

# Identification and Quantitation of $^{232}\text{Th}$ and $^{238}\text{U}$ Decay Series Members

*Analytical Peculiarities  
due to Sampling and  
Sample Origin*



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# Identification and Quantitation of $^{232}\text{Th}$ and $^{238}\text{U}$ Decay Series Members

1. Naturally Occurring Radionuclide's (NOR's) in the *Earth's* Crust
2. Activity Concentration vs. Elemental Concentration
3. Chemistry – Members of  $^{232}\text{Th}$  and  $^{238}\text{U}$  decay series
4. Mineral Mining, Beneficiation/Treatment and Processing
  - a. Mobile Phase - Gas/Oil/Water Production,
  - b. Ore

# 1

## **Naturally Occurring Radionuclide's (NOR's) in the *Earth's* Crust**

# Earth's Crust – Element Concentrations (ppm[w])

Rank	Z	Symbol	ppm(w)	Rank	Z	Symbol	ppm(w)	Rank	Z	Symbol	ppm(w)	Rank	Z	Symbol	ppm(w)
1	8	O	460000,000	21	23	V	160,000	41	62	Sm	6,500	61	69	Tm	0,490
2	14	Si	280000,000	22	28	Ni	120,000	42	64	Gd	5,700	62	53	I	0,470
3	13	Al	82000,000	23	37	Rb	75,000	43	66	Dy	5,700	63	49	In	0,210
4	26	Fe	57000,000	24	30	Zn	75,000	44	92	U	4,200	64	51	Sb	0,200
5	20	Ca	43000,000	25	74	W	69,000	45	68	Er	3,200	65	48	Cd	0,150
6	11	Na	25000,000	26	29	Cu	64,000	46	72	Hf	3,000	66	47	Ag	0,078
7	12	Mg	24000,000	27	58	Ce	63,000	47	70	Yb	2,700	67	80	Hg	0,076
8	19	K	21000,000	28	60	Nd	37,000	48	35	Br	2,500	68	34	Se	0,050
9	22	Ti	6100,000	29	57	La	37,000	49	55	Cs	2,400	69	83	Bi	0,017
10	1	H	1400,000	30	39	Y	31,000	50	4	Be	2,400	70	46	Pd	0,011
11	15	P	1100,000	31	27	Co	28,000	51	50	Sn	2,300	71	78	Pt	0,004
12	25	Mn	980,000	32	21	Sc	24,000	52	33	As	2,000	72	79	Au	0,004
13	6	C	980,000	33	7	N	20,000	53	63	Eu	1,900	73	75	Re	0,002
14	9	F	470,000	34	31	Ga	19,000	54	73	Ta	1,900	74	76	Os	0,002
15	16	S	430,000	35	3	Li	18,000	55	32	Ge	1,500	75	52	Te	0,001
16	56	Ba	420,000	36	41	Nb	18,000	56	67	Ho	1,300	76	44	Ru	0,001
17	38	Sr	370,000	37	90	Th	12,000	57	42	Mo	1,200	77	45	Rh	0,001
18	17	Cl	260,000	38	82	Pb	12,000	58	65	Tb	1,100	78	77	Ir	0,001
19	24	Cr	200,000	39	5	B	9,400	59	81	Tl	0,690				
20	40	Zr	180,000	40	59	Pr	9,000	60	71	Lu	0,500			Total Crust	101%

# Earth's Crust– Element Concentrations (ppm[w])

## incl. Elements with Naturally Occurring Radioisotopes (I)

Rank	Z	Symbol	ppm(w)	Rank	Z	Symbol	ppm(w)	Rank	Z	Symbol	ppm(w)	Rank	Z	Symbol	ppm(w)
1	8	O	460000,000	21	23	V	160,000	41	62	Sm	6,500	61	69	Tm	0,490
2	14	Si	280000,000	22	28	Ni	120,000	42	64	Gd	5,700	62	53	I	0,470
3	13	Al	82000,000	23	37	Rb	75,000	43	66	Dy	5,700	63	49	In	0,210
4	26	Fe	57000,000	24	30	Zn	75,000	44	92	U	4,200	64	51	Sb	0,200
5	20	Ca	43000,000	25	74	W	69,000	45	68	Er	3,200	65	48	Cd	0,150
6	11	Na	25000,000	26	29	Cu	64,000	46	72	Hf	3,000	66	47	Ag	0,078
7	12	Mg	24000,000	27	58	Ce	63,000	47	70	Yb	2,700	67	80	Hg	0,076
8	19	K	21000,000	28	60	Nd	37,000	48	35	Br	2,500	68	34	Se	0,050
9	22	Ti	6100,000	29	57	La	37,000	49	55	Cs	2,400	69	83	Bi	0,017
10	1	H	1400,000	30	39	Y	31,000	50	4	Be	2,400	70	46	Pd	0,011
11	15	P	1100,000	31	27	Co	28,000	51	50	Sn	2,300	71	78	Pt	0,004
12	25	Mn	980,000	32	21	Sc	24,000	52	33	As	2,000	72	79	Au	0,004
13	6	C	980,000	33	7	N	20,000	53	63	Eu	1,900	73	75	Re	0,002
14	9	F	470,000	34	31	Ga	19,000	54	73	Ta	1,900	74	76	Os	0,002
15	16	S	430,000	35	3	Li	18,000	55	32	Ge	1,500	75	52	Te	0,001
16	56	Ba	420,000	36	41	Nb	18,000	56	67	Ho	1,300	76	44	Ru	0,001
17	38	Sr	370,000	37	90	Th	12,000	57	42	Mo	1,200	77	45	Rh	0,001
18	17	Cl	260,000	38	82	Pb	12,000	58	65	Tb	1,100	78	77	Ir	0,001
19	24	Cr	200,000	39	5	B	9,400	59	81	Tl	0,690				
20	40	Zr	180,000	40	59	Pr	9,000	60	71	Lu	0,500			Total Crust	101%

Cosmogenic

Primordial

# Earth's Crust– Element Concentrations (ppm[w])

## incl. Elements with Naturally Occurring Radioisotopes (II)

Rank	Z	Symbol	ppm(w)	Rank	Z	Symbol	ppm(w)	Rank	Z	Symbol	ppm(w)	Rank	Z	Symbol	ppm(w)
1	8	O	460000,000	21	23	V	160,000	41	62	Sm	6,500	61	69	Tm	0,490
2	14	Si	280000,000	22	28	Ni	120,000	42	64	Gd	5,700	62	53	I	0,470
3	13	Al	82000,000	23	37	Rb	75,000	43	66	Dy	5,700	63	49	In	0,210
4	26	Fe	57000,000	24	30	Zn	75,000	44	92	U	4,200	64	51	Sb	0,200
5	20	Ca	43000,000	25	74	W	69,000	45	68	Er	3,200	65	48	Cd	0,150
6	11	Na	25000,000	26	29	Cu	64,000	46	72	Hf	3,000	66	47	Ag	0,078
7	12	Mg	24000,000	27	58	Ce	63,000	47	70	Yb	2,700	67	80	Hg	0,076
8	19	K	21000,000	28	60	Nd	37,000	48	35	Br	2,500	68	34	Se	0,050
9	22	Ti	6100,000	29	57	La	37,000	49	55	Cs	2,400	69	83	Bi	0,017
10	1	H	1400,000	30	39	Y	31,000	50	4	Be	2,400	70	46	Pd	0,011
11	15	P	1100,000	31	27	Co	28,000	51	50	Sn	2,300	71	78	Pt	0,004
12	25	Mn	980,000	32	21	Sc	24,000	52	33	As	2,000	72	79	Au	0,004
13	6	C	980,000	33	7	N	20,000	53	63	Eu	1,900	73	75	Re	0,002
14	9	F	470,000	34	31	Ga	19,000	54	73	Ta	1,900	74	76	Os	0,002
15	16	S	430,000	35	3	Li	18,000	55	32	Ge	1,500	75	52	Te	0,001
16	56	Ba	420,000	36	41	Nb	18,000	56	67	Ho	1,300	76	44	Ru	0,001
17	38	Sr	370,000	37	90	Th	12,000	57	42	Mo	1,200	77	45	Rh	0,001
18	17	Cl	260,000	38	82	Pb	12,000	58	65	Tb	1,100	78	77	Ir	0,001
19	24	Cr	200,000	39	5	B	9,400	59	81	Tl	0,690				
20	40	Zr	180,000	40	59	Pr	9,000	60	71	Lu	0,500			Total Crust	101%

Cosmogenic

Primordial >>>> Secondary (ex decay series)

# $^{232}\text{Th}$ & $^{238}\text{U}$ Decay Characteristics

$^{232}\text{Th}$	$10^{10}$ y	
$^{228}\text{Ra}$	6 y	
$^{228}\text{Ac}$		$\gamma$
$^{228}\text{Th}$	2 y	( $\gamma$ )
$^{224}\text{Ra}$	4 d	( $\gamma$ )
$^{220}\text{Rn}$		
$^{216}\text{Po}$		
$^{212}\text{Pb}$		$\gamma$
$^{212}\text{Bi}$		$\gamma$
$^{212}\text{Po}$ & $^{208}\text{Tl}$		$\gamma$
$^{208}\text{Pb}$	stable	

Primordial **N**aturally **O**ccurring **R**adionuclide's (**NOR's**)  $^{232}\text{Th}$  and  $^{238}\text{U}$  are special as they are heading a series of successive nuclear decays, thereby transmuting nuclei and changing chemical behaviour

Listed in *Earth's Crust Element Concentrations: Th, Pb, U, Tl, Bi*  
**not** listed: Ra, Ac, Rn, Po, Pa  
 if undisturbed > secular equilibrium  
 (on a geological time scale)

$^{238}\text{U}$	$10^9$ y	
$^{234}\text{Th}$		( $\gamma$ )
$^{234\text{m}}\text{Pa}$		
$^{234}\text{U}$		( $\gamma$ )
$^{230}\text{Th}$		( $\gamma$ )
$^{226}\text{Ra}$	1600 y	( $\gamma$ )
$^{222}\text{Rn}$	4 d	
$^{218}\text{Po}$		
$^{214}\text{Pb}$		$\gamma$
$^{214}\text{Bi}$		$\gamma$
$^{214}\text{Po}$		
$^{210}\text{Pb}$	22 y	( $\gamma$ )
$^{210}\text{Bi}$		
$^{210}\text{Po}$	138 d	
$^{206}\text{Pb}$	stable	

(radio)isotopes: (radio)isotopes within a specified element, e.g.  $^{38}\text{K}$ ,  $^{39}\text{K}$ ,  $^{40}\text{K}$ ,  $^{41}\text{K}$ ,  $^{42}\text{K}$ ,  $^{43}\text{K}$

(radio)nuclides: (radio)nuclides of various elements, e.g.  $^1\text{H}$ ,  $^{12}\text{C}$ ,  $^{35}\text{Cl}$ ,  $^{40}\text{K}$ ,  $^{57}\text{Fe}$

# Specific Activity vs. Activity Concentration

In agreement with the general use of the term *specific* and the definition of *activity* the **specific activity** (SA) should be the activity of 1 g of the radionuclide itself. Consequently **specific activity** is a constant physical quantity or physical property of a naturally occurring radionuclide *e.g.*

$$^{40}\text{K} \quad \text{SA} = \lambda \times N_{\text{AV}} / M_{\text{A}}[^{40}\text{K}] = \ln(2) \times N_{\text{AV}} / (M_{\text{A}}[^{40}\text{K}] \times T_{1/2}) = 2.59 \times 10^5 \text{ Bq}[^{40}\text{K}]/\text{g}[^{40}\text{K}]$$

**Activity concentration** (AC) is a measurable quantity of an identified naturally occurring radionuclide in a product / residue / waste matrix. The naturally occurring radionuclide is present at an impurity level, whereas the product / residue / waste matrix is determining the chemical and physical properties of the “material”. AC may be expressed as the (radio)activity in an identified naturally occurring radionuclide (subseries) per unit of mass or volume *e.g.* 300 Bq[<sup>222</sup>Rn]/Nm<sup>3</sup>[natural gas], 5 Bq[<sup>228</sup>Ra]/L[effluent] or 3 Bq[<sup>226</sup>Ra<sub>eq</sub>]/g[scale].



