid, C_0 in the initial concentration in the liquid, F is the fraction of liquid remaining, and D is the distribution coefficient.

The equation for the trace-element concentration in the solid that is crystallizing from the melt and is removed immediately from contact with the liquid is:

$$\frac{c_S}{c_0} = DF^{(1-D)}$$

where C_s in the concentration of the trace element in the instantaneous solid, C_0 in the initial concentration in the liquid, F is the fraction of liquid remaining, and D is the distribution coefficient.

The equation for the trace-element concentration in the bulk solid that has been separated from the liquid is:

$$\frac{C_S}{C_0} = \frac{1 - (F)^D}{1 - F}$$

where C_s in the concentration of the trace element in the bulk solid, C_0 in the initial concentration in the liquid, F is the fraction of liquid remaining, and D is the distribution coefficient.

3) Calculate the value of C_L/C_0 using the equation for Rayleigh fractionation for various degrees of melting (F) and for different values of D ranging from 0.1 to 10. Plot the results on a C_L/C_0 vs F diagram.

What happens to the concentration of the trace element in the liquid as F changes for values of D > 1 (compatible trace element)? How does this compare to the equilibrium case?

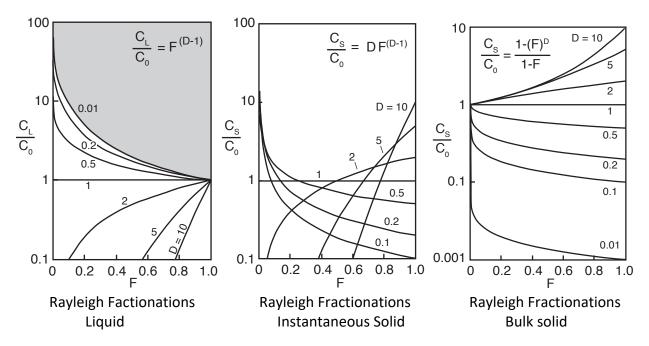
4) Calculate the value of C_S/C_0 for the instantaneous solid using the equation for Rayleigh fractionation for various degrees of melting (F) and for different values of D ranging from 0.1 to 10. Plot the results on a C_S/C_0 vs F diagram.

How does the behavior of the trace elements in the solid differ between the Rayleigh case and the equilibrium case? Why does C_s/C_0 decrease so rapidly in the instantanceous solid when D > 1?

5) Calculate the value of C_s/C_0 for the bulk solid using the appropriate Rayleigh equation for various degrees of melting (F) and for different values of D ranging from 0.1 to 10. Plot the results on a C_s/C_0 vs F diagram.

How does the behavior of the trace elements in the solid differ from the instantaneous case? What is going on that explains this difference. Why does the bulk solid not match the solid in the equilibrium case, especially for D > 1?

[Answers:



On the C_L/C_0 diagram, when D > 1, the trace elements are preferentially extract into the crystals from the melt, as in the equilibrium case. But in this case, because the crystals are removed from the system, the liquid composition evolves much more quickly and to more extreme levels of depletion. The crystals have lower trace-element concentrations that the original melt, but they are always extracting a higher fraction of the trace elements from the melt, as given by the distribution coefficient, thereby depleting the liquid in trace elements. For D < 1, the trace elements preferentially remain in the melt, as in the equilibrium case, so as crystallization proceeds, the melt becomes increasingly enrich in trace elements. But because the crystals are removed from contact with the liquid as they form, the trace-element concentrations in the melt increase. The shaded region at the top of the liquid diagram cannot be reached in the liquid during fractionational crystallization.

The middle diagram above shows the composition of the instantaneous solid as a function of F. When D > 1, the concentration of trace elements in the crystal is always greater than that in the liquid, but as each crystal forms and is removed from the system, it removes a high proportion of the trace elements from the liquid. The next crystal forms from a depleted melt, and thus gets less of the trace elements. As this continues, the liquid is rapidly stripped of its trace elements and that last crystals to form have to pull trace elements out of a very depleted liquid. When D < 1, the crystal takes only a little bit of trace elements and leaves most of them in the liquid. The concentration in the liquid builds up. Each subsequent crystal grows from a more-enriched liquid, so even though it takes only a small amount of trace elements, the amount is higher than it was in the first crystal. As the amount of liquid gets very small, the concentration of trace elements can get quite high in the last crystals to form.

The right-hand diagram shows the behavior of the integrated bulk solid that has been removed from contact with the liquid. When D > 1, the crystals that form are initially enriched in trace elements. Each subsequent crystal that is removed from the liquid and added to the bulk solid brings down the total trace element abundances because each is forming from a depleted liquid. The composition of the total solid approaches that of the bulk system so the curve goes to 1. For D < 1, the trace element abundances in the solid start out very low, but each subsequent crystal obtains slightly higher abundances and the concentrations in the liquid build up. As the amount of liquid remaining becomes small, the concentration of trace elements becomes high. The last crystals are enriched in trace elements (see middle diagram) and the trace element abundances in the total solid approach the concentrations in the bulk system.

