Nebular and Parent Body Alteration of Chondritic Meteorites: Aqueous Alteration and Thermal Metamorphism

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Talk Outline

Aqueous Alteration

- Introduction and Overview
- Evidence for aqueous alteration
  - Low T alteration
  - Fluid-assisted metamorphism.
- Chemical and isotopic effects
- Alteration scenarios
  - Nebula
  - Preaccretionary
  - Asteroidal
- Conditions of alteration
- Microchemical environments
- Timescales of alteration
- Future work

PRIMORDIAL WATER IN EARLY SOLAR SYSTEM MATERIALS: KEY QUESTIONS

- What's the evidence?
  - Interaction of fluids with primary nebular materials
- How much?
- Was elemental mass transport involved? What scale?
- Where?
- Under what conditions?
- For how long?

HISTORY OF CHONDRITIC MATERIALS

Interstellar grains (stars)
Organic material (interstellar medium)

Molecular cloud collapse

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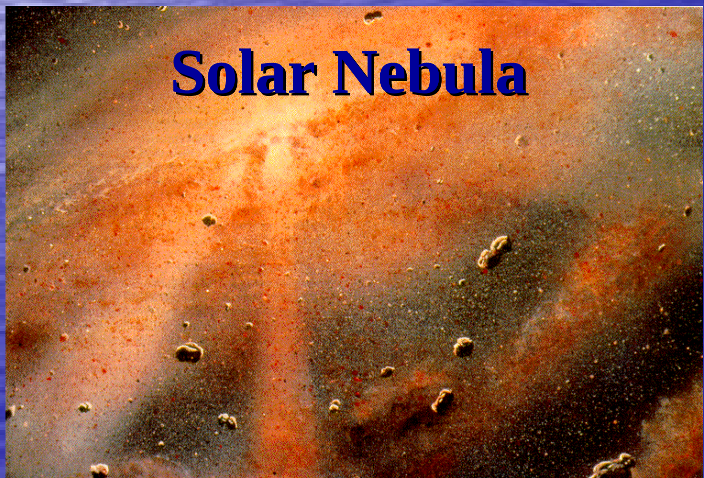


Accretion

CAIs
Chondrules
matrix

Aqueous alteration, heating

Secondary phases, carbonate

PRIMORDIAL WATER IN EARLY SOLAR SYSTEM MATERIALS

- Primordial water was widely available in early solar system and during accretion of asteroids.
- Record of interaction with water is present in almost all primitive chondrites.
- Alteration started early and water was available for extended periods of time (~10 Ma).
- Conditions of alteration were variable and reflects thermal structure of asteroids.

AQUEOUS ALTERATION: DEFINITION

- Alteration processes resulting from the interaction of water with an anhydrous protolith
- Has perturbed original mineralogy and chemistry of nebular materials
- Study of meteorites altered by water provides insights into the role of water in early solar system processes

IMPORTANCE OF AQUEOUS ALTERATION

- Widespread among early solar system materials (meteorites, IDPs).
- Almost all chondrite groups have been affected.
- Even meteorites that are considered as ‘dry’ show effects of interaction with water.
- Effects overprint primary nebular signatures.
- Need to understand effects to:
  - a) understand nebular processes
  - b) determine role and importance of water in evolution of chondritic materials

SOME TERMINOLOGY

- Aqueous alteration comes in many forms:
  - Low temperature, hydrothermal alteration
    - Alteration below ~200-300^{0}C, resulting in the formation of hydrous phases (phyllosilicates)
  - Fluid-assisted metamorphism
    - Thermal metamorphism in the presence of aqueous fluid above ~300^{0}C
  - Metasomatism
    - Change in bulk chemistry of meteorite as a result of interaction with aqueous fluids ~300^{0}C

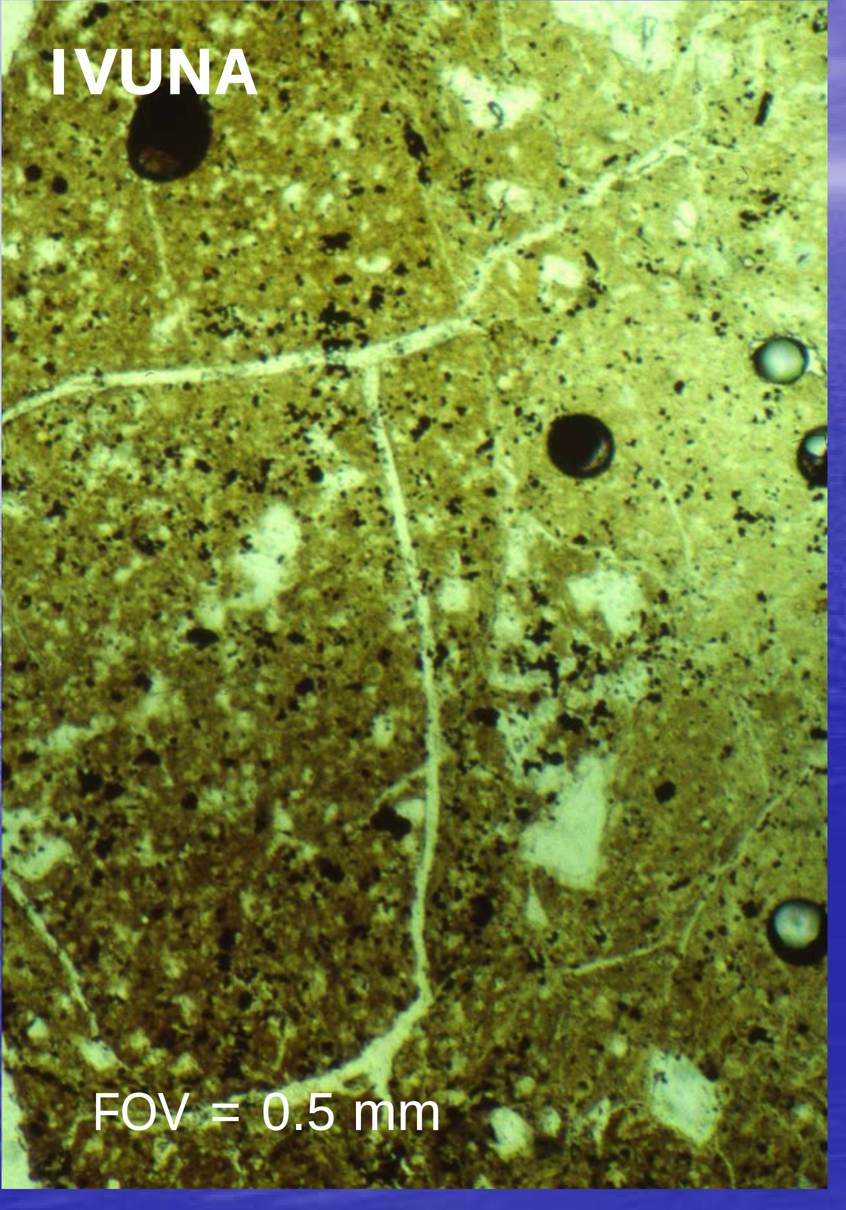
EVIDENCE FOR INTERACTION WITH WATER

- Replacement of primary nebular phases by secondary alteration products.
- Low temperature alteration commonly indicated by development of hydrous phases (serpentines, smectites).
  - Secondary carbonates, sulfates, oxides, sulfides, etc.
- Anhydrous silicates also formed by alteration under higher T regimes (fayalite, etc) – fluid assisted metamorphism/metasomatism.
- Alteration variable from complete to incipient, sometimes cryptic.

EVIDENCE FOR LOW T, AQUEOUS ALTERATION

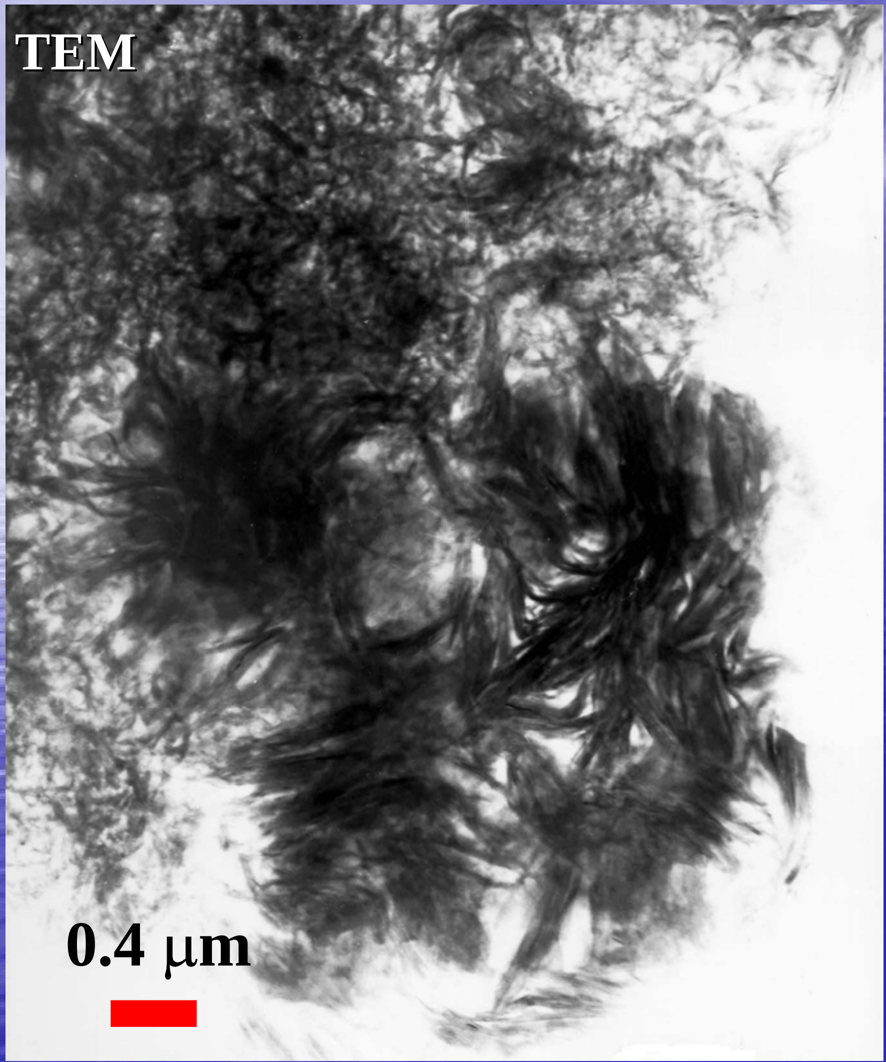
- Petrologic type 1 chondrites.
- Meteorites exhibiting very extensive evidence of interaction with aqueous fluids – e.g. phyllosilicates, carbonates, sulfates, etc.
- All primary anhydrous phases have been replaced – only rare, anhydrous phases remain as relicts.
  - CI – most completely altered (petrologic type 1) – only rare anhydrous phases
  - CM – some CM chondrites are completely altered.

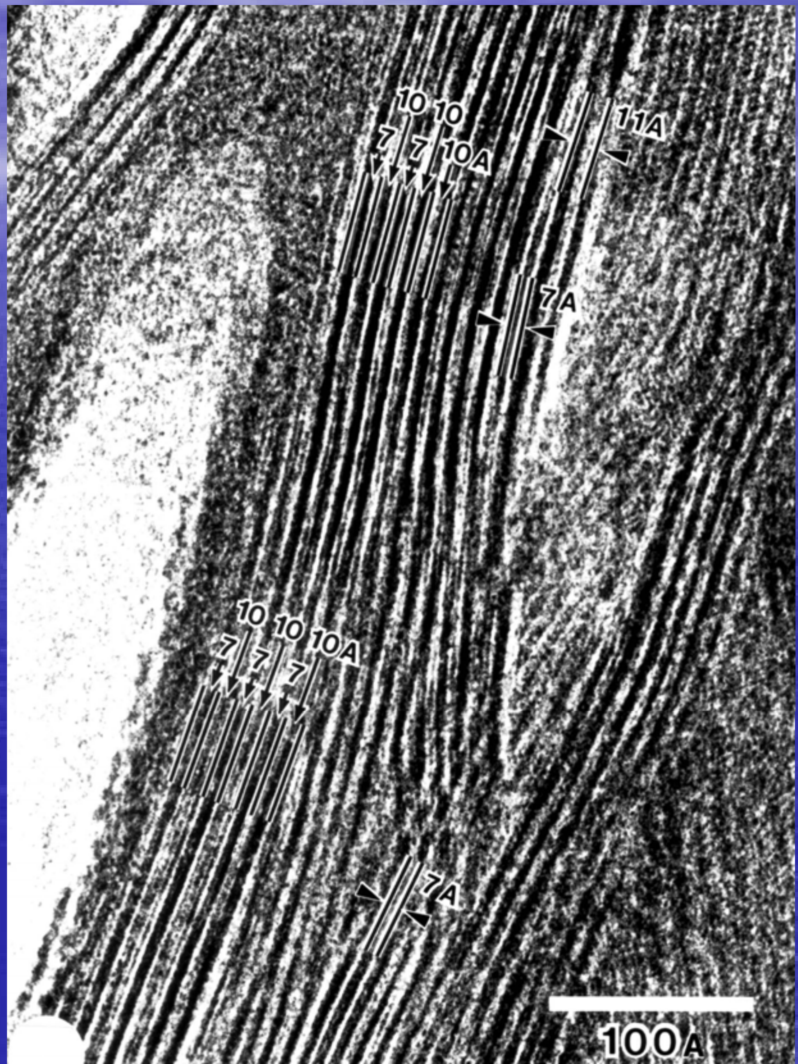
CI chondrites – Petrologic type 1



- Mineralogy
  - Phyllosilicates (saponite/smectite)
  - Carbonate (calcite, dolomite, breunnerite)
  - Sulfates (possibly terrestrial)
  - Magnetite
  - Ferrihydrite
- Veins of sulfate probably of terrestrial origin

CI chondrites – Phyllosilicates

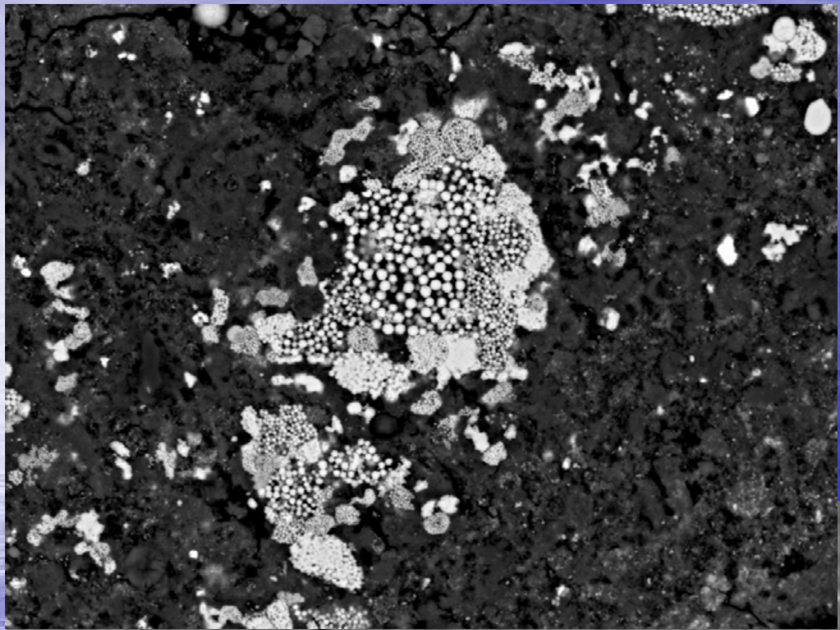


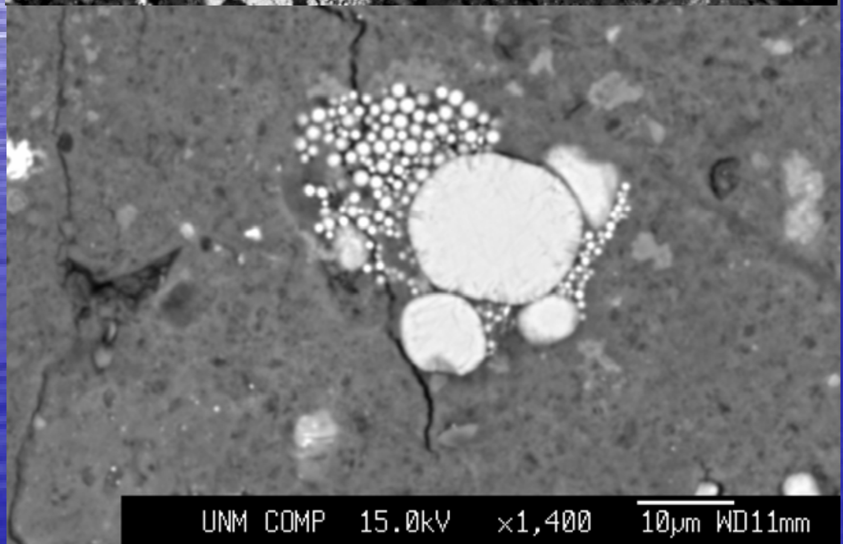


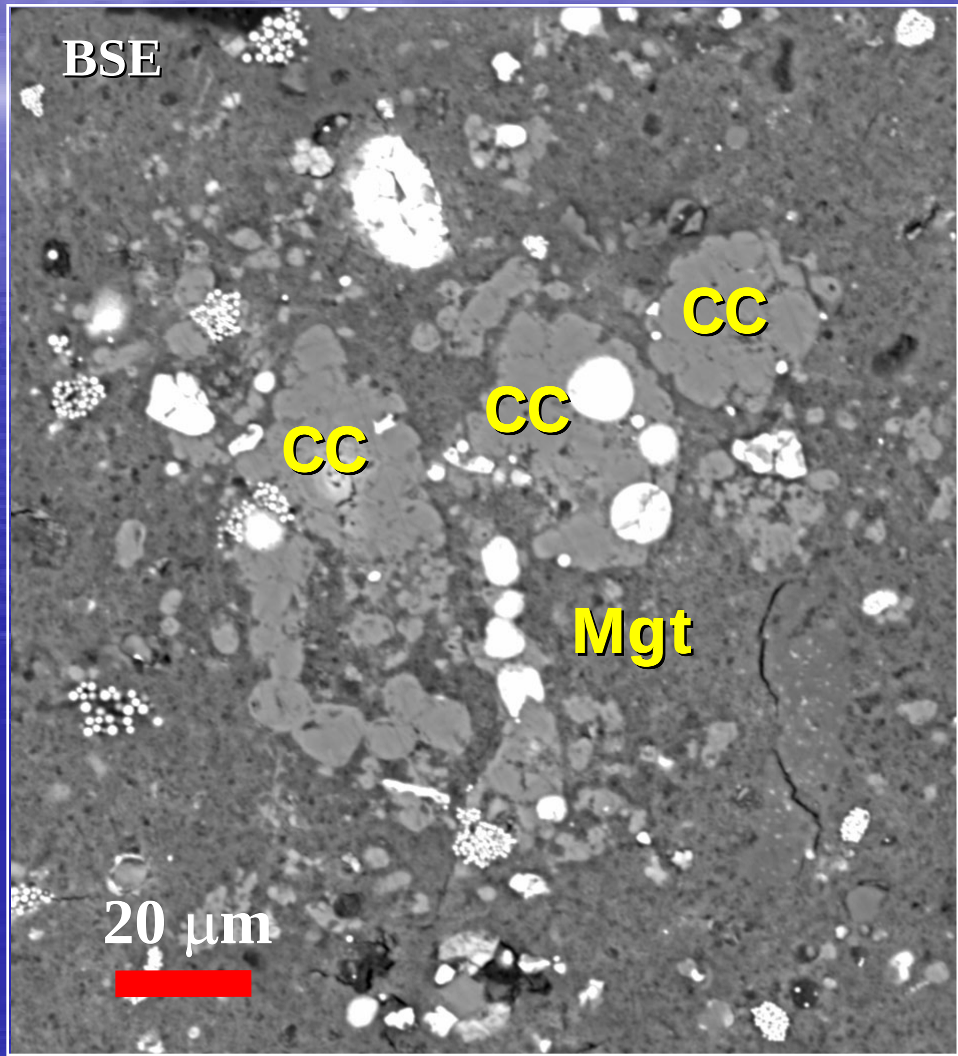
Coarse and fine-grained interlayered serpentine and saponite

Tomeoka and Buseck (1988)

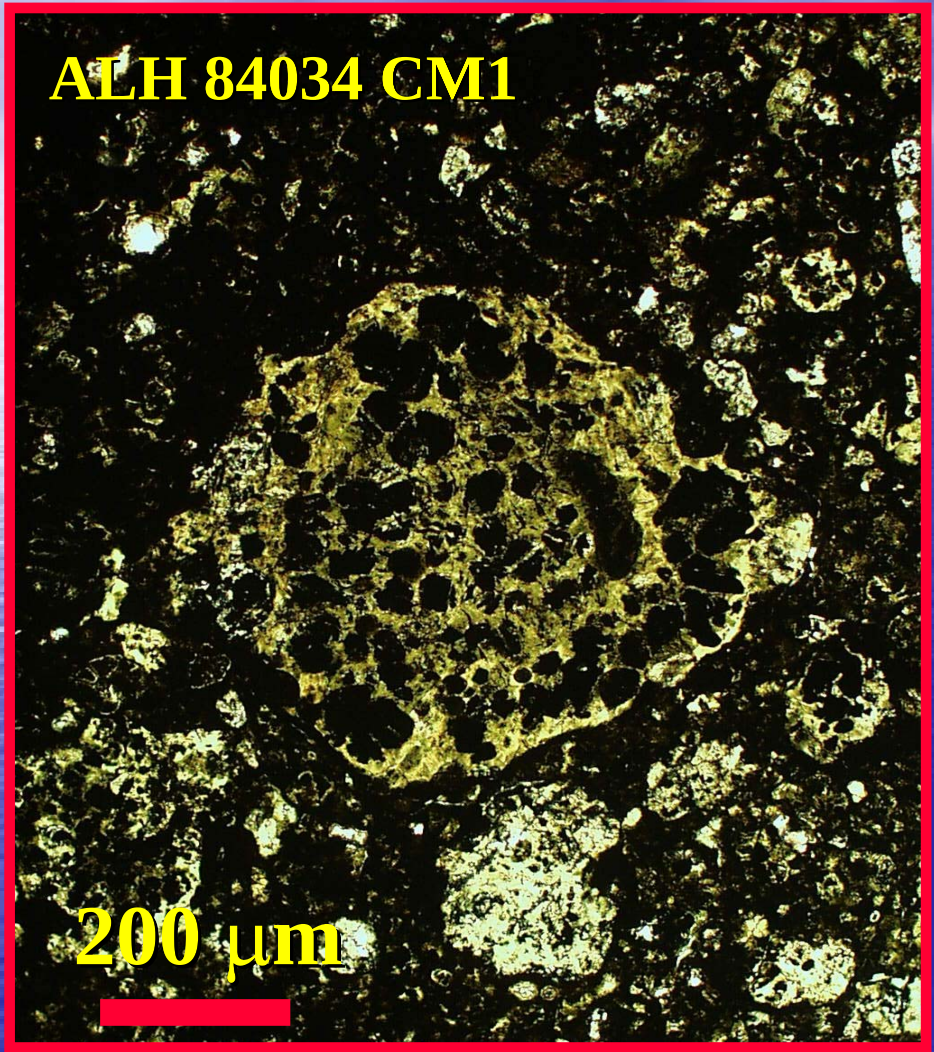
CI CHONDRITES - MINERALOGY







CM1 CHONDRITES

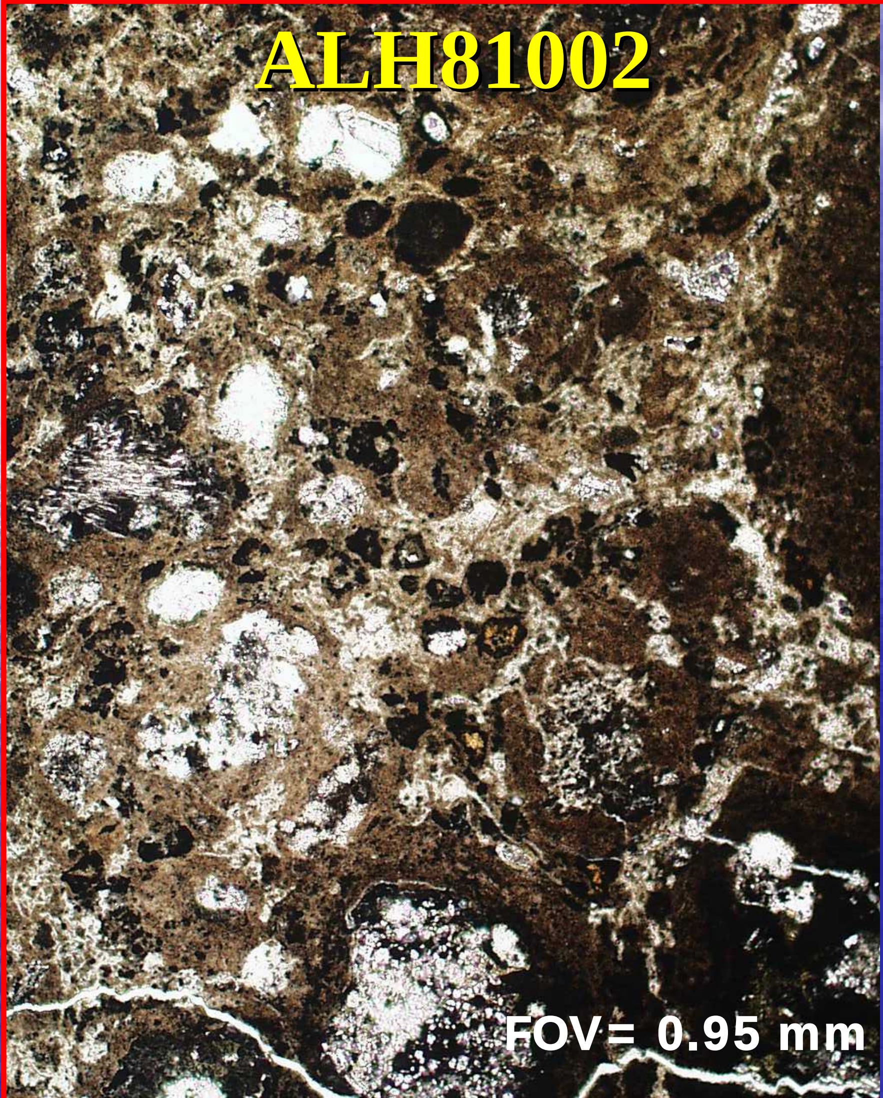


- Complete pseudomorphic replacement of chondrules
- Mineralogy
  - Serpentine
  - Magnetite
  - Carbonates (calcite and dolomite)
  - Chlorite

EVIDENCE FOR LOW T, AQUEOUS ALTERATION

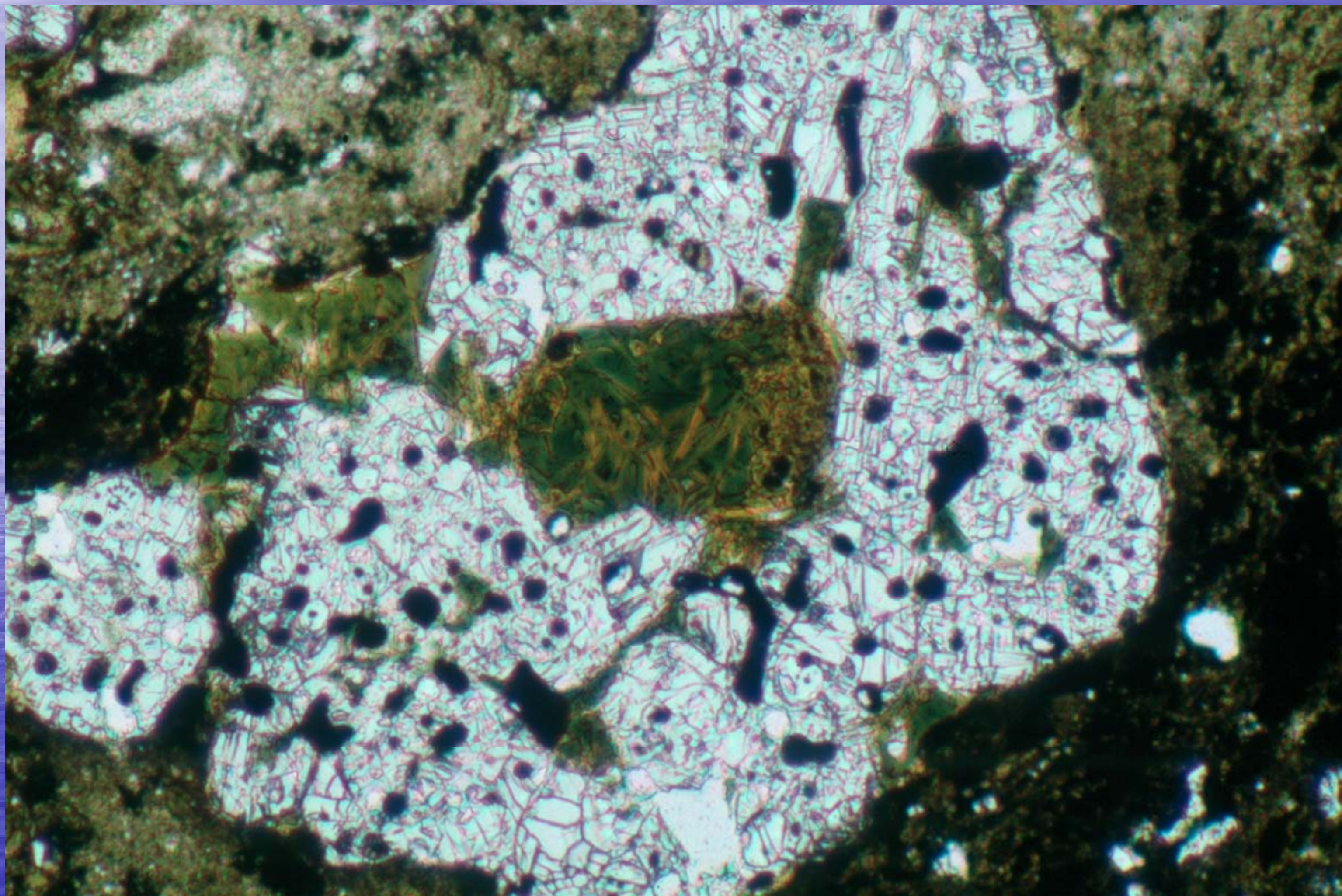
- Petrologic type 2 chondrites.
- Most CM chondrites:
  - significant, but not complete alteration.
  - matrix fully altered and chondrules partially to extensively altered.
  - CM2s exhibit wide degree of alteration – petrologic types 2 and 1.
- Most CR chondrites:
  - matrix fully hydrated and chondrules partially replaced. But generally less altered than CM2s.

