Gas Monitoring by QMS

Present Situation and Future Prospects

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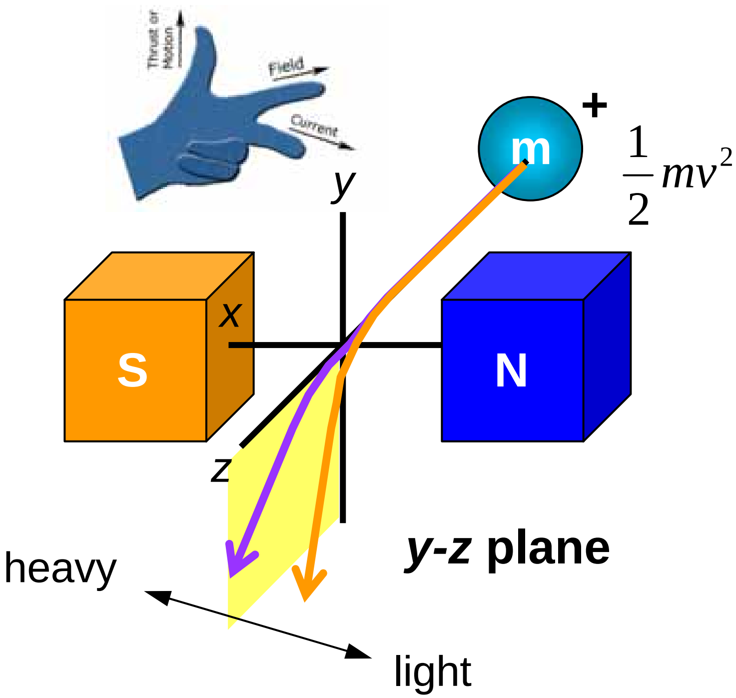
Outline

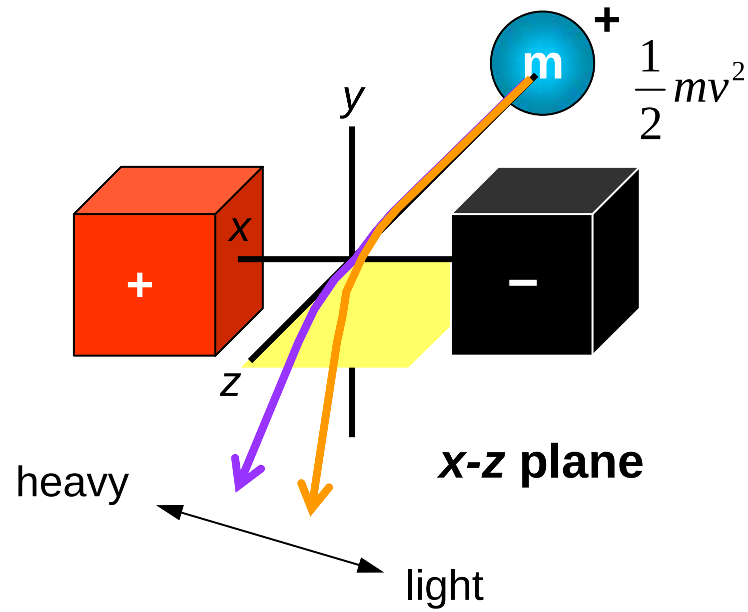
- Mass Spectrometry
- Gas Monitoring for Earthquake Research
- Gas Monitoring for Elemental Process Research
- Next Stage of Gas Monitoring by QMS

