ESS C109/C209 Final Due: June 14, 2007

Isotope geochemistry

Time limit: 3 hours

Note: This exam consists of two parts – a closed book part and an open book part.

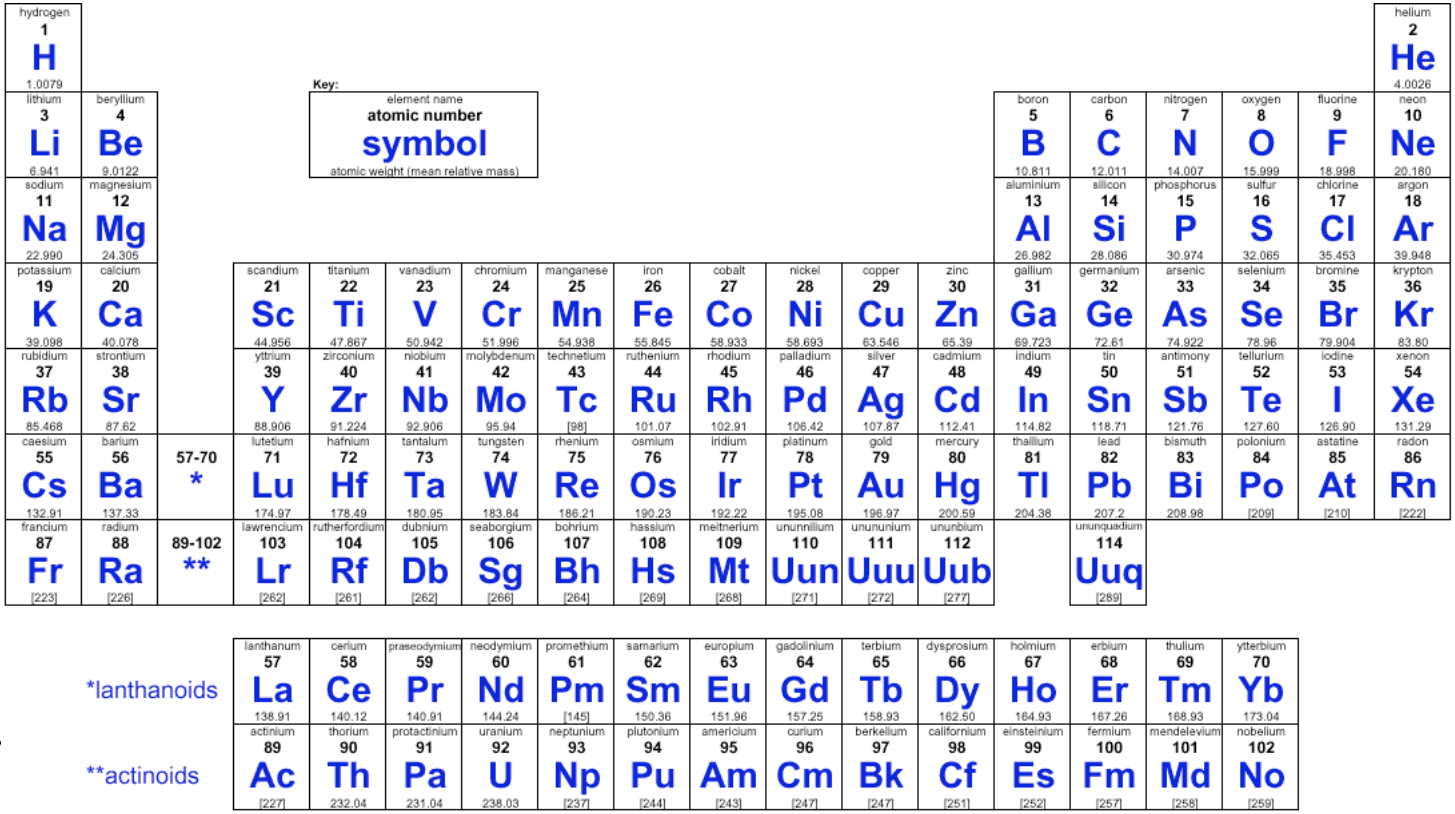
The first part is to be completed without looking at your textbook, isotopes & nuclides booklet, notes, or any other materials. You only need blank paper and a pen or pencil, and you may use the periodic table printed on the next page. No calculator is needed. Complete this part in one sitting.

The second part is open note and open book. You will want to have your nuclides booklet, copy of Faure and Mensing, and other notes handy. You may also want to have a calculator or spreadsheet program running. Time spent gathering these materials does not count against the two-hour time limit, and you may want to take break while you get ready – please don't start the second part of the test until you are ready, and try to complete it in one sitting.

Both parts are to be done on your own, without collaboration.

The closed-book portion begins on the --rd page. Please do not turn the page (or scroll down) until you are ready to begin.

