Development of a Laser Ablation Isochron K-Ar Dating Instrument for Landing Planetary Missions

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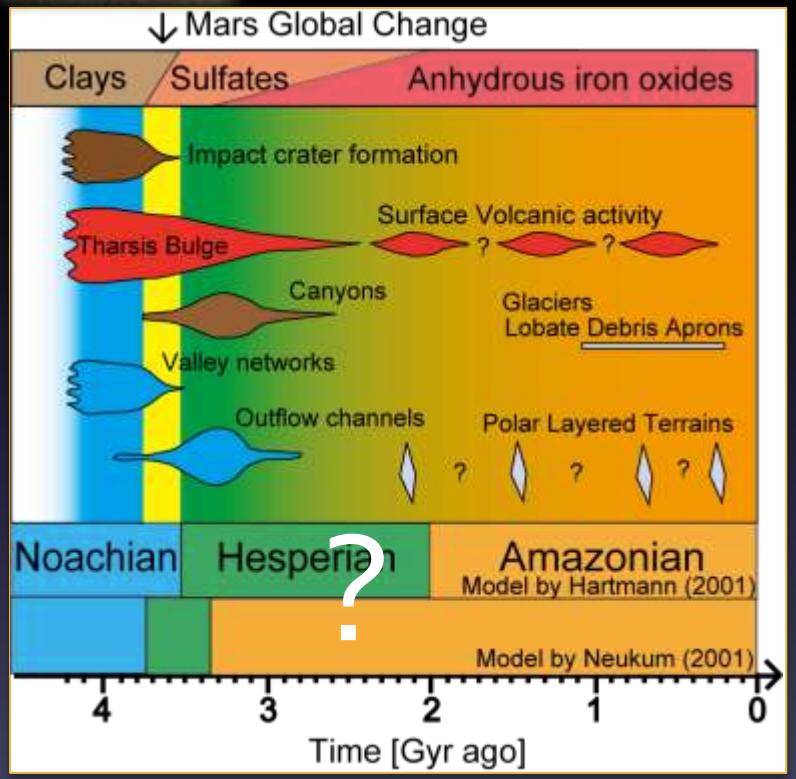
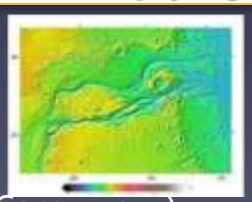
Issues on the solar system chronology:
Martian Absolute Chronology





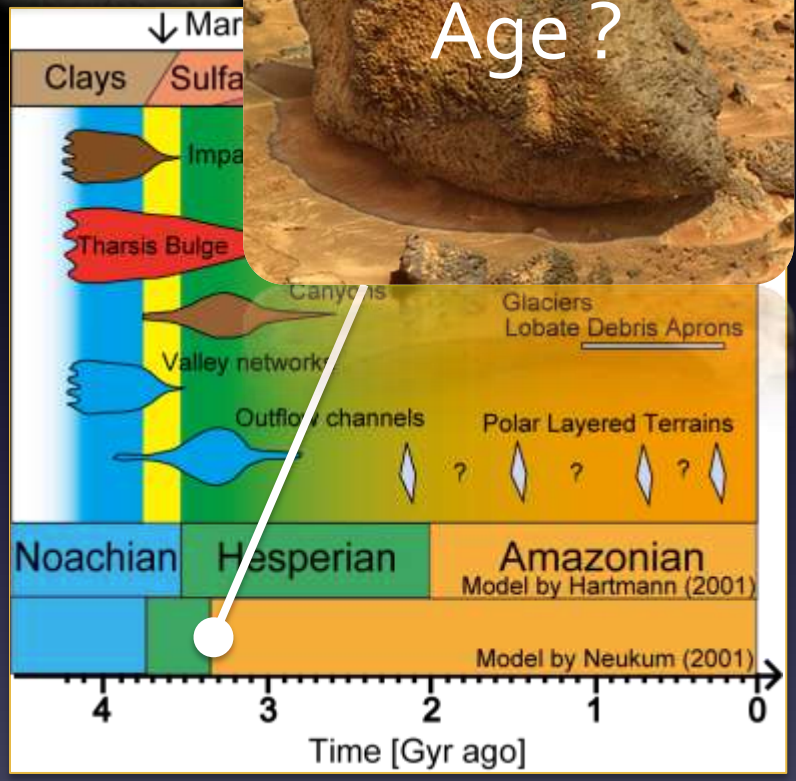
(Revised from Carr+, 2011)

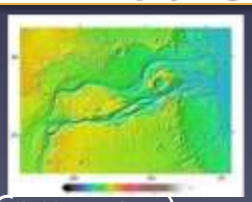
- Age
  - one of the most fundamental observables
  - Not many direct age measurements
- Knowing the ages of key geologic events greatly advance our understandings on Mars

Highly uncertain absolute age (Doran+ 2004)

- Moon/Mars impact flux ratio estimated by dynamical calculations (e.g., Ivanov, 2001)
- No direct information about age

Issues on the solar system chronology:
Martian Absolute Chronology





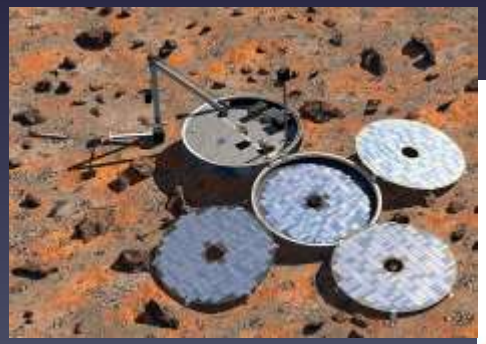
(Revised from Carr+, 2011)

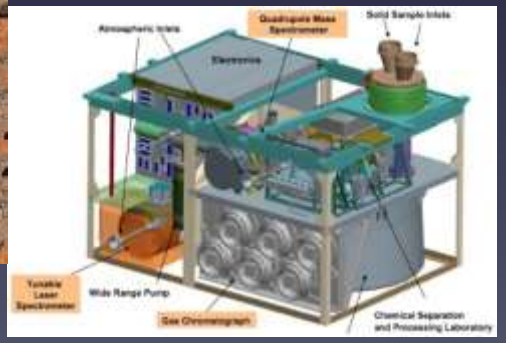
✓ In-situ age measurements

- Age data of known geologic unit
- Iterative measurements
- Contributions to sample return missions

