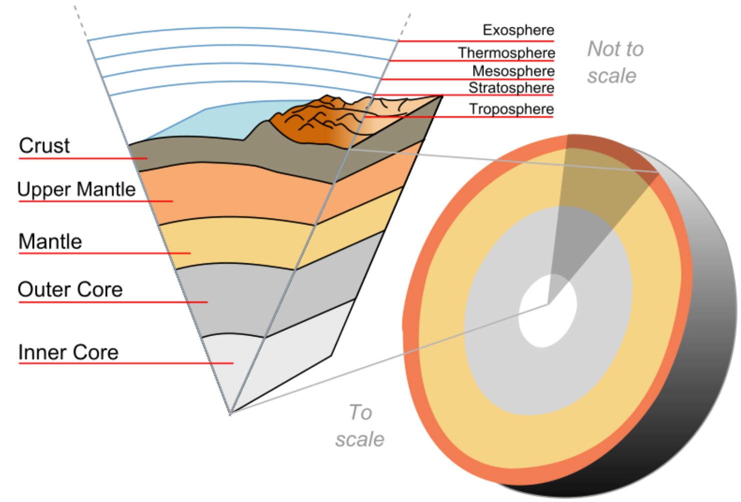
Tracing Time Scales of Fluid Residence and Migration in the Crust

R. Yokochi, N.C. Sturchio, R. Purtschert,
W. Jiang, G.-M. Yang, P. Mueller, Z.-T. Lu,
and B.M. Kennedy

The Crust



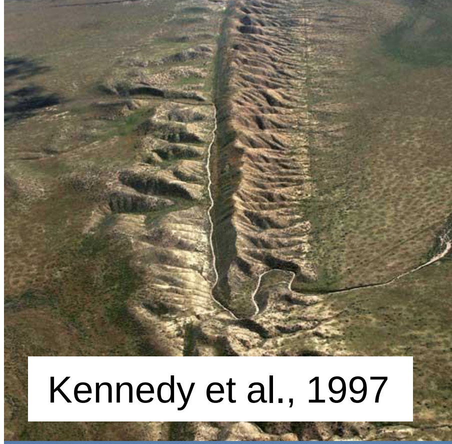
- The Crust?
  - Every naturally occurring solid you can see on Earth
  - 5-50km thick from the surface
  - Geological extract containing high concentration of U, Th, K (Production of ^{4}He, ^{21}Ne, ^{39}Ar, ^{40}Ar, ^{85}Kr, $^{131-136}Xe$)

- Fluids in the crust?
  - Groundwater (H_2O)
  - Natural gases/Petroleum (Hydrocarbons)
  - Volatiles associated with magmatism (CO_2-dominated)

