Subterranean production of ^{39}Ar and implications for Doe Canyon well gas

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^{36}Ar … primordial, stable
^{38}Ar … primordial, stable
^{40}Ar … radiogenic, stable
^{37}Ar … radioactive, $t_{1/2}$ = 35 d
^{39}Ar … radioactive, $t_{1/2}$ = 269 y
^{42}Ar … radioactive, $t_{1/2}$ = 32.9 y

Argon

Atmosphere

Argon the third most abundant gas (~1%)
^{40}Ar from degassing of Earth (decay of ^{40}K)
^{39}Ar produced cosmogenically: ^{40}Ar(n,2n)^{39}Ar
^{39}Ar/Ar = 8×10^{-16} → ~1 decay per sec per kg
^{40}Ar/^{36}Ar = 295

Underground

^{40}Ar produced by electron capture on ^{40}K
^{39}Ar nucleogenic production

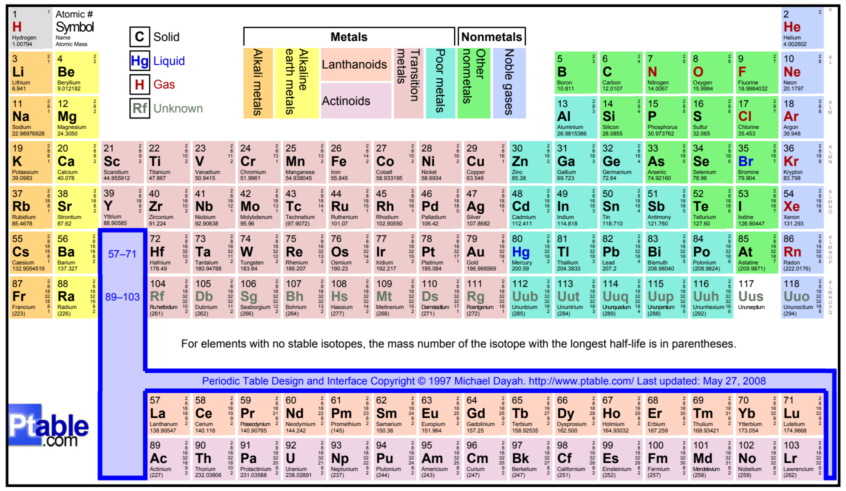
Interest in ^{39}Ar

- **Particle physics** – dark matter searches … seeking low radioactivity argon as target for WIMP detection
- **Hydrology** – environmental radioactive tracer … timescales and pathways of ground-water transport
- **Geophysics** – underground ^{39}Ar of nucleogenic (and not cosmogenic) origin carries signature of source rock composition, esp. concentration in K, Th, U

Geophysical interest

- O, Fe, Si, Mg make up 93% of Earth's mass
- + Al, Ca, Ni → 98% of Earth's mass

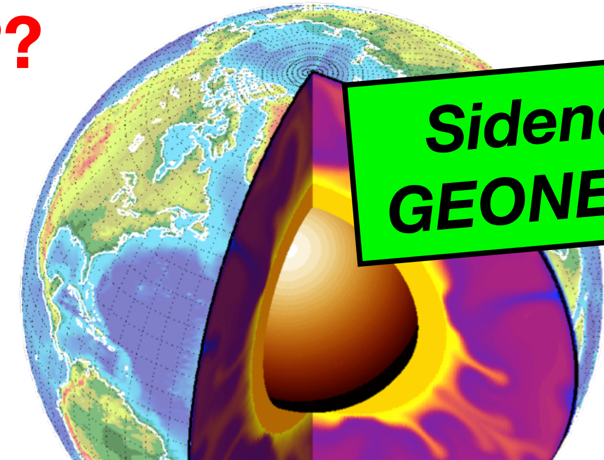
Chemistry of the Earth



- tens ppb of **U** (~10^{-8})
- four times as much **Th** (Th/U ~ 4)
- a few hundred ppm **K** (K/U ~ 10^4)
- Long-lived radionuclides ^{238}U, ^{232}Th, ^{40}K account for **>99%** of radiogenic heat produced in the Earth

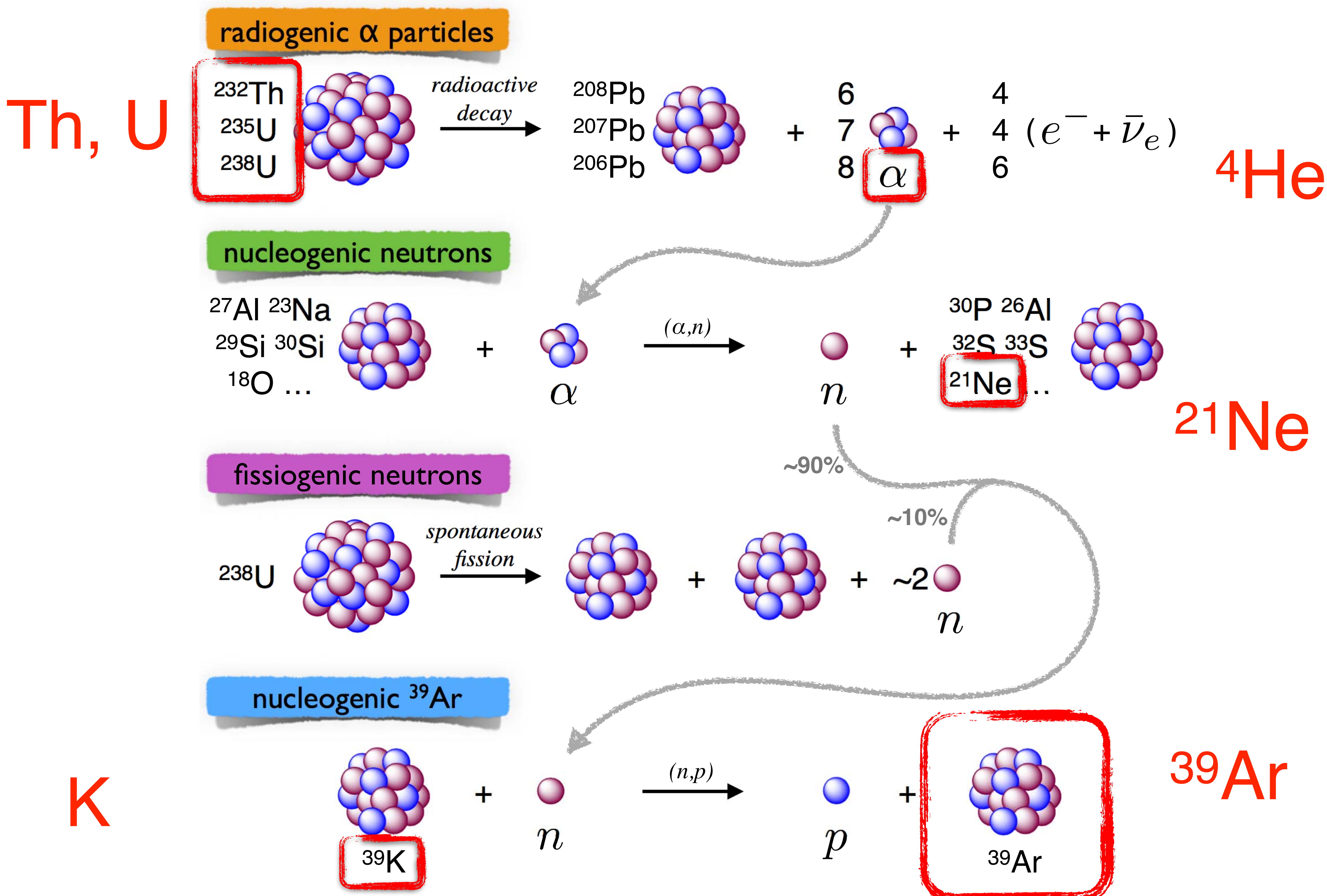
- **A factor of 3 uncertainty in the amount of U, Th, K in the Earth…**
- **How much power available to power plate tectonics, mantle convection?? Energy balance of the planet??**

Dynamics and thermal evolution of the Earth

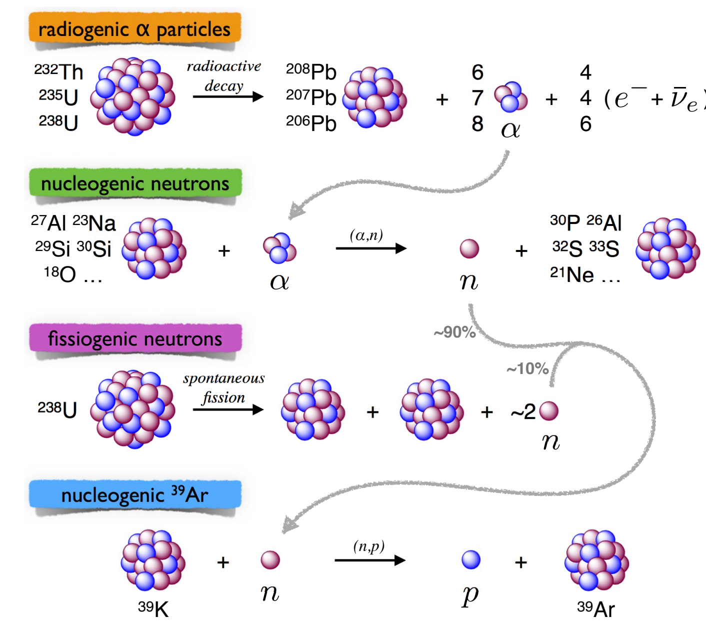


Sidenote: also GEONEUTRINOS

Underground production of noble gases



Calculating underground ^{39}Ar production



- Natural α particle energy spectrum:
  decay chains and spontaneous fission,
  inputs from NuDat (www.nndc.bnl.gov/nudat2)

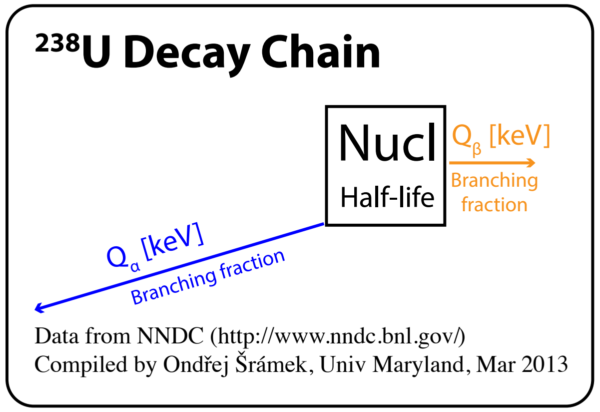
- Slowing and stopping of α particles:
  stopping power from SRIM-2013.00 (www.srim.org)

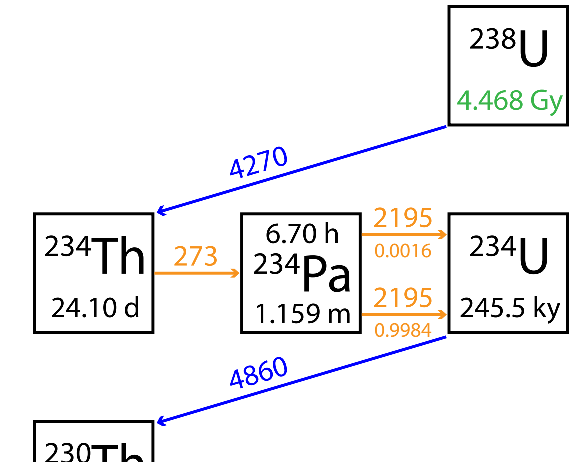
- Fast neutrons from (α,n) reactions on light targets:
  (α,n) cross sections from TALYS version 1.6 (www.talys.eu)

- ^{39}Ar from ^{39}K(n,p)^{39}Ar:
  using MCNP6, a general-purpose Monte Carlo N-Particle transport code (mcnp.lanl.gov)

