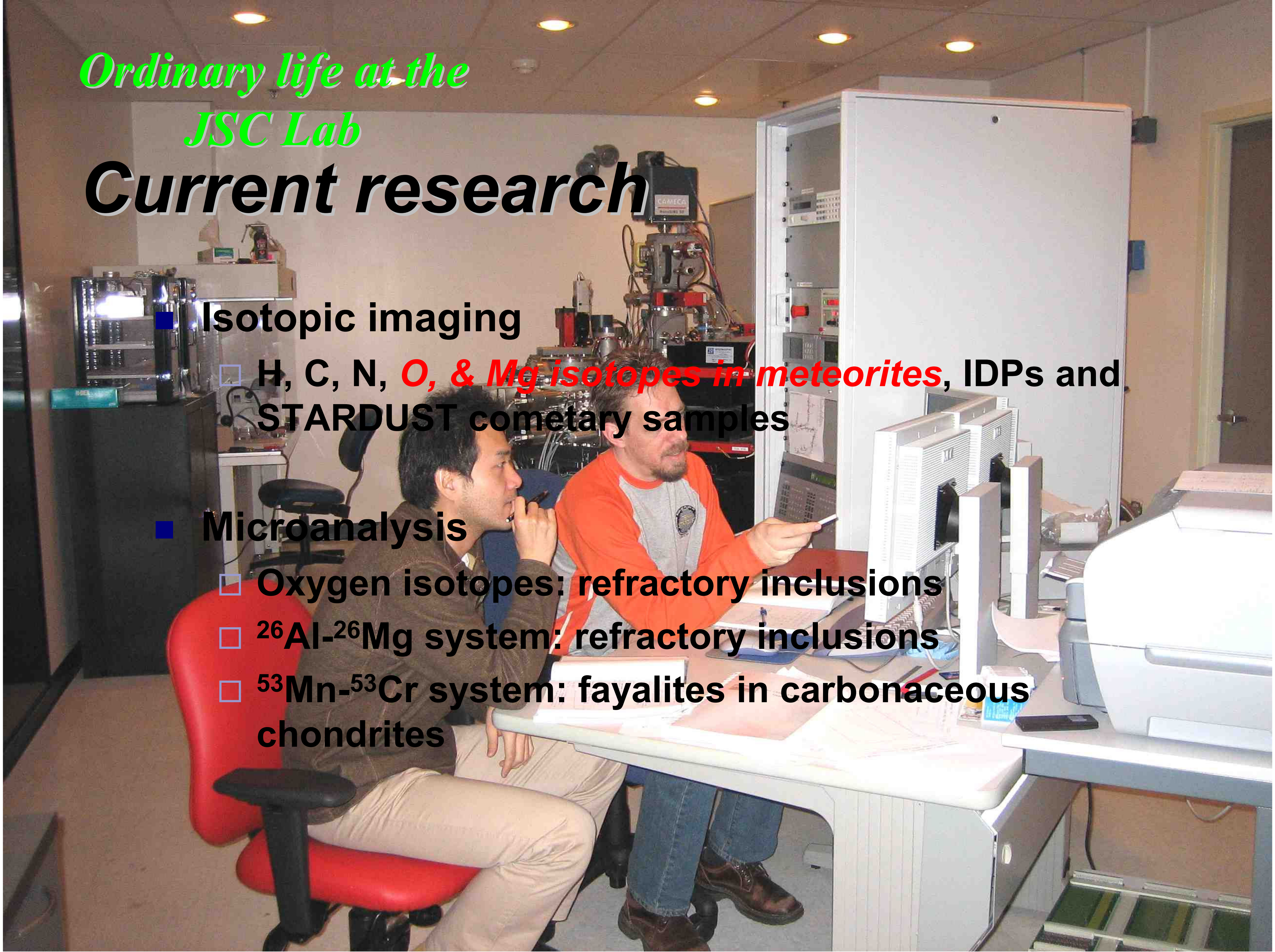
Isotopic imaging of refractory inclusions in meteorites with the NanoSIMS 50L