Fluids in the crust

Evidence of interaction with the crust

- Gradual addition of radiogenic/nucleogenic isotopes as flow distance increases


Kennedy et al., 1997


Torgersen et al., 1989
Lehmann et al., 2003


Ballentine et al., 2005
Gilfillan et al., 2008; 2009


Sano & Wakita, 1985
Kennedy et al., 1987

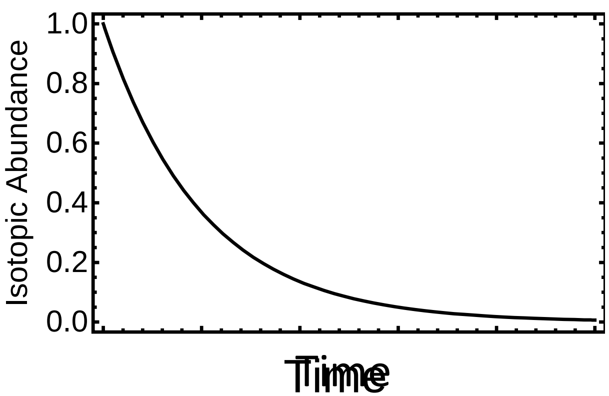
Pinti and Marty, 1995

Geochemical system in the crust

Initial

Beauty of
Noble gas radionuclides:
<u>Simplicity</u>

- Decay



Sample

Comoplicated …

Geochemical system in the crust

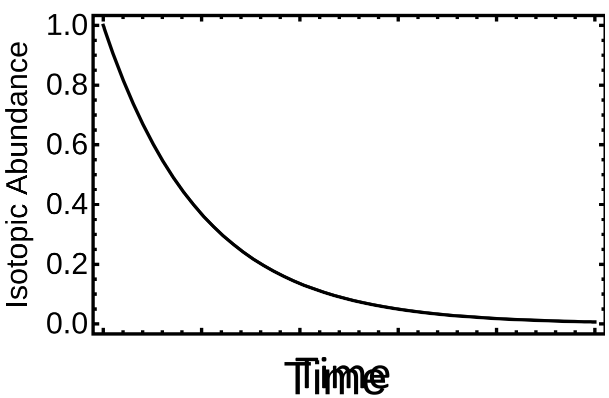
Initial

- Atmospheric
- Magmatic
- Other

Crustal

- Radiogenic
- Nucleogenic

- Decay



Surface

- Atmospheric contamination

Sample

Comoplicated …

Outline

1. Introduction: Fluids in the Crust

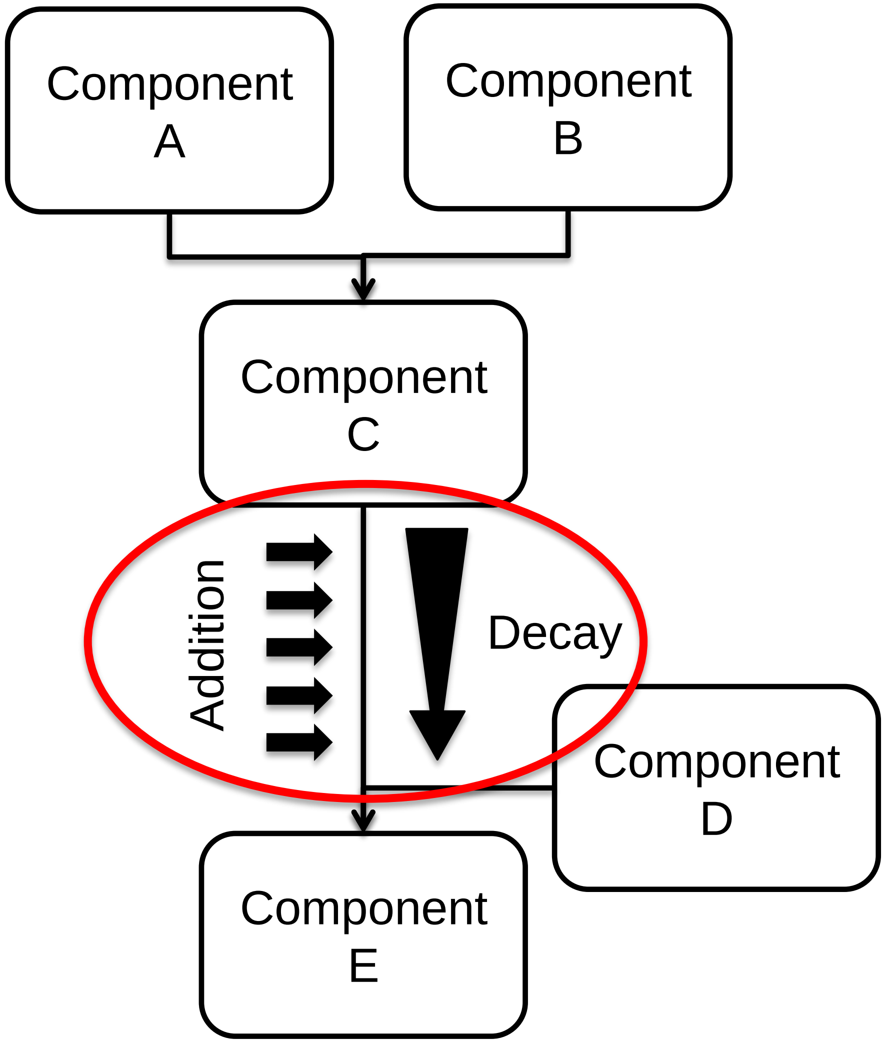
2. Theoretical analysis of complex geochemical system

1. Case study at Yellowstone National Park

Complex Geochemical System?

Processes

- Mixing
  - Episodic:
    - Magmatic volatiles
    - Atmosphere at different stages



Continuous addition of radioactive isotopes

Model:

Loss by decay

$$\frac{d\,{}^{i}C_{Tot}}{dt} = -\lambda_i \times {}^{i}C_{Tot} + \frac{d\,{}^{i}C_{R}}{dt}$$

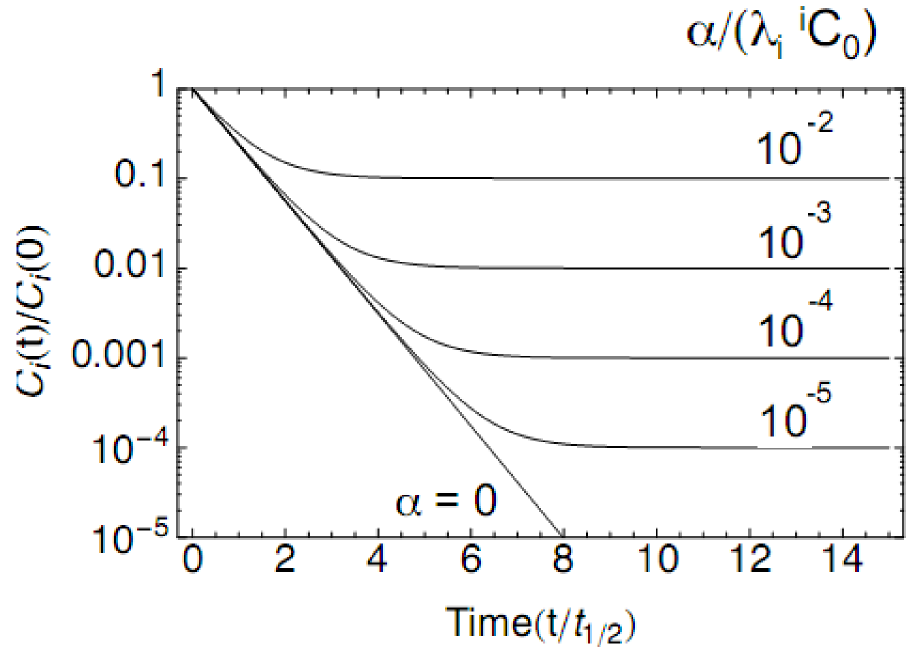
Addition
from the Crust

For $d^{i}C_{R}/dt = \alpha$ (constant):

$${}^{i}C(t) = {}^{i}C_0 \times e^{-\lambda_i t} + \frac{\alpha}{\lambda_i}(1 - e^{-\lambda_i t})$$

Supply-decay equilibrium

Modeled Isotopic abundance



Notes:

- Input rate determined once in equilibrium (α/λ)
- No direct implication on "Age"

Continuous addition of stable isotopes

Model:

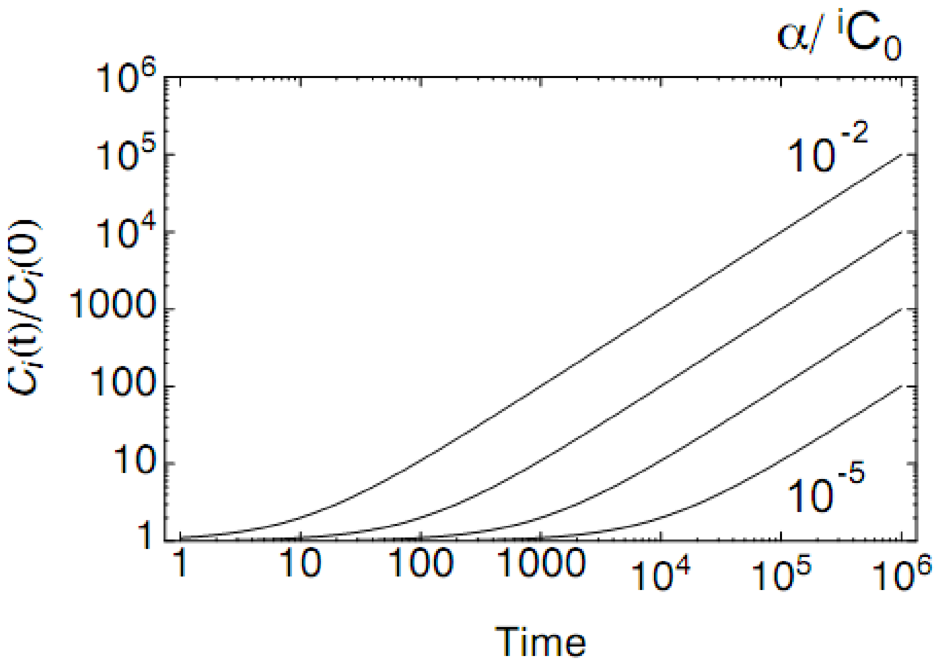
$$\frac{d\,{}^iC_{Tot}}{dt} = -\lambda \times {}^iC_{Tot} + \frac{d\,{}^iC_{R}}{dt}$$