Detailed discussion of trace-element partitioning can be found in Rollinson (1995) *Using Geochemical Data: evaluation, presentation, interpretation*. E-book (2014) and in Alberède F. (1995) Introduction to Geochemical Modeling. Cambridge University Press, Cambridge.543 pp.

Question 7.4: Generating a trace-element model of a natural system.

We have discussed REE patterns and shown how they can be used to infer something about the partitioning of trace elements, which in turn can tell you about geologic processes (Question 7.2). We also looked at the behavior of trace elements in systems undergoing melting a crystallization (Question 7.3). Suppose you have table of distribution coefficients for Rare Earth Elements in several igneous mineral such as olivine, pyroxene, plagioclase, apatite, and hornblende. The Table would look something like Table 7.1. Now suppose you have an silicate that is cooling down and crystallizing the minerals listed above. As they form, the crystals settle to the bottom of the magma chamber and become isolated from the melt. You know the temperature range over which each mineral crystallizes, and you know how much of each mineral will form. How would you model the trace element behavior of this system as it cools? What would the REE pattern of each mineral look like.

[Answer: We did not give you enough information to carry out a numerical model (although you could provide your own information and do the calculation). The goal here is to have you lay out the steps necessary to make a model like that described.

The outline of a model: Your data would have several dimensions. Each element would have a distribution coefficient and the evolution of its concentration could be modeled as discussed in question 7.3. You would create a model for each element in each mineral. From that data, you would extract the REE pattern for each mineral at several different levels of crystallization (e.g., every 10% crystallized). Every mineral would extract REEs at a different rate, so you would have to model how the REE concentrations in the liquid change as the minerals crystalize. Alberède (1995) outlines an example of such a calculation in his Chapter 9.]

Questions 8.1: Delta values for hydrogen isotopes

8.1. Delta values are widely used in stable-isotope geochemistry and cosmochemistry. For example, the equation for δD is:

 $\delta D = (((D/H)_{measured}/(D/H)_{VSMOW})-1)*1000$

Where $(D/H)_{VSMOW} = 155.76 \text{ ppm} (= 0.00015576 - 1.5576 \times 10^{-4})$

The Table below gives various D/H ratios ranging from very small to very large. Calculate the δD values for each of these ratios.

D/H Ratio	[Answers: δD]
100 x 0.00015576 = 0.015576	99000 ‰
10 x 0.00015576 = 0.0015576	9000 ‰
2 x 0.00015576 = 0.00031152	1000 ‰
1.5 x 0.00015576 = 0.00023374	500 ‰
0.00015576	0
0.75 x 0.00015576 = 0.00011682	-250 ‰
0.5 x 0.00015576 = 0.00007788	-500 ‰
0.1 x 0.00015576 = 0.000015576	-900 ‰
0.01*0.00015576 = 0.0000015576	-990 ‰

What do you notice about the delta values as the ratio gets larger? What is the largest delta value you can calculate?

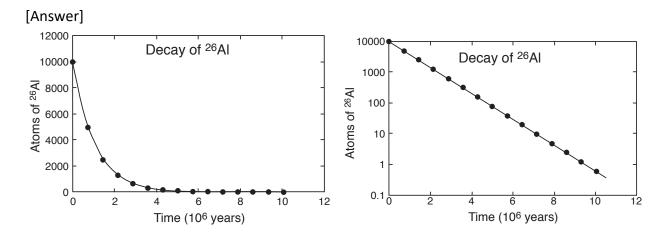
[Answer: The delta value grows proportional to the ratio. Two times the standard ratio gives +1000 ‰, four times the standard ratio gives 3000 ‰, and 8 times the standard ratio gives 7000 ‰. The largest delta value you can calculate is +infinity.]

What do you notice about the delta values as the ratio gets smaller? What is the smallest delta value you can calculate?

[Answer: The delta value shrinks as the ratio shrinks, but the farther the ratio gets from the standard ratio, the more slowly the delta value changes. The smallest delta value you can calculate is -1000 ‰.]

Questions 9.1: Construct plots of the decay of ²⁶Al over time.

a) Plot the curve for the day of ²⁶Al ($t_{1/2}$ = 717,000 years) starting with 10,000 atoms of ²⁶Al for a period of 10 million years. Plot the vertical axis on both linear and log scales.



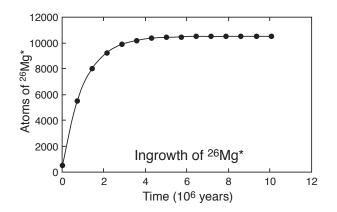
How many ²⁶Al atoms remain after three half-lives.

[Answer: 1250]

How many half-lives does it take for the initial 10,000 atoms to decay to less than 1 atom? Or, to say it another way, how many half-lives does it take for the abundance of ²⁶Al to drop by a factor of 10,000?

