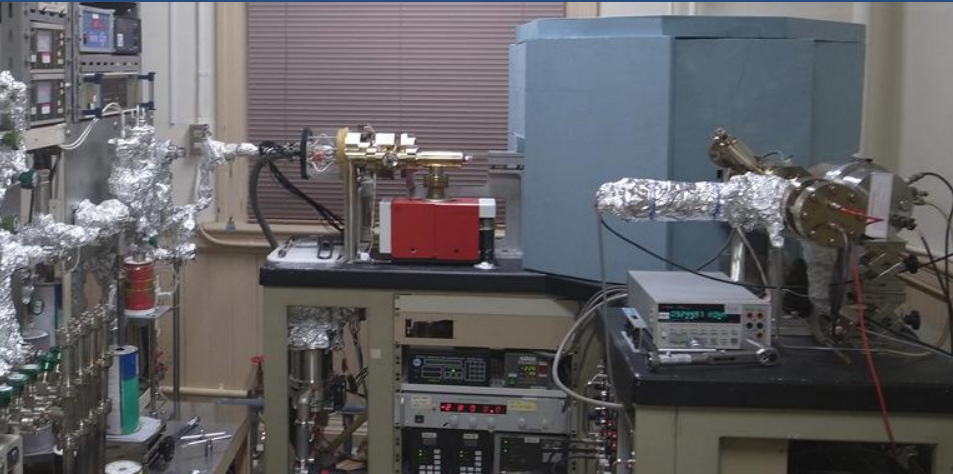


# Mantle metasomatism inferred from halogens and noble gases within mantle-derived materials



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## Acknowledgement

Satoko ISHIMARU (*Kumamoto University*) Shoji ARAI (*Kanazawa University*)

Masako YOSHIKAWA Tatsuhiko KAWAMOTO Yoshitaka KUMAGAI (*Kyoto University*)

Tetsuo KOBAYASHI (*Kagoshima University*) Keisuke NAGAO (*KOPRI*)

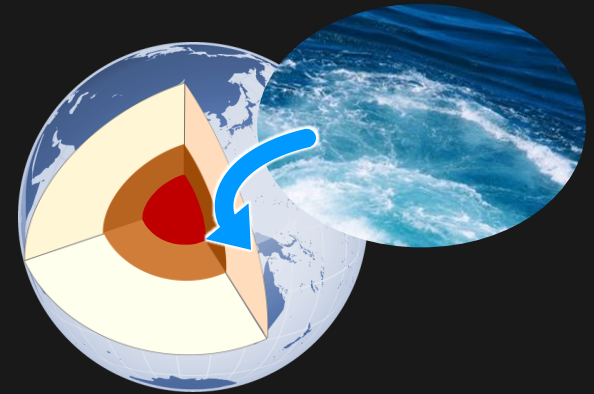
# Halogens & noble gases

## Powerful tracers of water

Strongly partitioned into water

Distinct compositions in each reservoir

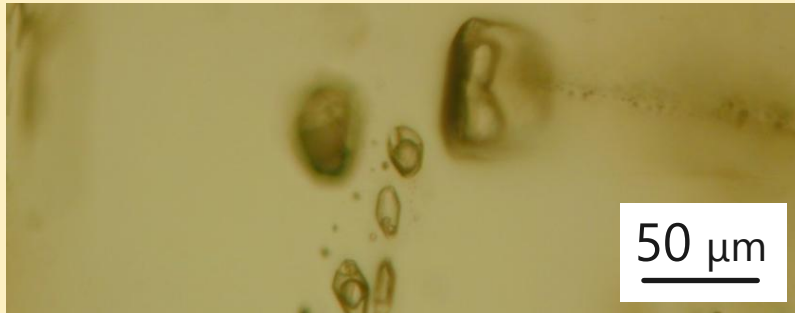
Scarce in the mantle



# Mantle xenoliths

○ **Primary information on slab-derived fluids**

Fluid inclusions in olivine



*Kawamoto et al. (2013)*

✘ **Low halogen concentration**

Halogen concentrations in DMM\*

Cl [ppm]	Br [ppb]	I [ppb]
0.5–6	2–8	0.04–0.8

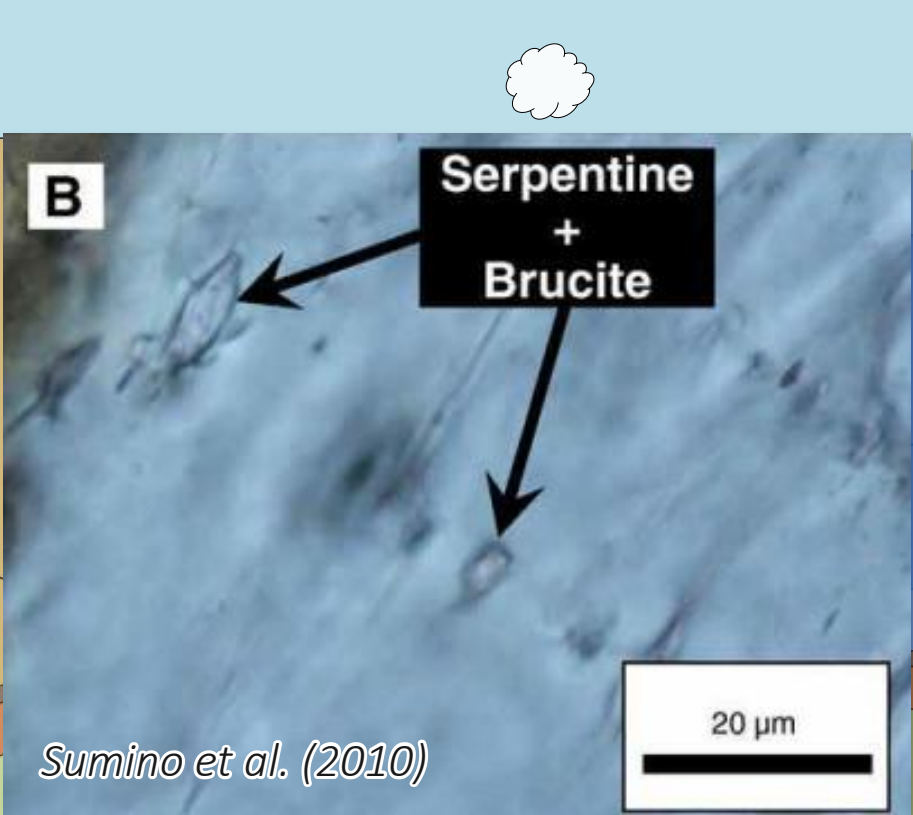
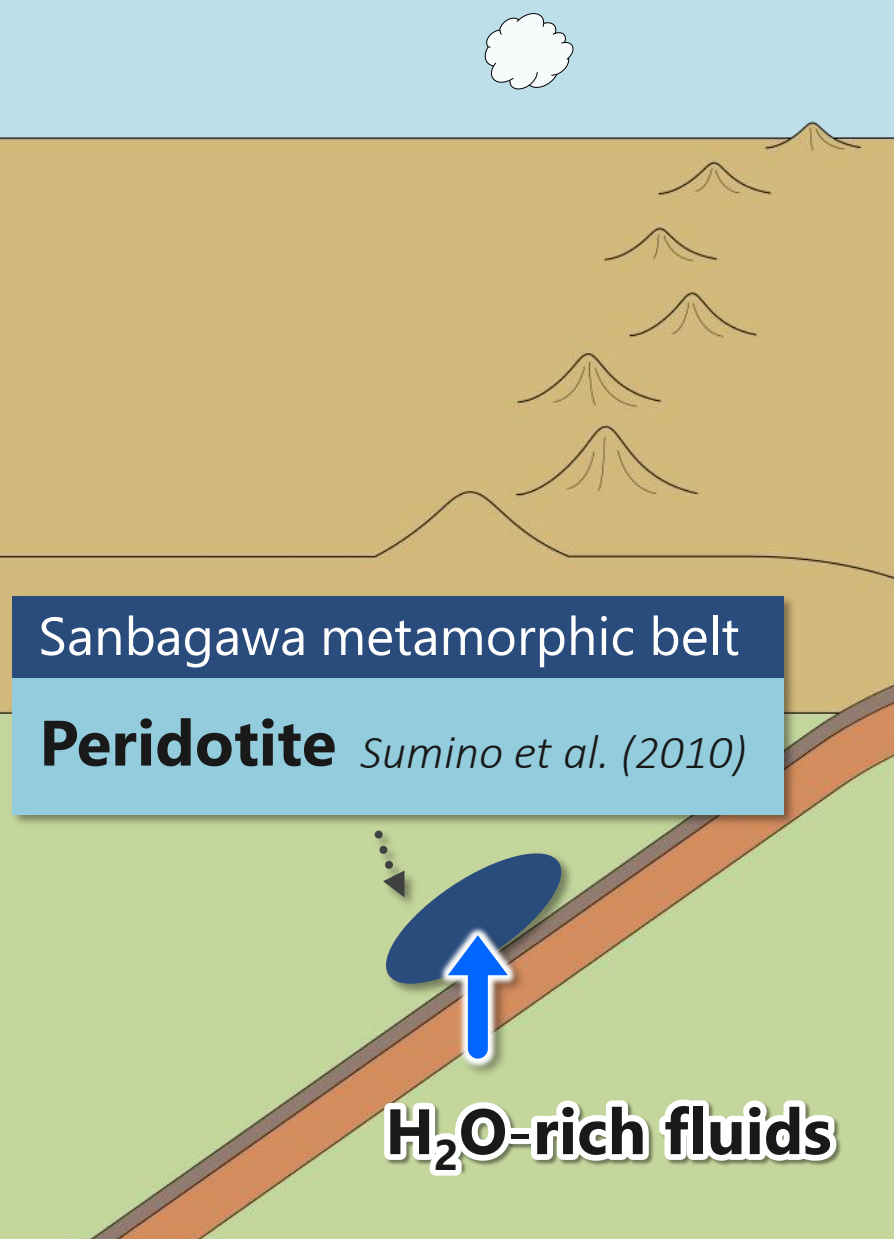
*Saal et al. (2002); John et al. (2011); Kendrick et al. (2012)*