Addition from the Crus

For $d^iC_R/dt = \alpha$ (constant):

$${}^iC(t) = {}^iC_0 + \alpha \times t$$

Modeled Isotopic abundance



Notes:

- Simple increase with time
- Input rate is unknown (assumed sometimes for ^4He)

Evolution of isotope ratios

Model

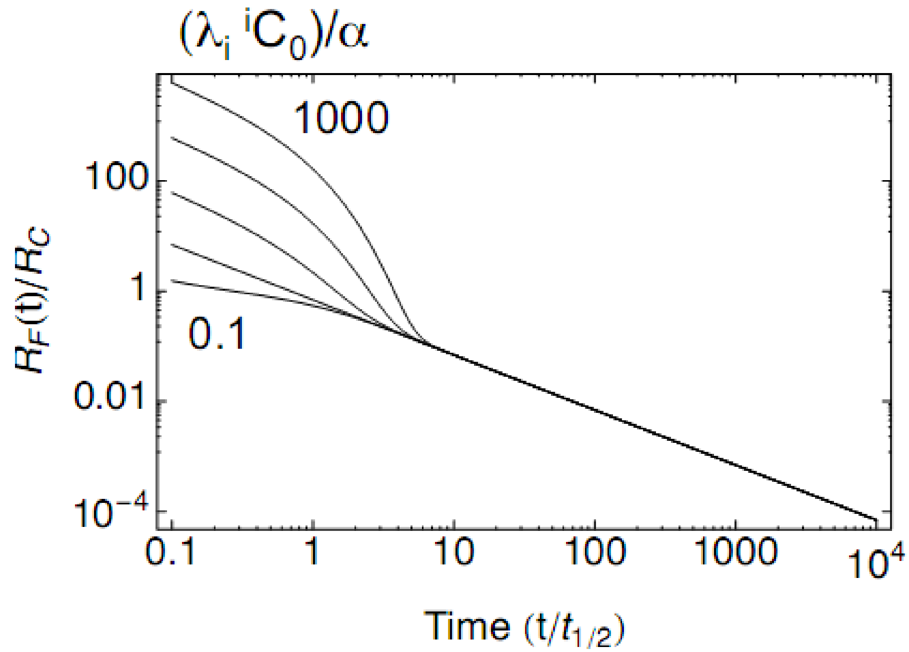
$$ {}^{ij}R_F(t) = \frac{{}^{i}C(t)}{{}^{j}C(t)} = \frac{{}^{i}C_0 \cdot e^{-\lambda_i t} + \frac{\alpha_i}{\lambda_i}(1 - e^{-\lambda_i t})}{{}^{j}C_0 + \alpha_j \cdot t} $$

$$ \rightarrow \frac{\alpha_i / \lambda_i}{{}^{j}C_0 + \alpha_j \cdot t} $$ Steady-state

$$ \rightarrow \frac{\alpha_i / \alpha_j}{\lambda_i \cdot t} $$ Initial correction

$$ \rightarrow \frac{{}^{ij}R_C}{\lambda_i \cdot t} $$ Common α

Modeled isotope ratios



Notes:

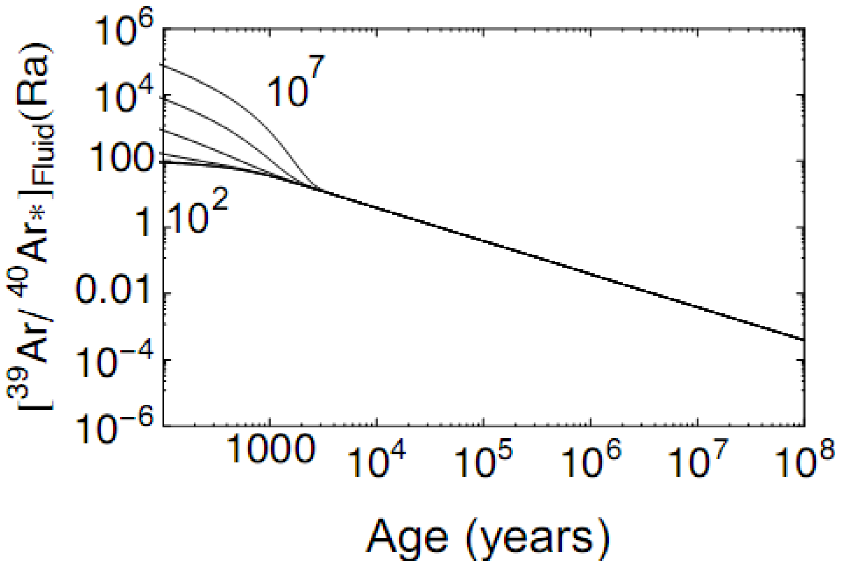
- Input rate from radionuclide
- Accumulation from stable isotope
- **New Chronometer!**

Applicable system

Isotopes

- Radioactive isotopes produced in-situ
  - ^{39}Ar by $^{39}K(n,p)^{39}Ar$
  - ^{85}Kr by ^{238}U fission
  - No significant ^{81}Kr
- Stable isotope
  - ^{4}He and ^{40}Ar
  - Concentrations of other non-radiogenic stable isotopes in rocks are low
- Similar α value: $^{39}Ar/^{40}Ar$