Motoo Ito and Scott Messenger

Robert M. Walker Laboratory for Space Science
NASA Johnson Space Center, ARES

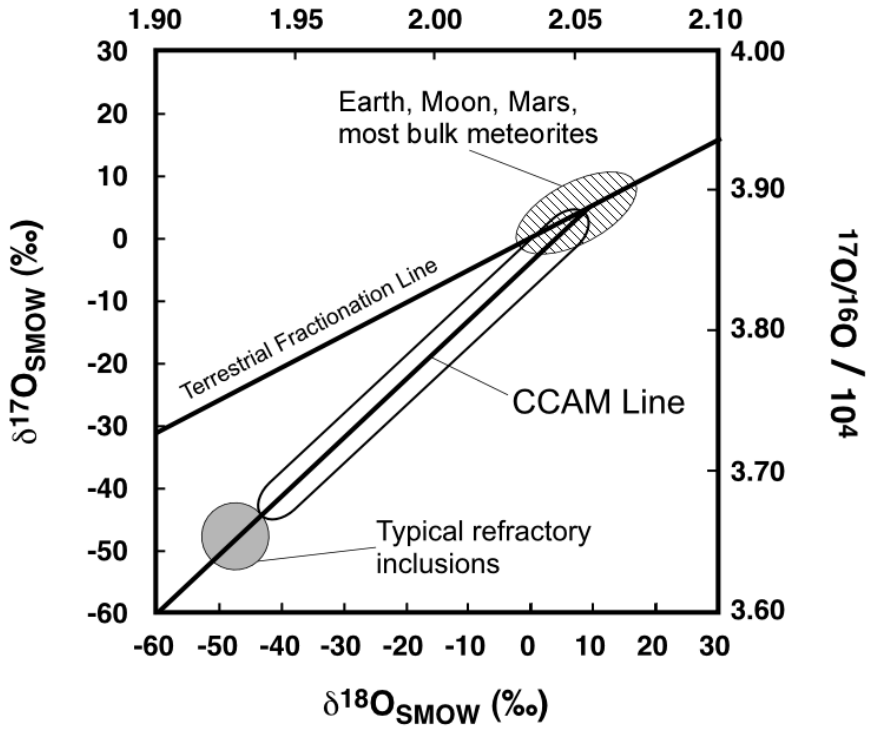


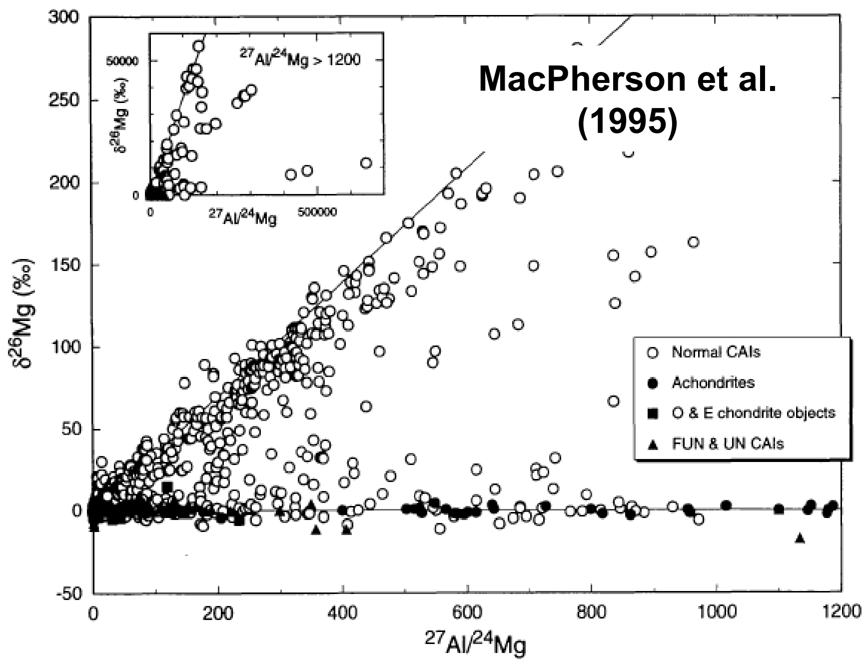
Ordinary life at the JSC Lab

Current research

- Isotopic imaging
  - H, C, N, *O, & Mg isotopes in meteorites*, IDPs and STARDUST cometary samples
- Microanalysis
  - Oxygen isotopes: refractory inclusions
  - ^{26}Al-^{26}Mg system: refractory inclusions
  - ^{53}Mn-^{53}Cr system: fayalites in carbonaceous chondrites

Clayton et al. (1973)





Refractory Inclusions or Ca, Al-rich inclusions (CAIs)

- Preserve records of "***the very early history of the solar system***".
- Anomalous isotopic compositions: O, Mg (e.g., Clayton et al., 1973; Lee et al., 1976)

CAIs require *high precision (~ few permil) isotopic measurements*

Progress in Isotopic Analysis of CAIs

~1 mm
few mg

- **Bulk analysis (1970~: e.g., Clayton et al., 1973)**
  - O isotopic anomalies in CAI minerals from Allende carbonaceous chondrite

~10 μm
few ng

- **Spot analysis (1989~: e.g., McKeegan, 1989; Yurimoto et al., 1994)**
  - Good agreement with bulk analysis
  - Heterogeneous O isotopic distributions within minerals

few μm
~0.4 ng

- **Stepped linear traverse analysis (1998~: e.g., Yurimoto et al., 1998; Ito et al., 2004)**

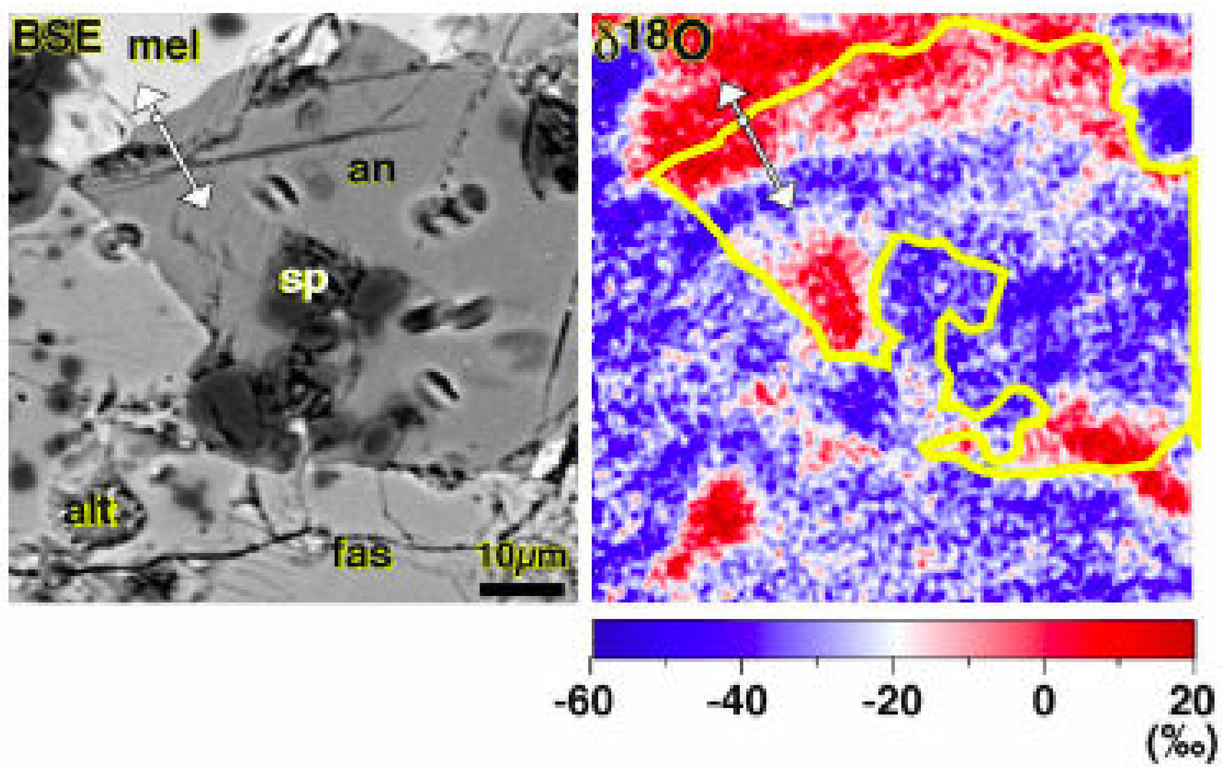
The μm-scale measurement by SIMS provide a new clue for these solar system objects.

Our Next Goal!

