Quantitative Questions: Supplement to Cosmochemistry by McSween and Huss

Table of Contents

Question 2.1. Calculate atomic weights.

a) Using the numbers from the Chart of the Nuclides (copied below), 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

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?

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

d) What is unusual about the atomic weight of tellurium compared to other elements?

Question 2.2. Atomic Binding Energy calculations.

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

Particle	Mass (grams)	Mass (Daltons)	Mass (MeV)
Proton	1.673×10^{-24}	1.00728	938.256
Neutron	1.675×10^{-24}	1.00866	939.550
Electron	9.110×10^{-28}		0.511

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

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

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

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 chondritic meteorites, an Al-rich chondrule and three different CAIs. Before we manipulate the data, let's just look at it.

Table 4.1: Data for question 4.1 about normalization

Element	Solar System Abundances	Al-rich Chondrule	Melilite-rich CAI	Hibonite-rich CAI	Hibonite-rich 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
Ho	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

1) 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?

2) 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.

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.

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, SiO_2 consists of two silicon atoms and one oxygen atom. The weight fraction of SiO_2 that is made up of silicon is (2*28.0855)/(2*28.0855+15.9994). Multiply this factor by the weight percent SiO_2 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.

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

Compound	Wt % Oxide	Element	Element Atomic Weight	Wt % Element	Wt. % Oxygen	Atom Fraction Element	Atom % Fraction Oxygen
SiO_2	52.92	Si	28.0855	24.74	28.18	0.88076	1.76153
Al_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_2O_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	Ca	40.078	14.27	5.70	0.35611	0.35611
Na_2O	0.35	Na	22.989770	0.26	0.090	0.01129	0.00565
K_2O	0.01	K	39.0983	0.0083	0.0017	0.00021	0.00011
		O	15.9994	43.84			2.73952

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 100% to convert from atom fraction to atom percent.

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

Compound	Subcalcic Augite	Pigeonite	Albite	Anorthite	Fayalite	Forsterite
SiO_2	49.68	49.72	67.41	44.17	30.56	41.07
TiO_2	0.56	0.85			0.72	0.05
Al_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_2O	0.65	0.23	10.97	0.79		
K_2O	0.15	0.12	0.36	0.05		
Total	99.94	98.78	100.22	99.23	100.31	100.40

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 for 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.

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

Element	Atom Fraction Element	Atom Fraction Oxygen	Atoms per 6 oxygen	Cations Partitioned	Cations per cite
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	
K	0.00021	0.00011	0.00047	0.00047	
O		2.73952			3.98539

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.

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.

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.

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/10^6 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
Be	0.6116	1490
B	18.816	964
Na	55,300	970
Mg	1,045,000	1340
Al	82,730	1650
Si	1,000,000	1340
S	426,600	648
K	3,607	1000
Ca	61,670	1518
Ti	2,574	1549
V	276.7	1455
Cr	13,340	1301
Mn	9,107	1190
Fe	872,700	1337
Co	2,270	1356
Ni	48,350	1354
Zn	1,212	684
In	0.1779	470
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
Ir	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).

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).

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

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.

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

Element	Olivine	OPX	Cpx	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	

Data table based on Rollinson (1993).

a) 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?

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.

$$D_{Bi} = x_1D_1 + x_2D_2 + x_3D_3 \ldots$$

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.

b) 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.

c) 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?]

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

Equilibrium melting and crystallization: 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 described 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.

a) 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?

b) 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 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?

Fractional crystallization: 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.

c) 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?

d) 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 instantaneous solid when D > 1?

e) 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?

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.

Questions 8.1: Delta values for hydrogen isotopes

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 ppm (= 0.00015576 – $1.5576 x10^{-4}$)

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
100 x 0.00015576 = 0.015576
10 x 0.00015576 = 0.0015576
2 x 0.00015576 = 0.00031152
1.5 x 0.00015576 = 0.00023374
0.00015576
0.75 x 0.00015576 = 0.00011682
0.5 x 0.00015576 = 0.00007788
0.1 x 0.00015576 = 0.000015576
0.01*0.00015576 = 0.0000015576

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

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

Question 9.1: Construct plots of the decay of ^{26}Al over time.

