



# **Environmental Isotope Geochemistry:** Radiogenic and Stable Isotopes

Lecturer:

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Arba Minch, Ethiopia, Oct 16, 2014

**ISOTOPE GEOCHEMISTRY** is a specialized field within earth sciences, however this discipline is applicable to almost all studies in natural sciences, including studies of solar system, earth geological evolution, and life sciences (i.e., biology, ecology, etc.)

### **ISOTOPE TRACING of planetary, geological and biological processes** ...

COSMOCHEMISTRY Planetary Sciences

GEOCHEMISTRY Earth Sciences

**BIOCHEMISTRY** Life Sciences









**ISOTOPES** – of certain element have the **same number of protons** (p<sup>+</sup>), but **distinct number of neutrons** (n<sup>0</sup>)





Mass Number – is a total number of protons and neutrons in the nucleus

Atomic Number – reflects a total number of protons in the nucleus





Nucleosynthesis (i.e. origin of elements) in stars is able to generate 'new' heavy isotopes:

- \* Proton-proton (H to He)
- \* Helium burning (He to C)
- \* **s-process** (neutron capture)
- \* **p-process** (proton capture)



These two processes are able to generate elements / isotopes **heavier than iron** (><sup>56</sup>Fe)

### Synthesis of Transuranium Elements by Neutron Bombardment

Plutonium isotopes, 239-Pu, 240-Pu and 241-Pu, are produced in nearly all nuclear reactors by neutron capture on naturally occurring uranium 238-U



SCIENTIFIC REPORTS | 2:304 | DOI: 10.1038/srep00304

OPEN

SUBJECT AREAS:

MASS SPECTROMETRY



## Isotopic evidence of plutonium release into the environment from the Fukushima DNPP accident

0.18 Fukushima Fukushima 0.16 S3 Litter S2 Litter NW 32km NW 26km 0.14 0.12 **Fukushima** Chernobyl J-Village soil 241Pu/239Pu 0.10 S 20km 0.08 A210.9901 0.06 0.04 Half-life of <sup>239</sup>Pu is 24 000 yrs 0.02 Global Atmospheric fallout fallout in Japan 1963-1979 0.00 0.15 0.20 0,25 0.30 0.35 0.40 0,45 Hence, it will disappear only after 120 000 yrs ! 240Pu/239Pu

**Isotope Analysis:** 

### Global transport of the human-made <sup>137</sup>Cs from Fukushima

Data indicate that other harmful radioactive isotopes such as <sup>90</sup>Sr and <sup>239</sup>Pu, were also released to the local environment at Fukushima (Zheng et al. 2012)



Hoeve & Jacobson, 2012 EES







## **Basics of Radiogenic Isotope Geochemistry**



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### Major Milestones in the Field of Isotope Geochemistry

- Discovery of **radioactivity** of uranium salts by Henry Becquerel in 1896
- By 1902, the radioactivity was discovered in several other elements (work of P. Currie, M. Sklodowska-Currie, E. Rutherford, F. Soddy)
- These workers also recognized that the process of radioactivity results in the emission of **alpha** and **beta particles**, and **gamma radiation**.
- In 1903, Curie and Laborde reported that radioactivity is an exothermic process (i.e. heat and energy is released), which had important implications for theories of Lord Kelvin and his estimates on the age of Earth (20 - 100 Ma) based simply on gradual cooling of Earth (with no additional source of heat).