Two-dimensional isotope heterogeneity

O Isotopic Imaging of CAIs by the IMS-1270/SCAPS

O isotopes in CAI minerals	***Required for measurement***
1. less than 5 % isotopic anomaly	1. High precision (~0.5 %)
2. Crystal boundary	2. High spatial resolution (~0.5 μm)
3. Distributions among/within minerals	3. Large area (10-50 μm)



- Nagashima et al (2004) found O isotopes are heterogeneously distributed
  - among minerals
  - within a mineral

GOAL: *Develop high precision μm-scale isotopic map in minerals with the NanoSIMS*

- **Key factors in achieving high precision isotopic images**
  1. Minimize variations in EM yield: HV adjusted to match PHD daily (check every 12-24h)
  2. Minimize sample charging (E-gun if necessary and Au (or C) film)
  3. Require flat sample surface without cracks
  4. Accurate QSA and deadtime corrections
  5. Reach steady state of the secondary ion beam following pre-sputtering procedure.
- **Spot analysis with high precision and high spatial resolution**
- **Capabilities of the JSC NanoSIMS for isotopic images**

O isotopic imaging

- **10 µm: $\delta^{17,18}O$ = ~ 2-3 ‰ (1σ)**
- **2-3 µm: $\delta^{17,18}O$ = ~ 5 ‰ (1σ)**
- **Reproducibility = ~ 2 ‰ (1σ)**
- **High spatial resolution = less than 0.4 µm**

Mg isotopic imaging

- **$^{27}Al/^{24}Mg$ (1σ) = ~ 9.5 % (Labradorite, $Al/^{24}Mg$ = 254)**
- **$\delta^{25}Mg$ (1σ) = 4.5 ‰, $\delta^{26}Mg$ (1σ) = 6.0 ‰. $\delta^{26}Mg$ excess (1σ) = 7.5 ‰**
- **Overall reproducibility of the ^{26}Mg excesses: Hibonite (1σ) = 1.5 ‰, Labradorite (1σ) = 2.0 ‰**

- **Data acquisition**
  - 256 x 256 - 512 x 512 pixels
  - Dwell time = 1000-3000 µs/pixel
  - Each imaging run consisted of 30-80 repeated scans acquired over a ~2-4 hour period

- Terrestrial standards
  - Instrumental mass fractionation
  - Differing sensitivities of EMs
  - Sensitivity factors if necessary

- San Carlos olivine
- Fayalite
- Madagascar hibonite
- Labradorite
- Augite
- Diopside
- Enstatite
- Chromite
- Titanite
- Spessartine
- Spinel
- Synthetic akermanite
- Synthetic gehlenite
- Synthetic forsterite
- Synthetic diopside
- Synthetic anorthite
- Ak70Geh30 glass

Analytical Conditions: *JSC NanoSIMS 50L*

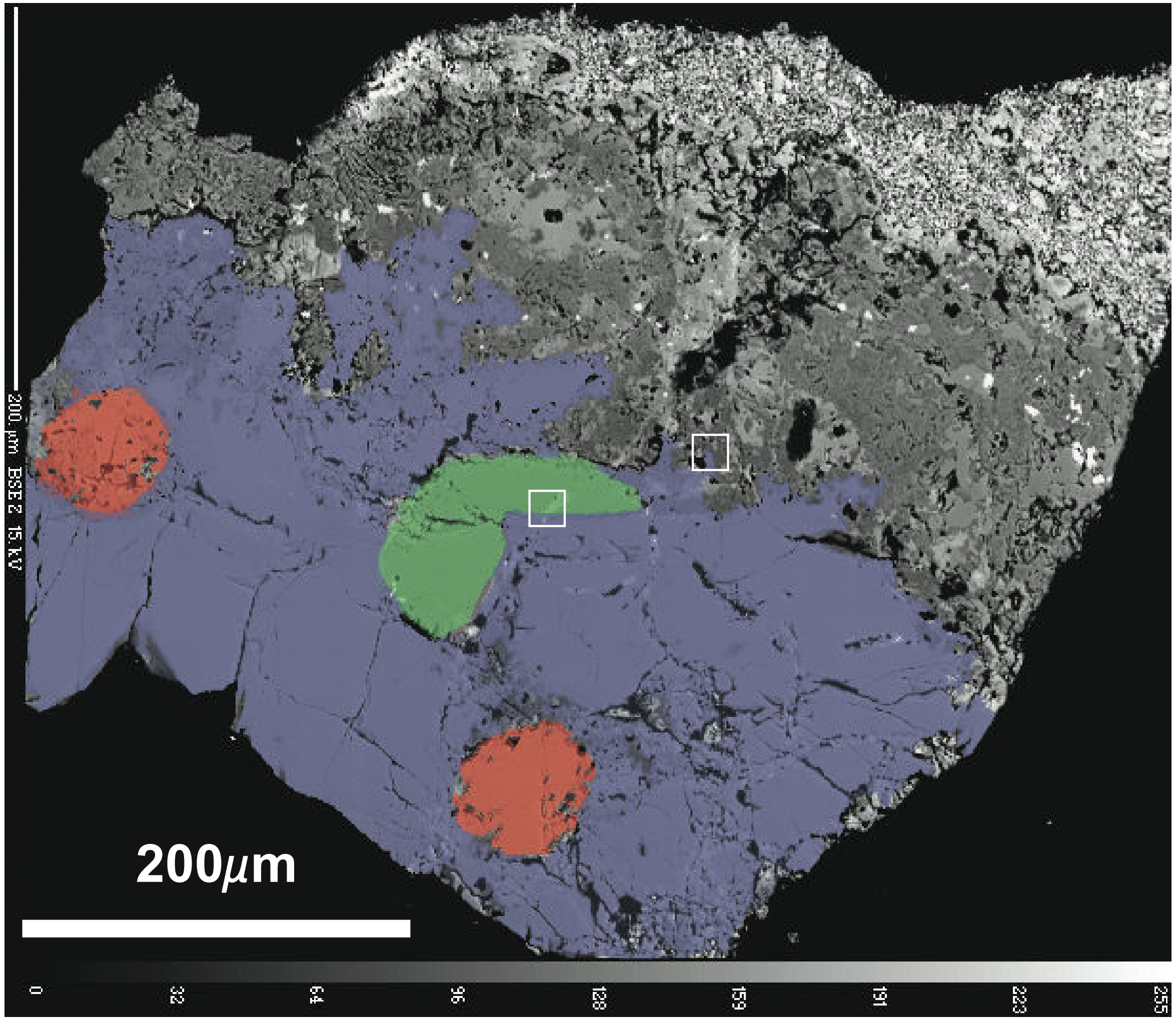
O Isotopic imaging

- Primary ions
  - Cs^+ ion beam
  - 100 nm beam rastered over 10 x 10 - 20 x 20 μm area
- Secondary ions
  - $^{16}O^-$, $^{17}O^-$, $^{18}O^-$, $^{28}Si^-$, $^{24}Mg^{16}O^-$ and $^{27}Al^{16}O^-$
- Isobaric Interferences
  - MRP> 9500 to separate ^{16}OH from ^{17}O peak (< 0.01 %)