CM, CR chondrites – Petrologic type 2

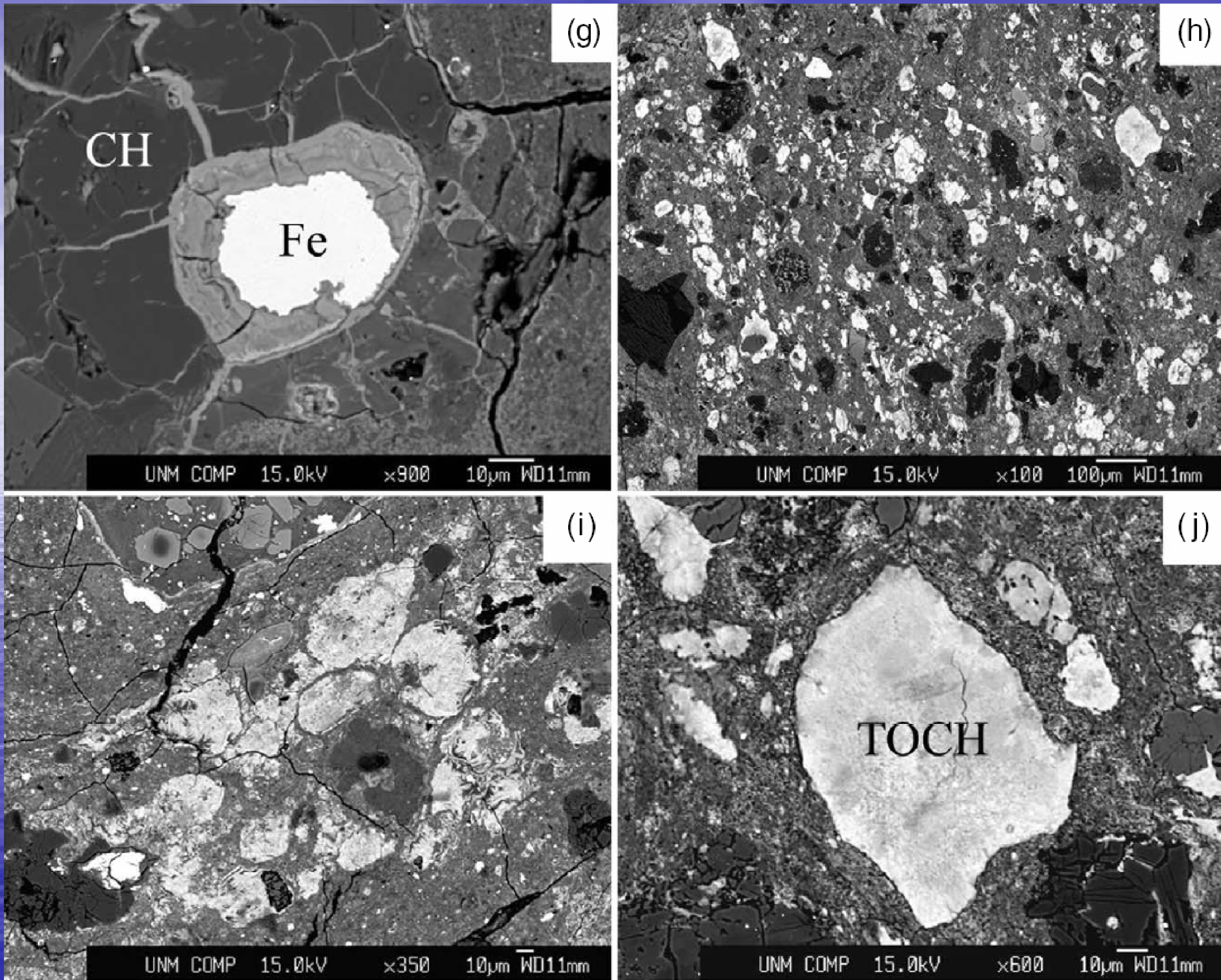



Murchison
CM2 carbonaceous chondrite

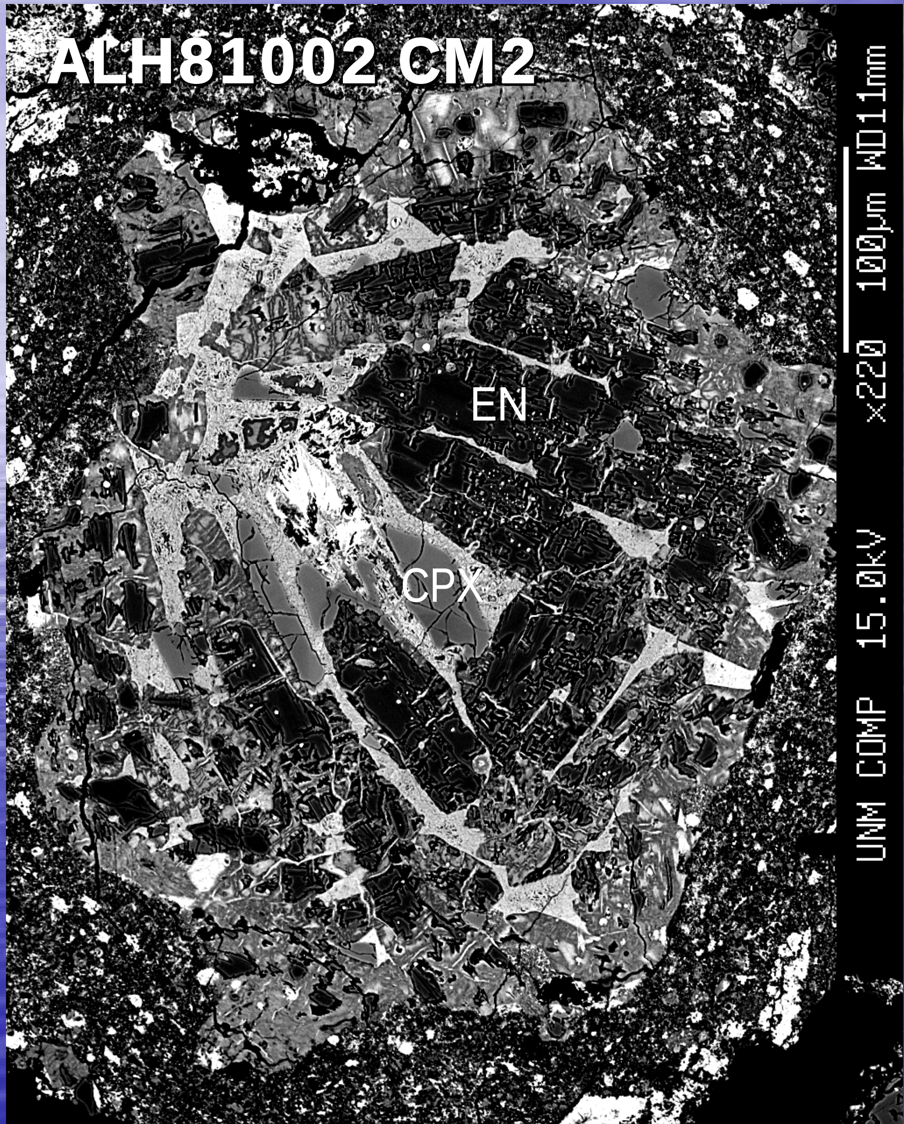
MINERALOGY OF CM CHONDRITES



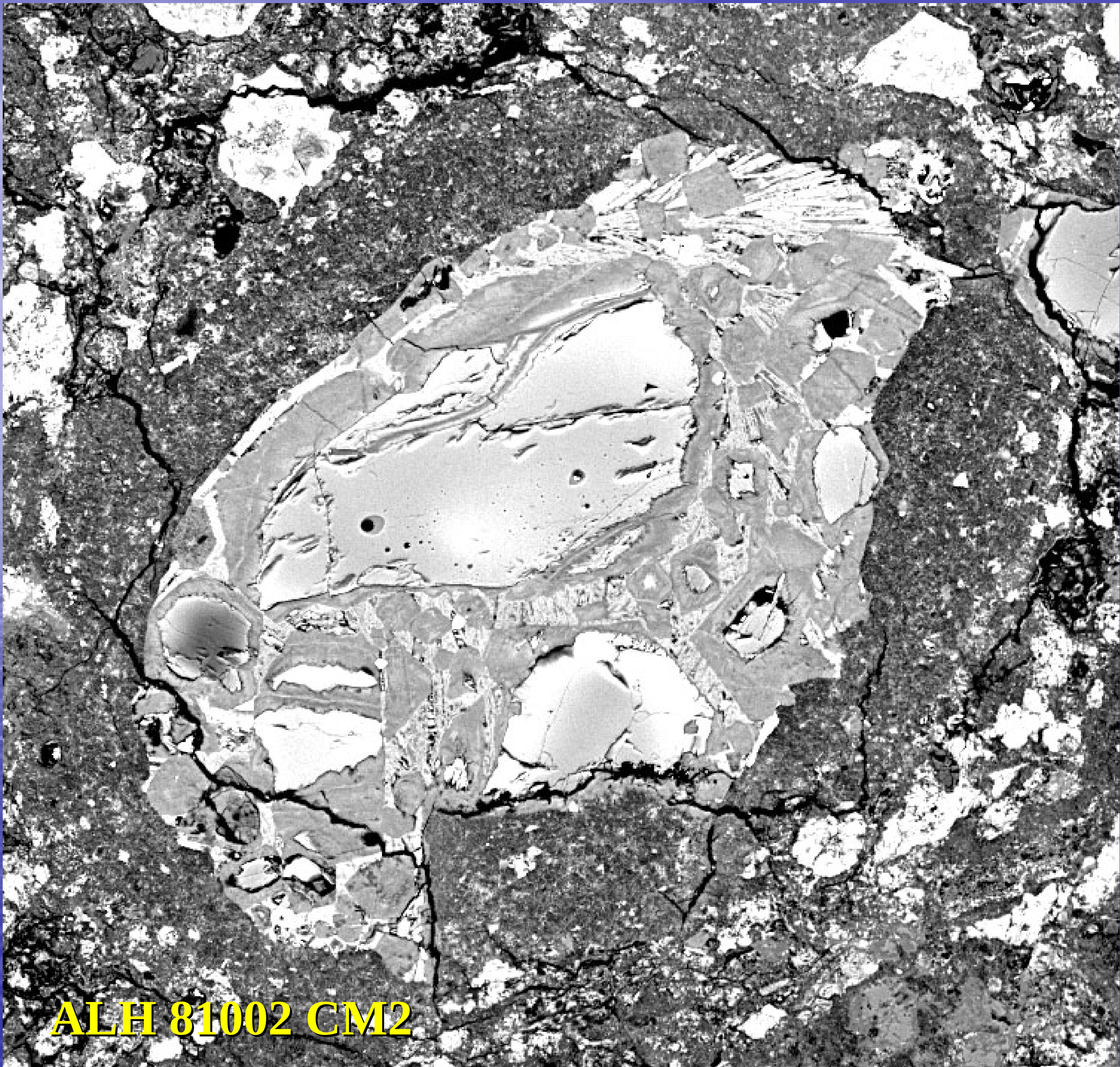
Murchison CM2 Partially altered chondrule


(g)
CH
Fe
UNM COMP 15.0kV ×900 10μm WD11mm
(h)
UNM COMP 15.0kV ×100 100μm WD11mm
(i)
UNM COMP 15.0kV ×350 10μm WD11mm
(j)
TOCH
UNM COMP 15.0kV ×600 10μm WD11mm

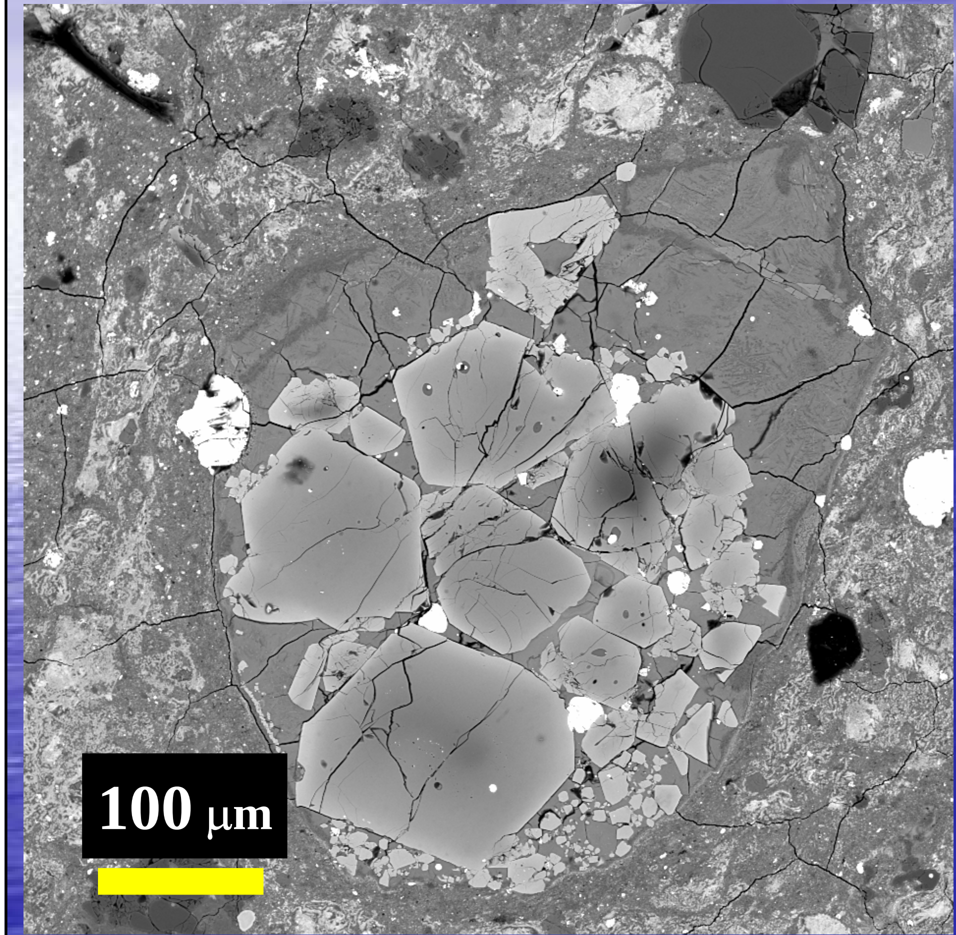
ALTERATION OF CHONDRULES

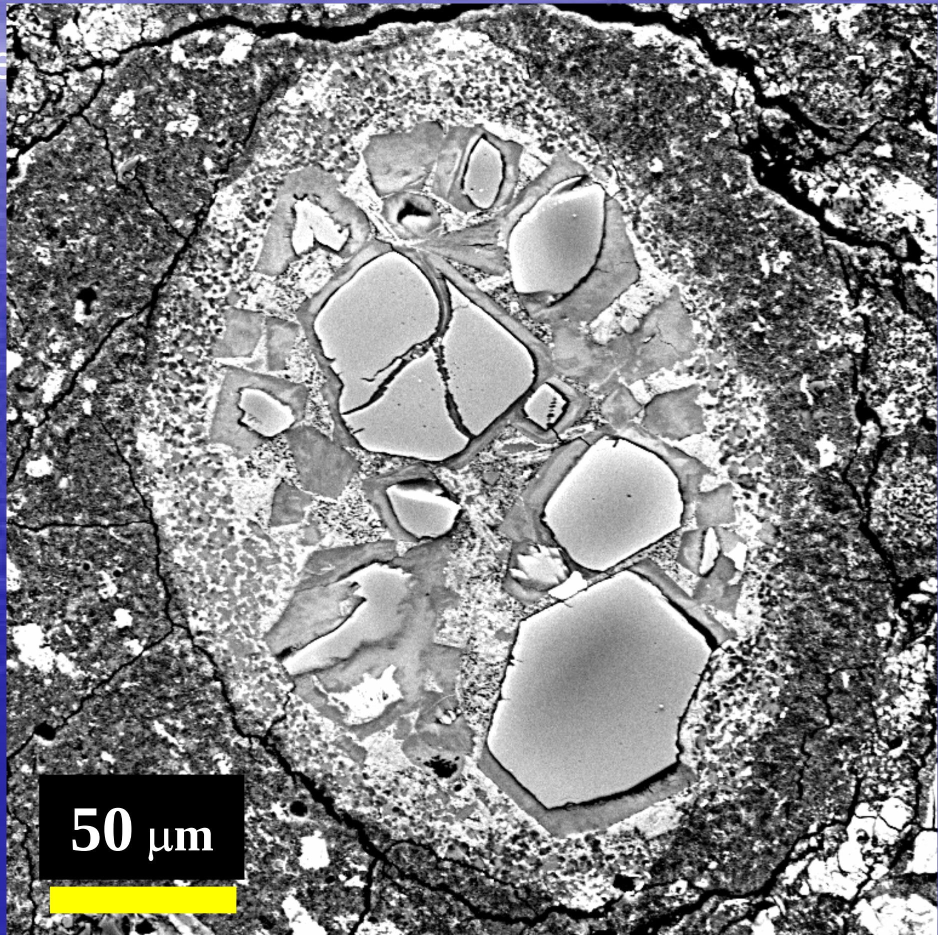


- Mesostasis – serpentine (cronstedite/Mg-Fe serpentine)
- Olivine/pyroxene – Mg-Fe serpentine
- Metal – tochilinite-cronstedtite intergrowths.


ALH 81002 CM2

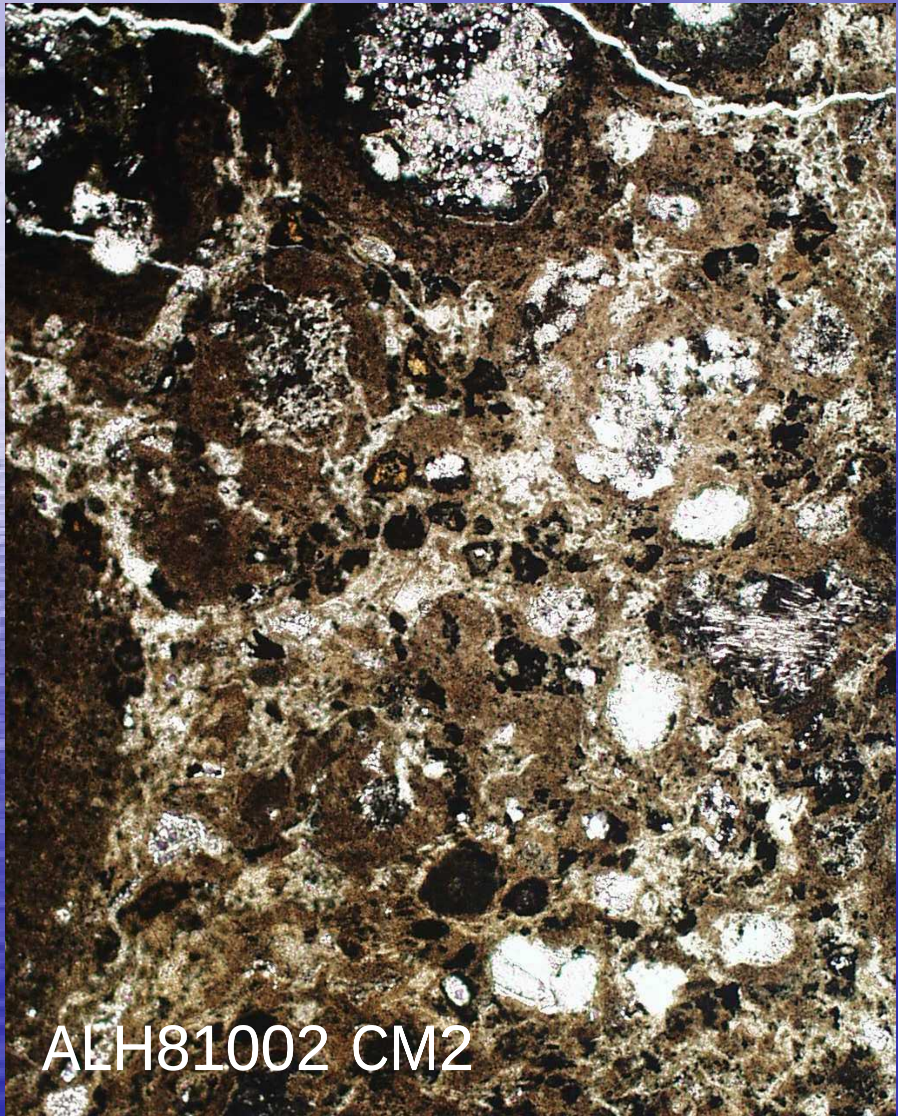
VARIABLE ALTERATION IN CM2 CHONDRITES



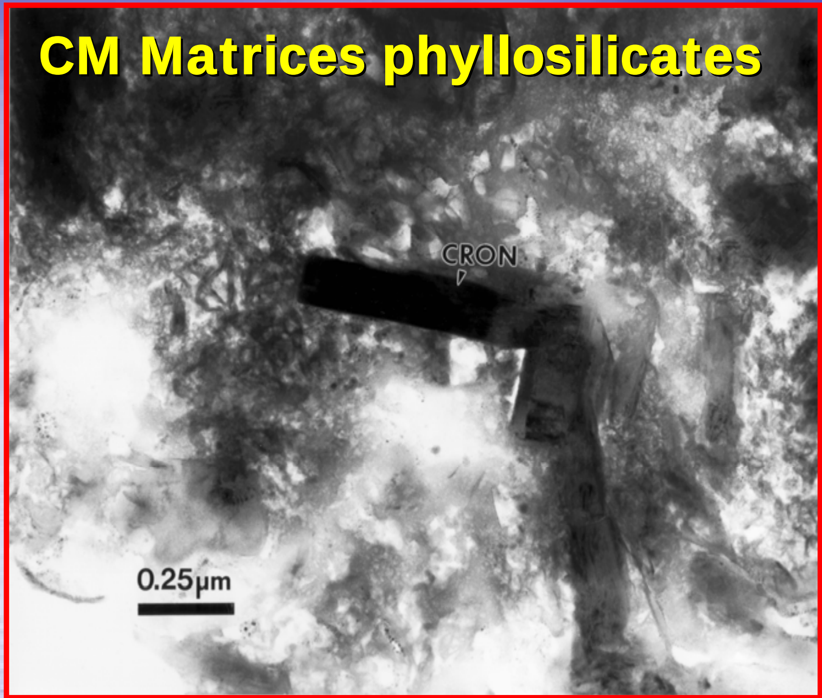


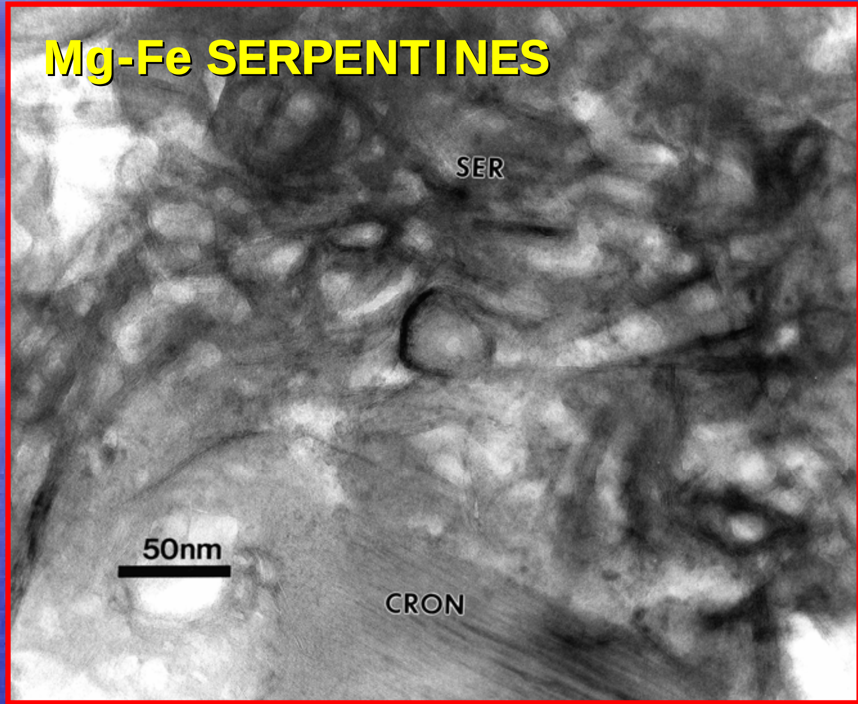
Y791198 Increasing alteration → **ALH81002**

ALTERATION OF MATRIX IN CM2

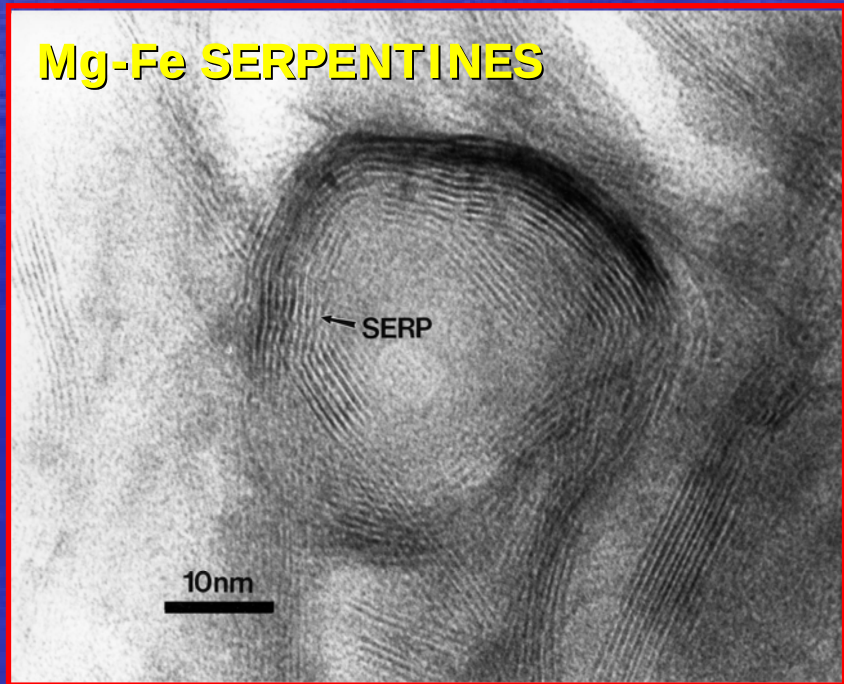


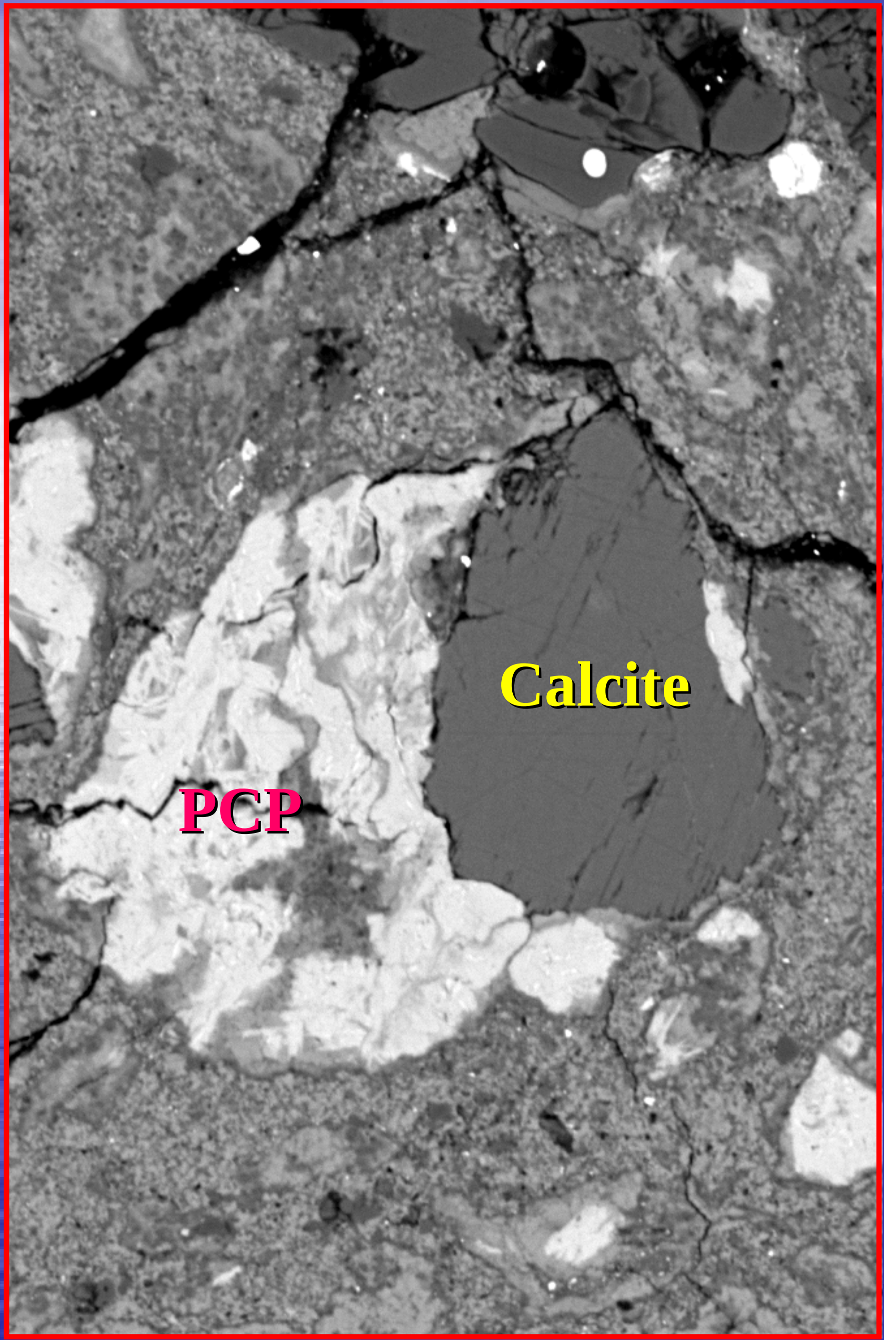
- Mineralogy – very fine-grained
  - Amorphous silicate material
  - serpentines (cronstedite and Mg-Fe serpentine)
- Tochilinite and tochilinite-cronstedtite intergrowths (formerly PCP).
- Sulfides – pentlandite, pyrrhotite
- Carbonates – mainly calcite, minor dolomite