### The rest is history..., and true beginning of the field of isotope geochemistry



**Radioactive decay** of elements occurs by three mechanisms (**beta** decay, **alpha** decay, **nuclear fission**), accompanied by emission of energy, i.e. **gamma rays (**γ**)** 

### <u>Beta (β) decay</u>

We recognize two types of beta-decay, i.e. **negatron** ( $\beta^-$ ) and **positron** ( $\beta^+$ ) decay depending whether a radioactive-nuclide has an excess or deficiency of neutrons

### **NEGATIVE Beta decay**

**Excess of neutrons** => emission of negatively charged beta particle (**negatron**,  $\beta^-$ )

**Neutron**  $\rightarrow$  **Proton** +  $\beta^-$  (negative-beta) +  $\underline{\upsilon}$  (anti-neutrino) +  $\gamma$  (gamma)

**Example:** Rubidium to Strontium Decay

 $^{87}_{37}$  Rb  $\rightarrow ^{87}_{38}$ Sr +  $\beta^-$  (negative-beta)



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### **POSITIVE Beta decay**

**Deficiency of neutrons** => emission of positively charged beta particle (**positron**,  $\beta^+$ )

**Proton**  $\rightarrow$  **Neutron** +  $\beta^+$  (positive-beta) +  $\upsilon$  (neutrino) +  $\gamma$  (gamma)

**Example:** Carbon to Boron Decay

 ${}^{10}_{6} \text{C} \rightarrow {}^{10}_{5} \text{B} + \beta^+ (positive-beta)$ 

## Chart of Nuclides (Selected Segment)





Number of Neutrons



### Alpha ( $\alpha$ ) decay

The emission of alpha particle, which is composed of two protons and two neutrons (and thus is identical to the nucleus of  ${}^{4}_{2}$ He), is described as:

 ${}^{\mathsf{M}}_{\mathsf{A}} \mathsf{X} \rightarrow {}^{\mathsf{M}-4}_{\mathsf{A}-2} \mathsf{Y} + \alpha \text{ (alpha-particle) + Energy}$  where  $\alpha = {}^{\mathsf{4}}_{\mathsf{2}} \mathsf{He}$ 

Example of the Alpha Decay: Uranium to Thorium Decay

 $^{238}_{92}$  U  $\rightarrow ^{234}_{90}$  Th +  $\alpha^{2+}$  (alpha-particle) + Energy

### **Nuclear Fission**

This decay process involves spontaneous fission of the nucleus of heavier isotopes (i.e. heavier than uranium), where the nucleus breaks into two or more unequal fragments, accompanied by the release of a large amount of energy.



### Law of Radioactivity

Rutherford and Soddy (1902) discovered that the rate of decay of a radioactive nuclide (N) at any instant is proportional to the number of atoms of the nuclide remaining at that instant:

 $-\frac{dN}{dt} = \lambda N \quad \text{where } \lambda \quad \text{is proportionality constant (or$ *decay constant* $)} \\ \text{and the$ *negative sign* $(-) indicate that the} \\ \text{amount of radioactive nuclide (N) decreases} \\ \text{with time (t).}$ 

Every radioactive-isotope decay system (such as e.g. Rb – Sr) has is own characteristic numerical value of the **decay constant** ( $\lambda$ ), and this is not affected by changes in the temperature, pressure, and chemical reactions

## **Decay Curves for Radioactive Isotopes**





### **Exponential Decay Curve**

## $N = N_0 e^{-\lambda t}$

where  $N_0$  represents the initial number of radioactive parent atoms and e is the base of natural logarithm (e = 2.71828)

### **Complementary Growth Curve**

 $D^* = N_0 (1 - e^{-\lambda t})$ 

where  $D^*$  represents the generation of stable daughter isotopes created by radioactive decay of  $N_o$  isotopes

## **Definition of Half-life for Radioactive Decay**



## <u>Half-life</u> $(T_{1/2})$

The half-life is defined as the time required for one half of a given number of the radioactive atoms to decay.