\*Depleted MORB Mantle

**Difficult to analyze**

**Few published studies**

# Halogens & noble gases subducted into the mantle



# Halogens & noble gases subducted into the mantle

## Similar halogen & noble gas signatures

### Marine sedimentary pore fluid

Enriched in organic material-derived iodine

*e.g. Muramatsu et al. (2007)*

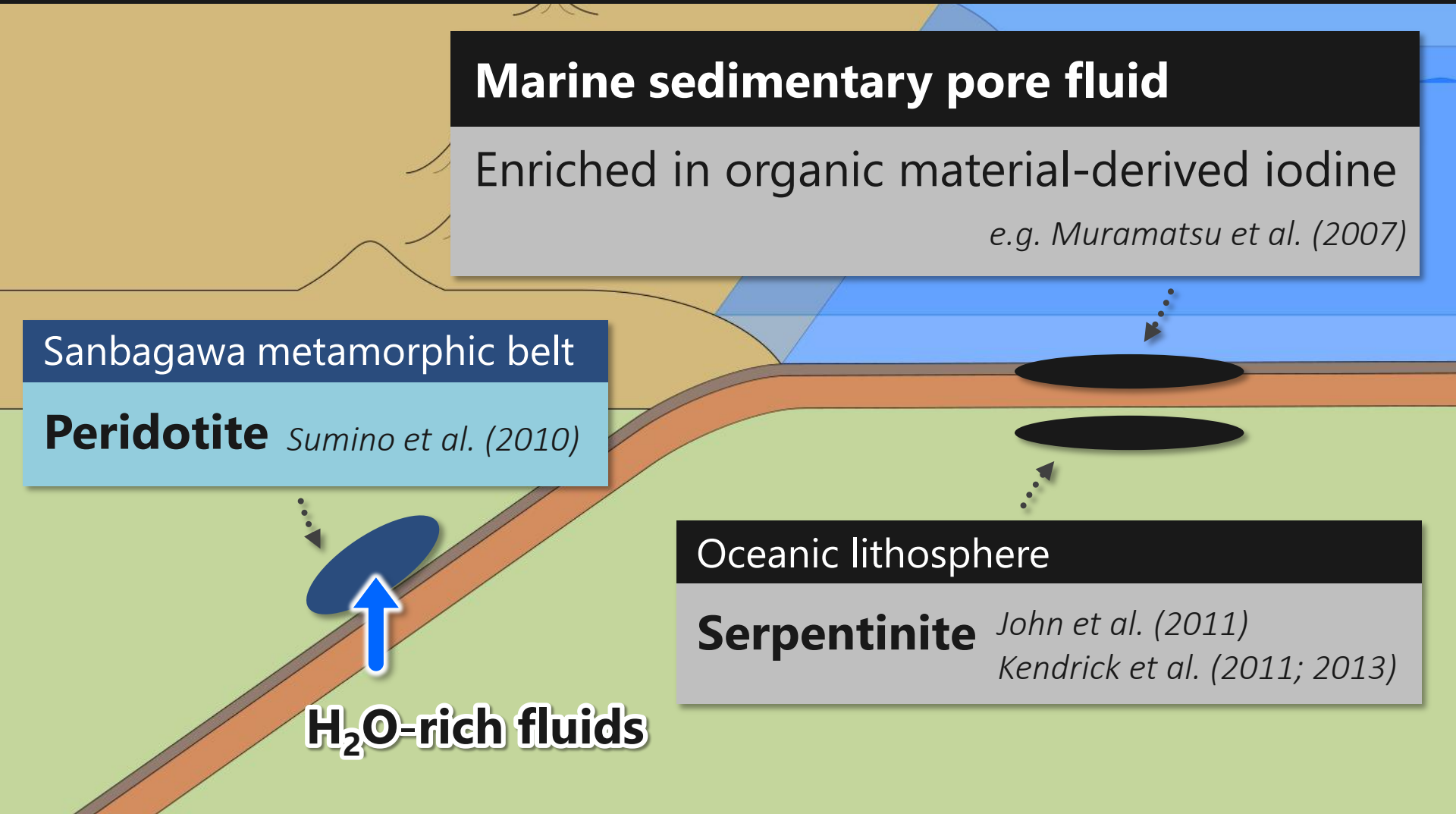
Sanbagawa metamorphic belt

**Peridotite** *Sumino et al. (2010)*

Oceanic lithosphere

**Serpentinite** *John et al. (2011)*  
*Kendrick et al. (2011; 2013)*

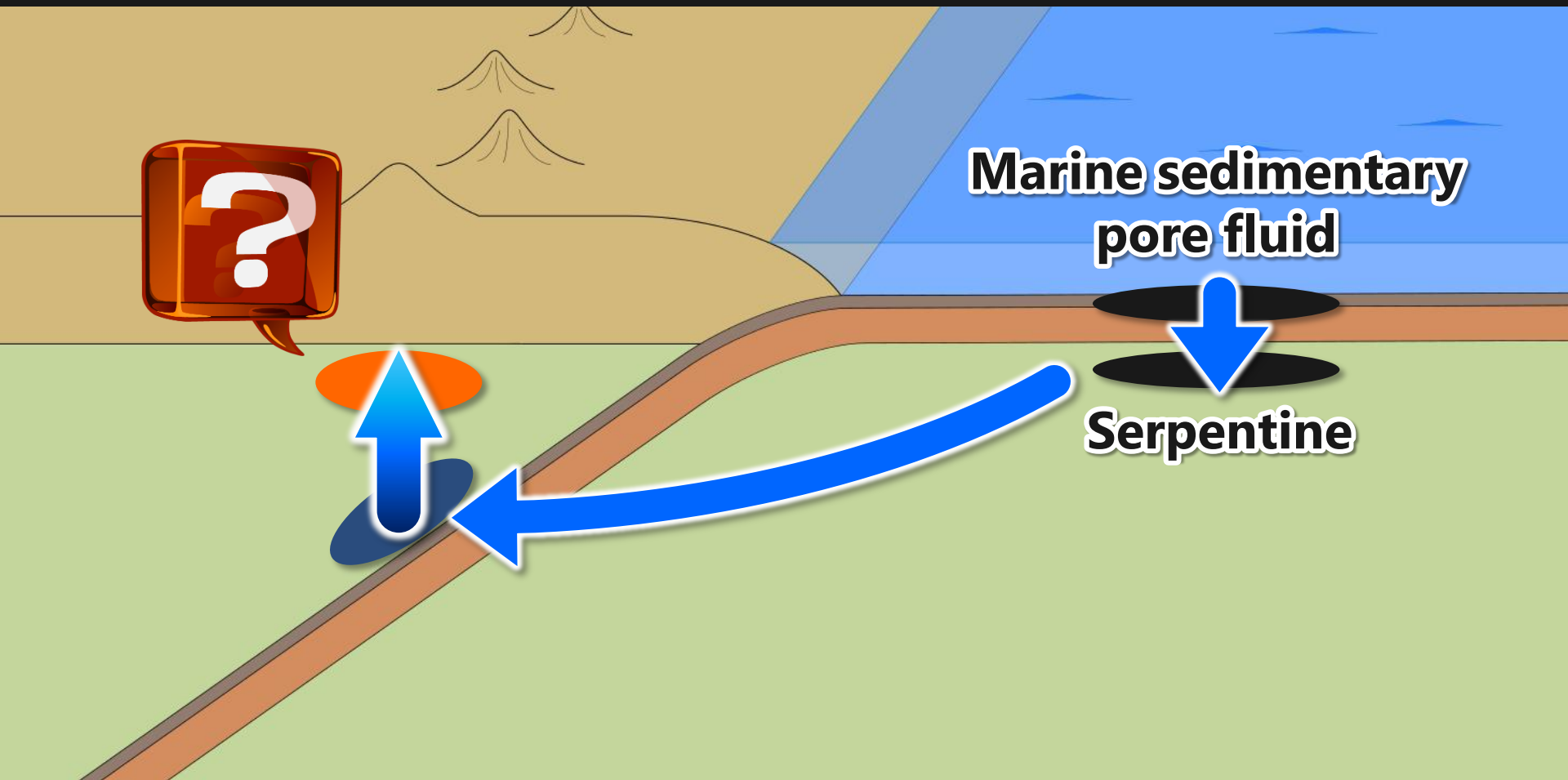
**H<sub>2</sub>O-rich fluids**



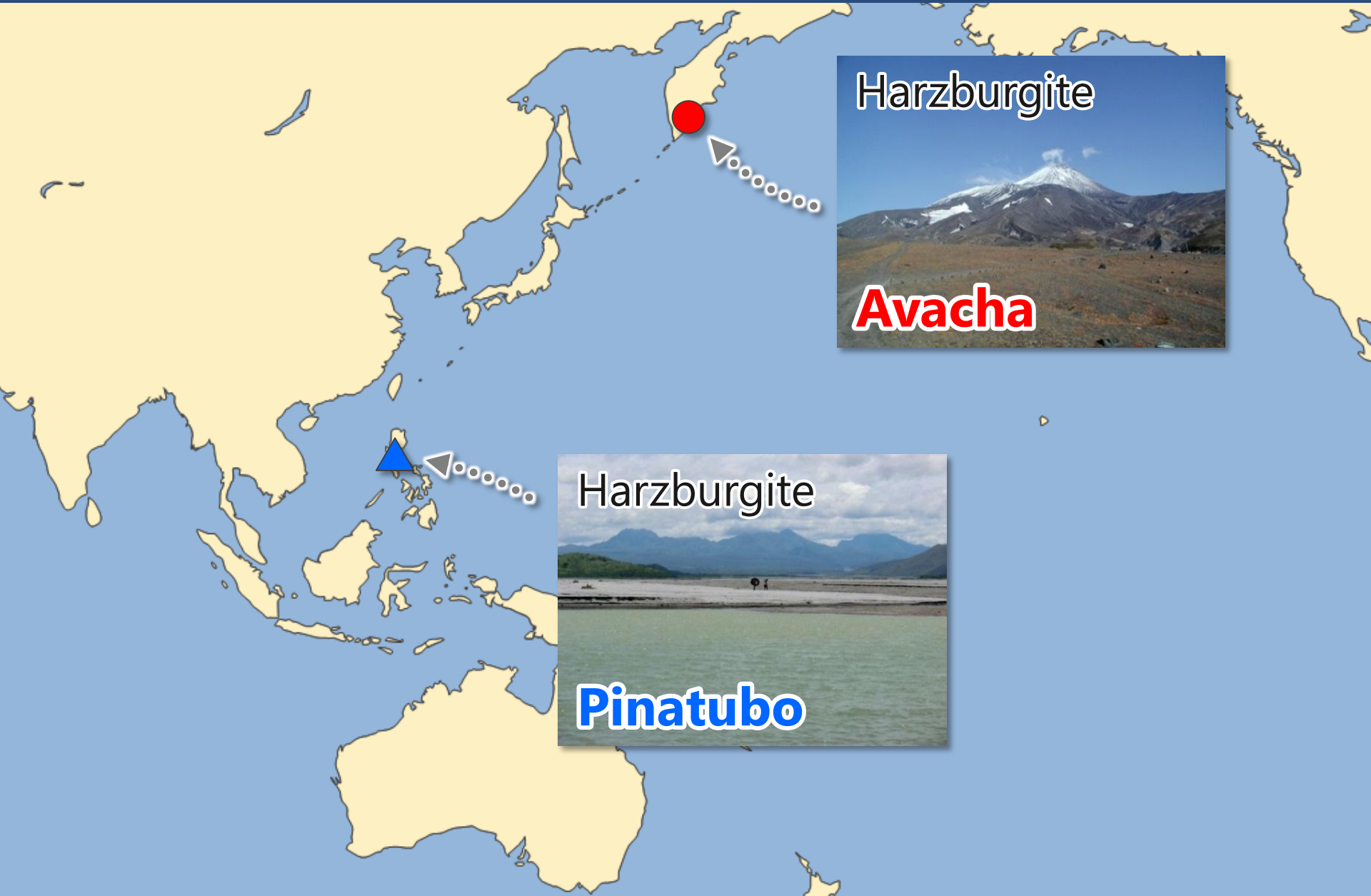
# Halogens & noble gases subducted into the mantle

Sedimentary pore fluid → Serpentine → Mantle?

Do they extend into the mantle?