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

b) How many ^{26}Al atoms remain after three half-lives.

c) 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 ^{26}Al to drop by a factor of 10,000?

d) Plot the curve for the ingrowth of radiogenic $^{26}Mg^*$ from the decay of ^{26}Al over 10 million years, assuming starting abundances of 510 atoms of ^{26}Mg and 10,000 atoms of ^{26}Al.

Question 9. 2. ^{26}Al-^{26}Mg data: Determining the initial $^{26}Al/^{27}Al$ ratio [$(^{26}Al/^{27}Al)_0$] 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 $(^{26}Al/^{27}Al)_0$ 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 ^{26}Mg* from the decay of ^{26}Al. 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 (δ^{26}Mg*) represents the excess of radiogenic ^{26}Mg* from the decay of ^{26}Al. 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 $^{27}Al/^{24}Mg$ 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	Δ^{26}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 values: $^{25}Mg/^{24}Mg$ = 0.12663; $^{26}Mg/^{24}Mg$ = 0.13932; $^{27}Al/^{24}Mg$ = 2.53

Material	$^{25}Mg/^{24}Mg$	$^{26}Mg/^{24}Mg$	$\Delta^{25}Mg$	$\Delta^{26}Mg$	$^{27}Al/^{24}Mg$
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 values: $^{25}Mg/^{24}Mg$ = 0.12663; $^{26}Mg/^{24}Mg$ = 0.13932; $^{27}Al/^{24}Mg$ = 30.12

CAI Spinel	$^{25}Mg/^{24}Mg$	$^{26}Mg/^{24}Mg$	$\Delta^{25}Mg$	$\Delta^{26}Mg$	$^{27}Al/^{24}Mg$
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	$^{25}Mg/^{24}Mg$	$^{26}Mg/^{24}Mg$	$\Delta^{25}Mg$	$\Delta^{26}Mg$	$^{27}Al/^{24}Mg$
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 $^{27}Al/^{24}Mg$ 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.

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.

3) Use the RSF values that you determined to calculate the true $^{27}Al/^{24}Mg$ 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 $^{27}Al/^{24}Mg$ ratios. The uncertainties in the true $^{27}Al/^{24}Mg$ ratios are the quadratic sum of the measurement uncertainty (2%) and the uncertainty in the RSF (1.3% for spinel and 3% for hibonite).

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:

$$\Delta^{25}Mg = \left(\left(\frac{\left({}^{25}Mg / {}^{24}Mg \right)_{sample}}{\left({}^{25}Mg / {}^{24}Mg \right)_{standard}} \right) - 1 \right) \times 1000$$

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:

$$\text{Uncertainty in } \Delta^{25}Mg = \left(\frac{\left({}^{25}Mg / {}^{24}Mg \right)_{uncertainty}}{\left({}^{25}Mg / {}^{24}Mg \right)_{standard}} \right) \times 1000$$

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 ^{26}Mg* 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 ^{26}Mg*, 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:

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

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

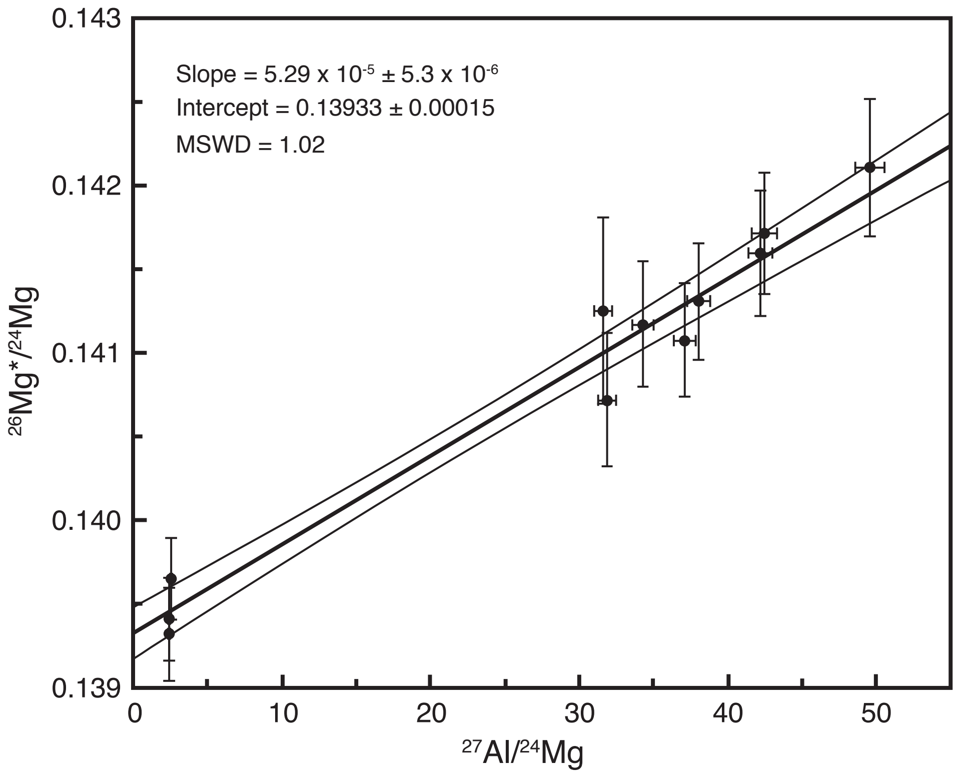
6) The final step in the analysis is to make an isochron diagram, which is a plot of $^{26}Mg^*/^{24}Mg$ on the Y axis versus $^{27}Al/^{24}Mg$ on the X-axis. The slope of the regression line on the isochron plot gives $(^{26}Al/^{27}Al)_0$ ratio for the CAI (see Chapter 9 for the derivation of this 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 be used.

Table 6: Data for the isochron plot for our CAI

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

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 ($(^{26}Al/^{27}Al)_0 = 5.25 \times 10^{-5}$; 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.

York D. (1969) Least squares fitting of a straight line with correlated errors. *Earth & Planetary Science Letters,* **5**, 320-324.

Question 9. 3: Calculating relative time differences between objects.

1) Below are a series of $^{26}Al/^{27}Al$ initial ratios [$(^{26}Al/^{27}Al)_0$] for objects that formed at different times from the same early solar system material reservoir. This reservoir had a $(^{26}Al/^{27}Al)_0$ ratio of 5.25 x 10^{-5} when the solar system formed. Using the half-life of ^{26}Al (Table 9.8) and the radioactive decay equation (equation 9.56), calculate the relative ages for the listed objects based on their $(^{26}Al/^{27}Al)_0$ 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}Al abundance that remained when each of the objects formed and enter that into the Table.

	$(^{26}Al/^{27}Al)_0$	DT (years)	Formation time (Ma)	Amount of initial ^{26}Al remaining.
#1	5.25×10^{-5}	0	4,567.3	100 %
#2	2×10^{-6}	3.4×10^{6}	4,563.9	3.8 %
#3	3.3×10^{-5}			
#4	7×10^{-7}			
#5	5.1×10^{-8}			
#6	2.2×10^{-5}			
#7	2×10^{-7}			
#8	1.2×10^{-5}			
#9	6×10^{-6}			
#10	1.2×10^{-8}			

2) Calculate the percentage of ^{26}Al that remains after 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 half-lives. Enter these numbers in new rows at the bottom of the table along with $(^{26}Al/^{27}Al)_0$, ΔT and formation time for each half-life. What is the approximate age of the youngest object that you can date using ^{26}Al?

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, ^{21}Ne, and ^{38}Ar. Assuming that the flux of cosmic rays is constant, the number of atoms of ^{21}Ne of ^{36}Ar produced in a small body traveling through space is given by:

$$N_s = P_s t \qquad 10.1.1$$

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.

1) 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 8×10^{10} atoms/gram/million years. What do you observe?

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 ^{10}Be, ^{26}Al, and ^{36}Cl. 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).

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

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:

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

[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 N_r versus time. Let's consider ^{26}Al, which has a decay constant of 9.667×10^{-7} (half-life of 7.17×10^{5} 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 (8×10^{10} atoms/gram/million years). What do you observe?

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 ^{26}Al 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 ^{26}Al 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 measure the number of atoms of ^{26}Al to be $3\text{x}10^{16}$, how could you tell whether the meteorite was exposed for about half a million years or about 11 million years?

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?

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) *Cosmic-ray 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.