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**Activity Concentration  
vs.  
Element Concentration**

# Basic Units & Terminology

## Activity Concentration vs. Element Concentration in a Matrix

### RADIOACTIVITY

**Becquerel** SI unit for radioactivity (Bq); concentration (Bq per unit of mass/volume):

**1 Bq equals 1 nuclear disintegration per second**

**Half-Life** time period, in which the total activity, is reduced to half its value

(e.g.  $^{238}\text{U}$   $5 \times 10^9$  years,  $^{226}\text{Ra}$  1600 years,  $^{222}\text{Rn}$  4 days,  $^{218}\text{Po}$  3 minutes,  $^{210}\text{Pb}$  22 years)

**Equilibrium** (secular -) can be reached in a 'closed' system between long-lived radioactive parent and substantially shorter-lived progeny.

### PHYSICS/CHEMISTRY

**mass/volume** Avogadro's number:  $6 \times 10^{23}$  atoms/mole

**$0,0224 \text{ Nm}^3/\text{mole} = M_A \text{ (g/mole)}$**

#### RADIOACTIVITY

**$300 \text{ Bq}[^{222}\text{Rn}]/\text{Nm}^3[\text{NG}]$**

**$10 \text{ Bq}[^{226}\text{Ra}]/\text{g}[\text{sample}]$**

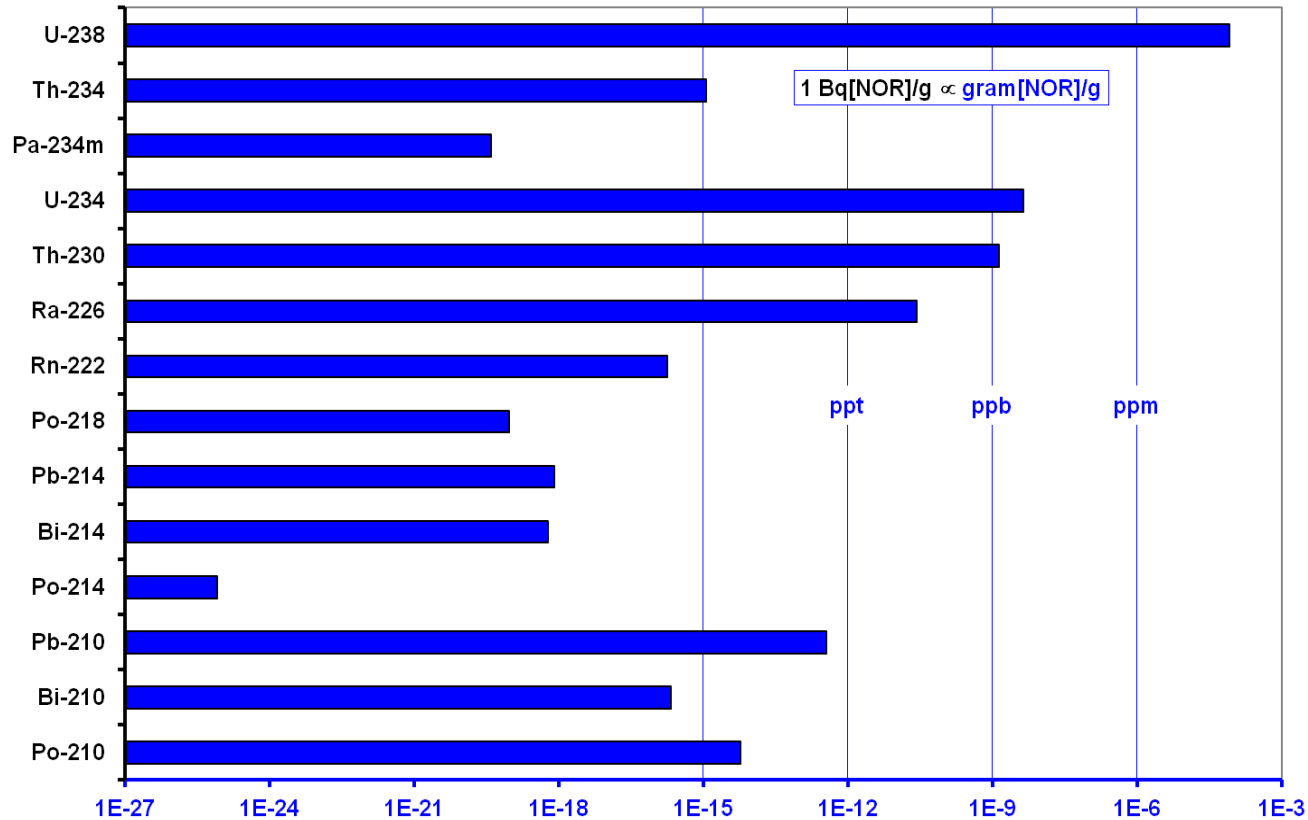
corresponds to

#### PHYSICS/CHEMISTRY

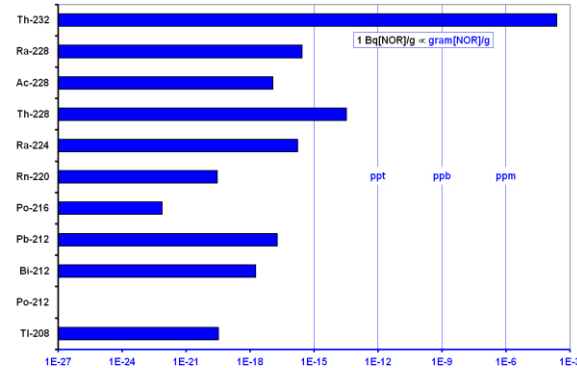
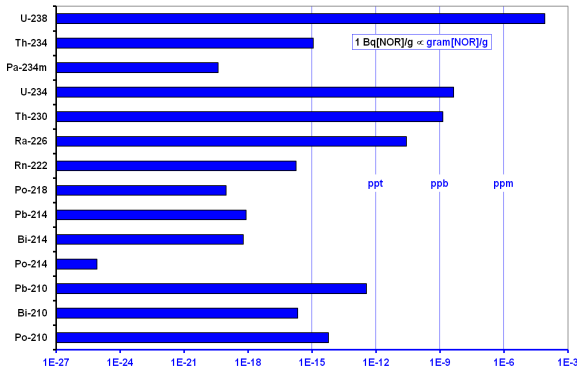
**$5 \times 10^{-18} \text{ Nm}^3[^{222}\text{Rn}]/\text{Nm}^3[\text{NG}]$**

**$3 \times 10^{-10} \text{ g}[^{226}\text{Ra}]/\text{g}[\text{sample}]$**

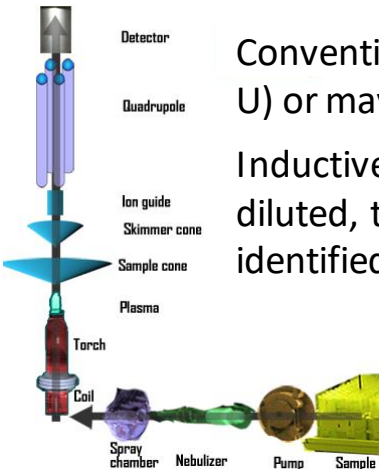
# Activity Concentration vs. "Chemical" Concentration



# Element Analysis



## ICP/MS

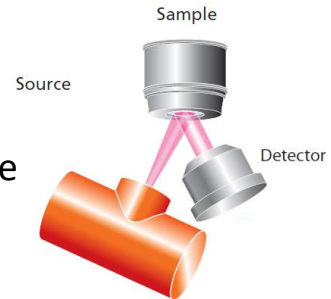


Conventional Element Analysis techniques are a good indicator, if NOR's are (Th and U) or may be (Pb, S in combination with group II ions) present in a sample

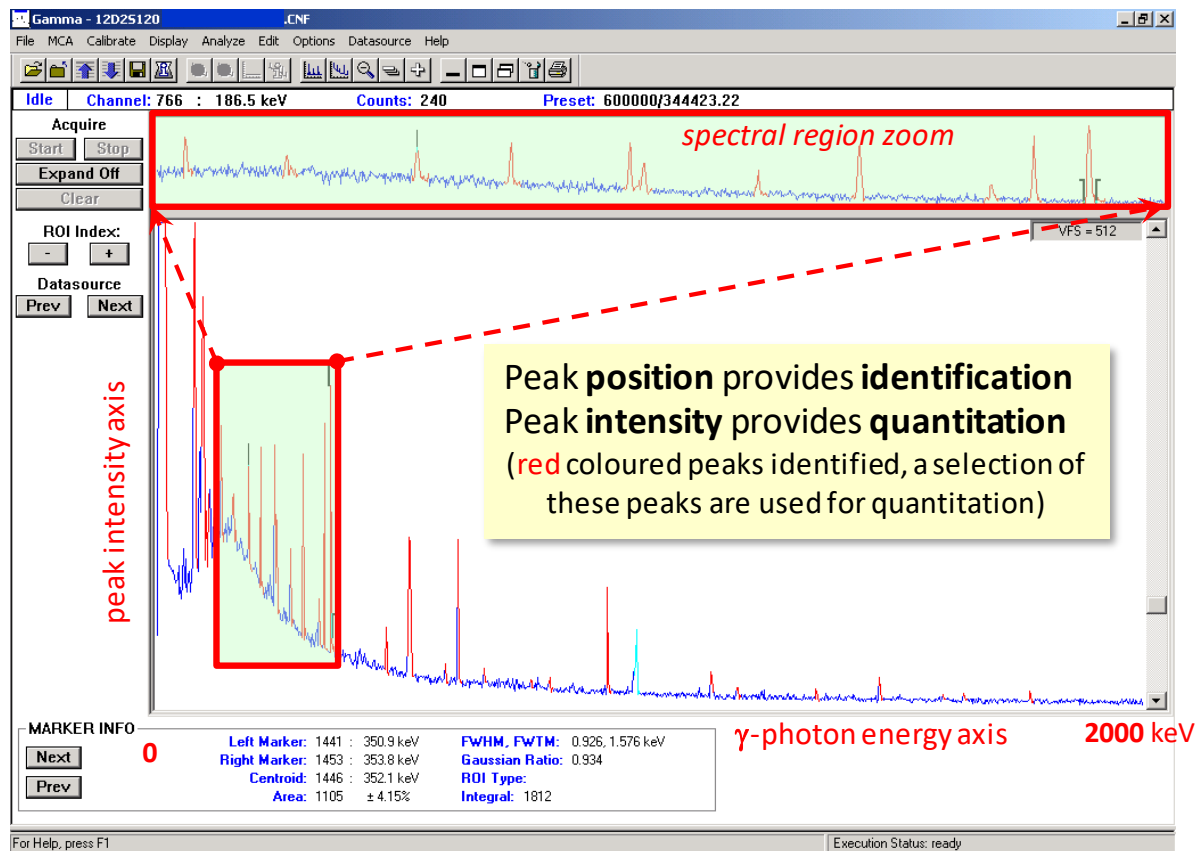
Inductively Coupled Plasma/Mass Spectroscopy (**ICP/MS**): sample digested and diluted, treated sample introduced into plasma, ionised element (isotopes) identified (mass) and quantified (peak area)