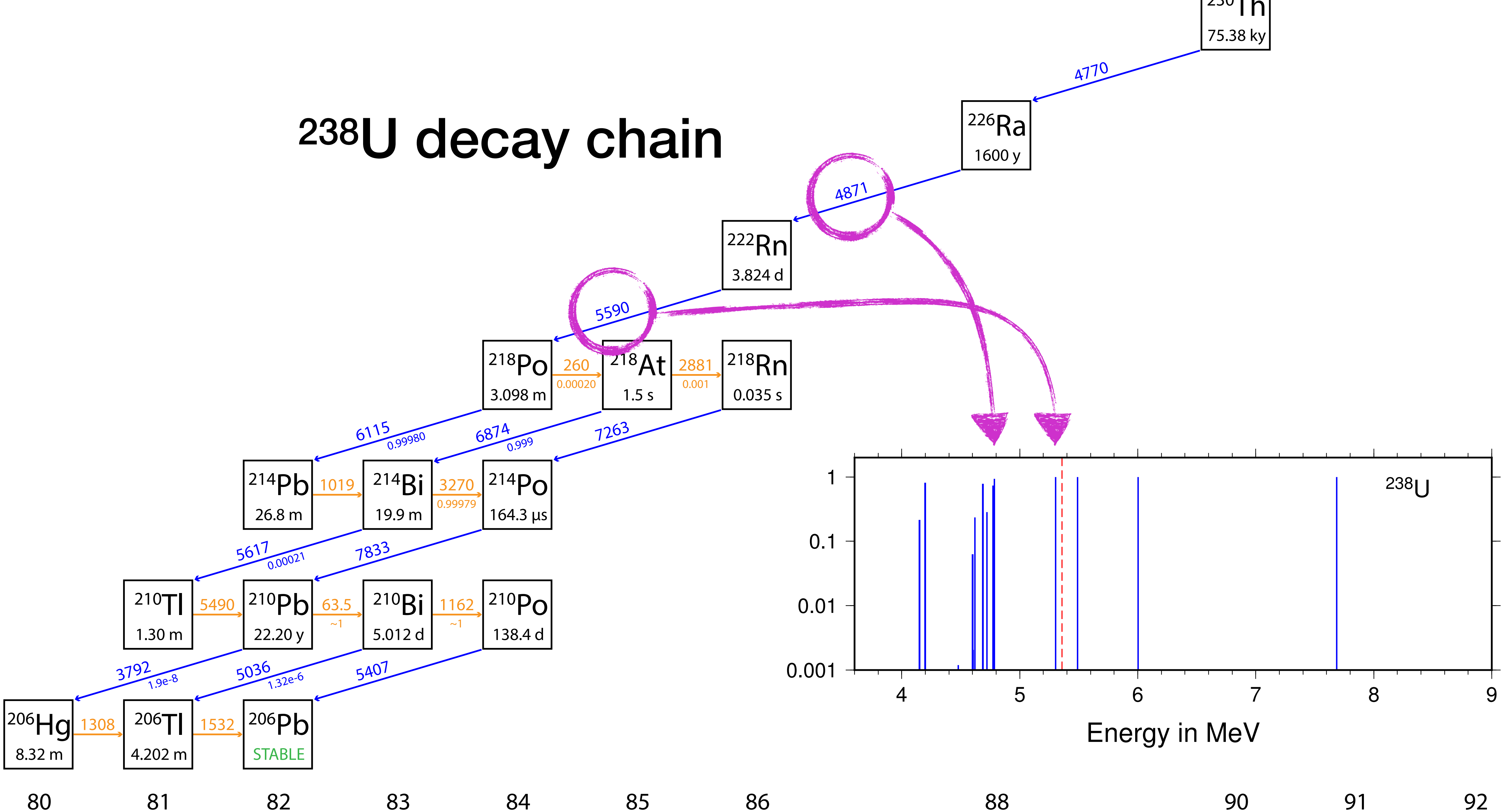
Šrámek, Stevens, McDonough, Mukhopadhyay, Peterson 2017
Geochim.Cosmochim.Acta doi:10.1016/j.gca.2016.09.040 (arXiv:1509.07436)