Previous missions

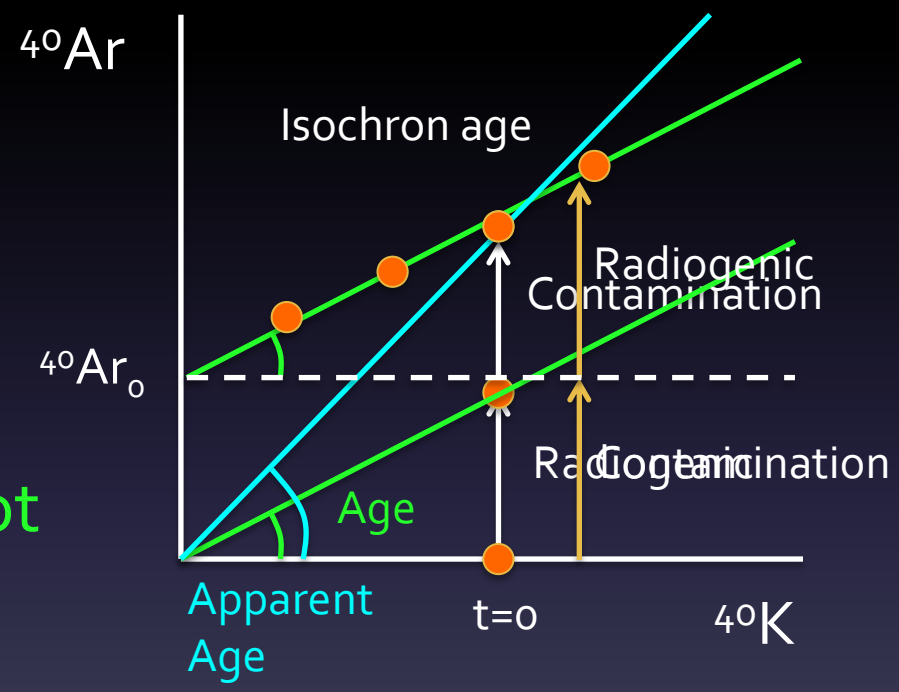
- Beagle 2, MSL
- Whole rock measurement of K-Ar age





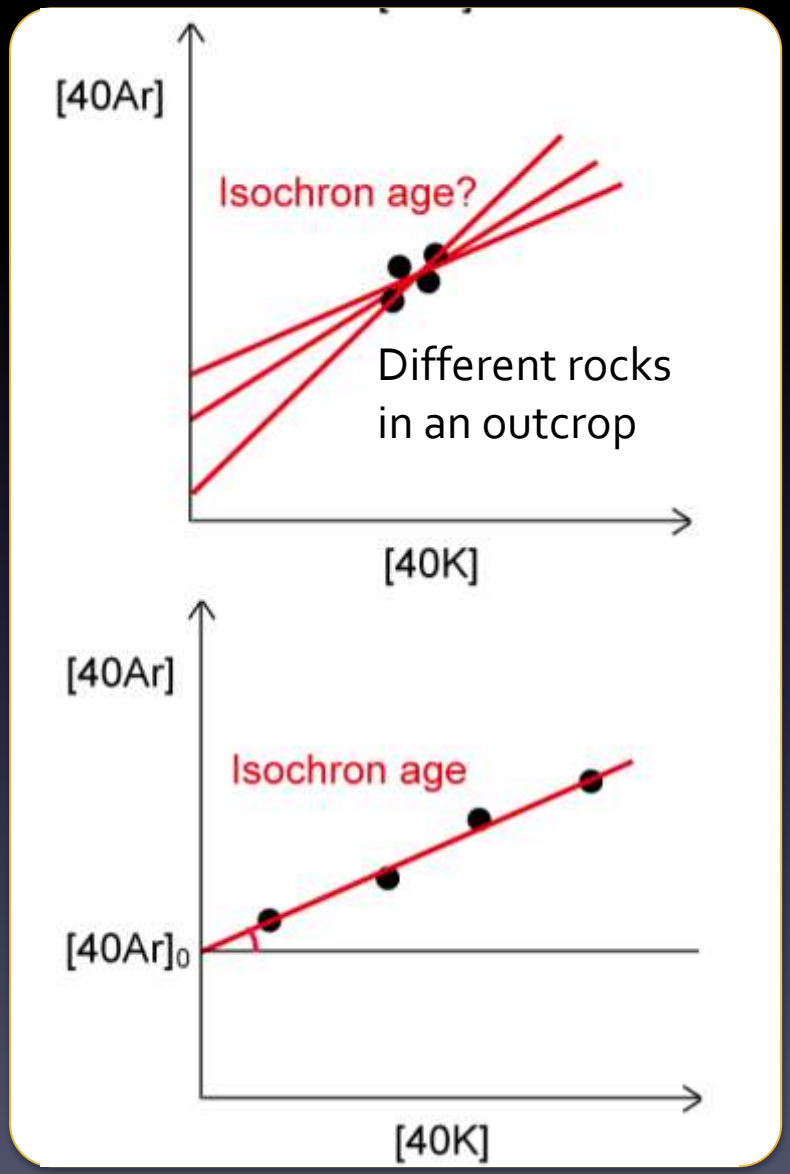
Principle of K-Ar measurement

- ^{40}K decays to ^{40}Ar
- Ideally, no ^{40}Ar at t=0
- Excess ^{40}Ar in Martian samples (Bogard+ 2008)
  - Whole rock analyses are not reliable
  - Isochron is needed to separate radiogenic ^{40}Ar from magmatic ^{40}Ar



Principle of K-Ar measurement

- Whole rock analysis
  - Small variation in bulk K
  - Less reliable isochron
- Measuring Ar/K in a small spot size (~mineral grain)
  - Cover large K range to obtain good isochron



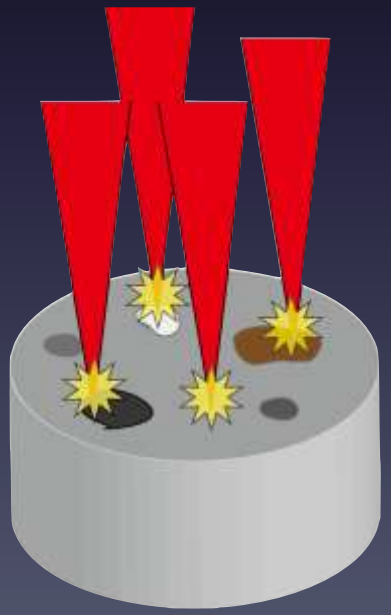
Ultimate Goal

- ✓ Develop an in-situ isochron dating instrument
  - Required accuracy:

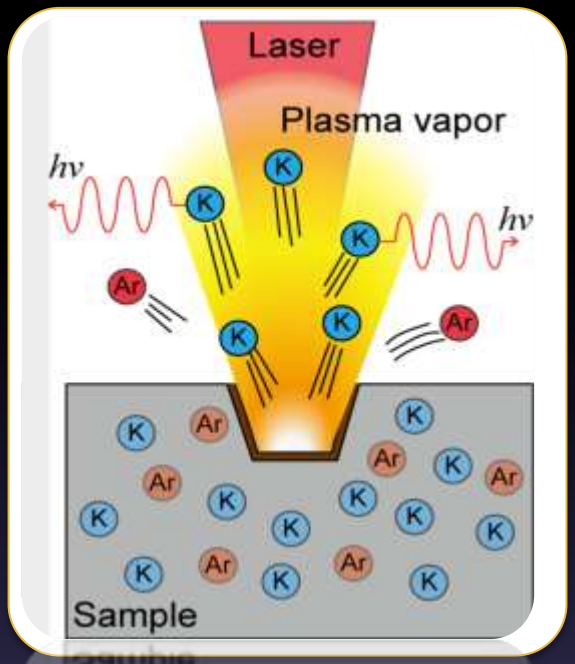
    10% for Martian Chronology mission (e.g., 3.0±0.3 Ga)