X-ray Fluorescence (**XRF**): sample milled (solids), transferred to sample cup (ultra thin mylar foil bottom), 40 keV X-ray irradiation, elements identified (energy fluorescent lines) and quantified (peak area)

## XRF



# Identification and Quantitation by $\gamma$ -Spectrometry



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# Chemistry – Members of $^{232}\text{Th}$ and $^{238}\text{U}$ decay series

# Periodic System

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18				
1	<b>H</b> Hydrogen 1.008	Atomic # Symbol Name Weight																2	<b>He</b> Helium 4.002602			
2	3 <b>Li</b> Lithium 6.94	4 <b>Be</b> Beryllium 9.012182	Metalloids										Other nonmetals		Halogens		Noble gases					
3	11 <b>Na</b> Sodium 22.989...	12 <b>Mg</b> Magnesium 24.305	Metals										Alkali metals		Alkaline earth metals		Lanthanoids		Transition metals		Post-transition metals	
4	19 <b>K</b> Potassium 39.0983	20 <b>Ca</b> Calcium 40.078	21 <b>Sc</b> Scandium 44.955...	22 <b>Ti</b> Titanium 47.867	23 <b>V</b> Vanadium 50.9415	24 <b>Cr</b> Chromium 51.9961	25 <b>Mn</b> Manganese 54.938...	26 <b>Fe</b> Iron 55.845	27 <b>Co</b> Cobalt 58.933...	28 <b>Ni</b> Nickel 58.6934	29 <b>Cu</b> Copper 63.546	30 <b>Zn</b> Zinc 65.38	31 <b>Ga</b> Gallium 69.723	32 <b>Ge</b> Germanium 72.63	33 <b>As</b> Arsenic 74.92160	34 <b>Se</b> Selenium 78.96	35 <b>Br</b> Bromine 79.904	36 <b>Kr</b> Krypton 83.798				
5	37 <b>Rb</b> Rubidium 85.4678	38 <b>Sr</b> Strontium 87.62	39 <b>Y</b> Yttrium 88.90585	40 <b>Zr</b> Zirconium 91.224	41 <b>Nb</b> Niobium 92.90638	42 <b>Mo</b> Molybdenum 95.96	43 <b>Tc</b> Technetium (98)	44 <b>Ru</b> Ruthenium 101.07	45 <b>Rh</b> Rhodium 102.90...	46 <b>Pd</b> Palladium 106.42	47 <b>Ag</b> Silver 107.8682	48 <b>Cd</b> Cadmium 112.411	49 <b>In</b> Indium 114.818	50 <b>Sn</b> Tin 118.710	51 <b>Sb</b> Antimony 121.760	52 <b>Te</b> Tellurium 127.60	53 <b>I</b> Iodine 126.90...	54 <b>Xe</b> Xenon 131.293				
6	55 <b>Cs</b> Caesium 132.90...	56 <b>Ba</b> Barium 137.327	57-71	72 <b>Hf</b> Hafnium 178.49	73 <b>Ta</b> Tantalum 183.84	74 <b>W</b> Tungsten 183.84	75 <b>Re</b> Rhenium 186.207	76 <b>Os</b> Osmium 190.23	77 <b>Ir</b> Iridium 192.217	78 <b>Pt</b> Platinum 195.084	79 <b>Au</b> Gold 196.96...	80 <b>Hg</b> Mercury 200.59	81 <b>Tl</b> Thallium 204.38	82 <b>Pb</b> Lead 207.2	83 <b>Bi</b> Bismuth 208.98...	84 <b>Po</b> Polonium (209)	85 <b>At</b> Astatine (210)	86 <b>Rn</b> Radon (222)				
7	87 <b>Fr</b> Francium (223)	88 <b>Ra</b> Radium (226)	89-103	104 <b>Rf</b> Rutherfordium (267)	105 <b>Db</b> Dubnium (268)	106 <b>Sg</b> Seaborgium (271)	107 <b>Bh</b> Bohrium (272)	108 <b>Hs</b> Hassium (270)	109 <b>Mt</b> Meitnerium (276)	110 <b>Ds</b> Darmstadtium (281)	111 <b>Rg</b> Roentgenium (280)	112 <b>Cn</b> Copernicium (285)	113 <b>Uut</b> Ununtrium (284)	114 <b>Fl</b> Flerovium (289)	115 <b>Uup</b> Ununpentium (288)	116 <b>Lv</b> Livermorium (293)	117 <b>Uus</b> Ununseptium (294)	118 <b>Uuo</b> Ununoctium (294)				
	57 <b>La</b> Lanthanum 138.90...	58 <b>Ce</b> Cerium 140.116	59 <b>Pr</b> Praseodym 140.90...	60 <b>Nd</b> Neodymium 144.242	61 <b>Pm</b> Promethium (145)	62 <b>Sm</b> Samarium 150.36	63 <b>Eu</b> Europium 151.964	64 <b>Gd</b> Gadolinium 157.25	65 <b>Tb</b> Terbium 158.92...	66 <b>Dy</b> Dysprosium 162.500	67 <b>Ho</b> Holmium 164.93...	68 <b>Er</b> Erbium 167.259	69 <b>Tm</b> Thulium 168.93...	70 <b>Yb</b> Ytterbium 173.054	71 <b>Lu</b> Lutetium 174.9668							
	89 <b>Ac</b> Actinium (227)	90 <b>Th</b> Thorium 232.03...	91 <b>Pa</b> Protactinium 231.03...	92 <b>U</b> Uranium 238.02...	93 <b>Np</b> Neptunium (237)	94 <b>Pu</b> Plutonium (244)	95 <b>Am</b> Americium (243)	96 <b>Cm</b> Curium (247)	97 <b>Bk</b> Berkelium (247)	98 <b>Cf</b> Californium (251)	99 <b>Es</b> Einsteinium (252)	100 <b>Fm</b> Fermium (257)	101 <b>Md</b> Mendelevium (258)	102 <b>No</b> Nobelium (259)	103 <b>Lr</b> Lawrencium (262)							

# Periodic System – Primordial and Secondary NOR's

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18																																
1	<b>H</b> Hydrogen 1.008	Atomic # Symbol Name Weight																	2	<b>He</b> Helium 4.002602																														
3	<b>Li</b> Lithium 6.94	<b>Be</b> Beryllium 9.012182											<b>B</b> Boron 10.81	<b>C</b> Carbon 12.011	<b>N</b> Nitrogen 14.007	<b>O</b> Oxygen 15.999	<b>F</b> Fluorine 18.998...	<b>Ne</b> Neon 20.1797																																
11	<b>Na</b> Sodium 22.989...	<b>Mg</b> Magnesium 24.305											<b>Al</b> Aluminum 26.981...	<b>Si</b> Silicon 28.085	<b>P</b> Phosphorus 30.973...	<b>S</b> Sulfur 32.06	<b>Cl</b> Chlorine 35.45	<b>Ar</b> Argon 39.948																																
19	<b>K</b> Potassium 39.0983	<b>Ca</b> Calcium 40.078	<b>Sc</b> Scandium 44.955...	<b>Ti</b> Titanium 47.867	<b>V</b> Vanadium 50.9415	<b>Cr</b> Chromium 51.9961	<b>Mn</b> Manganese 54.938...	<b>Fe</b> Iron 55.845	<b>Co</b> Cobalt 58.933...	<b>Ni</b> Nickel 58.6934	<b>Cu</b> Copper 63.546	<b>Zn</b> Zinc 65.38	<b>Ga</b> Gallium 69.723	<b>Ge</b> Germanium 72.63	<b>As</b> Arsenic 74.92160	<b>Se</b> Selenium 78.96	<b>Br</b> Bromine 79.904	<b>Kr</b> Krypton 83.798																																
37	<b>Rb</b> Rubidium 85.4678	<b>Sr</b> Strontium 87.62	<b>Y</b> Yttrium 88.90585	<b>Zr</b> Zirconium 91.224	<b>Nb</b> Niobium 92.90638	<b>Mo</b> Molybdenum 95.96	<b>Tc</b> Technetium (98)	<b>Ru</b> Ruthenium 101.07	<b>Rh</b> Rhodium 102.90...	<b>Pd</b> Palladium 106.42	<b>Ag</b> Silver 107.8682	<b>Cd</b> Cadmium 112.411	<b>In</b> Indium 114.818	<b>Sn</b> Tin 118.710	<b>Sb</b> Antimony 121.760	<b>Te</b> Tellurium 127.60	<b>I</b> Iodine 126.90...	<b>Xe</b> Xenon 131.293																																
55	<b>Cs</b> Caesium 132.90...	<b>Ba</b> Barium 137.327	57-71	<b>Hf</b> Hafnium 178.49	<b>Ta</b> Tantalum 183.84	<b>W</b> Tungsten 183.84	<b>Re</b> Rhenium 186.207	<b>Os</b> Osmium 190.23	<b>Ir</b> Iridium 192.217	<b>Pt</b> Platinum 195.084	<b>Au</b> Gold 196.96...	<b>Hg</b> Mercury 200.59	<b>Tl</b> Thallium 204.38	<b>Pb</b> Lead 207.2	<b>Bi</b> Bismuth 208.98...	<b>Po</b> Polonium (209)	<b>At</b> Astatine (210)	<b>Rn</b> Radon (222)																																
87	<b>Fr</b> Francium (223)	<b>Ra</b> Radium (226)	89-103	<b>Rf</b> Rutherfordium (267)	<b>Db</b> Dubnium (268)	<b>Sg</b> Seaborgium (271)	<b>Bh</b> Bohrium (272)	<b>Hs</b> Hassium (270)	<b>Mt</b> Meitnerium (276)	<b>Ds</b> Darmstadtium (281)	<b>Rg</b> Roentgenium (280)	<b>Cn</b> Copernicium (285)	<b>Uut</b> Ununtrium (284)	<b>Fl</b> Flerovium (289)	<b>Uup</b> Ununpentium (288)	<b>Lv</b> Livermorium (293)	<b>Uus</b> Ununseptium (294)	<b>Uuo</b> Ununoctium (294)																																
<table border="1"> <tr> <td>57</td> <td><b>La</b> Lanthanum 138.90...</td> <td><b>Ce</b> Cerium 140.116</td> <td><b>Pr</b> Praseodym 140.90...</td> <td><b>Nd</b> Neodymium 144.242</td> <td><b>Pm</b> Promethium (145)</td> <td><b>Sm</b> Samarium 150.36</td> <td><b>Eu</b> Europium 151.964</td> <td><b>Gd</b> Gadolinium 157.25</td> <td><b>Tb</b> Terbium 158.92...</td> <td><b>Dy</b> Dysprosium 162.500</td> <td><b>Ho</b> Holmium 164.93...</td> <td><b>Er</b> Erbium 167.259</td> <td><b>Tm</b> Thulium 168.93...</td> <td><b>Yb</b> Ytterbium 173.054</td> <td><b>Lu</b> Lutetium 174.9668</td> </tr> <tr> <td>89</td> <td><b>Ac</b> Actinium (227)</td> <td><b>Th</b> Thorium 232.03...</td> <td><b>Pa</b> Protactinium 231.03...</td> <td><b>U</b> Uranium 238.02...</td> <td><b>Np</b> Neptunium (237)</td> <td><b>Pu</b> Plutonium (244)</td> <td><b>Am</b> Americium (243)</td> <td><b>Cm</b> Curium (247)</td> <td><b>Bk</b> Berkelium (247)</td> <td><b>Cf</b> Californium (251)</td> <td><b>Es</b> Einsteinium (252)</td> <td><b>Fm</b> Fermium (257)</td> <td><b>Md</b> Mendelevium (258)</td> <td><b>No</b> Nobelium (259)</td> <td><b>Lr</b> Lawrencium (262)</td> </tr> </table>																			57	<b>La</b> Lanthanum 138.90...	<b>Ce</b> Cerium 140.116	<b>Pr</b> Praseodym 140.90...	<b>Nd</b> Neodymium 144.242	<b>Pm</b> Promethium (145)	<b>Sm</b> Samarium 150.36	<b>Eu</b> Europium 151.964	<b>Gd</b> Gadolinium 157.25	<b>Tb</b> Terbium 158.92...	<b>Dy</b> Dysprosium 162.500	<b>Ho</b> Holmium 164.93...	<b>Er</b> Erbium 167.259	<b>Tm</b> Thulium 168.93...	<b>Yb</b> Ytterbium 173.054	<b>Lu</b> Lutetium 174.9668	89	<b>Ac</b> Actinium (227)	<b>Th</b> Thorium 232.03...	<b>Pa</b> Protactinium 231.03...	<b>U</b> Uranium 238.02...	<b>Np</b> Neptunium (237)	<b>Pu</b> Plutonium (244)	<b>Am</b> Americium (243)	<b>Cm</b> Curium (247)	<b>Bk</b> Berkelium (247)	<b>Cf</b> Californium (251)	<b>Es</b> Einsteinium (252)	<b>Fm</b> Fermium (257)	<b>Md</b> Mendelevium (258)	<b>No</b> Nobelium (259)	<b>Lr</b> Lawrencium (262)
57	<b>La</b> Lanthanum 138.90...	<b>Ce</b> Cerium 140.116	<b>Pr</b> Praseodym 140.90...	<b>Nd</b> Neodymium 144.242	<b>Pm</b> Promethium (145)	<b>Sm</b> Samarium 150.36	<b>Eu</b> Europium 151.964	<b>Gd</b> Gadolinium 157.25	<b>Tb</b> Terbium 158.92...	<b>Dy</b> Dysprosium 162.500	<b>Ho</b> Holmium 164.93...	<b>Er</b> Erbium 167.259	<b>Tm</b> Thulium 168.93...	<b>Yb</b> Ytterbium 173.054	<b>Lu</b> Lutetium 174.9668																																			
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# Periodic System – Carrier   vs. Carrier Free

