

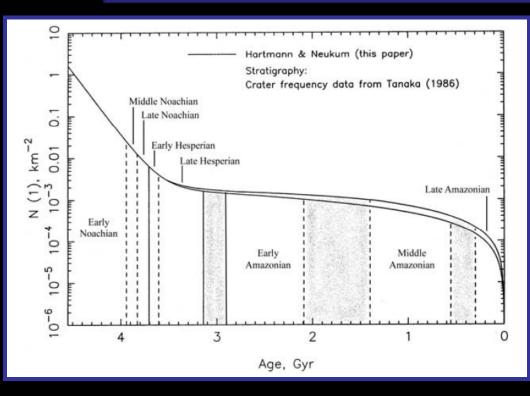
# A New Approach to In-Situ K-Ar Geochronology

Better than 10% precision on K/Ar ages with a single analytical instrument, easily accessible Ar extraction temperatures, and no mass determination required

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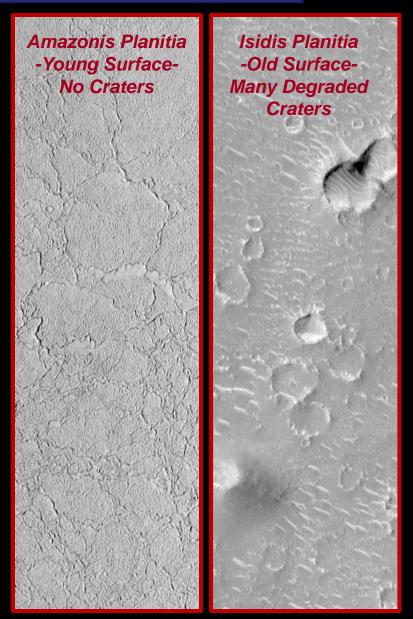
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## **Crater Counting Chronology**



#### The Two Major Assumptions (weaknesses):

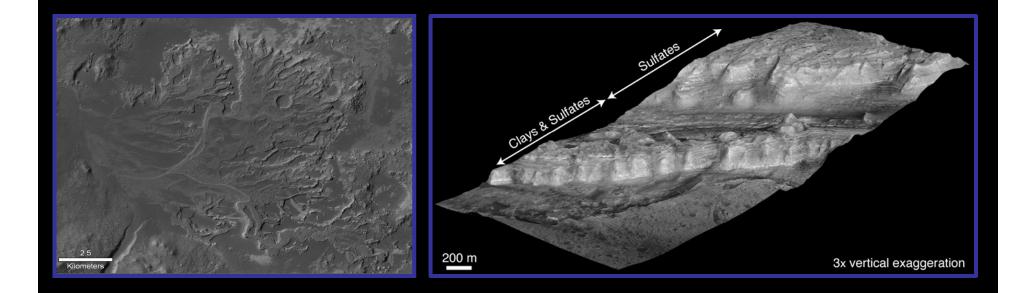
- 1. The lunar cratering rate can be scaled to an appropriate value for Mars
- 2. The geologically active surface of Mars (which erases and modifies craters in ways not experienced on the Moon) can be properly accounted for



## Why in-situ Geochronology?

### **Important Questions:**

- 1) When did aqueous activity occur on the Martian surface?
- 2) When did the Martian surface environment undergo major changes?
- 3) Does Mars record evidence of a late heavy bombardment?
- 4) Did Mars harbor a biosphere, and if so, exactly when?



## Why in-situ Geochronology?

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These are fundamentally questions of timing. Our understanding of absolute time on Mars is currently subject to the limitations of crater counting.

## **K-Ar Geochronology**

### What?

•  ${}^{40}\text{K} \rightarrow {}^{40}\text{Ar}, t_{1/2} = 1.3 \times 10^9 \text{ years}$ 

### Why?

- Applicable to basalt and K-bearing alteration phases including jarosite and alunite
- Useful over a wide range of age (10's of Ma to many Ga)
- Involves K, a major element (rather than trace elements, e.g., Rb-Sr, Sm-Nd, U-Pb)
- Martian targets of interest are likely to be old, and accordingly, have high Ar-concentration

## How are K-Ar Ages Measured on Earth?

- 1. Measure K-concentration by conventional techniques
- 2. Place a second weighed aliquot of sample into an MS
- 3. Heat sample to melting point (~1200°C<sup>+</sup> for basalts)
- 4. Measure isotopic composition and amount of Ar
- 5. Calculate K-Ar age using K/Ar concentration ratio

Weighing small aliquots of sample + Heating them above 1000°C = Some of the hardest things to do with spacecraft instrumentation.