Approach

K & Ar measured with LIBS+QMS



Spot analysis with laser ablation



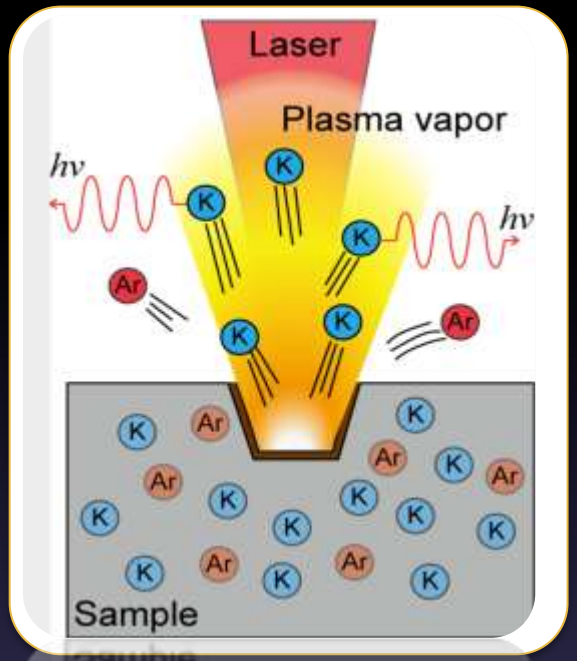
Advantages:

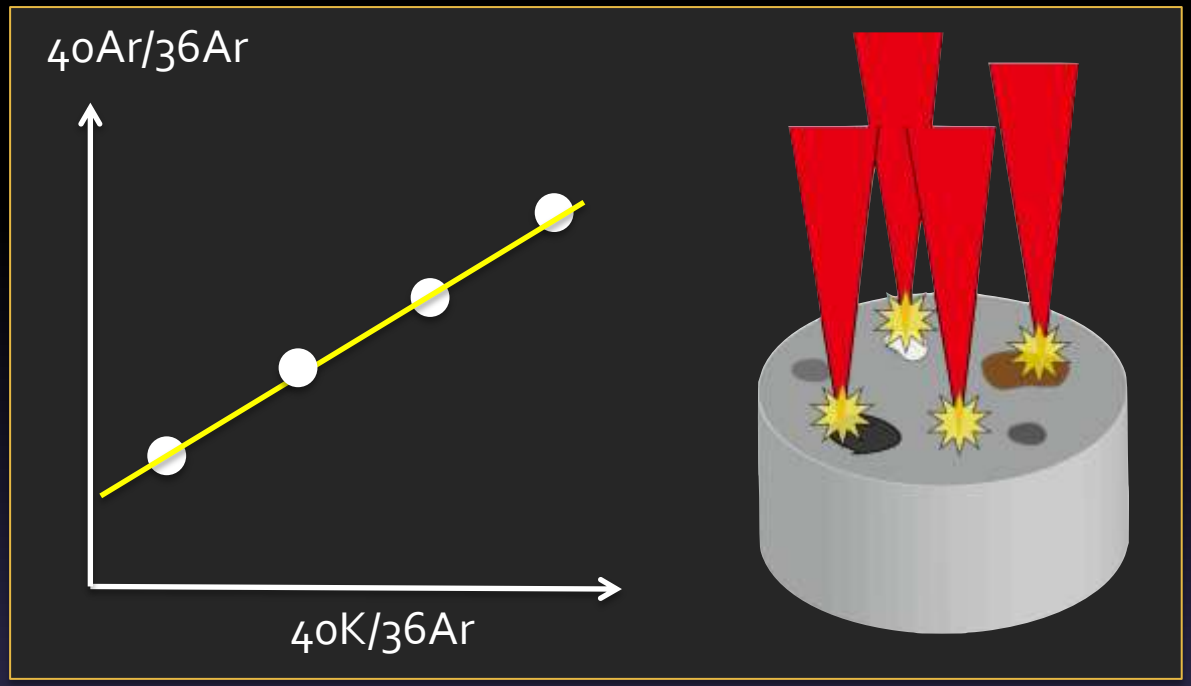
- ✓ K/Ar extracted & measured from the same spot(~500 μm)
- ✓ Ability of isochron measurements

Challenges:

- ✓ Weak K emission under the high-vacuum condition(<10^{-2} Pa)
- ✓ Small amount of Ar extracted by laser ablation