Answer: ~13.4 half-lives]

b) Plot the curve for the ingrowth of radiogenic ²⁶Mg* from the decay of ²⁶Al over 10 million years, assuming a starting abundances of 510 atoms.



Question 9. 2. ²⁶Al-²⁶Mg data: Determine the initial ²⁶Al/²⁷Al ratio [(²⁶Al/²⁷Al)₀] by ion probe

Sample: Calcium-aluminum inclusion (CAI) consisting of spinel and hibonite. Both minerals are highly resistant to metamorphism. This problem walks you through the steps to determine the $({}^{26}AI/{}^{27}AI)_0$ for this CAI.

Standards: Relative sensitivity factor (RSF). The ion probe ionizes each element with a different efficiency, so we need mineral standards with known elemental composition (usually determined by electron microprobe) for each mineral in our sample. From these standards, we can calculate a factor to correct for the differential ionization of aluminum and magnesium in the ion probe measurements, the RSF.

Instrumental Mass Fractionation (IMF): The ion probe also fractionates isotopes, and does so differently for each mineral. So we need mineral standards for each mineral in our sample with known magnesium isotopic composition. From these standards, we can calculate a factor to correct for the IMF for magnesium in spinel and hibonite. In this example, we are interested in radiogenic ²⁶Mg* from the decay of ²⁶Al. In most samples, the underlying magnesium falls on the terrestrial mass fractionation line. If this is true, then we can combine the instrumental mass fractionation and any intrinsic mass fractionation in the sample into a single factor to correct for all mass-dependent isotope fractionation.

Data: The Tables below contain data for our spinel standard and our hibonite standard, and for spinel and hibonite in our CAI. The measured isotope ratios are given along with the measurement uncertainties, which are dominated by counting statistics. Columns 4 and 5 give the delta values for these ratios relative to the terrestrial magnesium isotopic composition (official values). The delta values are given with capital delta, by convention for magnesium data. The deviation of a measurement from the terrestrial mass fractionation line is presented in terms of small delta (see below). This convention is confusing because oxygen isotope data are presented with small deltas. For magnesium, the small delta ($\delta^{26}Mg^*$) represents the excess of radiogenic ²⁶Mg* from the decay of ²⁶Al. You will calculate this number below.

Here are the data that we will use in this calculation. The first Table gives data for our spinel standard., the second for our hibonite standard, the third for spinel in the CAI, and the fourth for hibonite in the CAI. Note that the ²⁷Al/²⁴Mg ratio is given with a 2% uncertainty. This is larger than the uncertainty based on counting statistics and takes into account other systematic sources of error.

Material	²⁵ Mg/ ²⁴ Mg	²⁶ Mg/ ²⁴ Mg	Δ^{25} Mg	$\Delta^{ m 26} { m Mg}$	²⁷ Al/ ²⁴ Mg
Spinel	0.127071±0.000144	0.140313±0.000192	3.48±1.14	7.13±1.38	2.081±0.042
Spinel	0.126899±0.000122	0.139918±0.000183	2.12±0.96	4.29±1.31	2.109±0.042
Spinel	0.126626±0.000135	0.139331±0.000198	-0.03±1.07	0.08±1.42	2.098±0.042
Official value	ues: ²⁵ Mg/ ²⁴ Mg = 0.12	.663; ²⁶ Mg/ ²⁴ Mg	g = 0.13932;	²⁷ Al/ ²⁴ N	√lg = 2.53

Material	²⁵ Mg/ ²⁴ Mg	²⁶ Mg/ ²⁴ Mg	$\Delta^{25} Mg$	$\Delta^{ m 26} { m Mg}$	²⁷ Al/ ²⁴ Mg
Hibonite	0.126606±0.000134	0.139221±0.000133	-0.19±1.06	-0.71±0.95	24.08±0.48
Hibonite	0.126684±0.000116	0.139306±0.000127	0.43±0.92	-0.10±0.91	23.53±0.47
Hibonite	0.127088±0.000155	0.140580±0.000198	3.62±1.22	9.04±1.42	24.28±0.49
Official value	es: ²⁵ Mg/ ²⁴ Mg = 0.12	663; ²⁶ Mg/ ²⁴ Mg	; = 0.13932;	²⁷ Al/ ²⁴ N	lg = 30.12
CAI Spinel	²⁵ Mg/ ²⁴ Mg	²⁶ Mg/ ²⁴ Mg	$\Delta^{25} Mg$	$\Delta^{ m 26} { m Mg}$	²⁷ Al/ ²⁴ Mg
Spinel #1	0.126205±0.000111	0.138387±0.000137	-3.36±0.88	-6.70±0.98	2.046±0.041
Spinel #2	0.126187±0.000101	0.138676±0.000103	-3.50±0.80	-4.62±0.74	2.118±0.042
Spinel #3	0.126126±0.000100	0.138304±0.000119	-3.98±0.79	-7.29±0.85	2.056±0.041
CAI Hibonite	e ²⁵ Mg/ ²⁴ Mg	²⁶ Mg/ ²⁴ Mg	$\Delta^{25} {\sf Mg}$	$\Delta^{ m 26} { m Mg}$	²⁷ Al/ ²⁴ Mg
Hibonite #1	0.127051±0.000164	0.143037±0.000192	3.32±1.30	26.68±1.38	39.47±0.79
Hibonite #2	0.127225±0.000133	0.142385±0.000174	4.70±1.05	22.00±1.25	29.52±0.59
Hibonite #3	0.127283±0.000144	0.142609±0.000198	5.16±1.14	23.61±1.42	27.25±0.54
Hibonite #4	0.126860±0.000153	0.142106±0.000165	1.82±1.21	20.00±1.18	33.59±0.67
Hibonite #5	0.126756±0.000146	0.141989±0.000173	1.00±1.15	19.16±1.24	33.83±0.68
Hibonite #6	0.126213±0.000136	0.140389±0.000176	-3.29±1.07	7.67±1.26	30.26±0.61
Hibonite #7	0.129637±0.000161	0.147337±0.000184	23.75±1.27	57.54±1.32	25.32±0.51
Hibonite #8	0.128068±0.000223	0.144418±0.000262	11.36±1.76	36.59±1.88	25.19±0.50