Mg isotopic imaging

- Primary ions
  - O^- ion beam
  - 400 nm beam rastered over 15 x 15 μm area
- Secondary ions
  - $^{27}Al^{++}$, $^{23}Na^+$, $^{24}Mg^+$, $^{25}Mg^+$, $^{26}Mg^+$, and $^{54}Fe^+$
- Isobaric Interferences
  - MRP> 8000 to resolve Mg hydride interferences at mass 25 and 26

CAI, EK1-6-3 from Allende

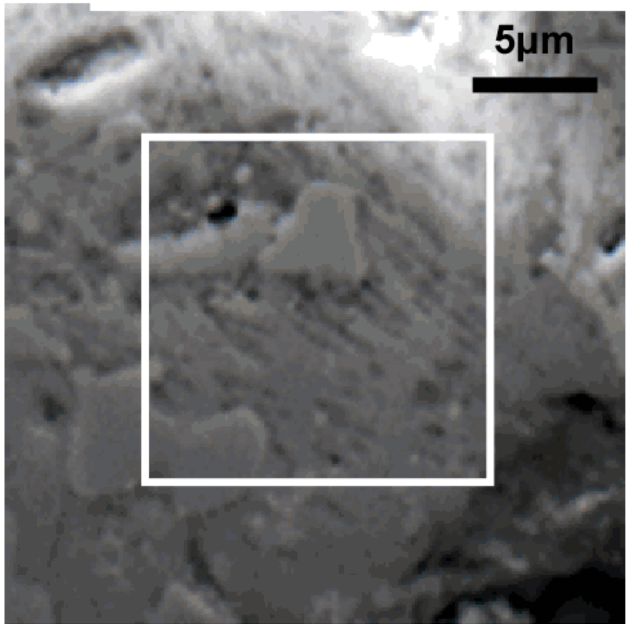


- **Melilite**
  - $Ca_2Al_2SiO_7$
  - $Ca_2MgSi_2O_7$
- **Anorthite**
  - $CaAl_2Si_2O_8$
- **Ti-rich pyroxene**
  - $Ca(Mg,Al,Ti)(Si,Al)_2O_6$

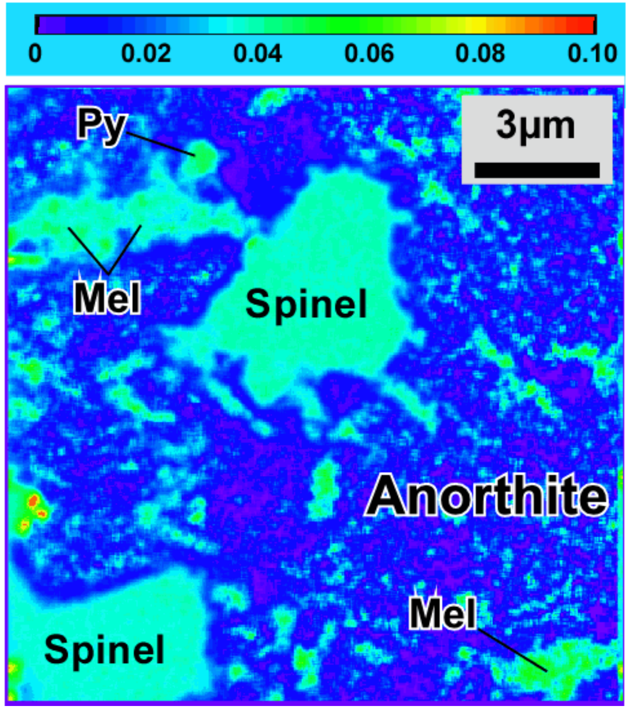
- Rim consists of different mineral aggregates: Fe-rich Sp, Pv, Fo (Fo60-80), Mel (~Åk8), An and Py.

Images of a part of the rim structure of a CAI, EK1-6-3

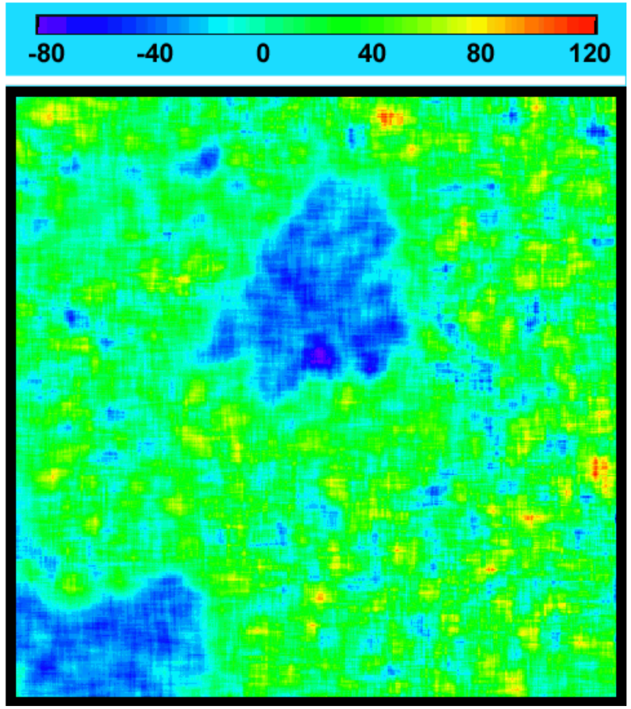
a) BSE image



b) Mg/Al elemental map



c) $\delta^{18}O$ isotope map



Ito and Messenger (2008)

Spot analysis (Ito and Messenger, 2007)
- **Anorthite: $\delta^{17,18}O$ = 0 to +10 permil**
- **Spinel : N/A**
- **Pyroxene: $\delta^{17,18}O$ = -20 to -30 permil**
- **Melilite: $\delta^{17,18}O$ = 0 to +5 permil**

