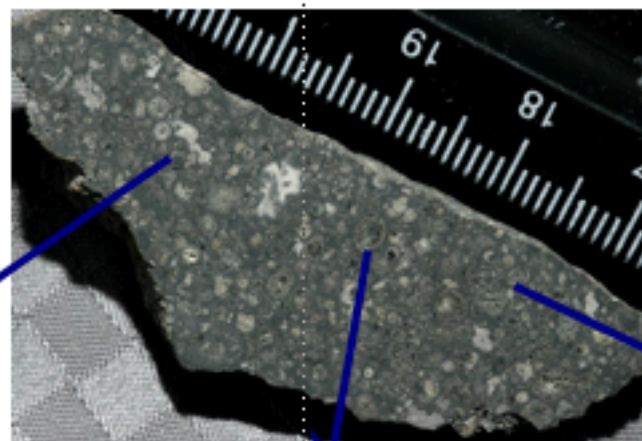
Calcium-Aluminum-rich Inclusions & Chondrules

Guy Libourel
CRPG-CNRS, Nancy, France

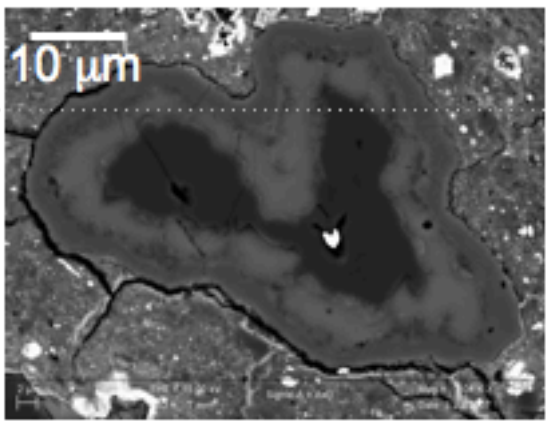
INSU
Institut national des sciences de l'Univers

CRPG

Constituents of Primitive Meteorites

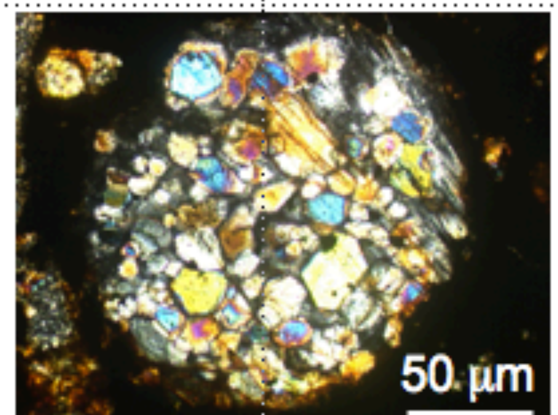


Allende CV3
(Mexico, fall, February 8, 1969)

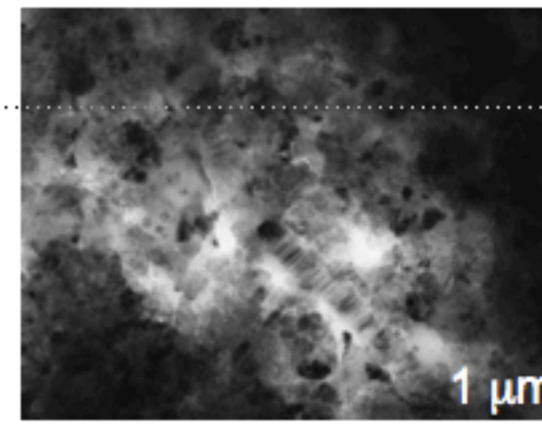


Ca - Al-rich inclusions (CAI)
(10 µm - 2 cm)

Oldest solids
in the solar system (t=0)
4,567 MA



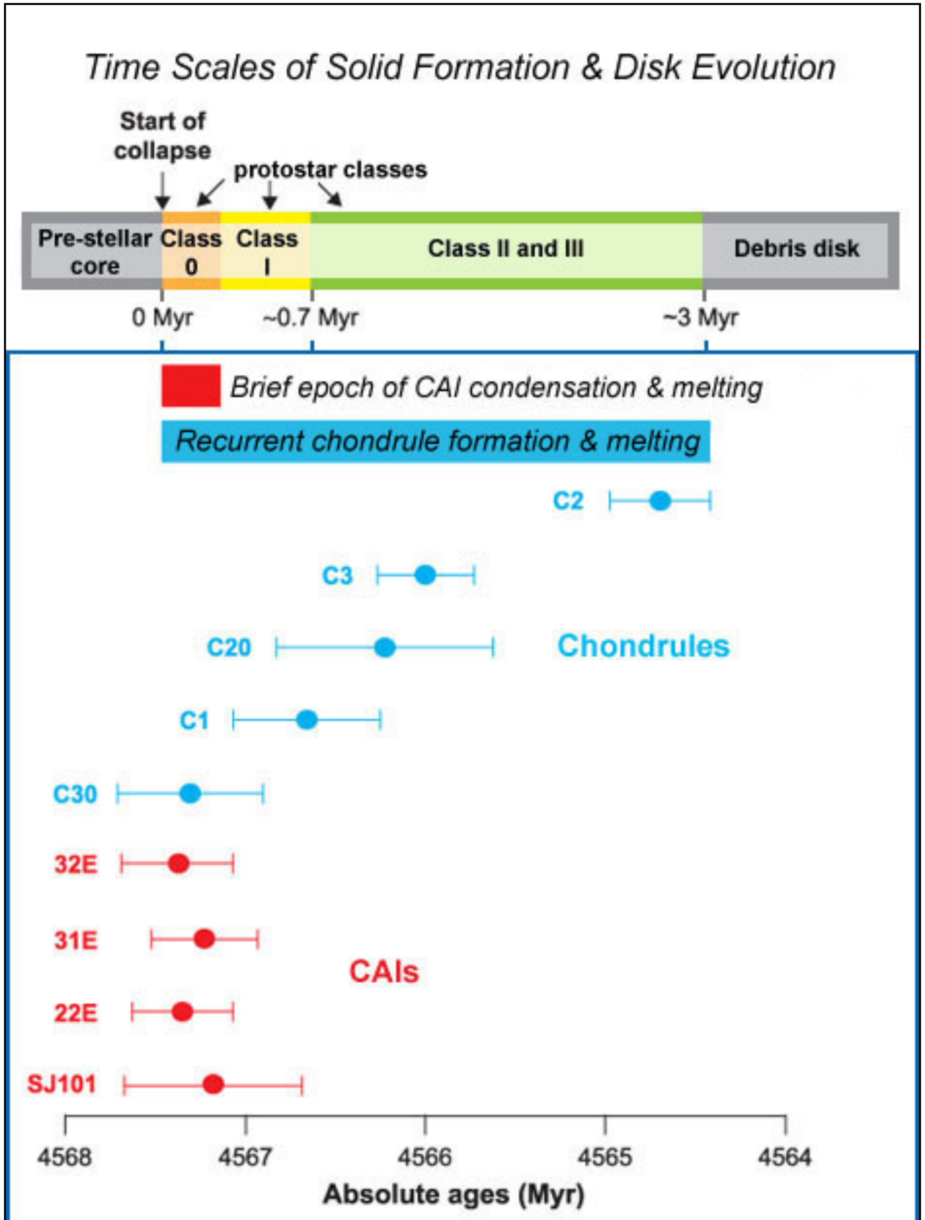
Chondrules
(10 µm - 0.2 cm)