Data reduction calculations:

1) The first step will be to determine the relative sensitivity factor (RSF) for aluminum and magnesium for each mineral. Determine the average ²⁷Al/²⁴Mg ratio for the standard spinel and hibonite measurements. Determine the uncertainty in these average values by calculating the standard deviation of measurement values for each.

[Answer: Average 27 Al/ 24 Mg for spinel standards: 2.096 ± 0.028 Average 27 Al/ 24 Mg for hibonite standards: 23.95 ± 0.77]

2) Compare the average ratio from the standard measurements with the true 27 Al/ 24 Mg ratio for each standard. The true ratio is given below the table for each standard. We use the isotope ratio rather than the elemental ratio because the ion probe measures only one isotope at a time. The RSF can be defined either as the true ratio divided by the measured ratio or the measured ratio divided by the true ratio. For this calculation we will *divide the true ratio by the measured ratio*, which gives an RSF of >1. What are the RSFs for spinel and hibonite in these measurements? What is the uncertainty in the RSF; propagate the uncertainty in the mean of the standard measurements to the RSF.

[Answer: RSF for spinel = 1.207 ± 0.016 RSF for hibonite = 1.257 ± 0.041] 3) Use the RSF values that you determined to calculate the true ²⁷Al/²⁴Mg ratios for the measurements in Tables 3 and 4. Because the RSF is defined as "true ratio/measure ratio", we must multiply the measured ratios for the CAI by the appropriate RSF to get the true ²⁷Al/²⁴Mg ratios. The uncertainties in the true ²⁷Al/²⁴Mg ratios are the quadratic sum of the measurement uncertainty (2%) and the uncertainty in the RSF (1.3% for spinel and 3% for hibonite).

[Answer: See Table 6 below.]

4) To determine the initial ratio $[({}^{26}Al/{}^{27}Al)_0]$ in our CAI, we need to correct the measured magnesium isotopic compositions for both intrinsic mass fractionation in the sample and for the instrumental fractionation produced by the ion probe. We will be using the delta values for this part of the exercise, so the first task is to make sure that we understand delta values and their uncertainties. Calculate the Δ^{25} Mg and Δ^{26} Mg values for each measurement from the measured ratios in the Tables above. The equation for Δ^{25} Mg is:

$$\Delta^{25} Mg = \left(\left(\frac{\binom{2^{5} Mg}{2^{4} Mg}}{\binom{2^{5} Mg}{2^{4} Mg}} - 1 \right) \times 1000 \right)$$

The equation of Δ^{26} Mg is analogous. Check your calculation against the values in the Tables above. How do you calculate the uncertainty on Δ^{25} Mg? The delta value calculates the difference between the measurement and the standard composition in parts per thousand. For the uncertainty, we just need to convert the uncertainty on the ratio into the same units as the delta values:

Uncertainty in
$$\Delta^{25}Mg = \left(\frac{\binom{2^5Mg}{2^4Mg}}{\binom{2^5Mg}{2^4Mg}}_{standard}\right) \times 1000$$

Make sure you can reproduce the delta values and their uncertainties in the Tables above before continuing.

5) If the underlying magnesium that makes up the CAI is isotopically normal (the same as the Earth), we can assume that the magnesium in the samples and standards, before addition of ²⁶Mg* to the magnesium in the CAI, will all plot on a single slope ~0.5 mass fractionation line. (Considerable effort has gone into determining the exact numerical value for the slope of the mass fractionation line, but we will not get into that here. For the purpose of this exercise, we will just assume a slope of 0.5.) If this is true, then the excess ²⁶Mg*, reported as δ^{26} Mg*, can be calculated from Δ^{25} Mg and Δ^{26} Mg using this equation:

$$\delta^{26}Mg^* = \Delta^{26}Mg - (2 \times \Delta^{25}Mg)$$

Calculate δ^{26} Mg* for each spinel and hibonite measurement for the CAI. Calculate the uncertainties for each of these values. The uncertainties for δ^{26} Mg come from the quadratic sum of the weighted uncertainties on Δ^{25} Mg and Δ^{26} Mg:

$$\delta^{26}Mg^*_{uncertainty} = sqrt((\Delta^{26}Mg_{uncertainty})^2 + (2 \times \Delta^{24}Mg_{uncertainty})^2)$$

Finally, we have to convert the δ^{26} Mg* values back into ratios in order to plot the data on a diagram where the slope of the isochron gives the initial ratio.