Natural α production

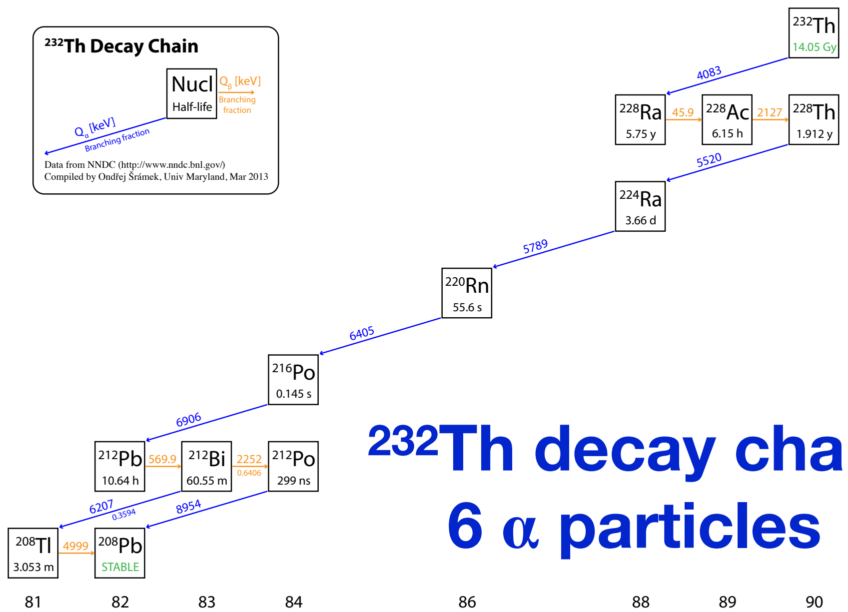




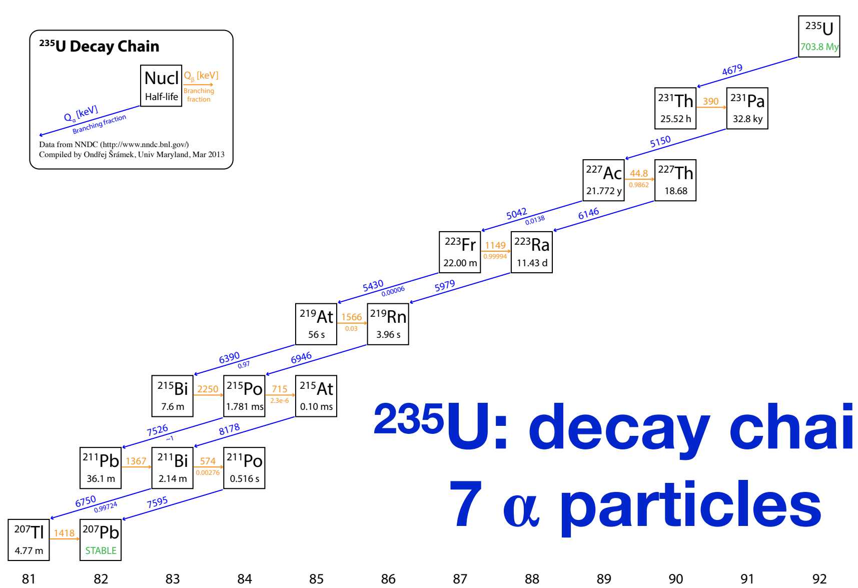
^{238}U decay chain



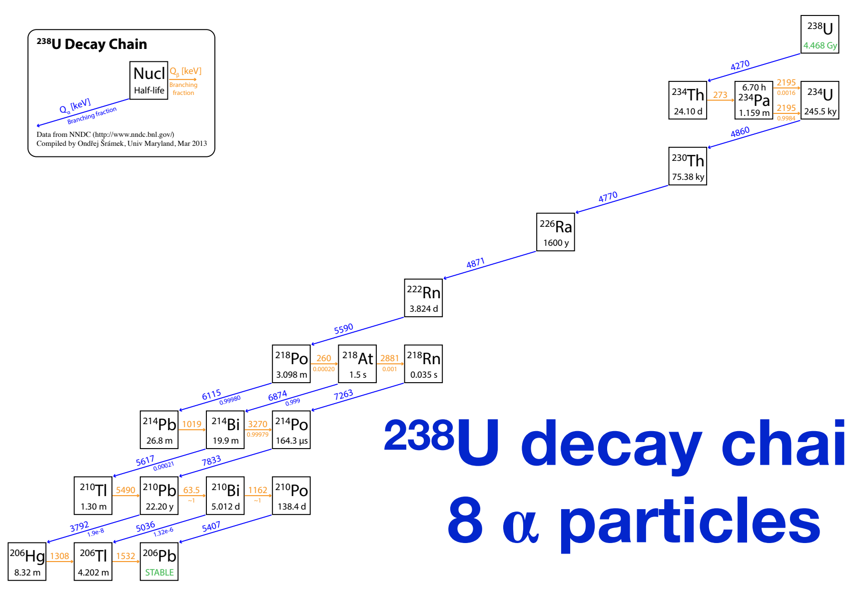
α energy spectrum



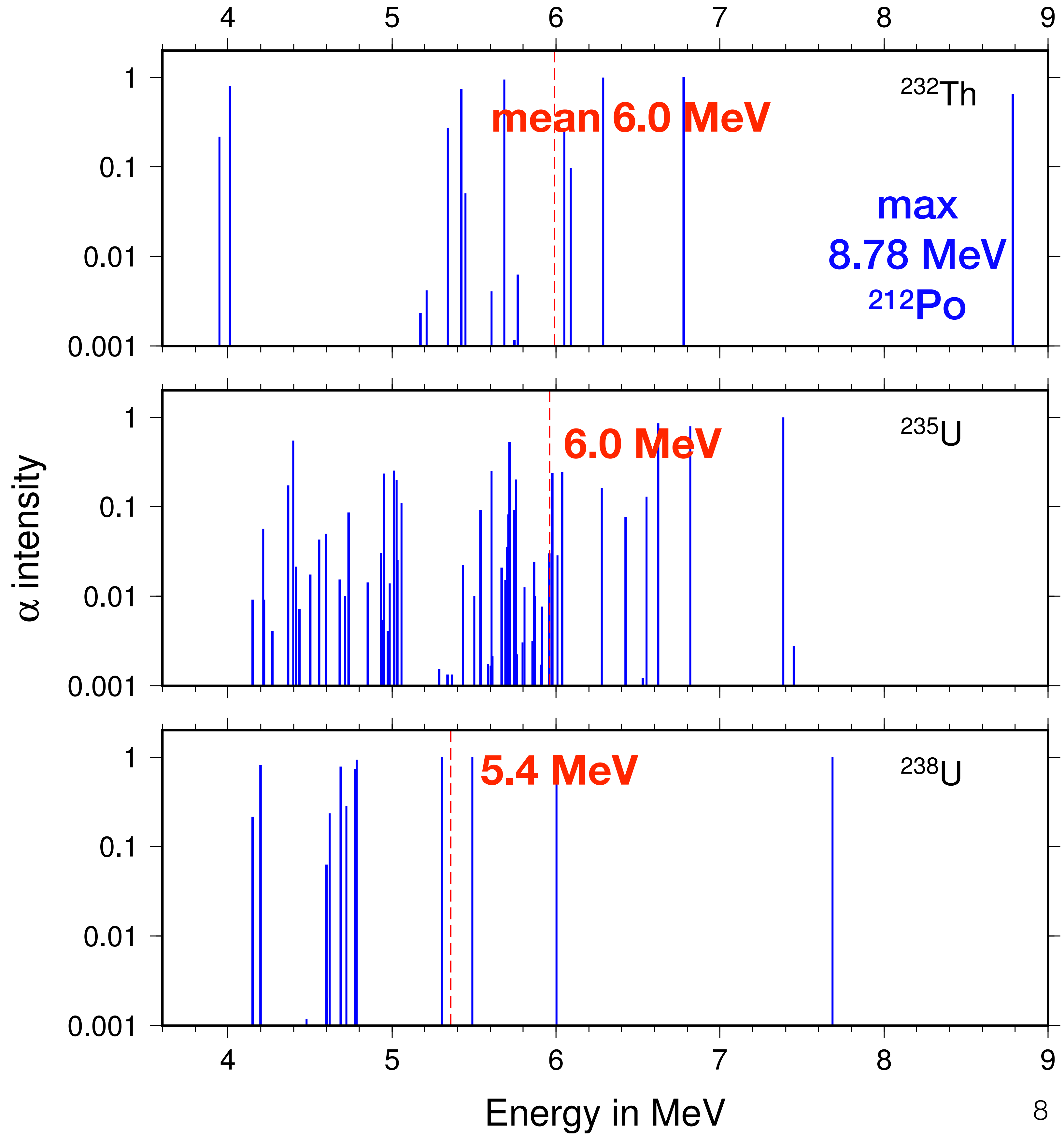
^{232}Th decay chain
6 α particles



^{235}U: decay chain
7 α particles



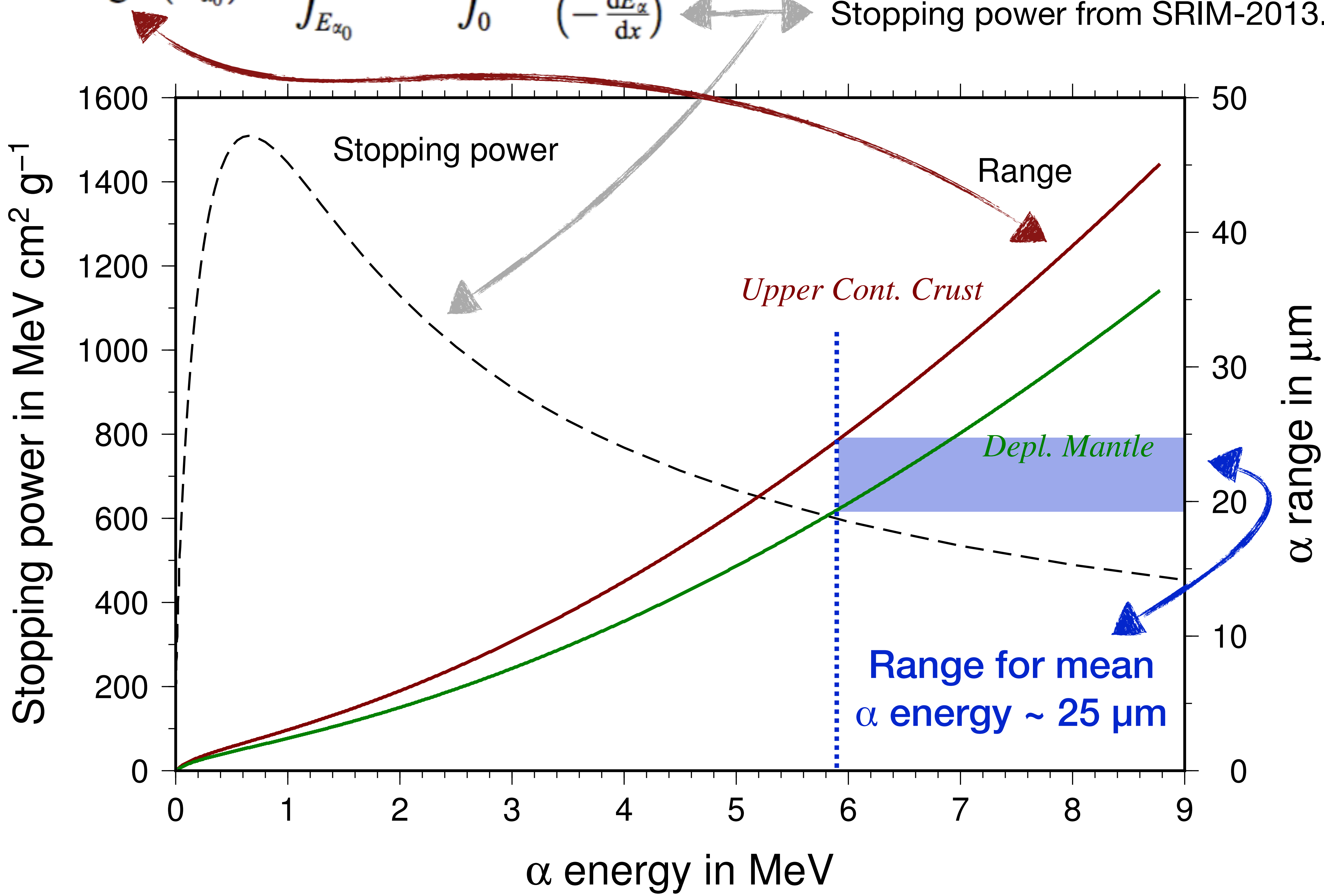
^{238}U decay chain
8 α particles

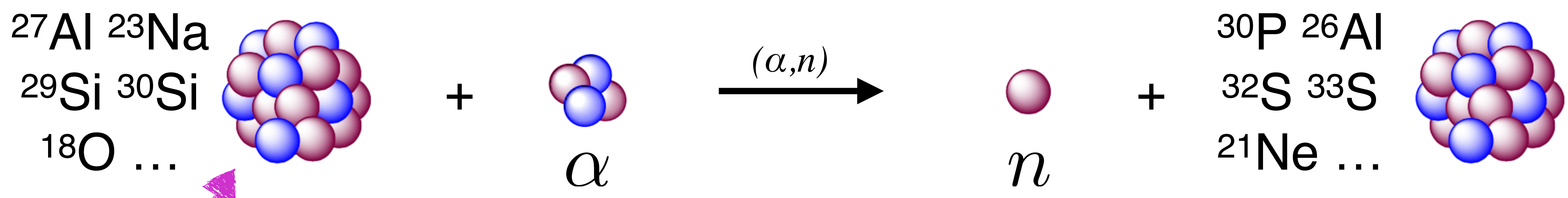


Travel distance of α particle in rock

$$\text{Range}\ (E_{\alpha_0}) = \int_{E_{\alpha_0}}^{0} \mathrm{d}x = \int_{0}^{E_{\alpha_0}} \frac{\mathrm{d}E_\alpha}{\left(-\frac{\mathrm{d}E_\alpha}{\mathrm{d}x}\right)}$$

Stopping power from SRIM-2013.00





(α,n) targets

Choice based on:
- natural abundance
- (α,n) cross section

Target	Product	Q	E_{th}	V_C
^{27}Al	^{30}P* → ^{30}Si	−2.6425	3.0345	6.8012
^{23}Na	^{26}Al* → ^{26}Mg	−2.9659	3.4823	5.9577
^{29}Si	^{32}S	−1.5258	1.7365	7.2107
^{30}Si	^{33}S	−3.4933	3.9598	7.1571
^{18}O	^{21}Ne	−0.6961	0.851	4.5626
^{26}Mg	^{29}Si	0.0341	–	6.3298
^{25}Mg	^{28}Si	2.6536	–	6.3838
^{19}F	^{22}Na* → ^{22}Ne	−1.9513	2.3624	5.0754
^{17}O	^{20}Ne	0.5867	–	4.6168
^{56}Fe	^{59}Ni* → ^{59}Co	−5.0961	5.4607	11.5272
^{41}K	^{44}Sc* → ^{44}Ca	−3.3894	3.7206	9.0555
^{48}Ti	^{51}Cr* → ^{51}V	−2.6853	2.9094	10.1118
^{13}C	^{16}O	2.2156	–	3.656
^{44}Ca	^{47}Ti	−2.1825	2.3812	9.3791

Energy threshold
of endothermic reactions

$$E_{th} = -\frac{m_1 + m_2}{m_2} Q$$

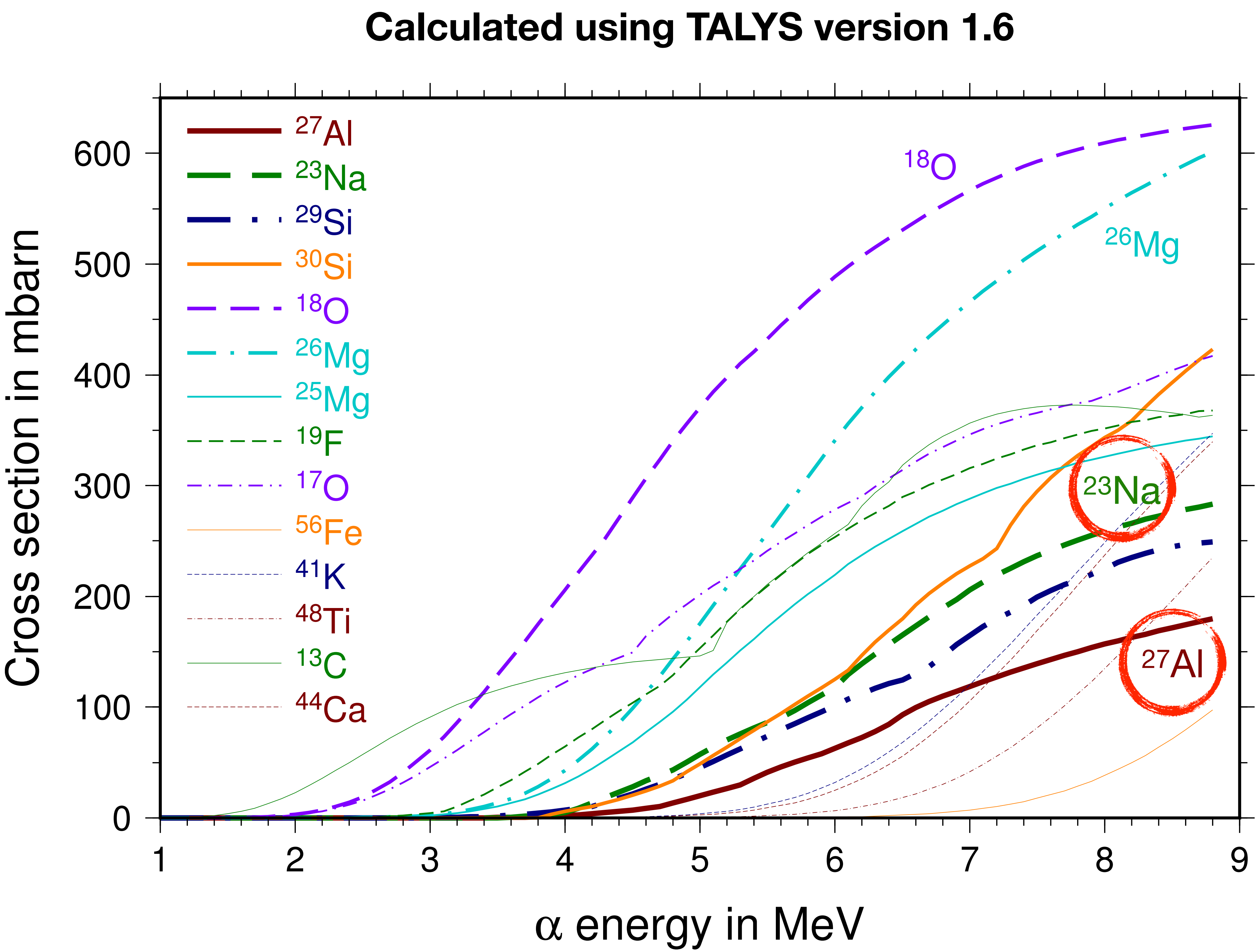
Coulomb barrier
EM repulsion between α & target
Restrictive for high *Z* targets.