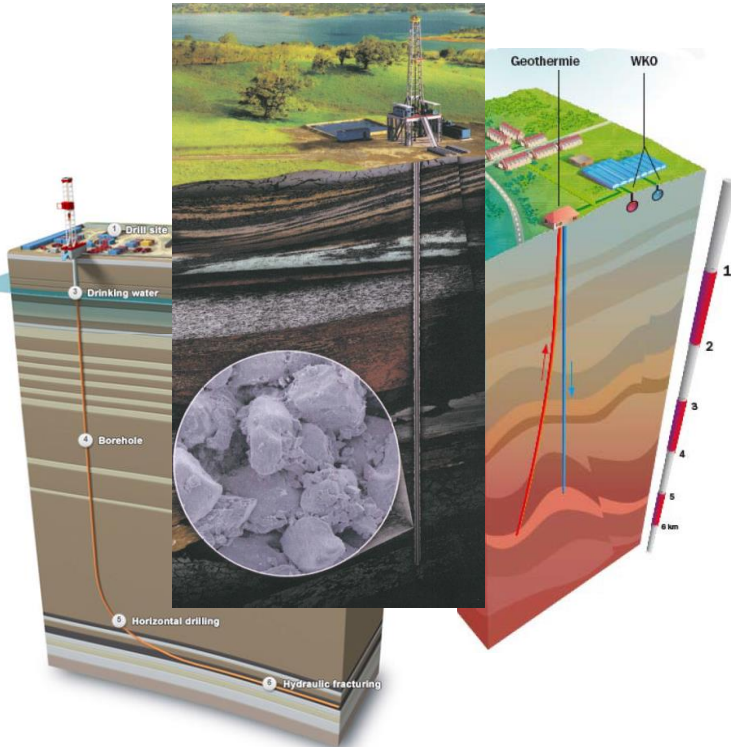
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18		
1	<b>H</b> Hydrogen 1.008	Atomic # Symbol Name Weight																	2	<b>He</b> Helium 4.002602
2	<b>Li</b> Lithium 6.94	<b>Be</b> Beryllium 9.012182											<b>B</b> Boron 10.81	<b>C</b> Carbon 12.011	<b>N</b> Nitrogen 14.007	<b>O</b> Oxygen 15.999	<b>F</b> Fluorine 18.998...	<b>Ne</b> Neon 20.1797		
3	<b>Na</b> Sodium 22.989...	<b>Mg</b> Magnesium 24.305											<b>Al</b> Aluminum 26.981...	<b>Si</b> Silicon 28.085	<b>P</b> Phosphorus 30.973...	<b>S</b> Sulfur 32.06	<b>Cl</b> Chlorine 35.45	<b>Ar</b> Argon 39.948		
4	<b>K</b> Potassium 39.0983	<b>Ca</b> Calcium 40.078	<b>Sc</b> Scandium 44.955...	<b>Ti</b> Titanium 47.867	<b>V</b> Vanadium 50.9415	<b>Cr</b> Chromium 51.9961	<b>Mn</b> Manganese 54.938...	<b>Fe</b> Iron 55.845	<b>Co</b> Cobalt 58.933...	<b>Ni</b> Nickel 58.6934	<b>Cu</b> Copper 63.546	<b>Zn</b> Zinc 65.38	<b>Ga</b> Gallium 69.723	<b>Ge</b> Germanium 72.63	<b>As</b> Arsenic 74.92160	<b>Se</b> Selenium 78.96	<b>Br</b> Bromine 79.904	<b>Kr</b> Krypton 83.798		
5	<b>Rb</b> Rubidium 85.4678	<b>Sr</b> Strontium 87.62	<b>Y</b> Yttrium 88.90585	<b>Zr</b> Zirconium 91.224	<b>Nb</b> Niobium 92.90638	<b>Mo</b> Molybdenum 95.96	<b>Tc</b> Technetium (98)	<b>Ru</b> Ruthenium 101.07	<b>Rh</b> Rhodium 102.90...	<b>Pd</b> Palladium 106.42	<b>Ag</b> Silver 107.8682	<b>Cd</b> Cadmium 112.411	<b>In</b> Indium 114.818	<b>Sn</b> Tin 118.710	<b>Sb</b> Antimony 121.760	<b>Te</b> Tellurium 127.60	<b>I</b> Iodine 126.90...	<b>Xe</b> Xenon 131.293		
6	<b>Cs</b> Caesium 132.90...	<b>Ba</b> Barium 137.327	57-71	<b>Hf</b> Hafnium 178.49	<b>Ta</b> Tantalum 183.84	<b>W</b> Tungsten 183.84	<b>Re</b> Rhenium 186.207	<b>Os</b> Osmium 190.23	<b>Ir</b> Iridium 192.217	<b>Pt</b> Platinum 195.084	<b>Au</b> Gold 196.96...	<b>Hg</b> Mercury 200.59	<b>Tl</b> Thallium 204.38	<b>Pb</b> Lead 207.2	<b>Bi</b> Bismuth 208.98...	<b>Po</b> Polonium (209)	<b>At</b> Astatine (210)	<b>Rn</b> Radon (222)		
7	<b>Fr</b> Francium (223)	<b>Ra</b> Radium (226)	89-103	<b>Rf</b> Rutherfordium (267)	<b>Db</b> Dubnium (268)	<b>Sg</b> Seaborgium (271)	<b>Bh</b> Bohrium (272)	<b>Hs</b> Hassium (270)	<b>Mt</b> Meitnerium (276)	<b>Ds</b> Darmstadtium (281)	<b>Rg</b> Roentgenium (280)	<b>Cn</b> Copernicium (285)	<b>Uut</b> Ununtrium (284)	<b>Fl</b> Flerovium (289)	<b>Uup</b> Ununpentium (288)	<b>Lv</b> Livermorium (293)	<b>Uus</b> Ununseptium (294)	<b>Uuo</b> Ununoctium (294)		
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**4**