Mass Spectrometry

<u>Principle</u>: Trajectory of a cation is determined by mass weight



<u>Magnetic Field</u>

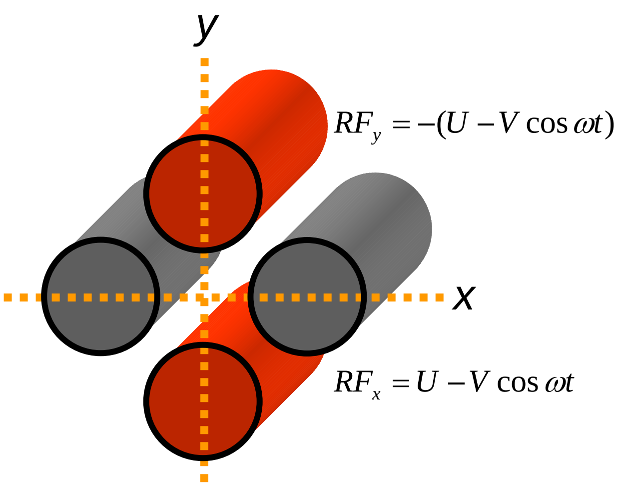


<u>Electric Field</u>

Gas composition can be analyzed by mass weight of molecules

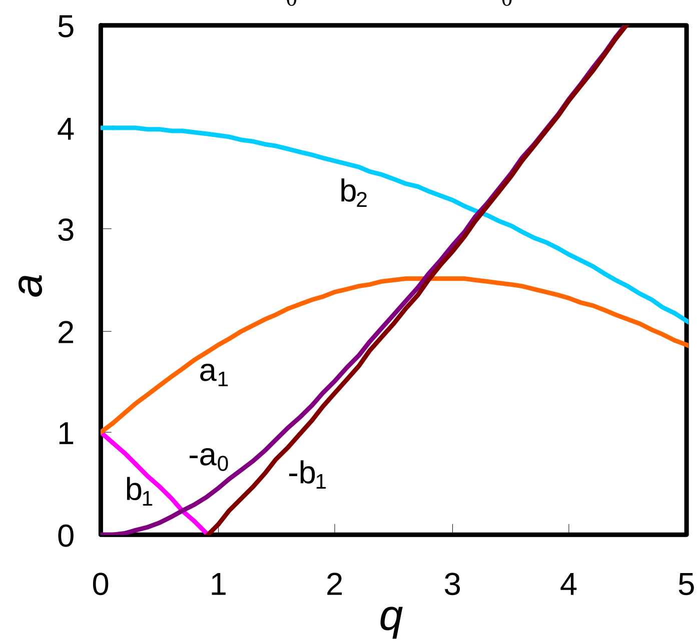
Quadrupole Mass Spectrometer (QMS)

Quadrupole: Motion of a cation is governed by Mathieu's equation



$$\frac{d^2x}{dt^2} + \frac{2Ze}{mr_0^2}(U - V\cos\omega t)x = 0$$

$$a = \frac{8ZeU}{mr_0^2\omega^2}, \quad q = \frac{4ZeV}{mr_0^2\omega^2}$$



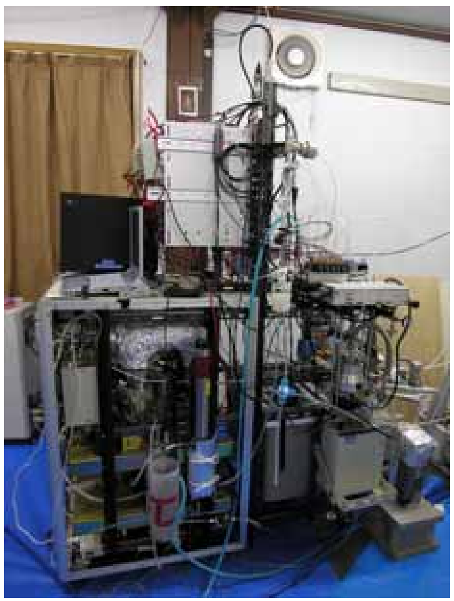
a-*q* stability diagram of Mathieu's equation

Quadrupole behaves as a mass filter under stated electronic condition

QMS as Gas Monitor

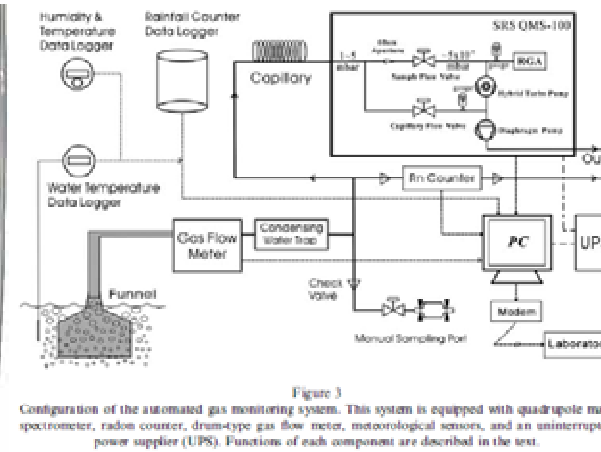
Advantage: Isotope analysis, High sensitivity, High time resolution

Gas monitoring using a QMS was realized by Takahata et al. in 1997.



Shimada, et al. (in preparation)

Tsunomori, et al. (submitted)



Yang, et al. (2006)

Quadrupole mass spectrometer is useful for a long-term observation

Gas Composition Change in Spring Water

Spring water gathers chemical substances from wide area

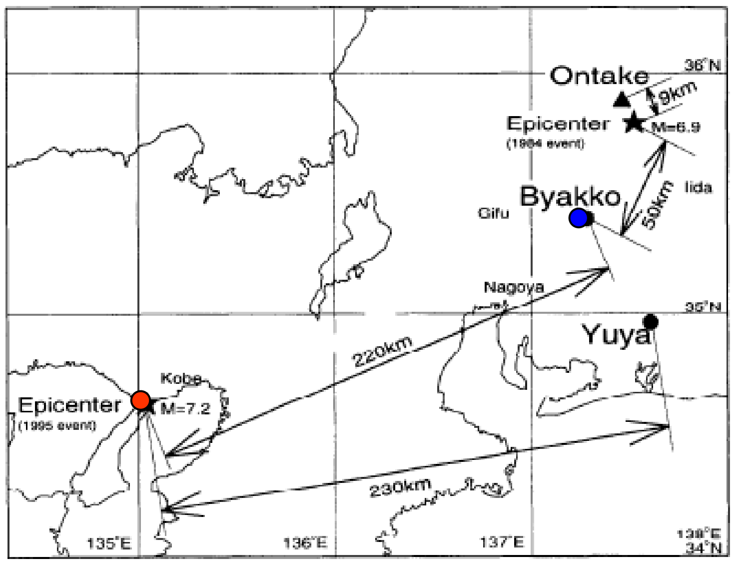


Fig. 1. Locations of monitoring sites (dots and triangle) and epicenters (stars) of two large events (1984 and 1995).