Objectives of this study

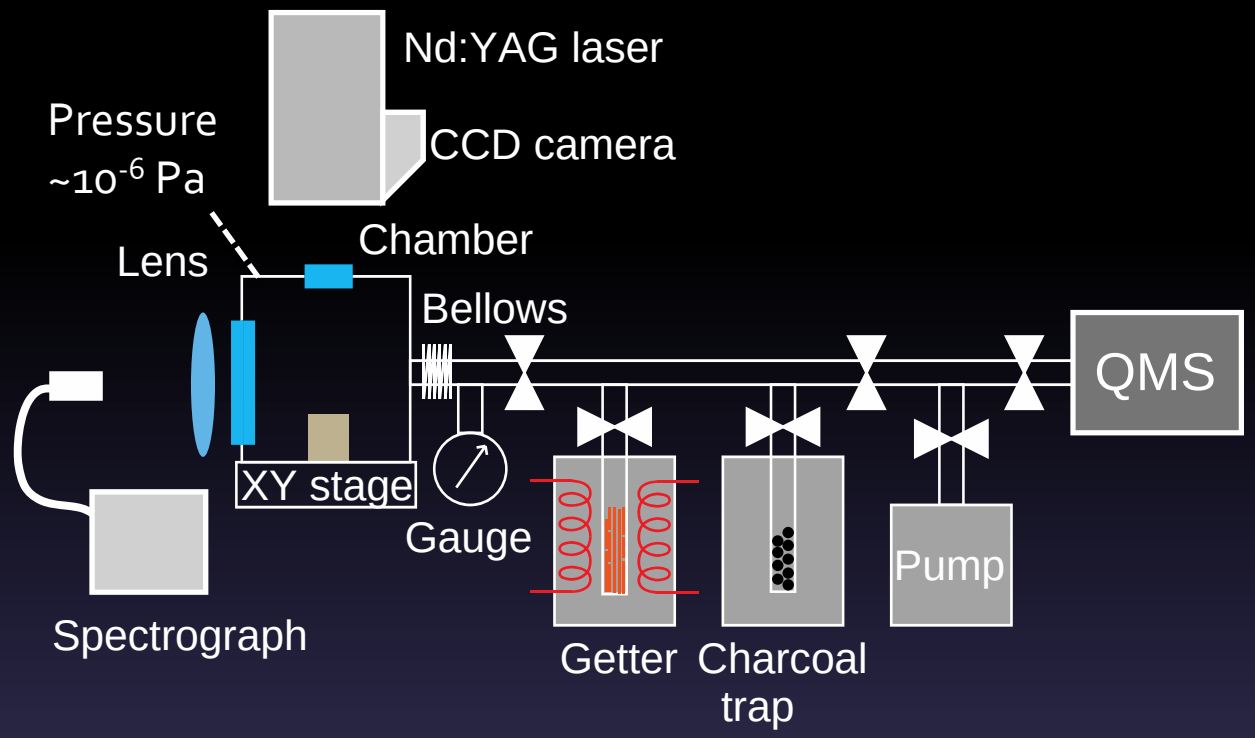




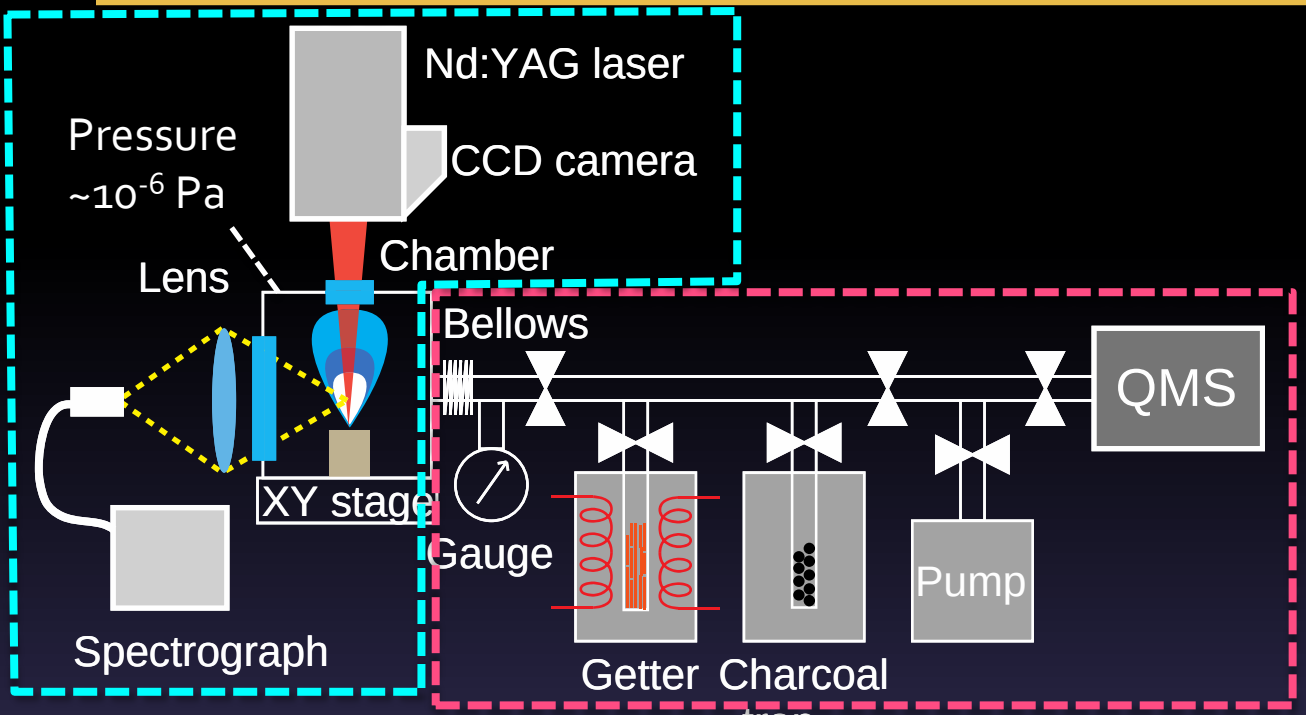
- ✓ Measure weak K emission under the high-vacuum condition
- ✓ Measure small amount of laser-released Ar
- ✓ Construct actual isochron ←*In progress*

Achieved

LIBS-QMS system

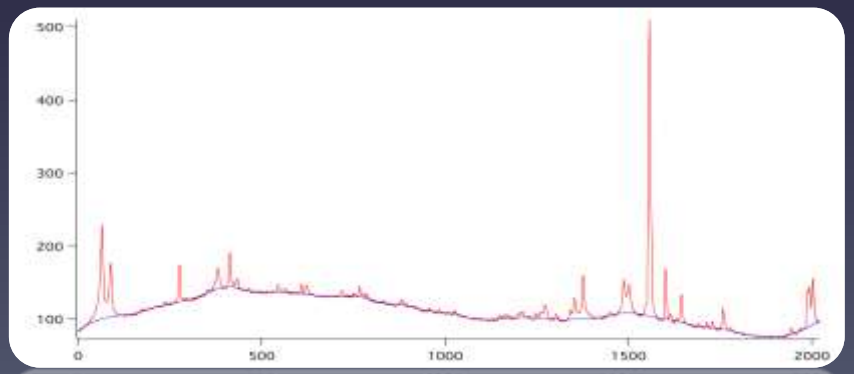


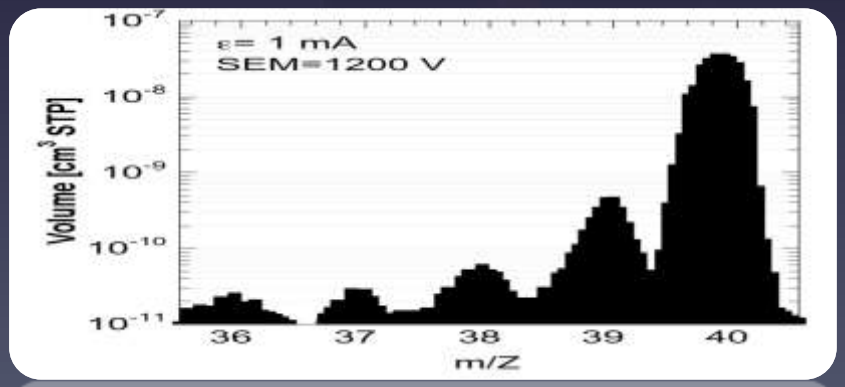
LIBS-QMS system



Laser-induced breakdown spectroscopy(LIBS) →K emission line

Quadrupole Mass Spectrometer (QMS)→^{40}Ar mass peak



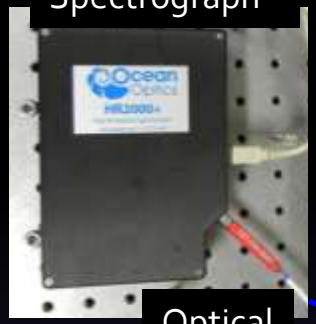


Instrument

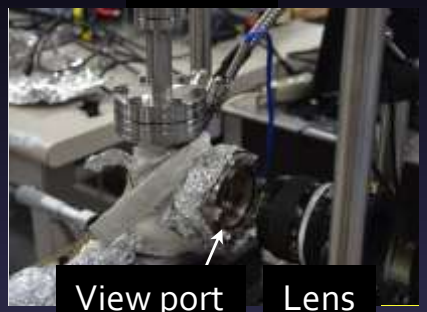
Experimental conditions

- Laser: Nd:YAG(λ=1064nm); pulse width 6 ns; energy 100 mJ; spot 500μm; 100 pulses
- Samples: USGS/NIST/AIST standard volcanic rocks
- Pressure: 1E-6 Pa
- Spectrometer: Non-gated CCD (Ocean Photonics)
- QMS: emission current=1mA, SEM=1200-1600V