# Mantle xenoliths from volcanic fronts



Harzburgite



**Avacha**

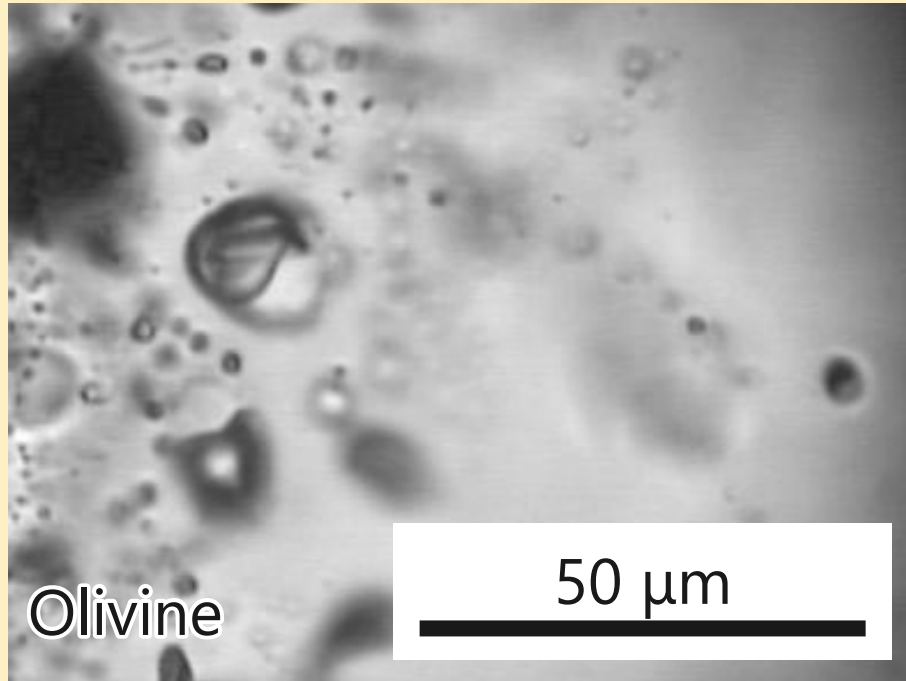
Harzburgite



**Pinatubo**

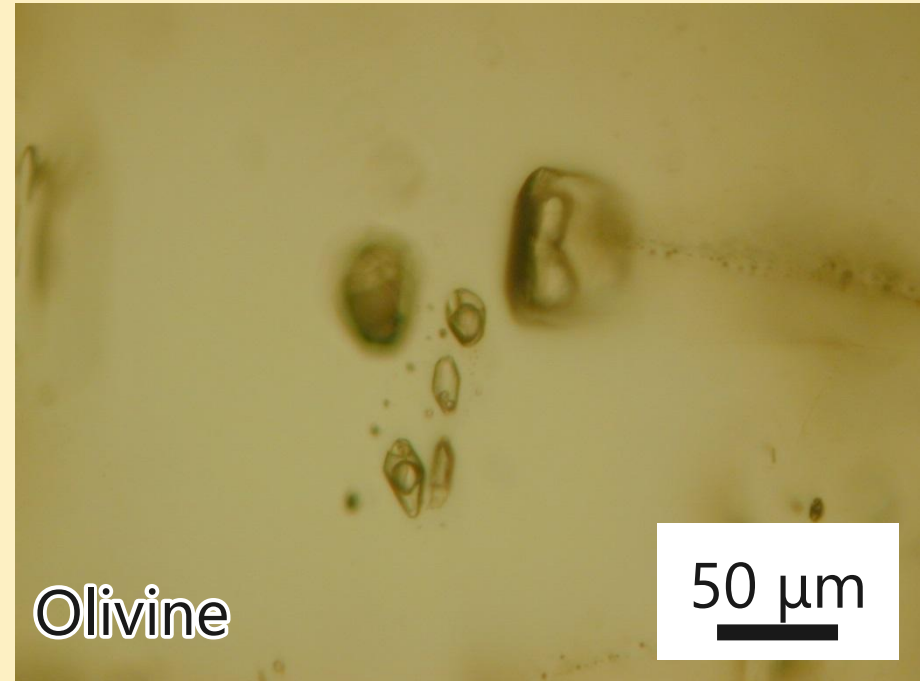
# H<sub>2</sub>O-rich fluid inclusions

## Avacha



*Ishimaru et al. (2007; personal comm.)*

## Pinatubo



*Kawamoto et al. (2013)*

**Pristine information on subducted water**

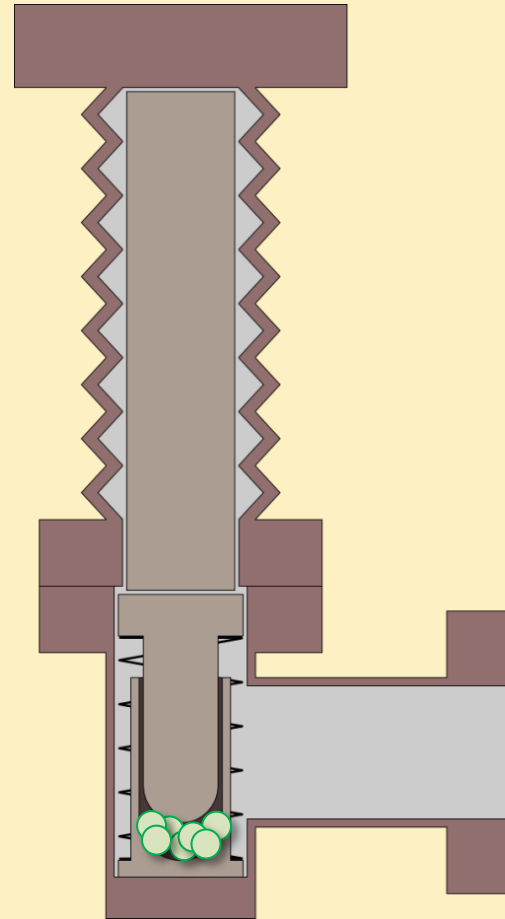
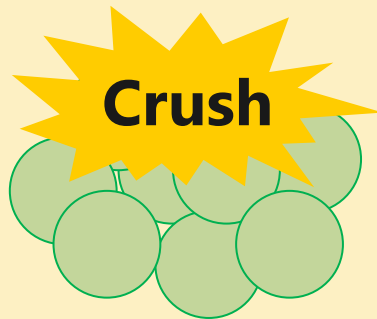


# Noble gas mass spectrometry

**Static operation** ► **High sensitivity, high precision**



# Noble gas extraction | *in vacuo* crushing

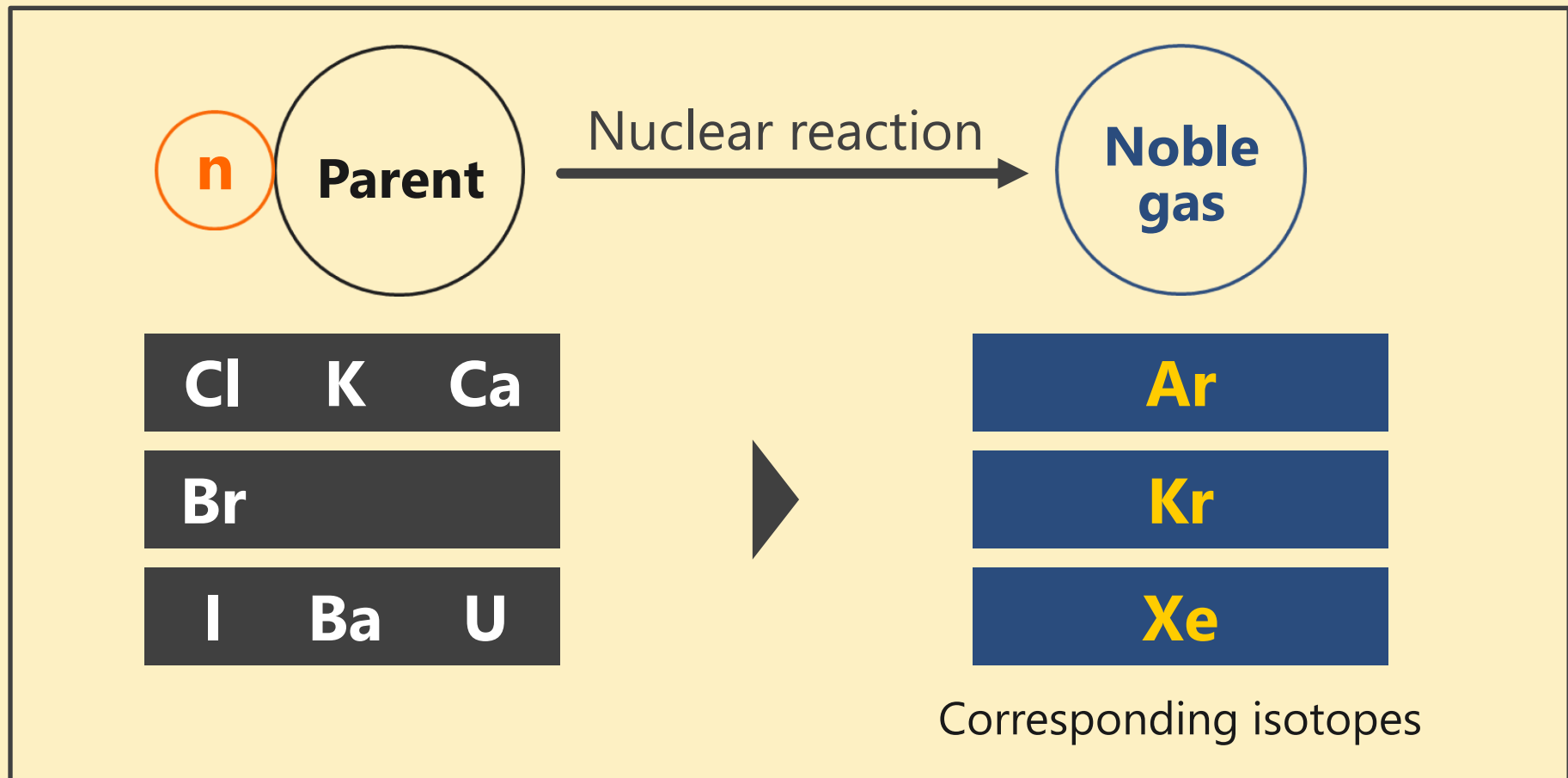


Selectively extract from fluid inclusions

# Halogen analysis by using noble gas MS

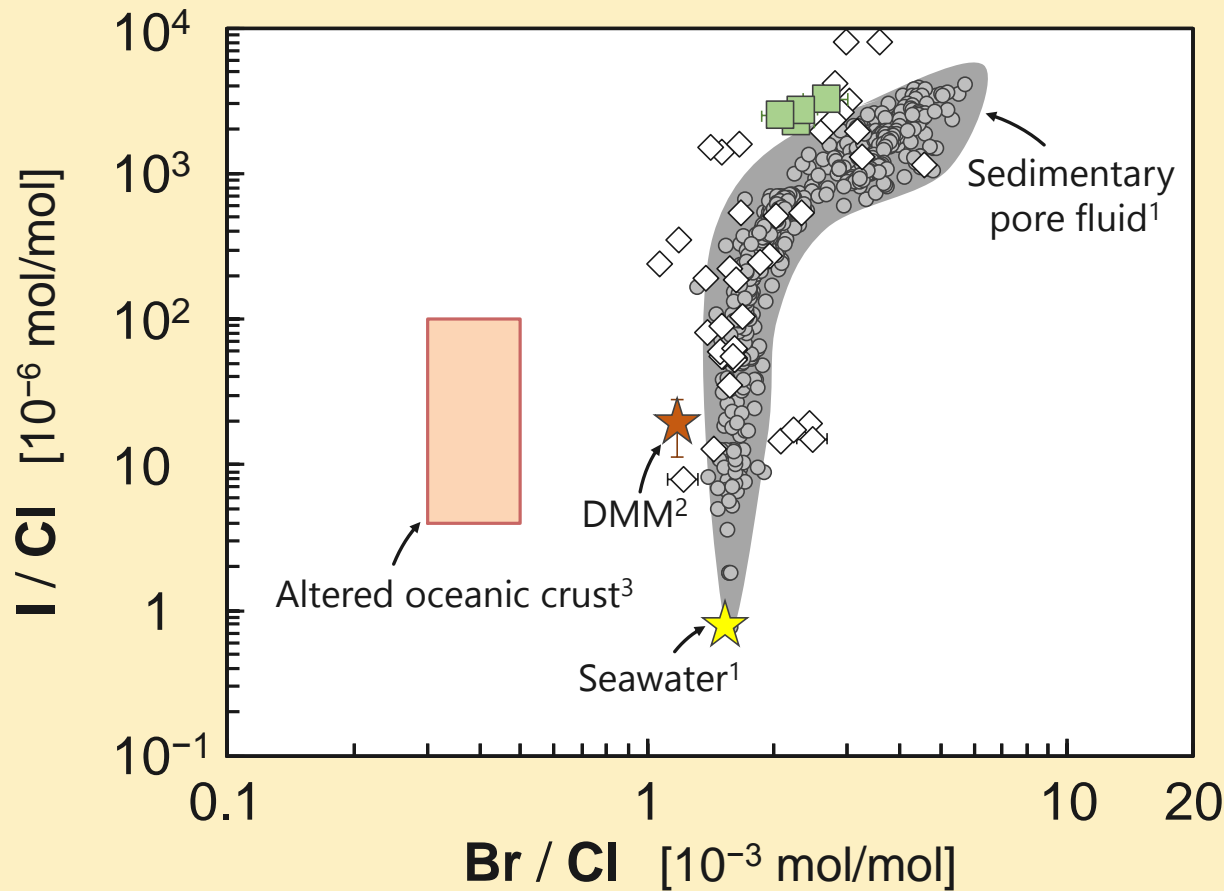
## An extension of the Ar-Ar and I-Xe dating methods

Neutron irradiation  $\longrightarrow$  Noble gas mass spectrometry



*e.g. Johnson et al. (2000)*

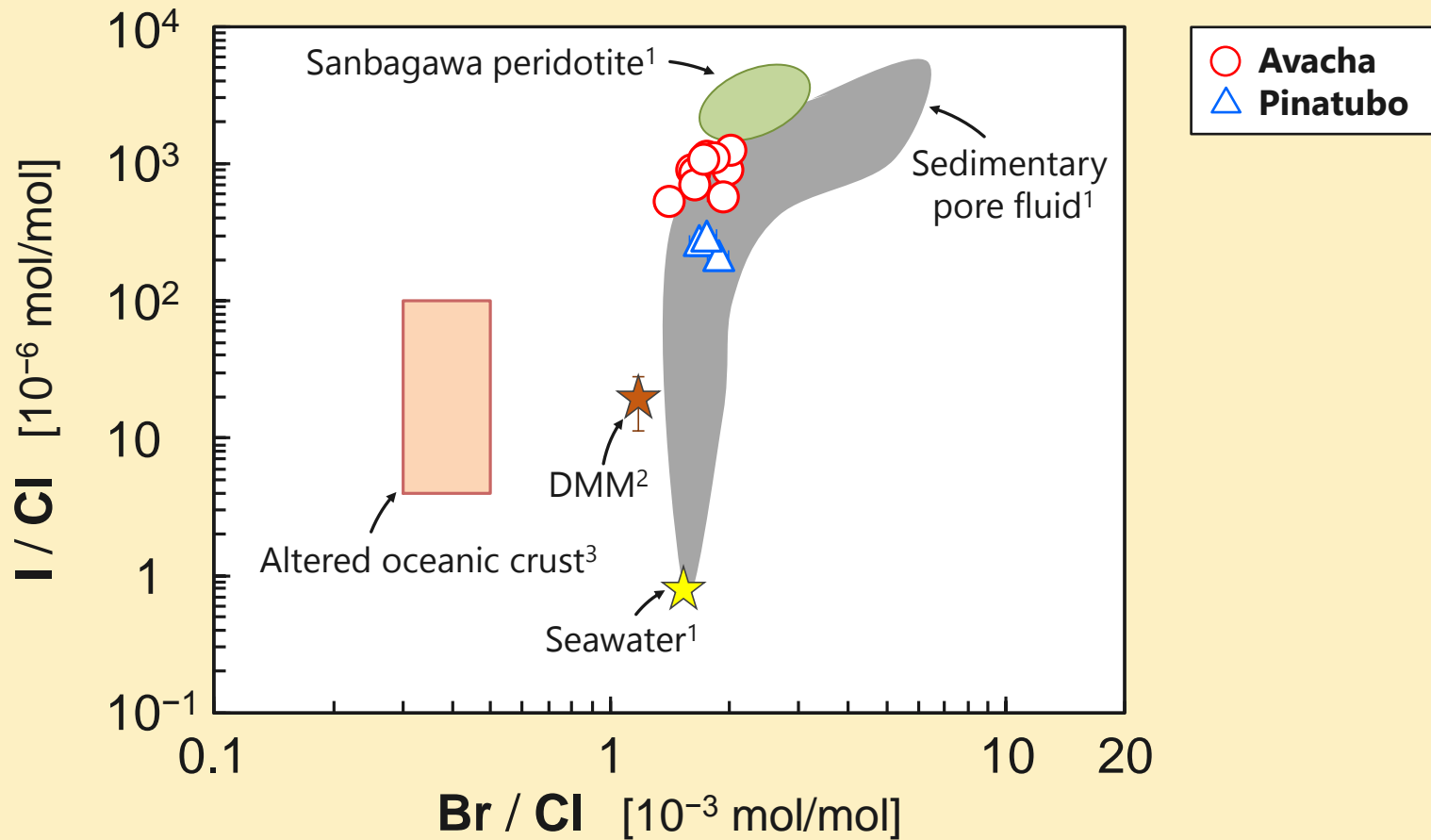
# Halogen elemental ratios | Cl / Br / I