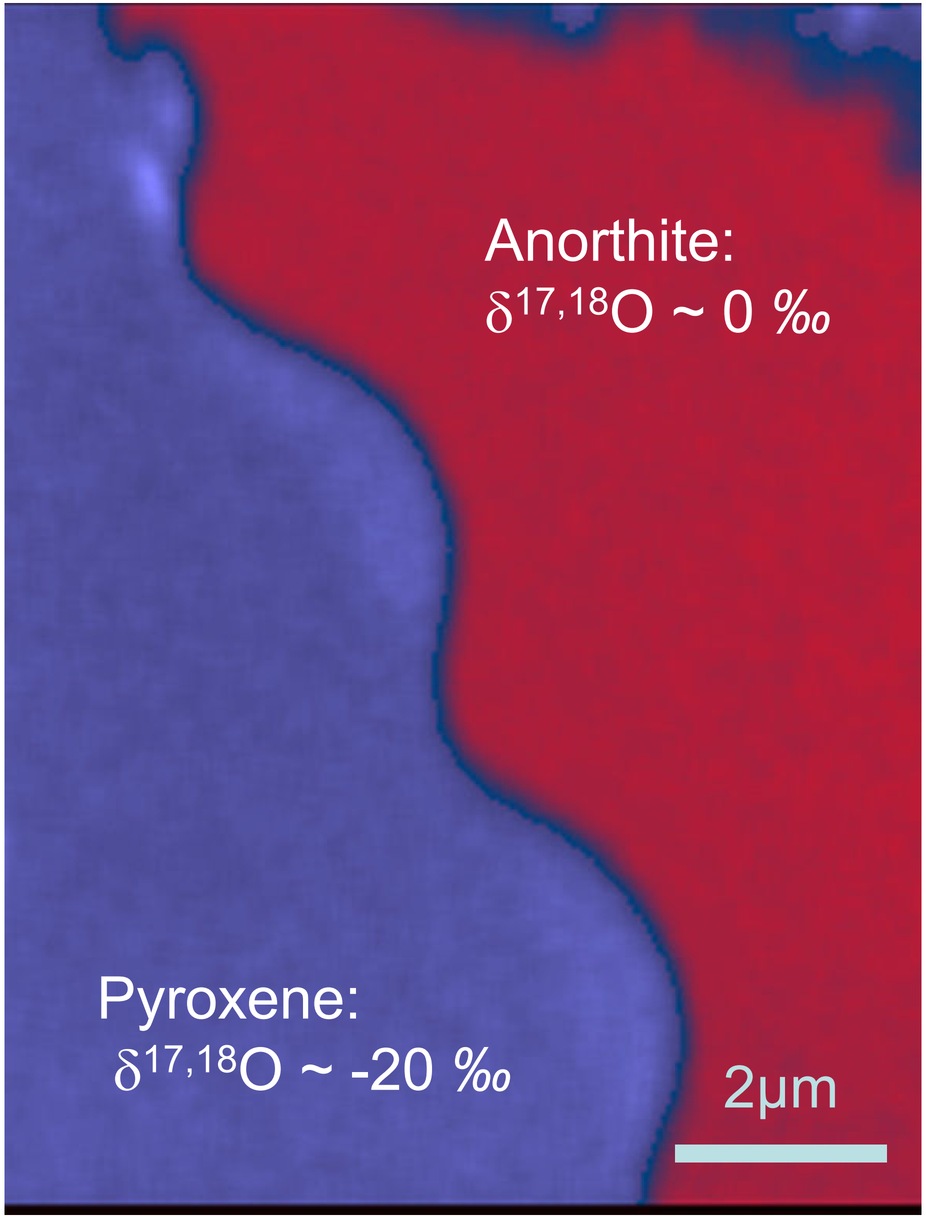
Isotope map (Ito and Messenger, 2008)
- **Anorthite matrix: $\delta^{17,18}O$ = +10 permil**
- **Spinel grains: $\delta^{17,18}O$ = -45 permil**
- **Pyroxene grain: $\delta^{17,18}O$ = -40 permil**
- **Melilite grains: $\delta^{17,18}O$ = +10 permil**

Strong isotopic disequilibrium among the minerals in the isotopic image

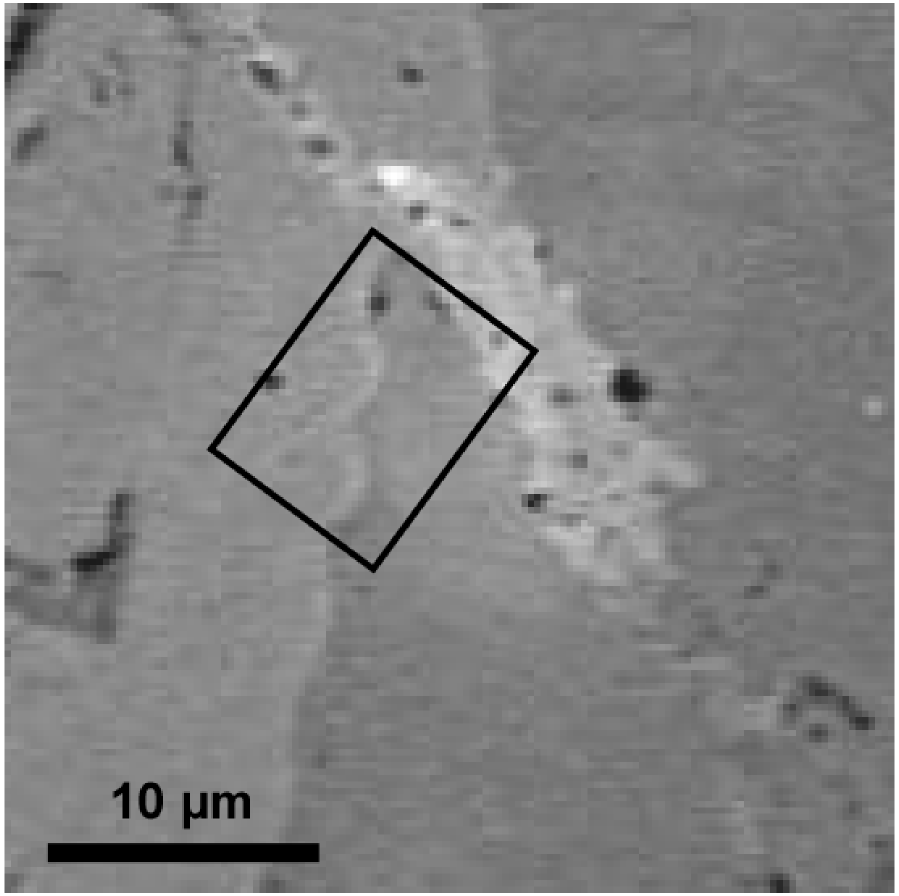
A closer look at the isotopic boundary between pyroxene and anorthite