Spectrograph

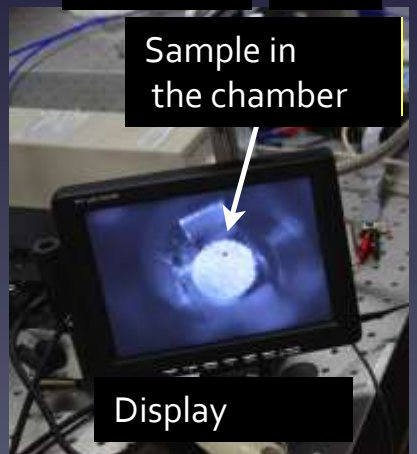


Optical Fiber



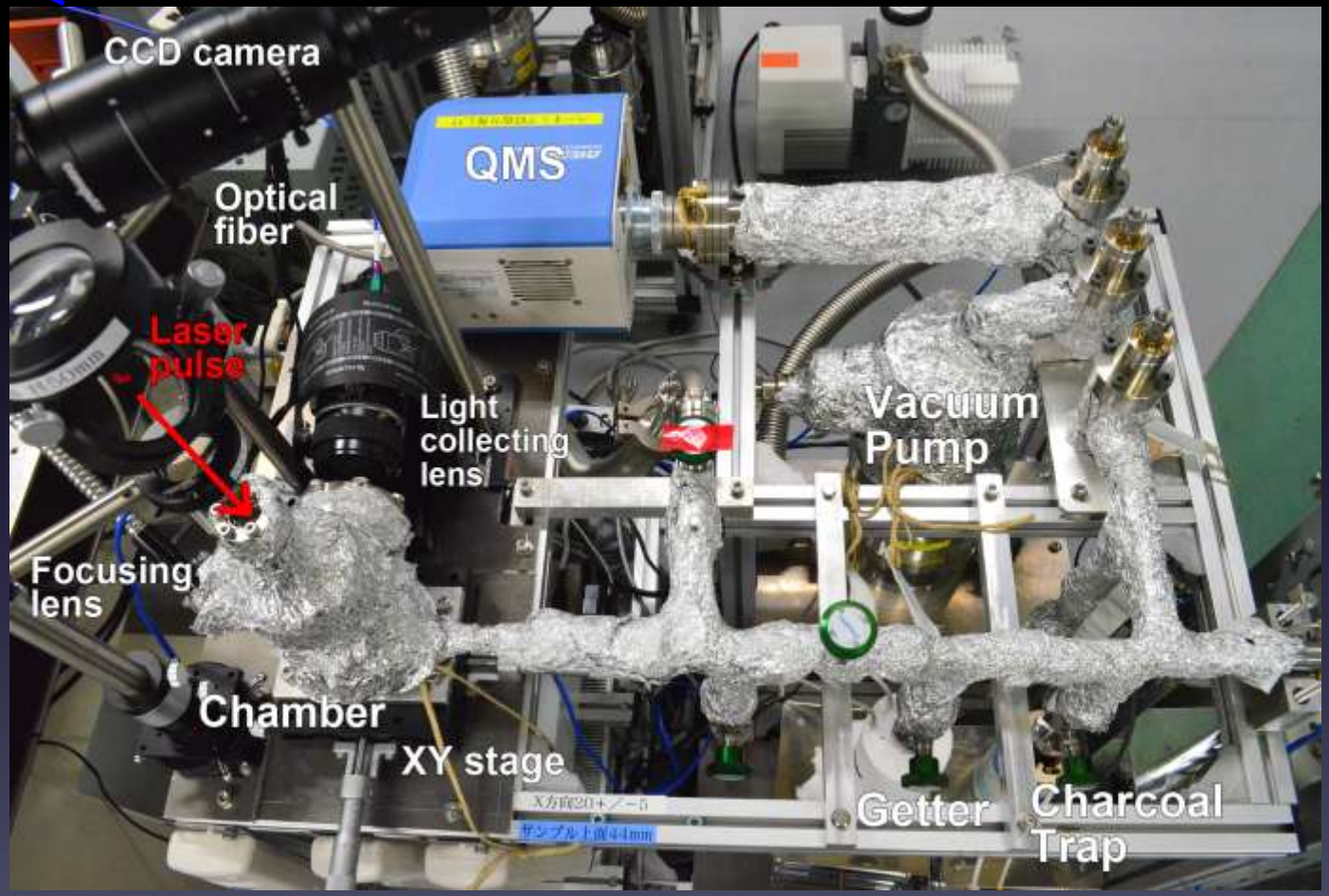
View port

Lens

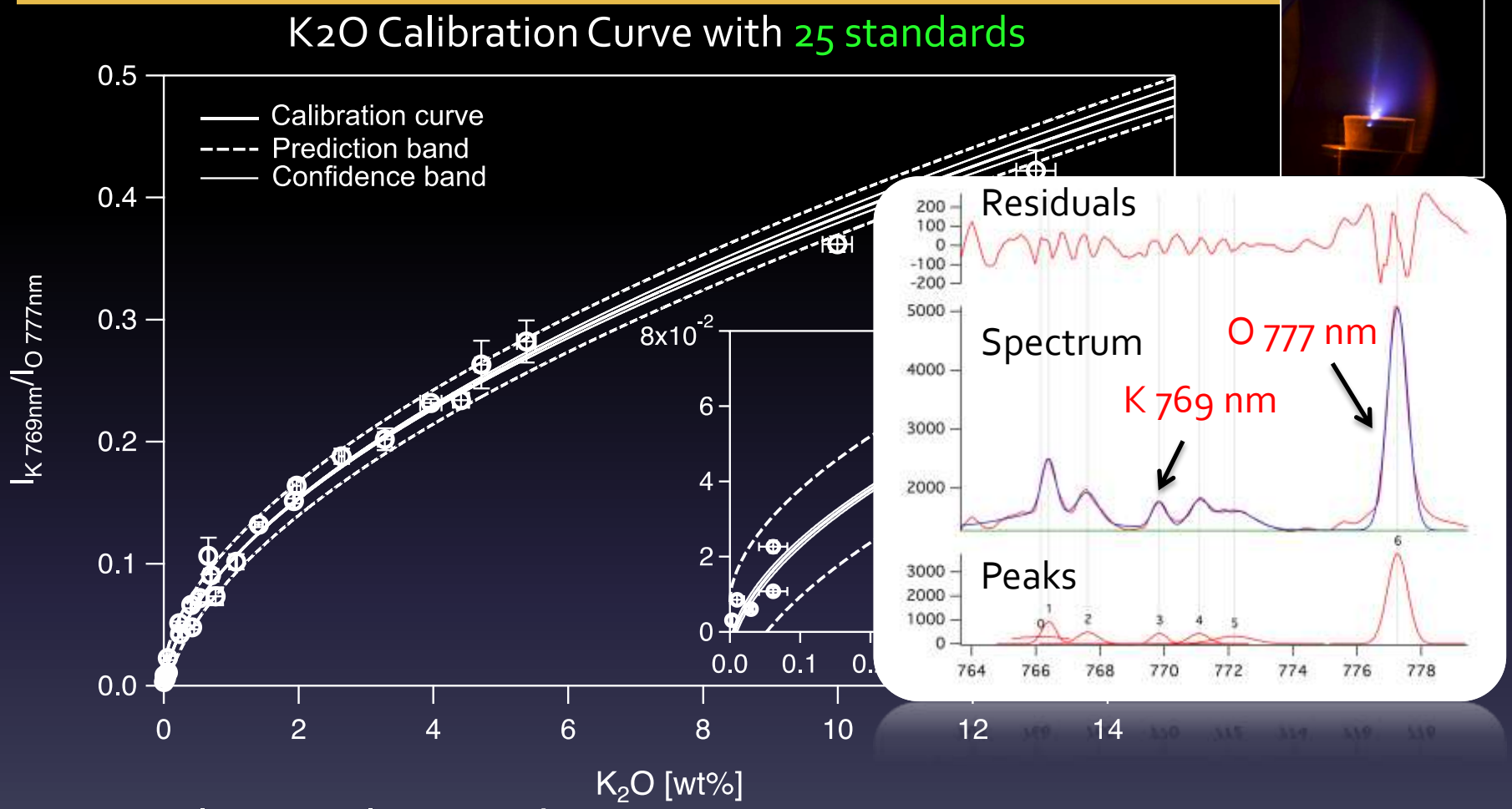


Sample in the chamber

Display

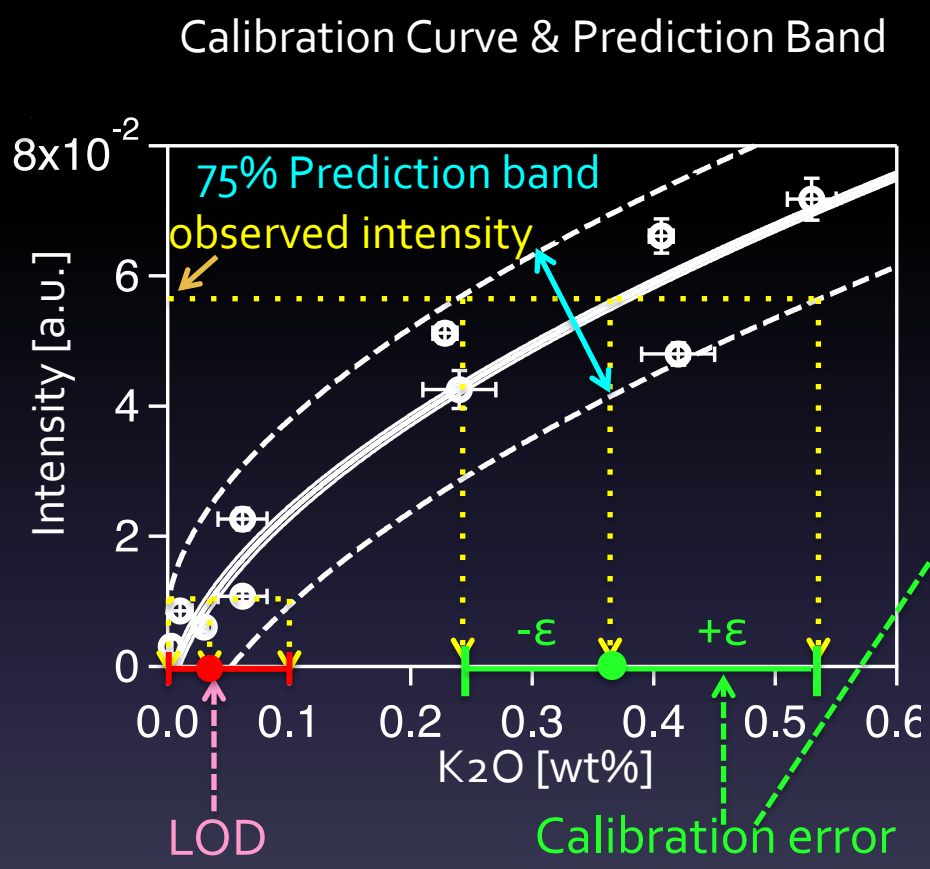


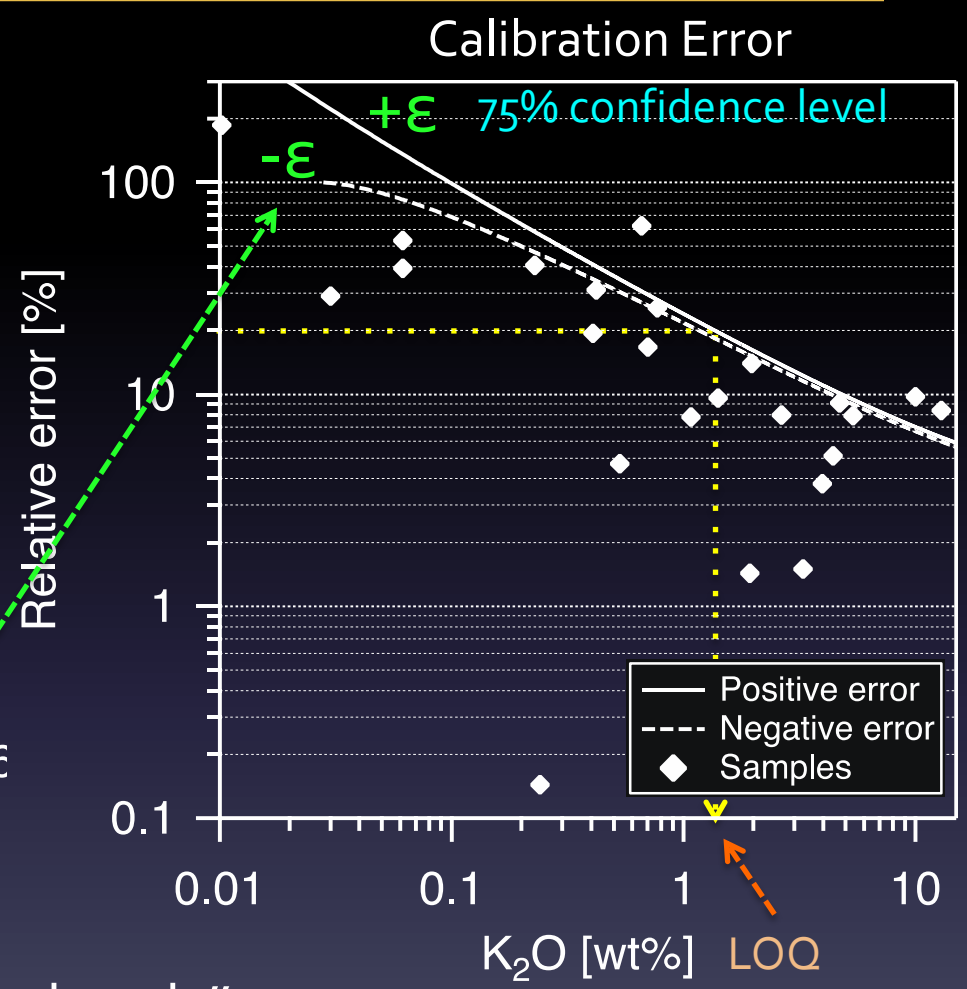
LIBS calibration model



- Internal normalization by O 777 nm line (Salle+ 2006)
- Power-law calibration curve

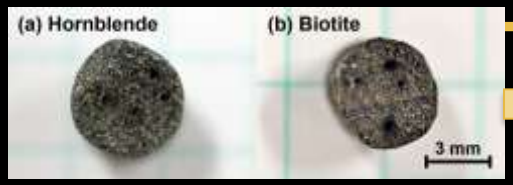
LIBS calibration results: Error &LOD





- Error estimated by "prediction bands" (Mermet+, 2007)
- Limit of Detection(LOD): 270 ppm
- Limit of Quantification(LOQ): 1 wt%