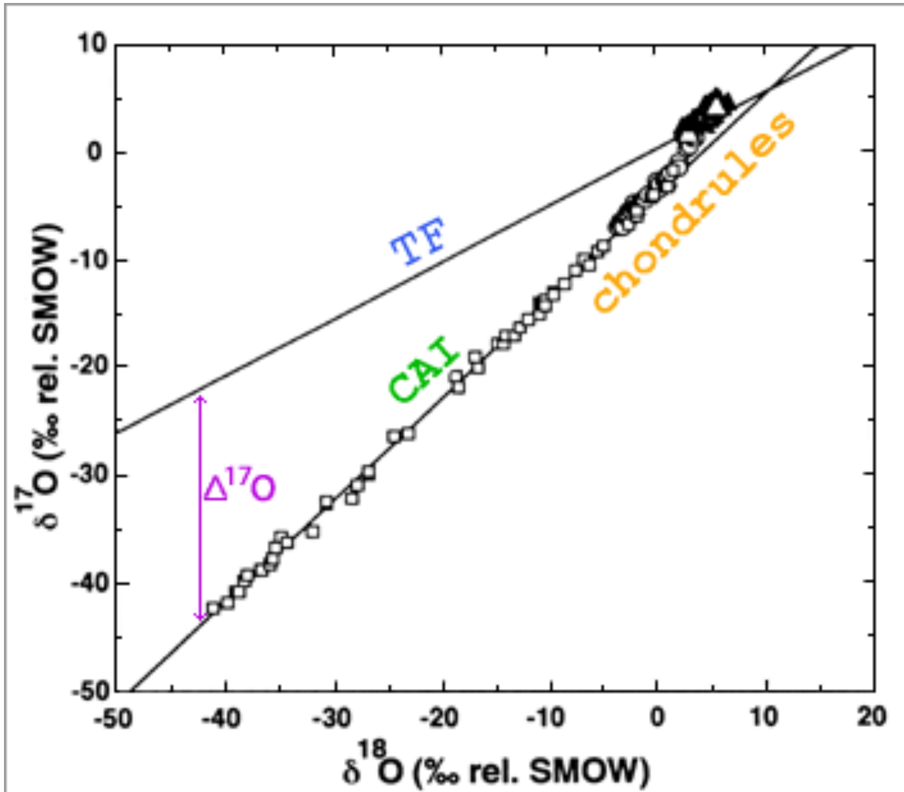
Matrix
(nm - 10s µm)

20-80 % by volume of primitive meteorites (chondrites)

CAIs and Chondrules



(From Connelly *et al.*, 2012, *Science*, v. 338, p.651-655, doi: 10.1126/science.1226919.)

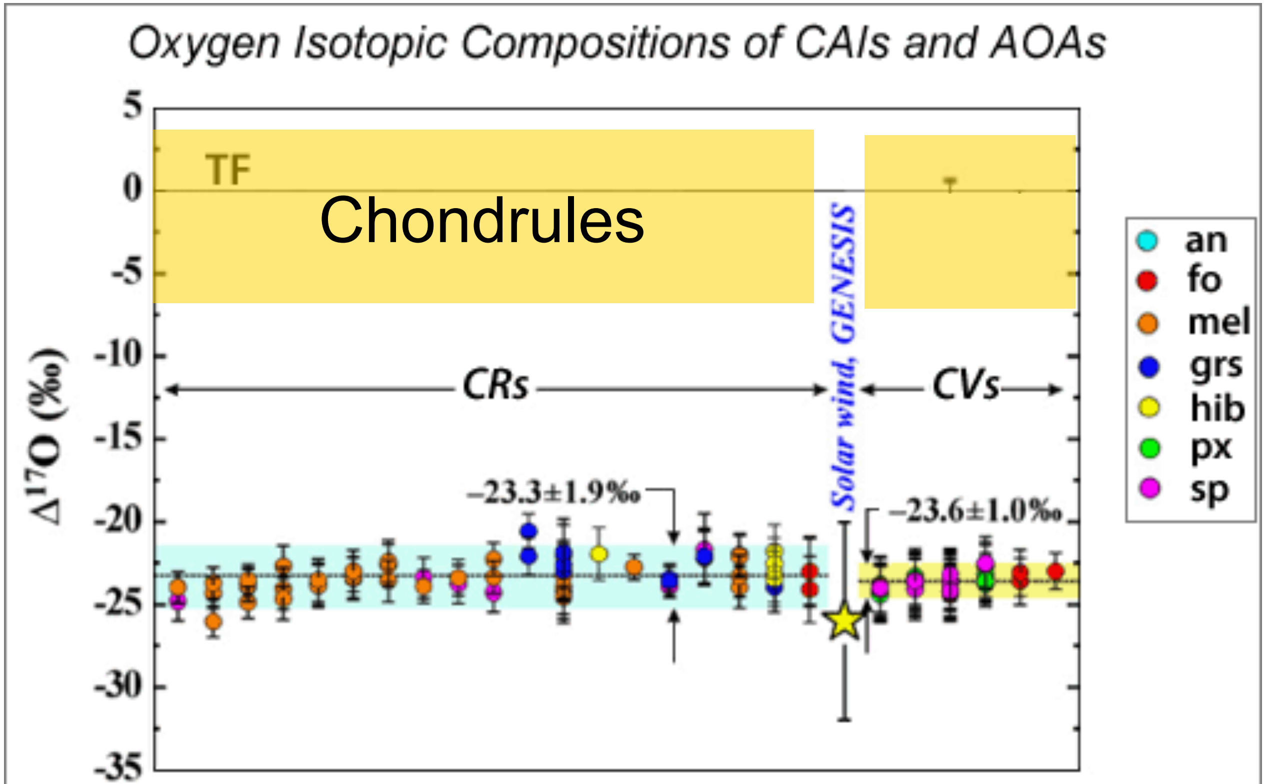


(From Clayton, R., 1993, Oxygen Isotopes in Meteorites, *Annu. Rev. Earth Planet. Sci.*, v.21, p. 123.)