$$V_C = \frac{1}{4\pi\epsilon_0}\frac{q_1 q_2}{r} = 1.4400\,\frac{Z_1 Z_2}{R_{int}[\mathrm{fm}]}\ \mathrm{MeV}$$

$$= \frac{1.4400\, Z_1 Z_2}{1.2(A_1^{1/3} + A_2^{1/3})}\ \mathrm{MeV},$$

⇒ Strong energy dependence of (α,n) cross sections

Cross section of (α,n) reaction



Only cross section comparison

Does not account for targets' natural abundance

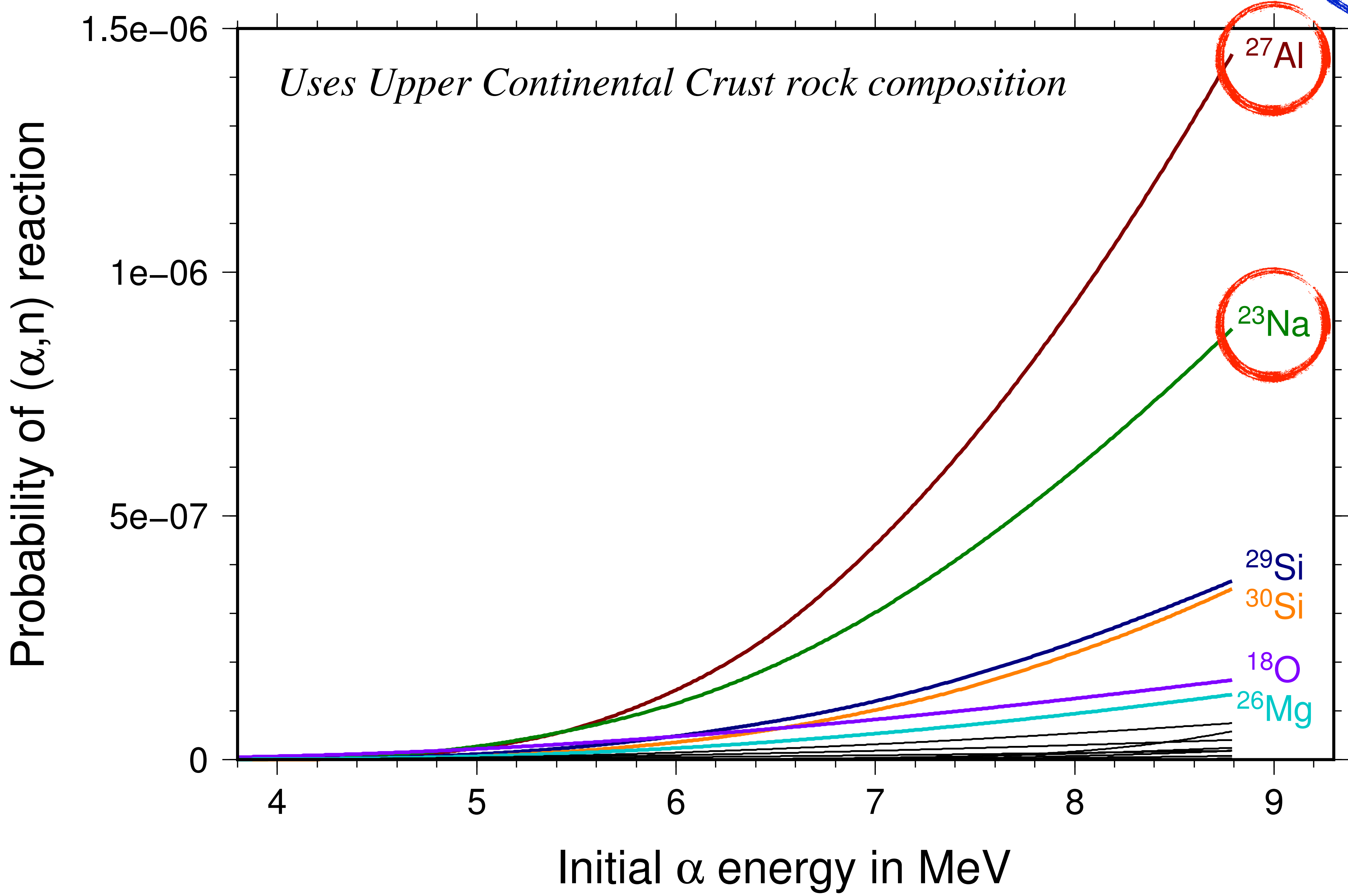
(α,n) neutron production

Thick target neutron production function
Probability that α particle of an initial energy participates in (α,n)

$$P_i(E_{\alpha_0}) = N_i \int_{E_{\alpha_0}}^{0} \frac{\sigma^i_{\alpha,n}(E_\alpha)}{\frac{dE_\alpha}{dx}} dE_\alpha$$

Atomic density of nuclide in rock

Accounts for rock composition



Neutron yield and neutron energy

Following α-decays
down the decay chain

Neutron yield

Neutrons per decay of 1 atom
of parent radionuclide

$$Y^i_{\alpha,n} = \sum_{k=1}^{\text{decays}} b_k \sum_{l=1}^{\text{levels}} f_{kl} P_i(E_{kl})$$

branching α intensity

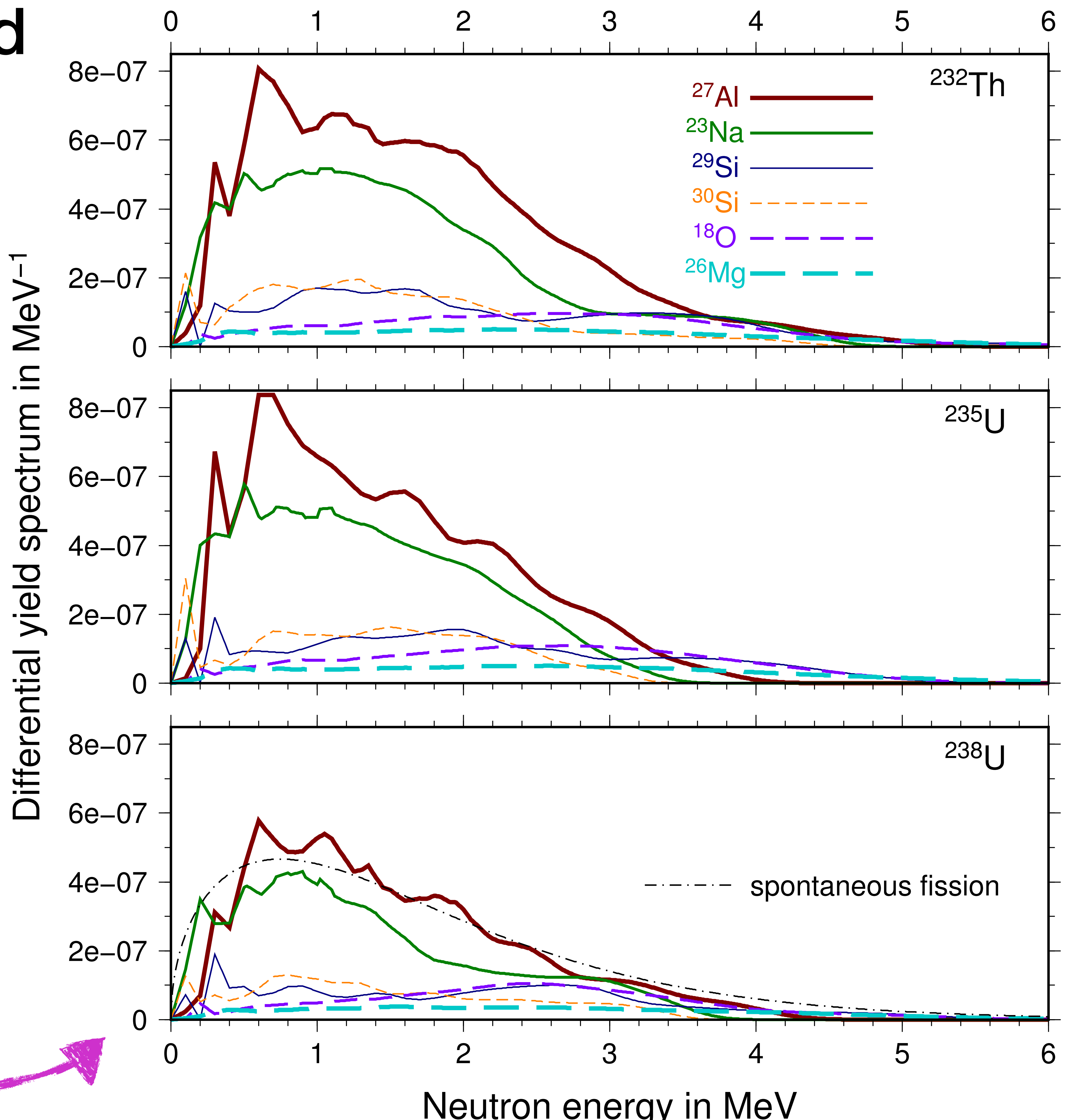
Differential neutron production function

$$P_i(E_{\alpha_0}) = N_i \int_{E_{\alpha_0}}^{0} \frac{\sigma^i_{\alpha,n}(E_\alpha)}{\frac{\mathrm{d}E_\alpha}{\mathrm{d}x}} \mathrm{d}E_\alpha$$

$$\frac{\mathrm{d}P_i}{\mathrm{d}E_n}(E_{\alpha_0}, E_n) = N_i \int_{E_{\alpha_0}}^{0} \frac{\frac{\mathrm{d}\sigma^i_{\alpha,n}}{\mathrm{d}E_n}(E_\alpha, E_n)}{\frac{\mathrm{d}E_\alpha}{\mathrm{d}x}} \mathrm{d}E_\alpha$$

Neutron yield spectrum

$$\frac{\mathrm{d}Y^i_{\alpha,n}}{\mathrm{d}E_n} = \dots$$

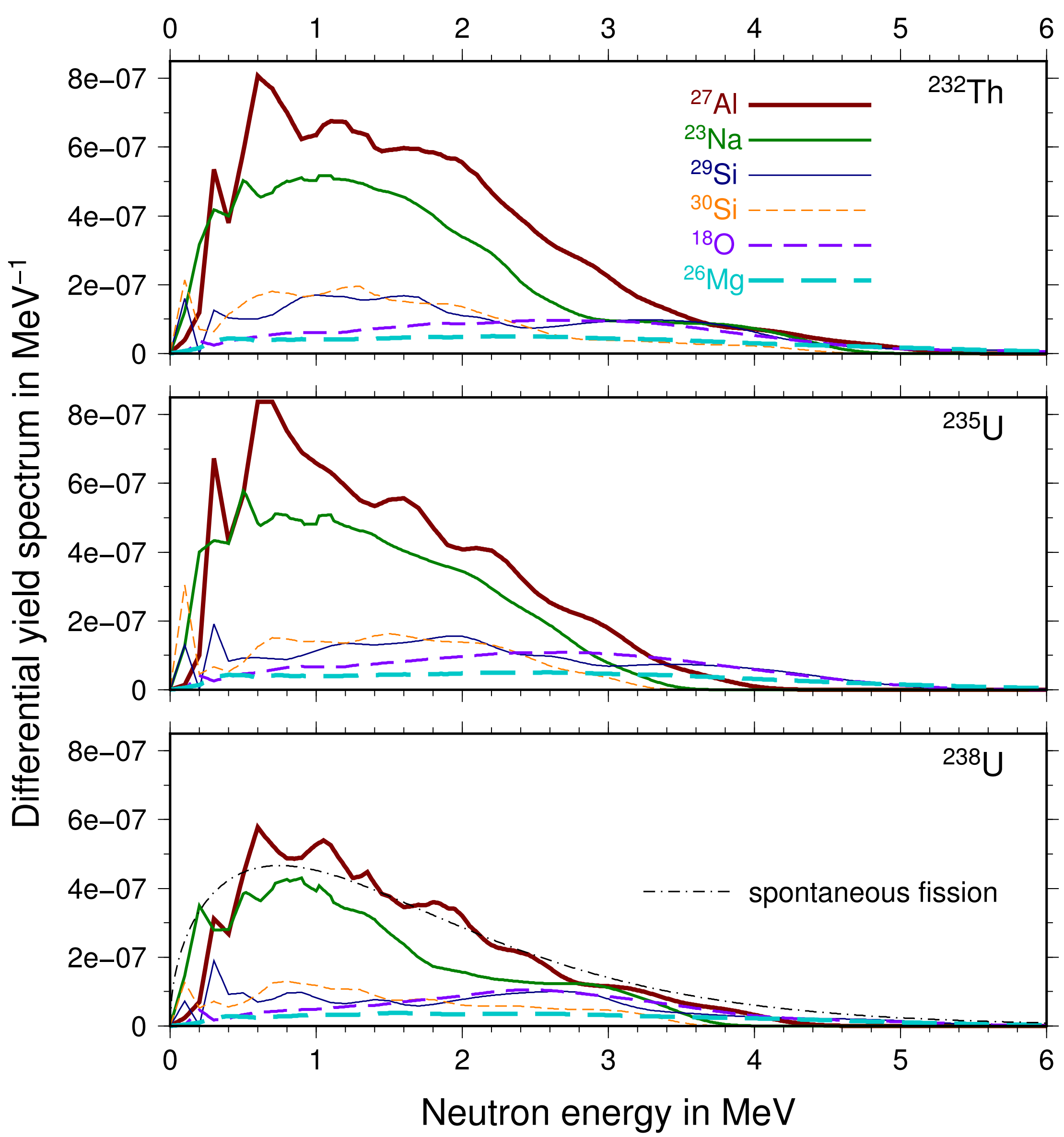


$^{39}K(n,p)^{39}Ar$

exothermic reaction
Q = 217.6 keV

^{39}K is 93.3% of natural potassium, there is ~2 wt% of K in shallow continental crust (global average)