If you find a mistake or typo, please let me know as soon as possible. Indicate the error in your answer to the affected question.


Key:
element name
atomic number
symbol
atomic weight (mean relative mass)
hydrogen 1 H 1.0079
helium 2 He 4.0026
lithium 3 Li 6.941
beryllium 4 Be 9.0122
boron 5 B 10.811
carbon 6 C 12.011
nitrogen 7 N 14.007
oxygen 8 O 15.999
fluorine 9 F 18.998
neon 10 Ne 20.180
sodium 11 Na 22.990
magnesium 12 Mg 24.305
aluminium 13 Al 26.982
silicon 14 Si 28.086
phosphorus 15 P 30.974
sulfur 16 S 32.065
chlorine 17 Cl 35.453
argon 18 Ar 39.948
potassium 19 K 39.098
calcium 20 Ca 40.078
scandium 21 Sc 44.956
titanium 22 Ti 47.867
vanadium 23 V 50.942
chromium 24 Cr 51.996
manganese 25 Mn 54.938
iron 26 Fe 55.845
cobalt 27 Co 58.933
nickel 28 Ni 58.693
copper 29 Cu 63.546
zinc 30 Zn 65.39
gallium 31 Ga 69.723
germanium 32 Ge 72.61
arsenic 33 As 74.922
selenium 34 Se 78.96
bromine 35 Br 79.904
krypton 36 Kr 83.80
rubidium 37 Rb 85.468
strontium 38 Sr 87.62
yttrium 39 Y 88.906
zirconium 40 Zr 91.224
niobium 41 Nb 92.906
molybdenum 42 Mo 95.94
technetium 43 Tc [98]
ruthenium 44 Ru 101.07
rhodium 45 Rh 102.91
palladium 46 Pd 106.42
silver 47 Ag 107.87
cadmium 48 Cd 112.41
indium 49 In 114.82
tin 50 Sn 118.71
antimony 51 Sb 121.76
tellurium 52 Te 127.60
iodine 53 I 126.90
xenon 54 Xe 131.29
caesium 55 Cs 132.91
barium 56 Ba 137.33
57-70 *
lutetium 71 Lu 174.97
hafnium 72 Hf 178.49
tantalum 73 Ta 180.95
tungsten 74 W 183.84
rhenium 75 Re 186.21
osmium 76 Os 190.23
iridium 77 Ir 192.22
platinum 78 Pt 195.08
gold 79 Au 196.97
mercury 80 Hg 200.59
thallium 81 Tl 204.38
lead 82 Pb 207.2
bismuth 83 Bi 208.98
polonium 84 Po [209]
astatine 85 At [210]
radon 86 Rn [222]
francium 87 Fr [223]
radium 88 Ra [226]
89-102 **
lawrencium 103 Lr [262]
rutherfordium 104 Rf [261]
dubnium 105 Db [262]
seaborgium 106 Sg [266]
bohrium 107 Bh [264]
hassium 108 Hs [269]
meitnerium 109 Mt [268]
ununnilium 110 Uun [271]
unununium 111 Uuu [272]
ununbium 112 Uub [277]
ununquadium 114 Uuq [289]
*lanthanoids
lanthanum 57 La 138.91
cerium 58 Ce 140.12
praseodymium 59 Pr 140.91
neodymium 60 Nd 144.24
promethium 61 Pm [145]
samarium 62 Sm 150.36
europium 63 Eu 151.96
gadolinium 64 Gd 157.25
terbium 65 Tb 158.93
dysprosium 66 Dy 162.50
holmium 67 Ho 164.93
erbium 68 Er 167.26
thulium 69 Tm 168.93
ytterbium 70 Yb 173.04
**actinoids
actinium 89 Ac [227]
thorium 90 Th 232.04
protactinium 91 Pa 231.04
uranium 92 U 238.03
neptunium 93 Np [237]
plutonium 94 Pu [244]
americium 95 Am [243]
curium 96 Cm [247]
berkelium 97 Bk [247]
californium 98 Cf [251]
einsteinium 99 Es [252]
fermium 100 Fm [257]
mendelevium 101 Md [258]
nobelium 102 No [259]

Ready?

Part 1: Closed book/closed notes. You may consult the periodic table on the previous page.

1) Electron capture is one type of spontaneous radioactive decay. List two more types of spontaneous decay, and give an example of each (i.e., an isotope that decays by that route, and the decay product).

2) The half-life of tritium (^{3}H, or T) is about 12 years. Let's assume we have a sample of purified lake water that has been sitting in a closed bottle in a radiation-proof lead safe for thirty years. The sample has a $^3H/^1H$ ratio of $1x10^{-18}$ today. Answer the following questions about this sample, and be sure to show your reasoning.
    a. What will the $^3H/^1H$ ratio be 12 years from now?
    b. What was the $^3H/^1H$ ratio 24 years ago?
    c. What will the decay rate (in decay/minute/ml) of ^{3}H in this sample be 12 years from now, relative to today?
    d. Describe a process that is responsible for creating the ^{3}H observed in natural waters (there is more than one correct answer).