CAIs average age is 4567.30 ± 0.16 My, which overlaps stage of Class 0 protostars. Chondrule formation began at the same time and continued for 2-3 My.

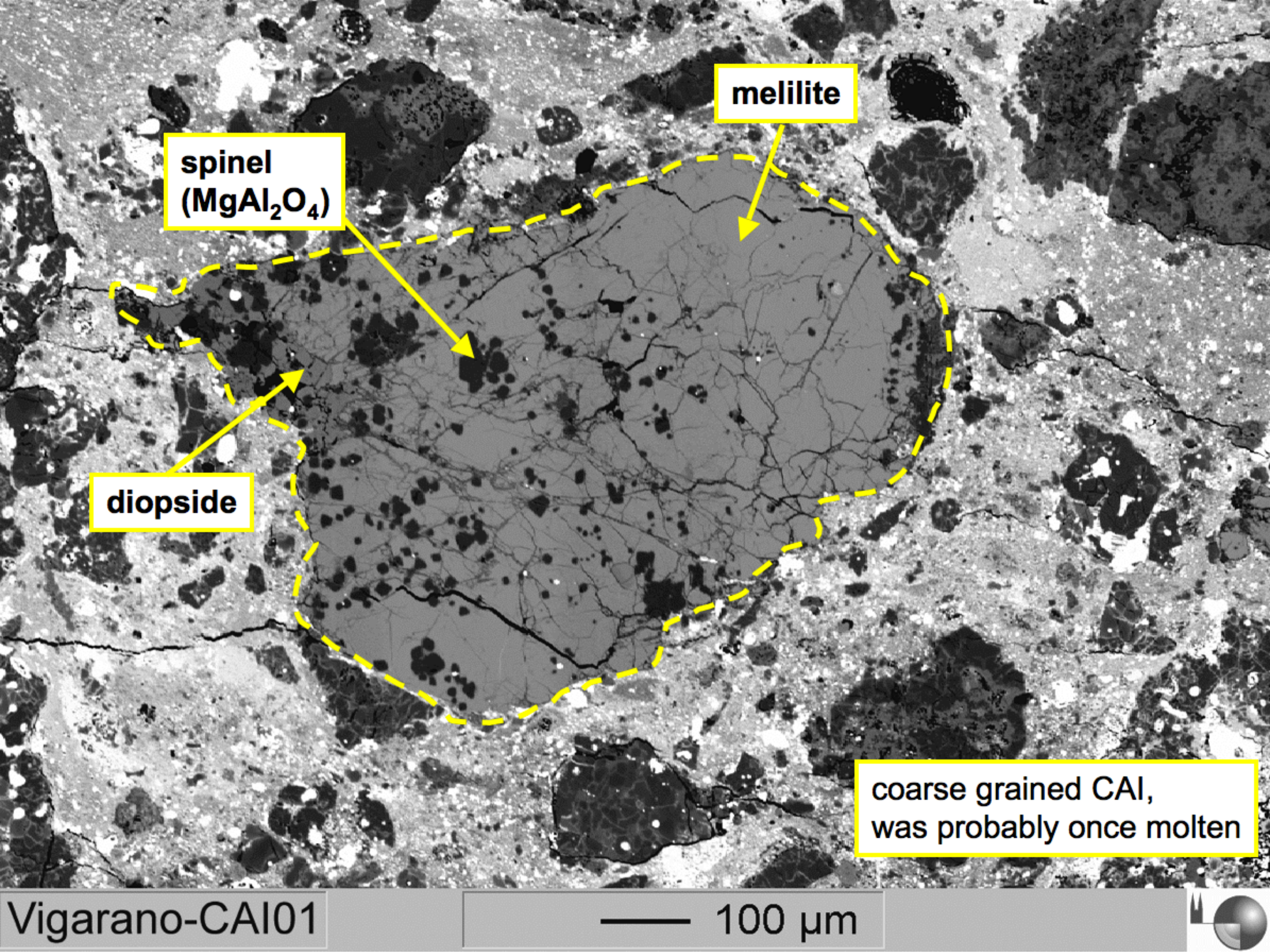
Calcium-aluminum-rich inclusions

CAIs



(From Krot *et al.*, 2010, *The Astrophysical Journal*, v. 713, p. 1159-1166.)

- Refractory inclusions (left) condensed from gas of solar composition with O-isotopes similar to the Sun (see Genesis data point).


melilite
spinel
($MgAl_2O_4$)
diopside
coarse grained CAI,
was probably once molten
Vigarano-CAI01
100 µm