# **Mineral Mining, Beneficiation/Treatment and Processing**

# Earth's Crust & Natural Resources - Mining

## Mobile Phase (Gas/Oil/Water)



## Surface Mine

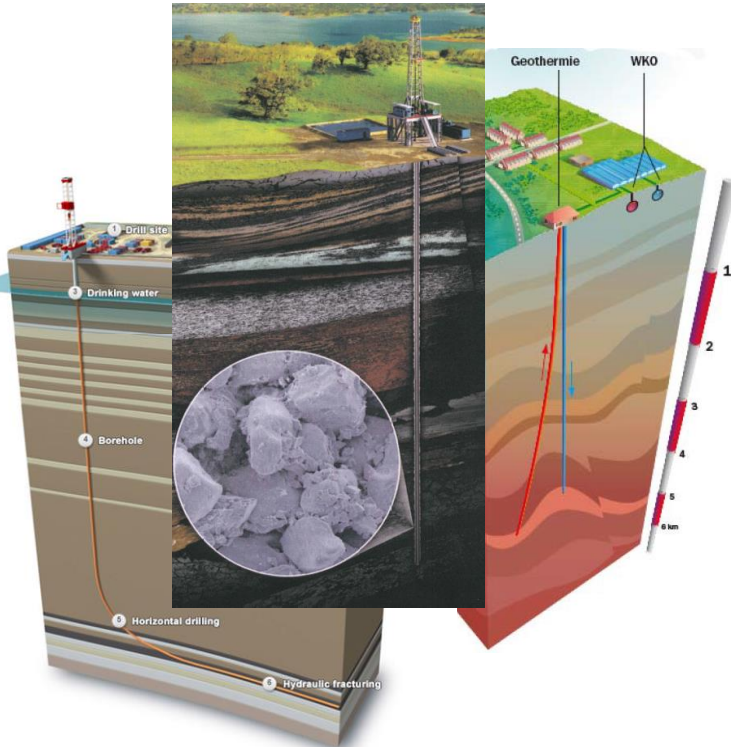


## Sub-surface Mine

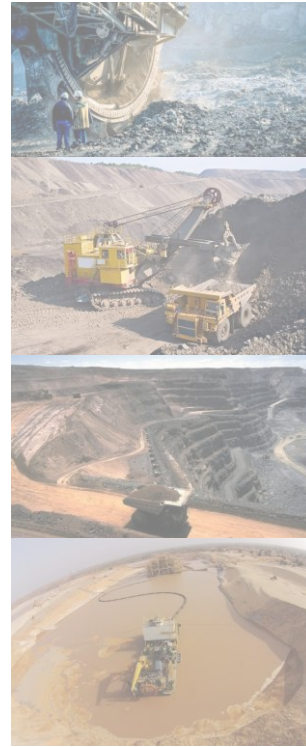


# Earth's Crust & Natural Resources – Mobile Phase Mining

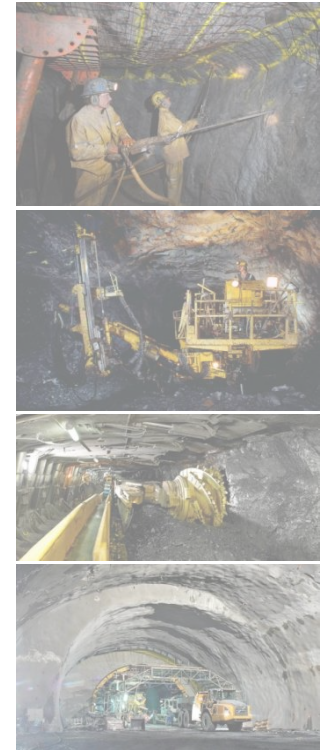
## Mobile Phase (Gas/Oil/Water)



## Surface Mine

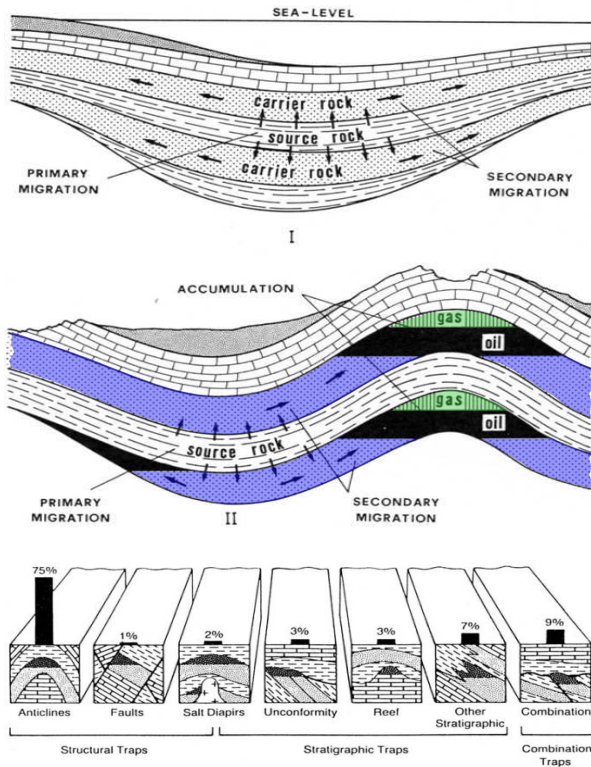


## Sub-surface Mine





# Gas/Oil Formation – Geological Time Scale

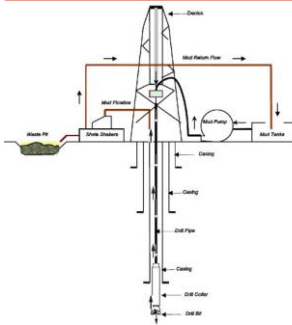


- hydrocarbon **source rocks** are sediments containing large amounts of organic matter (e.g. coal, organic rich shale)
- source rocks to have been buried to depths of at least 3 kilometers for a significant period of geological time (say up > **10<sup>6</sup> years**) before gas/oil is formed
- geological strata should be shaped in such a way that gas/oil escaping/seeping from source rock may be come **trapped** in a '**conventional**' reservoir
- most common **sandstone reservoir** with gas/oil/formation-water in the pores sealed by a dome-shaped sealing (salt [evaporite], shale) layer
- geological shale strata may contain gas/oil, that may be released by hydraulic fracturing ('**unconventional**' reservoir, e.g. shale gas/oil)

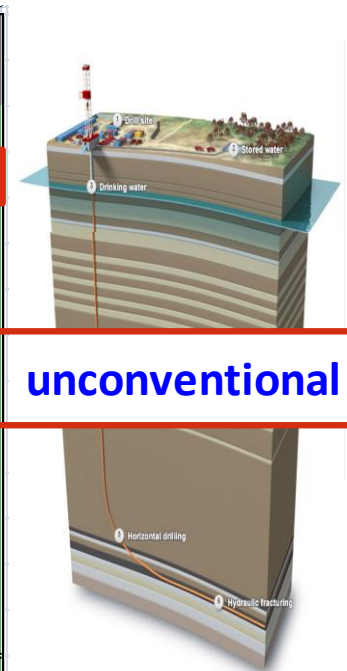
# NOR's in Sedimentary Rocks (Gas/Oil Reservoirs)

## K, Th & U - Element and Activity Concentrations

**conventional**



SEDIMENTARY ROCK CLASS	Potassium (K)		Thorium (Th)		Uranium (U)	
	%w	Bq/g	ppm(w)	Bq/g	ppm(w)	Bq/g
<b>DETRITAL</b>	2,1	0,66	12,4	0,050	4,8	0,059
<i>Sandstone &amp; Conglomerates</i>	1,2	0,37	9,7	0,039	4,1	0,050
Orthoquartzites	2,0	0,62	1,5	0,006	0,5	0,006
Arkoses	2,5	0,78	5,0	0,020	1,5	0,018
<b>Shale</b>						
Grey/Green	3,5	1,09	16,3	0,066	5,9	0,072
Black	3,0	0,94	13,0	0,053	3,0	0,037
<i>Clay</i>	0,6	0,19	8,6	0,035	4,0	0,049
<b>CHEMICAL</b>	0,6	0,19	14,9	0,060	3,6	0,044
<i>Carbonates</i>	0,3	0,09	1,8	0,007	2,0	0,025
Limestone	0,5	0,16	3,0	0,012	13,0	0,159
<i>Evaporites</i>					< 0,1	< 0,001
<b>EARTH'S CRUST</b>	2,1	0,66	12,4	0,050	4,2	0,051
<i>Top soil</i>	1,5	0,47	9,0	0,037	8,0	0,098
<i>Beach sands (unconsolidated)</i>			6,0	0,024	3,0	0,037

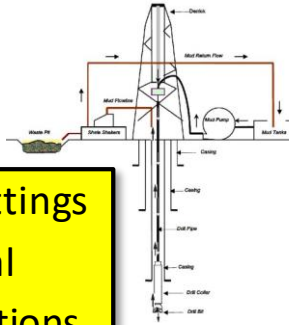


**unconventional**

# NOR's in Sedimentary Rocks (Gas/Oil Reservoirs)

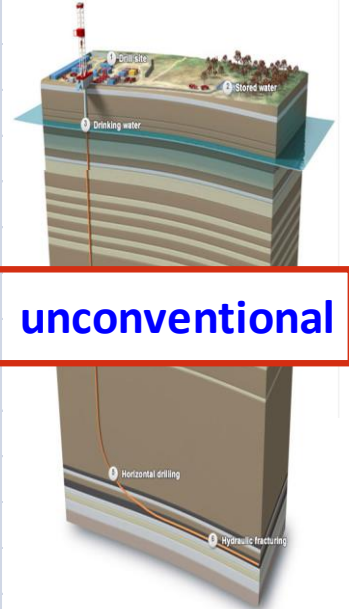
## K, Th & U - Element and Activity Concentrations

conventional



SEDIMENTARY ROCK CLASS	Potassium (K)		Thorium (Th)		Uranium (U)	
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Evaporites					< 0,1	< 0,001
<b>EARTH'S CRUST</b>	2,1	0,66	12,4	0,050	4,2	0,051
Top soil	1,5	0,47	9,0	0,037	8,0	0,098
Beach sands (unconsolidated)			6,0	0,024	3,0	0,037

unconventional



Drilling Cuttings  
Natural  
Concentrations

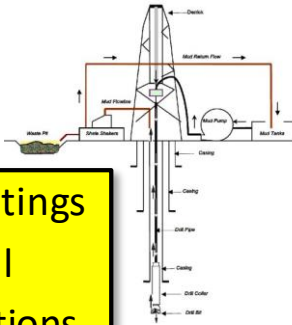
of K, Th & U

**NORM?**

# NOR's in Sedimentary Rocks (Gas/Oil Reservoirs)

## K, Th & U - Element and Activity Concentrations

**conventional**



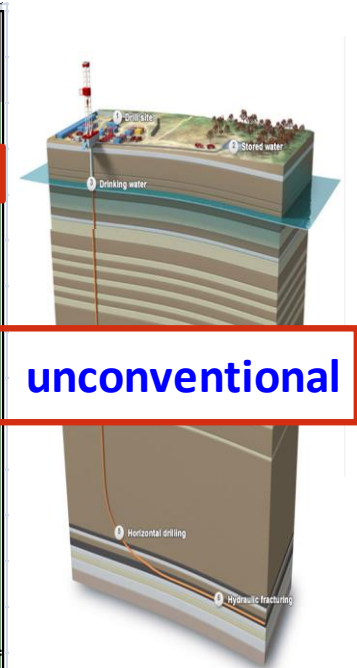
**Drilling Cuttings  
Natural  
Concentrations**

**of K, Th & U**

**NORM?**



SEDIMENTARY ROCK CLASS	Potassium (K)		Thorium (Th)		Uranium (U)	
	%w	Bq/g	ppm(w)	Bq/g	ppm(w)	Bq/g
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Beach sands (unconsolidated)			6,0	0,024	3,0	0,037