Neutron yield spectrum + rock composition



mcnp

^{39}Ar yield per decay of 1 atom of ^{232}Th / ^{235}U / ^{238}U

Results

Calculated with rock composition of Upper Continental Crust

Neutron yield per decay of 1 atom | **Neutron production rate per kg rock per year** | **^{39}Ar production rate per kg rock per year**

	Neutron yield (Y)			Neutron production rate (S_n)				^{39}Ar production rate ($S_{^{39}Ar}$)			
Target	^{232}Th	^{235}U	^{238}U	^{232}Th	^{235}U	^{238}U	Sum	^{232}Th	^{235}U	^{238}U	Sum
Upper Continental Crust											
^{27}Al	1.69e−6	1.48e−6	1.05e−6	2265.0	72.8	1107.0	3445.0	5.15	0.12	2.00	7.27
^{23}Na	1.15e−6	1.07e−6	7.66e−7	1547.0	52.5	805.6	2405.0	2.99	0.07	1.22	4.27
^{29}Si	4.74e−7	4.32e−7	3.13e−7	636.9	21.2	328.7	986.9	2.42	0.08	1.26	3.77
^{30}Si	4.09e−7	3.50e−7	2.53e−7	549.2	17.2	266.0	832.4	1.04	0.03	0.49	1.55
^{18}O	3.28e−7	3.51e−7	2.80e−7	441.4	17.2	294.2	752.8	2.30	0.09	1.41	3.80
^{26}Mg	2.01e−7	1.99e−7	1.43e−7	270.0	9.8	150.1	429.8	1.43	0.05	0.76	2.24
^{25}Mg	1.18e−7	1.19e−7	8.53e−8	158.1	5.8	89.8	253.7	1.00	0.04	0.59	1.64
^{19}F	6.95e−8	7.18e−8	5.36e−8	93.4	3.5	56.4	153.3	0.24	0.01	0.11	0.36
^{17}O	3.56e−8	3.77e−8	3.04e−8	47.9	1.8	31.9	81.6	0.27	0.01	0.17	0.46
^{56}Fe	3.86e−8	7.11e−9	9.45e−9	51.9	0.3	9.9	62.1	0.06	0.00	0.00	0.07
^{41}K	1.99e−8	1.14e−8	9.81e−9	26.7	0.6	10.3	37.6	0.06	0.00	0.02	0.08
^{48}Ti	1.30e−8	4.65e−9	4.92e−9	17.5	0.2	5.2	22.9	0.06	0.00	0.01	0.07
^{13}C	3.85e−9	4.12e−9	3.49e−9	5.2	0.2	3.7	9.0	0.04	0.00	0.03	0.08
^{44}Ca	5.97e−9	3.14e−9	2.82e−9	8.0	0.2	3.0	11.2	0.02	0.00	0.01	0.03
SF	2.35e−11	1.30e−10	1.14e−6	0.0	0.0	1198.0	1198.0	0.00	0.00	2.97	2.97
Total				6119	203	4360	10 680	17.1	0.49	11.1	28.7

~12% of fast neutrons from SF, the rest from (α,n)

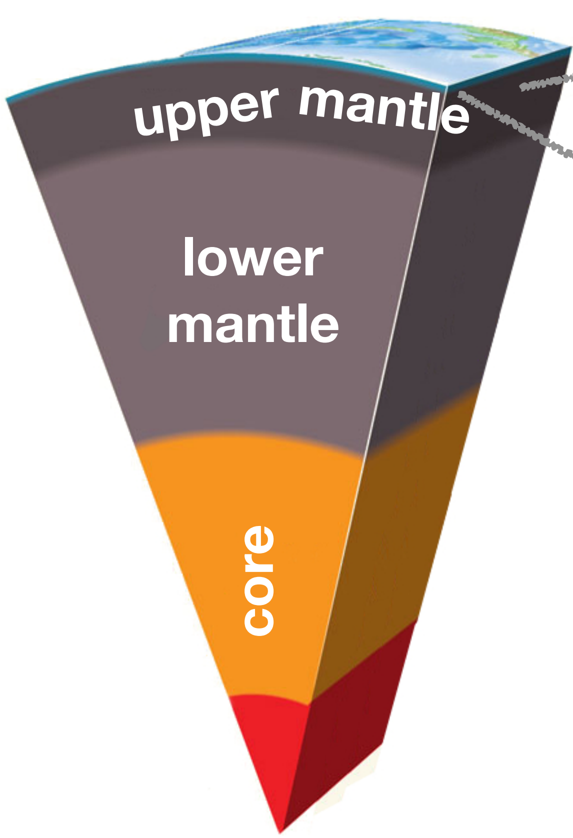
~11000 neutrons per year per kg rock

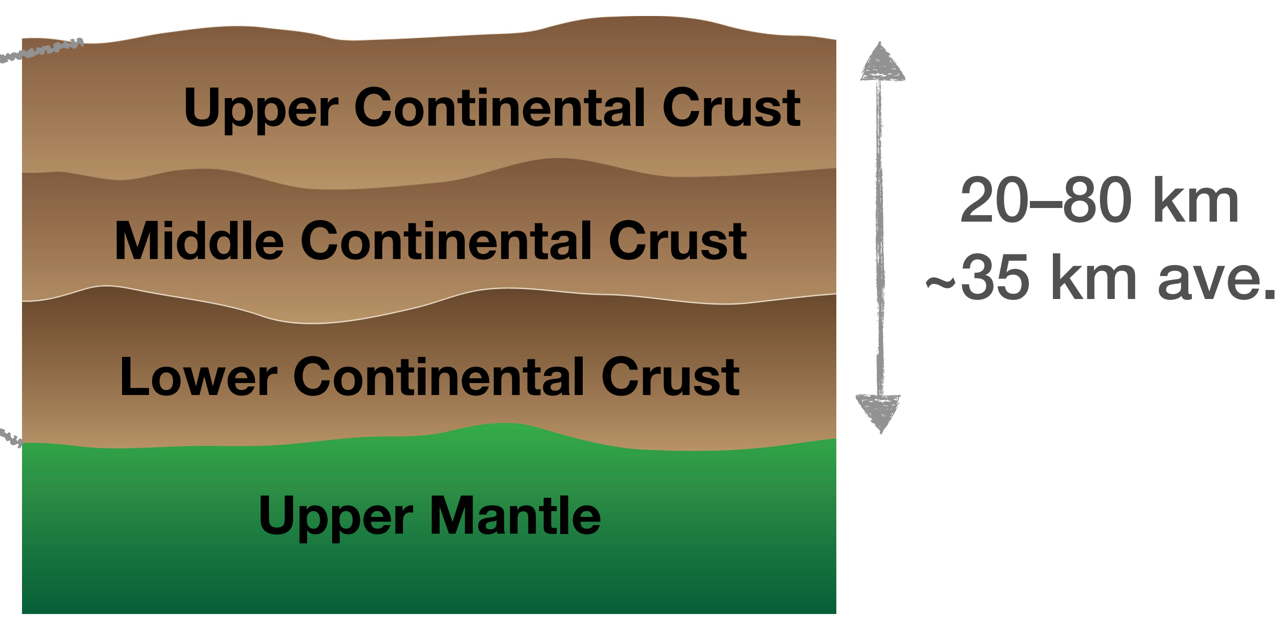
~30 ^{39}Ar atoms per year per kg rock

^{4}He, n, ^{21}Ne, ^{39}Ar production rates

Concentration of K, Th, U decreases with depth in the Earth

Weight fraction				Production rates, 1/(yr kg)			
K	Th	U	Composition	^{4}He	neutrons	^{21}Ne	^{39}Ar
2.32 %	10.5 ppm	2.7 ppm	Upper Continental Crust	1.64×10^{10}	10680	753	28.7
1.91 %	6.5 ppm	1.3 ppm	Middle Continental Crust	8.98×10^{9}	6114	416	13.9
0.51 %	1.2 ppm	0.2 ppm	Lower Continental Crust	1.53×10^{9}	1129	70.2	0.749
650 ppm	210 ppb	70 ppb	Bulk Oceanic Crust	3.79×10^{8}	260	15.8	0.0235
60 ppm	13.7 ppb	4.7 ppb	Depleted Upper Mantle	2.51×10^{7}	22.4	1.06	0.000257





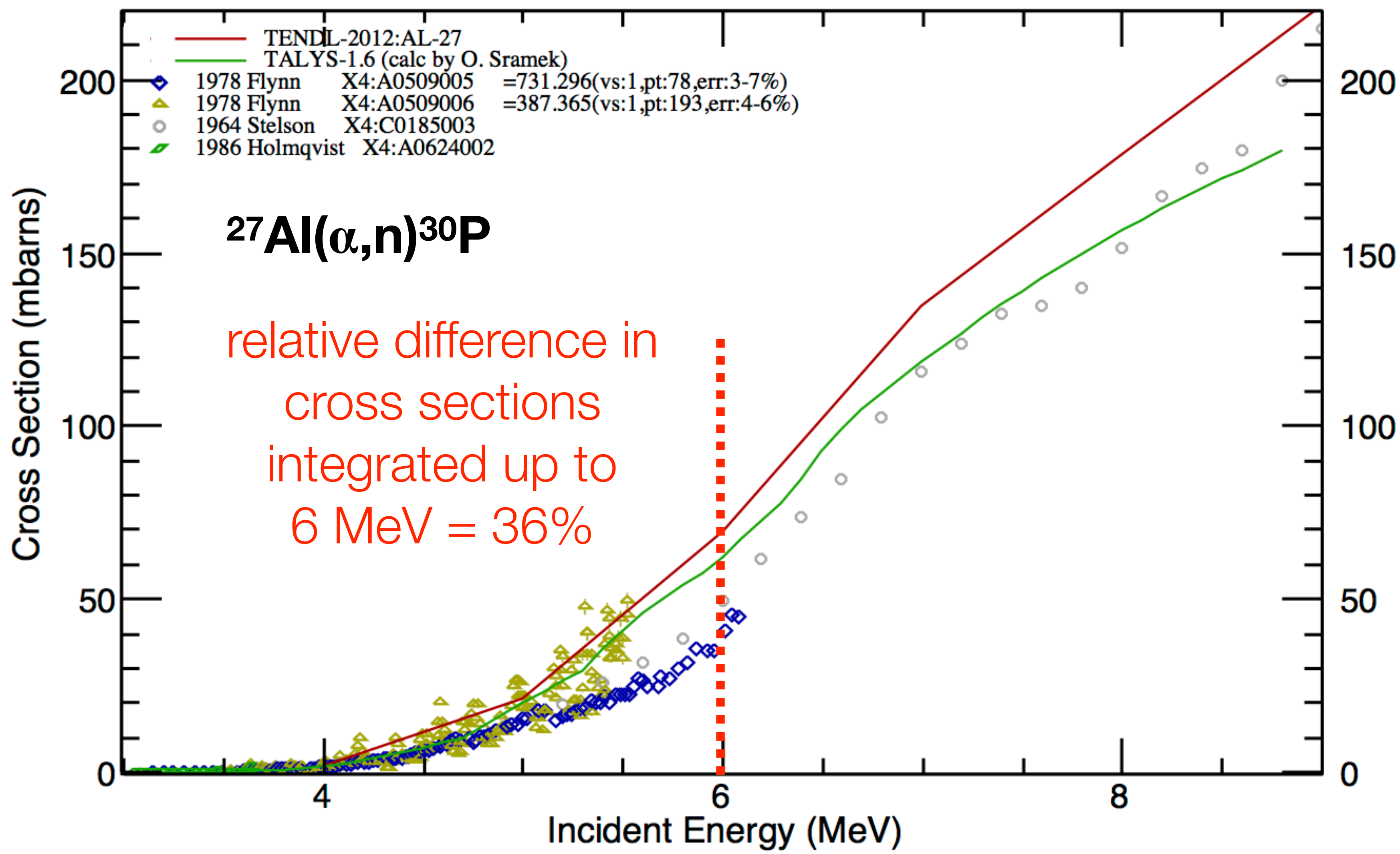
Rudnick & Gao 2014 doi:10.1016/B978-0-08-095975-7.00301-6
White & Klein 2014 doi:10.1016/B978-0-08-095975-7.00315-6
Salters & Stracke 2004 doi:10.1029/2003GC000597

Attempt at quantifying uncertainty

Assuming rock composition is known precisely (false…), what is uncertainty in the calculation?