CM Matrices phyllosilicates
CRON
0.25µm

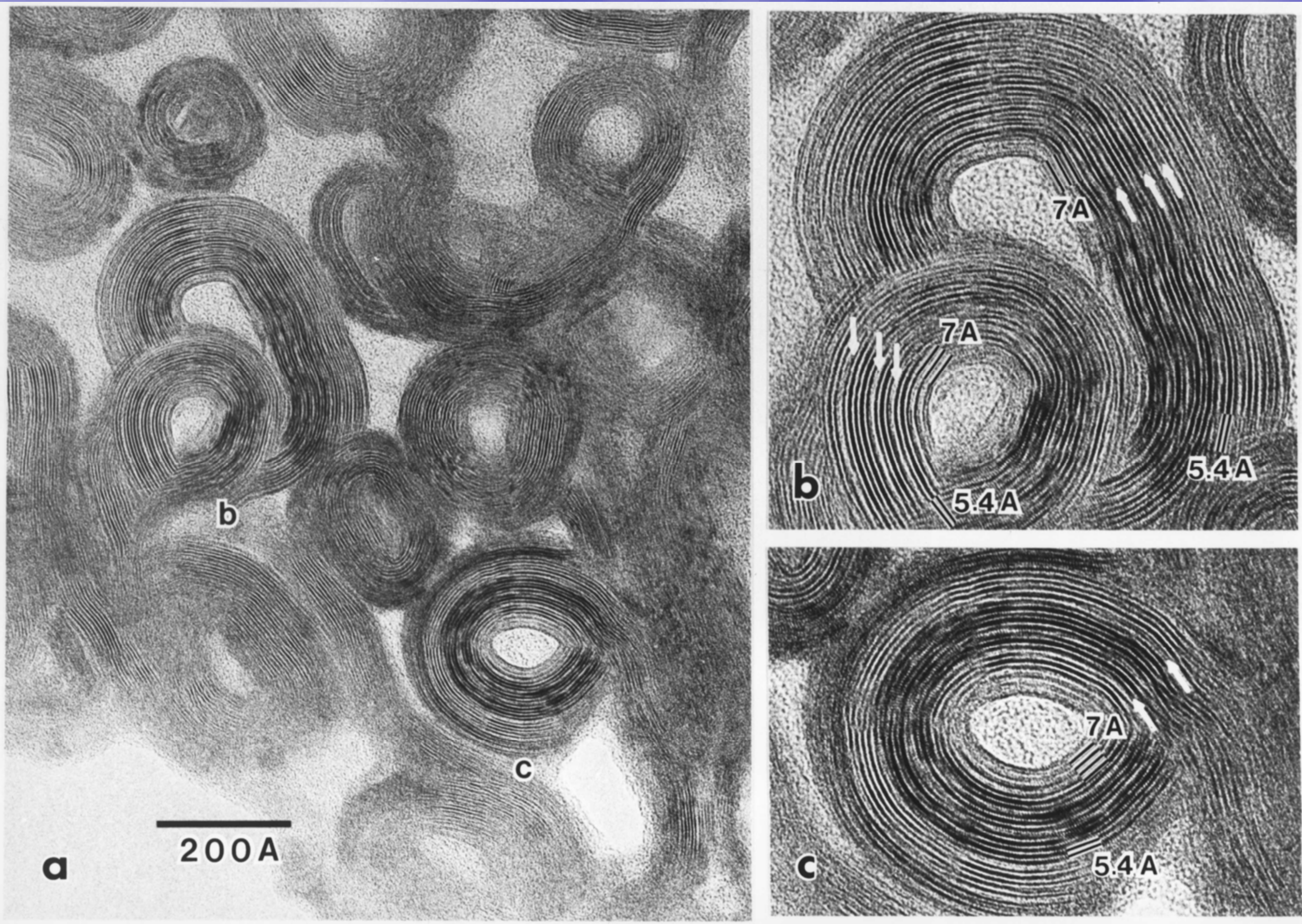

Mg-Fe SERPENTINES
SER
50nm
CRON


TOCHILINITE/CRONSTEDTITE
30nm


Mg-Fe SERPENTINES
SERP
10nm


Calcite
PCP


TOCHILINITE
40nm
TOCH



Courtesy Kazu Tomeoka

TOCHILINITE STRUCTURE

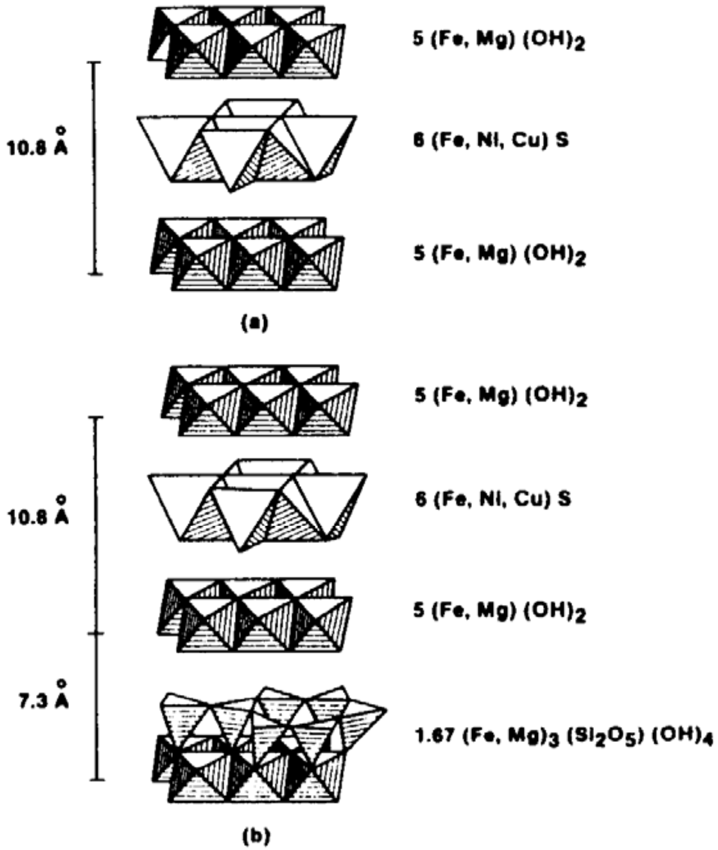
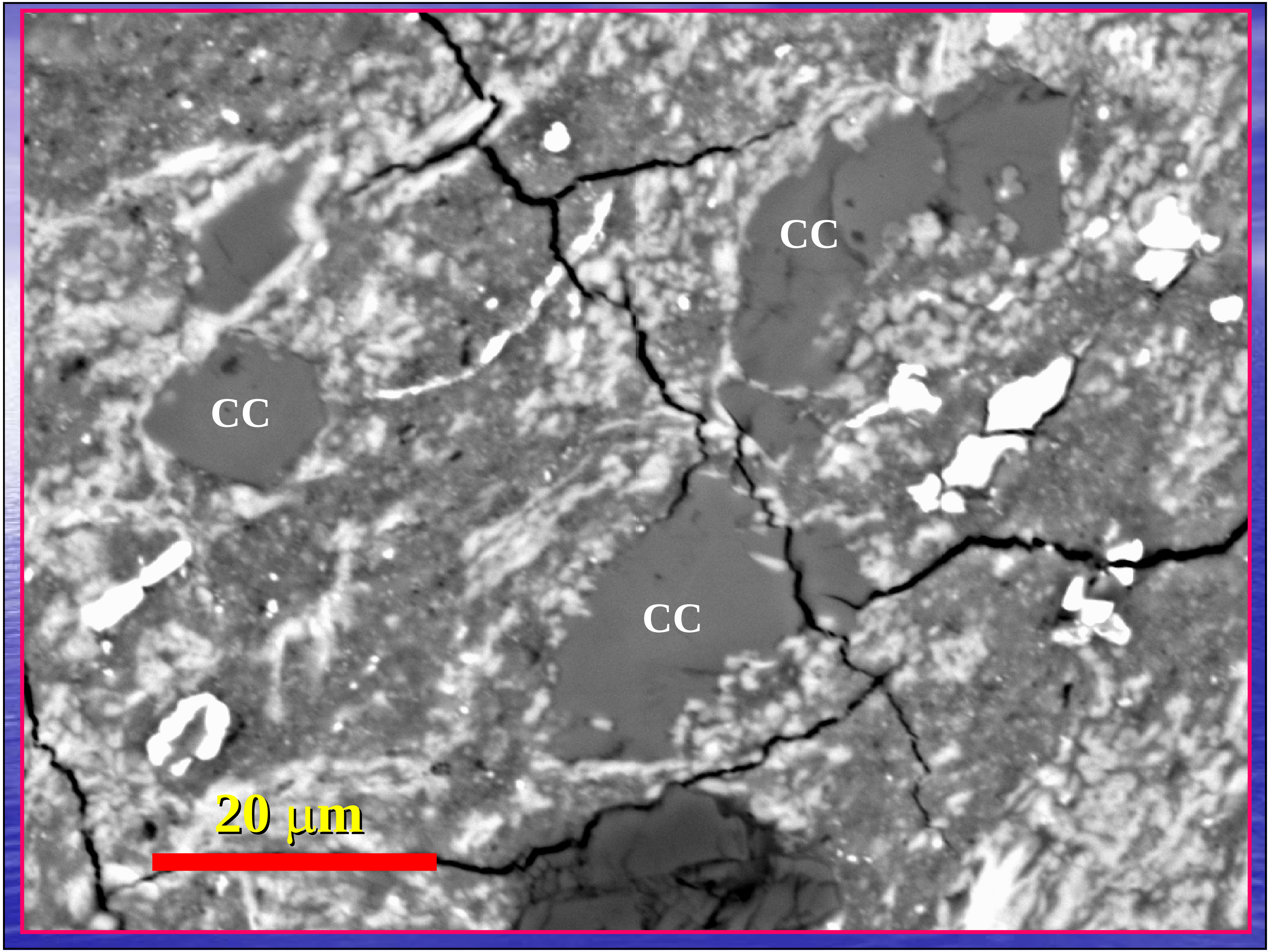
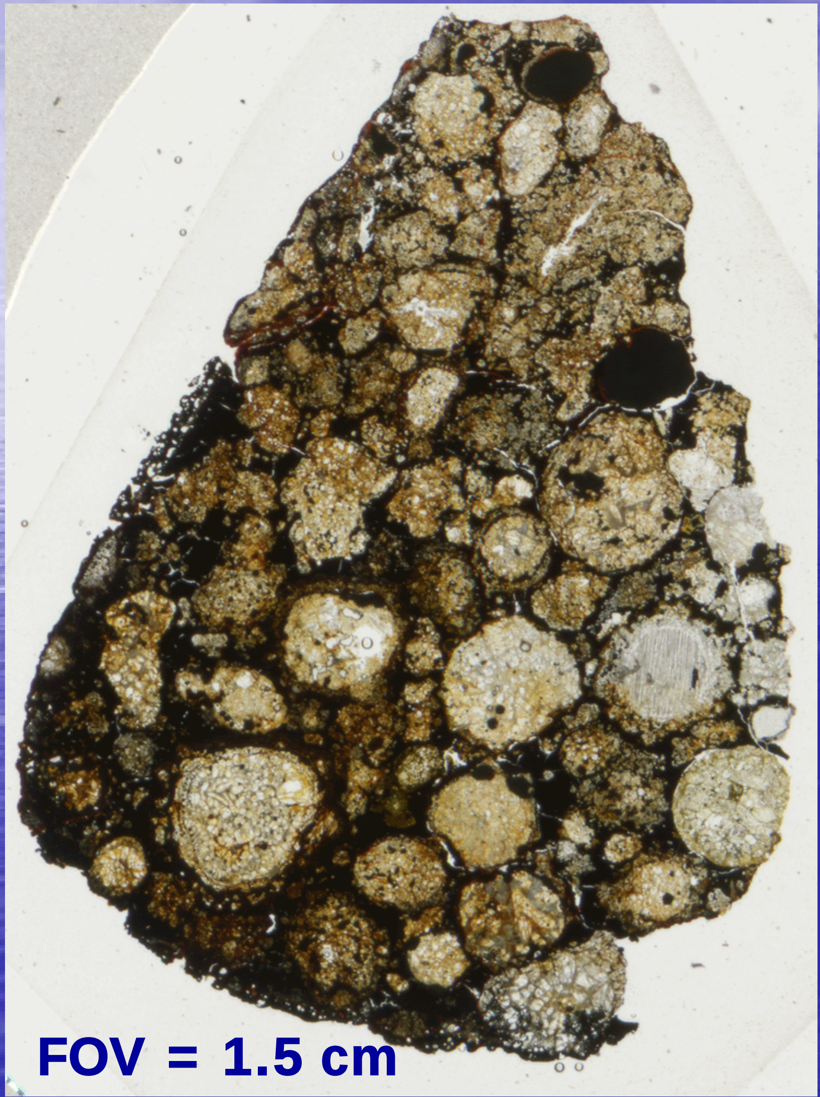


Fig. 3.4.7. Models for tochilinite phases. (a) Model of tochilinite, indicating sulfide and hydroxide layers. (b) Model of coherently interstratified tochilinite-serpentine, indicating the relative stacking of the sulfide, hydroxide and serpentine layers. Figure from Mackinnon and Zolensky (1984), reprinted by permission.



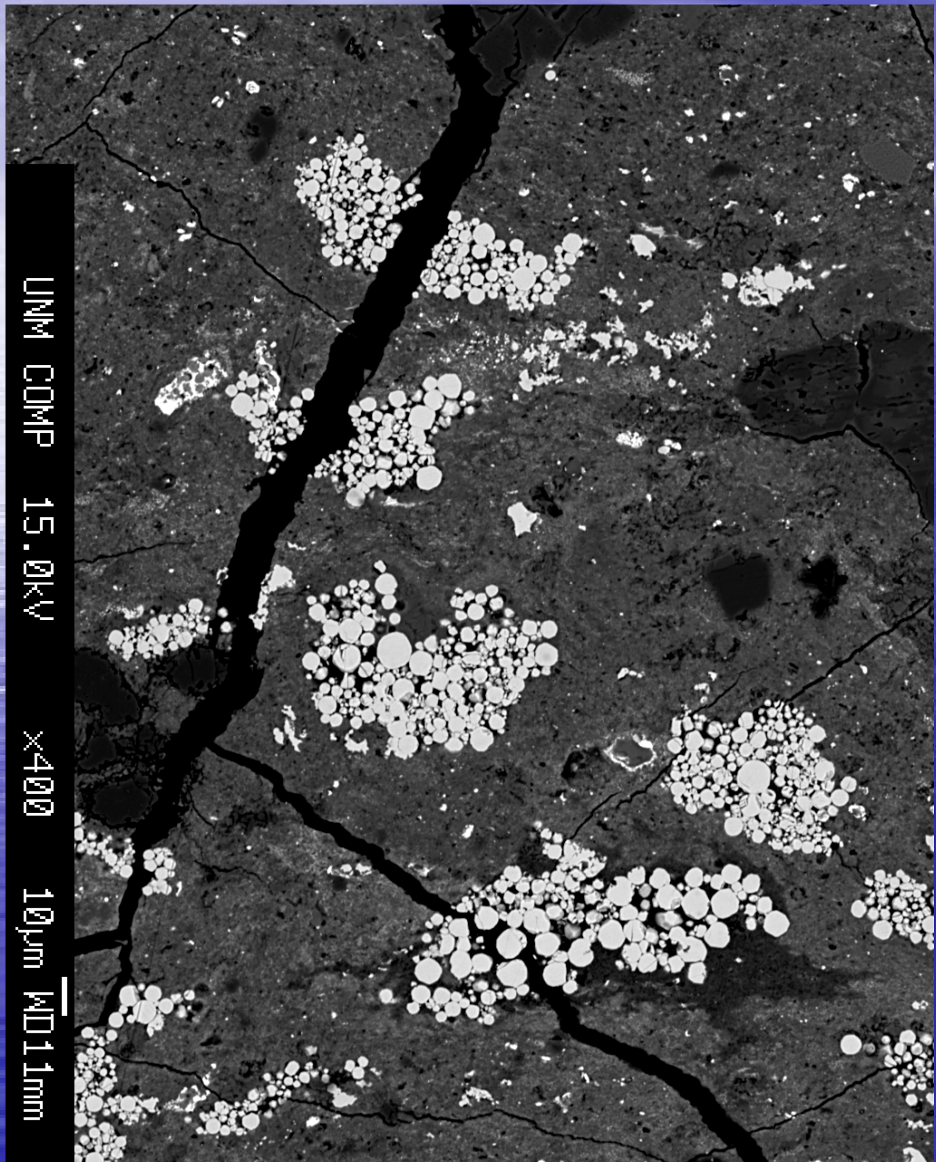
CC
CC
CC
20 µm

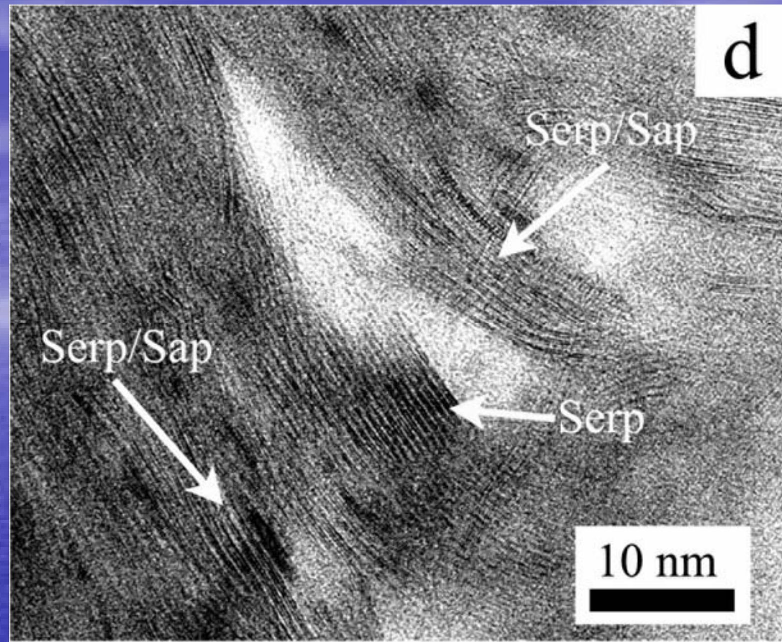
CR chondrites – Petrologic type 2

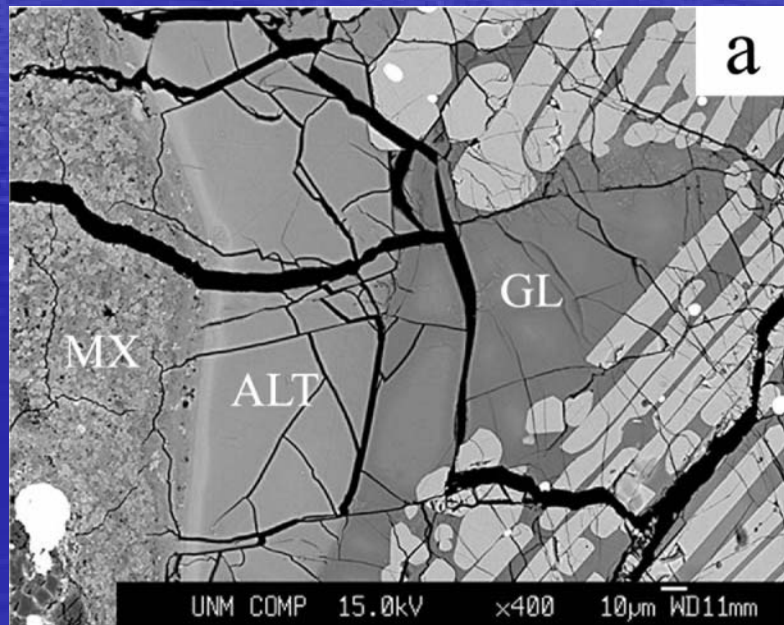


- Mineralogy
  - Serpentines and saponites (matrix and chondrules)
  - Magnetite
  - Pyrrhotite and pentlandite
  - Carbonate (calcite)
- Chondrules show variable alteration from weak to extensive replacement of chondrule mesostasis.

CR chondrite alteration



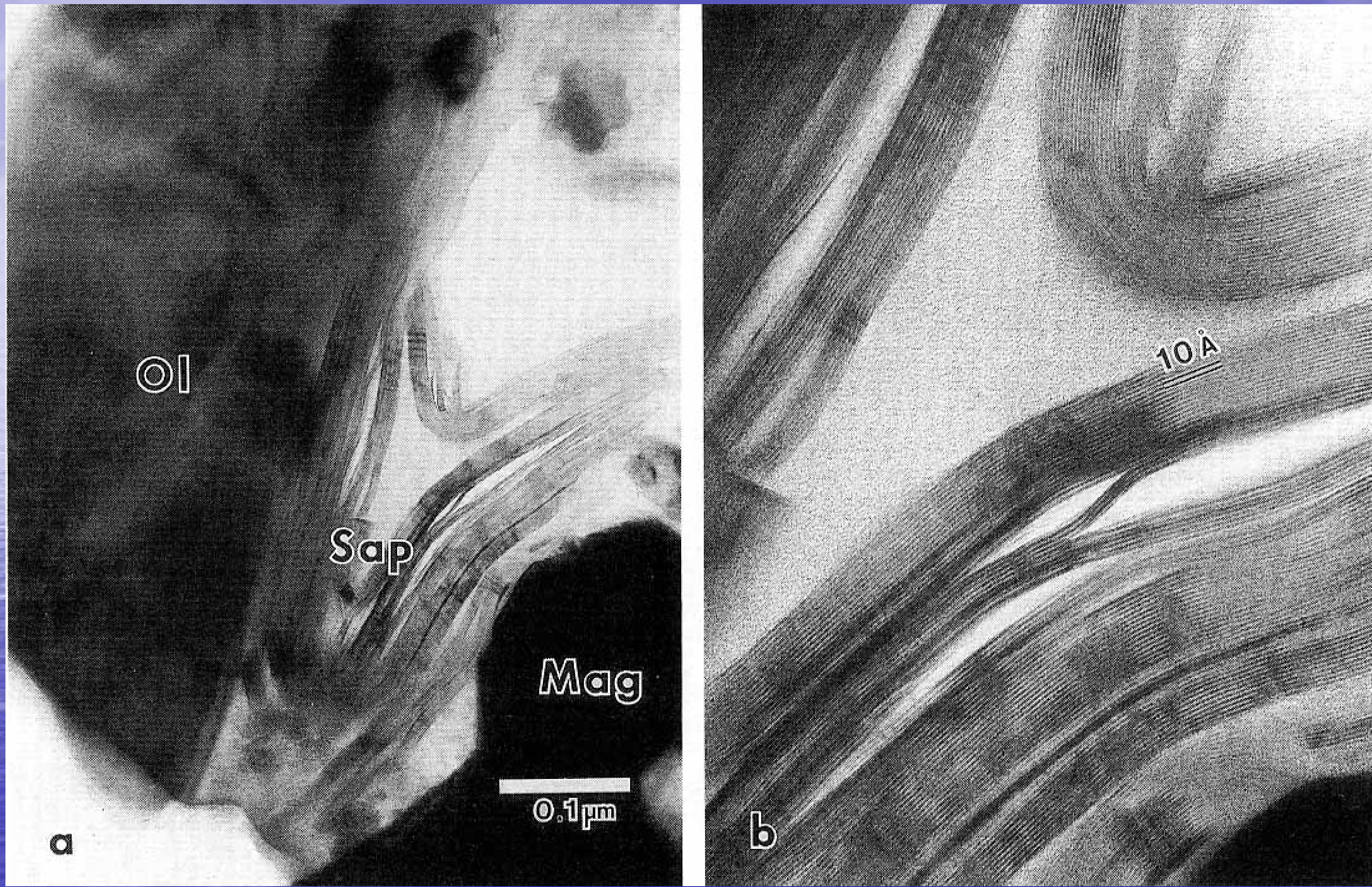




EVIDENCE FOR LOW T, AQUEOUS ALTERATION

- Petrologic type 3 chondrites – incipient evidence of aqueous alteration – phyllosilicates, Fe-oxides.
- CV (Ox_{Bali}) – alteration in matrix and chondrules
- CV (Ox_{All}) – rare phyllosilicates in chondrules and CAIs
- CO – mild localized alteration in matrix
- CR – some CR chondrites show very mild localized alteration effects in matrix and chondrules.
- UOC – matrix altered in lowest petrologic type.
- Unique chondrites – e.g. LEW 85332 for example.

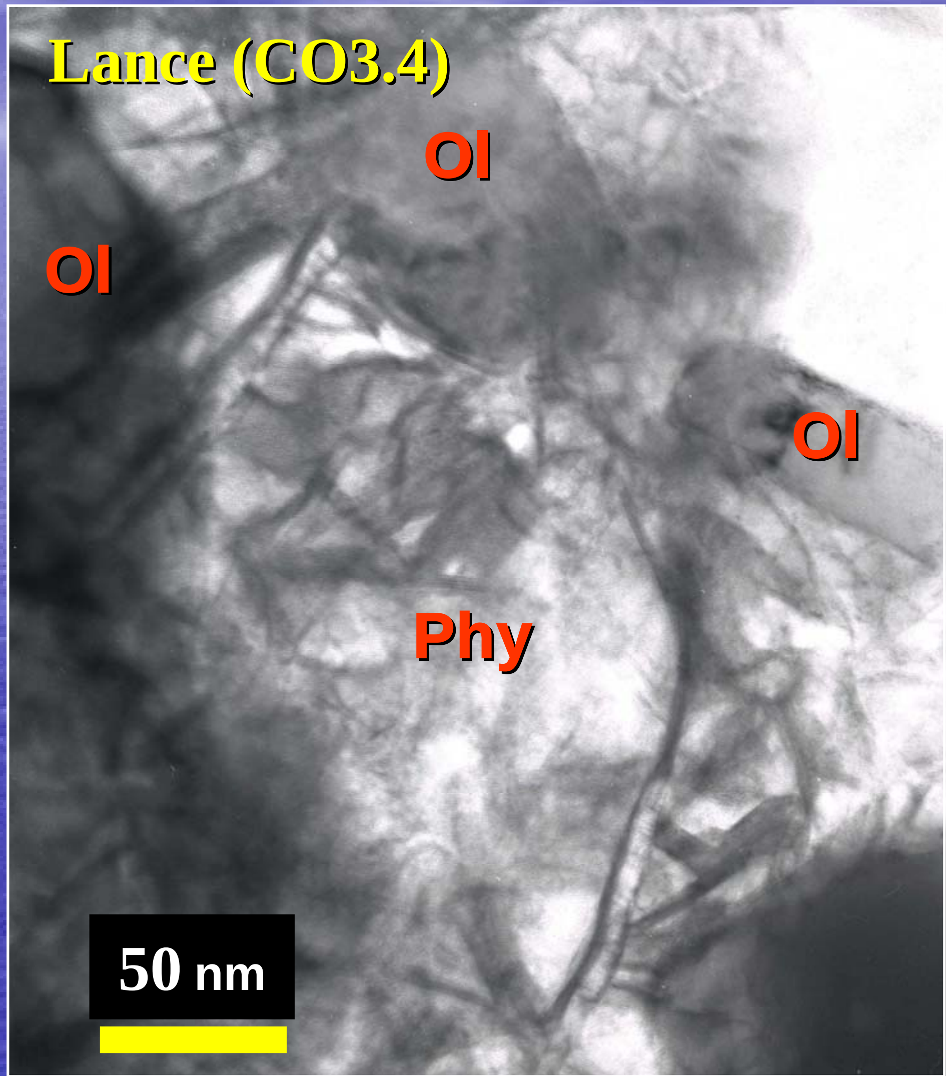
CV3 chondrite alteration



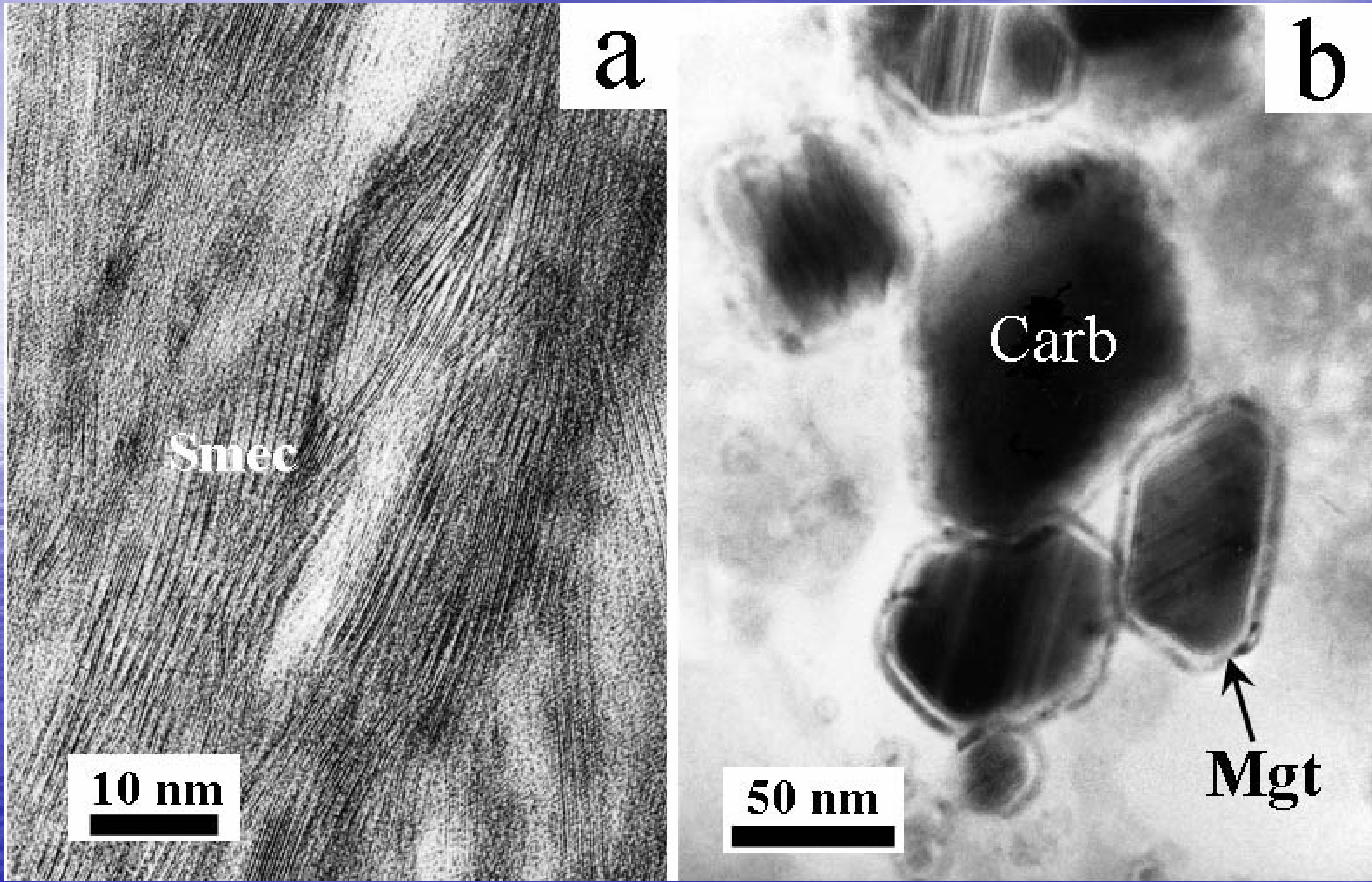
Phyllosilicates in Mokoia matrix - saponite

Tomeoka (1990) GCA

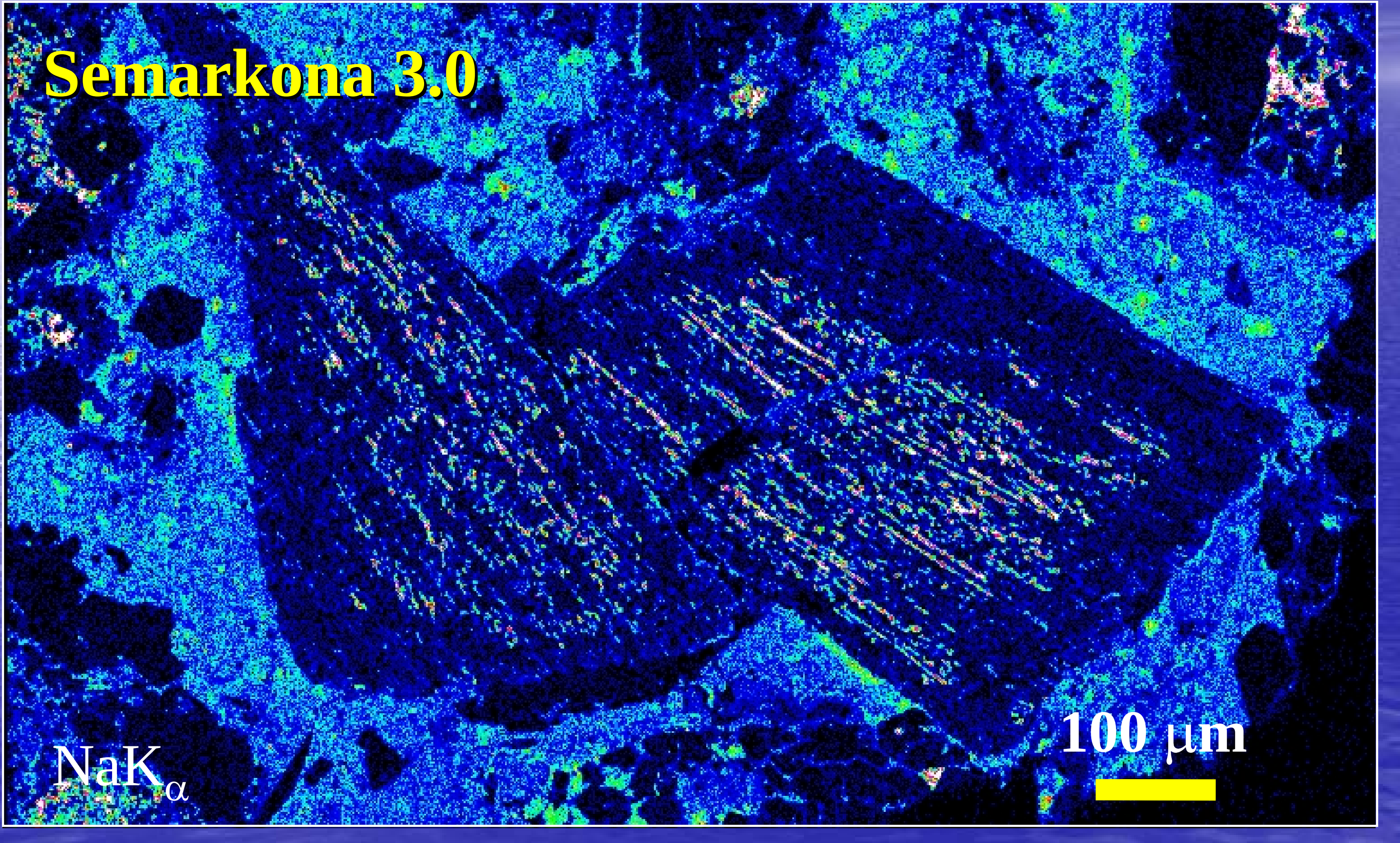
Incipient alteration – CO, CV3, UOCs



UNEQUILIBRATED ORDINARY CHONDRITES (SEMARKONA)



UNEQUILIBRATED ORDINARY CHONDRITES

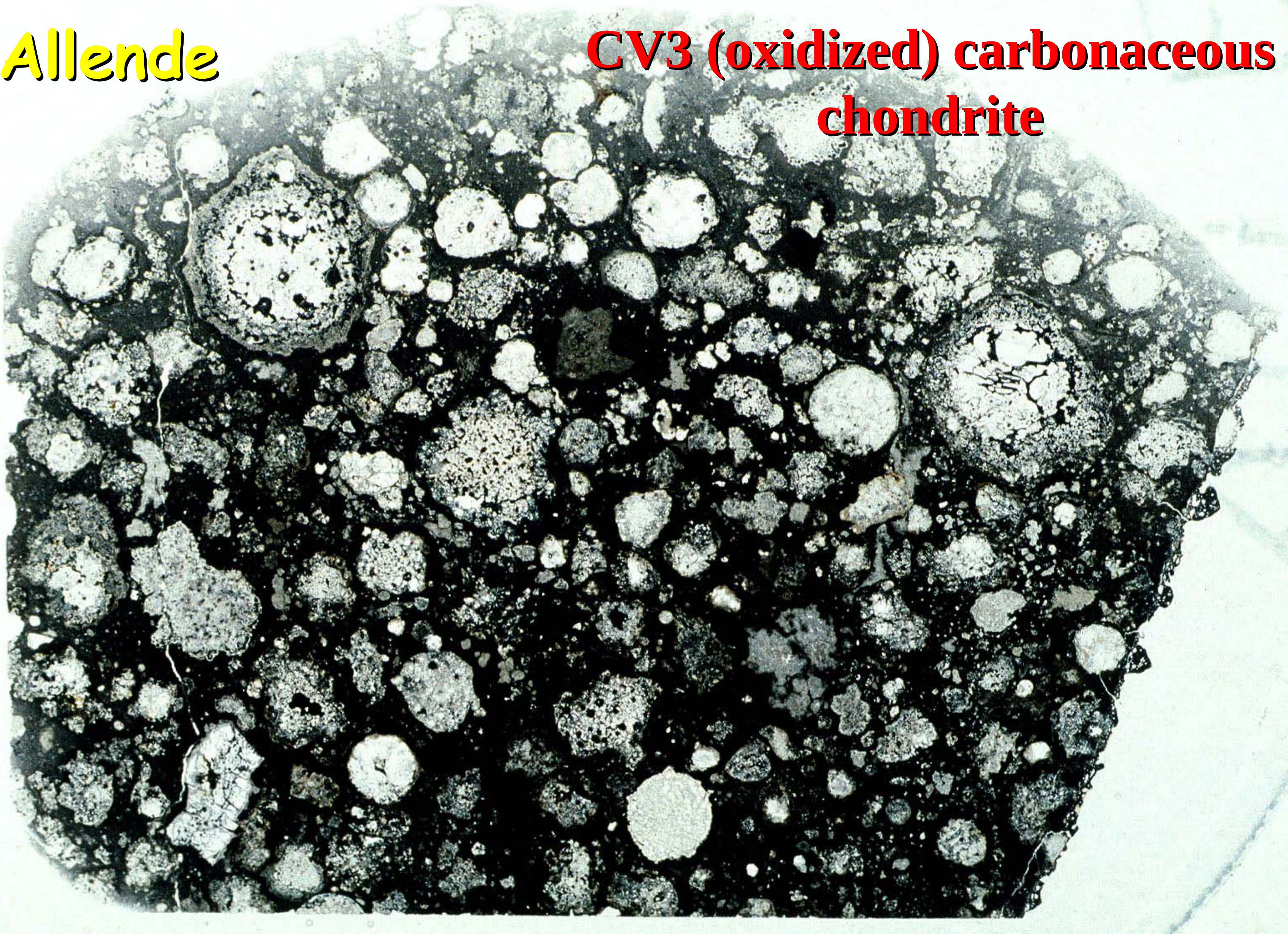


FLUID-ASSISTED METAMORPHISM

- Interaction of anhydrous nebular materials with fluids at relatively high temperature (<300^{0}C).
- May be coupled with metasomatism.
- Most common in oxidized (Bali-like and Allende-like) CV chondrites and CO chondrites.
- Evidence of fluid interaction is cryptic – i.e. products are anhydrous.
- Isotopic evidence of fluid-mineral interaction is not always present.
- Alteration textures are complex.
- Mineralogy of replacement phases is diverse.