Monitored by a gas chromatograph with oxygen carrier.

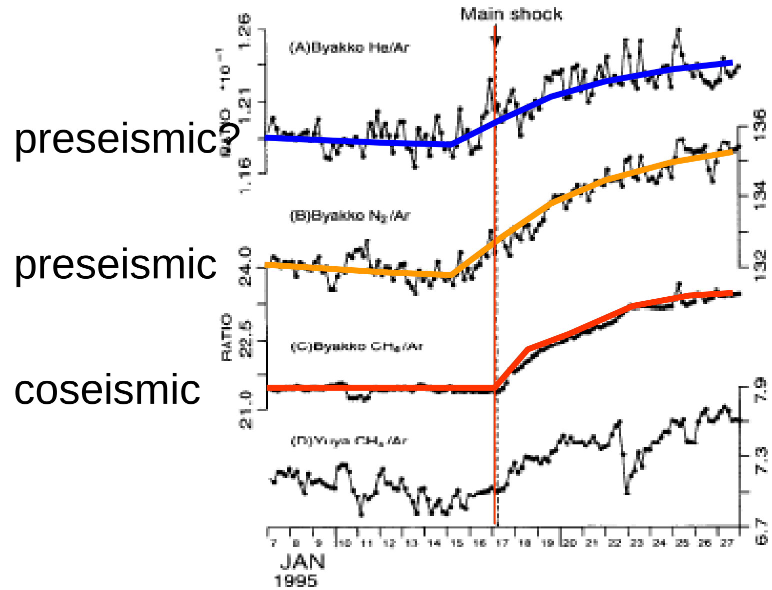
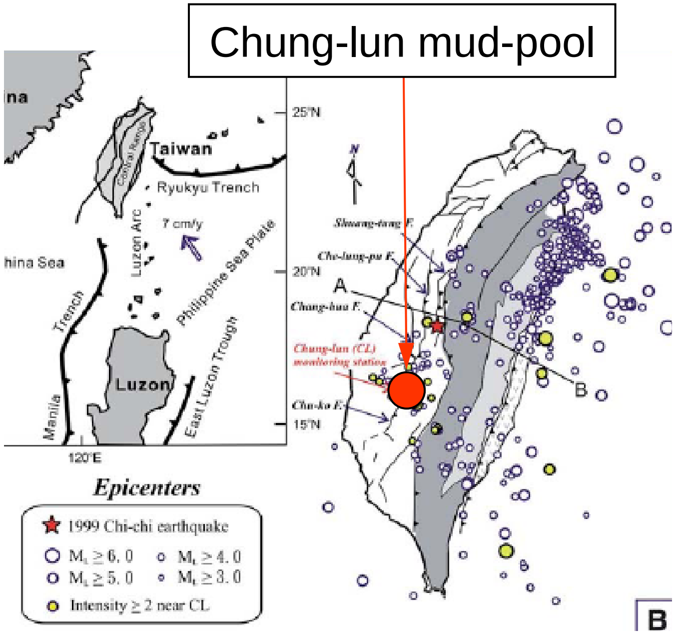


Fig. 3. Changes in gas concentration ratios at Byakko (A, B, C), and CH_4/Ar change at Yuya (D) for the 1995 event. Each point represents an average value during 4 hours (8 and 2 readings at Byakko and Yuya, respectively). Arrow indicates occurrence of the earthquake. Note that the N_2/Ar ratio began to increase 1 day before the event.

Sugisaki, et al. (1996)