Analysis	δ^{26} Mg*	²⁶ Mg*/ ²⁴ Mg
Spinel #1	0.016 ± 2.010	0.139322 ± 0.000280
Spinel #2	2.374 ± 1.758	0.139651 ± 0.000245
Spinel #3	0.668 ± 1.796	0.139413 ± 0.000250
Hibonite #1	20.03 ± 2.93	0.142111 ± 0.000409
Hibonite #2	12.60 ± 2.44	0.141076 ± 0.000340
Hibonite #3	13.29 ± 2.68	0.141172 ± 0.000374
Hibonite #4	16.36 ± 2.69	0.141600 ± 0.000375
Hibonite #5	17.17 ± 2.62	0.141712 ± 0.000365
Hibonite #6	14.26 ± 2.49	0.141307 ± 0.000347
Hibonite #7	10.05 ± 2.86	0.140720 ± 0.000399
Hibonite #8	13.88 ± 3.99	0.141254 ± 0.000556

[Answer:

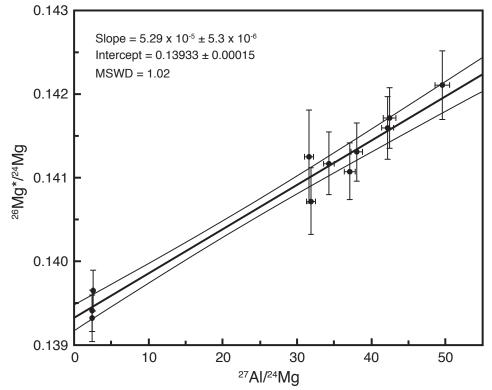
6) The final step in the analysis is to make an isochron diagram, which is a plot of ${}^{26}Mg^*/{}^{24}Mg$ on the Y axis versus ${}^{27}AI/{}^{24}Mg$ on the X-axis. The slope of the regression line on the isochron plot gives (${}^{26}AI/{}^{27}AI$)₀ ratio for the CAI (see Chapter 9 for the derivation of this diagram. The data that we will use are given in Table 6.

The best way to calculate the regression line on the isochron plot is to use a weighted linear regression that takes into account the uncertainties in both X and Y. Unfortunately, Excel does cannot make this plot. Regression methods that take into account the uncertainties in both X and Y and provide as output the slope and intercept of the isochron along with their uncertainties and a measure of the goodness of fit to the data are available in the literature (York, 1966, 1969; Williamson, 1968; Mahon, 1996; Ludwig 2003). For this exercise, one can use the program ISOPLOT, written by Ken Ludwig, which runs as an Add In in older versions of Excel. There is also now a web version, written in R, that can also be used.

Analysis	²⁷ Al/ ²⁴ Mg	²⁶ Mg*/ ²⁴ Mg
Spinel #1	2.470 ± 0.049	0.139322 ± 0.000280
Spinel #2	2.557 ± 0.051	0.139651 ± 0.000245
Spinel #3	2.482 ± 0.050	0.139413 ± 0.000250
Hibonite #1	49.61 ± 0.99	0.142111 ± 0.000409
Hibonite #2	37.10 ± 0.74	0.141076 ± 0.000340
Hibonite #3	34.25 ± 0.68	0.141172 ± 0.000374
Hibonite #4	42.22 ± 0.84	0.141600 ± 0.000375
Hibonite #5	42.52 ± 0.85	0.141712 ± 0.000365
Hibonite #6	38.03 ± 0.76	0.141307 ± 0.000347
Hibonite #7	31.83 ± 0.64	0.140720 ± 0.000399
Hibonite #8	31.66 ± 0.63	0.141254 ± 0.000556

Table 6: Data for the isochron plot for our CAI

Below is the final result. The data form a nice linear array. The regression line and the error envelope for the 95% confidence interval for the slope are shown. The slope of the regression line is statistically identical to the value that we believe represents the oldest objects that formed in the solar system ($({}^{26}AI/{}^{27}AI)_0 = 5.25 \times 10^{-5}$; see Chapter 10). The MSWD of ~1 indicates that the scatter in the data around the regression line is consistent with variations caused by counting statistics.



Isochron plot for the spinel hibonite CAI (data from Table 6). The three points at the left are spinel and the points on the right half of the diagram are hibonite. The initial ratio of 5.29×10^{-5} is consistent with the earliest-formed solar system objects.