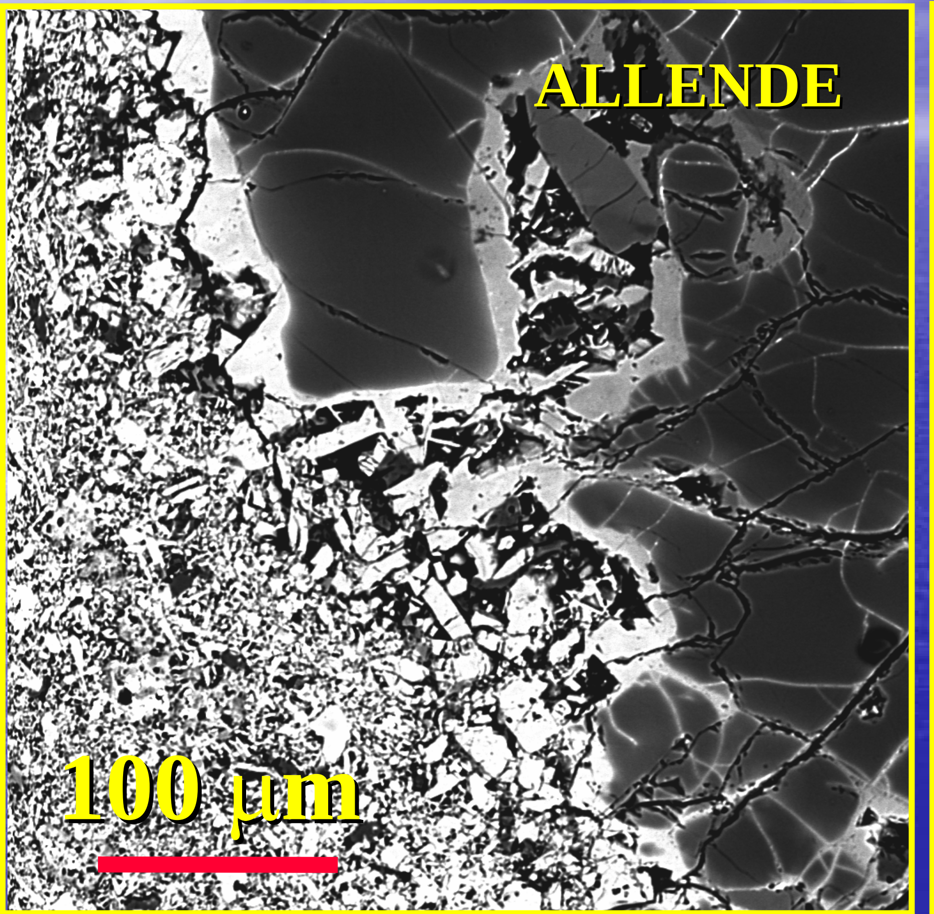
Allende

CV3 (oxidized) carbonaceous chondrite

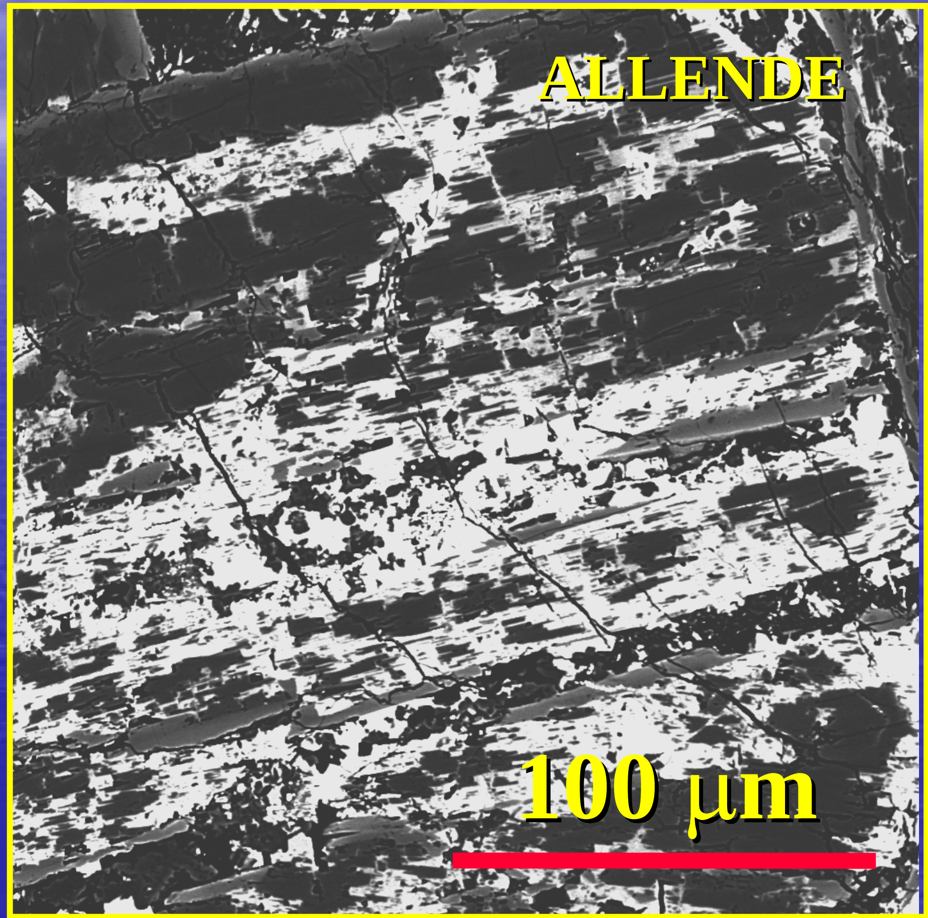


Field of view ~ 2.5 cms

Formation of fayalitic olivine

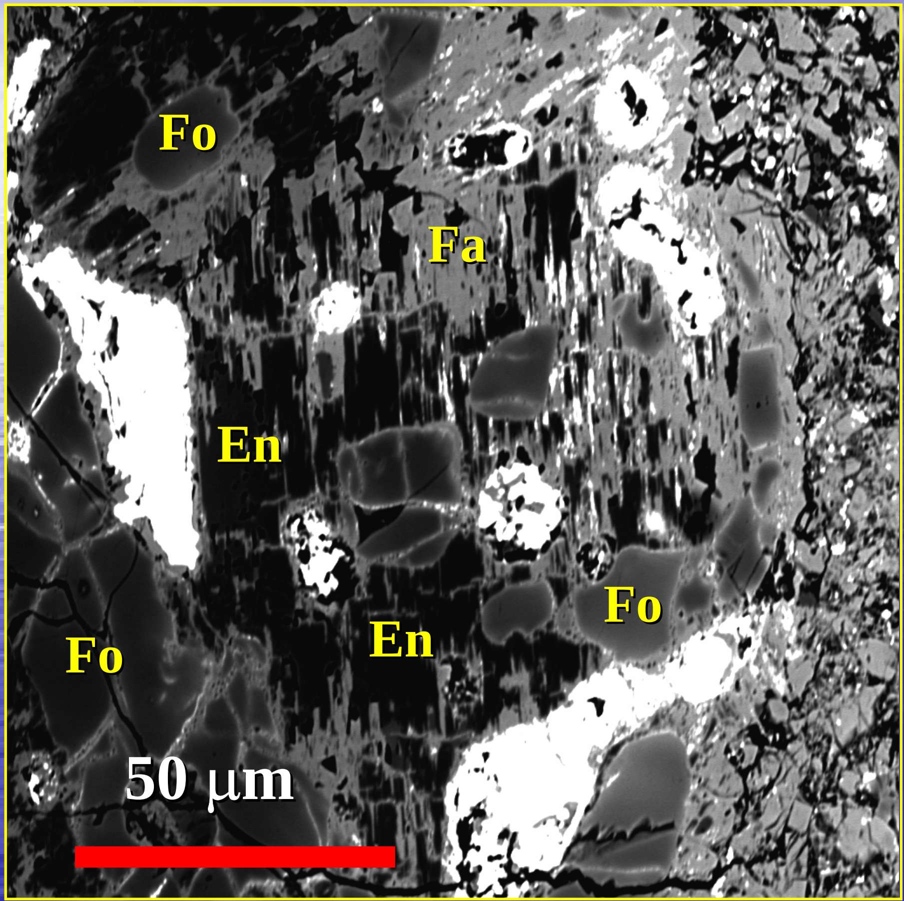


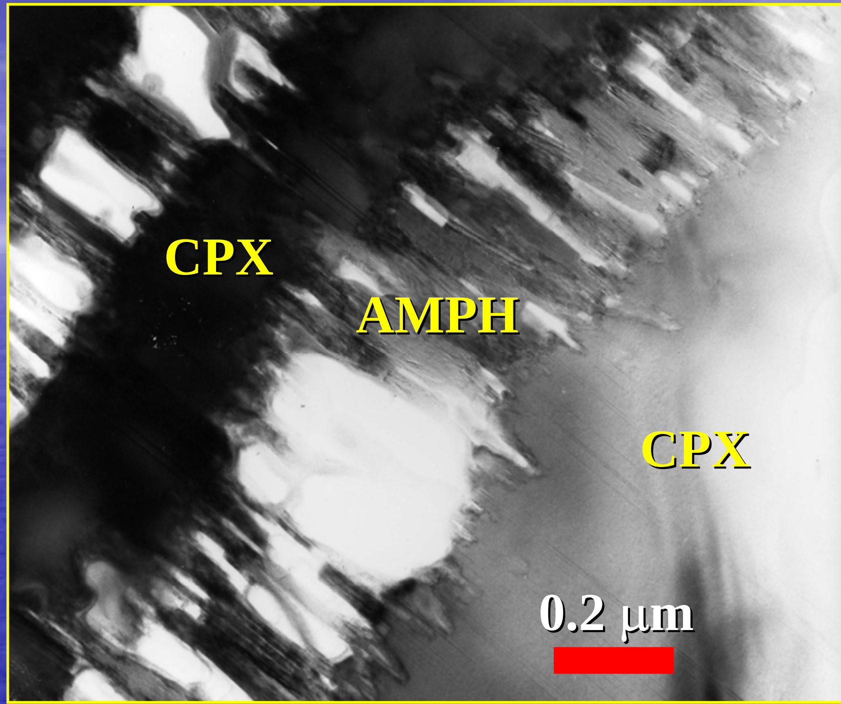
FAYALITIC OLIVINE OVERGROWTHS ON FORSTERITE

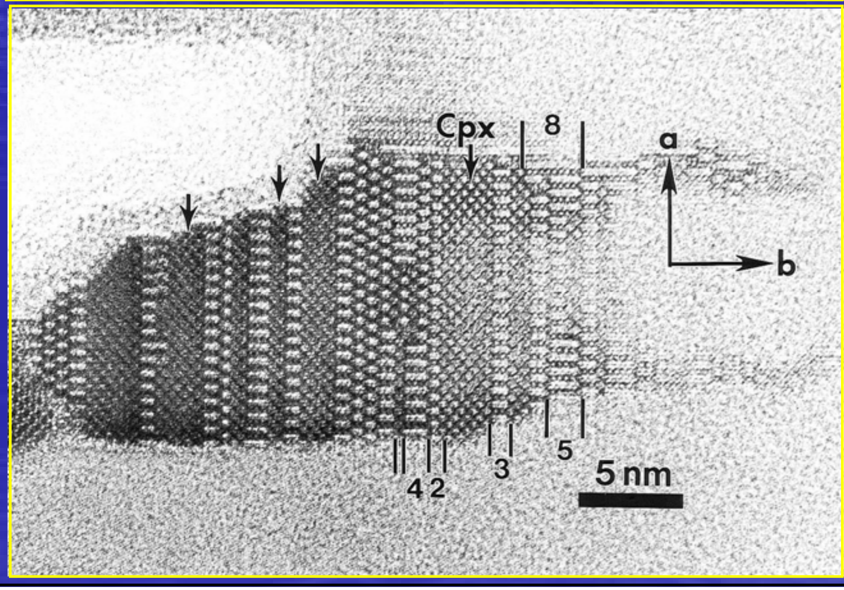


FAYALITIC OLIVINE REPLACING LOW-Ca PYROXENE

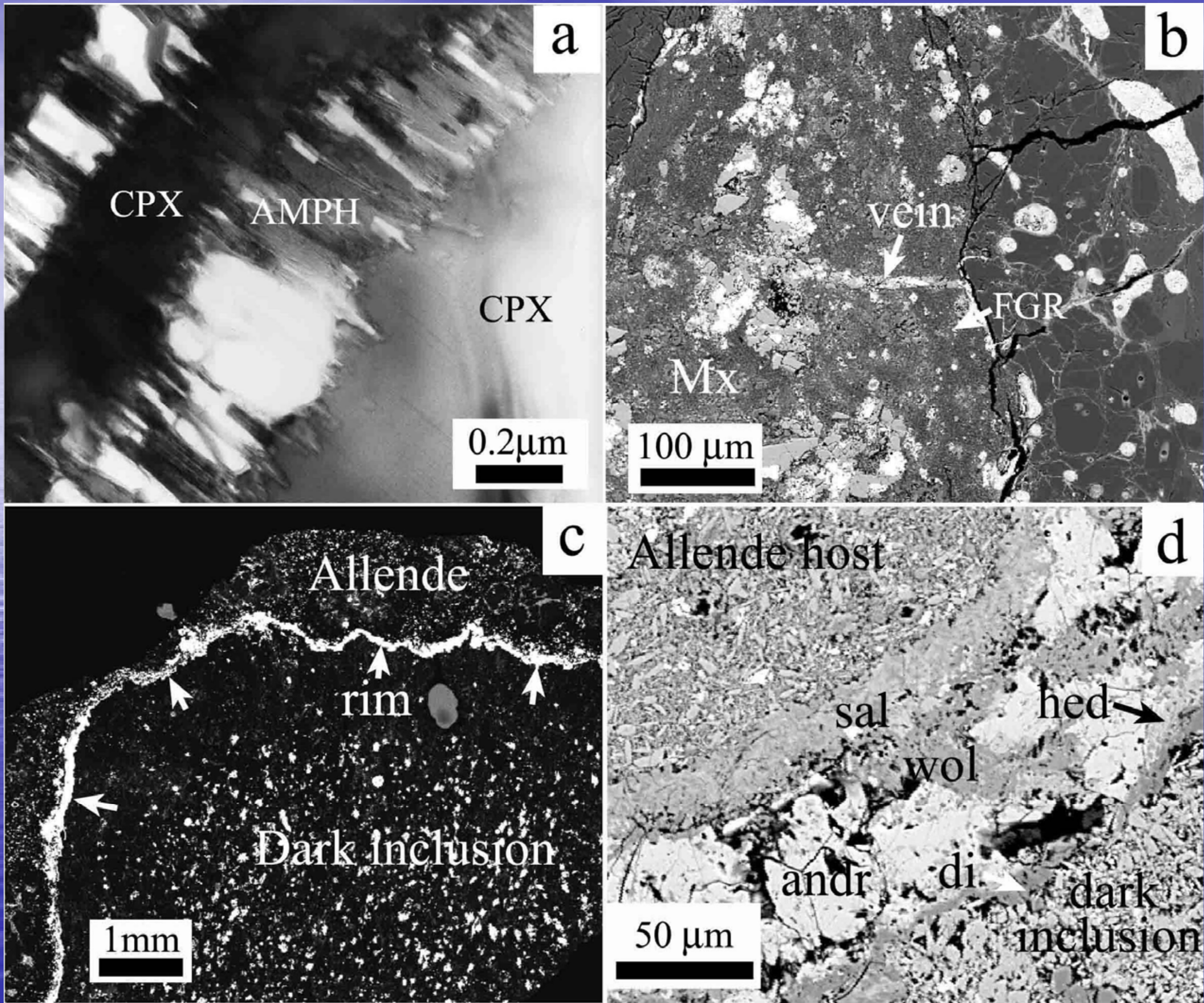
Replacement of enstatite by hydrous phases



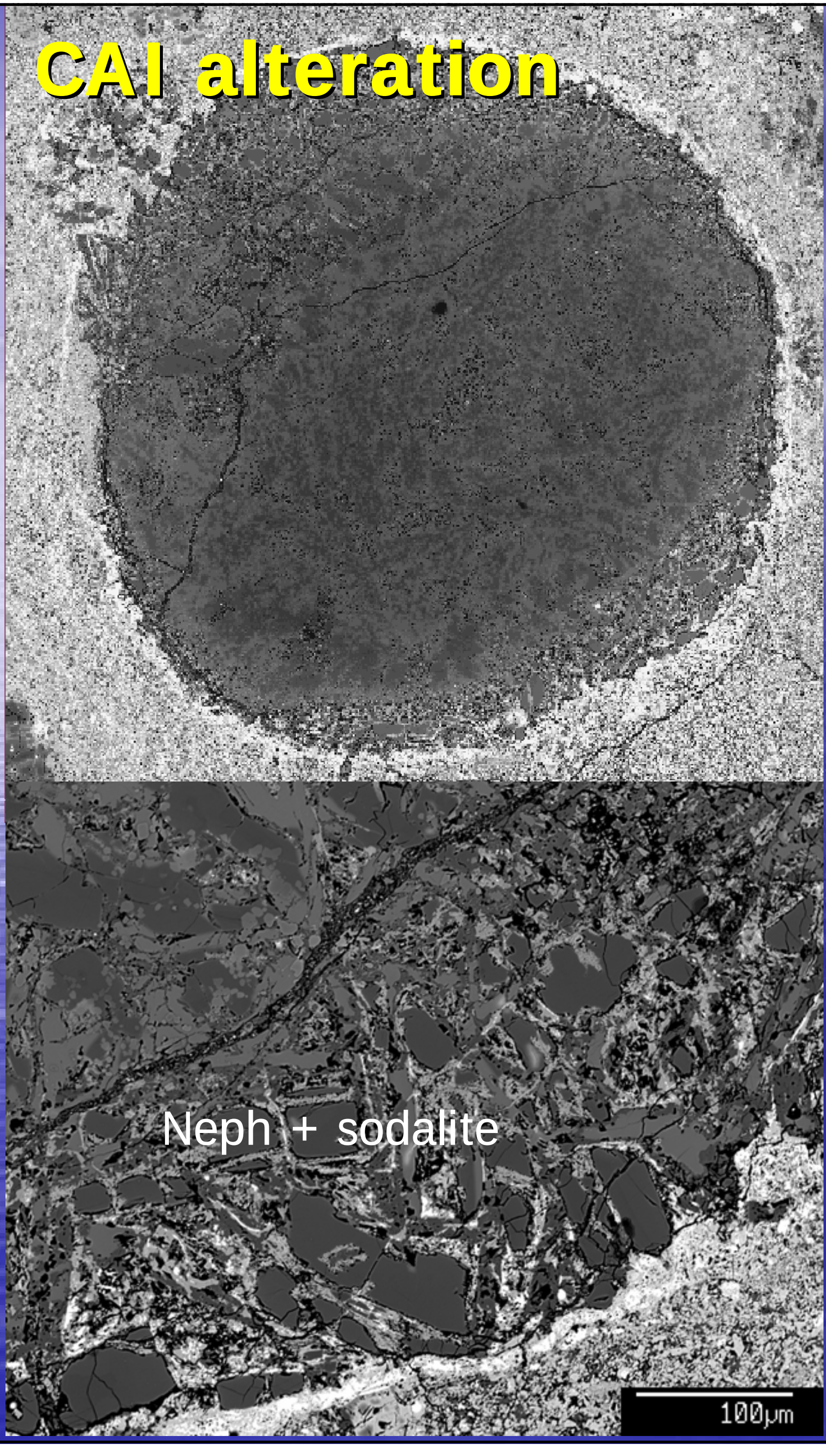


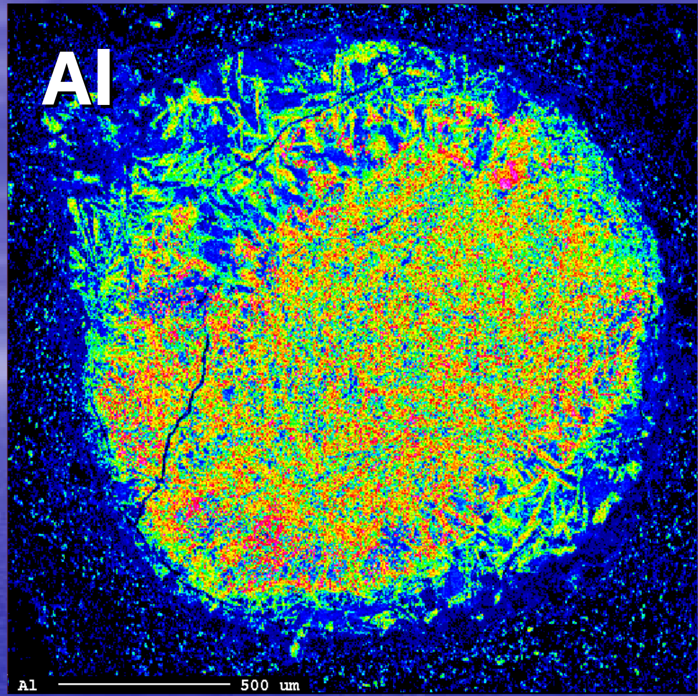


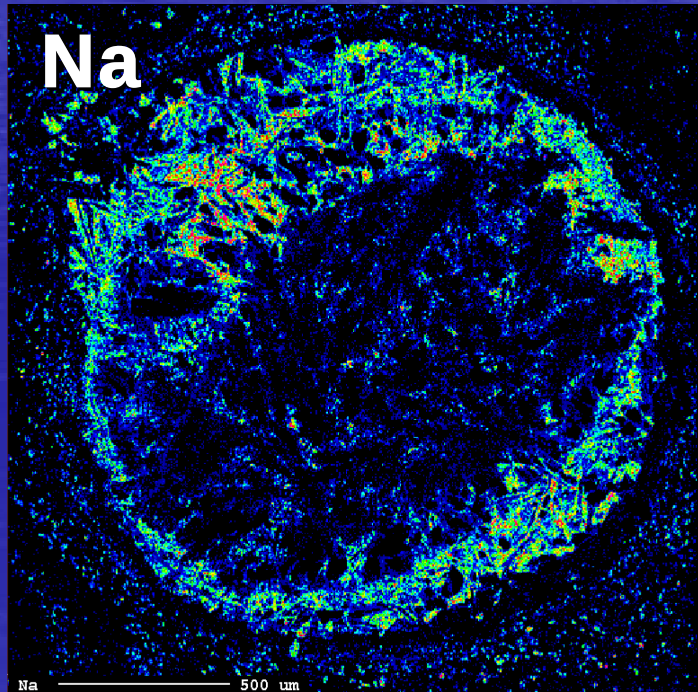
ALLENDE (oxidized CV3)


a
CPX
AMPH
CPX
0.2µm
b
vein
FGR
Mx
100 µm
c
Allende
rim
Dark inclusion
1mm
d
Allende host
sal
hed
wol
andr
di
dark inclusion
50 µm

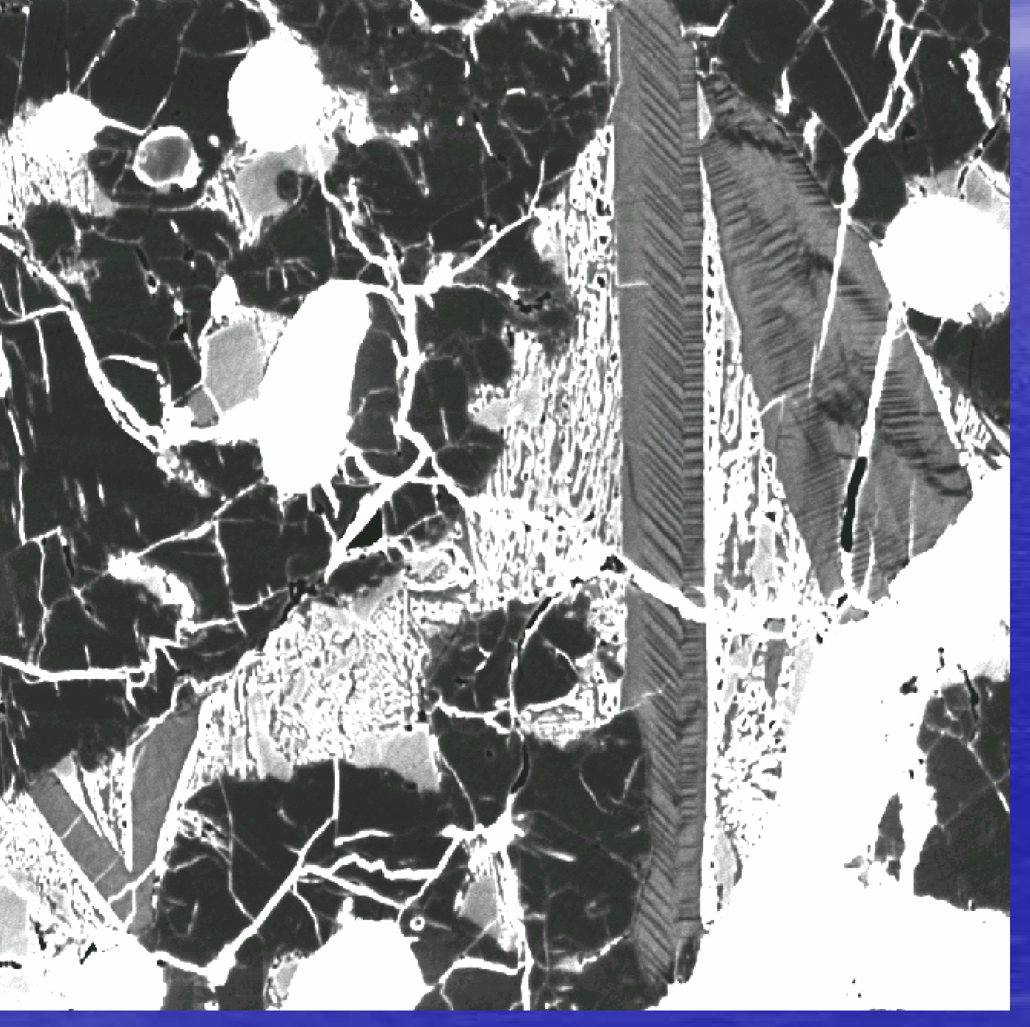
CAI alteration







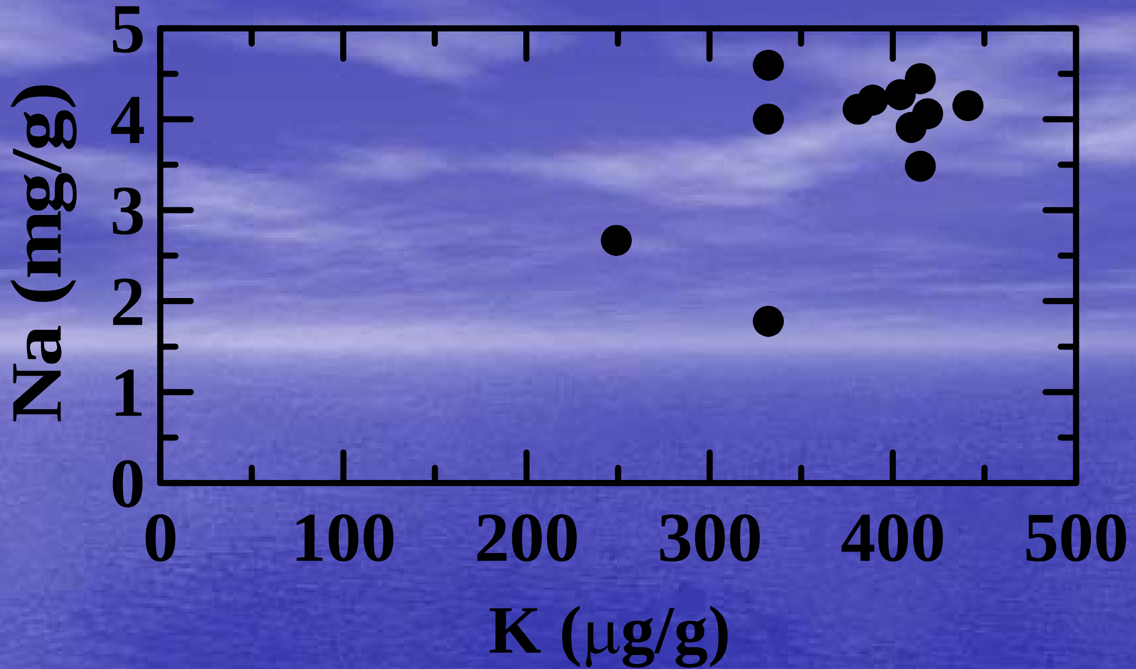
CO chondrites – plagioclase replacement by nepheline

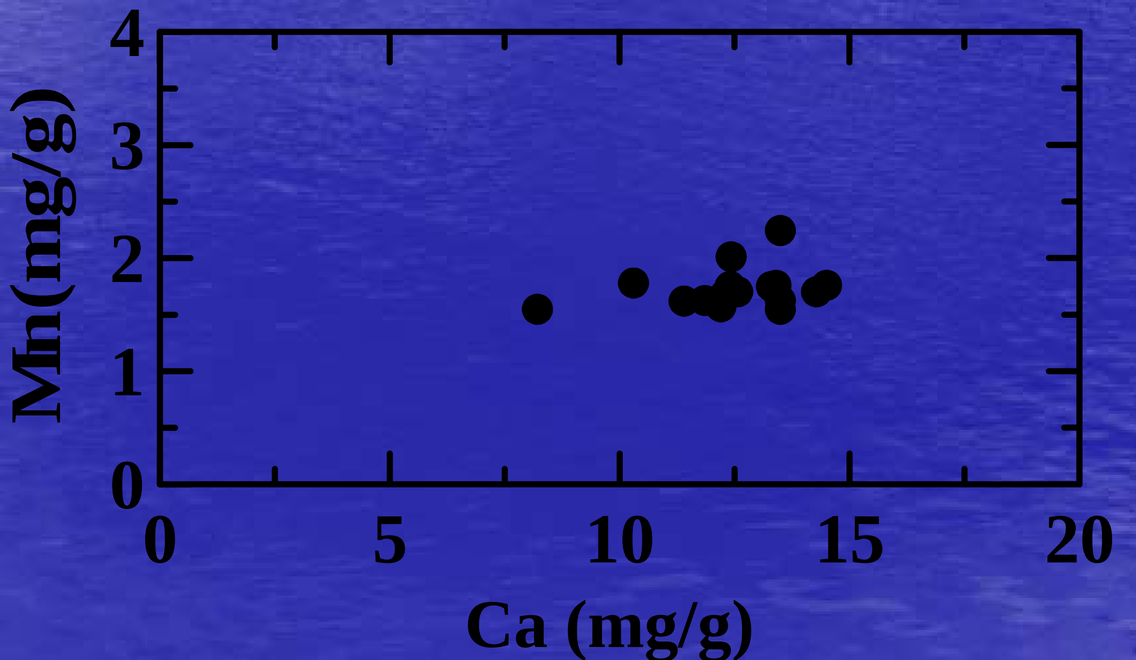


CHEMICAL AND ISOTOPIC EFFECTS OF AQUEOUS ALTERATION

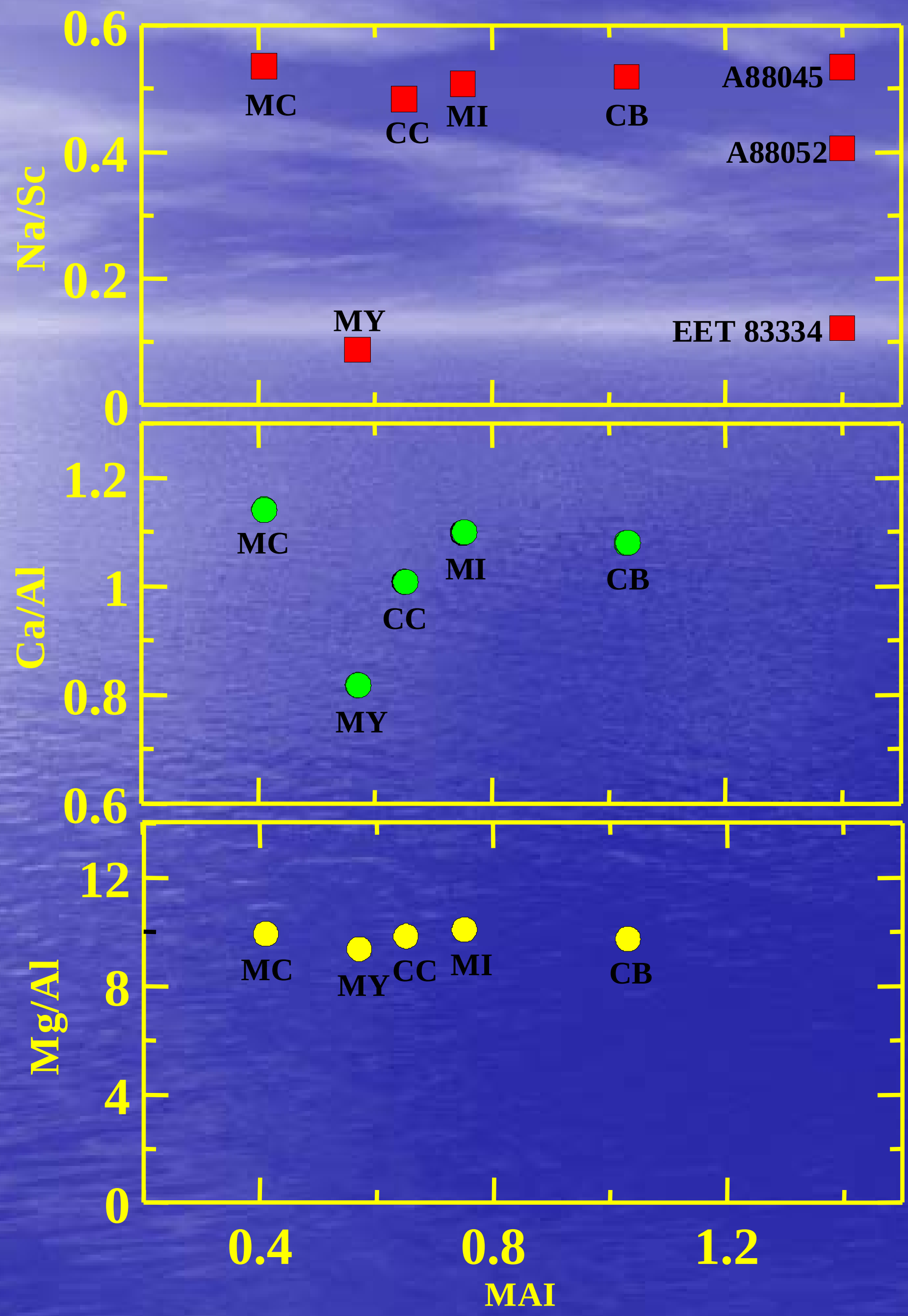
- Aqueous alteration in CI and CM chondrites is isochemical, but chemical exchange has occurred between different components.
- Metasomatism in CV chondrites has modified bulk chemistry (Reduced vs oxidized chondrites).
- Modification of oxygen isotopic composition by aqueous fluids (heavy isotope enrichment.