Thus, if  $t = T_{1/2}$ , then  $N = N_0 / 2$ 

Substituting this into equation for the exponential decay:  $N = N_0 e^{-\lambda t}$ , we obtain the following relation:



$$\frac{N_0}{2} = N_0 e^{-\lambda T_{1/2}}$$
 Hence,  $T_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda}$ 

## **Equations for Age Determination**

### **Isotope-Based Geochronology**

The relationship between the **radiogenic daughter isotopes** (**D**\*) and the **remaining radioactive parents** (**N**) can be expressed as:

 $D^* = N (e^{\lambda t} - 1)$ 

This equation is practical as both isotope parameters ( $D^*$  and N) are **measurable** quantities, and thus it represents the basis for the isotope geochronology used to determine the age of mineral/rock formation.

However, for realistic age calculations we have to consider the **total number** of radiogenic daughters (D), based on:  $D = D_0 + D^*$ 

where  $(D_0)$  is the initial number of daughters present in the sample at the time of its formation and  $(D^*)$  is the number of daughters produced by decay

Thus,  $D = D_0 + N (e^{\lambda t} - 1)$ 

General Equation for Age Determination



 $D = D_0 + N (e^{\lambda t} - 1)$  General Equation for Age Determination

This can be rearranged to yield the expression for (*t*), or the **age**:



### How do we estimate or determine the value for $D_0 \dots$ ?



### **Constraining the value for D\_0** (i.e. the initial number of radiogenic daughters)

The preferred procedure is based on the analysis of several samples (i.e. minerals) extracted from the same body of rock, so that these minerals will have identical age (t), and thus also identical initial daughter content ( $D_o$ )

For such a suite of "cogenetic" minerals the parameters  $D_0$  and t are constants, and thus the equation for the age determination ( $D = D_0 + N (e^{\lambda t} - 1)$ ) will form a straight line (called an *isochron*) in the coordinates of D and N.

### **Isochron:** represents a line connecting points of identical age

The slope (*m*) of an isochron is a function of the common age (*t*) of a suit of cogenetic samples, based on:

Slope:  $m = e^{\lambda t} - 1$  and thus the Age equals:  $t = \frac{1}{\lambda}$  In (m + 1)

## Isochrons: Rb-Sr Isotope System







### Table of Long-Lived Radioactive Nuclides

Parent	Daughter	<b>T<sub>1/2</sub></b> (yr)	$\lambda$ (yr <sup>1</sup> )	Iso	tope abundar of parent (%)	nce
40 19K	<sup>40</sup> <sub>18</sub> Ar	$1.19  imes 10^{10}$	$0.581 \times 10^{-10}$		0.01167	
40 19 K	<sup>40</sup> <sub>20</sub> Ca	$1.40  imes 10^{10}$	$4.962 \times 10^{-10}$		0.01167	
40K	$^{40}Ar + {}^{40}Ca$	$1.250  imes 10^{9}$	$5.543 \times 10^{-10}$		0.01167	
<sup>87</sup> <sub>37</sub> Rb	<sup>87</sup> <sub>38</sub> Sr	$48.8 imes10^{9}$	$1.42 \times 10^{-11}$	Rb-Sr	27.8346	
<sup>147</sup> <sub>62</sub> Sm	<sup>143</sup> <sub>60</sub> Nd	$1.06 \times 10^{11}$	$0.654  imes 10^{-12}$		15.0	
<sup>138</sup> 57La	<sup>138</sup> 58Ce	$2.70  imes 10^{11}$	$2.57 \times 10^{-12}$		0.09	
<sup>138</sup> 57La	<sup>138</sup> <sub>56</sub> Ba	$1.51 \times 10^{11}$	$4.59 \times 10^{-12}$		0.09	
<sup>138</sup> La	$^{138}_{58}$ Ce + $^{138}_{56}$ Ba	$96.8 \times 10^{9}$	$7.16 \times 10^{-12}$		0.09	
<sup>176</sup> <sub>71</sub> Lu	<sup>176</sup> <sub>72</sub> Hf	$35.7 \times 10^{9}$	$1.94 \times 10^{-11}$		2.600	
<sup>187</sup> <sub>75</sub> Re	<sup>187</sup> <sub>76</sub> Os	$45.6 \times 10^{9}$	$1.52 \times 10^{-11}$		62.602	
<sup>238</sup> <sub>92</sub> U	<sup>206</sup> <sub>82</sub> Pb	$4.468 \times 10^{9}$	$1.55125 \times 10^{-10}$		99.2743	
<sup>235</sup> <sub>92</sub> U	<sup>207</sup> <sub>82</sub> Pb	$0.7038 \times 10^{9}$	$9.8485 \times 10^{-10}$		0.7200	
<sup>232</sup> <sub>90</sub> Th	<sup>208</sup> <sub>82</sub> Pb	$14.010 \times 10^{9}$	$4.9475  imes 10^{-11}$		100.00	