References:

- Ludwig K. R. (2003) Isoplot-3.00, a Geochronological Toolkit for Microsoft Excel. *Berkeley Geochronology Center Special Publication No. 4*, 70 pp.
- Mahon K. I. (1996) The new "York" regression: Application of an improved statistical method to geochemistry. *International Geology Review*, **38**, 293-303.
- Williamson J. H. (1968) Least-squares fitting of a straight line. *Canadian Journal of Physics*, **46**, 1845-1847.
- York D. (1966) Least-squares fitting of a straight line. *Canadian Journal of Physics*, **44**, 1079-1086.
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Question 9. 3: Calculating relative time differences between objects.

Below are a series of $({}^{26}AI/{}^{27}AI)_0$ ratios for objects that formed at different times from the same early solar system material reservoir. This reservoir had a $({}^{26}AI/{}^{27}AI)_0$ ratio of 5.25 x 10⁻⁵ when the solar system formed. Using the half-life of ${}^{26}AI$ (Table 9.8) and the radioactive decay equation (equation 9.56), calculate the relative ages for the listed objects based on their $({}^{26}AI/{}^{27}AI)_0$ ratios. Enter the data into the Table below. What is the order of formation for the ten objects listed in the Table? You can put these relative ages on an absolute time scale if you know that the oldest object in your list formed at 4567.3 Ga. Enter the absolute formation times into the Table. Determine the percentage of the original ${}^{26}AI$ abundance that remained when each of the objects formed and enter that into the Table.

	(²⁶ AI/ ²⁷ AI) ₀	DT (years)	Formation time (Ma)	Amount of initial ²⁶ Al remaining.
#1	$5.25 imes 10^{-5}$	0	4,567.3	100 %
#2	2 × 10 ⁻⁶	$3.4 imes10^6$	4,563.9	3.8 %
#3	$3.3 imes 10^{-5}$			
#4	7 × 10 ⁻⁷			
#5	$5.1 imes10^{-8}$			
#6	$2.2 imes 10^{-5}$			
#7	2 × 10 ⁻⁷			
#8	$1.2 imes 10^{-5}$			
#9	$6 imes 10^{-6}$			
#10	$1.2 imes 10^{-8}$			

[Answer: see completed Table below. The order of formation of the ten objects is: #1, #3, #6, #8, #9, #2, #4, #7,#5, #10.]

Calculate the percentage of ²⁶Al that remains after 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 half-lives. Enter these numbers along with (²⁶Al/²⁷Al)₀, Δ T and formation time for each half-life. What is the approximate age of the youngest object that you can date using ²⁶Al.

	(²⁶ Al/ ²⁷ Al) ₀	DT (years)	Formation	Amount of initial ²⁶ Al
			time (Ma)	remaining.
#1	$5.25 imes 10^{-5}$	0	4,567.30	100 %
#3	$3.3 imes 10^{-5}$	$4.80 imes 10^5$	4,566.82	62.9 %
#6	2.2×10^{-5}	$9.00 imes 10^5$	4,558.30	41.9 %
#8	1.2×10^{-5}	$1.53 imes 10^6$	4,565.77	22.9 %
#9	6 × 10 ⁻⁶	$2.24 imes 10^6$	4,565.06	11.4 %
#2	2 × 10 ⁻⁶	$3.38 imes 10^6$	4,563.92	3.81 %
#4	7 × 10 ⁻⁷	$4.47 imes 10^6$	4562.83	1.33 %
#7	2 × 10 ⁻⁷	$5.76 imes 10^6$	4,561.54	0.39 %
#5	6 × 10 ⁻⁸	$7.01 imes 10^6$	4,560.29	0.114 %
#10	$1.2 imes 10^{-8}$	$8.67 imes10^6$	4,558.63	0.023 %
1 half-life	$2.63 imes 10^{-5}$	$7.15 imes 10^5$	4,566.58	50 %
2 half-lives	$1.31 imes 10^{-5}$	$1.43 imes10^6$	4,565.87	25 %
3 half-lives	$6.56 imes 10^{-6}$	$2.15 imes10^6$	4,565.15	12.5 %
4 half-lives	$3.28 imes 10^{-6}$	$2.87 imes 10^6$	4,564.43	6.25 %
5 half-lives	$1.64 imes10^{-6}$	$3.59 imes 10^6$	4,563.72	3.13 %
6 half-lives	$8.20 imes 10^{-7}$	$4.30 imes 10^6$	4,563.00	1.56%
7 half-lives	$4.10 imes 10^{-7}$	$5.02 imes 10^6$	4,562.28	0.78 %
8 half-lives	2.05×10^{-7}	$5.74 imes 10^6$	4,561.56	0.39 %
9 half-lives	$1.03 imes 10^{-7}$	$6.45 imes 10^6$	4,560.85	0.20 %
10 half-lives	$5.13 imes10^{-8}$	$7.17 imes10^{6}$	4,560.13	0.098 %

[Answer: see bottom half of the Table below. Most radiometric dating systems are useful for somewhere between seven and ten half-lives. After seven half-lives, the radionuclide abundance is down to less than 1% of what was present initially, and after ten half-lives, only about 0.1% of the original abundance remains.]