CM chondrite
bulk compositions

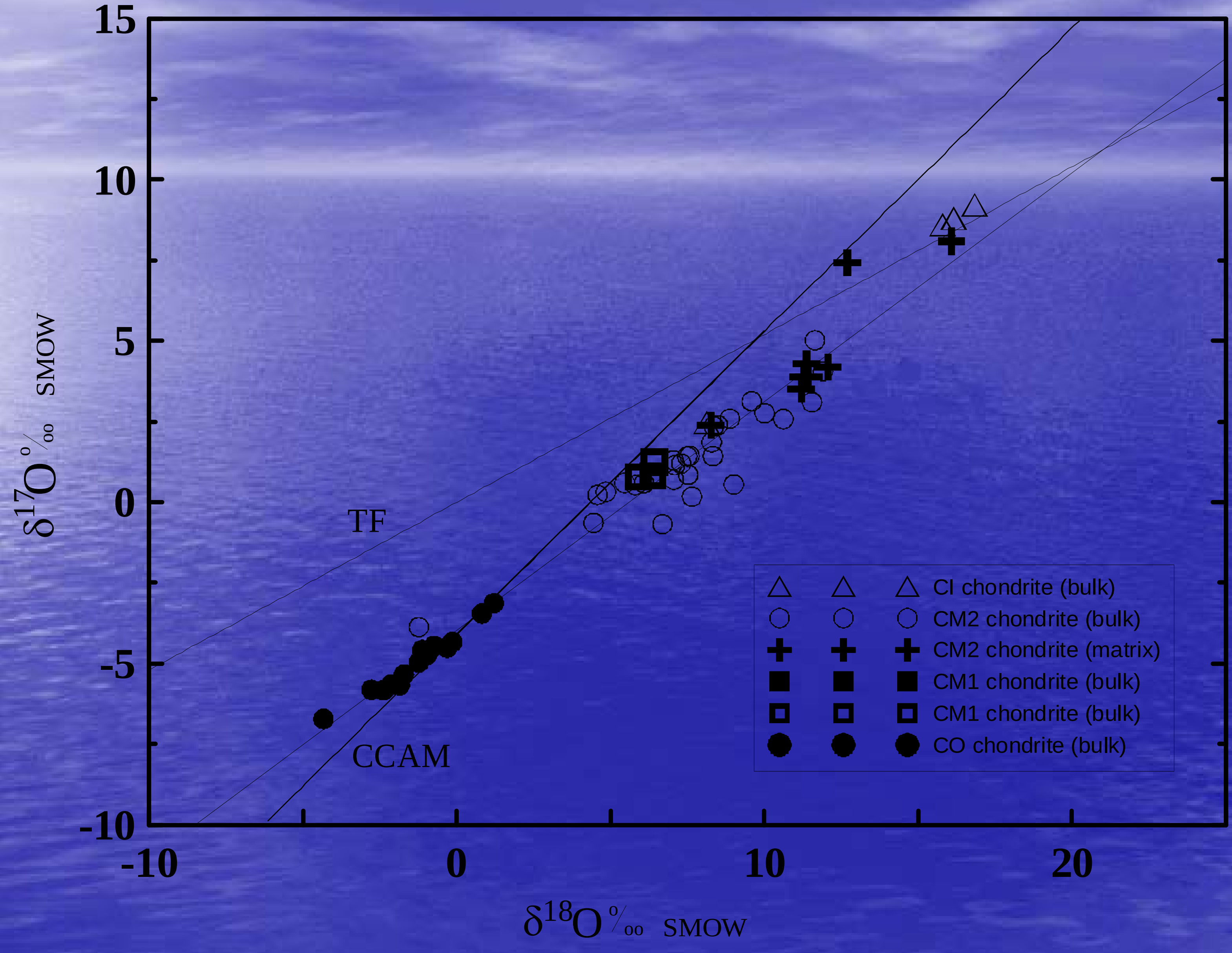




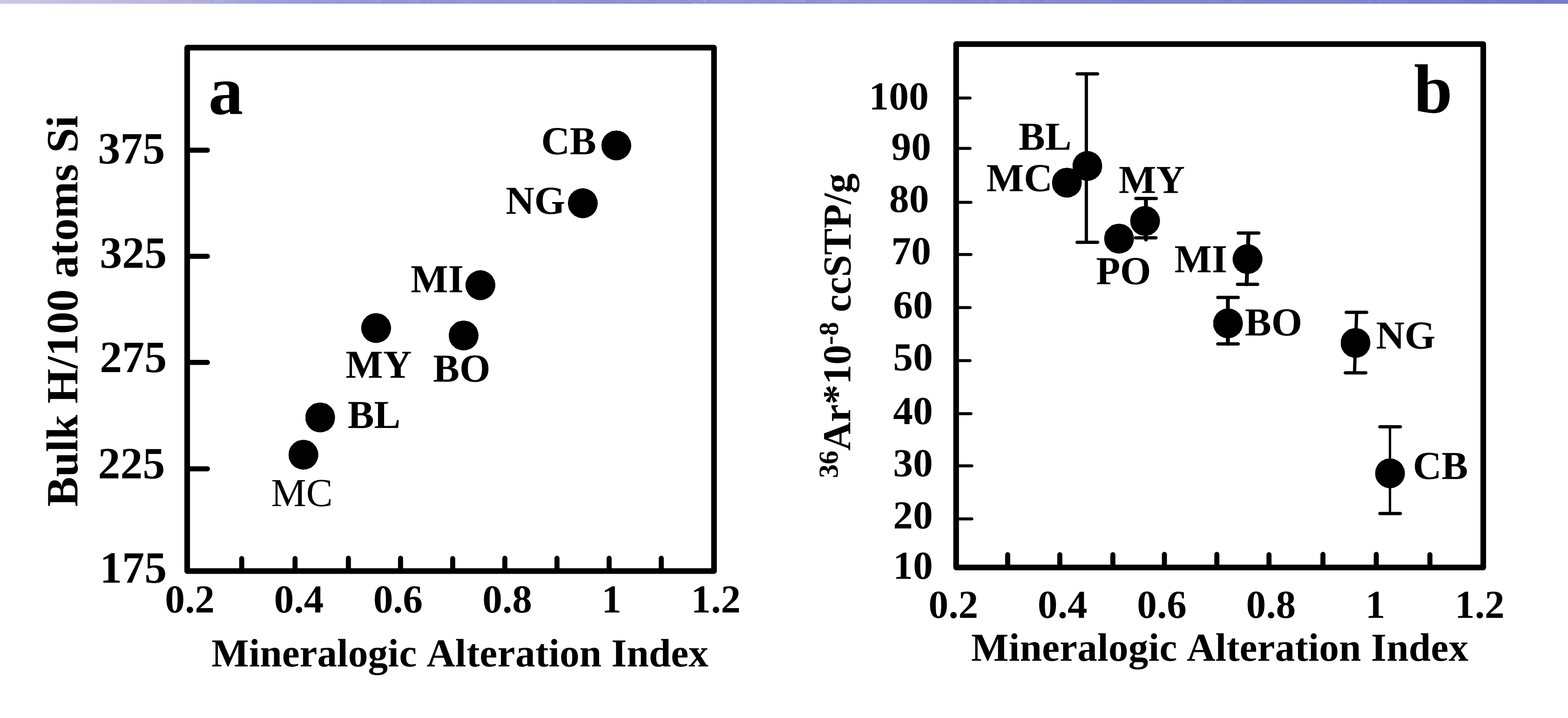
Bulk elemental ratios for CM chondrites vs Mineralogical Alteration Index



OXYGEN ISOTOPIC COMPOSITION OF CI, CM and CO CHONDRITES

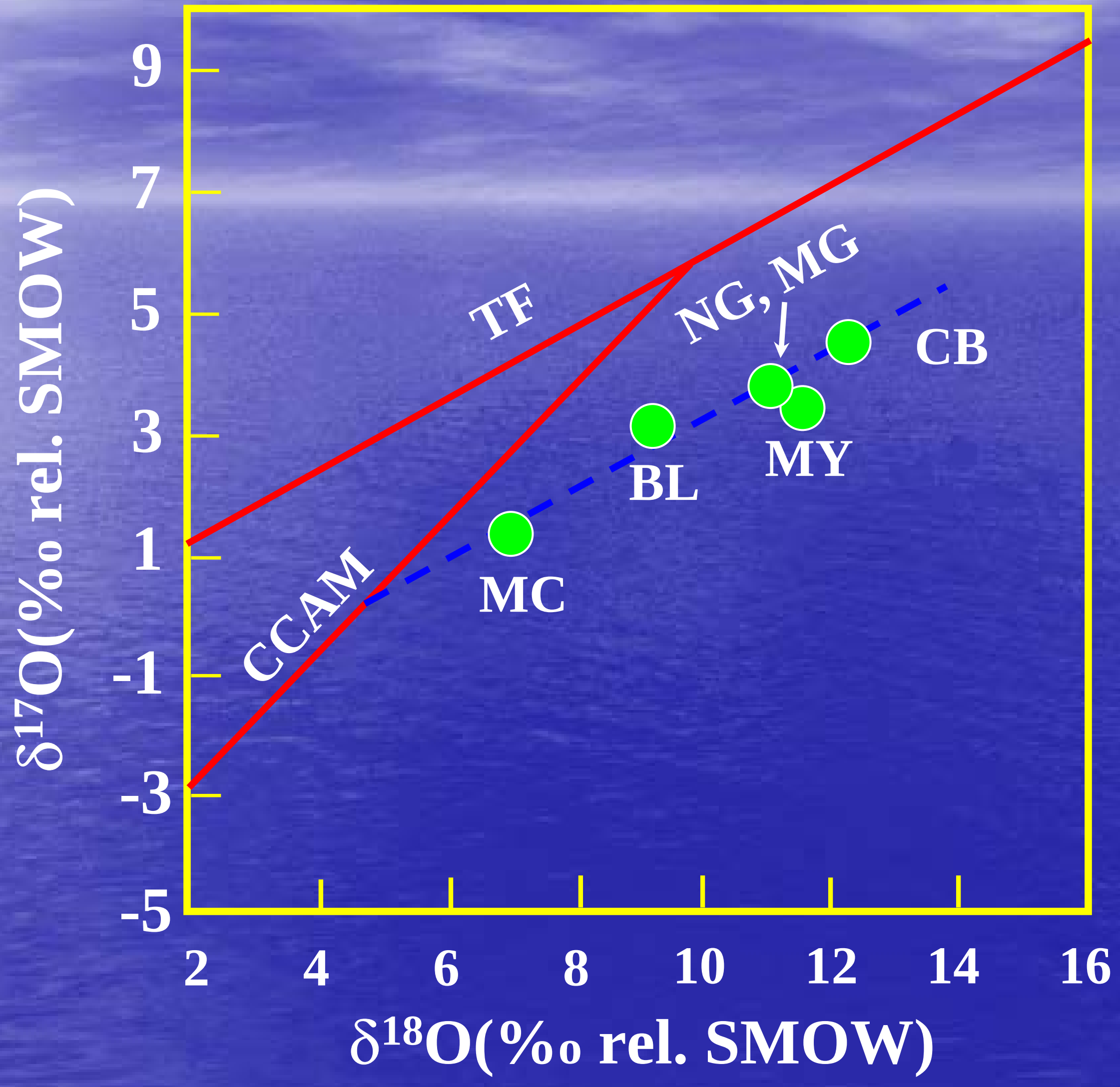


PROGRESSIVE ALTERATION OF CM CHONDRITES



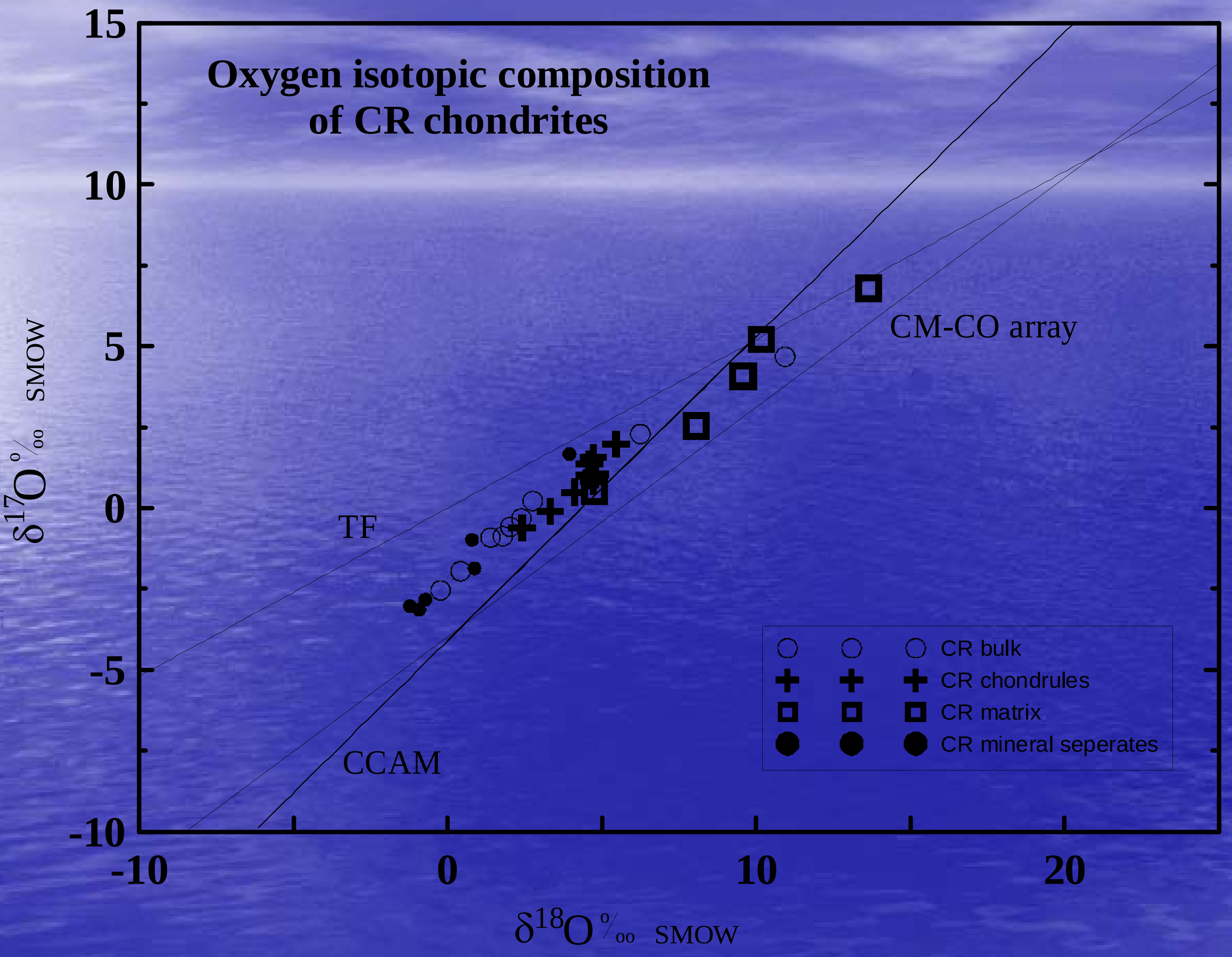
MAI (Browning et al. 1996) – measure of degree of alteration of CM chondrites

Oxygen isotopic composition of bulk CM2 chondrites

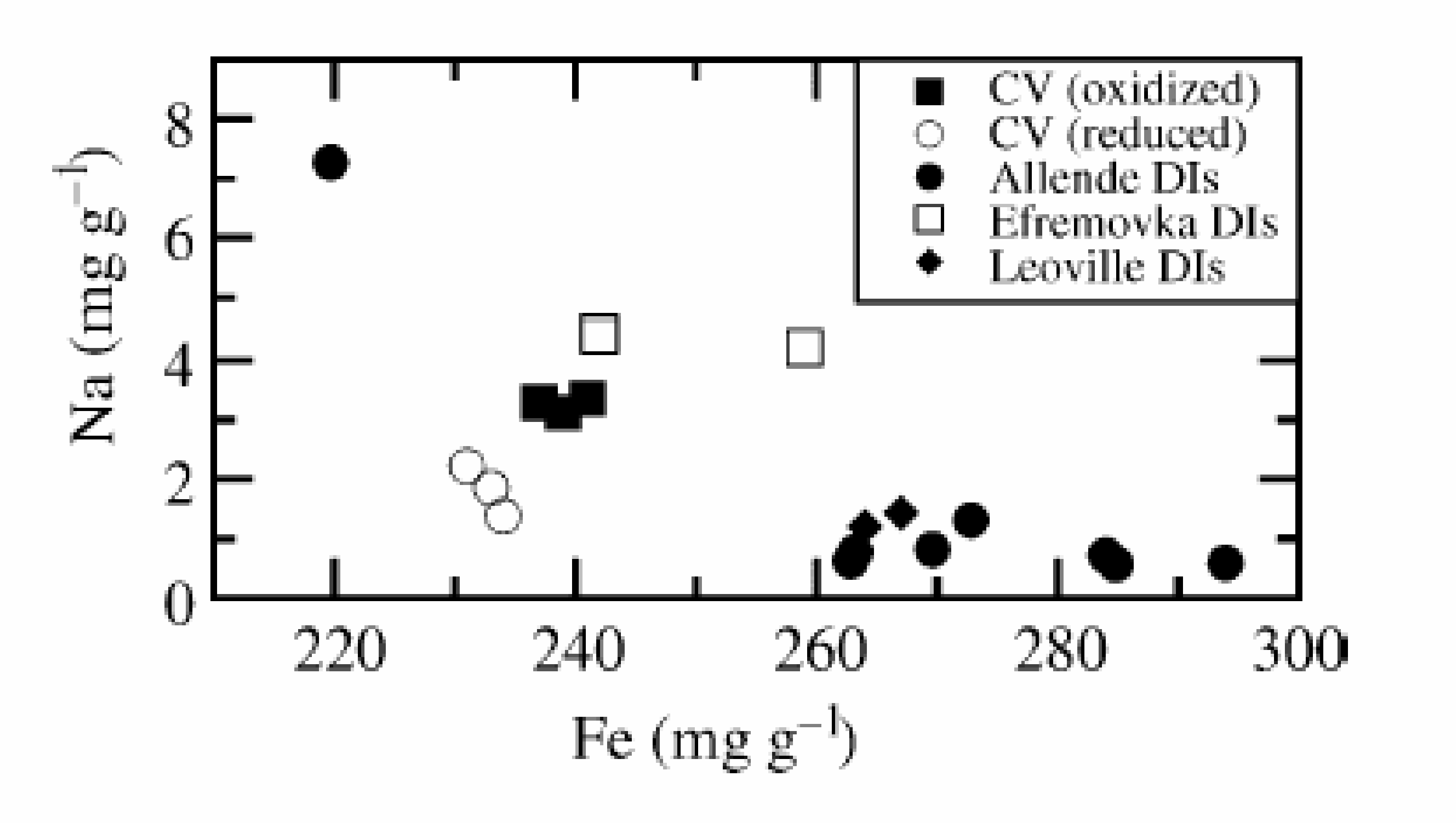


Enrichment in heavy isotopes generally correlates with MAI of Browning et al. (1996)

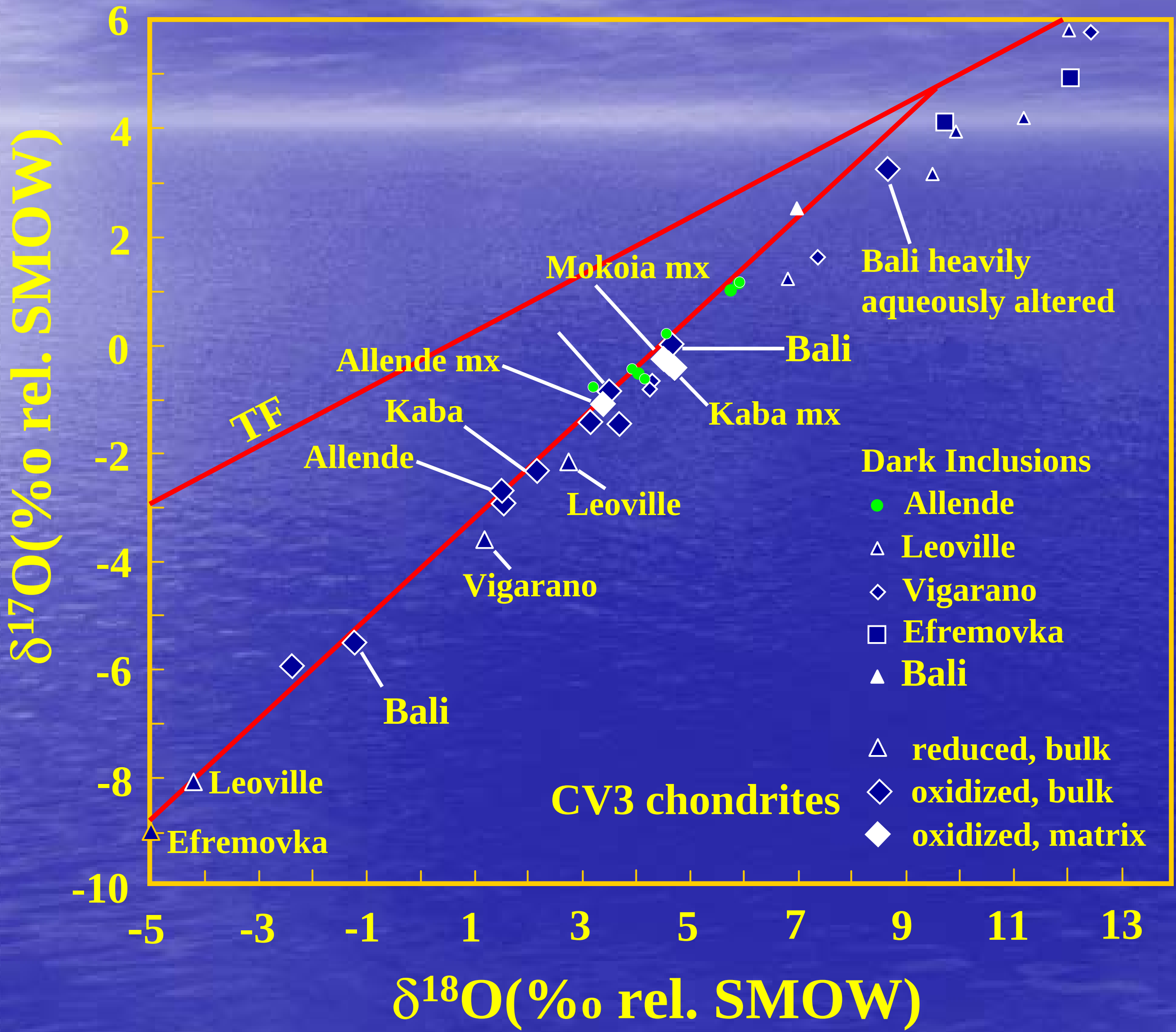
OXYGEN ISOTOPIC COMPOSITION OF CR CHONDRITES



BULK CHEMISTRY OF CV CHONDRITES



Oxygen isotopic compositions of CV chondrites



SCENARIOS FOR ALTERATION

- Nebular alteration
  - Gas-solid hydration reactions
  - Hydration caused by interaction of dust and ice during passage of shock waves in the nebula (Ciesla et al., 2003)
- Preaccretionary alteration
  - Alteration in small ephemeral protoplanetary bodies
- Parent body (in situ) alteration
- None are mutually exclusive
  - Challenge is discriminating between alteration in different environments.

GAS-SOLID NEBULAR REACTIONS

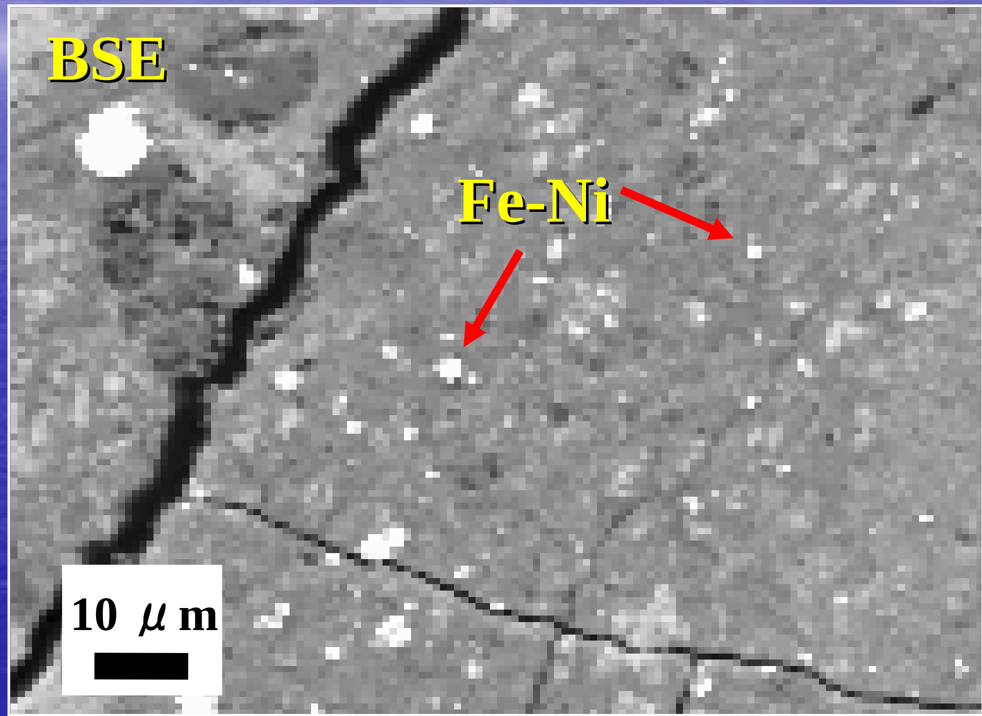
- Interaction of gaseous H_2O with nebular solids.
- May be kinetically inhibited (e.g. Fegley and Prinn) but may be enhanced by shock waves in solar nebula (Ciesla et al., 2003)
- Plausible, but:
  - Only causes hydration, no other chemical exchange occurs.
  - Doesn't readily explain local mass transport observed in altered chondrites.
- However, some hydrated phyllosilicates have been a source for water in chondritic parent bodies

PREACCRETIONARY ALTERATION MODEL

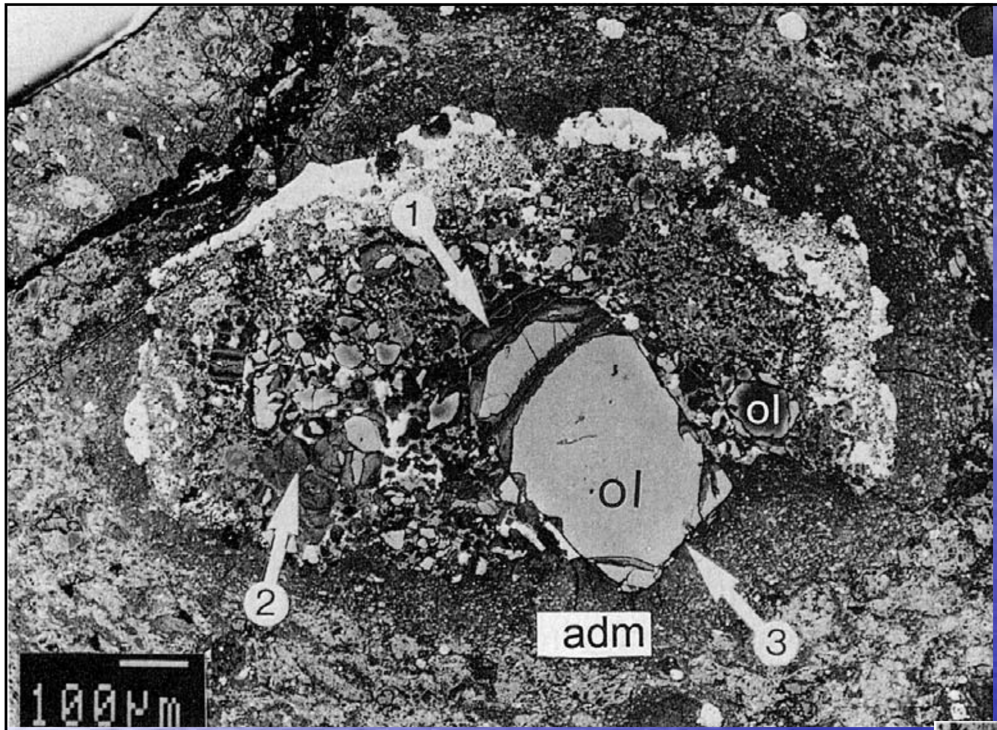
- Alteration of various chondritic components prior to final parent body accretion (e.g. Metzler et al. (1992); Bischoff, 1998).
- Altered chondrites represent mixture of materials altered to different degrees in different bodies.
- Alteration occurred in ephemeral protoplanetary bodies which were disrupted by impacts.
- Altered components mixed with unaltered nebular materials prior to accretion in asteroidal parent bodies.
- Proposed for some CM and CR chondrites

EVIDENCE FOR PREACCRETIONARY ALTERATION

- Juxtaposition of unaltered and altered phases in CM chondrites.
- Micron-sized metal grains embedded in hydrated fine-grained rims.
- Unaltered chondrule glass in contract with hydrated fine-grained rims.
- Unaltered fracture surfaces of olivine in chondrules in contact with hydrated fine-grained rims.