- Half-lives, branching ratios, α intensities … relatively small uncertainty <1%
- Stopping power for α particles … ~3.5%
- Cross sections of (α,n), (n,p) … challenging to estimate

Cross sections from TALYS compared to experimental data from EXFOR database. Difference in integrated cross sections used as an estimate of uncertainty.
… not satisfying but perhaps best approach given the lack of consistent uncertainty estimates



Attempt at quantifying uncertainty

	Uncert. est. %	Neutron % contrib.	^{39}Ar % contrib.
Decay data, α production	< 1		
Stopping power	3.5		
^{27}Al(α, n) cross section	36	32	25
^{23}Na(α, n) cross section	7.7	23	15
^{29}Si(α, n) cross section	7.3	9.2	13
^{30}Si(α, n) cross section	20	7.8	5.4
^{18}O(α, n) cross section	17	7.0	13
^{26}Mg(α, n) cross section	$10^{\dagger}$	4.0	7.8
^{25}Mg(α, n) cross section	$10^{\dagger}$	2.4	5.7
Spontaneous fission	1	11	10
Overall (α, n), neutron production	12		
Overall (α, n), ^{39}Ar production	10		
^{39}K(n, p) cross section	28		
Neutron production calculation	13		
^{21}Ne production calculation	17		
^{39}Ar production calculation	30		

%

Comparison to other studies

			This study:
Mei et al. 2009 10.1016/j.nima.2009.04.032			
Granitic rock composition:	‣ neutron production rate	5500	5400 ± 700
Mei et al. 2010 10.1103/PhysRevC.81.055802			
	‣ ^{39}Ar production rate	7	16 ± 5
		disagreement	
Yokochi et al. 2012 10.1016/j.gca.2012.04.034			
Cont. crust composition:	‣ ^{39}Ar production rate	24	13 ± 3
Yokochi et al. 2014 10.1016/j.chemgeo.2014.02.004			
"Lava Creek Tuff" rock	‣ ^{39}Ar production rate	120 ± 60	140 ± 40
			91 ± 26

SLOWN2 code calculation, assumes mono-energetic 2 MeV neutrons

35% decrease

Units:
neutrons/(kg yr)
atoms/(kg yr)

Plug-in formulae

Example: α particles from ^{238}U decay, neutrons by ^{18}O(α,n)

$$S_n = \chi_n(^{18}\mathrm{O}, ^{238}\mathrm{U}) \times A_\mathrm{O} \times A_\mathrm{U} = 2.27 \times 10^8 \times 0.480 \times 2.7 \times 10^{-6} = 294 \text{ neutrons/(year kg-rock)}$$

$$S_{39\mathrm{Ar}} = \chi_{39\mathrm{Ar}}(^{18}\mathrm{O}, ^{238}\mathrm{U}) \times A_\mathrm{O} \times A_\mathrm{U} \times A_\mathrm{K} = 4.68 \times 10^7 \times 0.480 \times 2.7 \times 10^{-6} \times 0.0232 = 1.41 \text{ atoms/(year kg-rock)}$$

Table of coefficients χ_n and χ_{39Ar}

		Neutron production			^{39}Ar production		
	Chain	^{232}Th	^{235}U	^{238}U	^{232}Th	^{235}U	^{238}U
(α, n) target	A	Th	U	U	Th	U	U
^{27}Al	Al	2.65e+9	3.31e+8	5.03e+9	2.59e+8	2.36e+7	3.92e+8
^{23}Na	Na	6.07e+9	8.02e+8	1.23e+10	5.04e+8	4.46e+7	8.02e+8
^{29}Si	Si	1.95e+8	2.53e+7	3.91e+8	3.19e+7	4.05e+6	6.46e+7
^{30}Si	Si	1.68e+8	2.05e+7	3.17e+8	1.37e+7	1.35e+6	2.51e+7
^{18}O	O	8.77e+7	1.33e+7	2.27e+8	1.97e+7	2.89e+6	4.68e+7
^{26}Mg	Mg	1.72e+9	2.41e+8	3.72e+9	3.92e+8	5.43e+7	8.13e+8
^{25}Mg	Mg	1.01e+9	1.44e+8	2.22e+9	2.75e+8	4.04e+7	6.33e+8
^{19}F	F	1.60e+10	2.34e+9	3.75e+10	1.78e+9	2.06e+8	3.17e+9
^{17}O	O	9.50e+6	1.43e+6	2.47e+7	2.34e+6	3.39e+5	5.70e+6
^{56}Fe	Fe	1.28e+8	3.35e+6	9.55e+7	6.81e+6	2.53e+4	1.62e+6
^{41}K	K	1.10e+8	8.92e+6	1.64e+8	1.06e+7	4.72e+5	1.22e+7
^{48}Ti	Ti	4.35e+8	2.20e+7	5.00e+8	5.88e+7	2.29e+6	5.89e+7
^{13}C	C	3.61e+8	5.48e+7	9.96e+8	1.31e+8	2.10e+7	4.02e+8
^{44}Ca	Ca	2.98e+7	2.22e+6	4.29e+7	3.96e+6	2.13e+5	4.80e+6
SF	1	3.01e+3	2.37e+3	4.44e+8	2.88e+2	3.09e+2	4.73e+7

☞ Python script at http://tinyurl.com/argon39

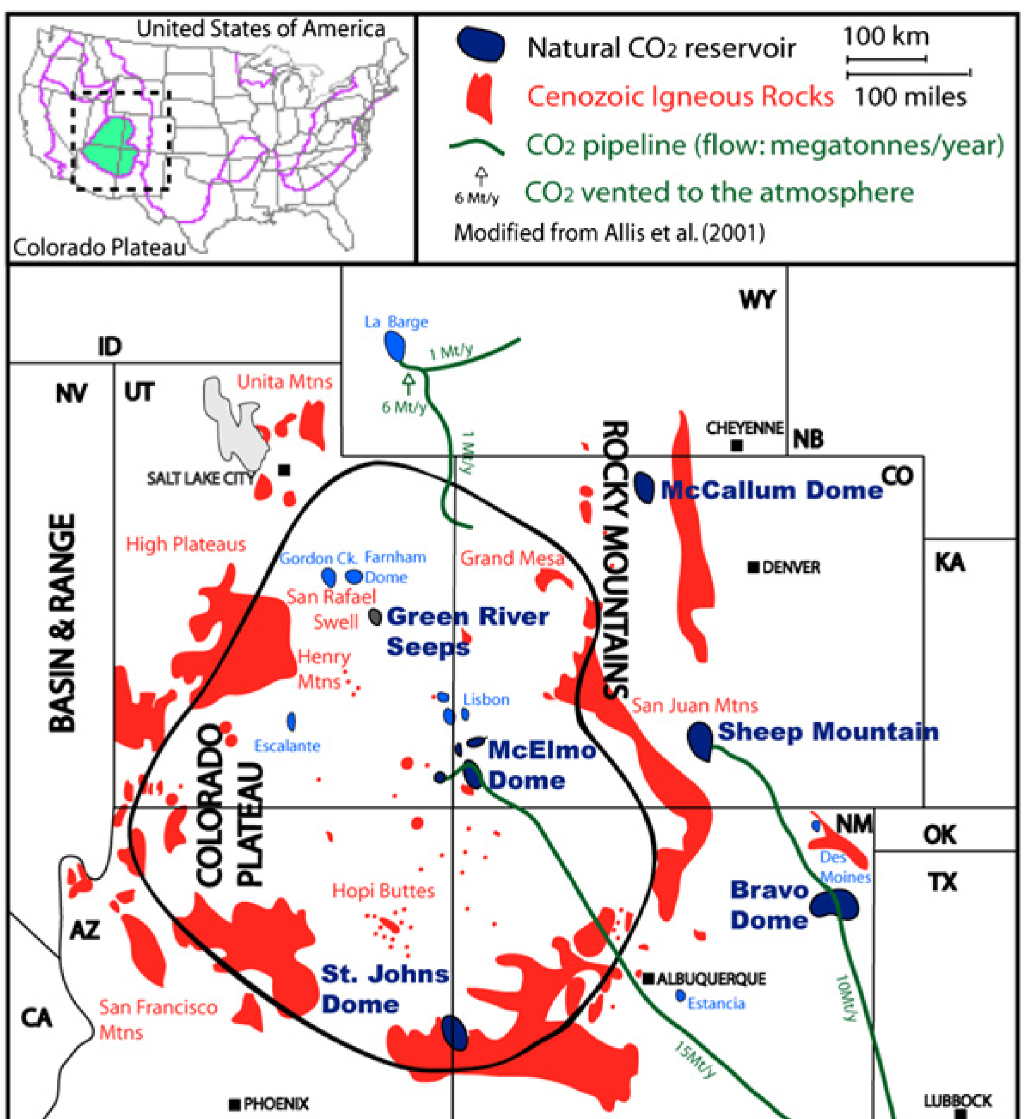
Origin of Colorado Plateau CO_2

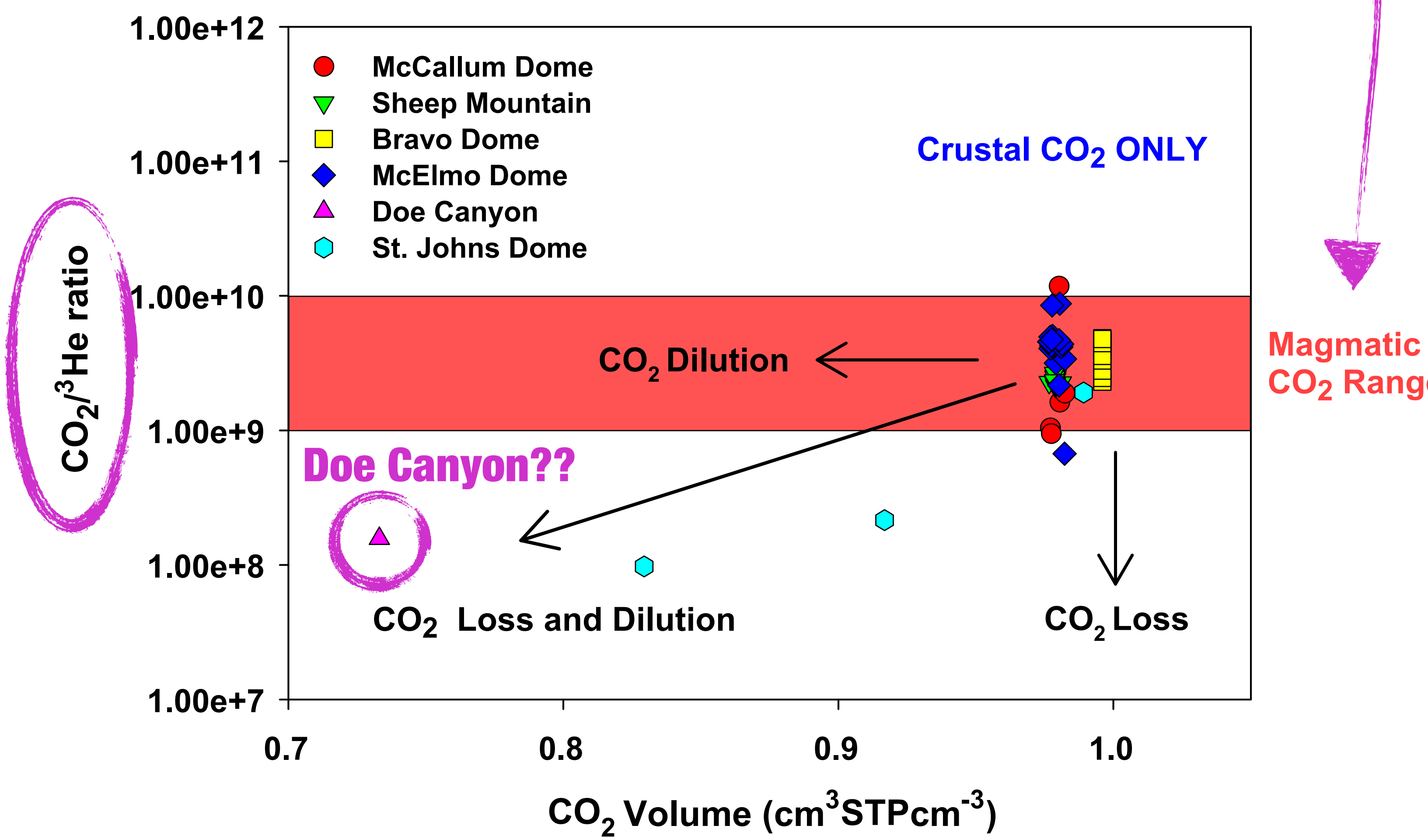
- methanogenesis
- oil field biodegradation
- kerogene decarboxylation
- hydrocarbon oxidation
- decarbonation of marine carbonates
- degassing of magmatic bodies