Question 10.1: Cosmic-ray-exposure ages and terrestrial ages of meteorites.

Cosmic rays are very energetic protons and other atomic nuclei that travel through space at relativistic velocities. When a cosmic ray encounters another atom, it can split that atom into smaller pieces, which are stable and radioactive isotopes of other elements. Measuring the amount of cosmic-ray-produced (cosmogenic) nuclides can provide a means of estimating how long a meteorite or planetary surface has been exposed to cosmic rays.

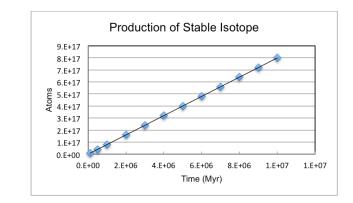
Examples of stable cosmogenic nuclides that can be used to investigate cosmic ray exposure include 3He, ²¹Ne, and ³⁸Ar. Assuming that the flux of cosmic rays is constant, the number of atoms of ²¹Ne of ³⁶Ar produced in a small body traveling through space is given by:

$$N_s = P_s t 10.1.1$$

where N_s is the number of stable atoms produced, P_s is the production rate, and t is time. There are many potential complications to getting quantitative results. For example, the production rate is a function of the cosmic ray flux, the size and shape of the body exposed to the cosmic rays, and the chemistry of the body, among other things. But the basic principles are straight-forward.

 Using data generated from equation 10.1.1 Make a plot of N_s versus time. We will assume a constant cosmic ray flux and no changes to the target body. The production rate can be arbitrary, but a ballpark number might be 8×10¹⁰ atoms/gram/million years. What do you observe?

[Answer:



The number of atoms of a stable nuclide increases linearly with time.]

Measurements of minor isotopes of noble gases generally give good measurements of exposure age. Noble gas atoms are used because the inherent abundance of these nuclides in most solids is very low, so the cosmogenic component is easy to see.

Cosmic rays also produce radioactive isotopes such as ¹⁰Be, ²⁶Al, and ³⁶Cl. But these isotopes start to decay with their characteristic half-lives as soon as they are created. The equation describing the change in the number of radioactive nuclides produced by interaction with a constant flux of cosmic rays as a function of time has two terms: a term for the production rate (the first term on the right side of equation 10.1.2) and a term for the decay of the newly produced nuclides (the second term on the right of equation 10.1.2).

$$\frac{dN_r}{dt} = P_r - \lambda N_r \tag{10.1.2}$$

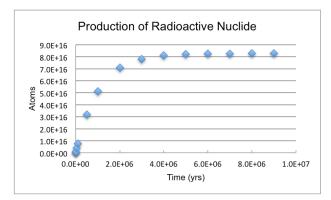
where N_r is the number of radioactive nuclides, P_r is the production rate, and λ is the decay constant. This equation is analogous to equation 9.2 in Chapter 9 of the Cosmochemistry textbook with the addition of a production term. Integrating this equation gives the number of radioactive cosmogenic nuclides at any time t:

$$N_r = \frac{P_r(1 - e^{-\lambda t})}{\lambda}$$
 10.1.3

[We leave as an exercise for the student the derivation of equation 10.1.3.]

2) Using data generated from equation 10.1.3, make a plot of Nr versus time. Let's consider ²⁶Al, which has a decay constant of 9.667×10⁻⁷ (half-life of 7.17×10⁵ yrs). Again, we will assume a constant cosmic ray flux and no changes to the target body. For comparison purposed, use the same production rate that you used for question 1 above (8×10¹⁰ atoms/gram/million years). What do you observe?

[Answer:

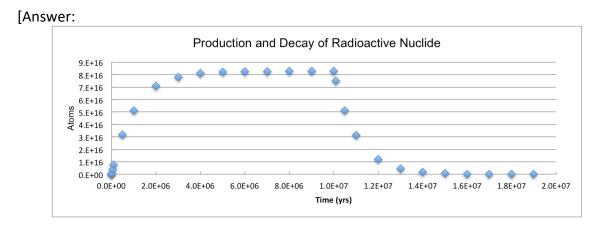


The number of radiogenic nuclides grows rapidly and nearly linearly at first. This is because they have not yet had time to decay. As time goes by, the radioactive decay becomes noticeable and the line describing the data begins to curve. After about 5 million years of exposure to cosmic rays, the number of ²⁶Al atoms in the target reaches a constant value as decay balances production. When the time, t, becomes long with respect to the half-life, the exponential term in equation 10.1.3 goes to zero and equation 10.1.3 approaches Nr =

Pr/ λ . How many half-lives for ²⁶Al are required before that number of ²⁶Al atoms in the target object has reached steady state?