5. Calculate the Rb-Sr isochron age and initial  ${}^{87}$ Sr/ ${}^{86}$ Sr ratio of a suite of whole-rock samples from the Amitsoq gneiss near Godthaab, Greenland, based on the following data ( $\lambda = 1.42 \times 10^{-11} \text{ a}^{-1}$ ).

Sample	<sup>87</sup> Rb/ <sup>86</sup> Sr	<sup>87</sup> Sr/ <sup>86</sup> Sr	
1	2.098	0.8245	
2	0.198	0.7096	
3	1.173	0.7668	
4	2.033	0.8191	
5	1.364	0.7791	
6	0.319	0.7163	

Slope: 
$$m = e^{\lambda t} - 1$$

Age: 
$$t = \frac{1}{\lambda} ln (m + 1)$$

6. Calculate a Rb–Sr date from the following analyses of a whole rock and its constituent minerals  $(\lambda = 1.42 \times 10^{-11} \text{ a}).$ 

<sup>87</sup> Rb/ <sup>86</sup> Sr	<sup>87</sup> Sr/ <sup>86</sup> Sr
1.173	0.7668
116.7	4.543
0.6437	0.7822
0.0633	0.7344
	<sup>87</sup> Rb/ <sup>86</sup> Sr 1.173 116.7 0.6437 0.0633

Note that the whole rock is sample 3 in Problem 5 and the biotite is sample 3 in Problem 4.

## Radiogenic Strontium Isotope (87Sr/86Sr) System



### **Evolution of** <sup>87</sup>**Sr**/<sup>86</sup>**Sr in Earth's geological reservoirs**





Simple mass-balance calculation indicate that **Sr in modern oceans** (0.709) originates about **3/4 from "continental" sources**, and about **1/4 from "mantle/ocean crust"** sources

Earth's Mantle (low Rb/Sr) <sup>87</sup>Sr/<sup>86</sup>Sr = 0.700





Veizer et al., 1999

## Seawater <sup>87</sup>Sr/<sup>86</sup>Sr Record of Earth's Tectonics History





Veizer et al., 1999



## **Radiogenic Isotopes in Environmental Studies**



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## <sup>87</sup>Sr/<sup>86</sup>Sr as Tracer of Ecosystem Processes



### Strontium isotopes as tracers of calcium (Ca<sup>2+</sup>) sources in forest ecosystems



Exchangeable-Ca<sup>2+</sup> (soils) + 2H<sup>+</sup> (acid rain)  $\Leftrightarrow$  Soil-2H<sup>+</sup>(acidification) + Ca<sup>2+</sup> (stream)

## **Study Location: Northeastern USA, Massachusetts**



N Manchester Study area Wachusett Mt. Worcester Providence New Haven New Haven New York New York

 Wachusett

 Machusett

 Output

 Output

Modified after Yanai et al. 2005

### We studied an old-growth forest, developed on a base-poor bedrock (i.e. granite + glacial till).

Located in the Wachusett Mountain State Reservation (MA, USA).