## How do we surmount these problems?

A work around to designing a spacequalified high temperature oven = FLUX ASSISTED MELTING

#### TABLE 3

Common fluxes used in sample decomposition by fusion<sup>1</sup>

| Flux  | Melting point $^{\circ}C$ |
|---|---------------------------|
| Lithium metaborate, LiBO <sub>2</sub>             | 845                       |
| Lithium tetraborate, $Li_2B_4O_7$                 | 930                       |
| Sodium peroxide, $Na_2O_2$                        | 480 (decomposed)          |
| Sodium carbonate, Na <sub>2</sub> CO <sub>3</sub> | 851                       |
| Sodium hydroxide, NaOH                            | 318                       |
| Potassium carbonate, $K_2CO_3$                    | 891                       |
| Potassium hydroxide, KOH                          | 360                       |
| Potassium pyrosulfate, $K_2S_2O_7$                | 419                       |
| Sodium pyrosulfate, $Na_2S_2O_7$                  | 403                       |
| Ammonium iodide, NH <sub>4</sub> I                | > 300 (starts to sublime) |

<sup>1</sup> Data from Potts (1987), Bock (1979), and Erdey et al. (1964).



SAM Pyrolysis oven can achieve 1000-1100°C

## How do we surmount these problems?

A work around to designing a space-qualified high precision analytical balance = DOUBLE ISOTOPE DILUTION



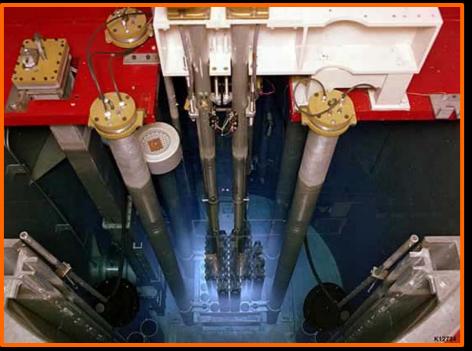
- Isotope dilution is the "gold standard" for laboratory measurements, yielding typical precisions of ~1%
- We employ a double-isotope spike containing <sup>41</sup>K and <sup>39</sup>Ar
- Here's how we cancel out the mass measurement:

$$\frac{{}^{40}Ar *}{{}^{40}K} = c * \frac{\left(\frac{{}^{40}Ar *}{{}^{39}Ar}\right) measured}{\left(\frac{{}^{39}K}{{}^{41}K}\right) measured} * \left(\frac{{}^{41}K}{{}^{39}Ar}\right) spike$$