Calcium-Aluminum-rich Inclusions WORLD

FoB

Type B1

Compact Type A

PLACS

AOA

Fluffy Type A

Hib-CTA

SHIB

Type B2

Sp-Px Inc

FUN

Hib-FTA

Wark-Lovering rim

Calcium-Aluminum-rich Inclusions WORLD

Gehlinite
$Ca_2Al_2SiO_7$

Spinel
$MgAl_2O_4$

Fassaite
$CaAl_2Si_2O_6$

Anorthite
$CaAl_2Si_2O_8$

Grossite
$CaAl_4O_7$

Ca-titanate
$Ca_4Ti_3O_{10}$

Melilite

Perovskite
$CaTiO_3$

Akermanite
$Ca_2MgSi_2O_7$

Krotite
$CaAl_2O_4$

Corundum
Al_2O_3

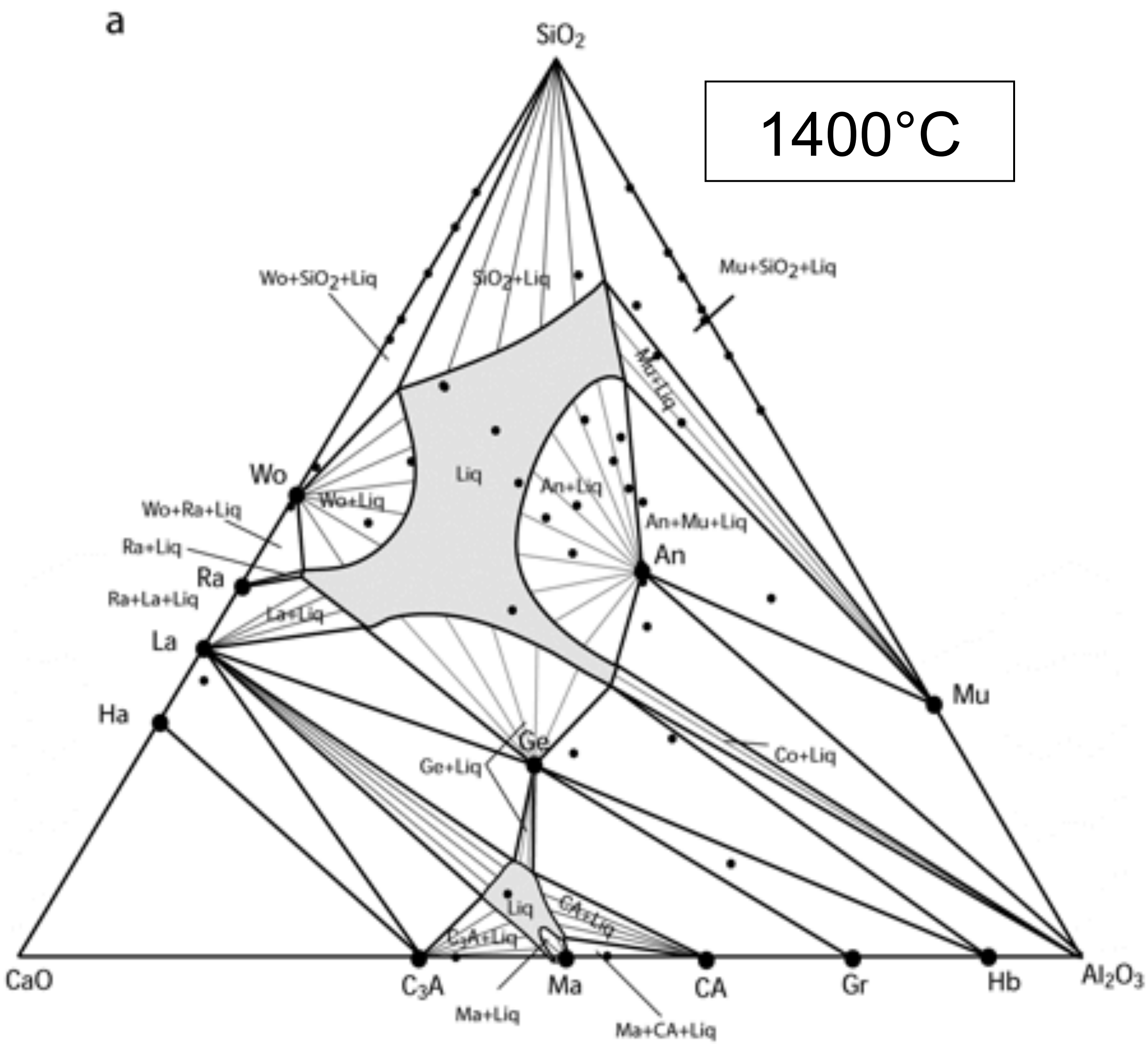
Hibonite
$CaAl_{12}O_{19}$

Dmisteinbergite
$CaAl_2Si_2O_8$

Diopside
$CaMgSi_2O_6$

Forsterite
Mg_2SiO_4