Gas Composition Change in Mud-Pool Bubble

Gas concentration in groundwater can be perturbated by many causes



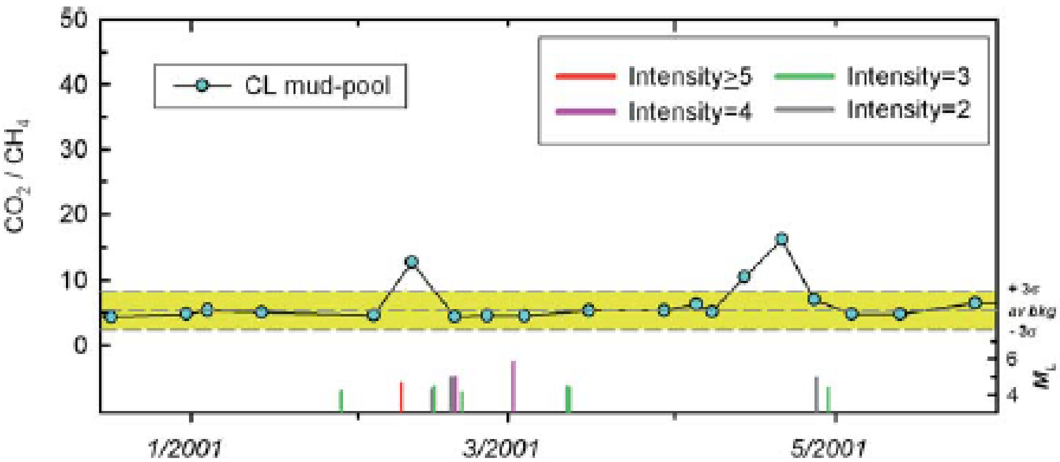


Figure 2

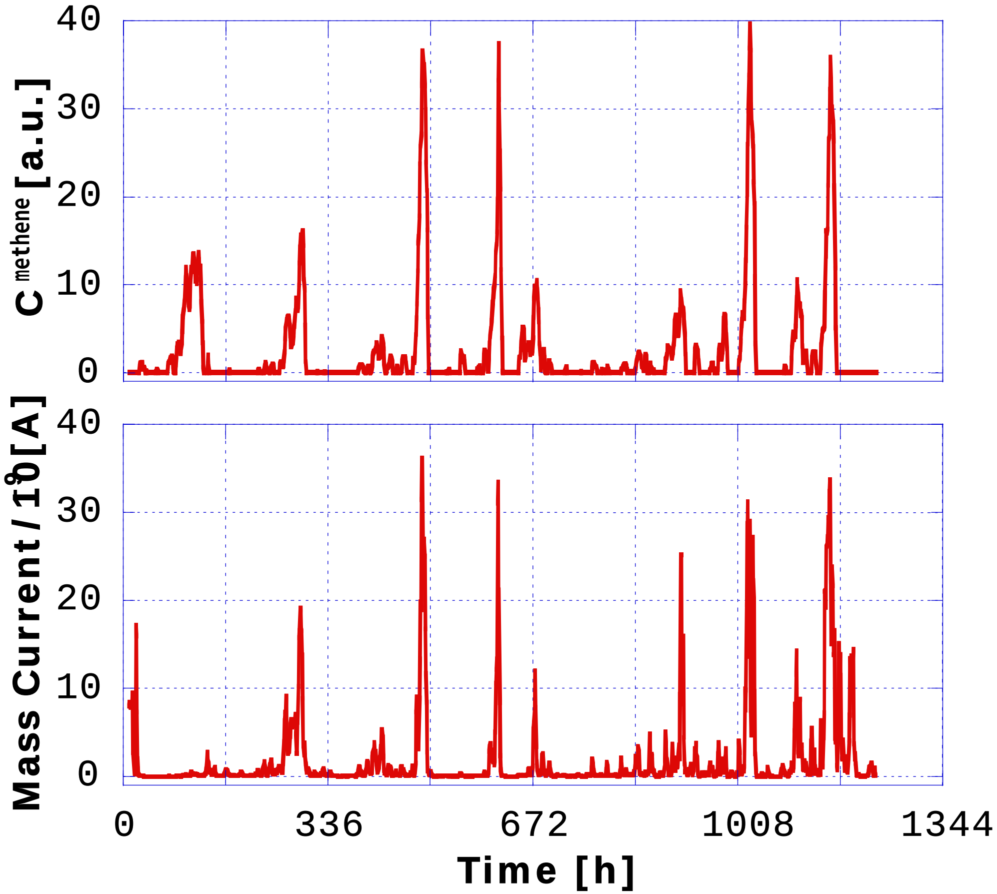
Variations in CO_2/CH_4 ratios of bubbling gases from the CL mud-pool. Earthquake data source is the same as shown in Figure 1.

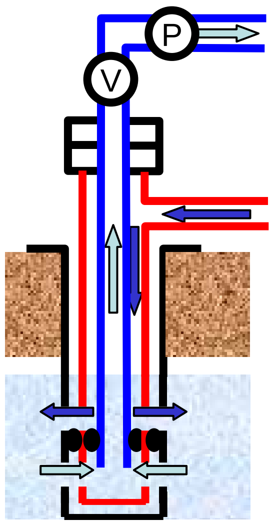
T.F. Yang, et al. (2006)