An example:



- Ar input from a reservoir rock with $^{39}Ar/^{40}Ar*$ ratio of 100 Ra.
- The ratio evolves independent of the input rate (for a constant $^{39}Ar/^{40}Ar*$ in the rock)

(GCA; Yokochi, Sturchio & Purtschert, 2012)

$^{39}Ar/^{40}Ar^*$ Chronometer

Details

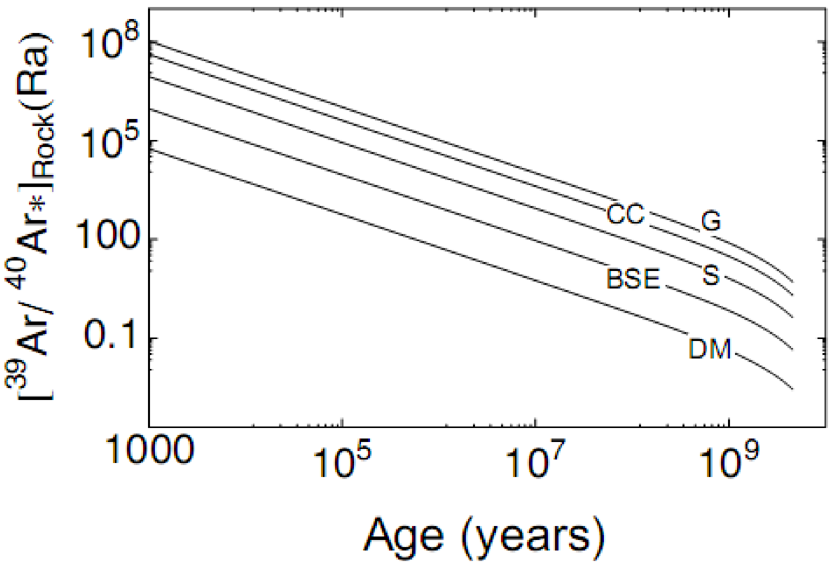
- Age

$$t_F \approx \frac{R_C}{R_F} \times \frac{1}{\lambda_{39}}$$

- Time range
  - Detectable $^{40}Ar/^{36}Ar$ anomaly relative to initial
  - Detectable amount of ^{39}Ar
  - Up to a few Myr (>>1800 yrs)

Difficulties+

Closed system Estimate



- Deviation associated with gas loss
- Production rate?
- Extent of source rock?

(GCA; Yokochi, Sturchio & Purtschert, 2012)

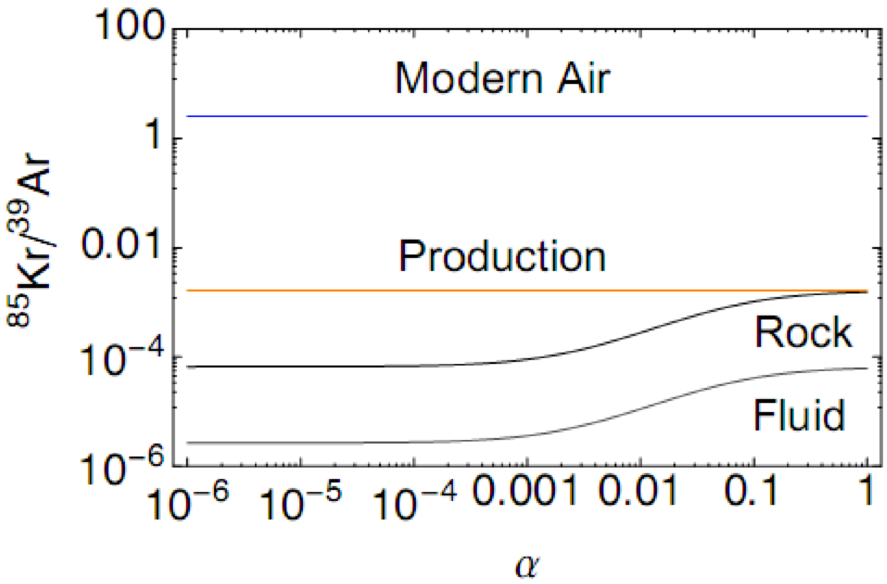
Krypton-85

Is subsurface ^{85}Kr significant?

- Production Rates
  - ^{85}Kr: 2.5-8 ×10^{-4} atoms/g/yr
  - ^{39}Ar: 0.04-0.9 atoms/g/yr

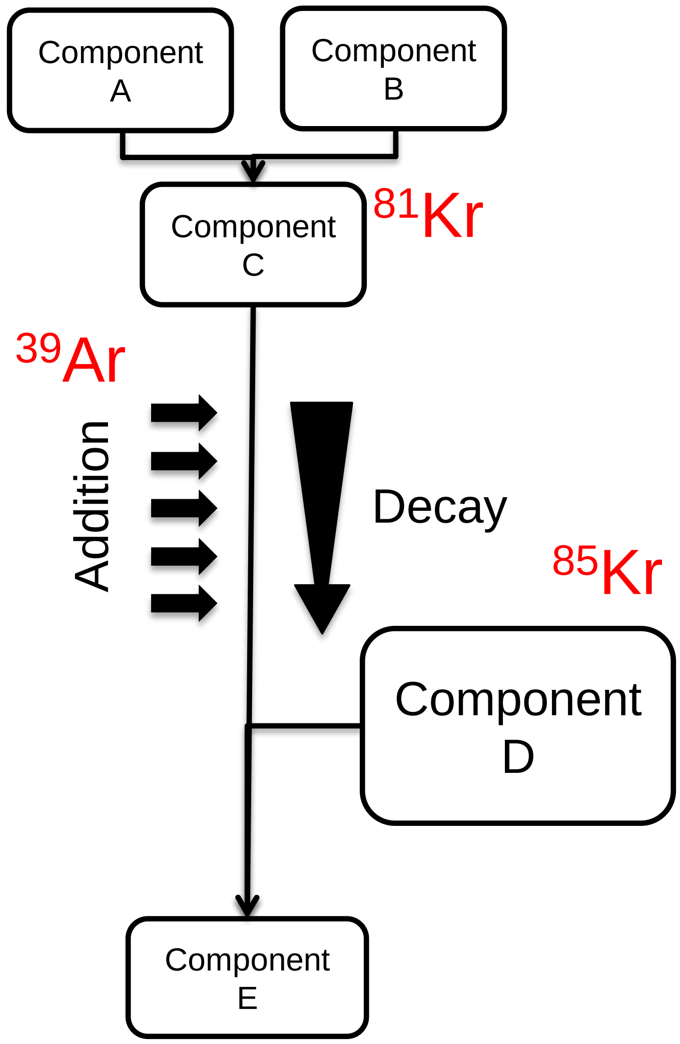
- ^{85}Kr/^{39}Ar: 0.001 -0.01
  - Modern Air >> Subsurface
  - Surface contamination dominates ^{85}Kr budget
  - Good tracer of shallow contamination