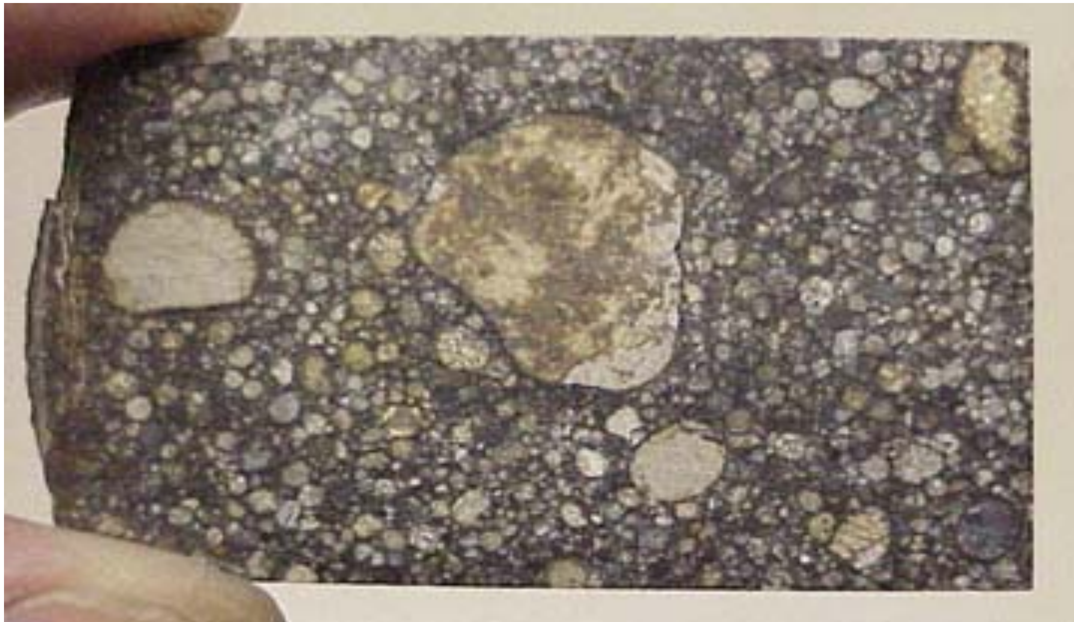
Calcium-Aluminum-rich Inclusions WORLD



Calcium-Aluminum-rich Inclusions

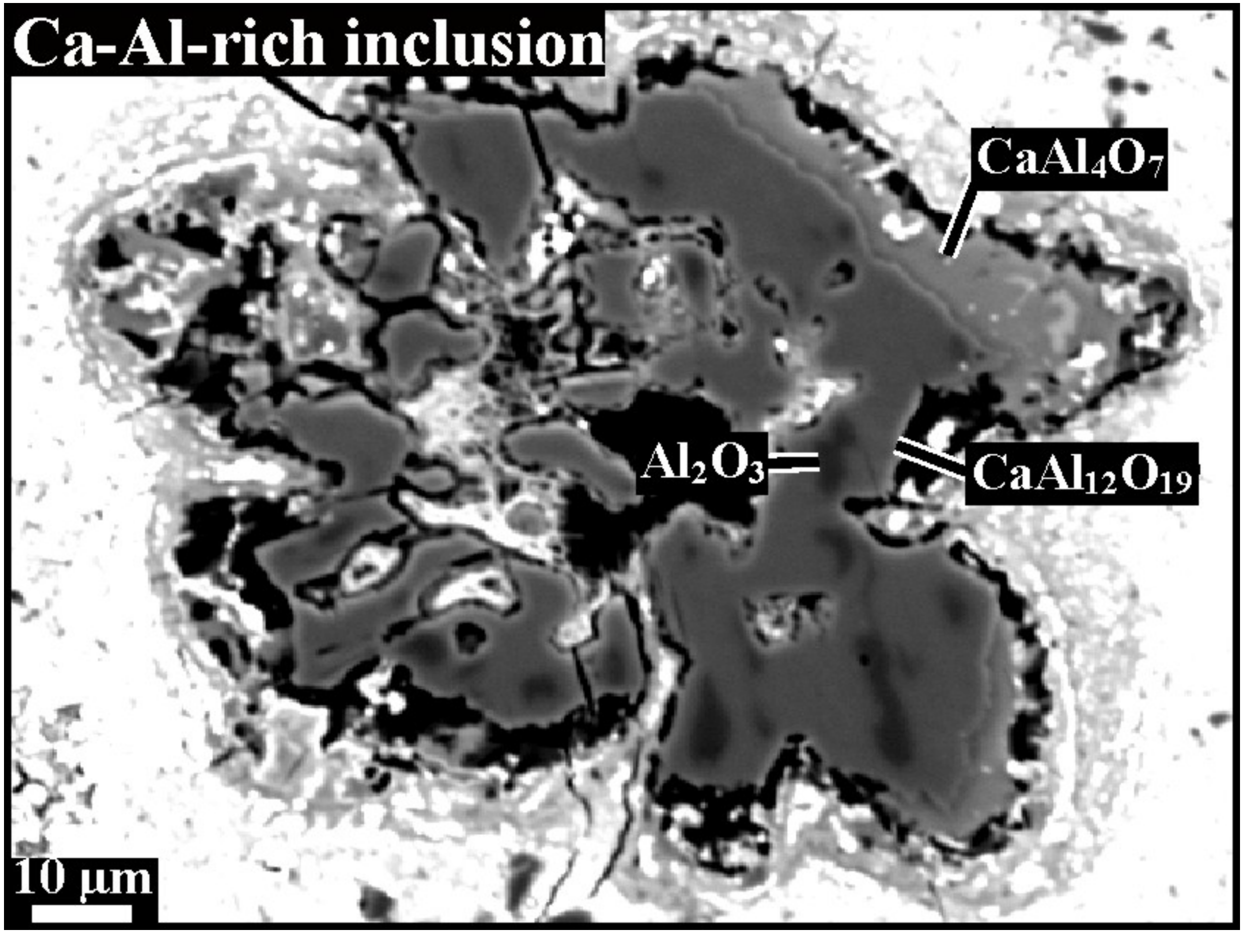
- Mineralogy and petrology
- Phase relations, thermodynamic
- Case study
- Experiments

CAI = refractory inclusion = White inclusion



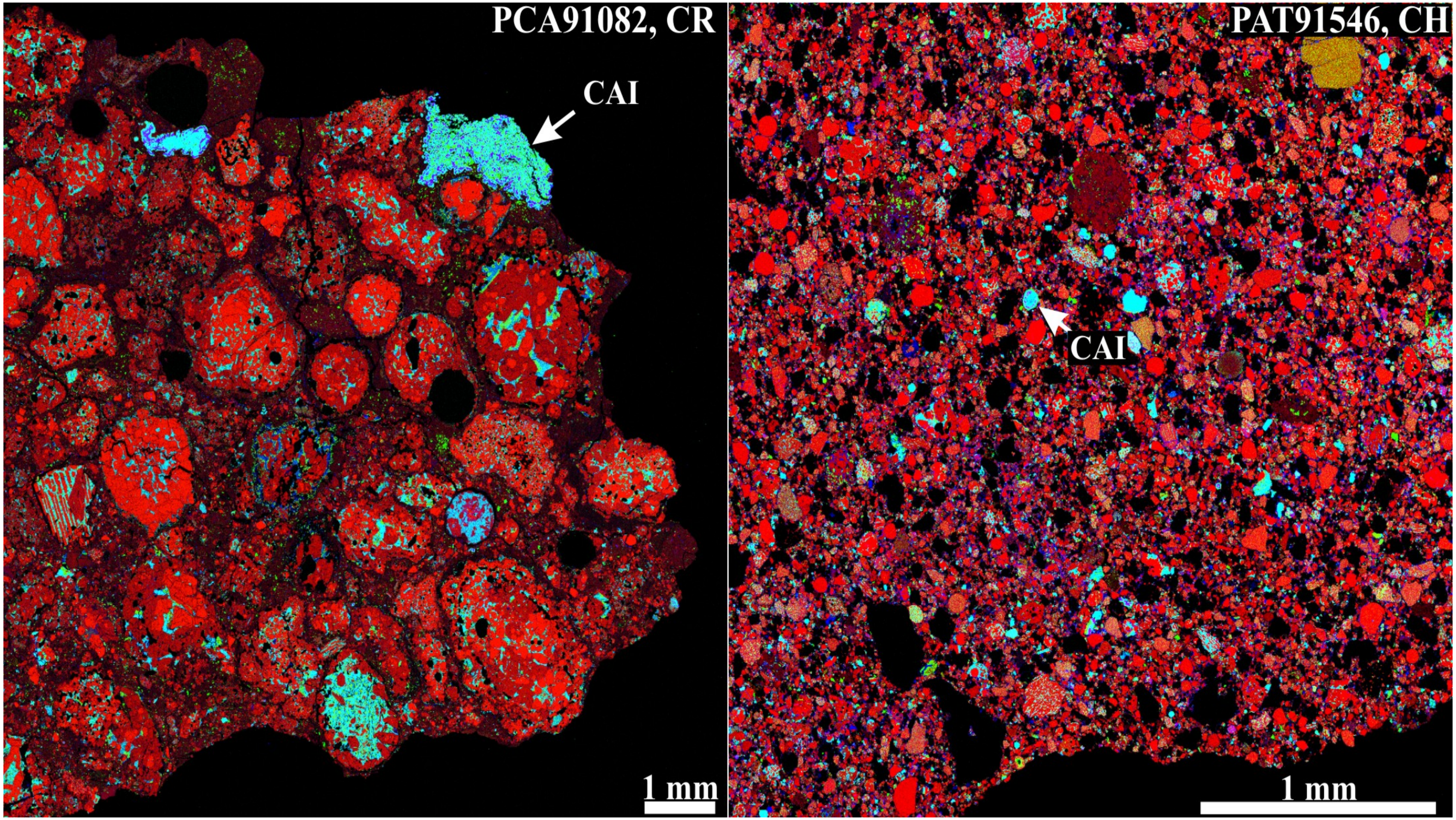
Allende CV3 meteorite (fall 1969)

CAI = refractory inclusion = White inclusion



Calcium-aluminum-rich inclusions

- minor component: 0.1-5 vol%
- large size range: 10 µm to several cm
- sizes of CAIs differ between chondrite groups: size-sorted in the nebula



~4.7 Ga ago, “protosun”