## Minerals identified in a local bedrock (i.e. granite):



Mineral	Chemical formula
Quartz	SiO <sub>2</sub>
K-feldspar	K AI Si <sub>3</sub> O <sub>8</sub>
Biotite	K (Mg, Fe) <sub>3</sub> (Al Si <sub>3</sub> O <sub>10</sub> ) (F, OH)
Plagioclase (with 40% anorthite)	Na Al Si <sub>3</sub> O <sub>8</sub> – <b>Ca</b> Al <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>
Apatite	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> (F,CI,OH)

### Major Ca-bearing minerals in our bedrock are: plagioclase and apatite

## Sampling of snow/rainwater, a soil profile, vegetation



Wachusett Mnt.



### **Vegetation (tree-coring)**



A sample of soil profile (credit to Adrien!)

Rainwater

## Ca/Sr and <sup>87</sup>Sr/<sup>86</sup>Sr variations in tree rings (red oak)





2008

## Sulfur emissions and <sup>87</sup>Sr/<sup>86</sup>Sr variations in tree rings



## Quantifying the fraction (flux) of atmospheric Ca source



Strontium isotope (<sup>87</sup>Sr/<sup>86</sup>Sr) data from tree-rings indicate that since the industrial revolution (after 1900) there has been significant increase (up to 20%) in atmospherically-derived sources of Ca to the ecosystem

Today, up to 80-90% of Ca used by trees originates from the atmosphere !



# ISOTOPE GEOCHEMISTRY

Nucleosynthetic Isotopes

Main processes:

- \* Proton-proton
- \* Helium burning
- \* s-process
- \* p-process

Applications: Cosmochemistry Nuclear safety Radiogenic Isotopes

Main processes:

- \* Radioactive decay
- \* Alpha emission
- \* Beta emission
- \* Gama radiation

Applications: Geochronology Isotope tracing Stable Isotopes

### Main processes:

- \* Isotope exchange
- \* Mass fractionation
- \* Kinetic effects
- \* Equilibrium effects

Applications: Stable-isotope tracing Quantifying processes



## **Basics of Stable Isotope Geochemistry**



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## **Stable Isotope Geochemistry**



**Isotope Fractionation** – is a natural process when stable isotopes of an element are being partitioned (i.e. separated) between two materials (minerals)



### Zero-point energy (E):

is the lowest possible energy that a quantum mechanical physical system may have

## E = hv/2

*v* is the frequency of vibration *h* is the Planck's constant

Thus, differences in the vibrational frequencies of two materials are the primary cause for stable isotope fractionation

Molecule with heavy isotopes has lower vibrational frequency, and thus lower E

### **Oxygen Isotope System**



- Oxygen
   <sup>16</sup>O (99.78%)
   <sup>17</sup>O (0.020%)
   <sup>18</sup>O (0.203%)
- Paleo-Thermometry
- Quantifying Water Cycle
- Rayleigh Distillation
- Ice Volume Effect



### **Oxygen Isotope System**



## **Delta Notation:**

Oxygen
 <sup>16</sup>O (99.78%)
 <sup>17</sup>O (0.020%)
 <sup>18</sup>O (0.203%)



## **Paleo-thermometry:**





### **Oxygen Isotope Paleo-Thermometry Equation**





The culturing temperature vs. the difference  $(\delta^{18}Oc - \delta^{18}Ow)$  (*i.e.*, the carbonate minus the water oxygen isotopic composition). The line is the best fit for the date and yields the following paleotemperature equation:  $\hat{t} = 17.00 - 4.52(\delta^{18}Oc - \delta^{18}Ow) + 0.03(\delta^{18}Oc - \delta^{18}Ow)^2$  with r = 0.95.