^{85}Kr/^{39}Ar ratios



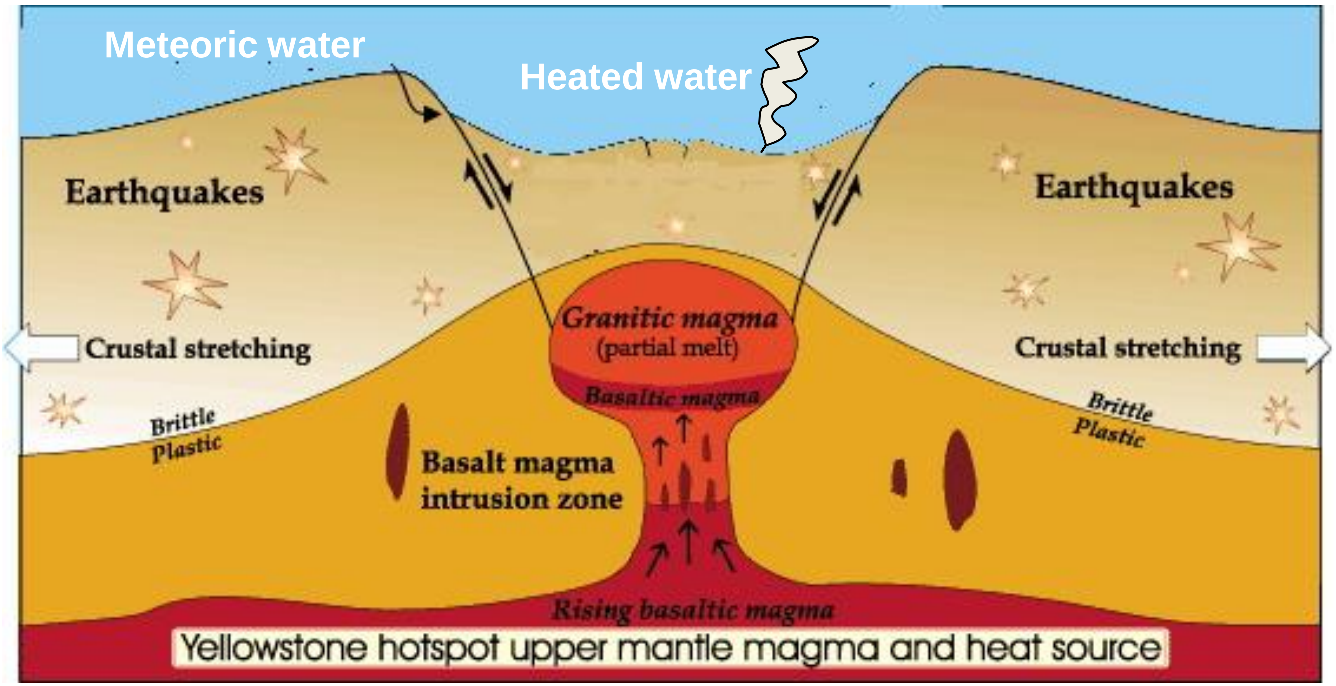
Summary 1: Model Study

- Subsurface-produced ^{39}Ar can serve as chronometer when combined with $^{40}Ar^*$.
- ^{85}Kr and $^{85}Kr/^{39}Ar$ ratio are ideal tracers of modern atmospheric contamination.
- There is no subsurface production of ^{81}Kr.




Case Study – Yellowstone National Park

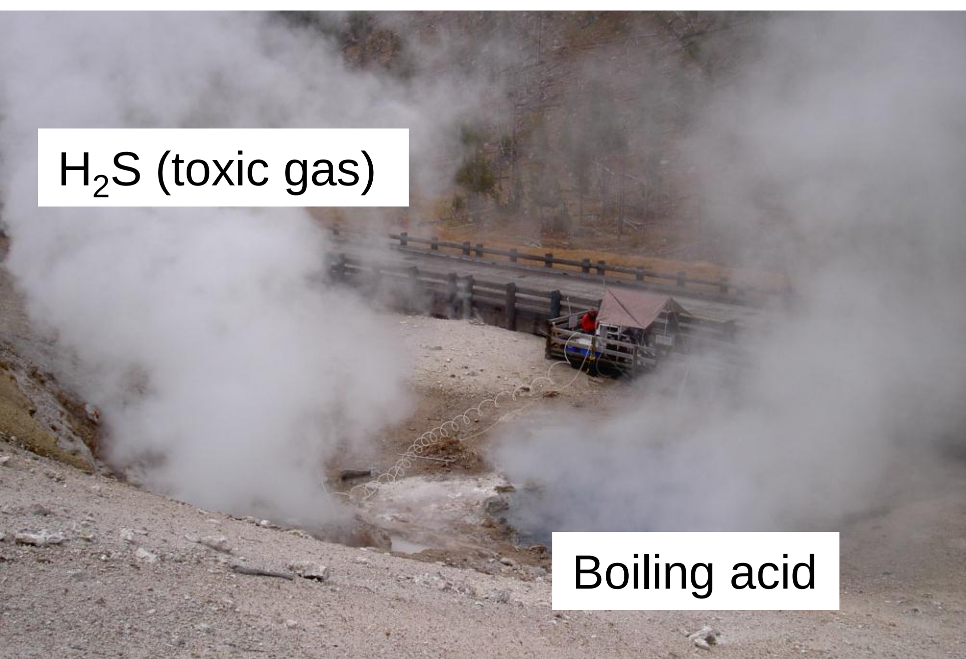

Motivation



- How much time does it take for the meteoric water to go down and come back up?