- first solids (inner Solar System) formed by gas/solid condensation

Gas-solid “condensation” of H_2O on a tree

Condensation calculations

- minerals that occur in CAIs condense at high temperatures

MAJOR ELEMENT CONDENSATION TEMPERATURES

Ideal Formula	Mineral Name	Solar System Composition (K)	Photospheric Composition (K)
Al_2O_3	Corundum	1677	1665
$CaAl_{12}O_{19}$	Hibonite	1659	1647
$CaAl_4O_7$	Grossite	1542	1531
$Ca_2Al_2SiO_7$	Gehlenite	1529	1519
$CaTiO_3$	Perovskite	1593	1584
$Ca_4Ti_3O_{10}$	Ca titanate	1578	1567
$Ca_3Ti_2O_7$	Ca titanate	1539	1529
$Ca_4Ti_3O_{10}$	Ca titanate	1512	1502
$CaTiO_3$	Perovskite	1441	1429
$MgAl_2O_4$	Spinel	1397	1387
$CaAl_2Si_2O_8$	Anorthite	1387	1378
Mg_2SiO_4	Forsterite	1354	1346
$MgSiO_3$	Enstatite	1316	1308
$CaMgSi_2O_6$	Diopside	1347	1339
Fe	Fe alloy	1357	1351
Fe_3P	Schreibersite	1248	1245
FeS	Troilite	704	693
Fe_3O_4	Magnetite	371	365
H_2O	Water ice	182	181

NOTE.—At 10^{-4} bar total pressure.

CAI minerals

➡ minerals rich in Ca, Al and Ti (CAIs)

from Lodders (2003) *Astrophys. Journal*

Condensation calculations

- condensation temperatures increase with increasing pressure

Condensation temperatures are **always** a function of

- pressure
- oxygen fugacity
- thermodynamic data used

Condensation temperatures can be given for

- minerals (*in-out*)

Table 3. Temperatures of appearance and disappearance of stable condensates at several representative total pressures in the pressure regime where liquids are not stable.

Condensate \ P^{tot} (atm)	1×10^{-6}		1×10^{-5}		1×10^{-4}		1×10^{-3}	
	In	Out	In	Out	In	Out	In	Out
Corundum	1571	1481	1633	1558	1699	1643	1770	1740
Hibonite	1485	1292	1562	1350	1647	1421	1743	1500
Perovskite	1471	1257	1537	1317	1609	1380	1688	1448
$CaAl_2O_4$								
Melilite ss								1444
Corundum								
Spinel ss								1409
Plagioclase ss								
Rankinite								
Fassaite ss								
Spinel ss								
Forsterite								
Plagioclase ss								
Sphene								
Enstatite								
Spinel ss	1161		1196		1217		1221	
Ti_3O_5							1386	1361
Ti_4O_7			1252	1217	1324	1216	1361	1217
Sphene	1222		1217		1216		1217	
Metal	1214		1287		1370		1464	