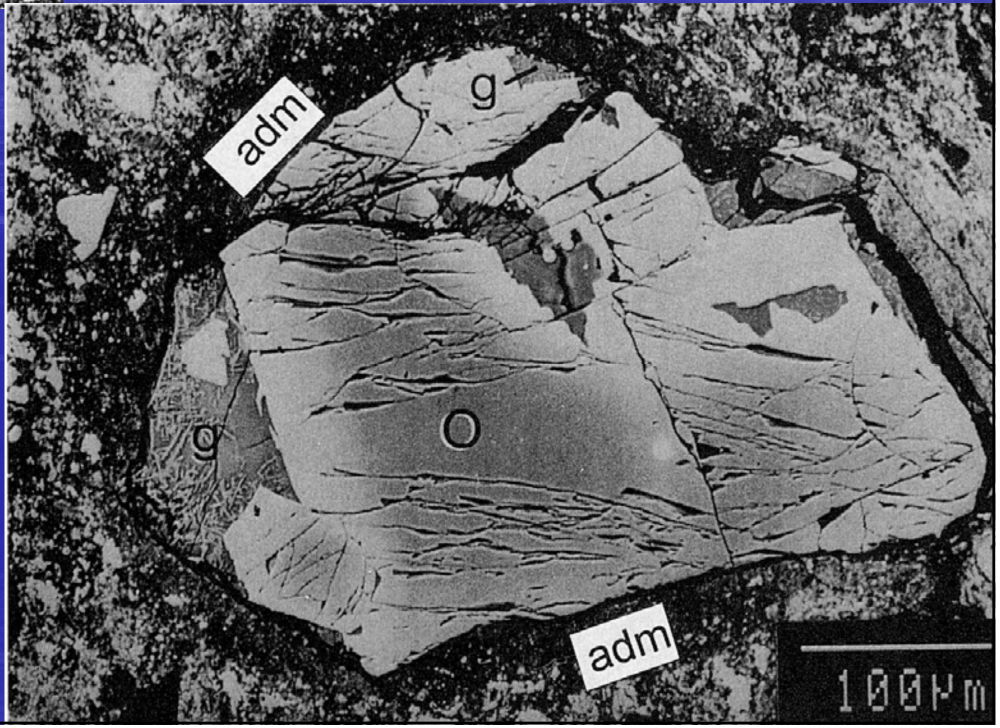


Y791198 CM2 – fine-grained rim



Lack of alteration of olivine on fracture surfaces in contact with hydrated fine-grained rims

Metzler et al. (1992) GCA



Apparently unaltered chondrule glass in contact with hydrated fine-grained rims

PREACCRETIONARY ALTERATION

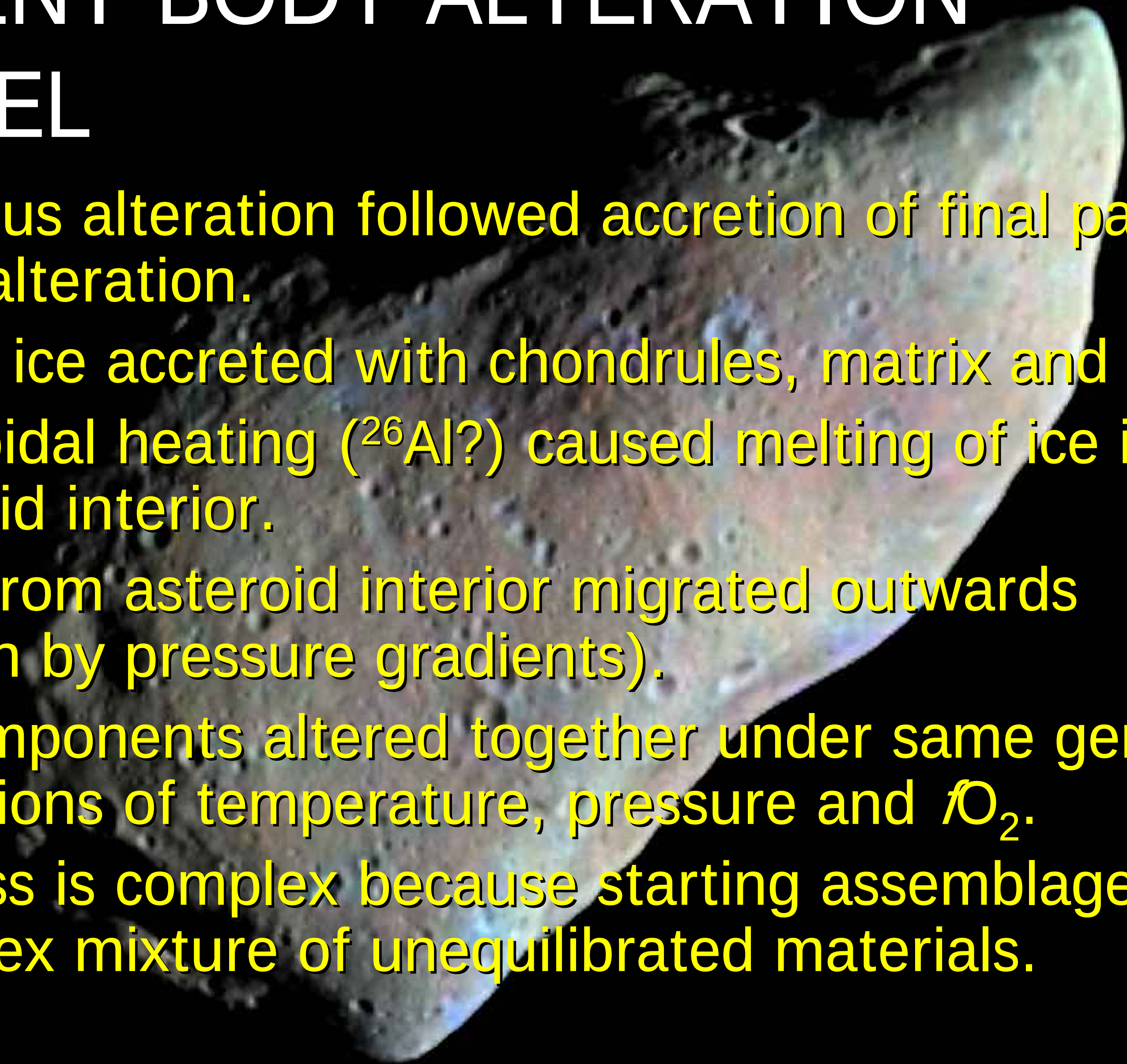
- Metal and chondrule glass are both very susceptible to aqueous alteration.
- Presence of unaltered metal and glass in contact with hydrous phases inconsistent with parent body alteration.
- Indicates mixing of altered and unaltered materials prior to accretion.
- No subsequent alteration (parent body) occurred after accretion.

PROBLEMS

- Evidence for preaccretionary alteration is present in meteorites which also have definitive evidence of parent body alteration.
- Other geochemical arguments can be put forward to explain observations.
- Some lines of evidence (e.g. unaltered chondrule glass) are very rare and poorly documented (i.e. no probe data for glass).

PARENT BODY ALTERATION MODEL

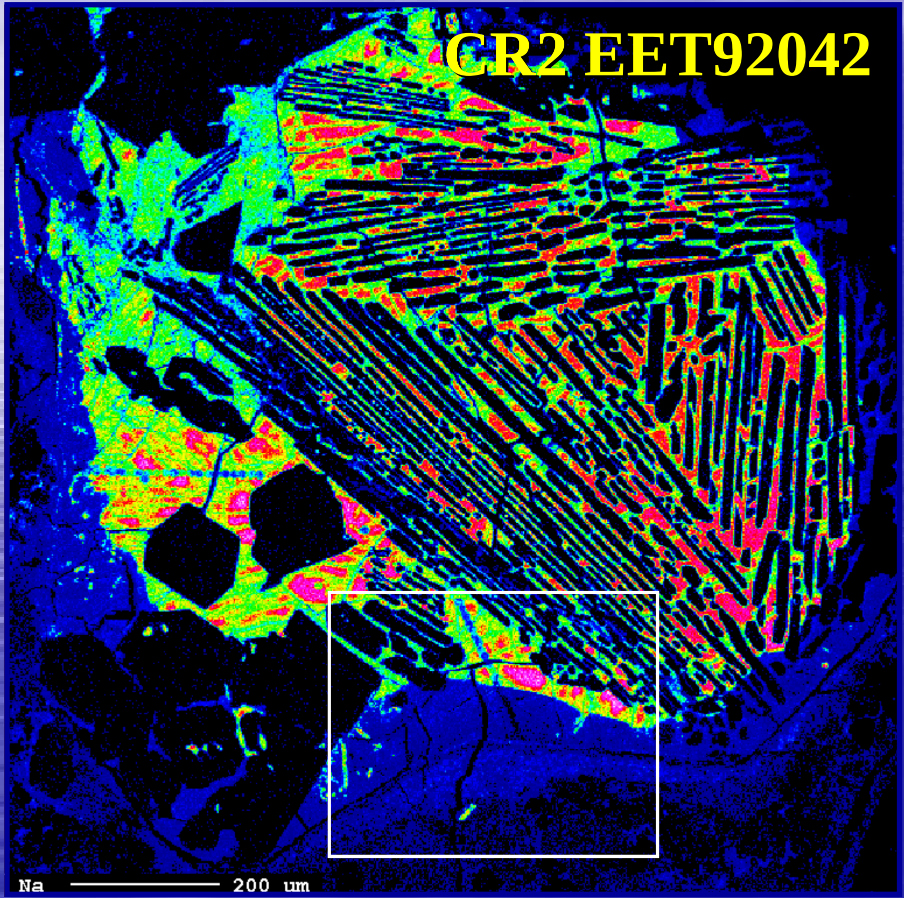
- Aqueous alteration followed accretion of final parent body alteration.
- Water ice accreted with chondrules, matrix and CAIs.
- Asteroidal heating (^{26}Al?) caused melting of ice in asteroid interior.
- Fluid from asteroid interior migrated outwards (driven by pressure gradients).
- All components altered together under same general conditions of temperature, pressure and fO_2.
- Process is complex because starting assemblage is complex mixture of unequilibrated materials.



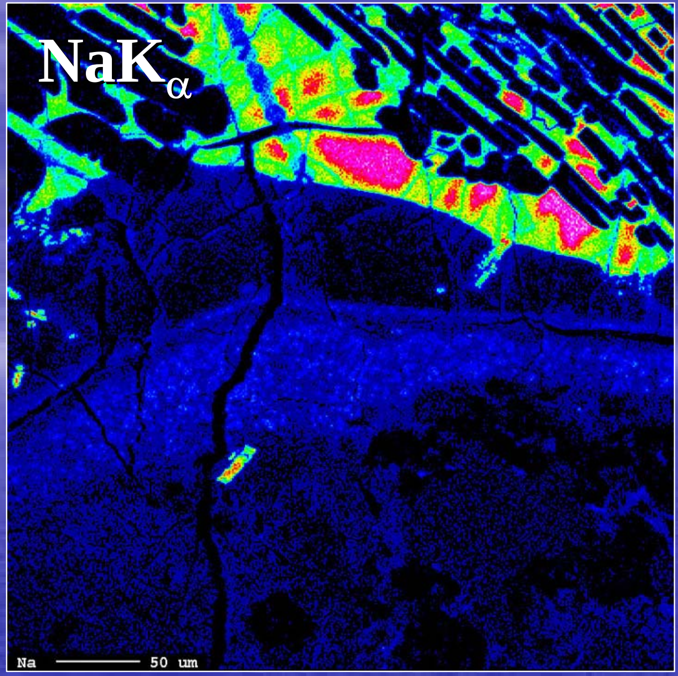
Evidence for asteroidal alteration

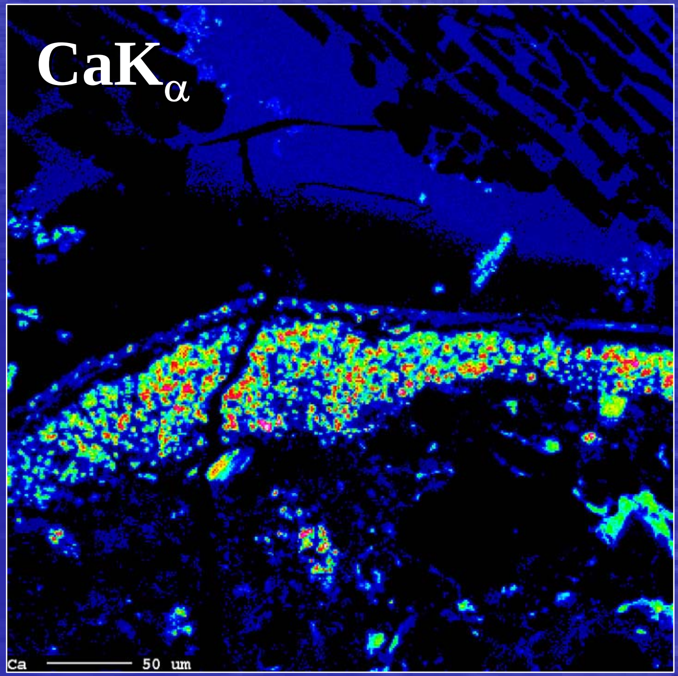
- Multiple lines of evidence
  - – Elemental exchange between chondrules and matrix.
  - – Presence of Fe-rich aureoles around metal grains
  - – Consistent degrees of alteration of different components in unbrecciated chondrites.
  - – Presence of alteration veins in CM chondrites (rare).
  - – Note: veins of sulfates in CI chondrites are probably terrestrial in origin.

Elemental exchange between chondrules and matrix in CR chondrites

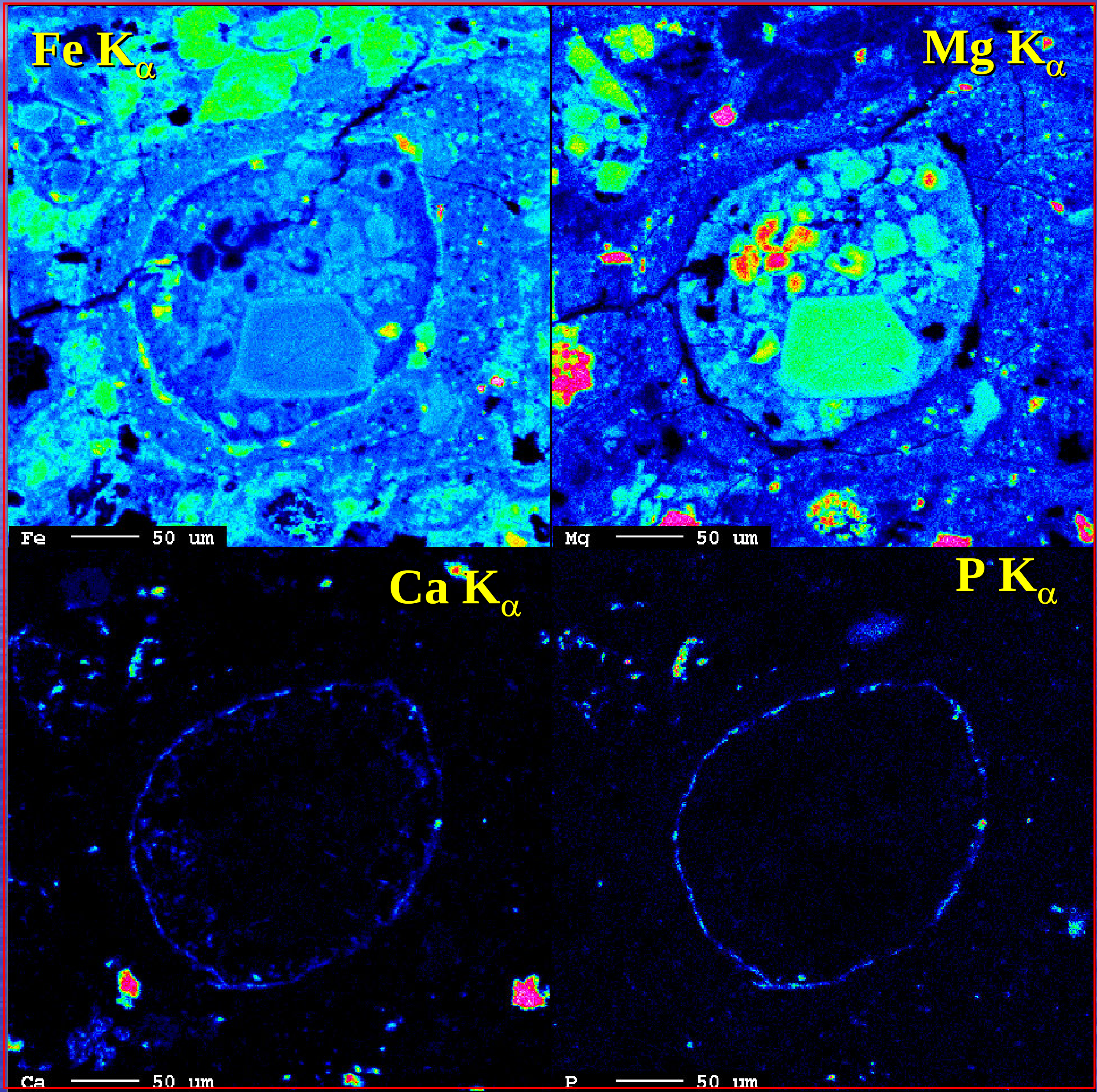


Sodium X-ray map

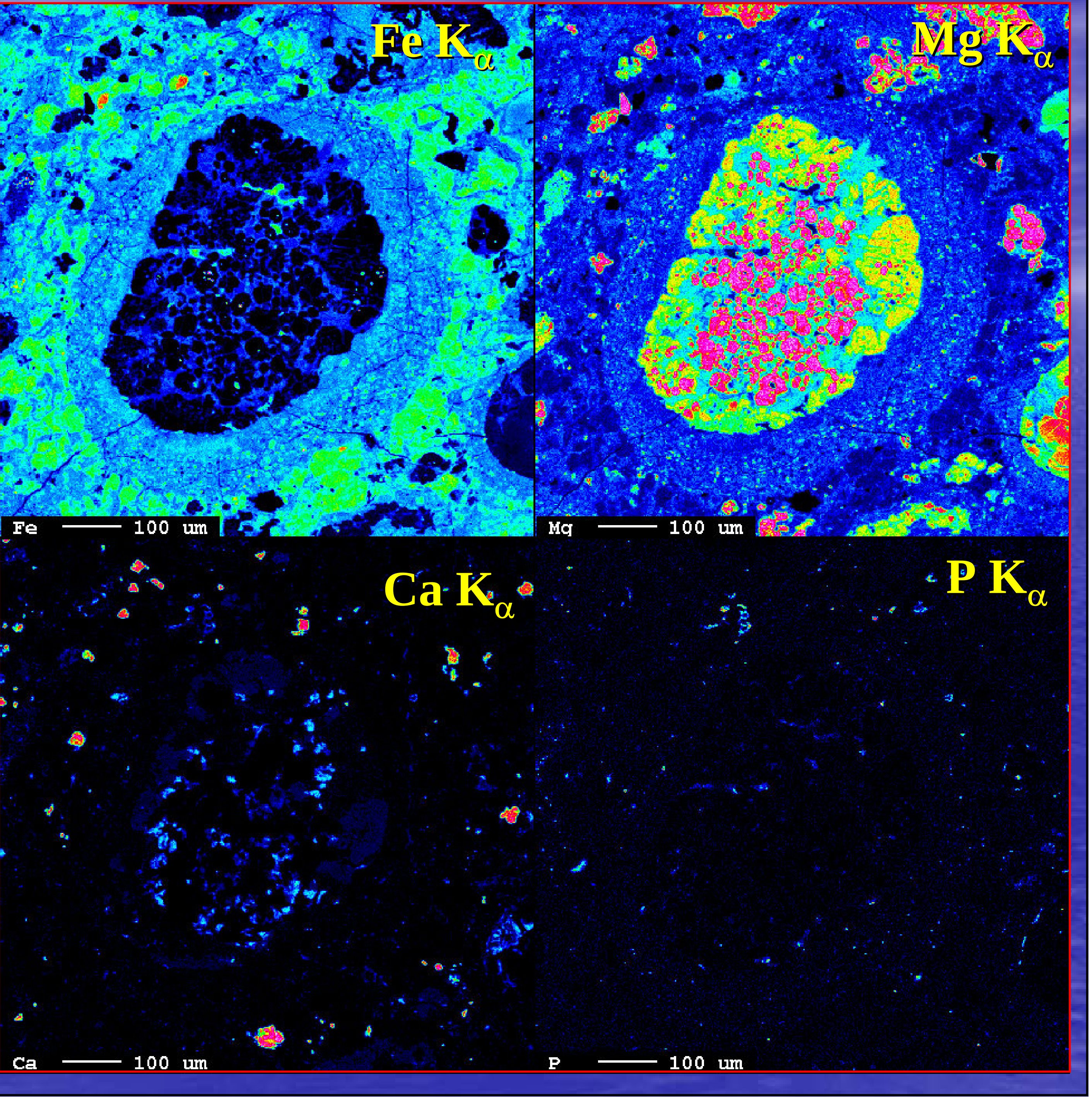


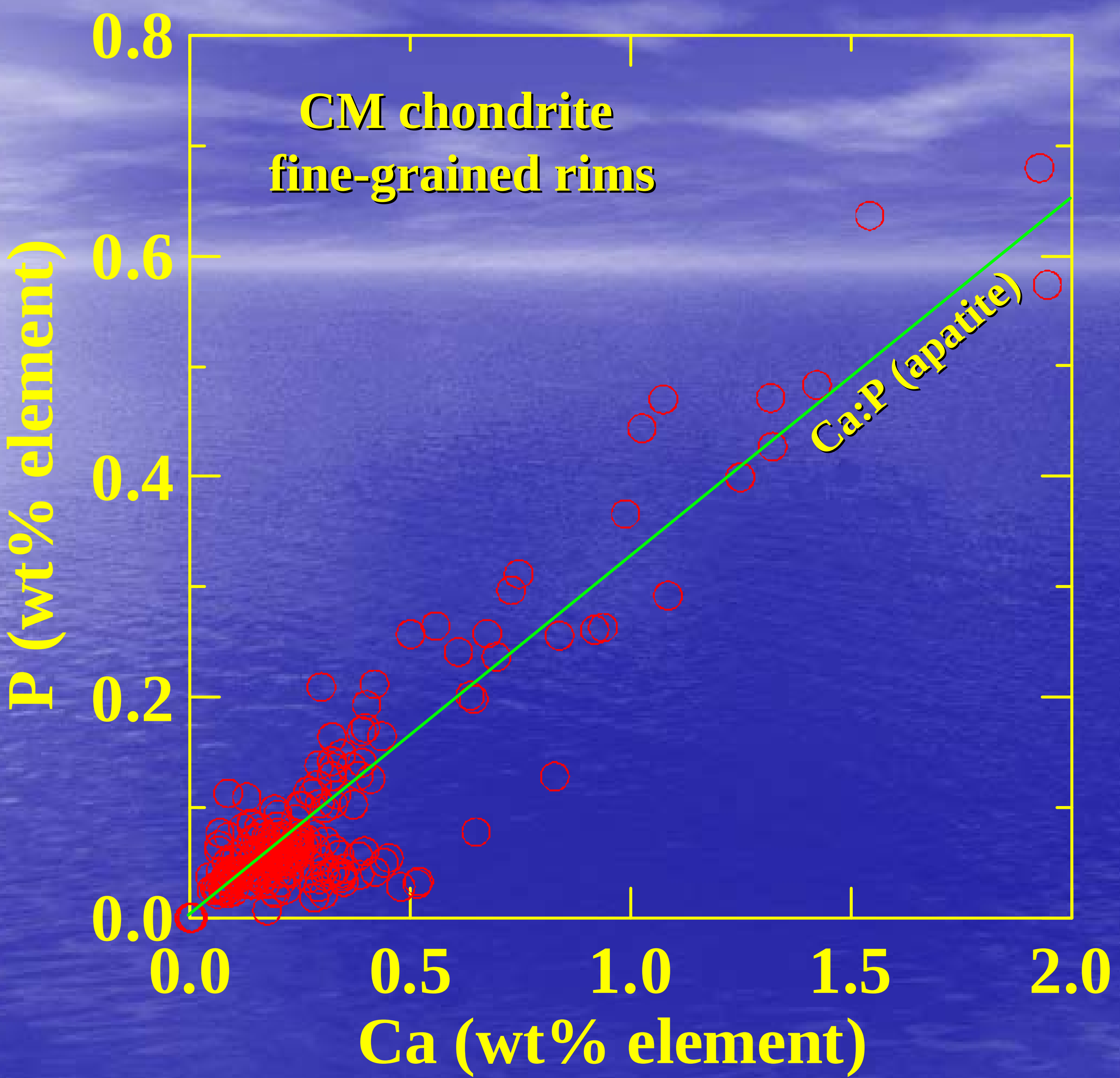


CM chondrites Calcium and P removal from chondrule glass in type IIA chondrules



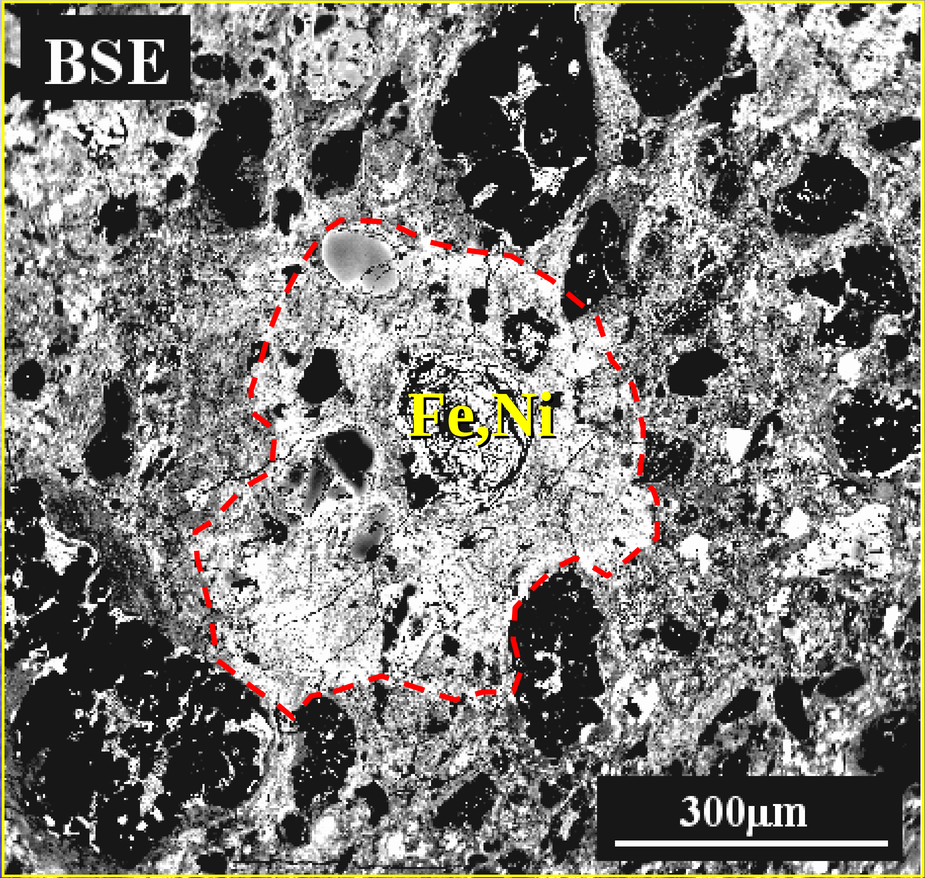
Y-791198
Type I
chondrule

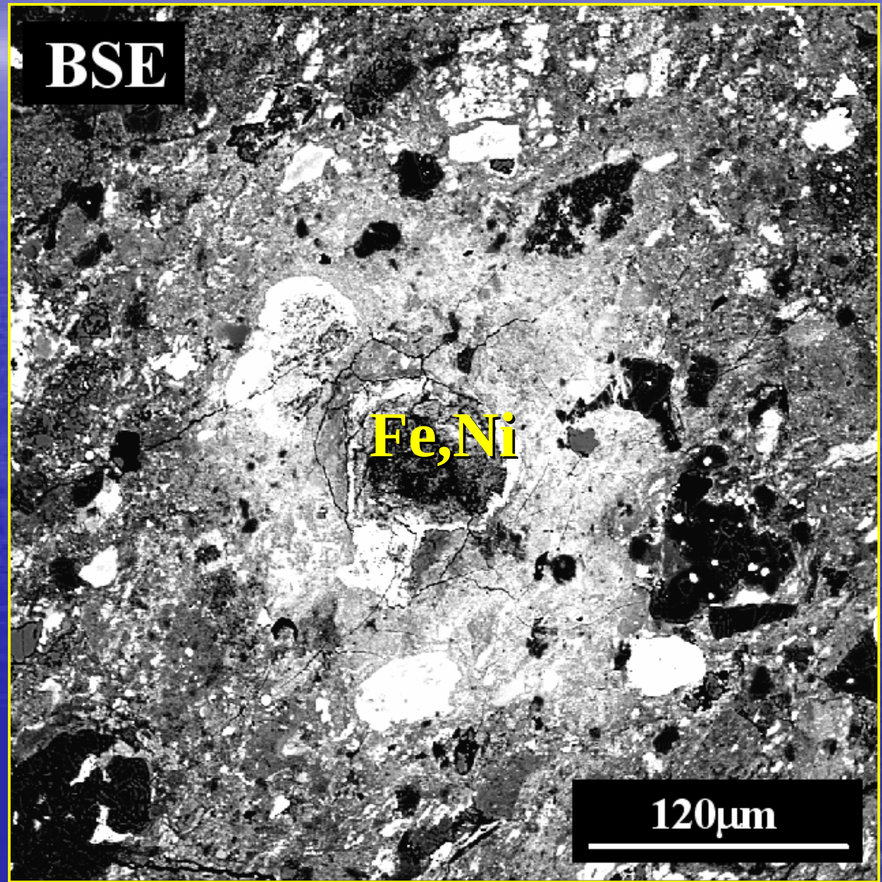




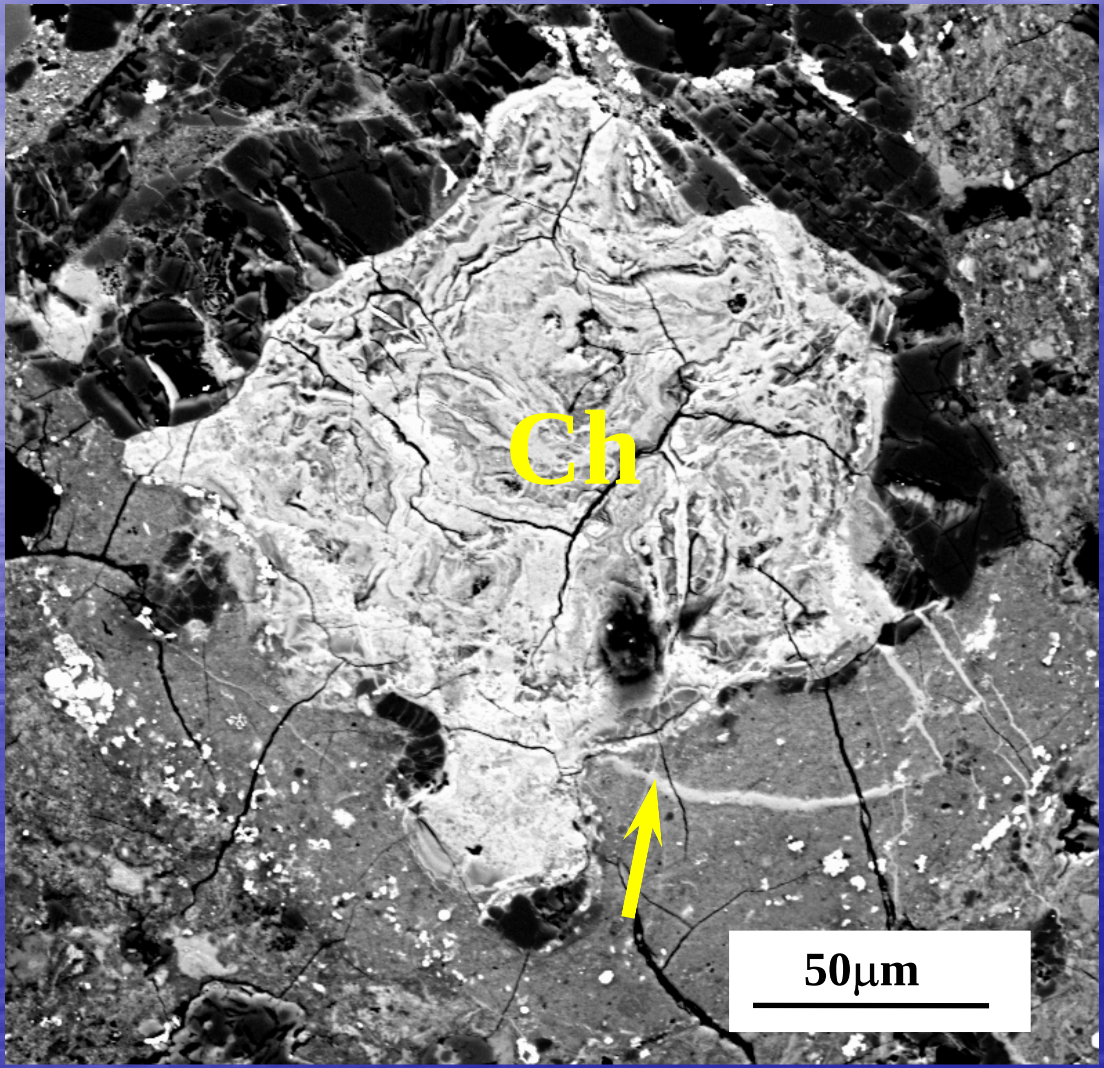
CM chondrite
fine-grained rims
Ca:P (apatite)
P (wt% element)
Ca (wt% element)
0.0
0.2
0.4
0.6
0.8
0.0
0.5
1.0
1.5
2.0

Fe-RICH AUREOLES IN CM CHONDRITES



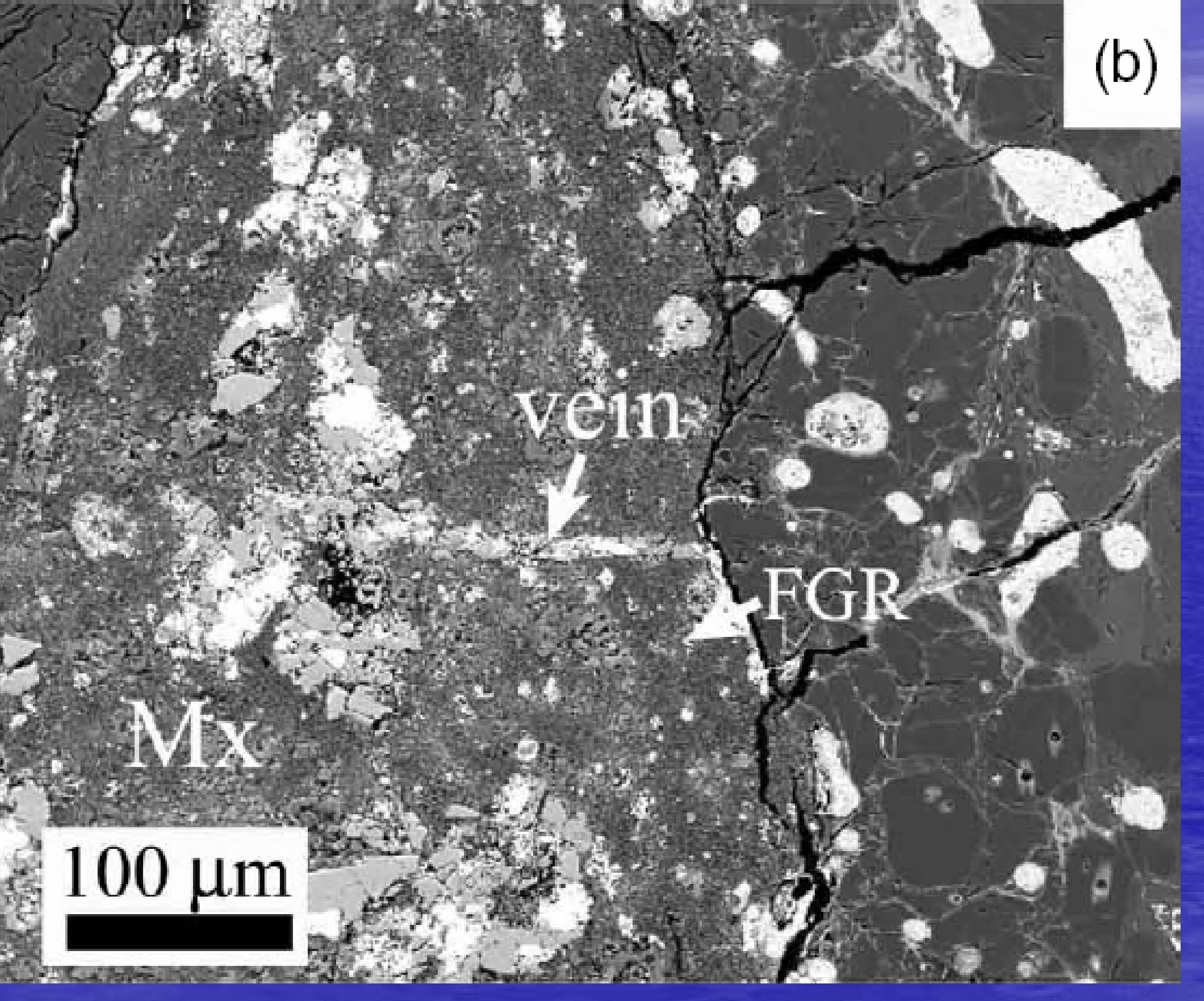


CROSS CUTTING VEINS



Fe-rich alteration veins from altered metal grain in Murchison (Hanowski and Brearley, 2000)

CROSS CUTTING VEIN IN MOKOIA (CV3 - ox)



Krot et al. (1998)

CONDITIONS OF ALTERATION

- Low temperature alteration (<~100ºC) – dominated by hydrous phases.
  - CI, CM, CR, CO, reduced CV, unequilibrated ordinary chondrites
- Rare evidence of alteration at intermediate temperatures (~200ºC, e.g., MAC88107, Krot et al., 2002). Hydrous + anhydrous phases
- Fluid-assisted metamorphism or metasomatism (300-500ºC) (Allende-like CV3s, some CO3s):
  - Alteration dominated by anhydrous phases, with minor phyllosilicates
  - CO chondrites, Allende-like CV3 chondrites, probably metamorphosed ordinary chondrites

pH conditions

- Equilibrium thermodynamic calculations for CM and CI (Zolensky et al. (1989) and Rosenberg et al. (2003) (CM).
- pH when ice melts is ~ neutral (pH7).
- As alteration proceeds, pH becomes progressively more alkaline – pH 12.
- Consistent with precipitation of calcite.
- But based on assumption of equilibrium.
- For complex disequilibrium assemblages, behavior is more complex.