Largely magmatic origin

⟹ Mantle signature in accompanying gases

low $CO_2/^3He$





Gilfillan et al. 2008 10.1016/j.gca.2007.10.009

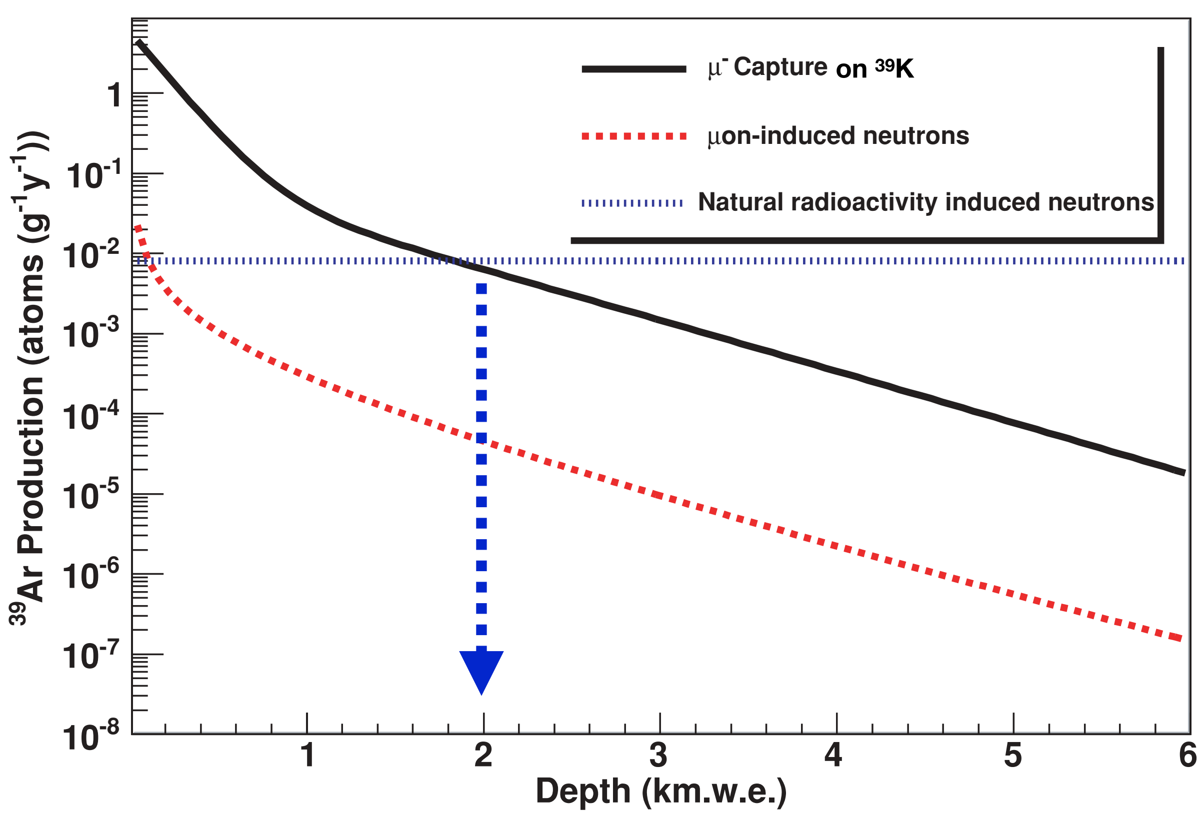
Doe Canyon CO_2 well gas

- Gas from deep CO_2 wells, spec. Doe Canyon, shows low level of ^{39}Ar
- ^{39}Ar activity a factor of 1400 ± 200 below atmospheric

DarkSide-50: 2016 10.1103/PhysRevD.93.081101

? Underground nucleogenic production in rock with sufficiently low K, Th, U concentration…?

Gas sequestered underground (negligible cosmogenic replenishment) with limited exchange…?

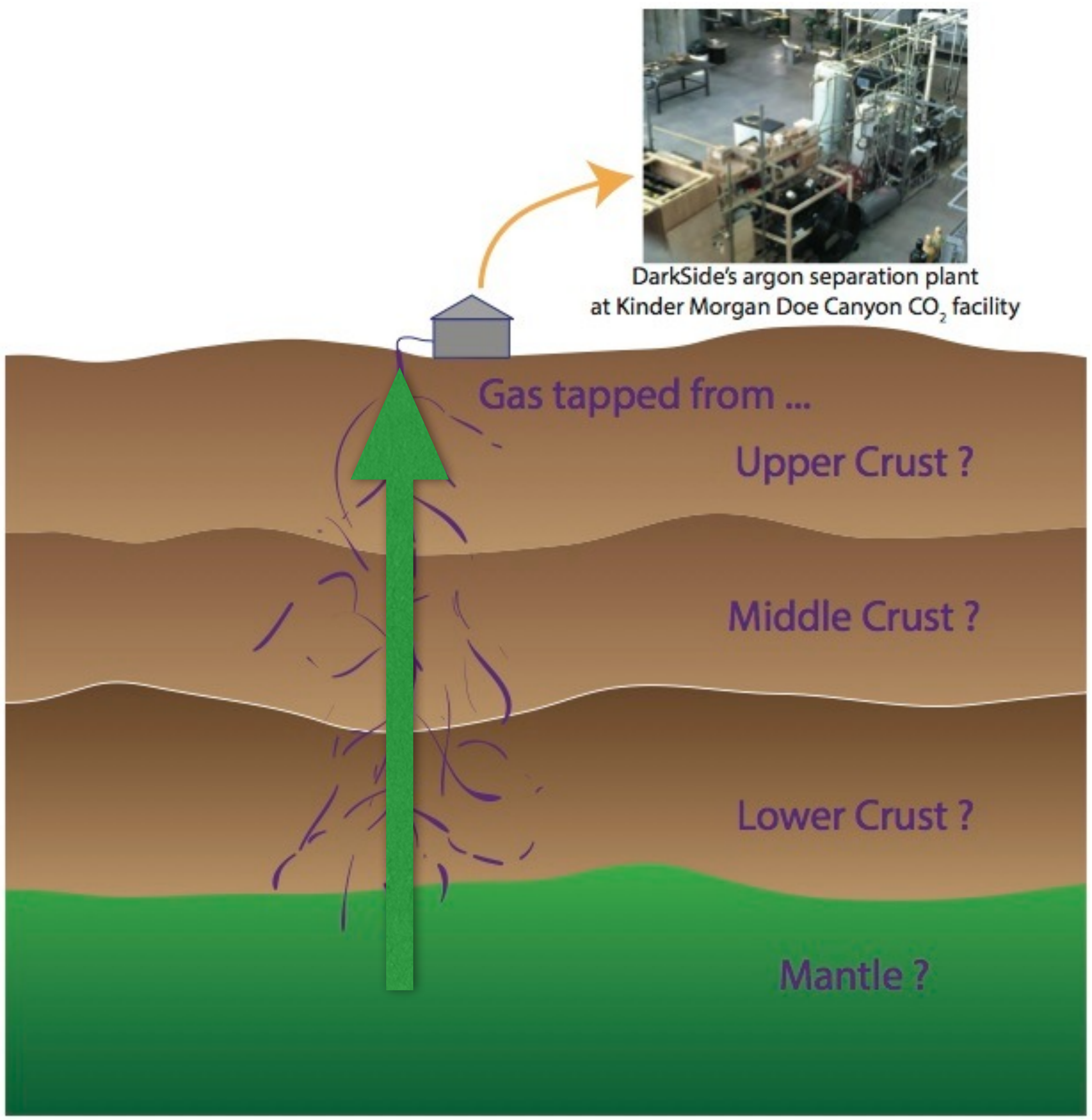


At depths >2000 m.w.e. nucleogenic ^{39}Ar production dominates

from Mei et al. 2010 10.1103/PhysRevC.81.055802

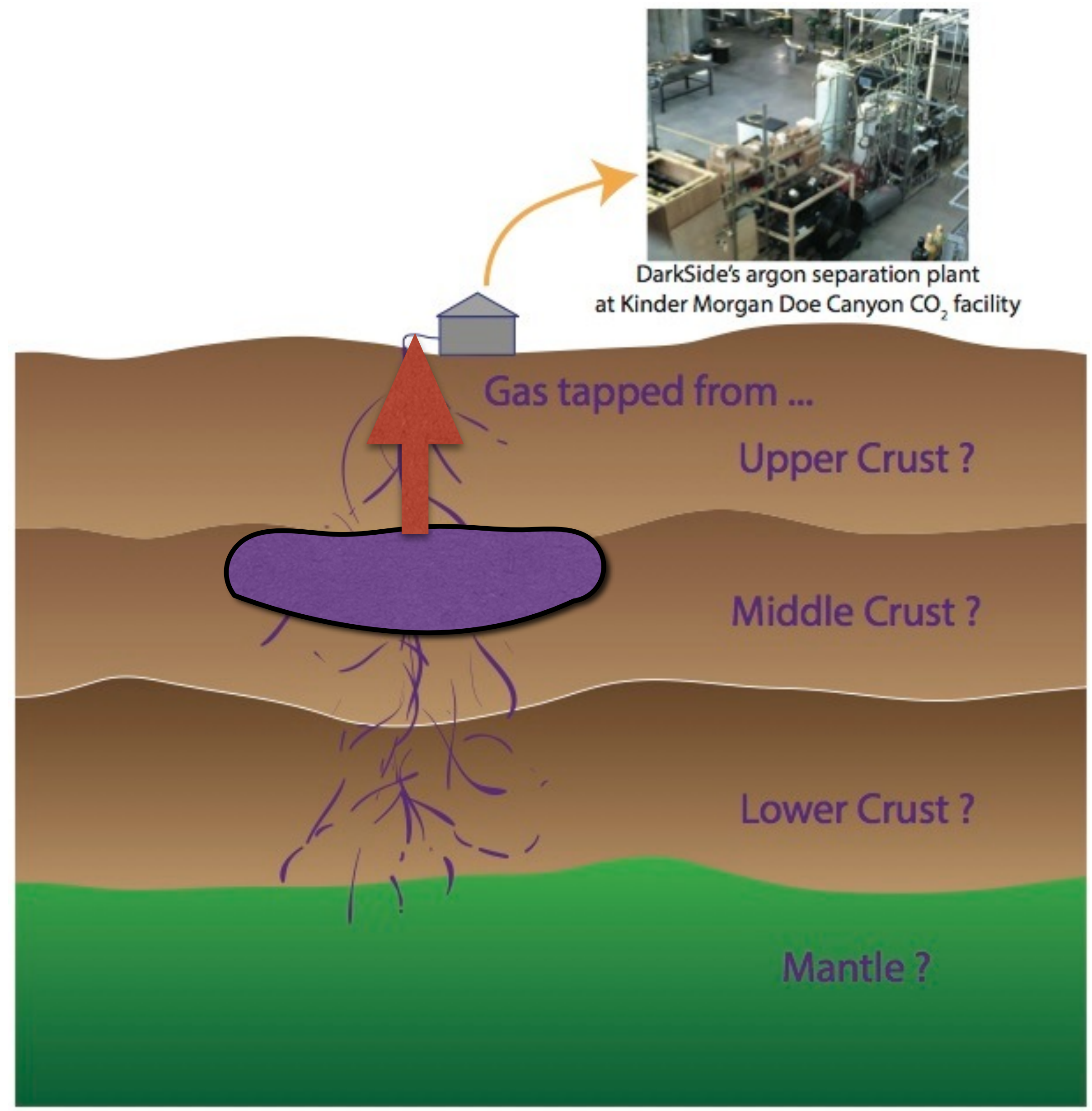
Doe Canyon CO_2 well gas

Message from the mantle?