increasing pressure → increasing condensation temperature

from Ebel and Grossman (2000) *Geochim. Cosmochim. Acta*

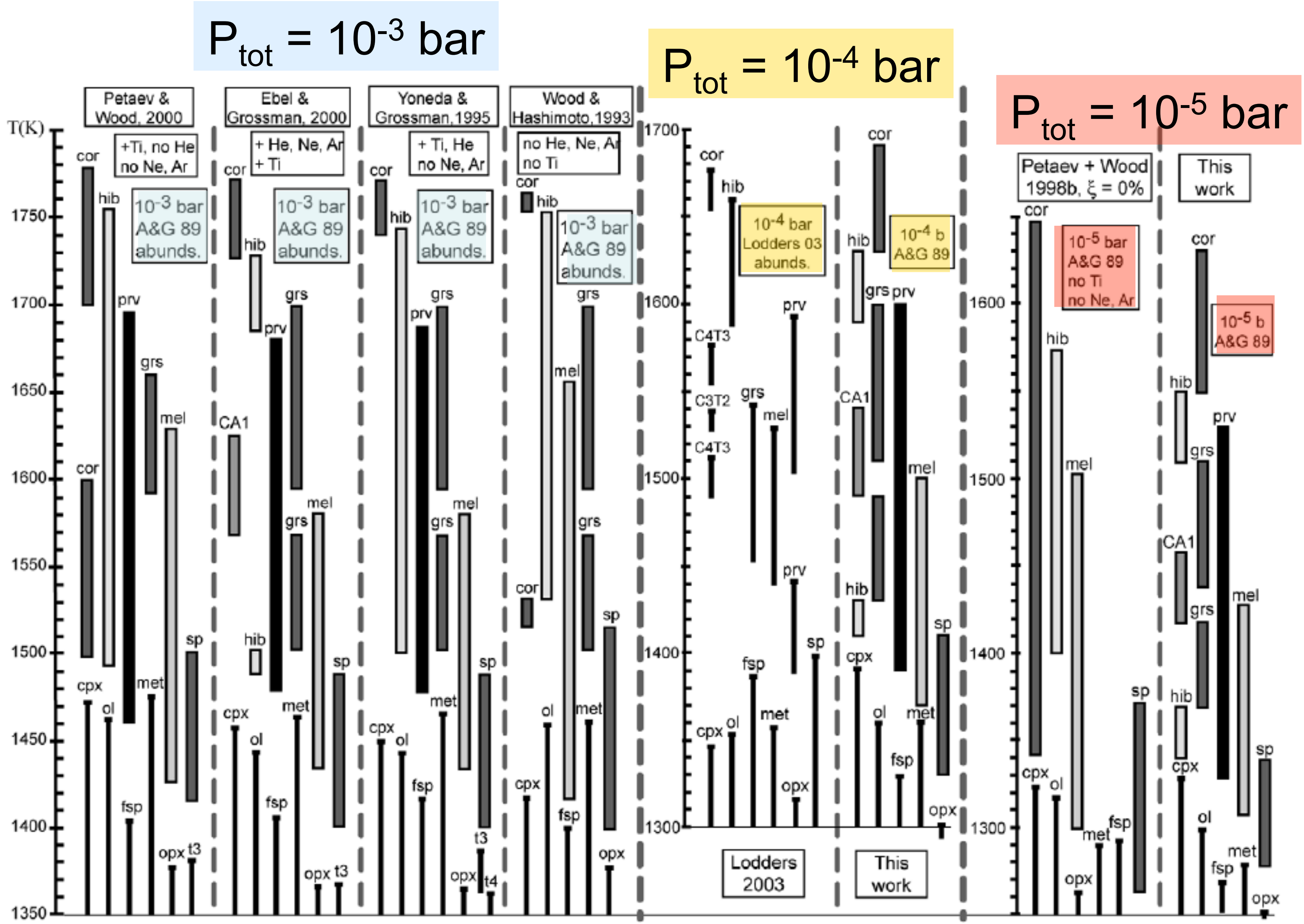
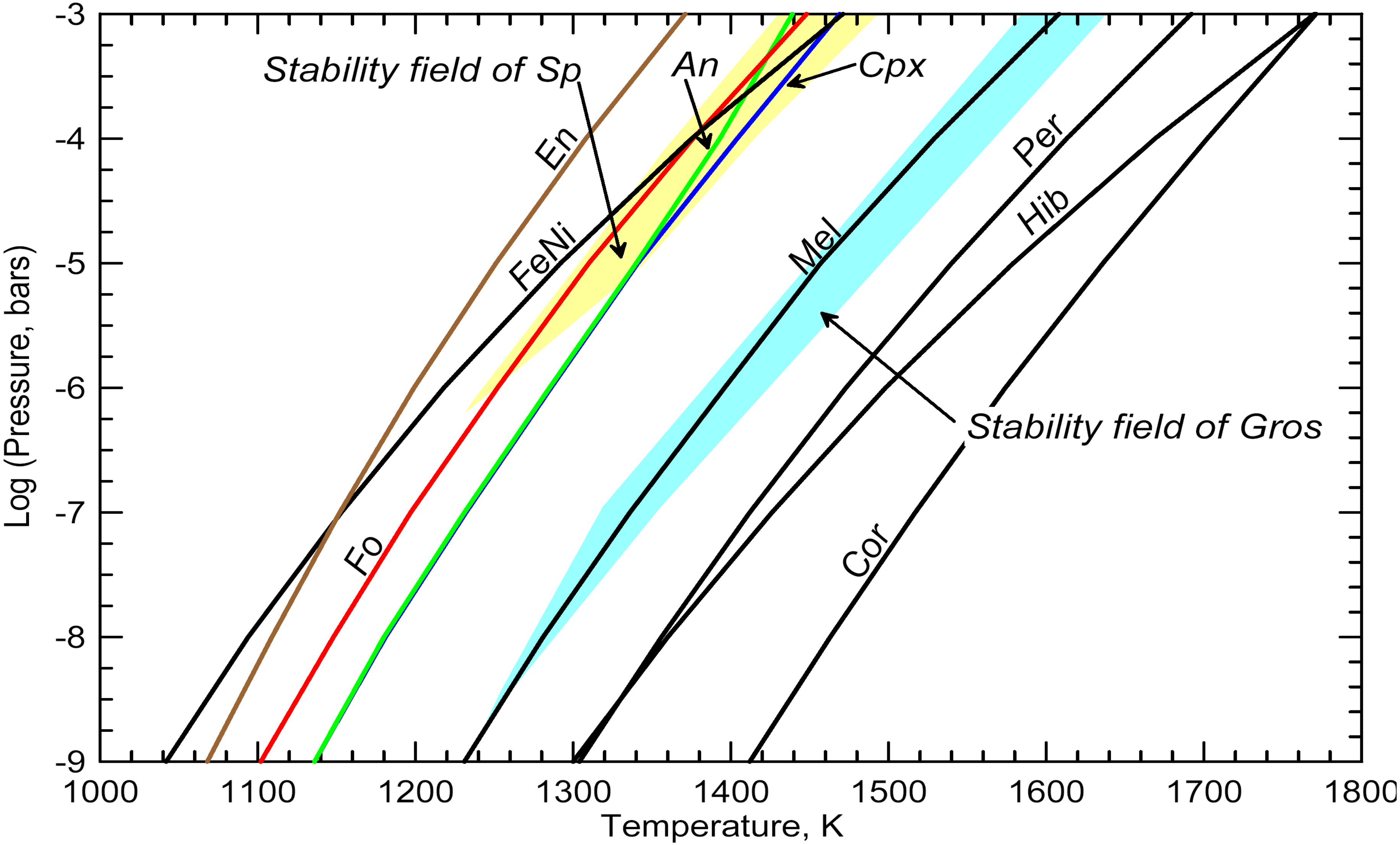
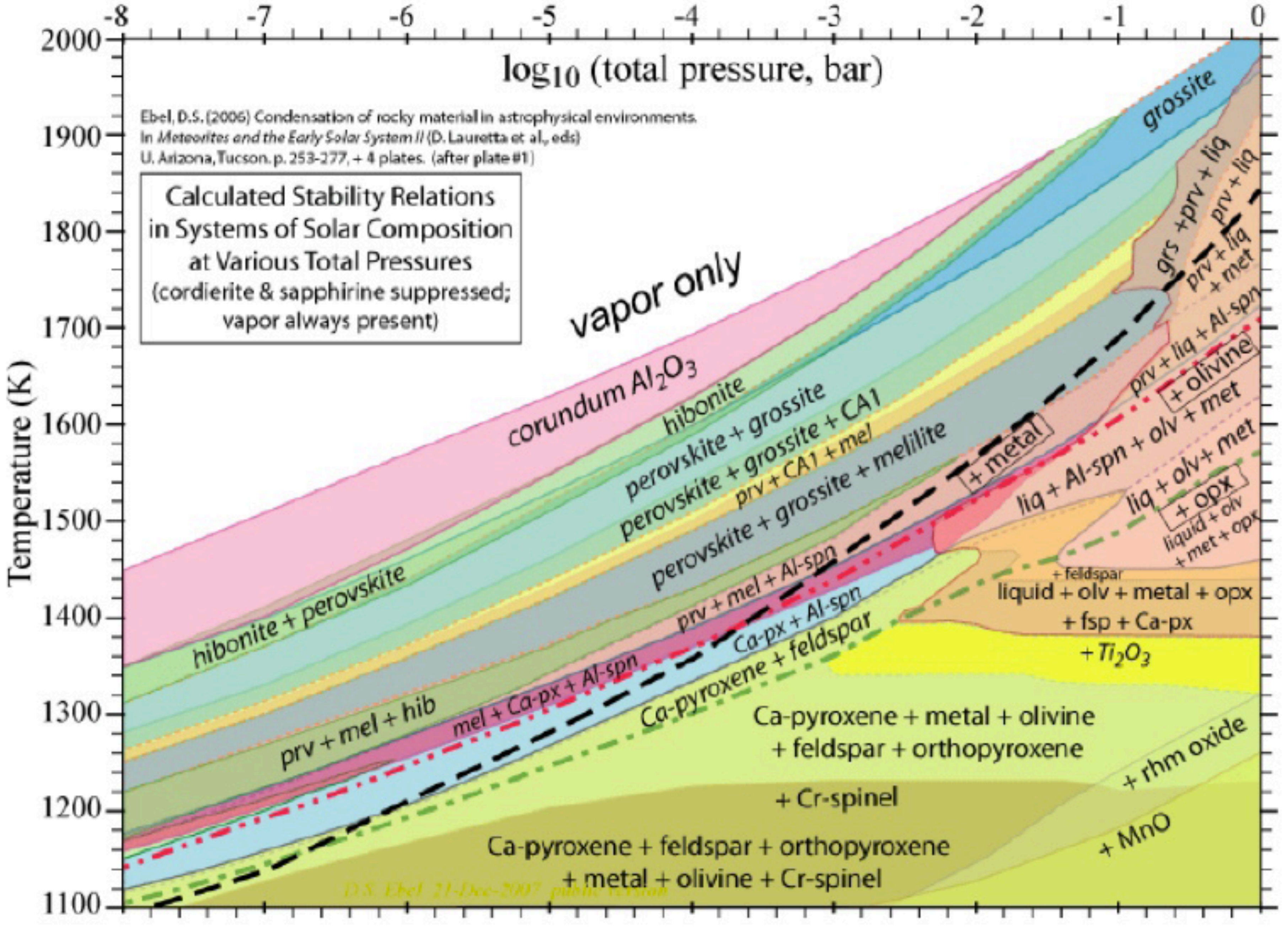