**unconventional**



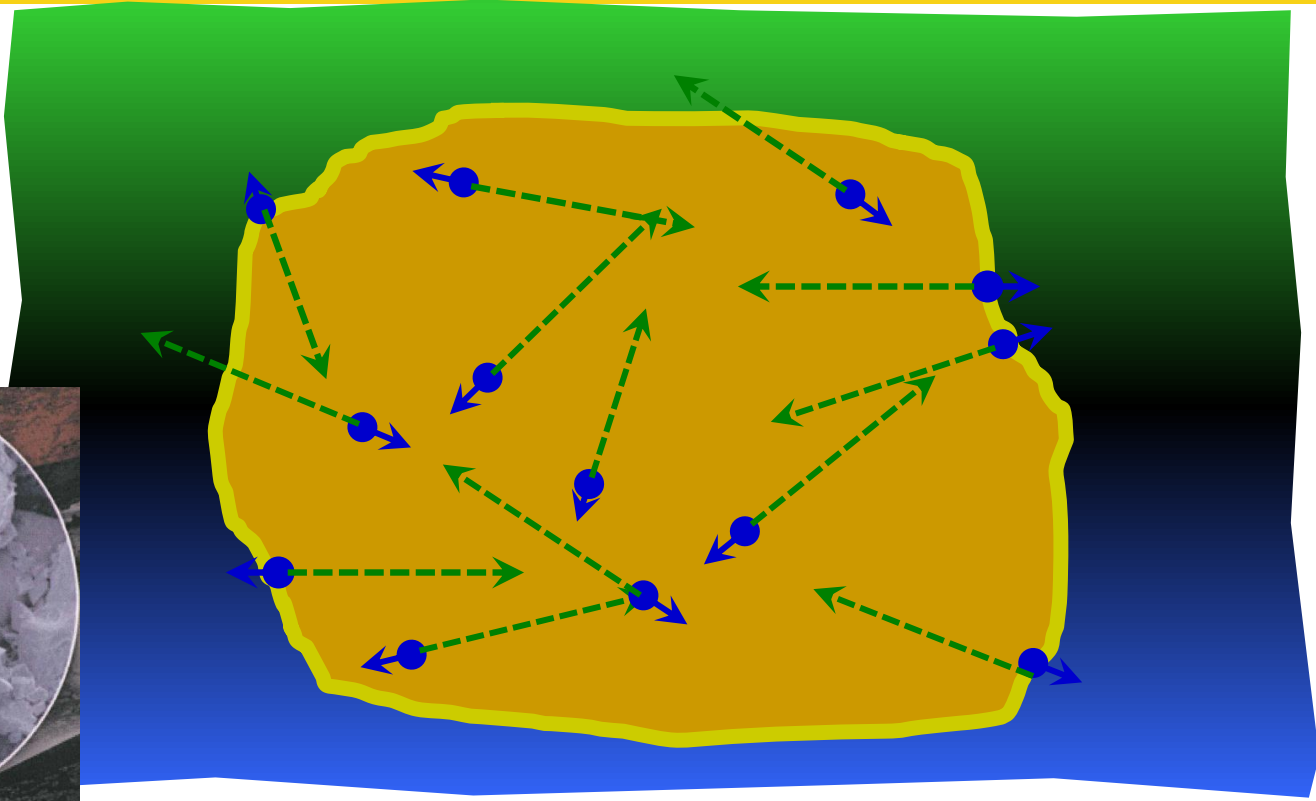
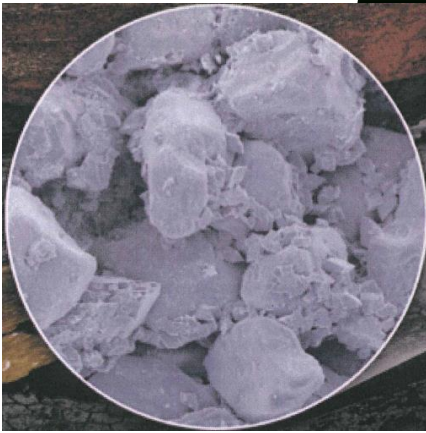
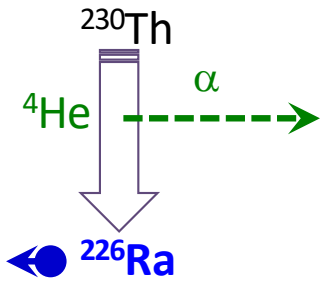
# NOR Geochemistry

## Gas/Oil/Water and Water Reservoir Conditions

element	$^{232}\text{Th}$ -series	$^{238}\text{U}$ -series	chemical behaviour	Diagenesis/ Accumulation
U uranium		$^{238}\text{U}$ , $^{234}\text{U}$	reducing environment: $\text{U}^{4+}$ insoluble, no $\text{UO}_2^{2+}$	remains inside or at surface of reservoir grains
Th thorium	$^{232}\text{Th}$ , $^{228}\text{Th}$	$^{234}\text{Th}$ , $^{230}\text{Th}$	reducing environment: $\text{Th}^{4+}$ very insoluble	
Ra radium	$^{228}\text{Ra}$ , $^{224}\text{Ra}$	$^{226}\text{Ra}$	alkaline-earth (Mg, Ca, Sr, Ba) $^{2+}_{\text{aq}}$ carrier for $\text{Ra}^{2+}$ ions	preference for and geo- chemically transported by aqueous phase
Rn radon	$^{220}\text{Rn}$	$^{222}\text{Rn}$	noble gas, very polarisable atoms	water/oil/gas phase partitioning
Pb lead		$^{210}\text{Pb}$	stable $\text{Pb}^{2+}_{\text{aq}}$ carrier for $^{210}\text{Pb}^{2+}$ ions	preference for and geo- chemically transported by aqueous phase

# Radiophysical and Radiochemical Phenomena

## $\alpha$ Recoil Stimulated Dissolution from/around a Sand Grain



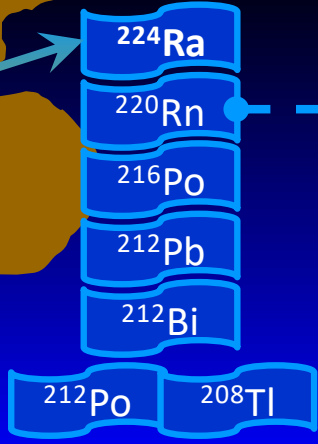
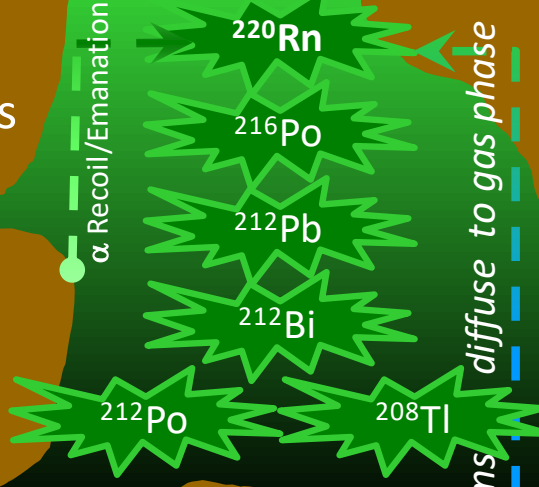
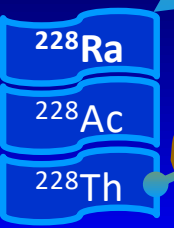
# Undisturbed Reservoir