<sup>1</sup>Sumino et al. (2010) & references therein; <sup>2</sup>Kendrick et al. (2012); <sup>3</sup>Chavrit et al. (2012)

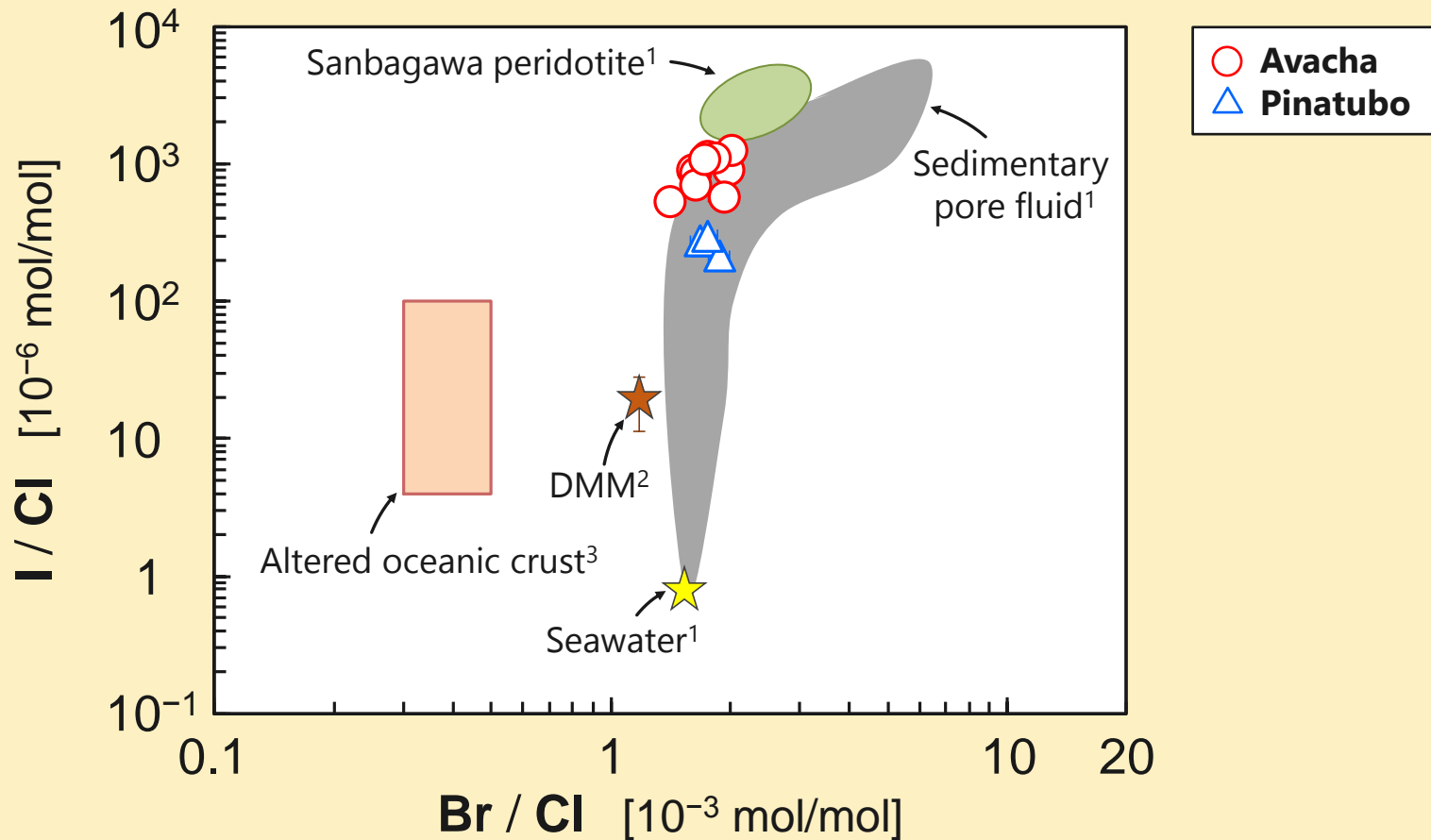
<sup>4</sup>John et al. (2011); <sup>5</sup>Kendrick et al. (2011; 2013)

# Halogen elemental ratios | Cl / Br / I



<sup>1</sup>Sumino et al. (2010) & references therein; <sup>2</sup>Kendrick et al. (2012); <sup>3</sup>Chavrit et al. (2012)

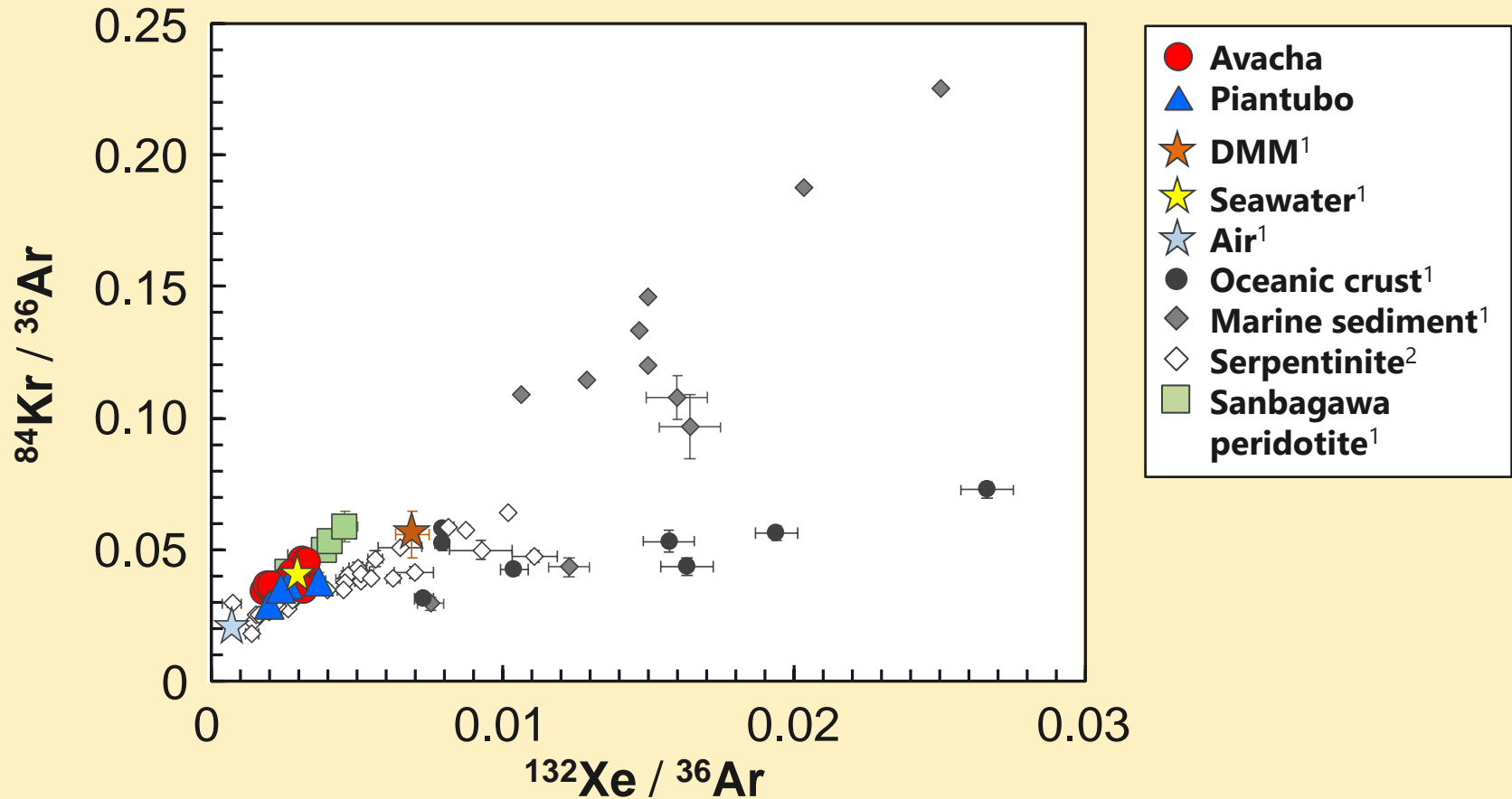
# Halogen elemental ratios | Cl / Br / I



Overlap with marine sedimentary pore fluid & serpentinite

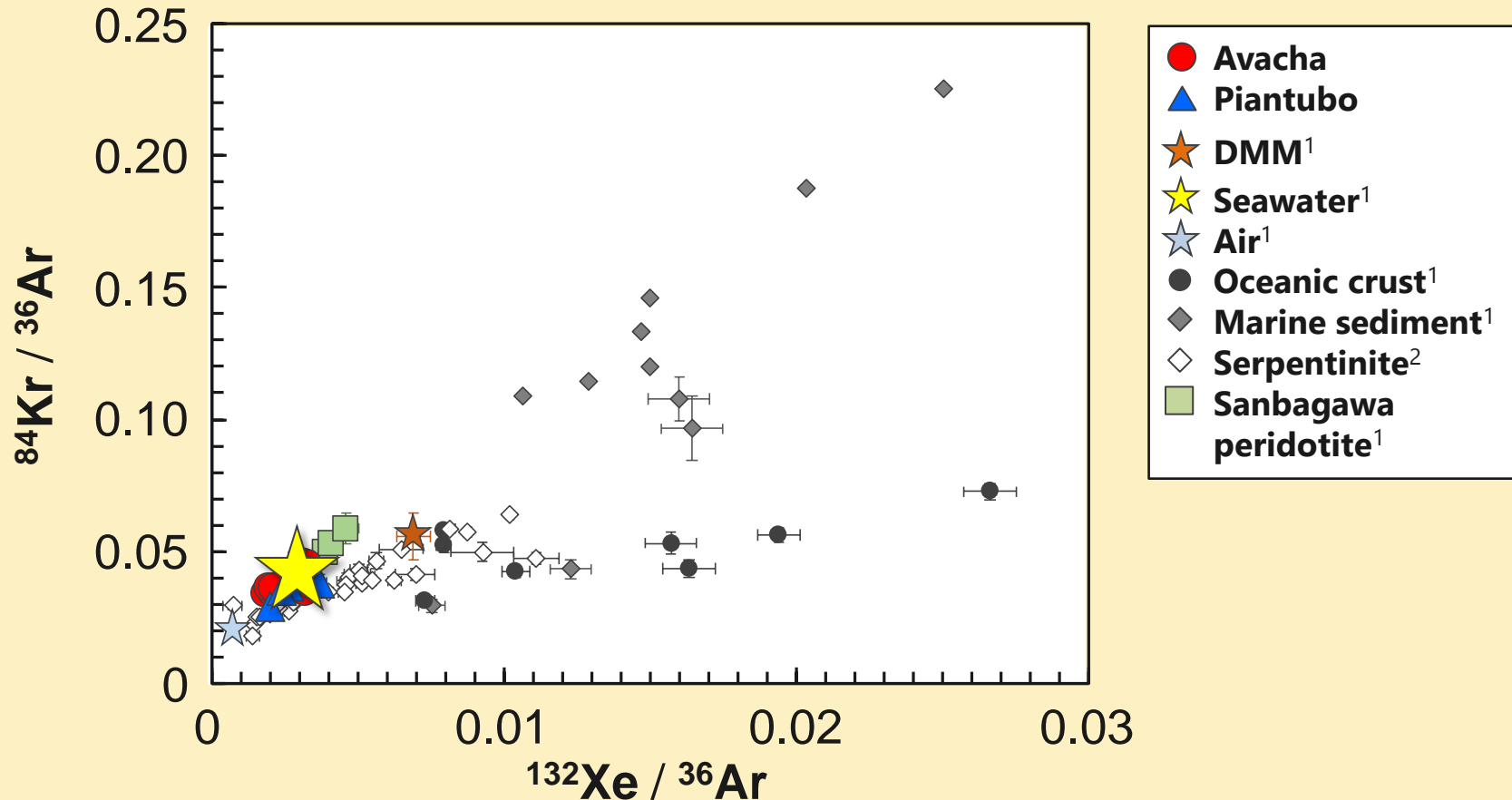
► Subducted from sedimentary pore fluid

# Noble gas elemental ratios | $^{36}\text{Ar} / ^{84}\text{Kr} / ^{132}\text{Xe}$



<sup>1</sup>Sumino et al. (2010) & references therein; <sup>2</sup>Kendrick et al. (2011; 2013)