## **Spike Synthesis**



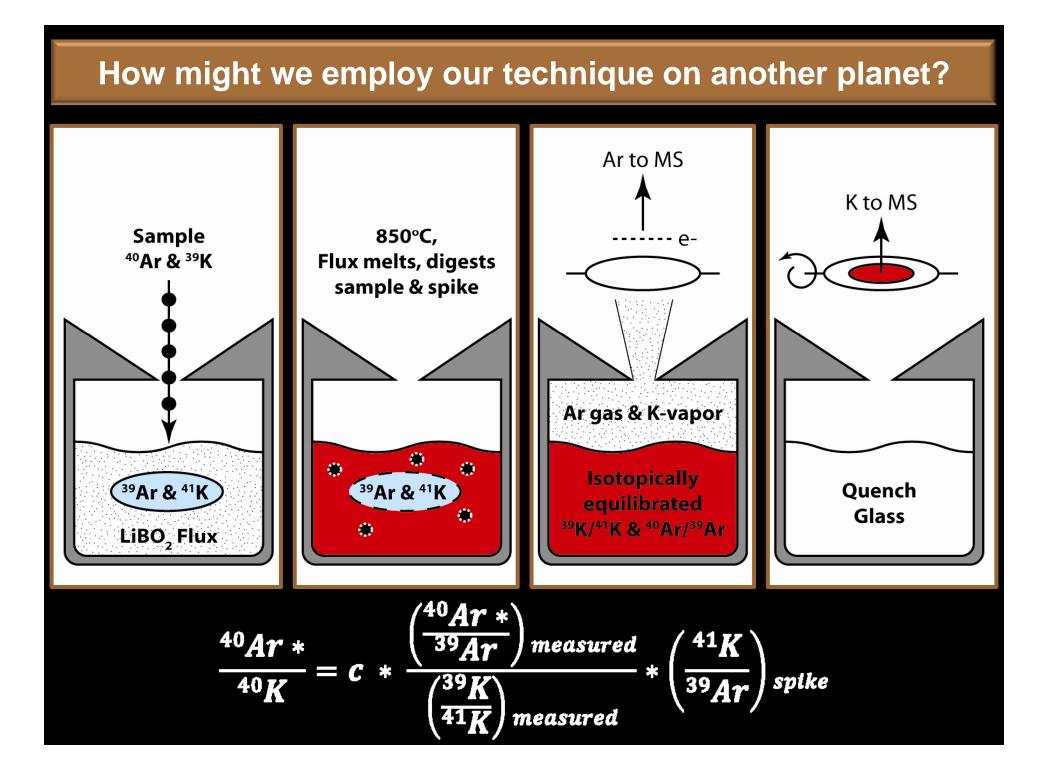
Caltech Petrology Lab



Oregon State University's TRIGA Reactor

Synthesized a glass containing known amounts of <sup>41</sup>K & <sup>39</sup>Ar:

- We did this by combining synthetic albite glass (NaAlSi<sub>3</sub>O<sub>8</sub>) with isotopically-enriched <sup>41</sup>KCl and melting them in a controlled atmosphere.
- This glass was irradiated, producing <sup>39</sup>Ar from the trace (~1%) <sup>39</sup>K present in the isotopically enriched <sup>41</sup>KCI.



### **Our First Age Measurement**

At present = no single instrument for both Ar & K measurement...

→ We are using 2 steps to perform this analysis using a basalt sample from the Viluy traps, Siberia (0.8 wt% K<sub>2</sub>O).

AIM: Measure an age of 354±2Ma

#### <u>Step 1</u>:

Combine flux (150mg) + basalt (15mg) + spike glass (1.5mg), in a crucible. Melt at 950°C, measure Ar-isotopic composition on Ken Farley's noble gas mass spectrometer at Caltech.

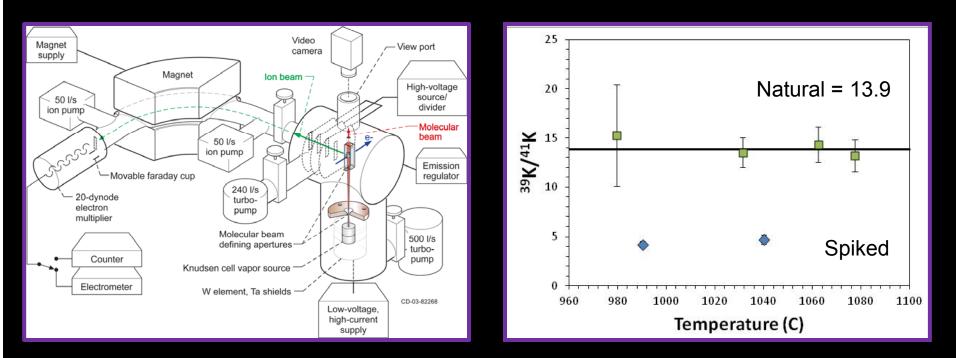


#### **Our First Age Measurement**

<u>Step 2</u>:

FedEx the cell to NASA Glenn Research Center, measure K isotopic composition on Nate Jacobson's Knudsen Effusion Mass Spectrometer.

AIM: Measure an age of 354±2Ma



**RESULT**: We calculate a preliminary age of 337 ± 30 Ma

#### Conclusions

- Developed and verified a technique that can be implemented for a flight instrument system. Basically consists of an oven and a mass spectrometer
  → Uses a mixture of basic geochemical practices developed in the mid-20<sup>th</sup> century, including K-Ar, flux digestion & isotope dilution
- 2. No mass measurement is required, high temperatures are not required, MS only has to measure isotope ratios, and no new technology development is required.
- 3. This double isotope dilution technique should yield in-situ whole rock ages with precision better than 10%.