Secular Equilibrium –  $^{232}\text{Th}$  Decay Series

GAS

OIL

WATER



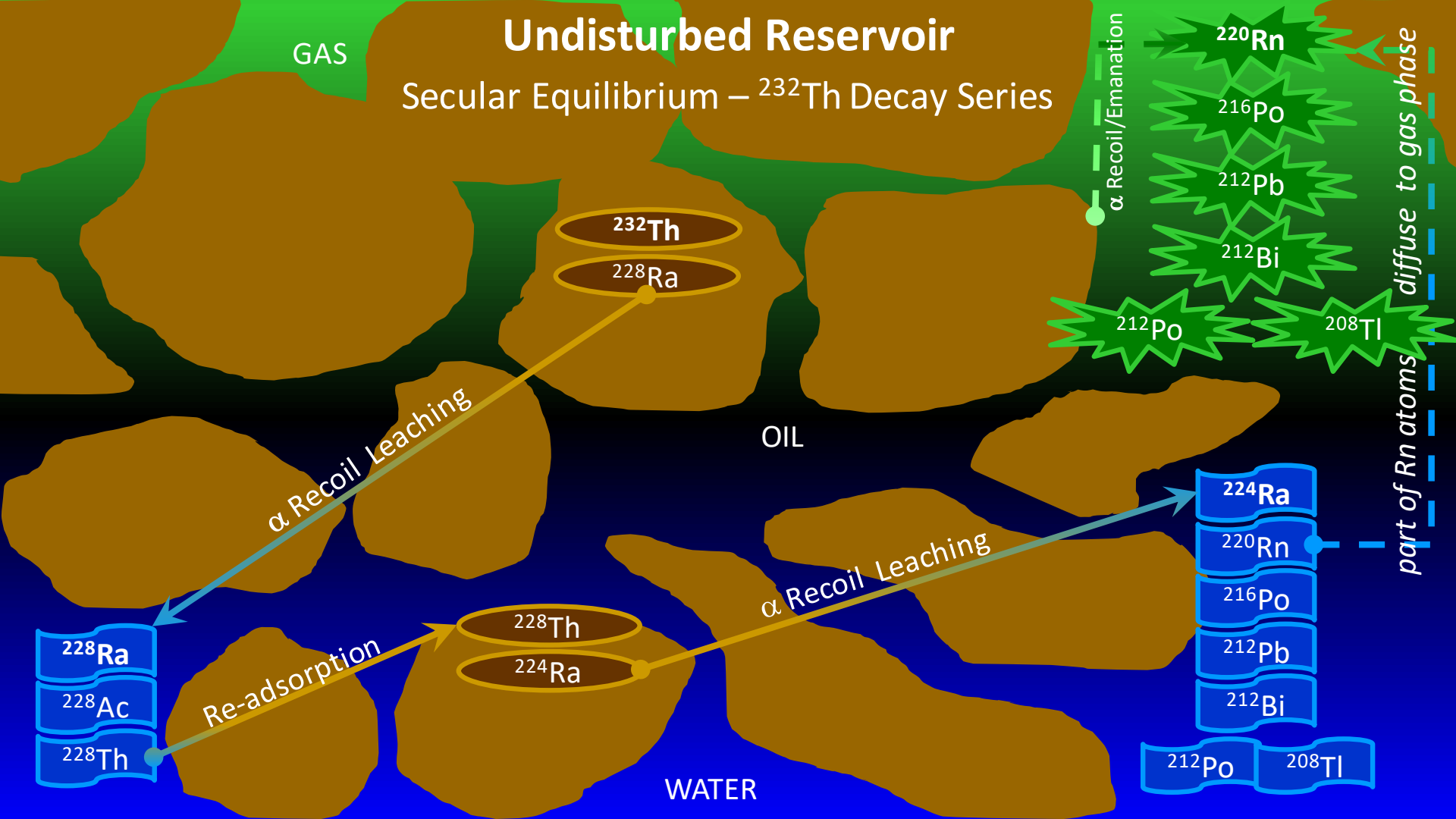
$\alpha$  Recoil Leaching

$\alpha$  Recoil Leaching

Re-adsorption

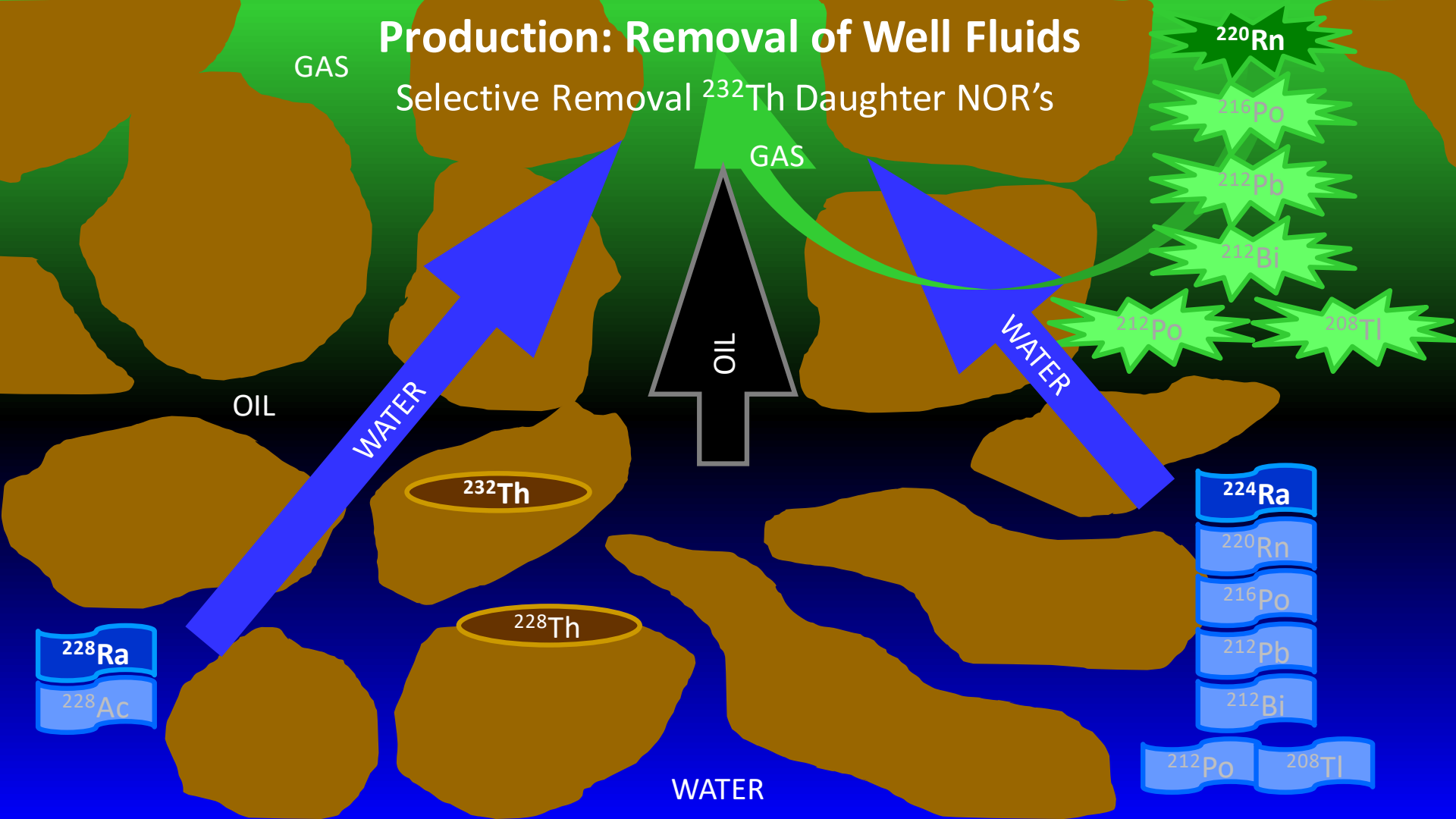
$\alpha$  Recoil/Emanation

diffuse to gas phase  
part of Rn atoms



# Production: Removal of Well Fluids

Selective Removal  $^{232}\text{Th}$  Daughter NOR's

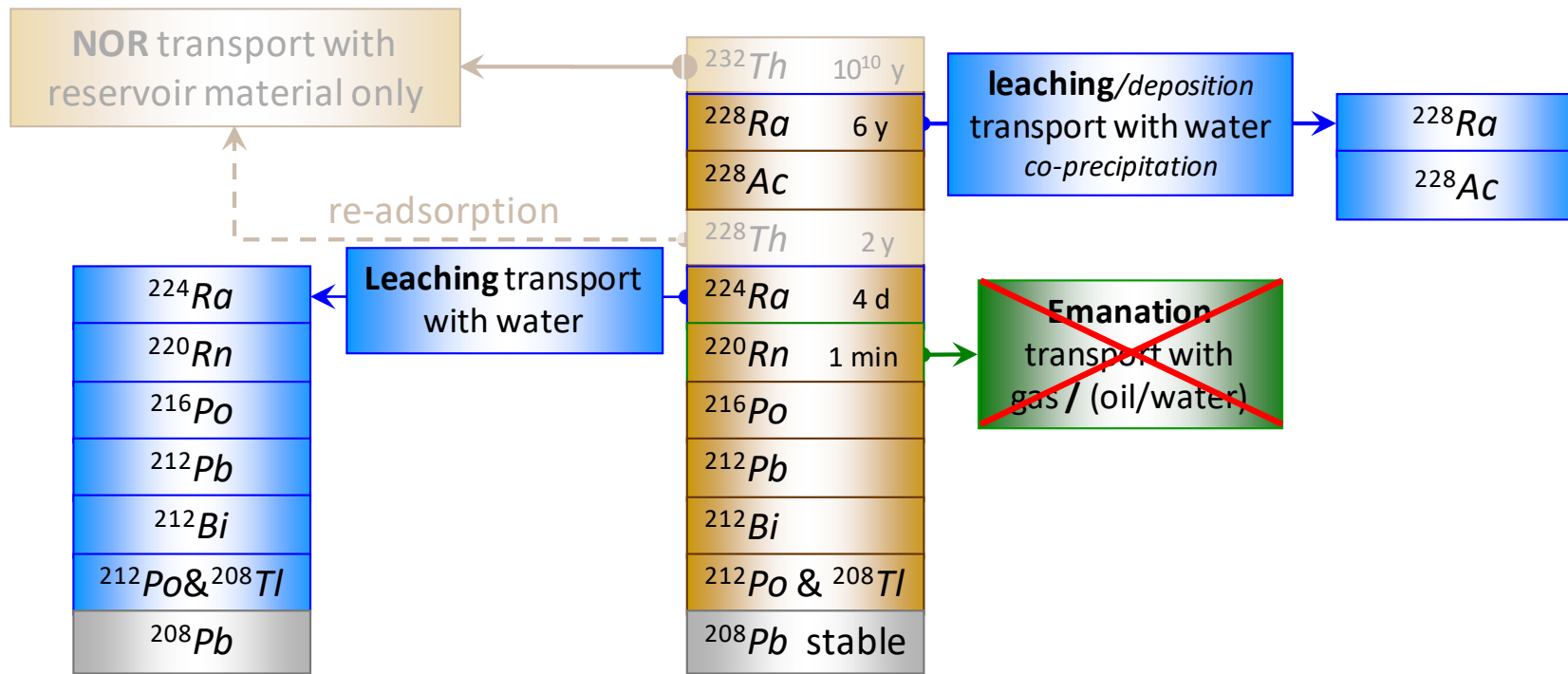


# NOR Characteristics – Well Fluids/Produced Water

$^{232}\text{Th}$  Decay Series

1 day after production

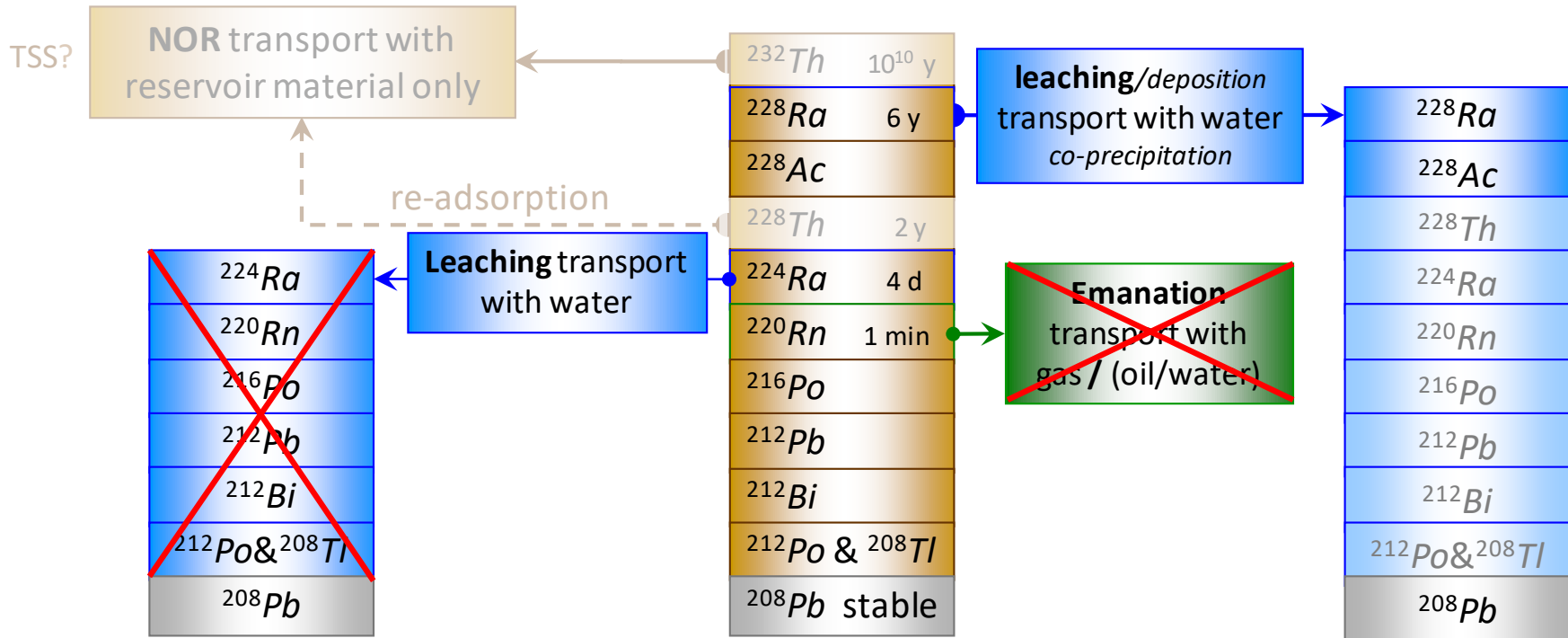
TSS?