# Noble gas elemental ratios | $^{36}\text{Ar} / ^{84}\text{Kr} / ^{132}\text{Xe}$



**Seawater-like  $^{36}\text{Ar} / ^{84}\text{Kr} / ^{132}\text{Xe}$  signatures**

Equivalent to marine sedimentary pore fluid

► **Subducted from sedimentary pore fluid**



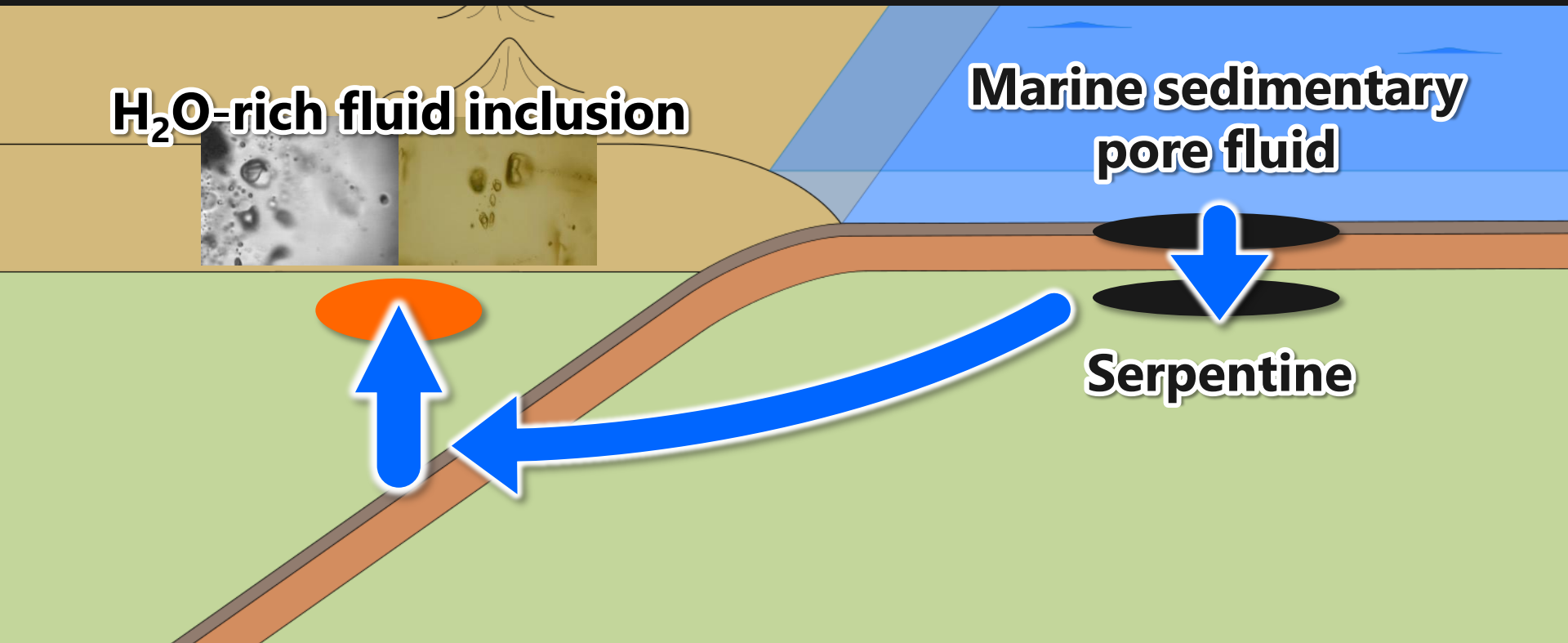
# Halogens & noble gases subducted into the mantle

Sedimentary pore fluid-like signatures in H<sub>2</sub>O



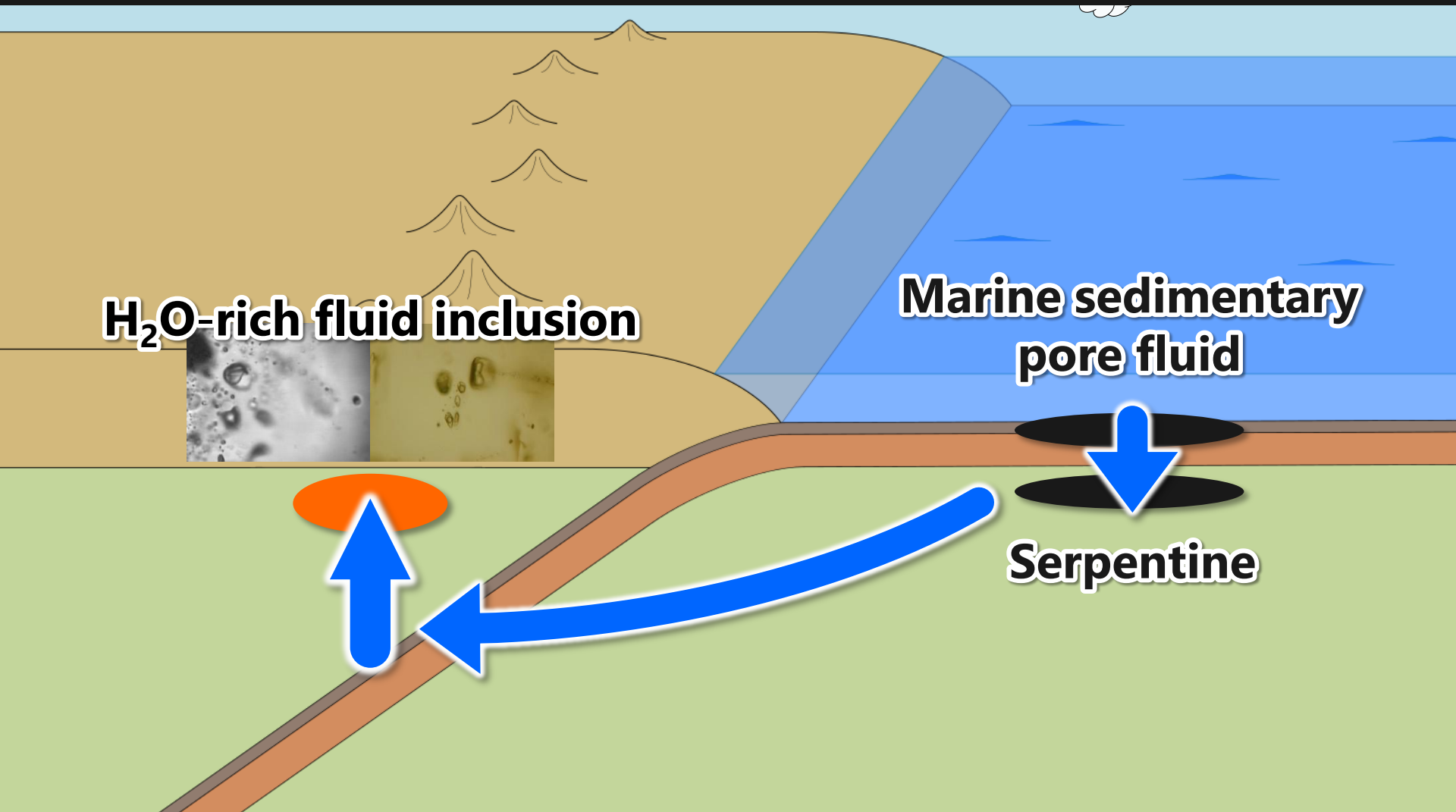
**Sedimentary pore fluid-derived water is subducted.**

Probably carried by serpentine



# Serpentine-derived water beneath volcanic front

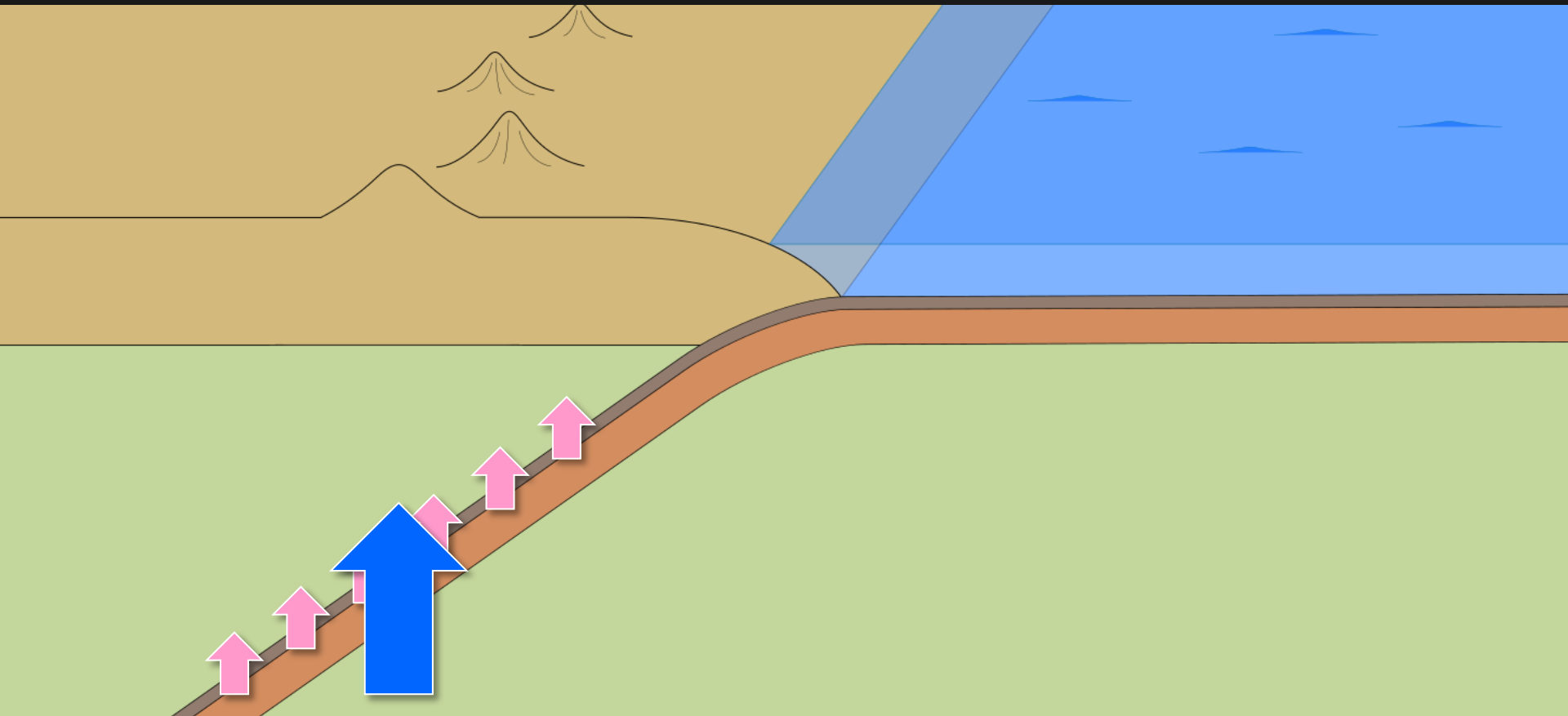
Oceanic crust ?    Sediment ?



# Serpentine-derived water beneath volcanic front

Oceanic crust ? Sediment ?