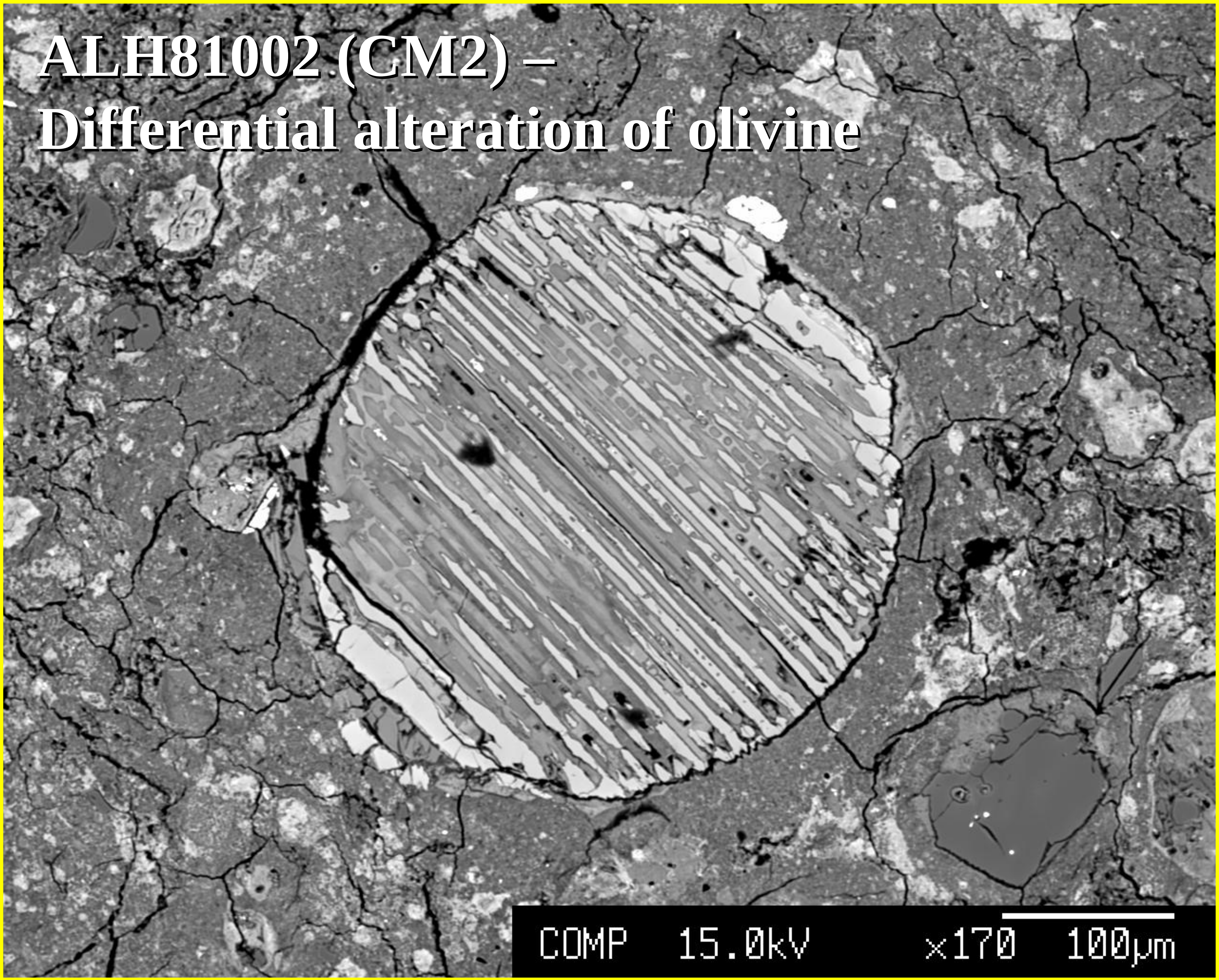
MICROCHEMICAL ENVIRONMENTS

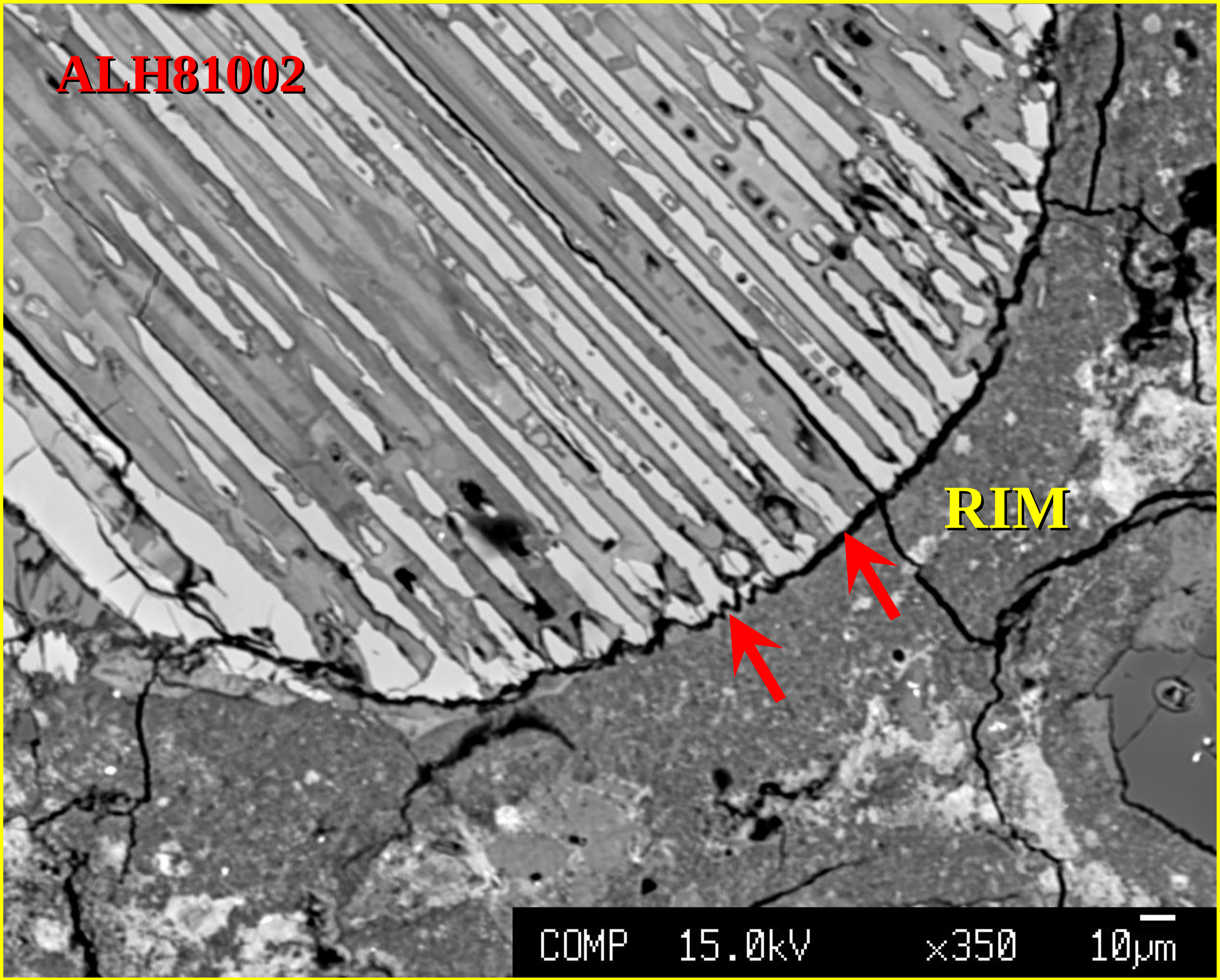
- Localized (scale <200 µm to mms) variations in geochemical conditions in CM and CR chondrites.
- Caused by localized chemical reactions that control pH.
- Differences in pH between matrix and chondrules.
- pH in chondrules was more acidic than matrix.
- Precipitation of soluble elements controlled by localized variations in pH.
- Possible explanation of isochemical alteration in CM chondrites, even if fluid flow occurred.

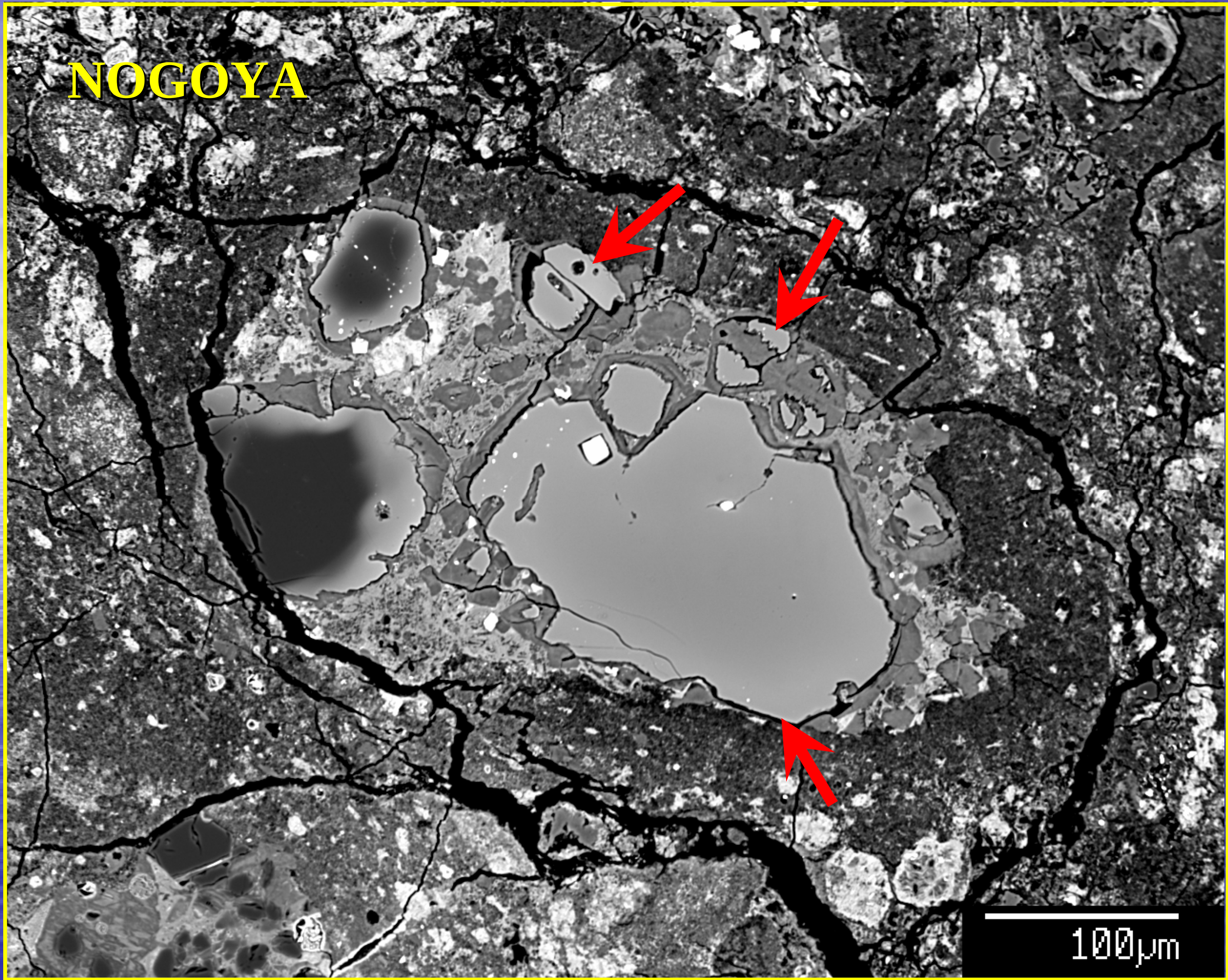
EVIDENCE FOR MICROCHEMICAL ENVIRONMENTS (CM chondrites)

- Differential alteration of olivine on interior vs exterior of olivines
  - Olivine in interior of chondrules altered preferentially to those in contact with matrix
- Absence of calcite replacing Ca-bearing mesostasis in chondrules (too acidic)
- Precipitation of calcite outside chondrules in matrix (more alkaline)
- Precipitation of Ca-phosphates at interface between chondrules and fine-grained rims
  - Ca-phosphate insoluble under acidic conditions
  - Precipitation at pH boundary 'metasomatic reaction front'.
- Fe-rich aureoles in CM chondrites
  - Precipitation of insoluble Fe^{3+} oxides at reaction front.

ALH81002 (CM2) – Differential alteration of olivine

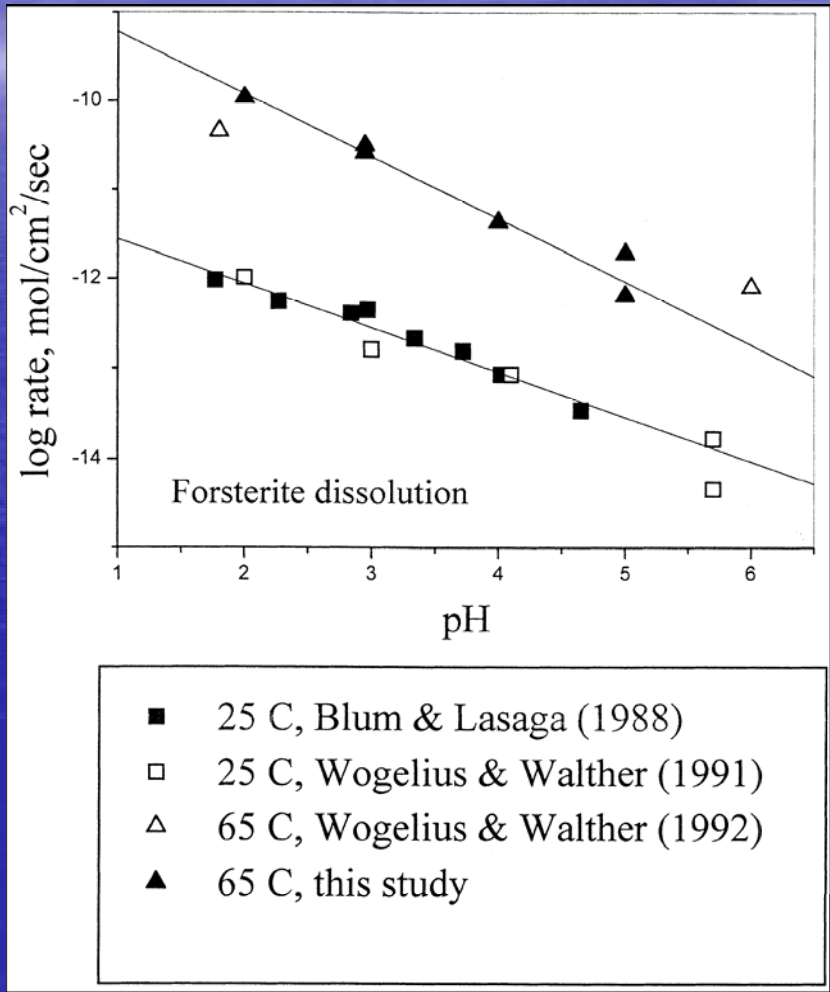



ALH81002
RIM
COMP 15.0kV ×350 10μm


NOGOYA
100μm

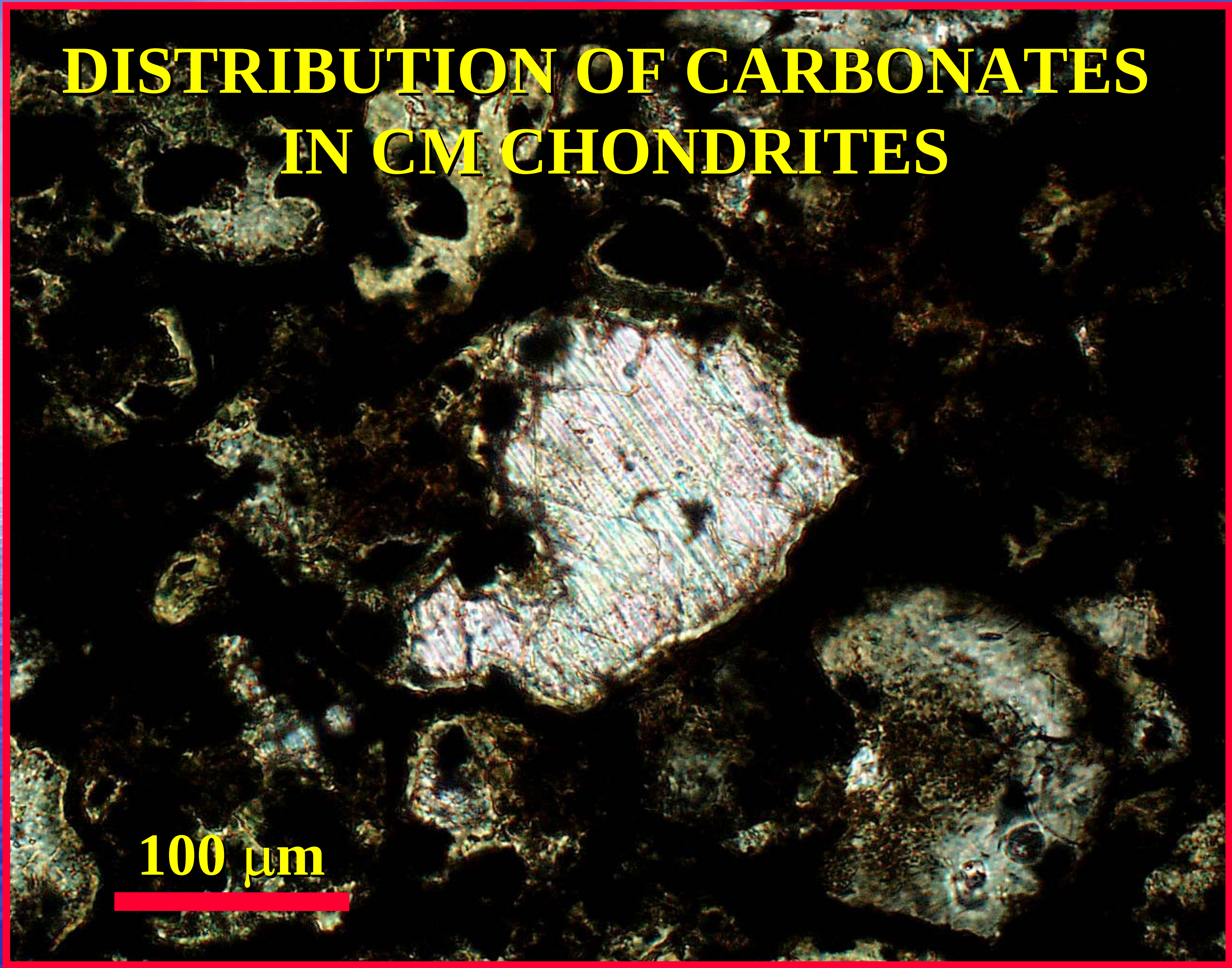
Alteration behavior of FeO-rich chondrule olivine

- Solubility of olivine is strong function of pH.
- More acidic solutions favor more rapid dissolution.
- Lower pH in interior of chondrules?

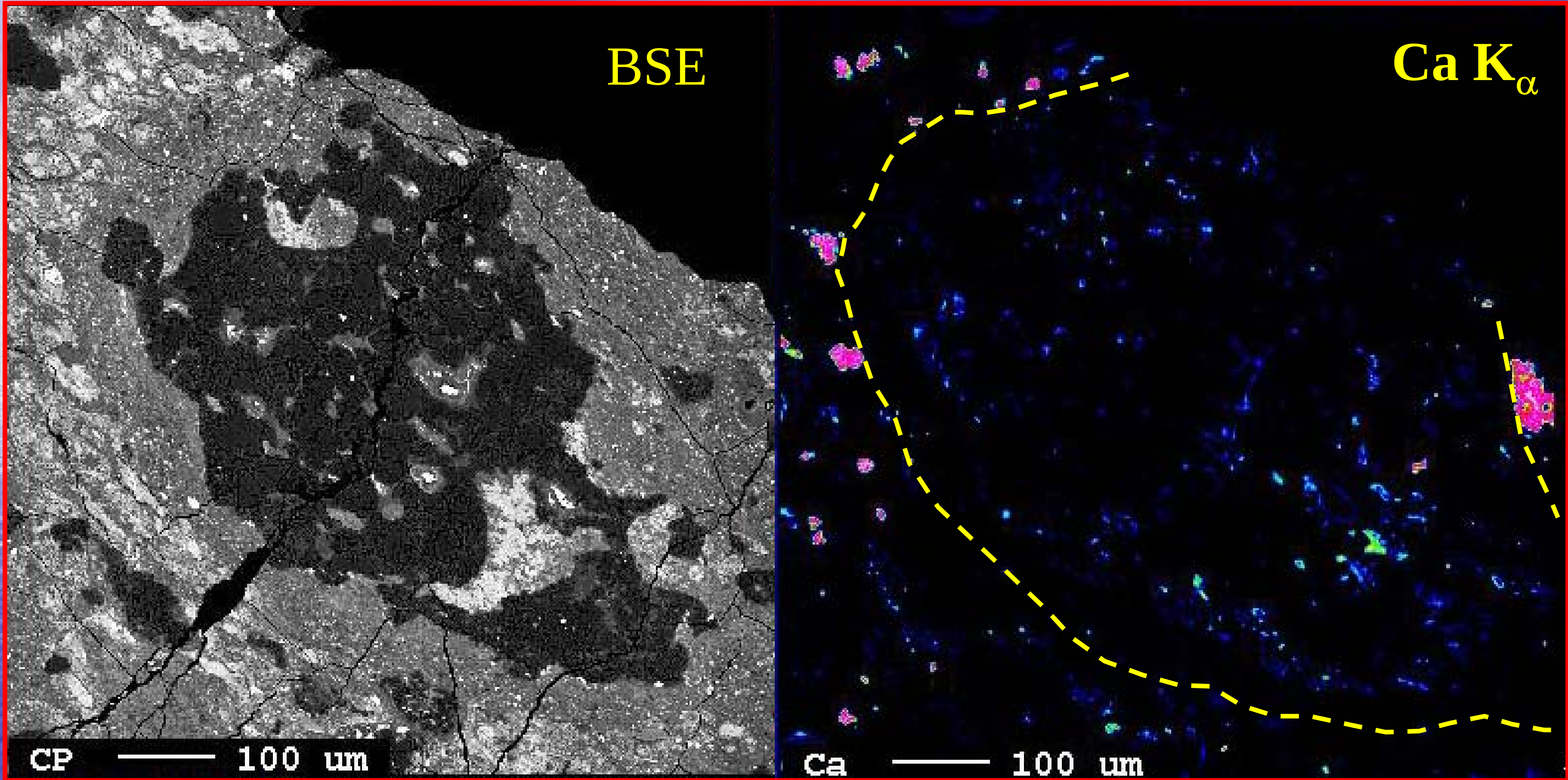


Chen and Brantley 2000

DISTRIBUTION OF CARBONATES IN CM CHONDRITES



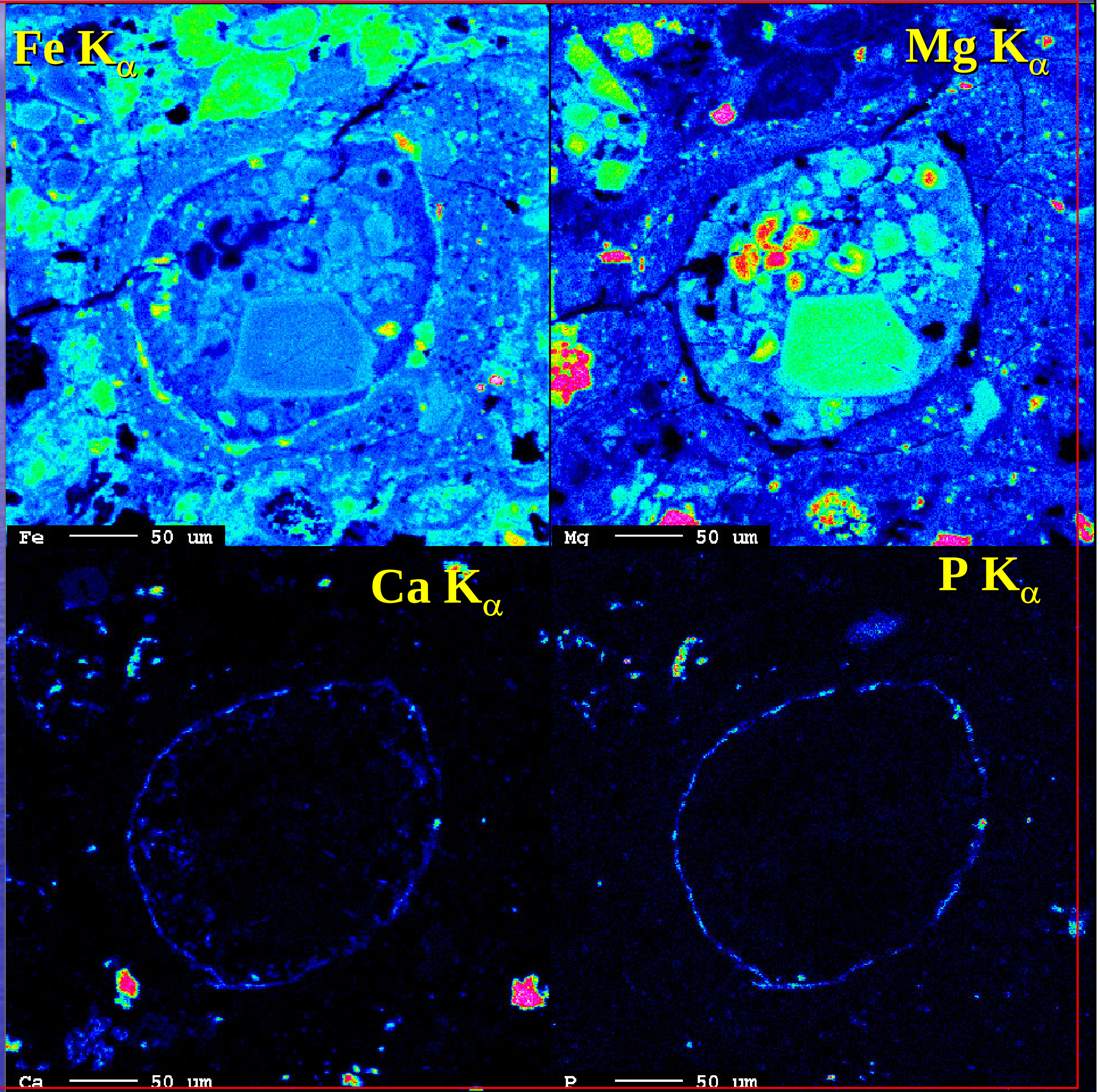
Y-791198 Type I chondrule

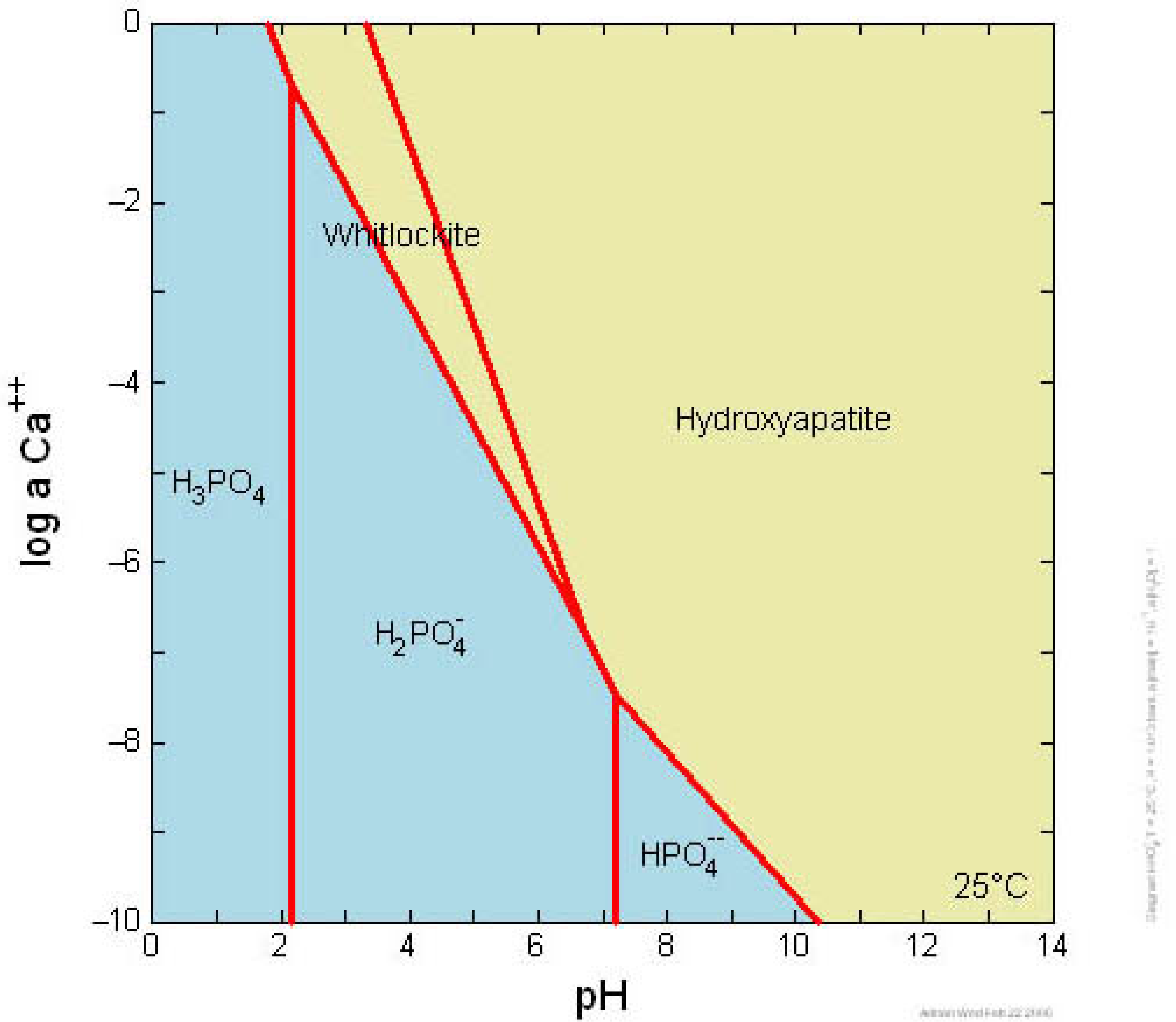


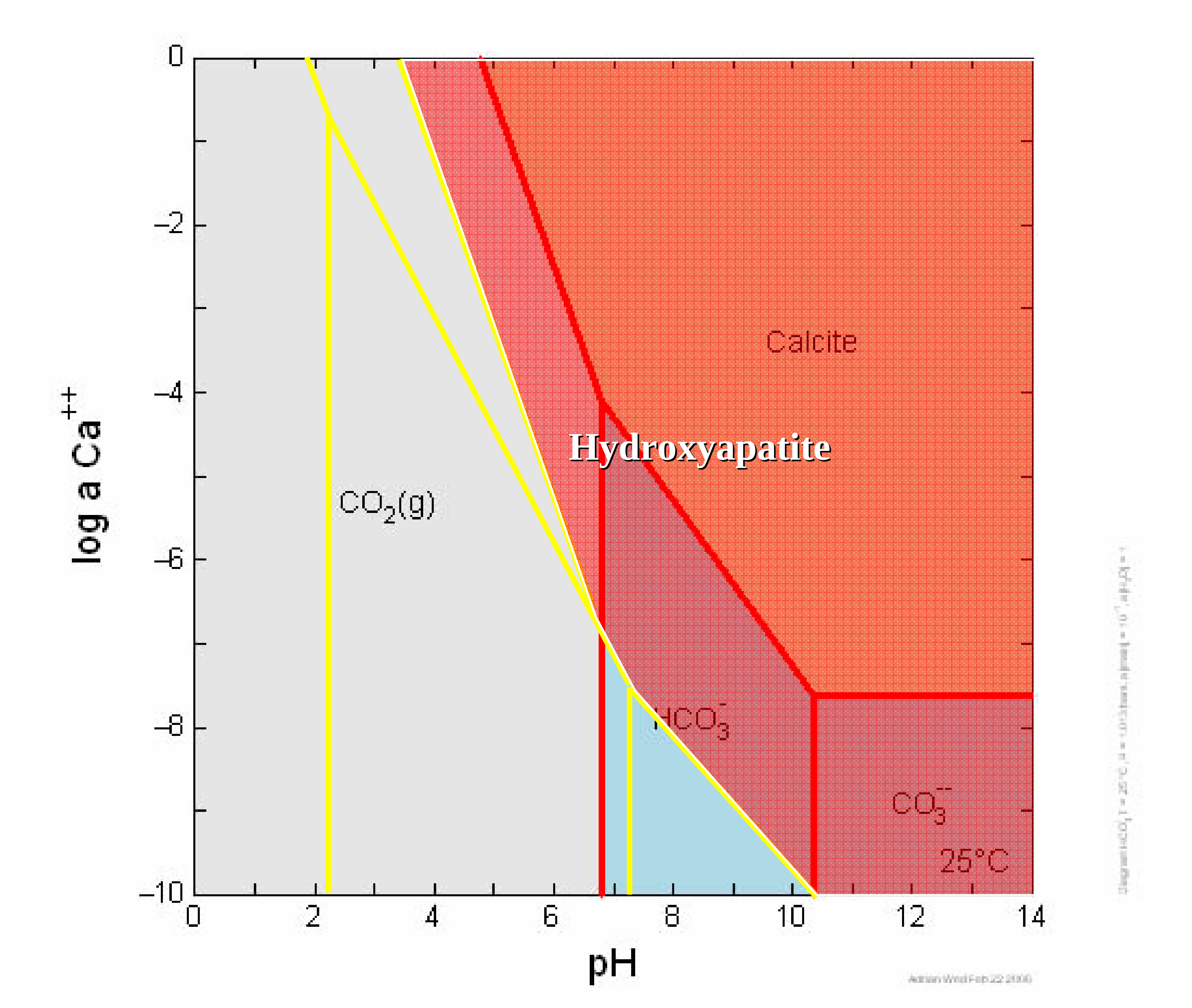
- Calcite occurs outside chondrules and outside fine-grained rims (higher pH in mx)