# NOR Characteristics – Well Fluids/Produced Water – Scale/Sludge

$^{232}\text{Th}$  Decay Series

1 year after production



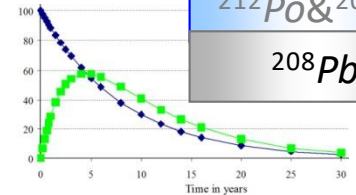
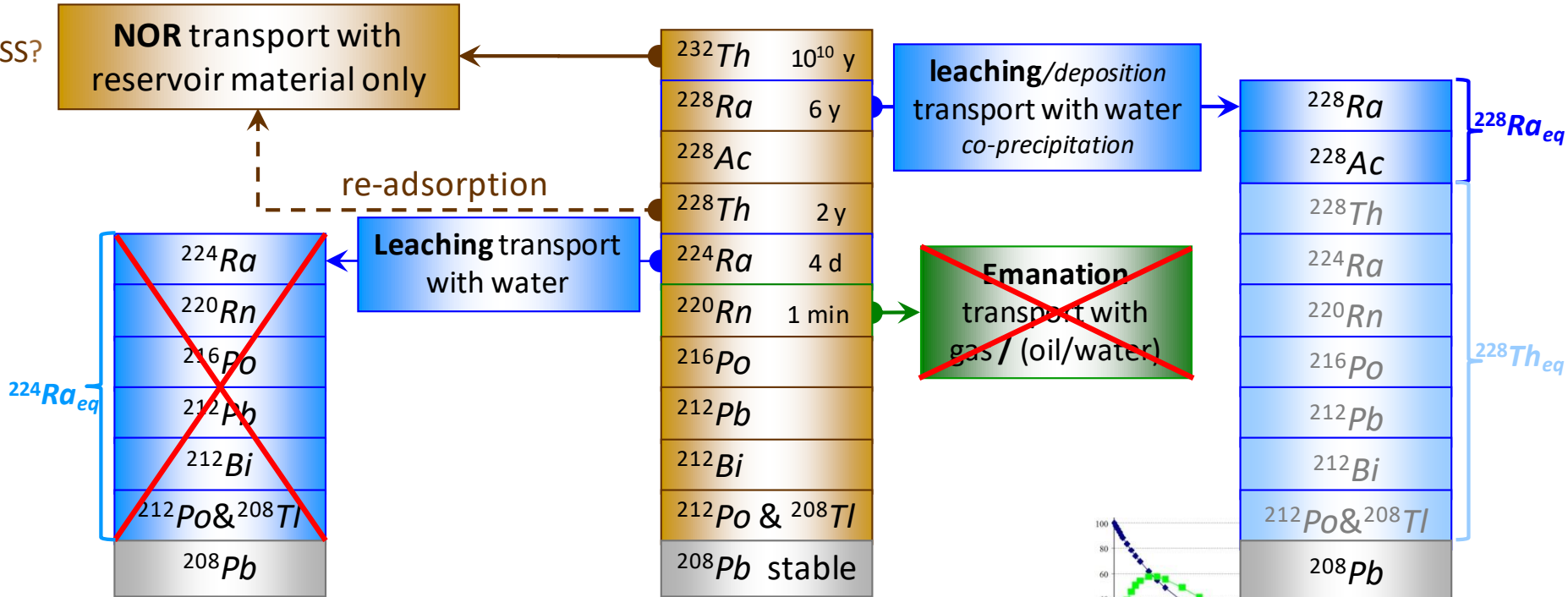
# NOR Characteristics – Mobile Phase Mining

## $^{232}\text{Th}$ Decay Series

## overview

Notation  $^{232}\text{Th}$ -series  
 $^{228}\text{Ra}_{\text{eq}}$  and  $^{228}\text{Th}_{\text{eq}}$

TSS?

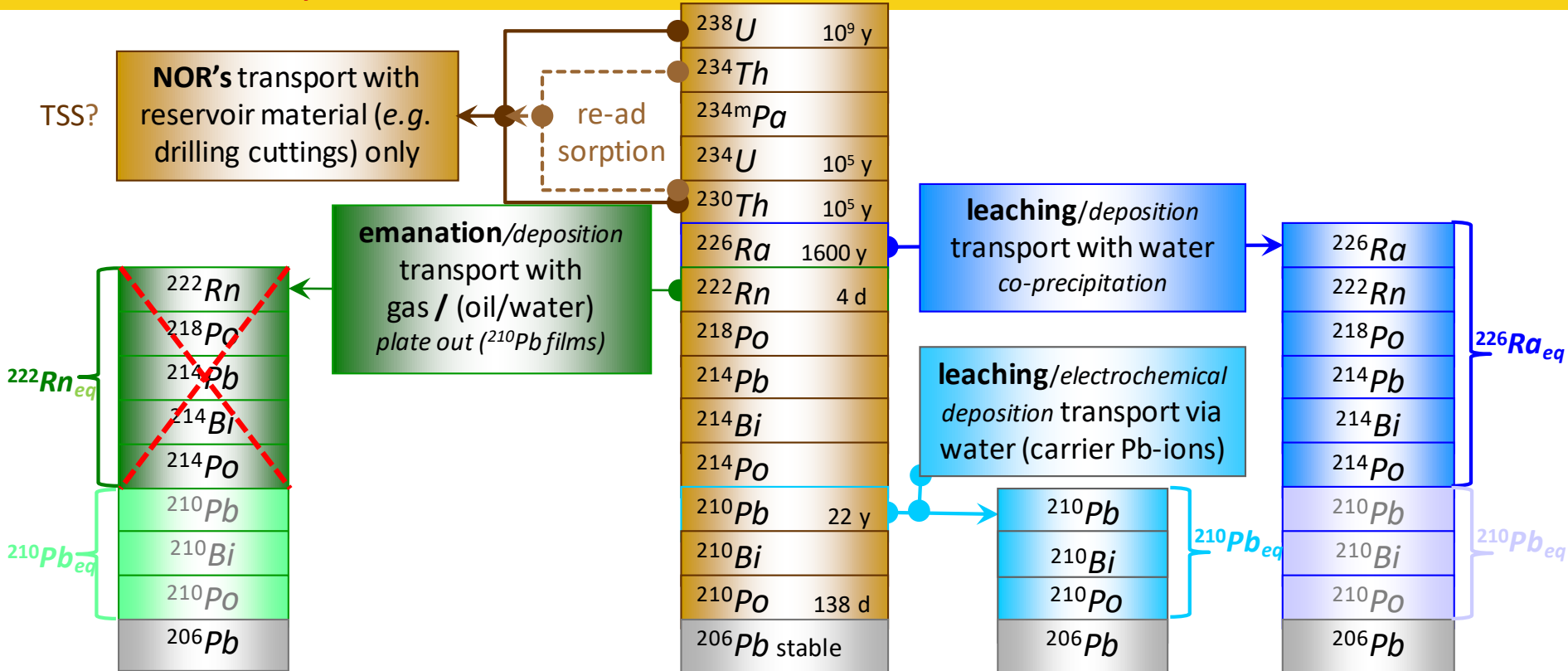


# NOR Characteristics – Mobile Phase Mining

$^{238}\text{U}$  Decay Series

overview

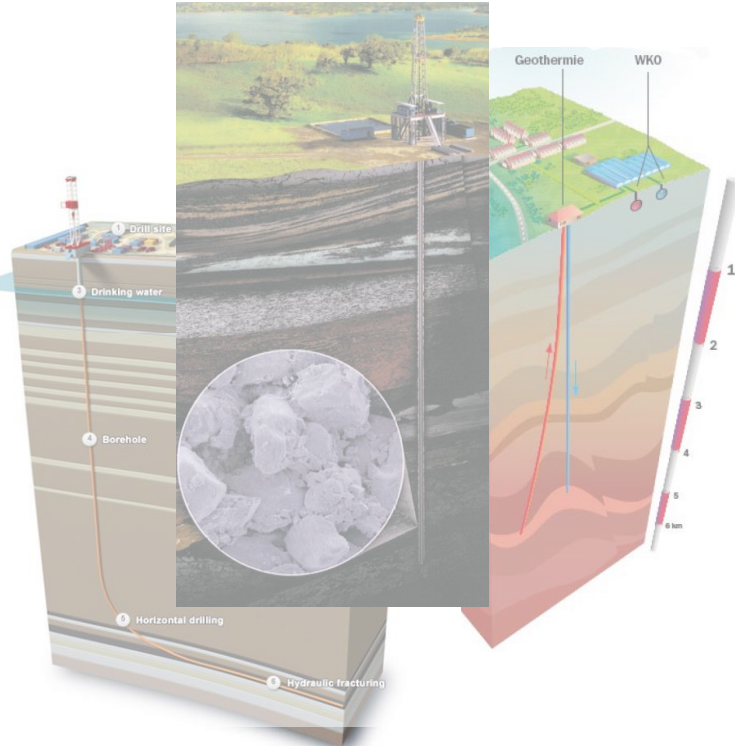
Notation  $^{238}\text{U}$ -series  
 $^{226}\text{Ra}_{\text{eq}}$  and  $^{210}\text{Pb}_{\text{eq}}$





# Earth's Crust & Natural Resources – Ore Mining

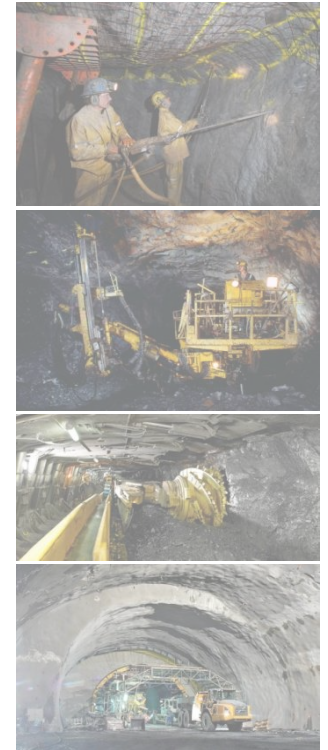
## Mobile Phase (Gas/Oil/Water)



## Surface Mine



## Sub-surface Mine



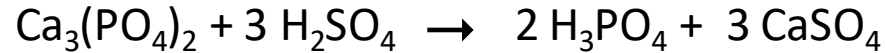
# Mining & Beneficiation



- Commercially exploited sedimentary phosphate deposits close to Earth's surface ( $\pm 10$  m).
- Overburden (set aside for mine remediation) and phosphate ore will be broken up.
- Truck loading and transport to nearby crushing facility and beneficiation plant.
- Beneficiation via wet screening ('washing'), flocculation, and other special physical-chemical treatments to enhance the phosphate rich fraction
- All NOR's are still there, no (severe) disturbance of secular equilibria.

# Wet Processing – Phosphoric Acid Production

- Beneficiated phosphate ore digested by  $\text{H}_2\text{SO}_4$  (sulphuric acid), thereby producing  $\text{CaSO}_4$  (phosphogypsum) and  $\text{H}_3\text{PO}_4$  (phosphoric acid)



- **U**: present in phosphate rock as  $\text{U}^{4+}$  and  $\text{U}^{6+}$ . Digestion reduces any  $\text{U}^{6+}$  to  $\text{U}^{4+}$ , open air acid filtration oxidises  $\text{U}^{4+}$  to  $\text{U}^{6+}$ , forming uranyl ions ( $\text{UO}_2^{2+}$ ) complexing with phosphates.
  - 90%–95% U in rock migrates to  $\text{H}_3\text{PO}_4$ .
  - 5%-10% U in rock migrates to phosphogypsum (unreacted rock)
- **Th**: partitions depending on the actual process conditions and characteristics of phosphate rock. Either 75% to  $\text{H}_3\text{PO}_4$  or 75% to phosphogypsum
- **Ra**: 75% to 95% in phosphate rock migrates to phosphogypsum
- **Pb**: conflicting reports, either all to  $\text{H}_3\text{PO}_4$  or to phosphogypsum
- **Po**: is reported to migrate for 80% to 100% to phosphogypsum

# Conclusions

- **Refrain from the term Specific Activity**
- Take account of the type of industry unwillingly producing NORM
  - U, Th** only relevant during ore mining, beneficiation and processing; not relevant for mobile phase mining industry (excl. U solution mining)
  - Ra, Pb** dissolves in aqueous process streams, deposits (exceeding solubility products/electrochemically) from aqueous process streams
  - Rn** only relevant for open industrial systems
  - Pb, Po** expelled from high temperature processes, deposits at cooler places (ducts, vents)
- $\alpha$ -recoil stimulates chemical leaching into the mobile phase (*geochemical time scale*)
- Transport carrier vs. carrier-free (*production/processing time scale*)
- NOR's may appear both in product and by-product (waste/residue) streams
- Have only relevant NOR's (in sub-equilibrium) reported



Q&A