Monitoring subsurface gas must be helpful for earthquake prediction

Spike-like Methane Concentration Change

Gas concentration in groundwater can be perturbated by many causes





$$C = \frac{C_{max}}{1 + \exp(-r(w - w_0))}$$

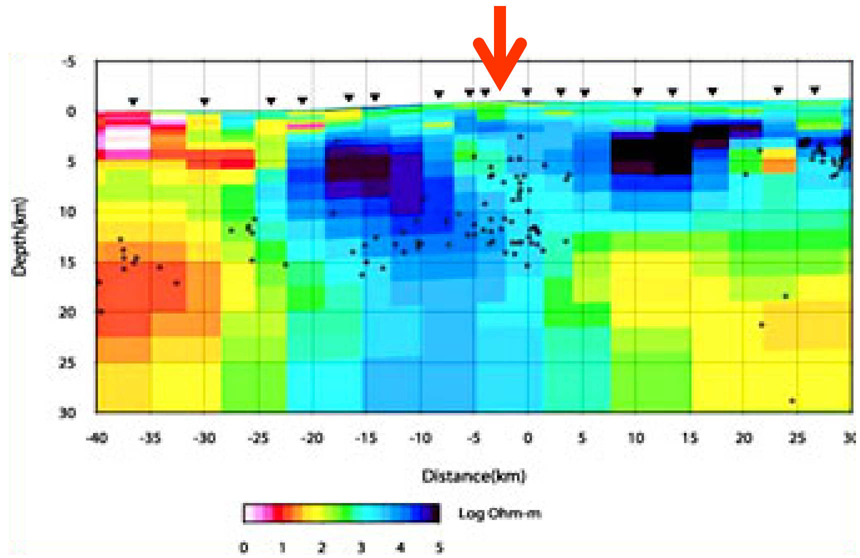
Tsunomori, et al. (submitted)

Groundwater flow affect methane concentration in groundwater, too

Spring Water of Active Fault

Active fault is connected to a focal region

ppm	Miya-kawa rv.	Spring Water
Na	3.3	333.1
NH_4	0.0	0.0
K	1.5	4.5
Mg	1.0	4.2
Ca	15.2	14.9
Cl	2.3	199.2
NO_3	0.3	0.0
SO_4	3.9	3.5
HCO_3	53.2	610.8



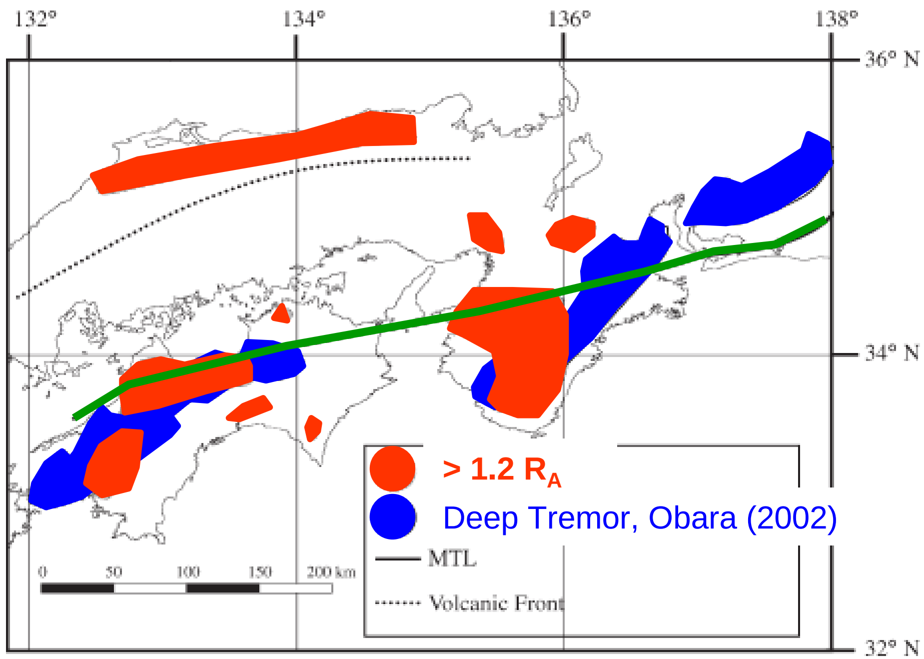
	Air	Spring Water #1	Spring Water #2
$^3He/^4He\ /10^{-6}$	1.4	2.42	2.39
^4He (ppm)	5.6	778	763

Shimada, et al. (in preparation)

Deep subsurface gas is included in fault gas

$^3He/^4He$ and Low Frequency Tremor

Low frequency tremor is thought to be related to fluid generation in the crust



Dogan, et al. (2007)

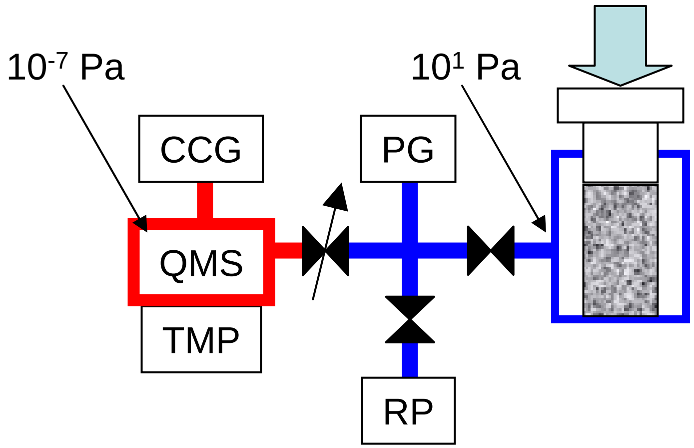
Spatio-temporal monitoring of $^3He/^4He$ will be a powerful tool for constraining the underground structure