Erez et al. (1983) (planktonic *G. sacculifer* laboratory experiment)

Hence, an increase in the δ<sup>18</sup>O values of marine carbonates of 1 per mil, corresponds to the cooling of seawater temperatures of about 4 °C (0.25 ‰ per 1°C)

### **Marine Record of Glacial-Interglacial Oscillations**



### Marine Oxygen Isotope and Climate Record over 65 Ma



#### Global Climate 65 Ma to Present 27 APRIL 2001 VOL 292 SCIENCE www.sciencemag.org James Zachos,<sup>1\*</sup> Mark Pagani,<sup>1</sup> Lisa Sloan,<sup>1</sup> Ellen Thomas,<sup>2,3</sup> Katharina Billups<sup>4</sup> Antarctic Ice Sheet 0

**Global deep ocean** oxygen isotope record from foraminifer shells



Global deep ocean temperature record corrected for ice-volume

### **Ice-Volume Effect and Oxygen Isotopes**





Figure 9.22. Cartoon illustrating how  $\delta^{18}$ O of the ocean changes between glacial and interglacial periods.



### Weighted Annual S<sup>18</sup>O



Source: IAEA Database

## **Rainout Effect and Rayleigh Distillation**











### **Rainout Effect – Rayleigh Distillation**





Figure 27.1. Fractionation of <sup>18</sup>O during cooling of water vapor from an initial temperature of 25 °C to - 20 °C with condensation of rain and subsequently of ice. Initial  $\delta^{18}O_{vapor} = -10\%$ .

## Oxygen Isotopes ( $\delta^{18}$ O) in Global Precipitation



## **Rainout Effect** = Global Distillation Process



Figure 3: Illustration of Oxygen-18 depletion with latitude. Taken from Herring (2006).

## Stable Isotopes ( $\delta^{18}O$ , $\delta^{2}H$ ) in Global Precipitation



### **Global Meteoric Water Line (GMWL)**

Isotopic composition of precipitation from all over the world, plotted in  $\delta^2$ H versus  $\delta^{18}$ O graphs, are strongly correlated according to the equation:

 $\delta^2 \mathbf{H} = \mathbf{8}^* \ \delta^{18} \mathbf{O} + \mathbf{10}$ 

The GMWL has typical slope of 8 and intercept of about 10 per mil

Increased evaporation of waters (e.g. in arid regions) lowers the slope of the MWL





## **Isotope Tracing of Metal Contamination**



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## **Application of Stable Isotopes to Enviro. Problems**



### **Isotope Tracing of Metal Contamination (Cr) in Ground Waters**



Contaminant plume can be monitored by using **Cr(VI) concentration data**, yet this approach **may be misleading**, and thus Cr isotope data are needed!

## **Speciation of Chromium in Aqueous Environments**



Hexavalent Chromium (Cr<sup>VI</sup>): Soluble, Mobile and Highly Toxic

Trivalent Chromium (Cr<sup>III</sup>): Insoluble, Relatively Immobile and Less Toxic



## Monitoring Cr(VI) Reduction with Concentration Data





Cr isotopes can help !

### Reduction of Cr<sup>VI</sup> to Cr<sup>III</sup> and associated "isotope fractionation"



Ellis et al. (2002).



## Quantifying the amount of reduced toxic Cr<sup>VI</sup> in a reservoir with $\delta^{53}$ Cr proxy $\delta^{53}$ Cr = [( $\delta^{53}$ Cr<sub>Initial</sub> + 1000) f ( $\alpha - 1$ )] + 1000

where **f** is the fraction of unreacted  $Cr^{VI}$  remaining, and  $\alpha$  is the fractionation factor

Rayleigh Model			
	THEORY	Fraction f	Calculated
F reactant		prod/	Remaining
remaining	Initial solution	reac	reac
			d53Cr
F	d53Cr (init)	f (Cr reduc)	(remain)
1	0	0,9965	0,0
0,9	0	0,9965	0,4
0,8	0	0,9965	0,8
0,7	0	0,9965	1,2
0,6	0	0,9965	1,8
0,5	0	0,9965	2,4
0,4	0	0,9965	3,2
0,3	0	0,9965	4,2
0,2	0	0,9965	5,6
0,1	0	0,9965	8,1
0,05	0	0,9965	10,5