Boundary between Pyroxene and Anorthite

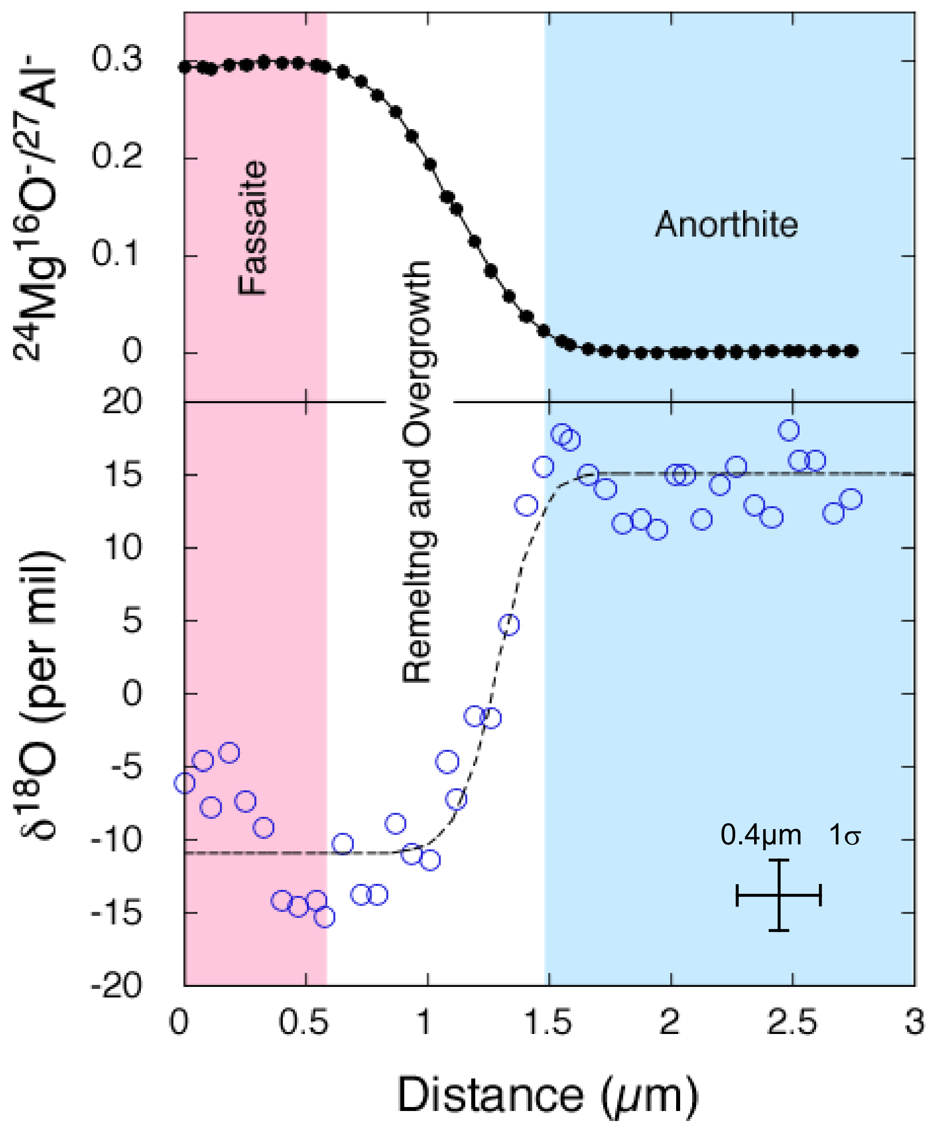
$^{28}Si/^{27}Al$ secondary ion image



BSE Image



Line Profile between Pyroxene and Anorthite

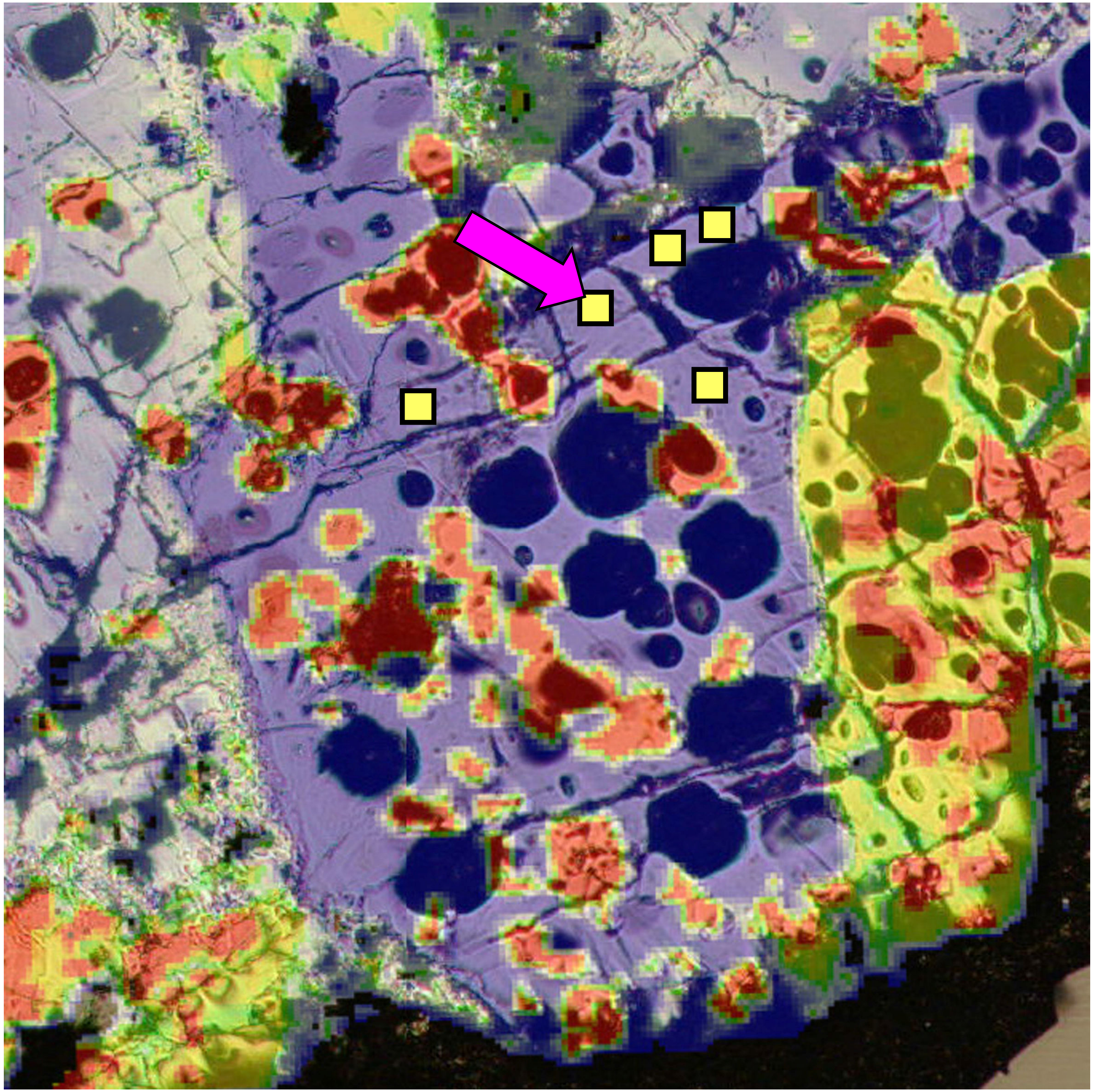


- Homogeneous O isotopic distribution within the anorthite and fassaite.
- Sharp O isotopic boundary (< 0.4 µm) between two phases.
  - Equivalent to spatial resolution of the profile

- The ***CAI*** experienced very fast cooling (**8-15°C/h**) following transient heating.