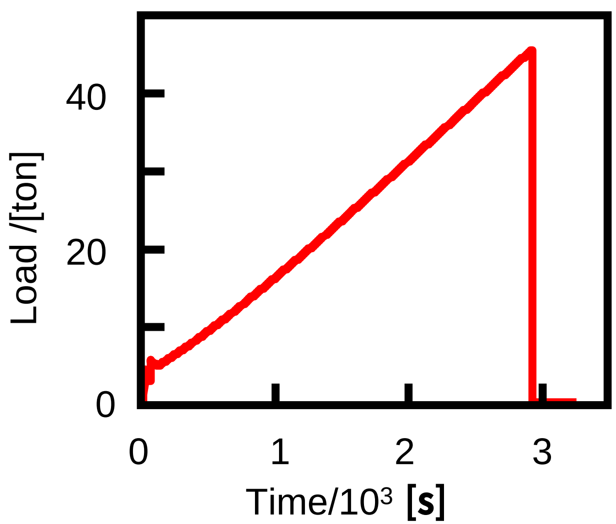
Gas Monitoring for Earthquake Research

- Monitoring subsurface gas must be helpful for earthquake prediction
- Groundwater flow also affect methane concentration in groundwater
- Deep subsurface gas is included in fault gas
- Spatio-temporal monitoring of $^{3}He/^{4}He$ will be a powerful tool for constraining the underground structure

Methane Emission under Compressive Force

Cylindrical granite is uni-axially compressed in a vacuum chamber

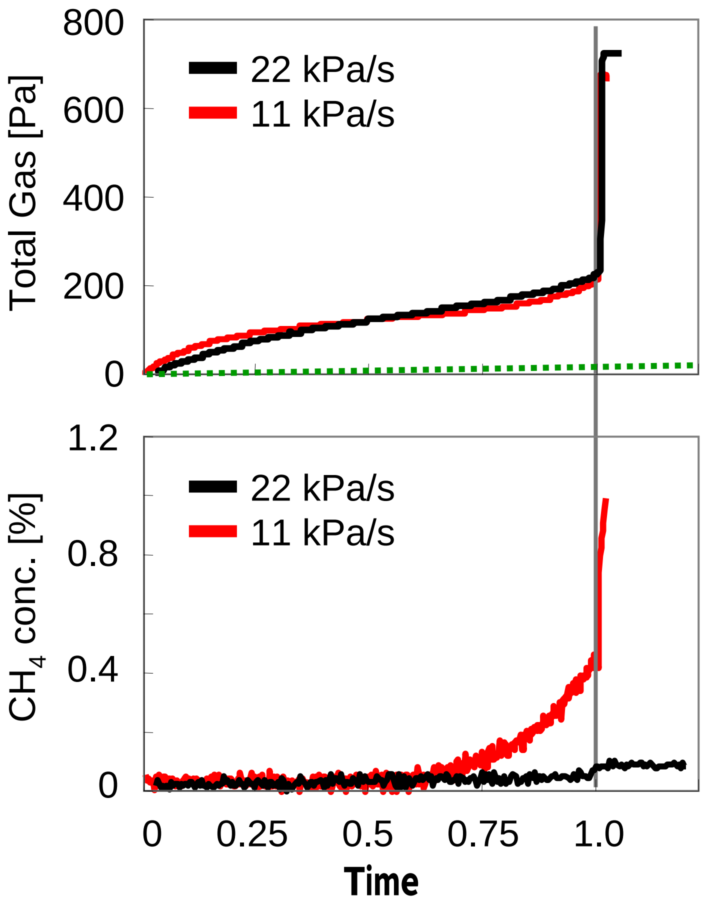




Inada Granite (Ibaragi, Japan)
Size: 0.5-4.0mm
Quartz 31%, Feldspar 63%,
Biotite 4%