3) Arrange these elements in order of increasing ionic radius in their most common (positive) oxidation states: Na, Mg, Al, Si. Explain your reasoning. Which would be most likely to substitute for calcium in a mineral like calcite?

4) In a couple of paragraphs, explain what a concordia diagram is, and what it is used for. Feel free to include sketches and/or equations.

5) Starting from the definitions of $\alpha_{Y\text{-}Z}$ (in this case for $^{18}O/^{16}O$) and $\delta^{18}O$ in terms of isotope ratios, show that

    $$\alpha_{Y\text{-}Z} = (1000 + \delta^{18}O[Y])/(1000 + \delta^{18}O[Z])$$

    where $\delta^{18}O[Y]$ is the $\delta^{18}O$ of Y, and $\delta^{18}O[Z]$ is the $\delta^{18}O$ of Z.

6) What are the isotopic standards for hydrogen, carbon, oxygen and sulfur? If there is more than one isotopic standard for an element, you only have to list one of them.

7) Briefly describe the geographic and climatological distribution of oxygen isotopes in modern precipitation (rain & snow). Feel free to add sketches and figures.

8) One long-term concern with global warming is that the ice caps on Greenland and Antarctica will shrink, leading to sea-level rise. How would melting ice caps affect the δD of the ocean?

9) An actively photosynthesizing C3-type leaf is carefully sealed in an air-filled chamber (harder than it sounds, trust me). Sketch a plot of the $\delta^{13}C$ vs. ppm (abundance) of CO_2 in the air as photosynthesis proceeds in this closed system.

END OF PART 1!

Ready for part two?

Part 2: Open book / open notes. Be sure to show your work & reasoning.

10) What properties distinguish high-precision geochronology isotope systems from typical isochron systems? What are the most important high-precision geochronometers, and what types of natural samples can they be used to study?

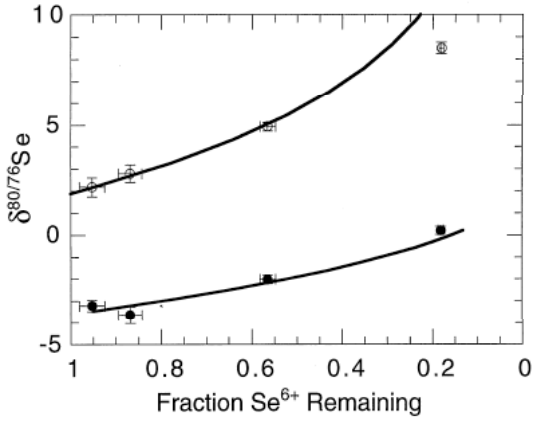
11) Based on the observed $\delta^{18}O$ trends in ice cores and marine carbonates, briefly discuss the relative rates at which ice caps grow and wane.

12) One of the early methods of uranium enrichment for refinement of nuclear fuel involved diffusion of the gaseous molecule UF_6 through tiny pores. Calculate the α for $^{238}U/^{235}U$ fractionation in pinhole diffusion of UF_6. Should the diffused gas or residual gas be collected, if nuclear fuel needs to be enriched in ^{235}U?

13) In a paragraph or two, summarize your favorite student presentation.