- Davis et al. (1992): trace element distributions
- Stolper and Paque (1986): crystallization sequence
- MacPherson et al. (1984): Reverse zoning of melilite

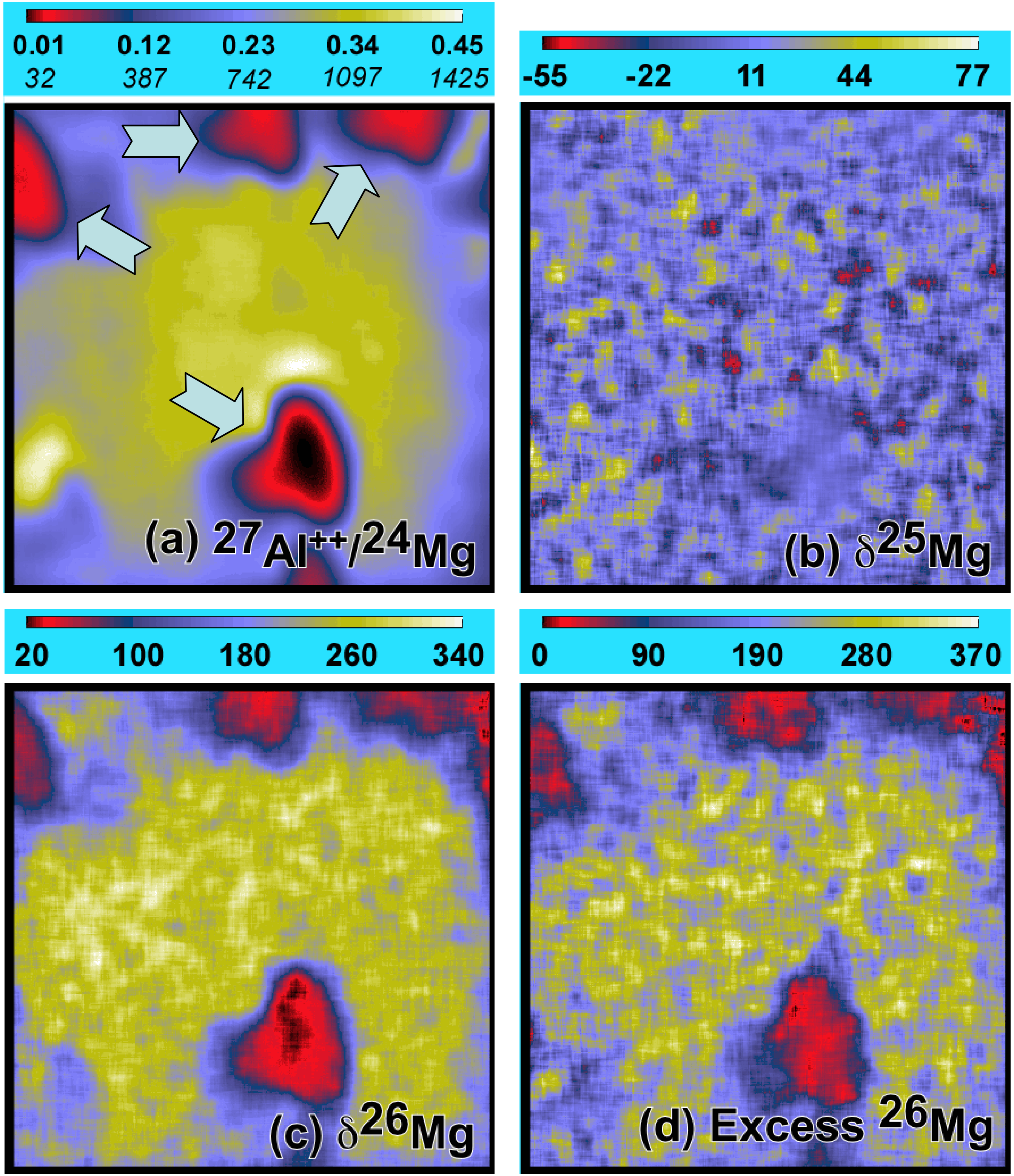
HN3-1c: coarse-grained Type-B1 CAI from Allende



- **Minerals (Nagahara et al., 1987)**
  - **Melilite** (Åk30-60)
  - **Spinel**
  - **Anorthite**
  - **Fassaite**
- **O isotopic ratio (Mayeda et al., 1986)**
  - $\delta^{17,18}O$ **~ 0 ‰ for Anorthite and Melilite**
  - $\delta^{17,18}O$ **~ -40 ‰ for Fassaite and Spinel**
- **$(^{26}Al/^{27}Al)_0$ (Koike et al., 1994)**
  - **$(3\text{-}5) \times 10^{-5}$**