Methane Emission and Compressive Rate

Methane concentration in the chamber is analyzed by a QMS

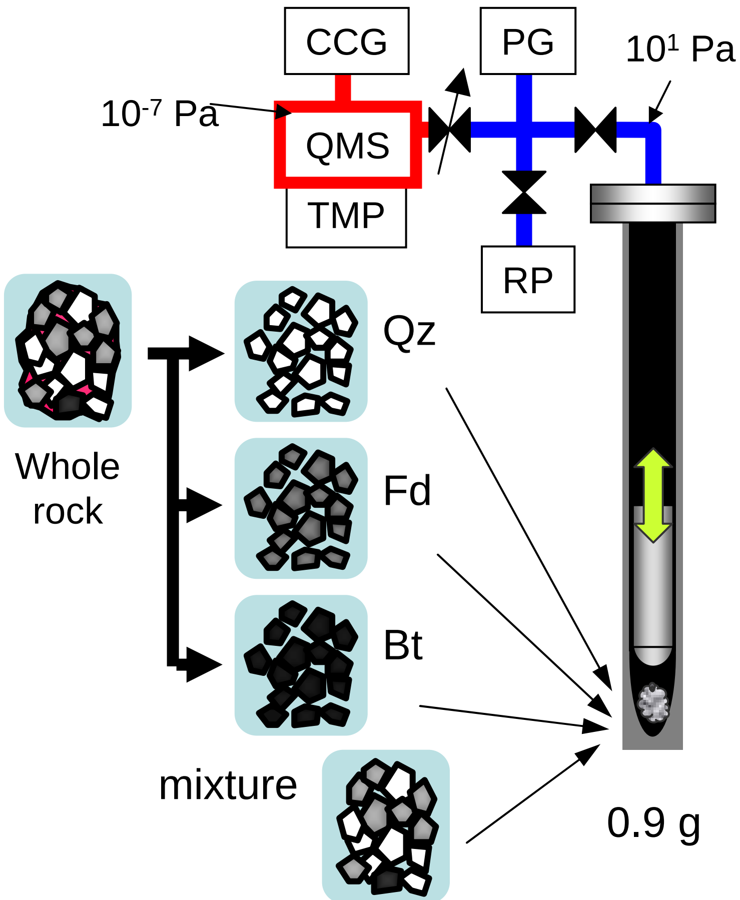


Koizumi, et. al (in preparation)

Temporal change of methane concentration seems to depend on compressive rate

Methane Concentration in a Rock

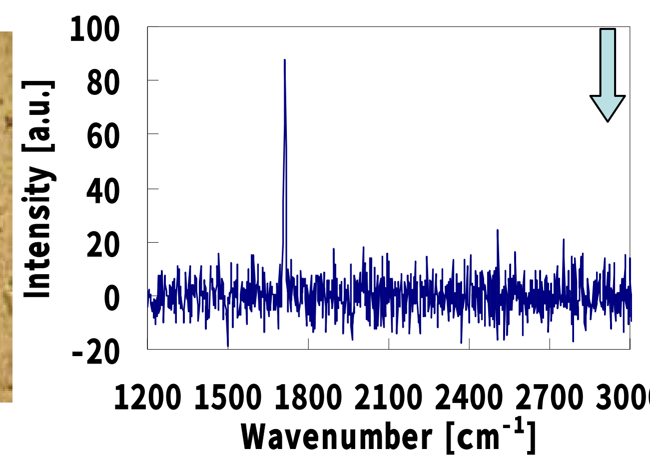
Methane source is thought to be minerals



	CH_4 conc. [cm^3STP/g]	
Qz	0.20	±0.06
Fd	0.08	±0.05
Bt	0.4	±0.1

	CH_4 conc. [cm^3STP/g]	
Granite	0.17	±0.06
Mixture	0.14	±0.05
Calc.*	0.14	±0.06

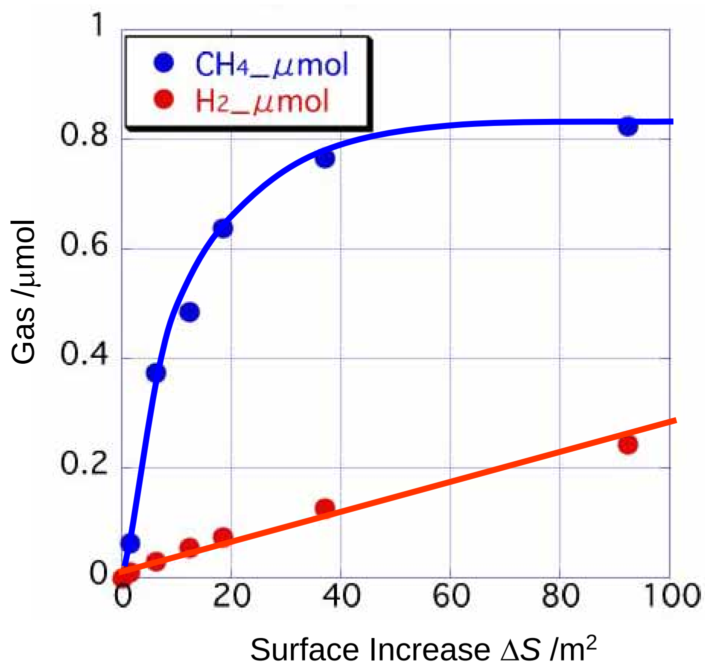
*** Inada Granite:** Qz 31%, Fd 63%, Bt 4%



Methane concentration may reflect the amount of cracks generated in a rock

Methane Included in a Rock

Granitic rocks of Atotsugawa active fault were grinded in a closed cell



$$C(\Delta S) = A\left(1 - \exp(-k\Delta S)\right)$$

Emission phenomenon

$$C(\Delta S) = B\Delta S$$

Mechano-chemical reaction

Saito, et. al (in preparation)

Methane is not reaction product but included in a rock

Gas Monitoring for Elemental Process Research

- Emission behavior of methane from a granite seems to depend on compressive rate.
  - The dependency is being confirmed now.
- The methane source is inclusions in minerals
- The amount of methane emitted may indicate degrees of crack generation.

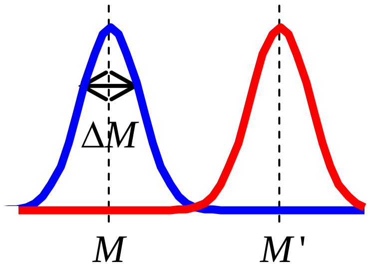
Next Stage of Gas Monitoring by QMS

- Spatio-temporal monitoring of $^3He/^4He$ must be important for earthquake prediction research.
  - Active fault zone
  - Area above focal region of low frequency tremor
  - Hot spring

- High performance mass spectrometer is definitely required.