Y-791198 Type II chondrule

- Ca-phospate precipitated at interface between chondrule and fine-grained rim.
- Ca and P leached from chondrule glass, precipitate at pH front – more alkaline in fine-grained rims




Whitlockite
Hydroxyapatite
H_3PO_4
$H_2PO_4^-$
HPO_4^{--}
25°C
log a Ca^{++}
pH
0
−2
−4
−6
−8
−10
0
2
4
6
8
10
12
14

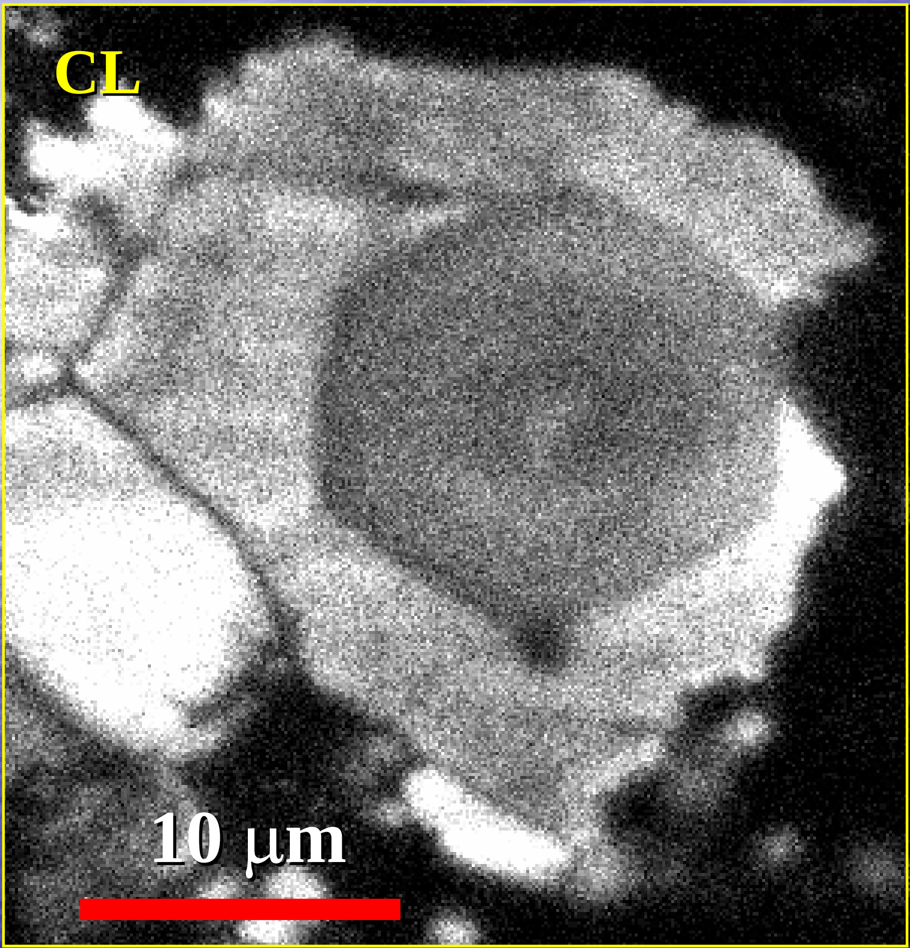


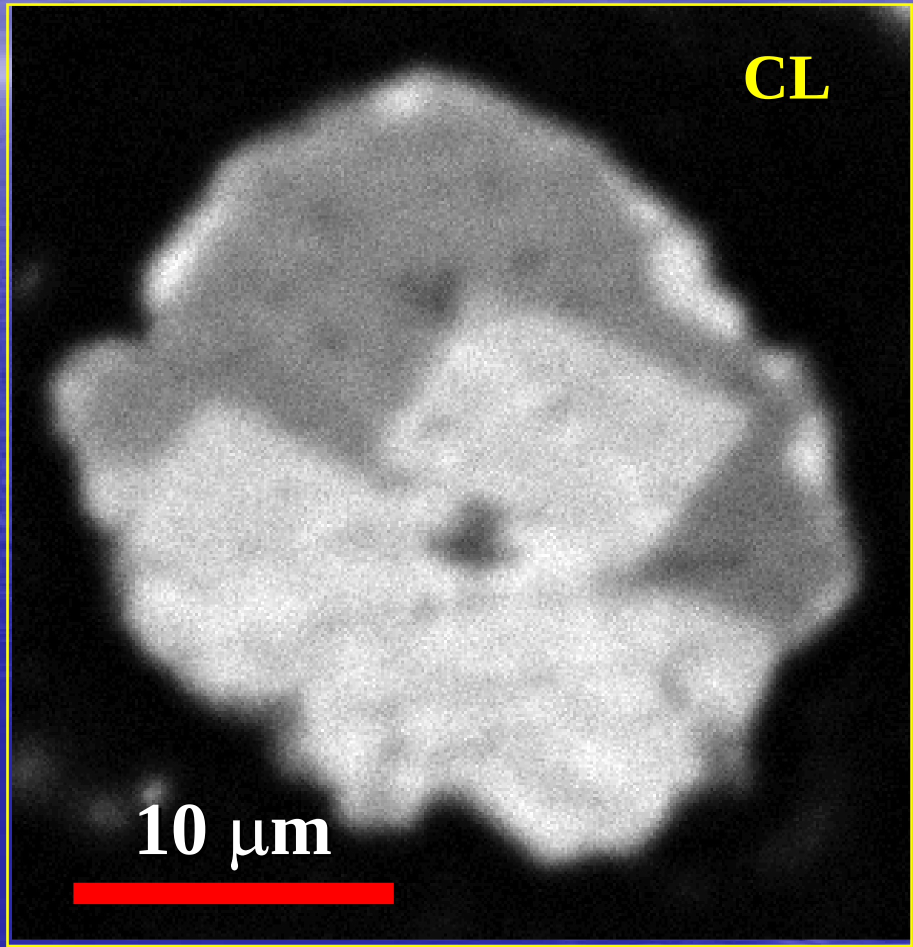
0
−2
−4
−6
−8
−10
log a Ca++
0
2
4
6
8
10
12
14
pH
Calcite
Hydroxyapatite
CO2(g)
HCO3-
CO3--
25°C

IMPLICATIONS

- Higher pH in rims may be result of rapid hydrolysis reactions that consumed protons.
  - e.g. geochemical modeling indicates evolution of fluids to alkaline compositions (e.g. Zolensky et al., 1993).
- Why was pH lower in chondrule interiors?
  - Acidic in interior of chondrules – hydrolysis of Si-rich glass, producing H_2SiO_4?
  - Alteration of sulfide in interior of type IIA chondrules?
- These small scale variations in pH may have prevented extensive mobilization and transport of soluble elements such as Ca.

EVIDENCE FOR EPISODIC ALTERATION - CARBONATES





THERMAL MODELS FOR PARENT BODIES OF CARBONACEOUS CHONDRITES (CI and CM)

- Several modeling studies:
  - Grimm and McSween (1989), Wilson et al. (1999), Coker and Cohen, Young et al.
- Each makes different assumptions about
  - A) initial conditions
  - B) processes such as fluid flow, convection, venting of gases, etc.
- Requires knowledge of numerous different parameters
  - e.g. porosity, permeability, thermal conductivity, reaction kinetic.

INITIAL CONDITIONS

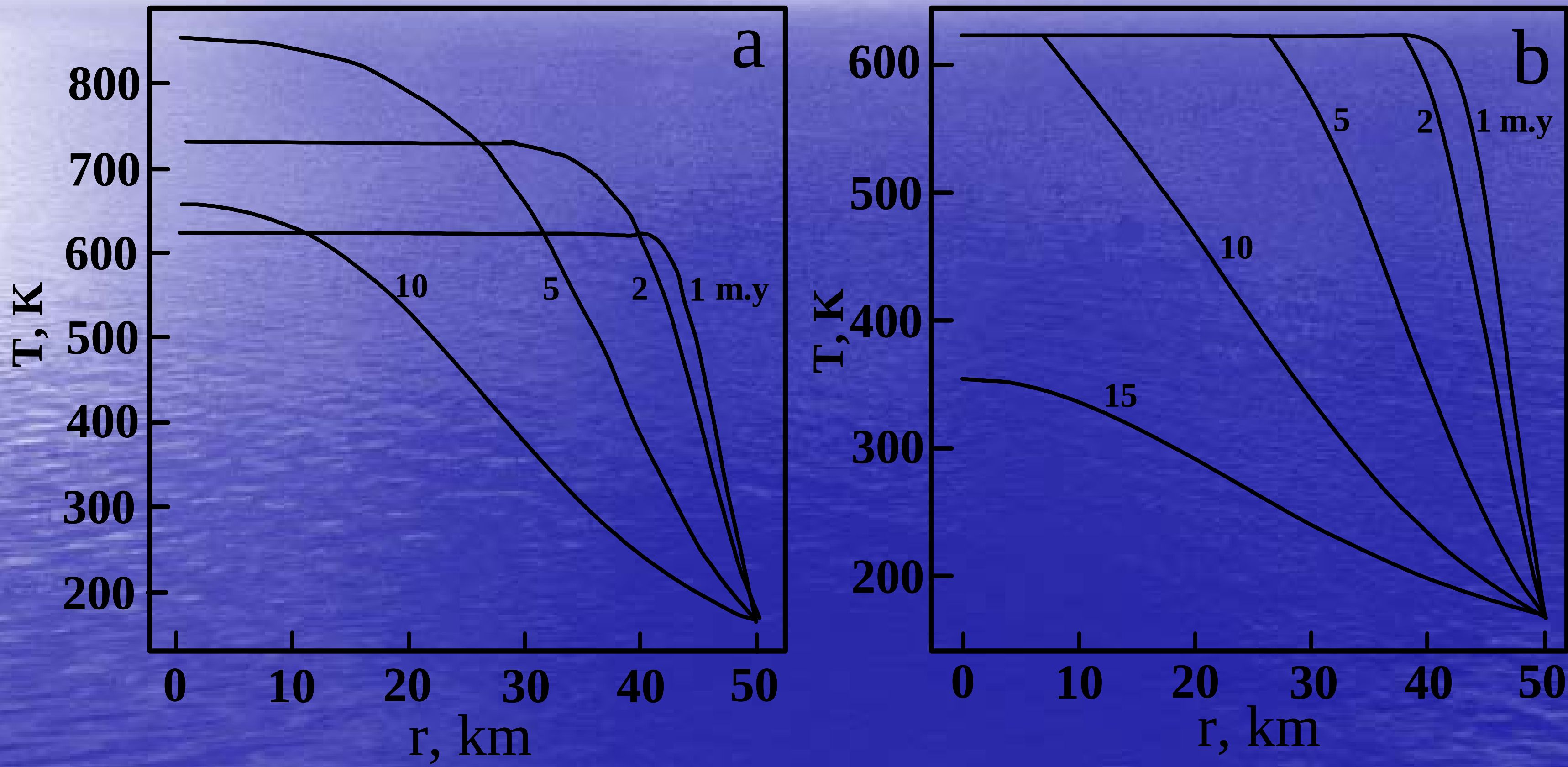
- Most models assume:
  - Initial asteroid diameter = 100 km
  - Accretion temperature 170-180K
  - Water accreted as ice, volume fraction 0.2-0.4
  - Heating by decay of ^{26}Al – initial $^{26/27}$Al ratio >canonical value.
  - Heating causes melting of ice initial in asteroid interior.
  - Lquid water interacts with primary nebular materials to form hydrous phases.
  - Hydration occurs by model reactions.

KEY RESULTS

- Hydration reactions are strongly exothermic.
- For volume fraction of ice = 0.3, 6 times as much heat is released by hydration as is required to melt all ice.
- If hydration reactions are rapid (~10^4 years) causes heat pulse within asteroid.
- Causes rapid rise in temperature.
- Effects of heat pulse are mitigated if convection (Grimm and McSween, 1989) or fluid flow (Young et al., 1999) occur.
- Unless venting of gases occurs catastrophic disruption of asteroid will occur due to pressure buildup (Wilson et al., 1999).

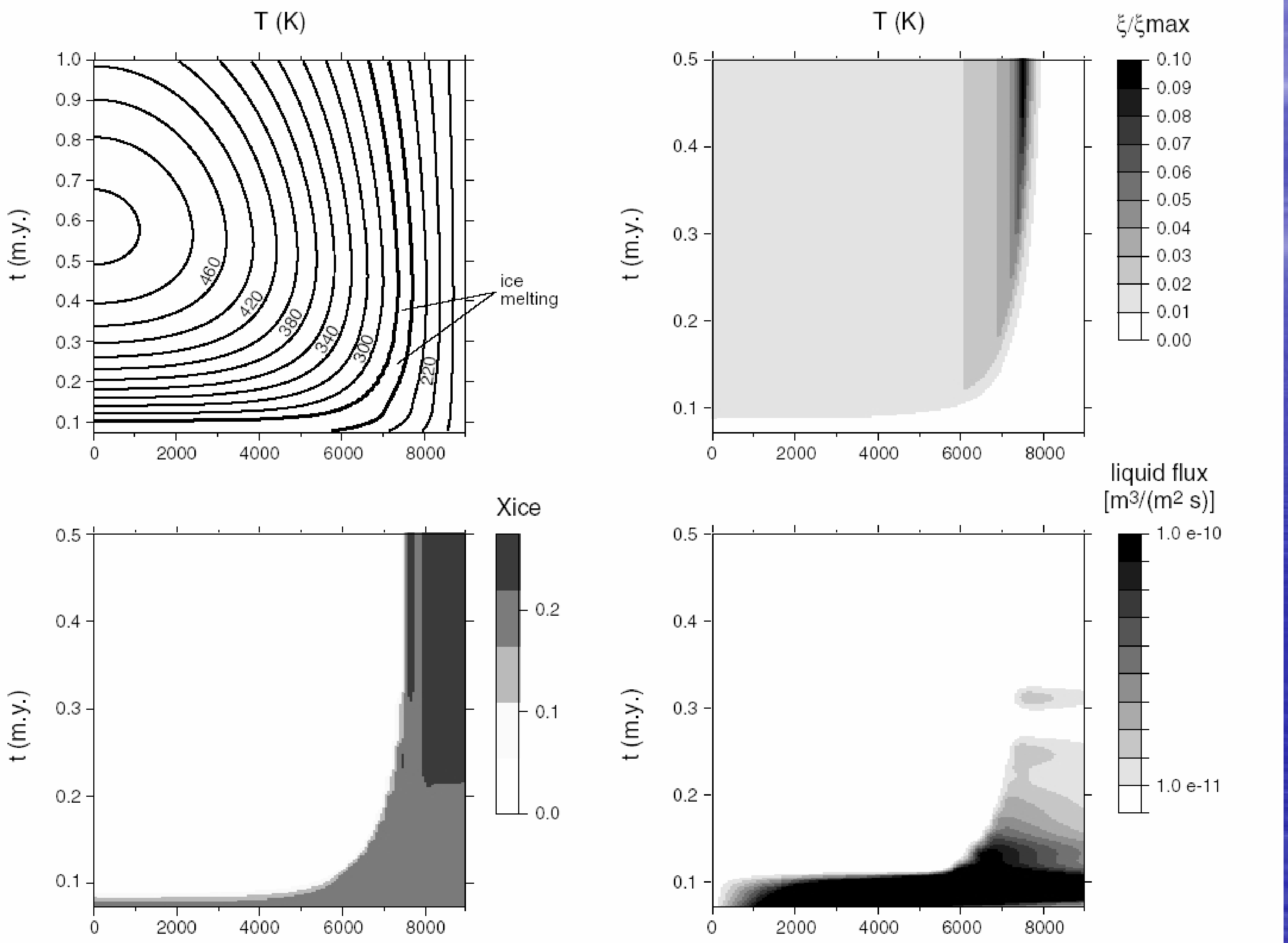
THERMAL MODELS FOR CM CHONDRITES

$^{26/27}Al = 1.2 \times 10^{-6}$ $^{26/27}Al = 1.2 \times 10^{-6}$



CM parent body (ice fraction = 0.2) CI parent body (ice fraction = 0.4)

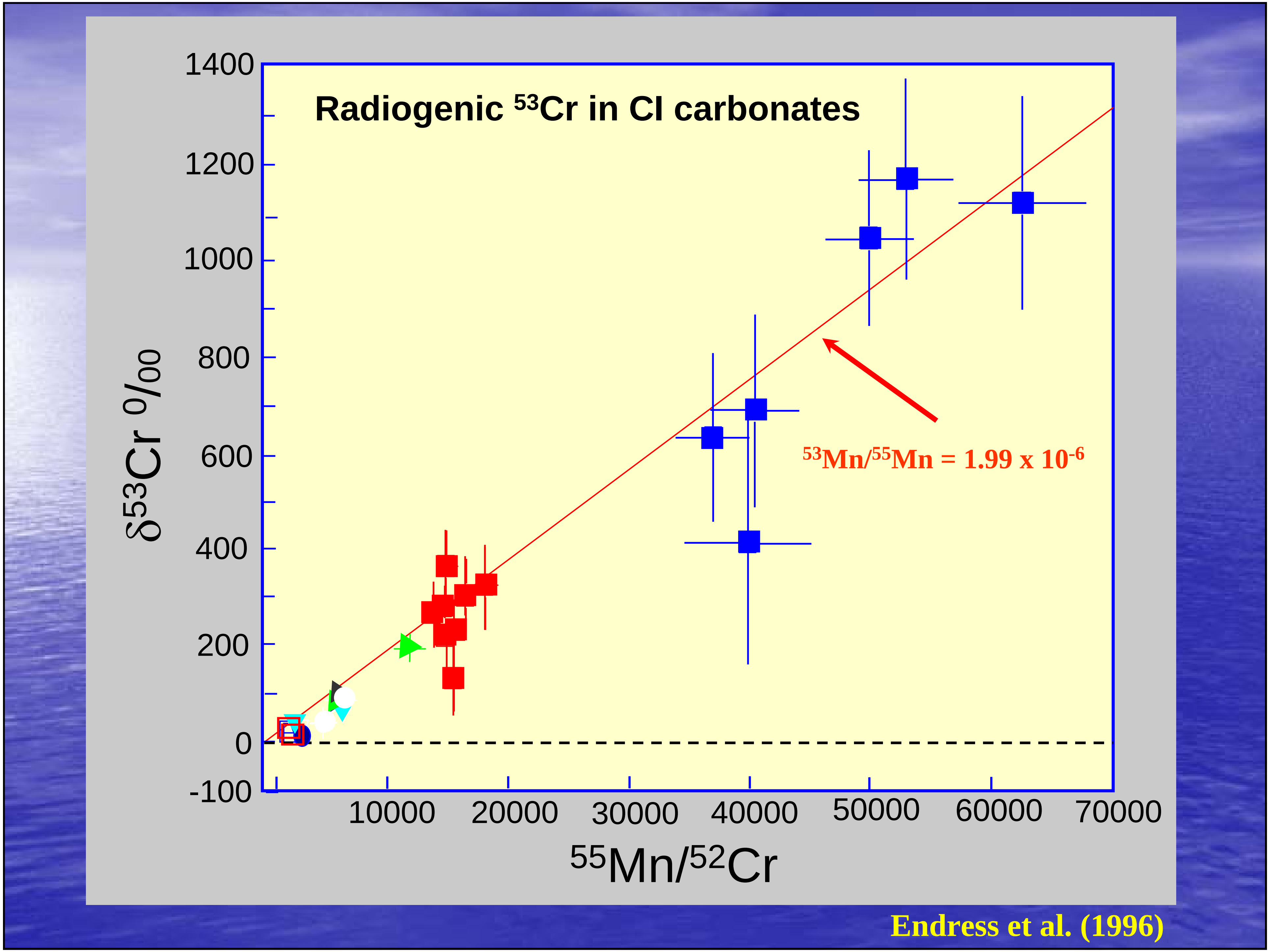
Grimm and McSween (1989)

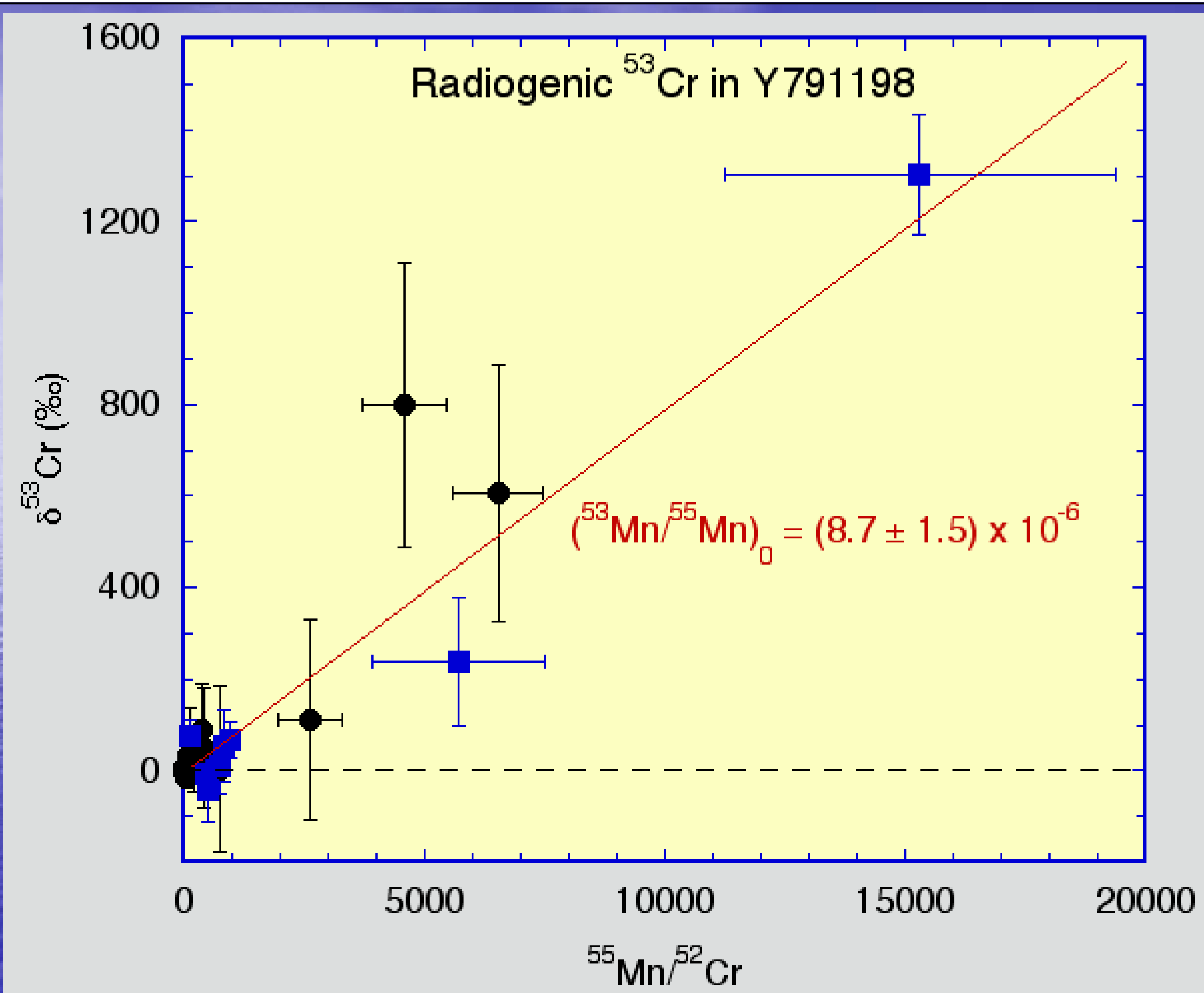


Young et al. (1999)

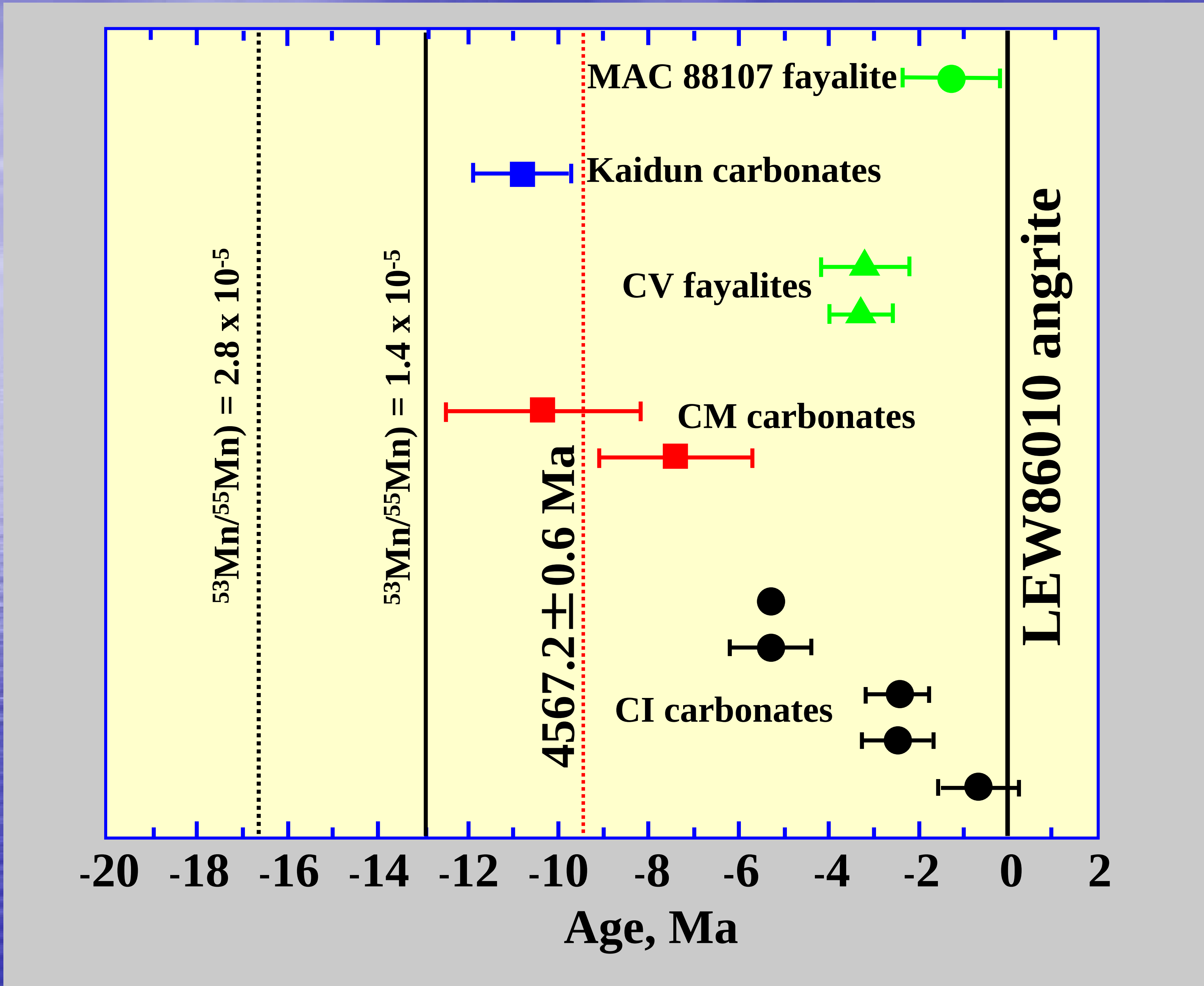
TIMING AND DURATION OF ALTERATION

- Constraints from geochronometers based on short-lived radionuclies – Mn-Cr, I-Xe.
- Mn-Cr of carbonates in CI and CM chondrites
  - – alteration commenced early (with ~1-2 Ma of CAI formation)
- Low T (<100ºC) alteration extended for up to ~10 Ma.


Radiogenic ^{53}Cr in CI carbonates
δ^{53}Cr $^{0}/_{00}$
^{55}Mn/^{52}Cr
^{53}Mn/^{55}Mn = 1.99 x 10^{-6}
1400
1200
1000
800
600
400
200
0
-100
10000
20000
30000
40000
50000
60000
70000
Endress et al. (1996)



Brearley and Hutcheon (2002)



Krot et al. (2006) MESS II

KEY ISSUES FOR FUTURE WORK

- Developing robust criteria for differentiating between asteroidal and preaccretionary alteration.
- Improved understanding of mineral-fluid reactions and fluid chemistry at the microscale.
- Timescales of alteration:
  - Improving chronology of alteration using short-lived radioisotopes
- Improved understanding of mass transfer during alteration –
  - why is alteration usually isochemical?
- Better integration of mineralogical data with thermal models of asteroids.
  - Static or fluid flow?