Gas from low K, Th, U source rock?

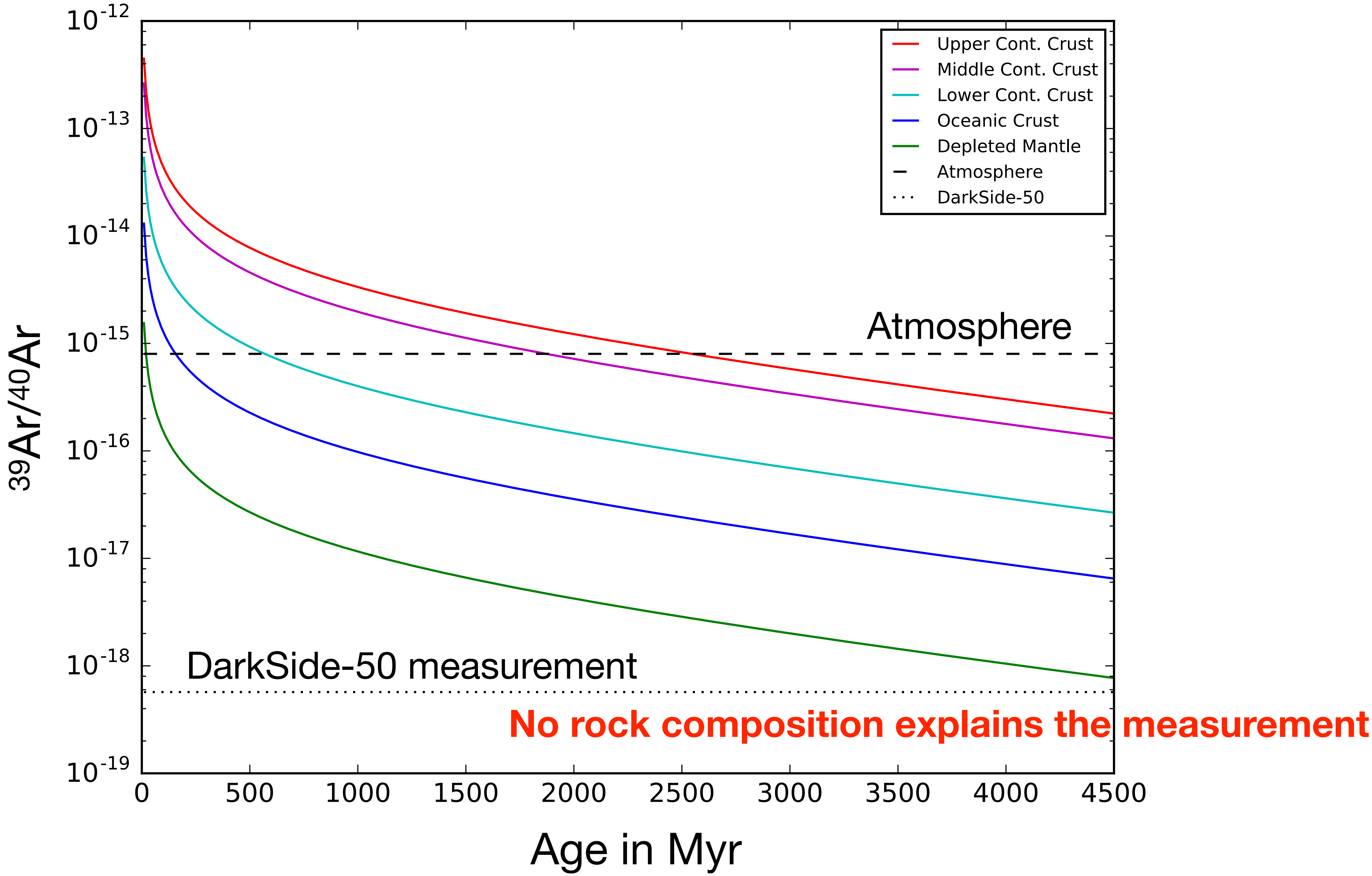
Or story of the crust?



Accumulation of gas in isolated reservoir in the crust?

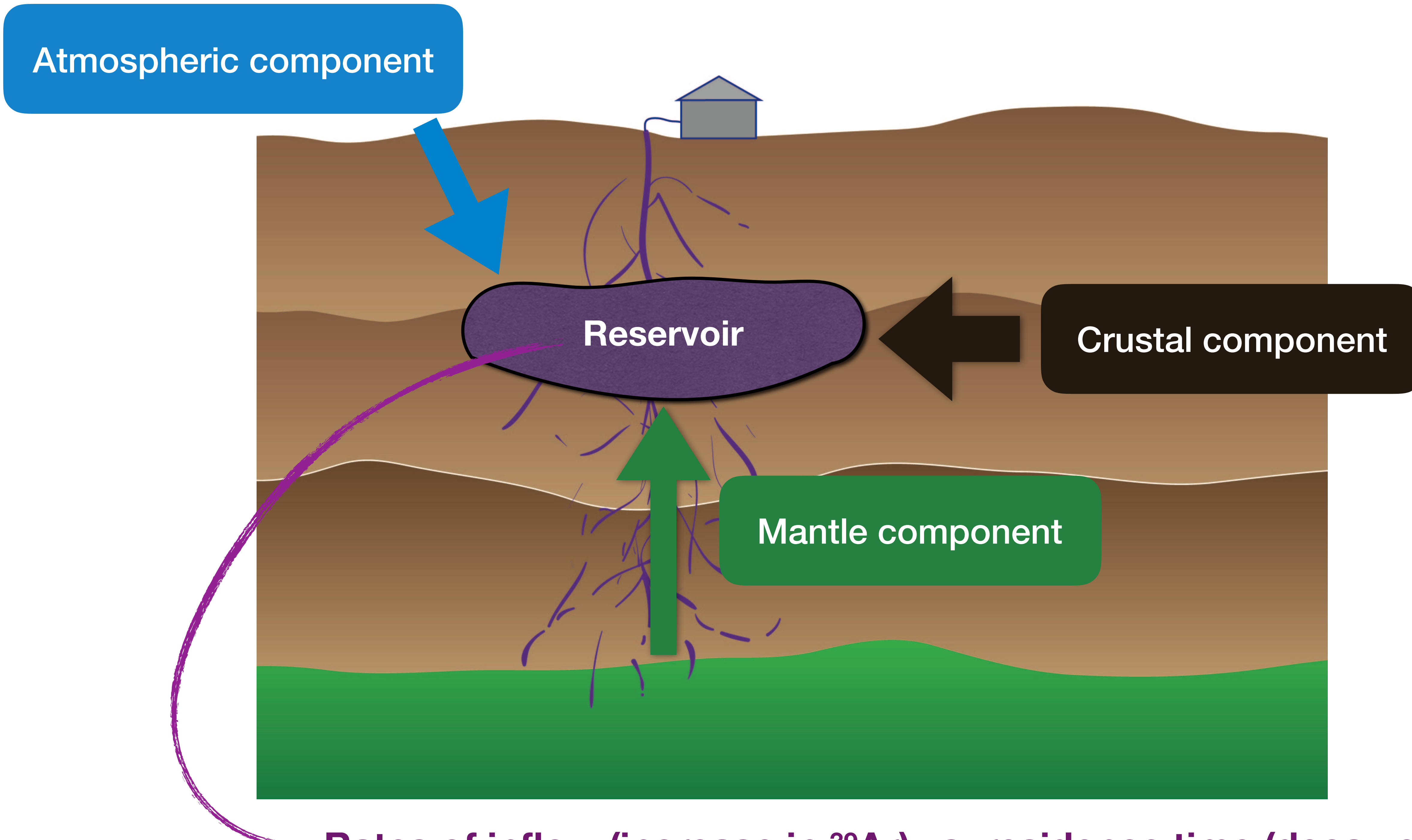
Predicting $^{39}Ar/^{40}Ar$ produced underground

Accumulation of ^{39}Ar and ^{40}Ar over time from initially degassed rock



How to explain anomalously low ^{39}Ar?

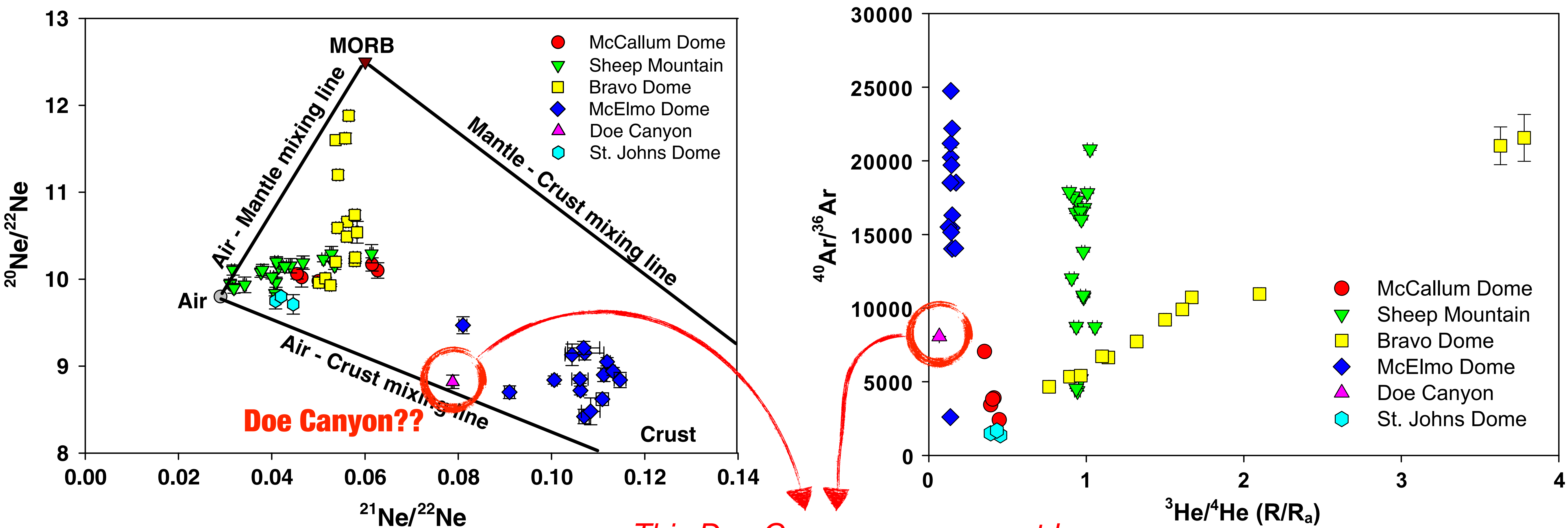
Argon sequestered at depth with no ^{39}Ar production nor influx →
^{39}Ar activity lowered by a factor of 1400 in **2800 years** (~10.5 half-lives with $t_{1/2}$ = 269 yr)



Rates of inflow (increase in ^{39}Ar) vs. residence time (decay of ^{39}Ar)

Noble gas isotopic constraints

Gilfillan et al. 2008 10.1016/j.gca.2007.10.009



This Doe Canyon gas may not be representative of DarkSide gas!

^{20}Ne, ^{21}Ne, ^{22}Ne nucleogenic

Well defined end-member ratios for air, crust, mantle

^{3}He, ^{36}Ar primordial
^{4}He, ^{40}Ar radiogenic

Noble gas isotopes can provide some clues.

Need measurements of actual DarkSide gas.

Summary

- Calculation of underground nucleogenic production of ^{39}Ar: α particles from natural radioactivity, fast neutrons from (α,n) on light targets and from spontaneous fission, ^{39}Ar from ^{39}K(n,p)

- Evaluation for several representative rock compositions, plug-in formulae to evaluate for an arbitrary rock-like composition.

- Estimate of calculation uncertainty (30% for ^{39}Ar production rate) and comparison to previous results.

- Low ^{39}Ar level in Doe Canyon gas is puzzling – isotopic composition suggests both atmospheric and crustal contribution to the magmatic origin gas, low ^{39}Ar requires $\gg$3000 year isolation.

- Possible scenario: Gas of magmatic origin with mantle signature, mixes with crustal and atmospheric components, sequestered in an underground reservoir for sufficient time.

- Measurement of noble gas isotopic composition of Doe Canyon well gas is needed.

Thank you.