**Overwhelmed by serpentine-derived water**



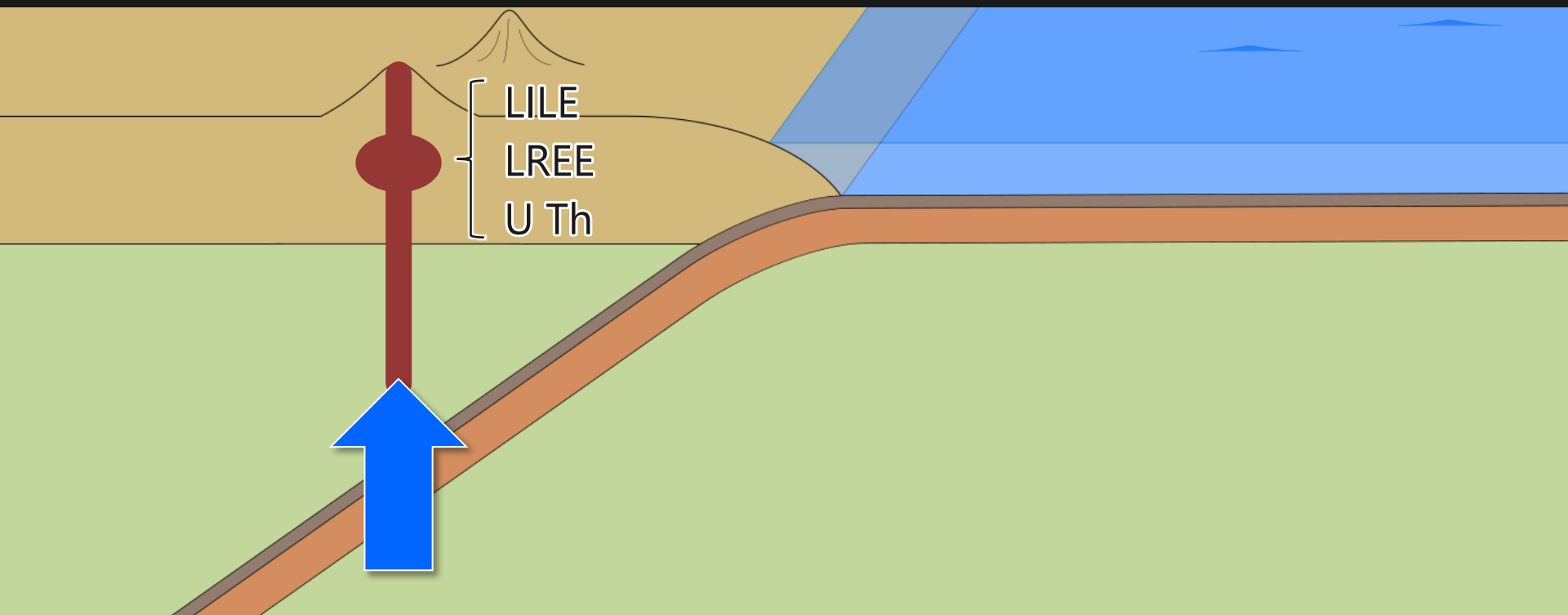
# Serpentine-derived water beneath volcanic front

## Trace elements in arc magmas

Major source of water beneath volcanic front is **serpentine**.

*e.g. Herman & Green (2001); Skora & Blundy (2010)*

**This study | Major source of water is serpentine.**



# Bilateral program between RFBR & JSPS

*Deep mantle cycling of crustal components  
and formation of **diamon**diferous lithology  
in the sublithospheric mantle*

*1/4/2015 – 31/3/2017*



## **Russia**

(Titles omitted)

D.A. Zedgenizov A. Ragozin V. Kalinina M. Kolesnichenko A. Bobrov

E. Sirotkina A. Tamarova

## **Japan**

H. Kagi T. Irifune H. Sumino H. Ohfuji K. Komatsu Y. Orihashi A. Shinozaki

M. Nishi T. Kunimoto T. Arimoto M. Kobayashi

# Previous studies | Halogens in diamonds

*Johnson et al. (2000) GCA, 64, 717-732*

## **Noble gas and halogen geochemistry of mantle fluids: Comparison of African and Canadian diamonds**

L. H. JOHNSON,<sup>1</sup> R. BURGESS,<sup>1,\*</sup> G. TURNER,<sup>1</sup> H. J. MILLEDGE,<sup>2</sup> and J. W. HARRIS<sup>3</sup>

*Burgess et al. (2002) EPSL, 197, 193-203*

## **Constraints on the age and halogen composition of mantle fluids in Siberian coated diamonds**

R. Burgess<sup>a,\*</sup>, E. Layzelle<sup>a</sup>, G. Turner<sup>a</sup>, J.W. Harris<sup>b</sup>

*Burgess et al. (2009) GCA, 73, 1779--1794*

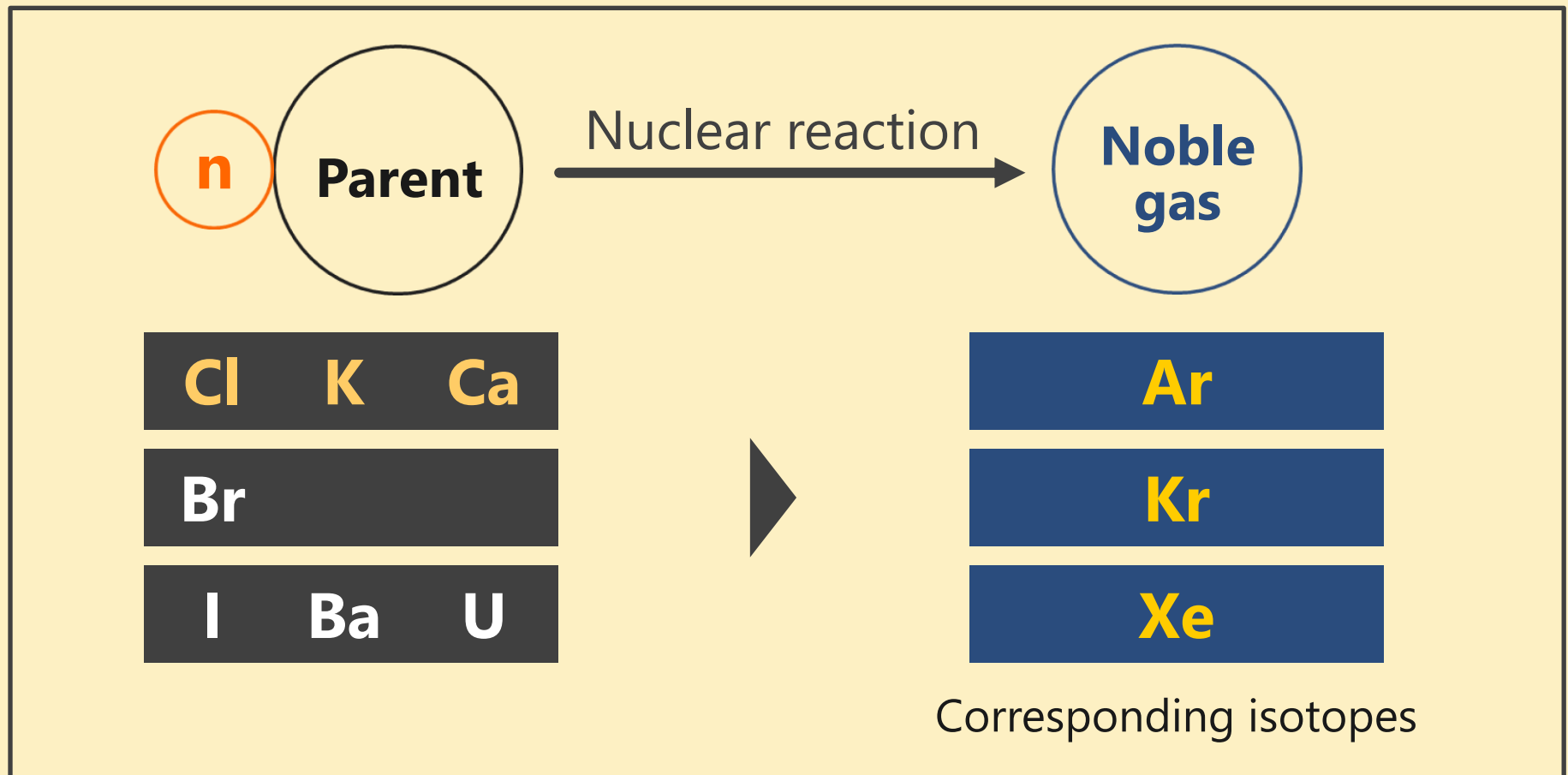
## **Volatile composition of microinclusions in diamonds from the Panda kimberlite, Canada: Implications for chemical and isotopic heterogeneity in the mantle**

Ray Burgess<sup>a,\*</sup>, Pierre Cartigny<sup>b</sup>, Darrell Harrison<sup>a</sup>, Emily Hobson<sup>a</sup>, Jeff Harris<sup>c</sup>

# Previous studies | Halogens in diamonds

## An extension of the Ar-Ar and I-Xe dating methods

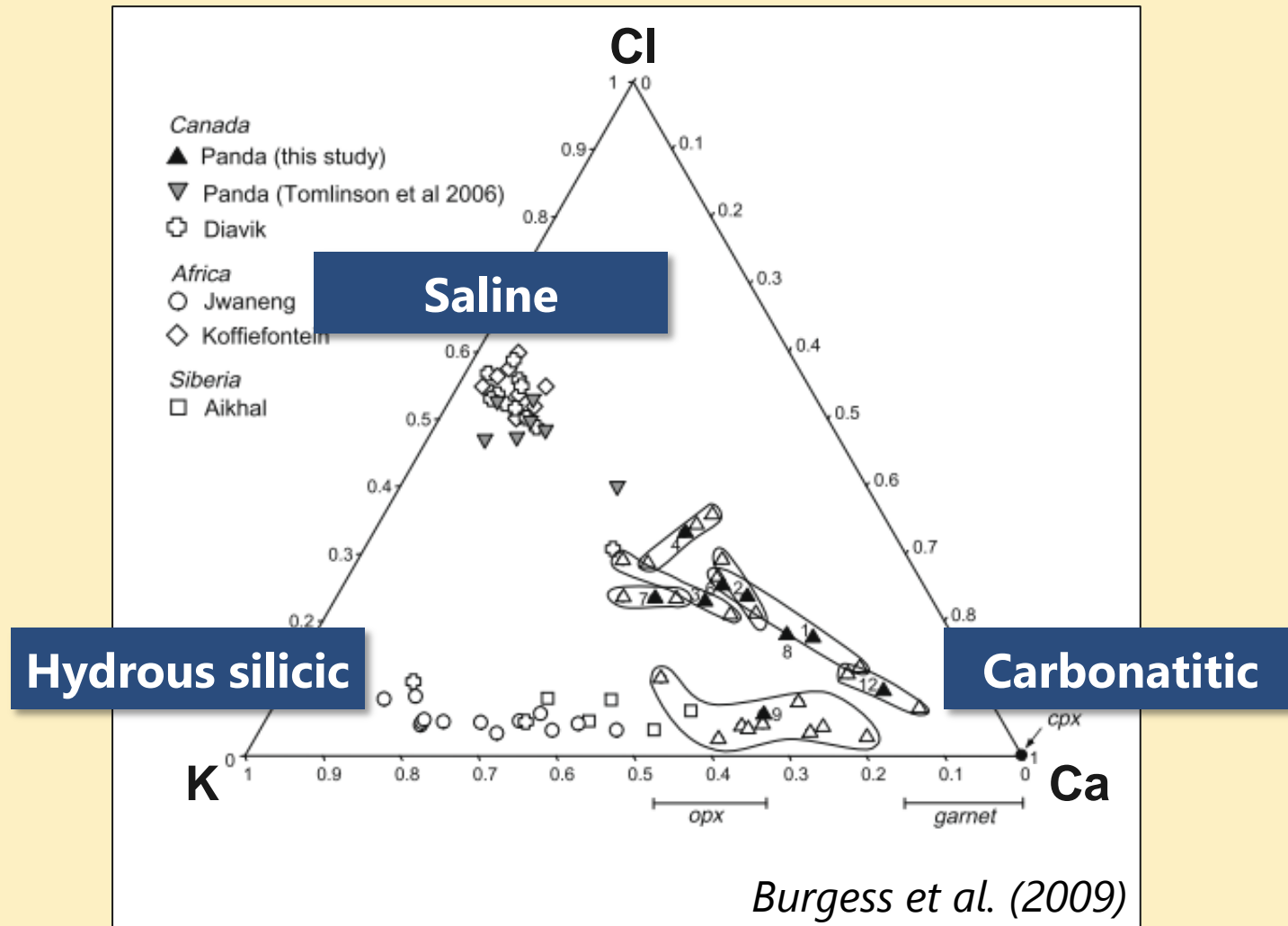
Neutron irradiation  $\longrightarrow$  Noble gas mass spectrometry



