The Argon Geochronology Experiment (AGE)

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**K-Ar dating**

Radioactive decay

$^{40}\text{K} \rightarrow ^{40}\text{Ar} \left( T_{1/2} = 1.3 \times 10^9 \text{ yrs} \right)$

Measure abundance of $^{40}\text{K}$, $^{40}\text{Ar}$; Calculate time since last thermal event

**Cosmic ray exposure dating**

Nuclear reactions produce

$^3\text{He}$, $^{20,21,22}\text{Ne}$, $^{36,38}\text{Ar}$

Measure abundances of O, Si, Mg, Ca, Fe, etc., $^3\text{He}$, $^{20,21,22}\text{Ne}$, $^{36,38}\text{Ar}$. Calculate time within ~1m of surface where reactions have occurred.
AGE flow diagram

1. Acquire sample, load into crucible.
2. Do LIBS analysis for elemental abundances.
3. Load sample into vacuum, pump down.
5. Analyze gas (Paul trap).
6. Measure volume, calculate mass.
Vacuum System Schematic
Sample Manipulation Mechanism

Samples are contained in the “dimples” visible on each arm. Sample loading is to the right, the vacuum system (not attached) to the left.
Operation of the LIBS Instrument

Components of the LIBS Instrument

L = Nd:YAG laser  FOC = fiber optic
M = mirror        S = spectrograph
LP = laser pulse  AD = array detector
CL = lens         GE = electronics
P = plasma        C = computer
T = target
Heating is via six tungsten filaments (two shown). The series of radiation shields makes it possible to achieve a sample temperature of 1500°C with minimal radiation losses.
QMSA Sensor Overview
The packaged TGA prior to launch

The TGA on ISS
Results ... mass spectra ...

UDMH QMSA SPECTRUM

| a | HCN or CCH₃ |
| b | CH₃N or CHCH₃ |
| c | CH₂N or CH₂CH₂ |
| d | CH₂NH or CH₂CH₂ |
| e | C₃N |
| f | CHCN |
| g | CN₂ |
| h | CHN₂ |
| i | CH₂N₂ or CH₂CHN |
| j | CH₃N₂ or CH₃CHN |
| k | CH₃N₂H or (CH₃)₂N |
| l | CH₃N₂H₂ or (CH₃)₂NH |
| m | CH₄CHN₂ |
| n | CH₃CH₂N₂ |
| o | (CH₃)₂N₂ |
| p | (CH₃)₂N₂H |
| q | (CH₃)₂N₂H₂ |
| r | ?? |

Intensity (counts)

Mass Number (u)
The Quadrupole Ion Trap Mass Spectrometer

Quadrupole ion trap and Quadrupole mass filter invented by Paul and Steinwedel in 1960

W. Paul awarded Nobel Prize in Physics 1989
How does the trapping really work?

Consider applying a voltage to the ring electrode

Say 1000 \( V_{0-p} \) at 1 MHz

Create an ion in this quadrupole field

Pause and look at potential surface

Ion rolls down slope to trap center = radial focusing

Ion reaches trap center, can continue downhill = axial defocusing

Restart voltage, ring at -1000 V end-cap at 0 V, rotate figure by 90°

Get axial focusing and radial defocusing

Balance focusing and defocusing forces – can trap the ion!
Further miniaturization to a System-on-a-Chip (SoC) is proceeding.
Argon Isotopes with Paul Trap and Digital RF Board

$^{36}\text{Ar} : 0.34\%$ (0.337%)
$^{38}\text{Ar} : 0.09\%$ (0.063%)
$^{40}\text{Ar} : 99.57\%$ (99.600%)
Isotope Ratios for Neon

"High Precision" Paul Trap, Gen 3 rf board, 1MHz rf frequency

Ion Signal (counts)

$m/z$
How do we balance the forces?

In practice $U = 0 \rightarrow a_z = 0$; operate along this line

$$q_z = \frac{4eV}{mr_0^2\Omega^2}$$

$$-a_z = \frac{8eU}{mr_0^2\Omega^2}$$

Can see that for $a_z = 0$ the stable/unstable boundary occurs at $q_z = 0.908$. 

stability boundary on $a_z = 0$ line

$q_x = 0.908$
Mass Discrimination by DC Offset on Trap Ring

Mass Selective Accumulation

Discriminating against $^4$He by applying a DC offset to the rf trapping potential
"High Precision" Paul Trap, Gen 3 rf board, 1MHz rf frequency

VDC = 21.35V
VDC = 20.70V

$m/z = 4$, FWHM = 0.02 amu

$m/z = 3.6$

[m/z spectrum graph]

Ion Signal (counts)
Elemental Abundances with the LIBS

(a) LIBS calibration for K in basalts, at 7 torr pressure.

(b) Comparisons with two martian meteorites.

(c) Blind test comparison of LIBS (solid line) to actual abundances for two “unknown” basalt samples.
Progress Summary

Sample Introduction and Heating

• developed a 6-armed sample loading mechanism
• developed a resealable (elastomer) vacuum chamber
• developed radiatively-heated sample oven for operation to 1500° C

Laser-Induced Breakdown Spectroscopy (LIBS)

• conducted lab & field tests of a high- and low-resolution spectrograph
• tested a suitable Nd:YAG Q-switched laser (1 Hz, 6-10 ns, 20-25 mJ/pulse)
• quantitatively detected K and other elemental abundances in minerals

Miniature Quadrupole and Paul Trap MS

• assembled and tested a QMSA system to interface to the sample oven
• designed & tested a new-type digital RF generator board with excellent control of frequency and THD
• using the Paul Trap, demonstrated good isotope separation for the gases $^{20,21,22}$Ne$^+$, $^{36,38,40}$Ar$^+$, $^{32,34}$S$^+$, and $^{83,84}$Kr$^+$
• demonstrated static operation of a commercial RGA with loading from sample oven
• demonstrated sensitivity to $10^{-12}$ torr $P_{Ar}$ with RGA, at $10^{-9}$ torr total background pressure
• characterized background evolution of Ar from oven while cold, and while hot (& empty).