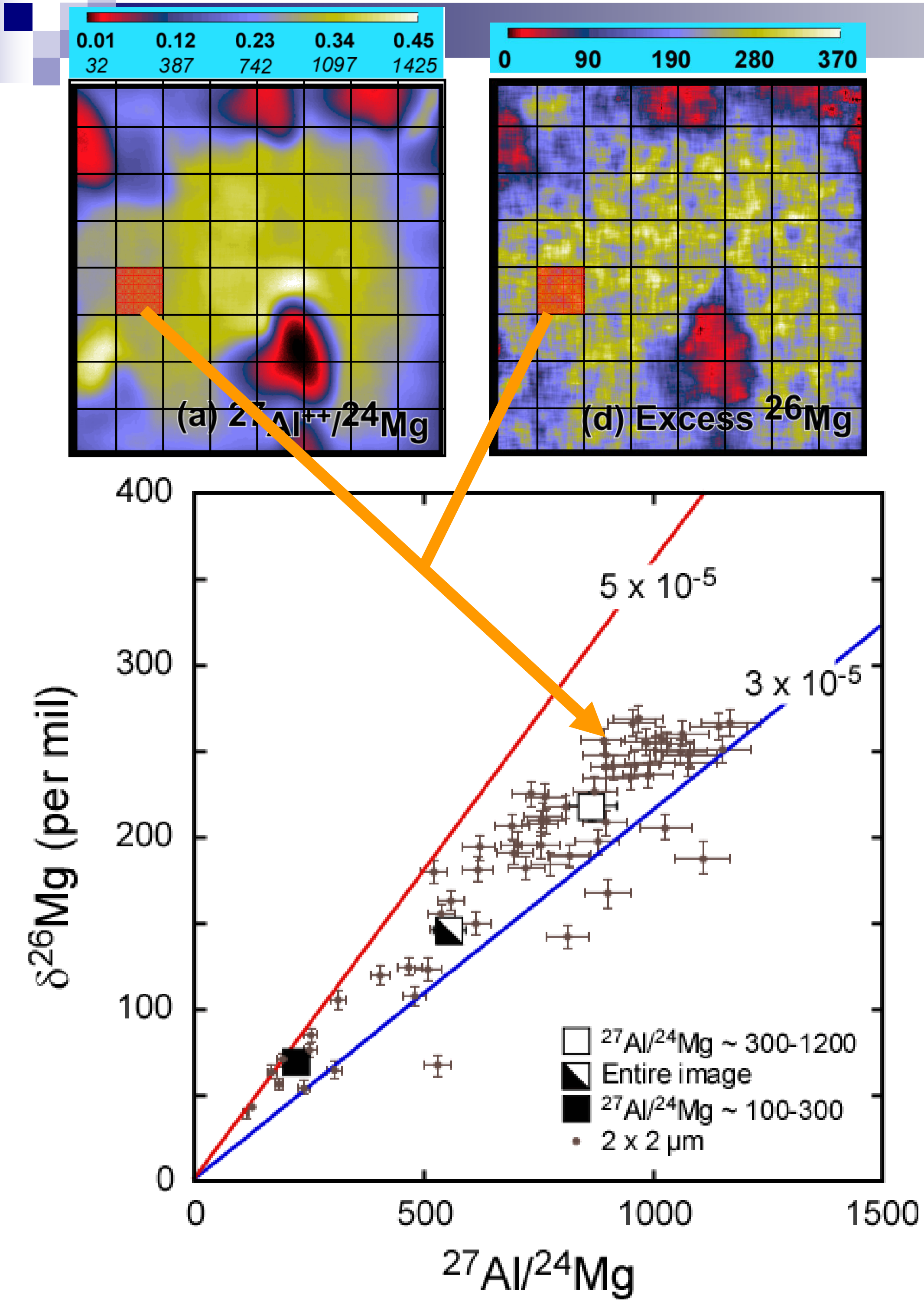
Mg isotope map

- 15 x 15 μm
- Smoothed by convolving each pixel with a 0.4 x 0.4 μm bin
- Excess ^{26}Mg = $\delta^{26}Mg - 2 \times \delta^{25}Mg$

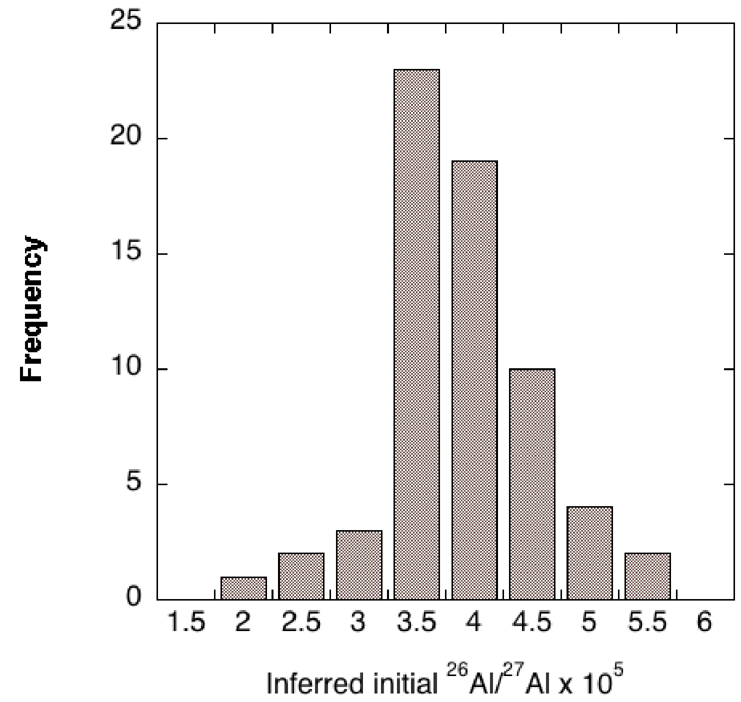


☻ **Several small Mg-rich grains in the Al/Mg ratio image of anorthite**

☺ **All bins show ^{26}Mg excesses: up to 370 ‰**



- ☺ $^{27}Al/^{24}Mg$: 100-1200
- ☺ Excess ^{26}Mg : 40-270 ‰
- ☺ $(^{26}Al/^{27}Al)_0$ = 1.8 to 5.2 x 10^{-5}



Initial $^{26}Al/^{27}Al$ ratio

- This study
  Image: (3.7 +- 0.4) (2σ) x 10^{-5}
  Spot: (3.4 +- 0.4) x 10^{-5}
- Previous study (Koiike et al.,1994)
  ims 3f = (3.12 +- 0.13) x 10^{-5}

Summary

- We established O and Mg isotope map techniques in mineral with the NanoSIMS 50L

- **Isotope map**
  - Consistent results with previous spot analyses
  - Isotopic images show strong isotopic disequilibrium among the mineral grains

- **O isotope map + Line Profile between two minerals**

  Sharp O isotopic boundary (< 0.4 μm) between two phases.

  >> Very rapid cooling following transient heating.

- We found heterogeneous Mg isotopic distributions and Al/Mg ratio in anorthite (15 x 15 μm) reflect a history of thermal alteration.

Future JSC NanoSIMS works

- **Trace element measurement (i.e., rare earth elements)**
  - REE elemental map

- **Mg and O isotopic measurements with Faraday cups**
  - 1 Sigma <= 0.12 % (Std-Err <= 0.04%) for FC-FC measurements of $^{18}O/^{16}O$ isotopic ratio

- **Developments of depth profile method, traverse analysis and elemental imaging for diffusion samples**
  - High spatial resolution capability is good for a sample with short diffusion profile