*e.g. Johnson et al. (2000)*

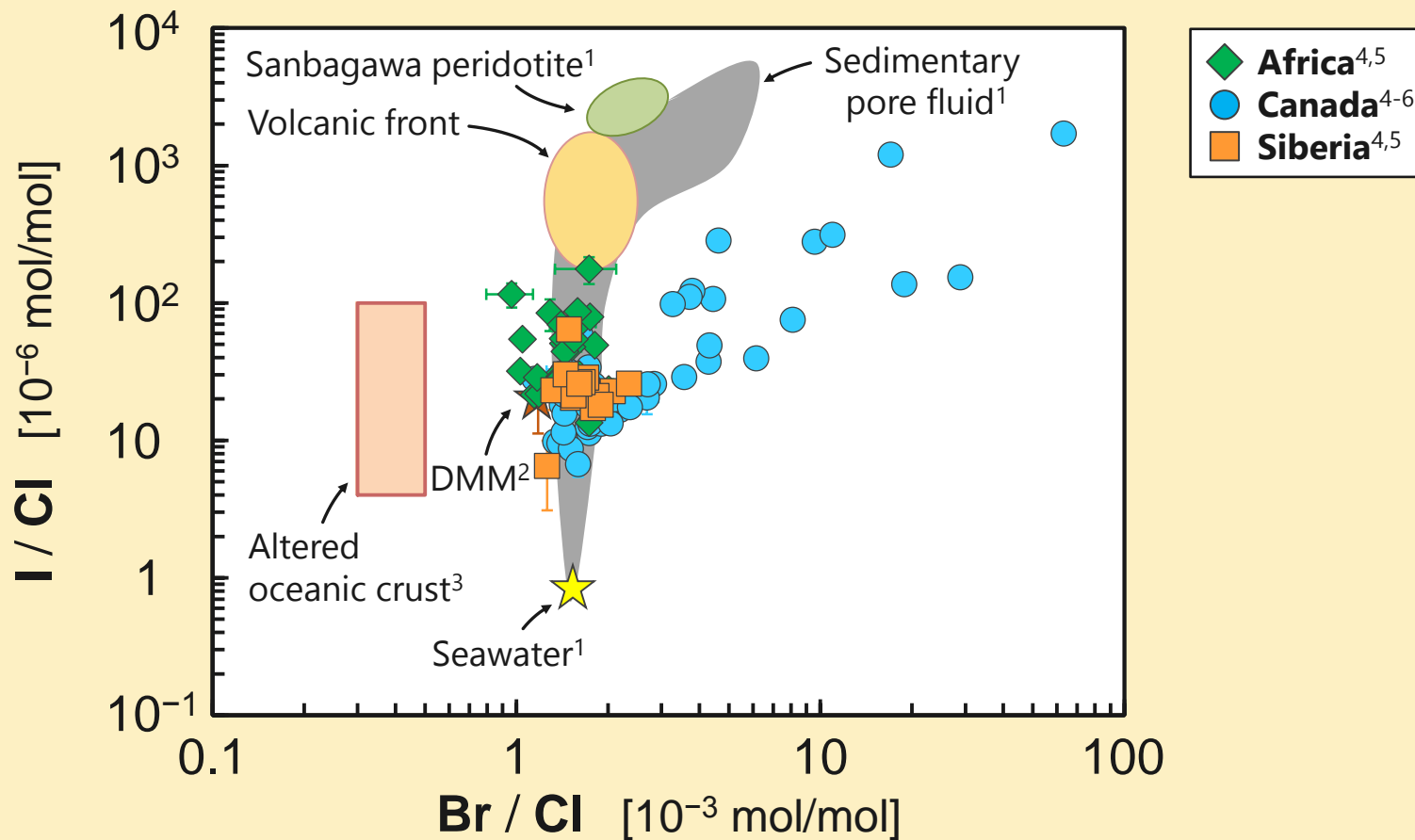
# Previous studies | Halogens in diamonds

## Compositions and origins of diamond-forming fluids





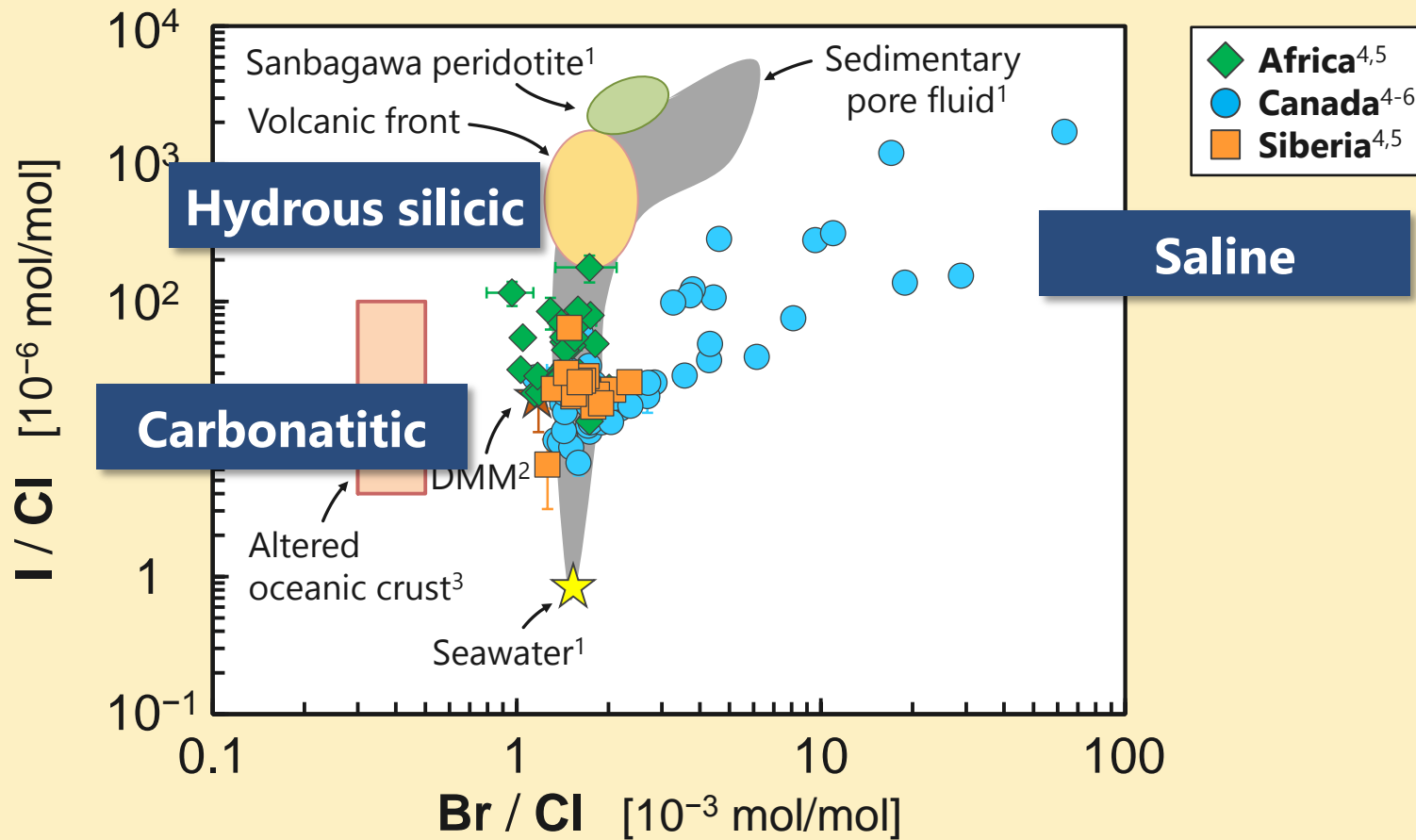
# Previous studies | Halogens in diamonds



<sup>1</sup>Sumino et al. (2010) & references therein; <sup>2</sup>Kendrick et al. (2012); <sup>3</sup>Chavrit et al. (2012)

<sup>4</sup>Johnson et al. (2000); <sup>5</sup>Burgess et al. (2002); <sup>6</sup>Burgess et al. (2009)

# Previous studies | Halogens in diamonds



- **Carbonatitic** ➤ DMM-like
- **Hydrous silicic** ➤ High  $I / Cl$
- **Saline** ➤ High  $I / Cl$  &  $Br / Cl$

# Future studies on diamonds

## Halogen & noble gas compositions along depth

**Constrain depth information** ← (From residual pressure?)



**Halogen & noble gas analysis**

Homogeneous?

Heterogeneous?

Relationship between depth?

Subduction related?



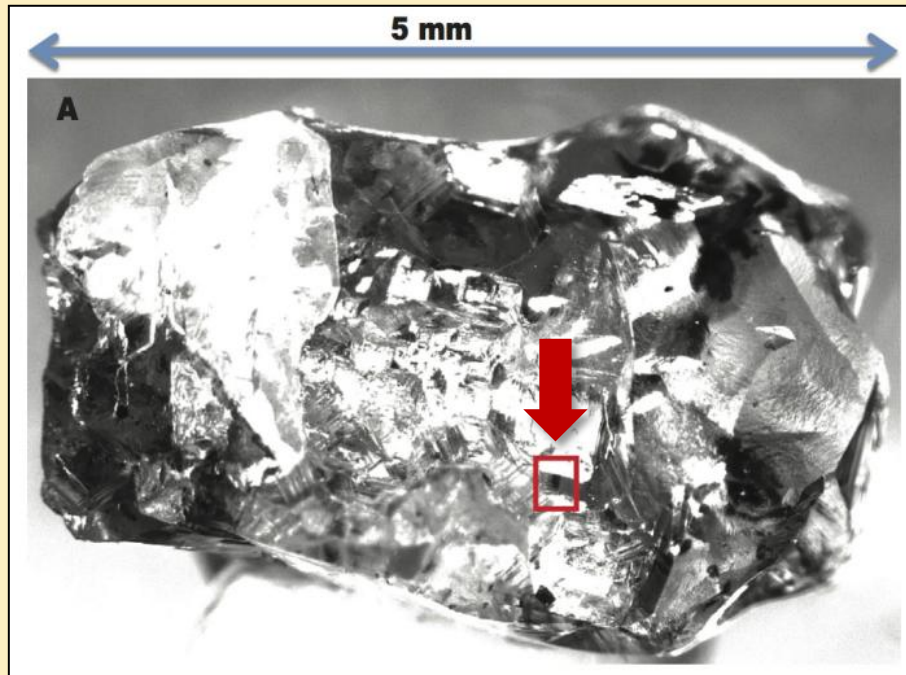
**Information on fluid distribution in the mantle**

# Future studies on diamonds

## Deep diamonds

### Lower mantle

### Transition zone



## Ringwoodite inclusion

1 wt.% H<sub>2</sub>O in transition zone

Subduction origin?

Juvenile water?

⋮

*Pearson et al. (2014)*

## Halogens & Noble gases

(The most ?) powerful tracers of subducted water in the mantle

## H<sub>2</sub>O-rich fluid inclusions within mantle xenoliths

The best medium to investigate slab-derived fluids

## Sedimentary pore fluid-like halogens & noble gases

- Sedimentary pore fluid-derived water is subducted.
- This subducted water is carried by serpentine.
- Serpentine is major source of water beneath volcanic front.