Participants


Fieldwork



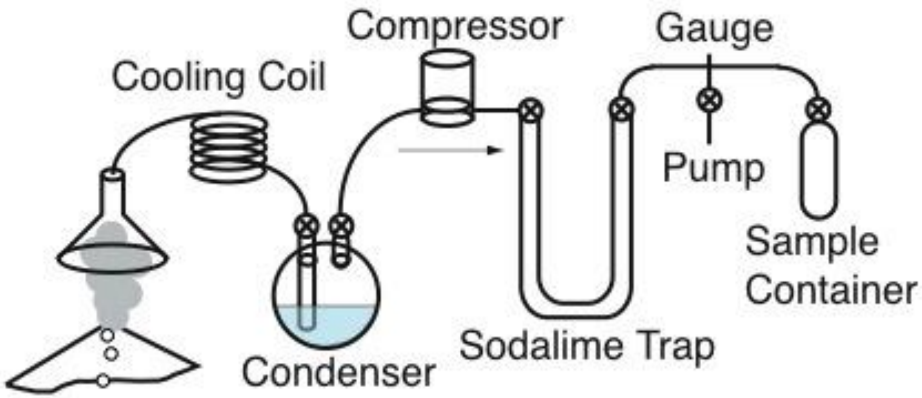

Beryl Spring

Frying Pan

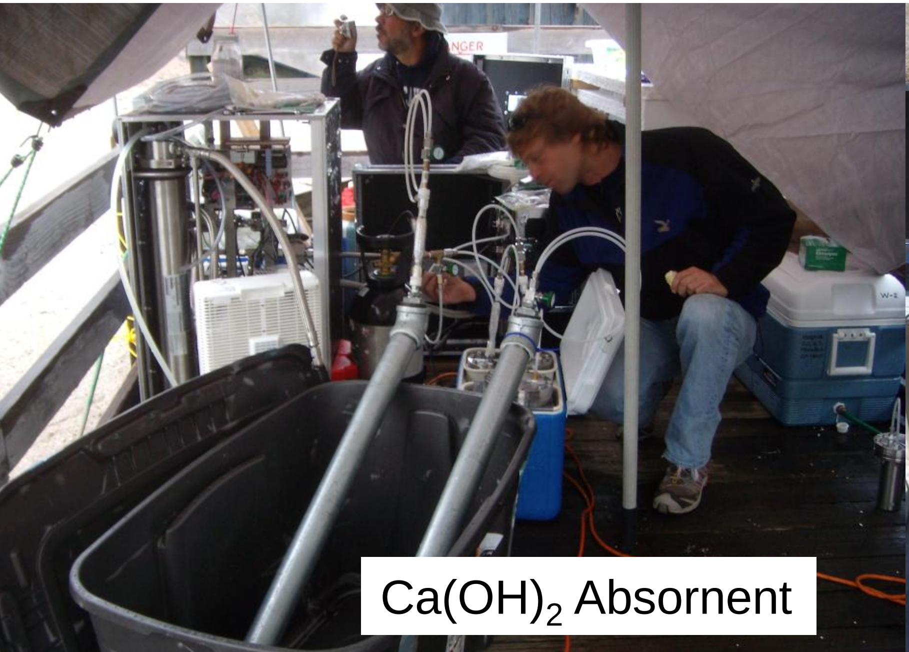
Sampling Sites

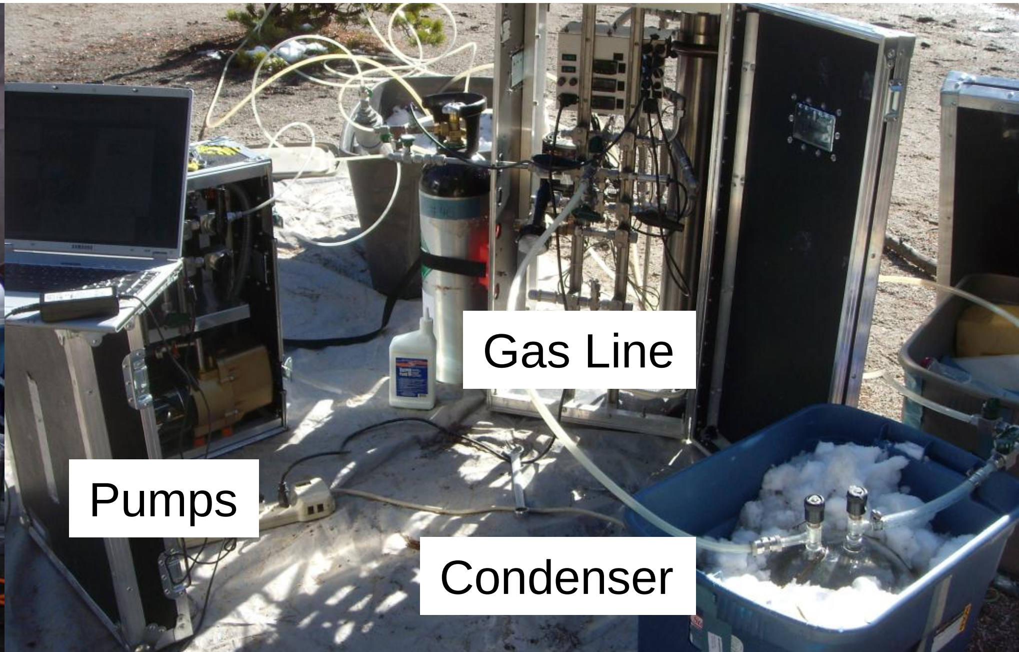

Mud Volcano


Ojo Caliente



Sampling Method





Data

ATTA Laboratory, Physics Division, Argonne National Laboratory, Argonne, IL 60439
(630)252-4123 www.phy.anl.gov/mep/atta/