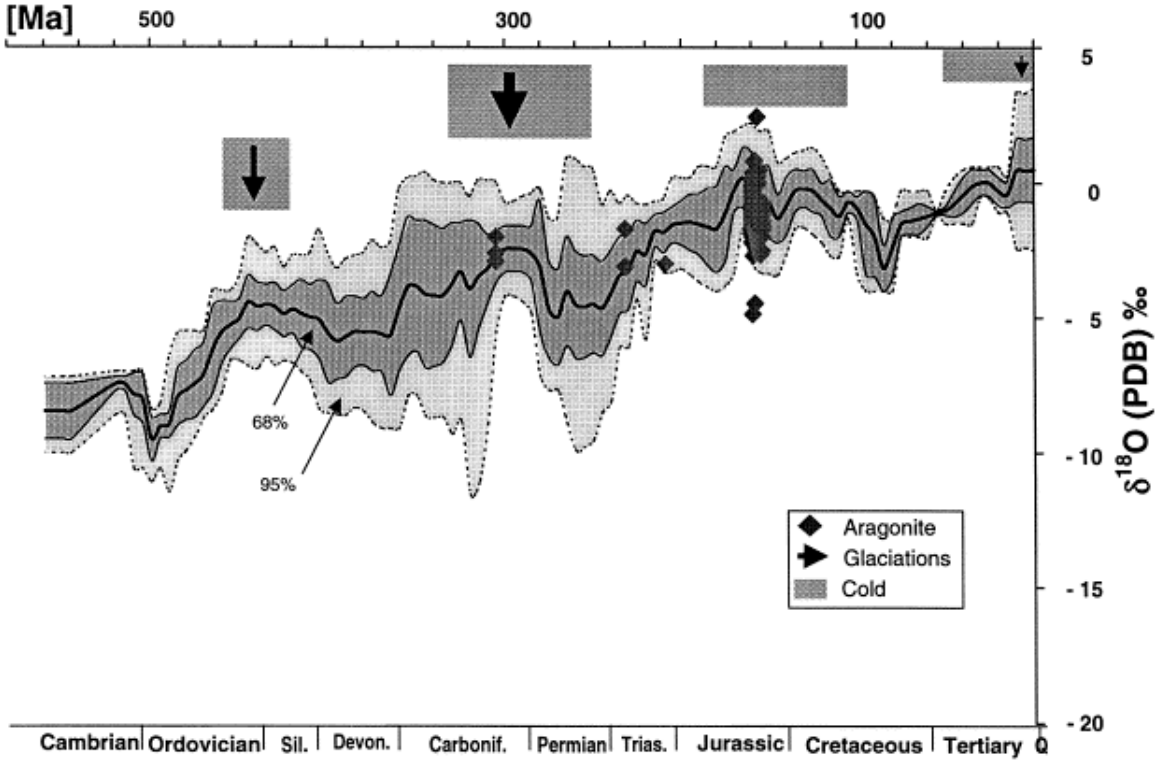
ANSWER 2 out of the 3 questions below

14) Selenium is a trace element in fresh waters in streams and lakes, and can become toxic if it is too concentrated. Much like sulfur, it occurs in a variety of oxidation states in nature, depending on the local chemical conditions. Selenium isotope measurement techniques have been developed (in part by Tom Johnson, now at the University of Illinois) as a method to trace selenium cycling and understand the accumulation and remediation of selenium-polluted habitats.
    a. Arrange the following species in order of increasing $^{80}Se/^{76}Se$ at equilibrium: SeO_3^{2-}, H_2Se, SeO_4^{2-}, Se(s). Explain your reasoning.
    b. The figure below (copied from a paper by Johnson and coworkers) shows the results of a laboratory experiment where SeO_4^{2-} is reduced to SeO_3^{2-}. The unfilled circles show the $\delta^{80}Se$ of SeO_4^{2-}, and the filled circles show the $\delta^{80}Se$ of accumulated SeO_3^{2-}. Is this result consistent with your answer in part (a)? (Note that $\delta^{80/76}Se = \delta^{80}Se$, i.e. deviation of the sample $^{80}Se/^{76}Se$ ratio from a standard material.)



    c. What chemical mechanism other than equilibrium fractionation might cause the observed trends?
    d. Does this look like a batch equilibrium process, or Rayleigh distillation?
    e. Compare the magnitude of the selenium isotope fractionation during selenium reduction to the sulfate-isotope fractionation observed during sulfate reduction. Why is the sulfur isotope fractionation larger?

15) The figure below is a compilation of $\delta^{18}O$ measurements of marine carbonates from Veizer et al. (1999). These are thought to reflect precipitation of calcite in equilibrium with seawater, and have been selected to sample locations near the equator. Assuming equilibrium fractionation and seawater $\delta^{18}O_{VSMOW} = 0$, estimate the maximum equatorial seawater temperatures during the Tertiary, Cretaceous, and Cambrian periods. Make sure to keep PDB and SMOW straight! Other than temperature changes, what might cause this variation in calcite $\delta^{18}O$ over time?



16) The Skaergaard Intrusion is one of world's best studied igneous bodies. It is thought to have formed approximately 56 million years ago when Mg and Fe-rich magma intruded into the crust of what is now the east coast of Greenland. The magma subsequently solidified, and the upper half of the intrusion was transformed into a giant hydrothermal system as water flushed through the hot rock. Assume that the initial $\delta^{18}O_{VSMOW}$ of the intrusion is +6, and the δD is –70, and that the $\delta^{18}O_{VSMOW}$ of the hydrothermal water is –16, with δD = –110. Make a plot of δD vs. $\delta^{18}O$, showing the initial water & rock. If the rock is 0.2‰ H and 45% O by mass, and the water is 11% H and 89% O by mass, plot the trajectory on this figure followed by the rock as it reacts with progressively greater amounts of hydrothermal fluid. Assume a batch reaction, and that there is no equilibrium oxygen or hydrogen isotope fractionation between the rock and fluid. How much water is needed to lower the $\delta^{18}O_{VSMOW}$ of the rock to –5? To lower the δD to –90?

YOU ARE FINISHED! Have a great Summer.