Age measurement of reference samples



Baking

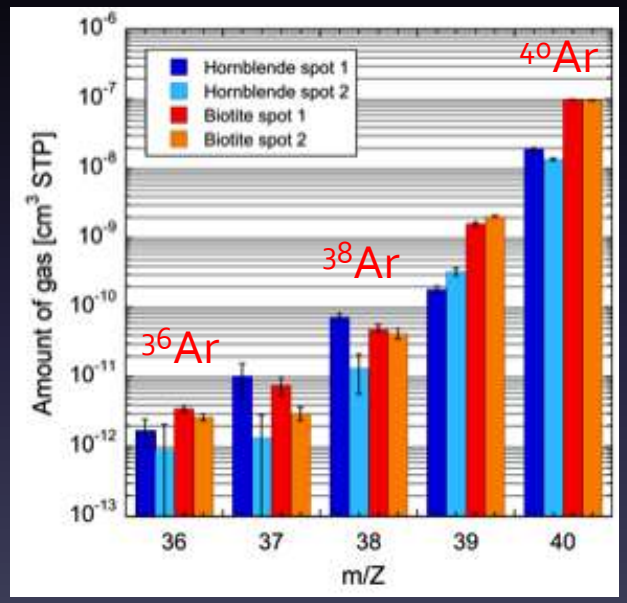
180°C 24 h

Laser irradiation

500 pulses, 2 Hz

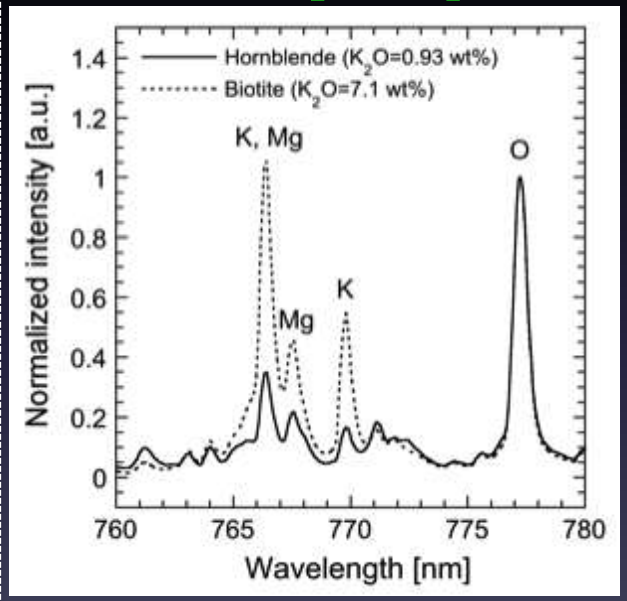
Purification of gas

QMS: ^{40}Ar [mol]

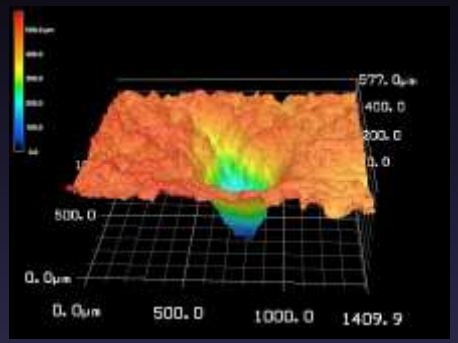


* Atmospheric mixing subtracted by $^{40}Ar_{atm}=296\times{}^{36}Ar$

LIBS: K2O [wt%]



Microscope: V [cm^3]



Assumed density:

~2.9 [g/cm^3]

$^{40}Ar_{rad}$ [mol]

^{40}K [mol]

Age [Ga]

Age determination results

	Hornblende			Biotite		
						
	Spot 1	Spot 2	Known	Spot 1	Spot 2	Known
K_2O [wt%]	1.13±0.25	0.87±0.22	0.93*	6.9±0.6	7.4±0.6	7.0*
Crater volume [10^{-5} cm^3]	4.3±0.5	4.0±0.4	-	4.5±0.6	4.4±0.3	-
Density [g/cm^3]	2.9±0.3	2.9±0.3	-	3.1±0.3	3.1±0.3	-
^{40}K [10^{-12} mol]	3.5±0.8	2.5±0.6	-	24±4	25±3	-
$^{40}Ar_{rad}$ [10^{-13} mol]	8.3±0.4	5.7±0.3	4.9	42±1	42±1	43
Age [Ga]	2.1±0.3	2.1±0.3	1.74*	1.8±0.2	1.7±0.2	1.80*

Age determination turns out to be rather accurate.

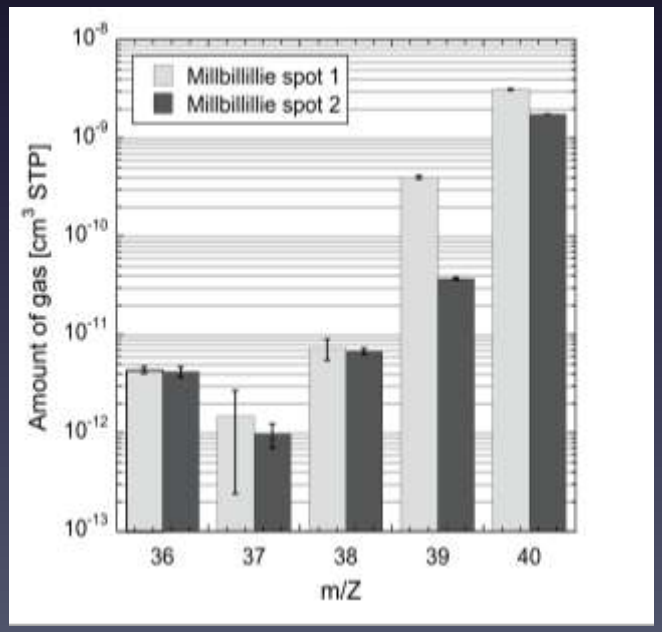
*Nagao, personal comm. (2012)

Dating a Eucrite

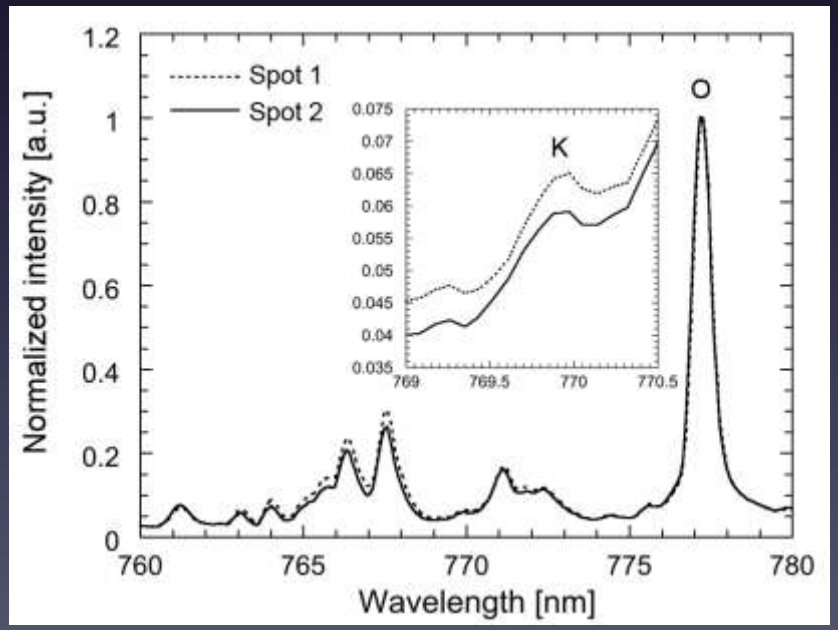
Millbillillie: K2O=~500 ppm (Miura+, 1998)
K-Ar age=3.2±0.4 Ga (Michel & Eugster, 1994)