**Halogens & noble gases in diamonds should be investigated.**



## Unknown samples

Isotope ratios

Concentrations



Neutron-derived isotopes

## Standard samples

Conversion factors

- Ar-Ar standards  
*e.g.* Hb3Gr GA1550
- I-Xe standards  
*e.g.* Shallowater Bjurböle



**Compositions of unknown samples**

$$[^{36}\text{Ar}]_m = [^{36}\text{Ar}]_t + [^{36}\text{Ar}]_{\text{Ca}} + [^{36}\text{Ar}]_{\text{Cl}}$$

$$[^{37}\text{Ar}]_m \exp(\lambda_{37\text{Ar}} t) = [^{37}\text{Ar}]_{\text{Ca}}$$

$$[^{38}\text{Ar}]_m = [^{38}\text{Ar}]_t + [^{38}\text{Ar}]_{\text{K}} + [^{38}\text{Ar}]_{\text{Ca}} + [^{38}\text{Ar}]_{\text{Cl}}$$

$$[^{39}\text{Ar}]_m \exp(\lambda_{39\text{Ar}} t) = [^{39}\text{Ar}]_{\text{K}} + [^{39}\text{Ar}]_{\text{Ca}}$$

$$[^{40}\text{Ar}]_m = [^{40}\text{Ar}]_{t+r} + [^{40}\text{Ar}]_{\text{K}}$$



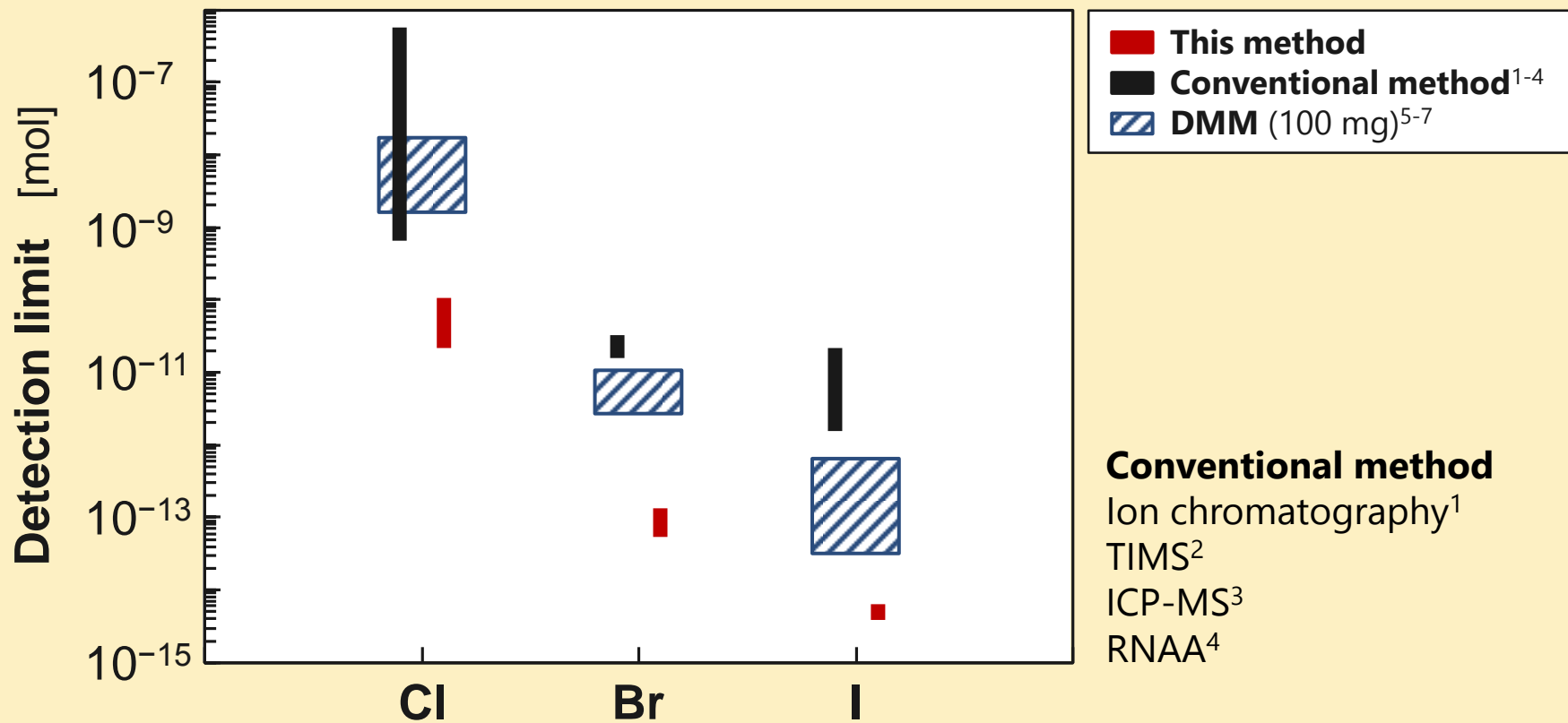
$$[^{36}\text{Ar}]_m = [^{36}\text{Ar}]_t + [^{36}\text{Ar}]_{\text{Ca}} + [^{36}\text{Ar}]_{\text{Cl}}$$

$$[^{37}\text{Ar}]_m \exp(\lambda_{37\text{Ar}} t) = [^{37}\text{Ar}]_{\text{Ca}}$$

$$[^{38}\text{Ar}]_m = [^{38}\text{Ar}]_t + [^{38}\text{Ar}]_{\text{K}} + [^{38}\text{Ar}]_{\text{Ca}} + [^{38}\text{Ar}]_{\text{Cl}}$$

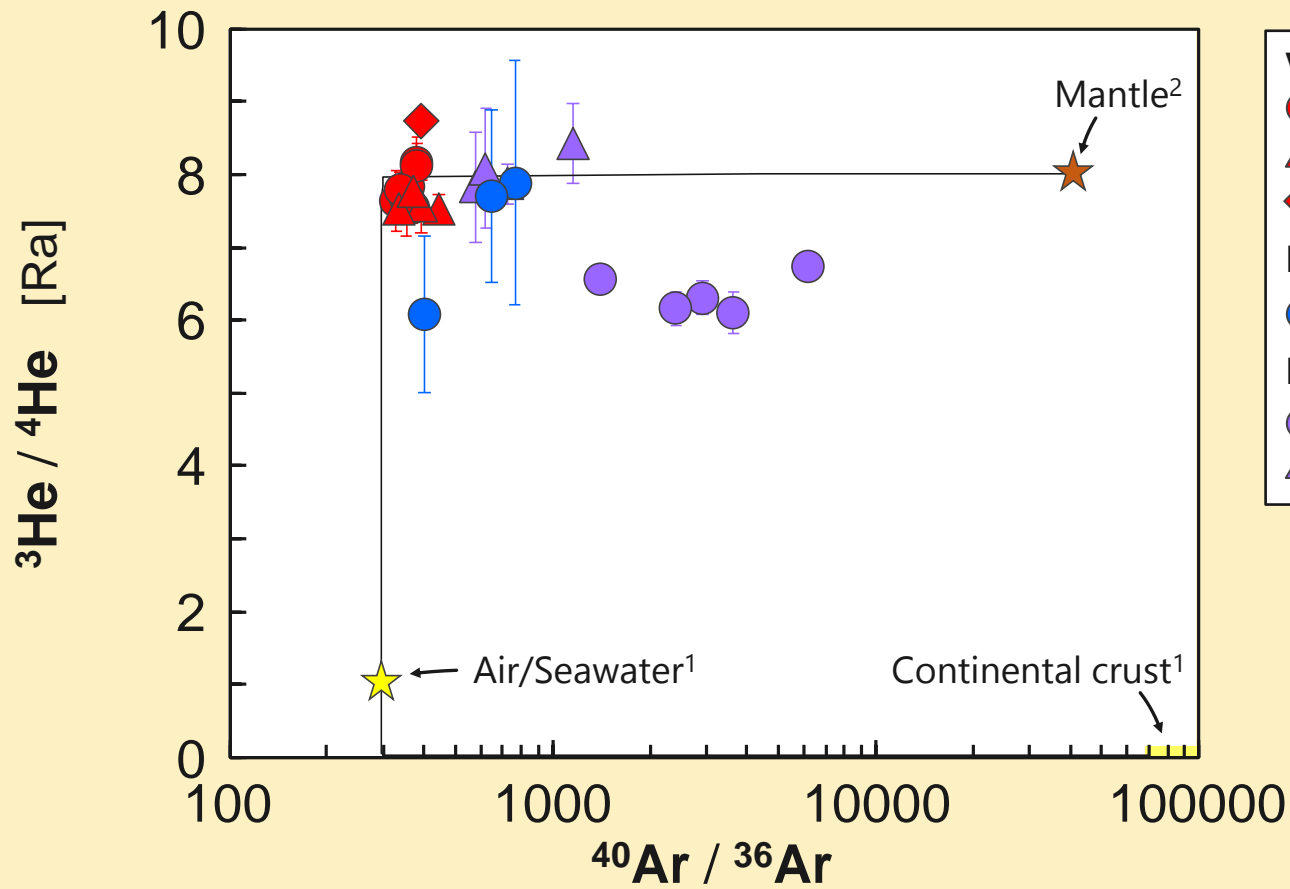
$$[^{39}\text{Ar}]_m \exp(\lambda_{39\text{Ar}} t) = [^{39}\text{Ar}]_{\text{K}} + [^{39}\text{Ar}]_{\text{Ca}}$$

$$[^{40}\text{Ar}]_m = [^{40}\text{Ar}]_{t+r} + [^{40}\text{Ar}]_{\text{K}}$$

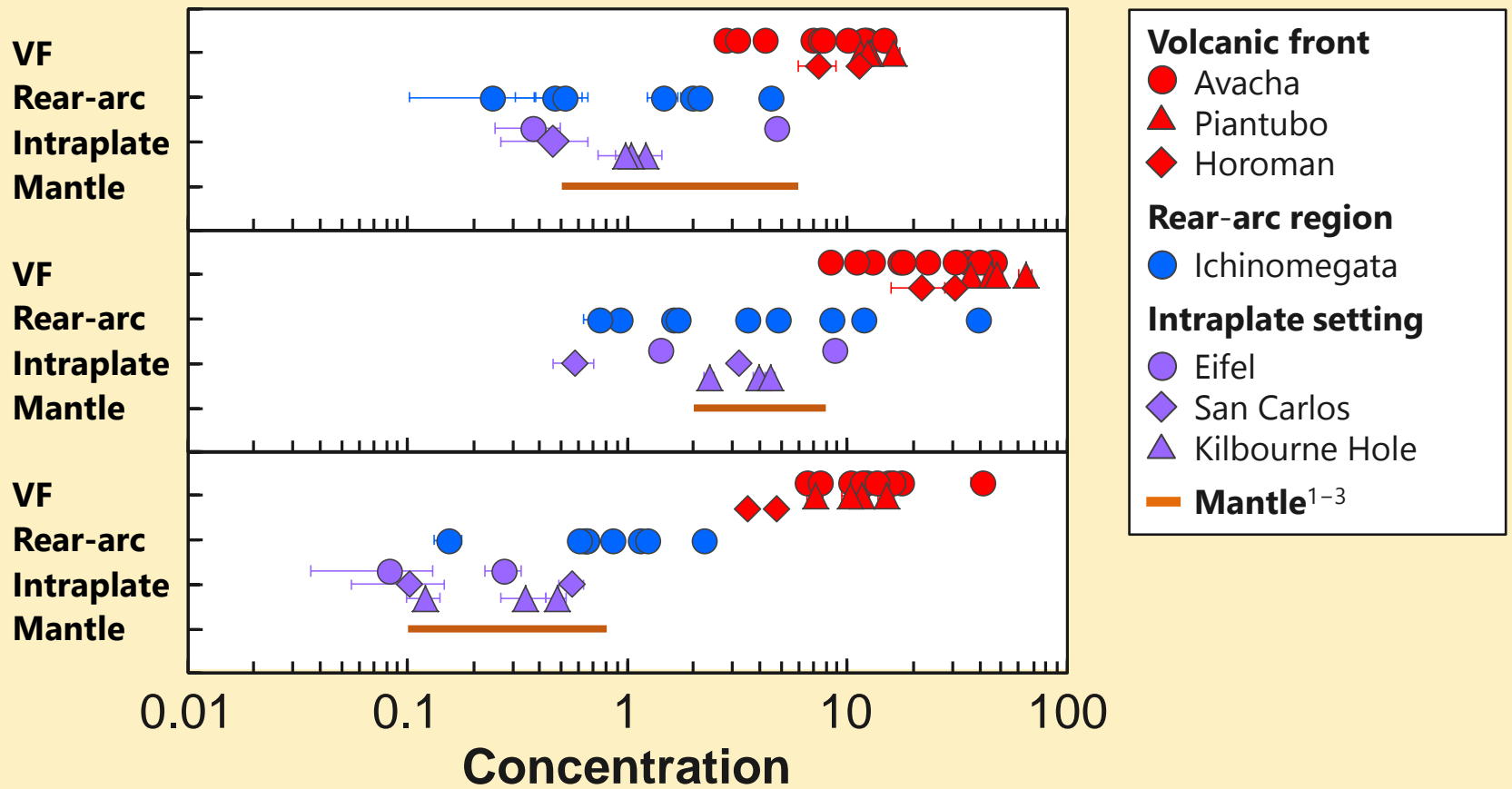


<sup>1</sup>Michel & Villemant (2003); <sup>2</sup>Fujitani & Nakamura (2006); <sup>3</sup>Chai & Muramatsu (2007)

<sup>4</sup>Ozaki & Ebihara (2007); <sup>5</sup>Saal et al. (2002); <sup>6</sup>John et al. (2011); <sup>7</sup>Kendrick et al. (2012)



<sup>1</sup>Ozima & Podosek (2002); <sup>2</sup>Holland & Ballentine (2006)



<sup>1</sup>Saal et al. (2002); <sup>2</sup>John et al. (2011); <sup>3</sup>Kendrick et al. (2012)

# Serpentine-derived water beneath volcanic front

Partition coefficients of trace elements  $D^{\text{fluid/melt}}$   
LILE

$\text{H}_2\text{O} + \text{NaCl} > \text{H}_2\text{O}$  Kepler (1996); Kawamoto et al. (2014)

This study | **Slab-derived fluids contain halogens.**