Suppose now that our object that is being irradiated by cosmic rays suddenly is shielded from cosmic rays. This can happens when a meteorite falls to Earth. The Earth's magnetic field and atmosphere stop the vast majority of the cosmic rays before they reach the Earth's surface. Some do penetrate to the altitude where commercial airliners fly, so passengers and crew are irradiated during flight. Airline crews have to worry at some level about their exposure to cosmic rays. When the meteorites falls to Earth, it is shielded from cosmic rays, to the production of cosmogenic nuclides stops.

3) What would the curve for ²⁶Al as a function of time look like if after 10 million years of cosmic ray irradiation, a meteorite fell to Earth? Using the same input data that you used for question 2, generate a plot of the number of ²⁶Al atoms as a function of time for a total of 10 million years. Now, using equation 9.3 from the Cosmochemistry textbook, calculate a curve for the decay of 26Al starting with the number of atoms that was generated during 10 million years of irradiation. Add the new data to the end of the data that you calculated for the irradiation. Make a plot. What do you see?



The radioactive nuclide decays away following the normal decay equation. But notice now that the number of atoms of the radioactive nuclide can be the same for more than one time.

4) If you only have the number of atoms of ²⁶Al (e.g., 3x10¹⁶), how could you tell whether the meteorite was exposed for about half a million years or about 11 million years?

[Answer: Cosmic rays produce many different cosmogenic nuclides at the same time. Some are stable and some are not. If you were to measure both ²¹Ne and ²⁶Al, you can distinguish which possibility give the real exposure age.]

In addition to the cosmic ray exposure age, cosmogenic nuclides can give the "terrestrial age" of a meteorite, i.e. the time since the meteorite fell to Earth and became shield from cosmic

rays. If the meteorite was exposed long enough to reach the steady state abundance for a radioactive nuclide, then when it fell to Earth and was shielded, the number of nuclides decreased following the decay curve you plotted in question 3.

5) How can you be sure that the radioactive nuclide(s) reached the steady-state abundance so you can use it to determine the terrestrial age?

[Answer: You know the half-lives of the radionuclides that are produced from cosmic rays. All of the nuclides in a meteorite were produced in the same irradiation episode. So you can compare the measure abundances for two or more radionuclides with the expected abundances as a function of time. You also have the stable nuclides. Taken together, if the irradiation history is simple, it should be possible to derive a unique irradiation history for your meteorite, giving both the exposure age and the terrestrial age.

Caution: This discussion of cosmogenic nuclides and how they can be used for dating has not probed the details of getting reliable data from real samples. This is a hard business. If you want to learn more about it, we suggest looking at Herzog G.F. and Caffee M. W. (2014) Cosmicray exposure ages of meteorites. In Treatise on Geochemistry, 2nd Edition, Vol. 1: Meteorites and Cosmochemical Processes, Davis, A. M., editor, pp. 419-453, Elsevier, Oxford, and references therein.

Derivation of equation for production and decay of radioactive isotopes produced by cosmic ray interactions.

The differential equation describing the production and decay of a radioactive isotope produced by a constant flux of cosmic rays has two terms: a term for the production rate (the first term on the right side of equation 10.1.4 below) and a term for the decay of the newly produced nuclides (the second term on the right of equation 10.1.4). The production term is just a constant production rate (by definition—the equation could be modified to include a more complicate function). The decay term is equation 9.2 from the Cosmochemistry textbook.

$$\frac{dN_r}{dt} = P_r - \lambda N_r$$
 10.1.4

where N_r is the number of radioactive nuclides, P_r is the production rate, and λ is the decay constant. To integrate this equation, we define:

$$x = P_r - \lambda N_r$$
 10.1.5
$$dx = -\lambda dN_r$$

and

$$lx = -\lambda dN_r$$

When $N_r = 0$, then $x = P_r$.

Re-arrange and integrate:

$$\frac{dx}{dN_r} = -\lambda$$
$$dN_r = \frac{1}{-\lambda}dx$$

From this equation and equations 10.1.1 and 10.1.2:

$$\frac{1}{-\lambda}dx \cdot \frac{1}{dt} = x$$
$$\frac{1}{x}dx = -\lambda dt$$

Integrate

 $\int_0^x \frac{1}{x} dx = -\lambda \int_0^t dt$ $\ln x(t) - \ln x(0) = -\lambda t - -\lambda 0$

We know that at t = 0, N_r = 0, so x = P_r. We also know that $-\lambda(0) = 0$. So:

$$\ln x - \ln P_r = -\lambda t$$
$$\frac{x}{P_r} = e^{-\lambda t}$$

Substitute back in for x:

Take the log of both sides

$$\frac{P_r - \lambda N_r}{P_r} = e^{-\lambda t}$$

$$P_r - \lambda N_r = P_r e^{-\lambda t}$$

$$P_r (1 - e^{-\lambda t}) = \lambda N_r$$

$$N_r = \frac{P_r (1 - e^{-\lambda t})}{\lambda}$$

This is the equation that describes the number of radioactive nuclides present at any one time in an object that has been exposed to a constant flux of cosmic rays.