Development of High Resolution QMS

Mass weight of ³He is very close to that of HD

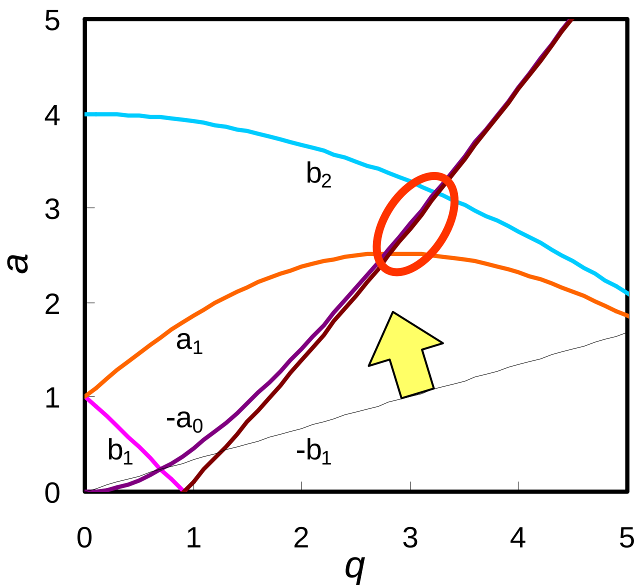


$$\frac{M}{\Delta M} = \frac{0.126}{0.16784 - (U/V)} \geq 500$$

$$\frac{U}{V} = \frac{a}{2q} \geq 0.168$$

$$\frac{a}{q} \geq 0.336$$

	Molecule	Weight [u]
3	**$^3He^+$**	**3.016030**
	T^+	3.016050
	HD^+	**3.021825**
	H_3^+	3.023475
4	**$^4He^+$**	**4.002600**
	HT^+	4.023875
	D_2^+	4.028204
	H_2D^+	4.029650

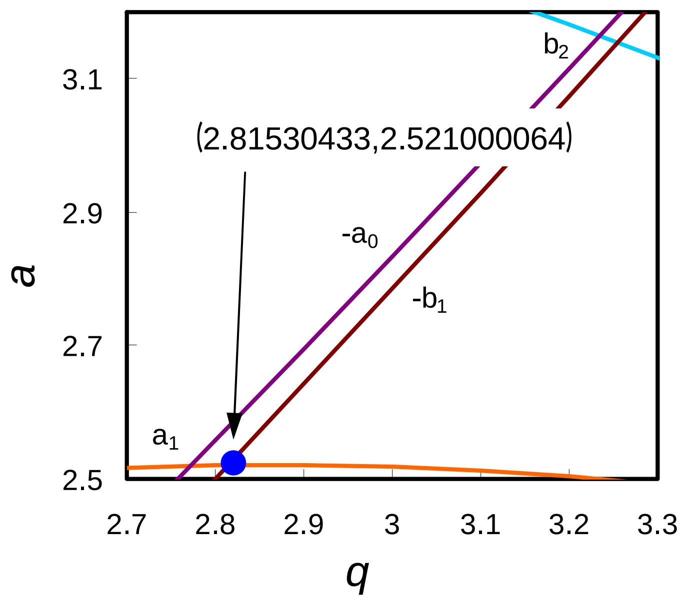


QMS should be driven in the second stability region

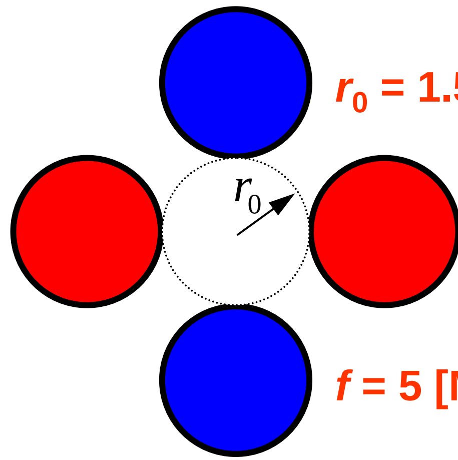
Requirement for High Resolution QMS

Quadrupole must be driven in the second stability region

Second Stability Region



$$q = 2.81, a = 2.53$$



r_0 = 1.5 [mm]

f = 5 [MHz]

$$e = 1.6021773349 \times 10^{-19}$$

$$u = 1.66053873 \times 10^{-27}$$

$$m : 1 \sim 5$$

$$q = \frac{4eV}{m r_0^2 \omega^2} \qquad V : 10.35 \sim 51.74$$

$$a = \frac{8eU}{m r_0^2 \omega^2} \qquad U : 4.66 \sim 23.29$$

Problem is only to make an electric circuit for RF voltage generation

Summary

- Gas monitoring is powerful tool for groundwater (geochemical) research related to earthquakes
- Laboratory experiments are important for understanding mechanism of observation results
- Spatio-temporal monitoring of $^{3}He/^{4}He$ must be important for earthquake prediction research.