Atom Trap Trace Analysis (ATTA) Report

Report No. 002 **Report Date** 08 Dec 2011 **Project Name** Yellowstone

Samples supplied by: Neil Sturchio (UIC), Reika Yokochi (Chicago), Roland Purtschert (Bern)

Samples analyzed by: Wei Jiang, Guo-Min Yang, Peter Mueller, Zheng-Tian Lu (ANL)

Wei Jiang
12-08-2011

ATTA trace No.	Sample No.	Sampling comments	Sampling Date	Size (micro-L)	ATTA Date	^{85}Kr (dpm/cc)	^{81}Kr sample / air	ATTA Lab comments
10014	S12	Frying Pan Air, #41	20 Feb 2008	~10	01 Nov 2011	56.2 ± 2.6	1.03 ± 0.057	Local Air
10015	S15	Frying Pan	05 Mar 2008	~10	03 Nov 2011	43.6 ± 2.2	1.03 ± 0.065	
10016	S18	Ojo Caliente	18 Mar 2008	~10	06 Nov 2011	36.9 ± 1.9	1.06 ±0.063	
10017	S14	Beryl	07 Mar 2008	~3.4	08 Nov 2011	51.1 ± 3.1	0.971 ± 0.090	(air contamination,%99.7 air, P_N2/P_Kr=250 on RGA)
10020	S17	MV1, #42	22 Feb 2008	~1.4	15 Nov 2011	33.4 ± 6.3	1.66 ± 0.33	← Interesting!
10024	S4	MV2, #43	18 Feb 2008	~7	06 Dec 2011	58.9 ± 3.0	0.92[illegible].061	(Sample cylinder valve leak)

Notes

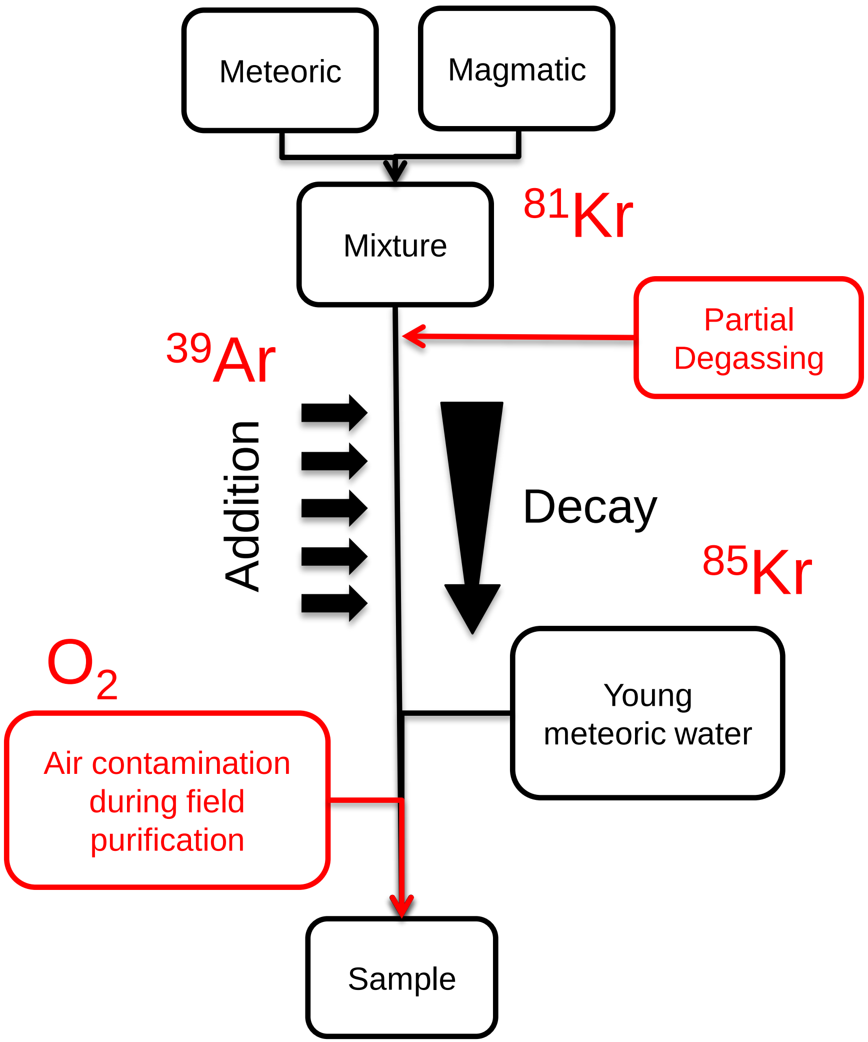
- ^{85}**Kr** ($t_{1/2}$ = 10.76 ± 0.02 yr) abundance is reported in the traditional unit of dpm/cc (decays per minute per cc STP of krypton).
  - Conversion: 100 dpm/cc corresponds to the isotopic ab
  - The reported ^{85}Kr value is as measured on the ATTA a … te.
- ^{81}**Kr** ($t_{1/2}$ = 229 ± 11 kyr) abundance is reported as the sample