- Microscope images

- QMS Spectra



- LIBS Spectra



Dating a Eucrite

	Eucrite		
	Spot 1	Spot 2	Known
K_2O [ppm]	120±520	120±520	500±100*
Crater volume [10^{-5} cm^3]	7.5±0.5	6.6±0.2	-
Density [g/cm^3]	2.9±0.2	2.9±0.2	-
^{40}K [10^{-14} mol]	6.6±23.4	5.8±20.5	-
$^{40}Ar_{rad}$ [10^{-13} mol]	1.4±0.1	7.85±0.03	-
Age [Ga]	5.5±6.1	4.8±5.9	3.2±0.4#

*Miura+ (1998), #Michel & Eugster (1994)

- Literature K2O is close to the LOD(~270 ppm) and smaller than Limit of Quantification(~1 wt%)
- Age measurement is still challenging due to low K2O concentrations.

Dating a Eucrite

	Eucrite with literature K_2O		
	Spot 1	Spot 2	Known
K_2O [ppm]	*500±100*	*500±100*	500±100*
Crater volume [10^{-5} cm^3]	7.5±0.5	6.6±0.2	-
Density [g/cm^3]	2.9±0.2	2.9±0.2	-
^{40}K [10^{-14} mol]	*2.7±0.5*	*2.4±0.4*	-
$^{40}Ar_{rad}$ [10^{-13} mol]	1.4±0.1	7.85±0.03	-
Age [Ga]	*3.2±0.3*	*2.6±0.3*	3.2±0.4#

*Miura+ (1998), #Michel & Eugster (1994)

- Age error is largely due to poor K2O accuracy.
- Using literature K2O value yields consistent ages with reported K-Ar age.

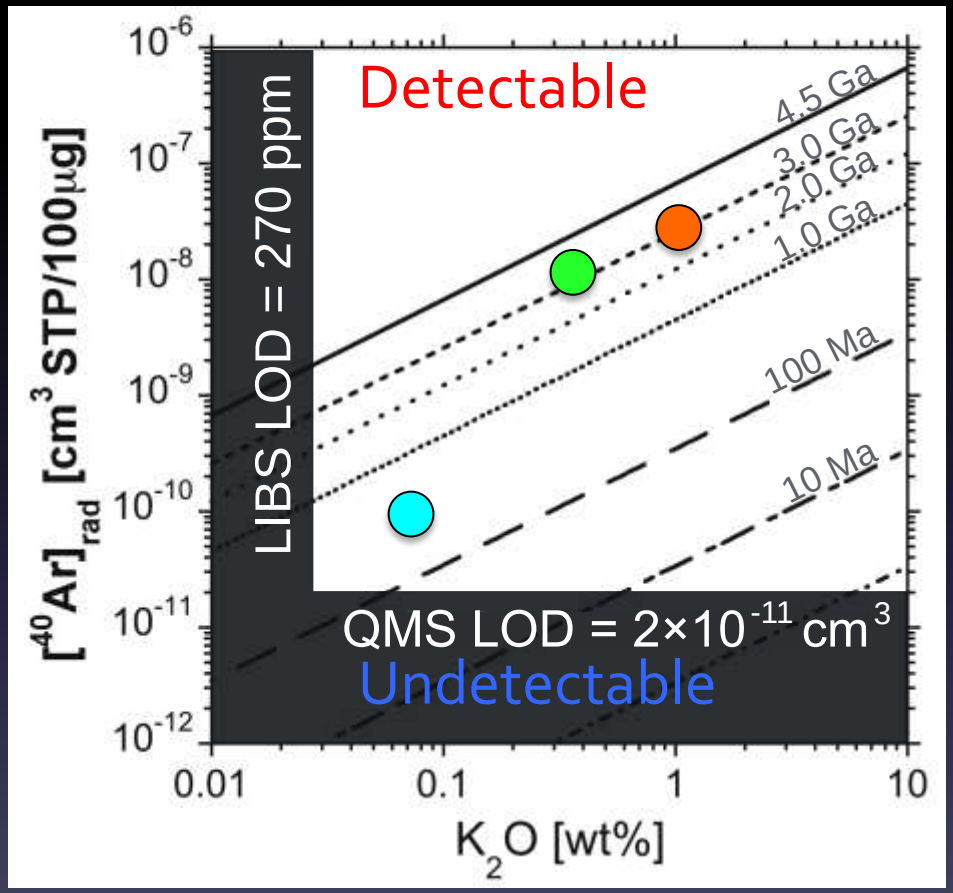
Dating a Eucrite

	Eucrite		
	Spot 1	Spot 2	Known*
$^{40}Ar/^{36}Ar$	710±60	420±50	650±150
$^{38}Ar/^{36}Ar$	1.7±0.4	1.6±0.2	~1.5
^{40}Ar [10^{-5} cm^3 STP/g]	1.4±0.2	0.9±0.1	1.1-1.5
^{36}Ar [10^{-8} cm^3 STP/g]	2.1±0.3	2.0±0.2	2.0-2.4

*Miura+ (1998)

- Amount & isotope ratio of Ar are consistent with reported values
  → QMS analyses in the small spot worked well.

Applicability of instrument: Detection limits



Three key samples we might encounter on Mars

- **Hesperian-Amazonian bdry. lava flow**
  - K2O~ 1 wt%[a]?
  - Age~ 2-3 Ga[b]?
- **Shergottites[c]**
  - K2O~ 700 ppm
  - Age~ 200 Ma
- **Tharsis basalt**
  - K2O~ 3000 ppm[d]?
  - Age~ 3.5 Ga[b]?

a Ming+ (2008)
b Neukum+ (2010)
c Bogard+ (2008)
d Boyton+ (2008)

- Our method will be able to measure key geologic units.
- Obtaining isochron and improving accuracy for low K are future work.

Conclusions

1. In-situ K-Ar dating instrument developed
   - Coupling LIBS & QMS
2. Age measured for mineral samples
   - 1.8±0.1 Ga for 1.80 Ga biotite & 2.1 ±0.3 Ga for 1.74 Ga hornblende with 10-15% age determination error
3. Argon accurately measured for a Eucrite
   - Challenges lie in accurate K_2O measurements when concentration is low.
4. Detection limit quantified
   - 270 ppm of K_2O, 2×10^{-11} cm^3 STP of ^{40}Ar
   - Accurate K_2O measurements at > 1 wt%

   →Measure Mars geologic units can be measured
5. Future work
   - Constract actual isochron
   - Further reduction of measurement error