Need to be evaluated in future work

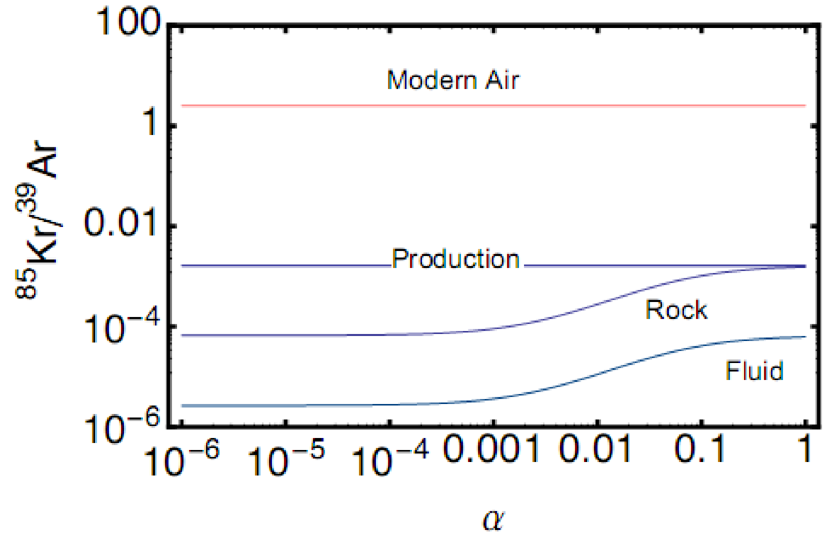
Data Analysis

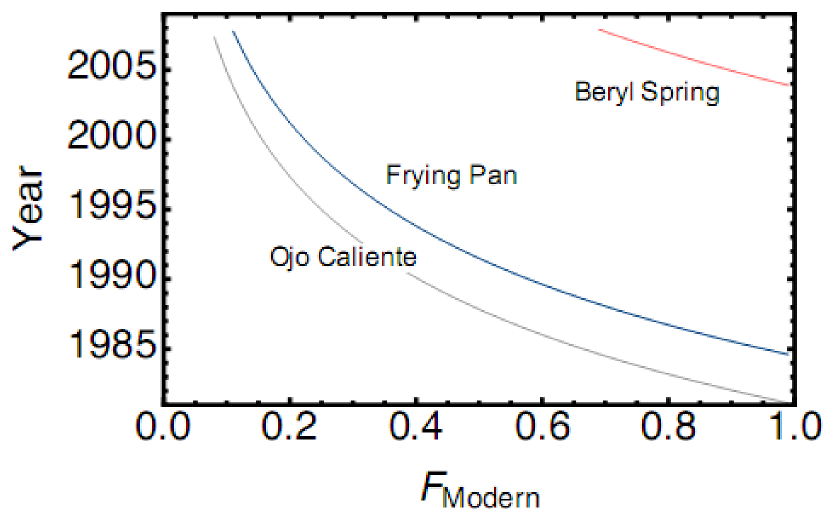
Other Data

- Chemical composition (UIC)
  - O_2 >%
  - Correction for air contamination during sampling
- Noble gas isotopes (LBNL)
  - $^3He/^4He$ and $^{40}Ar/^{36}Ar$ variation
  - Partial degassing (Kennedy et al., 1985)
- ^{39}Ar (Purtschert et al., 2009)
  - ^{39}Ar >> Atmospheric (up to ×6)



Discussions 1: ^{85}Kr





Fraction of young air
In the samples

- Clear contribution of modern ^{85}Kr
- Total: 36-74% Kr contamination during sampling = corrected
- Fraction of young air contribution depends on the age of the air component.
- Lower limit on the fraction of modern ^{81}Kr = Upper age limit goes up (Although measured values were atmospheric)

Discussions 2: ^{39}Ar

Reservoir Rocks and Production Rates

- Lava Creek Tuff

  Age: 640 kyr

  $^{39}Ar_{pro}$: 0.79 atoms/g/yr

  $^{39}Ar/^{40}Ar^{*}=1.3\times10^{5}$ Ra

- Central Plateau Member

  Age: 160 kyr

  $^{39}Ar_{pro}$: 0.57 atoms/g/yr

  $^{39}Ar/^{40}Ar^{*}=9.2\times10^{4}$ Ra

Fluid Data Analysis

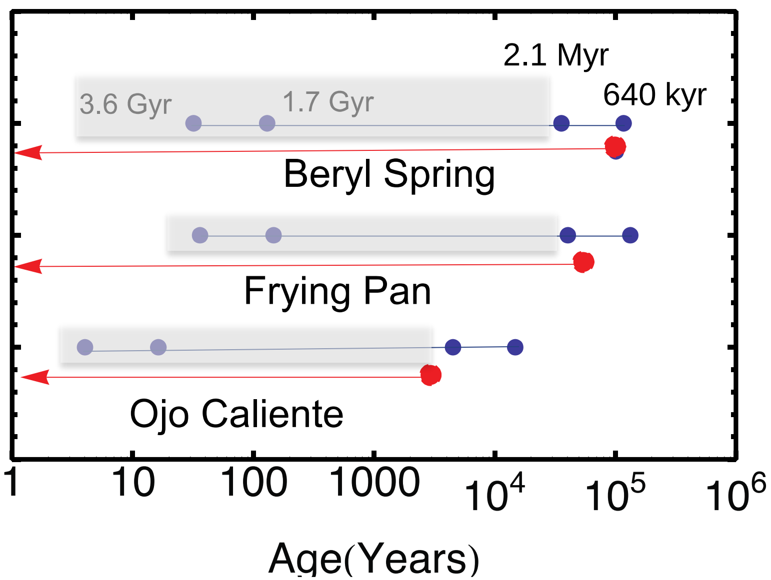
$$t_F \approx \frac{R_C}{R_F} \times \frac{1}{\lambda_{39}}$$

- Ages (for closed system)
  - Frying Pan: 130 kyr
  - Beryl Spring: 115 kyr
  - Ojo Caliente: 16 kyr

- External flux?
  - Ar from older reservoir =>younger age

Summary 2: YNP

Chronological Constraints



- Geothermal activity over >100 kyr (^{39}Ar age) if noble gas source is the reservoir rock
- ^{81}Kr age: Consistent with Ar age

Discussions

- The chronometer will improve if another parameter determines
  - The fraction (or age) of young meteoric component (^{81}Kr)
  - The source of radiogenic/nucleogenic isotopes (^{39}Ar) (reservoir rock vs. Pre-Cambrian basement)
- Systematic, multi-component study is essential for interpreting the complex system

Conclusions

- Nucleogenic ^{39}Ar, an obstacle of ventilation age dating, can serve as a chronometer when combined with $^{40}Ar^*$.

- Isotopic abundances of noble gas radionuclides in geothermal gases from Yellowstone National Park were analyzed for the first time, suggesting long water residence time in the crust

- Systematic, multi-component study is essential for interpreting the complex system

- $^{39}Ar/^{40}Ar^*$chronometer is applicable for old groundwater dating as well as tracing the time scale of fluid migration in a variety of scenarios including analogue and pilot studies of CO_2 sequestration and the formation of petroleum or natural gas reservoirs.

- Looking forward to new data!