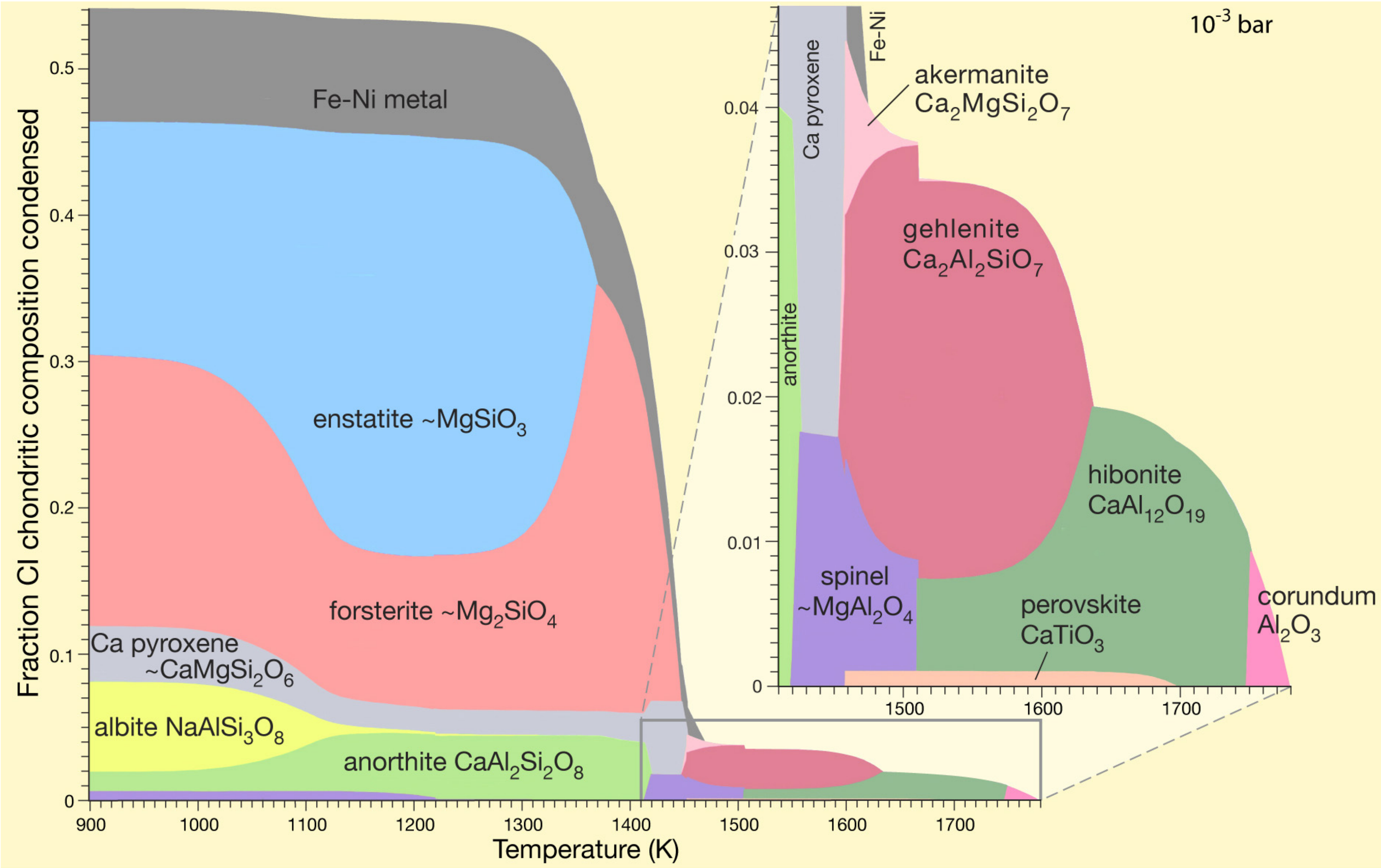
Fig. 1. Comparison of published results for vapor of solar composition (see section 3.1.2). Mineral abbreviations are t3 = Ti_3O_5, t4 = Ti_4O_7, C4T3 = $Ca_4Ti_3O_{10}$, C3T2 = $Ca_3Ti_2O_7$, sp = Al-spinel, cpx = Ca-pyroxene, and as listed in Table 1.



Petaev et al., 2005



log10 (total pressure, bar)
Temperature (K)
Ebel, D.S. (2006) Condensation of rocky material in astrophysical environments.
In Meteorites and the Early Solar System II (D. Lauretta et al., eds)
U. Arizona, Tucson. p. 253-277, + 4 plates. (after plate #1)
Calculated Stability Relations
in Systems of Solar Composition
at Various Total Pressures
(cordierite & sapphirine suppressed;
vapor always present)
vapor only
corundum Al2O3
hibonite
grossite
perovskite + grossite
perovskite + grossite + CA1
prv + CA1 + mel
perovskite + grossite + melilite
hibonite + perovskite
prv + mel + hib
mel + Ca-px + Al-spn
prv + mel + Al-spn
Ca-px + Al-spn
Ca-pyroxene + feldspar
+ metal
+ olivine
liq + Al-spn + olv + met
liq + olv + met
+ opx
liquid + olv + met + opx
+ feldspar
liquid + olv + metal + opx
+ fsp + Ca-px
+ Ti2O3
Ca-pyroxene + metal + olivine
+ feldspar + orthopyroxene
+ Cr-spinel
Ca-pyroxene + feldspar + orthopyroxene
+ metal + olivine + Cr-spinel
+ rhm oxide
+ MnO
grs + prv + liq
prv + liq
prv + liq + met
prv + liq + Al-spn
D.S. Ebel 21-Dec-2007 public version



Courtesy of A. Davis

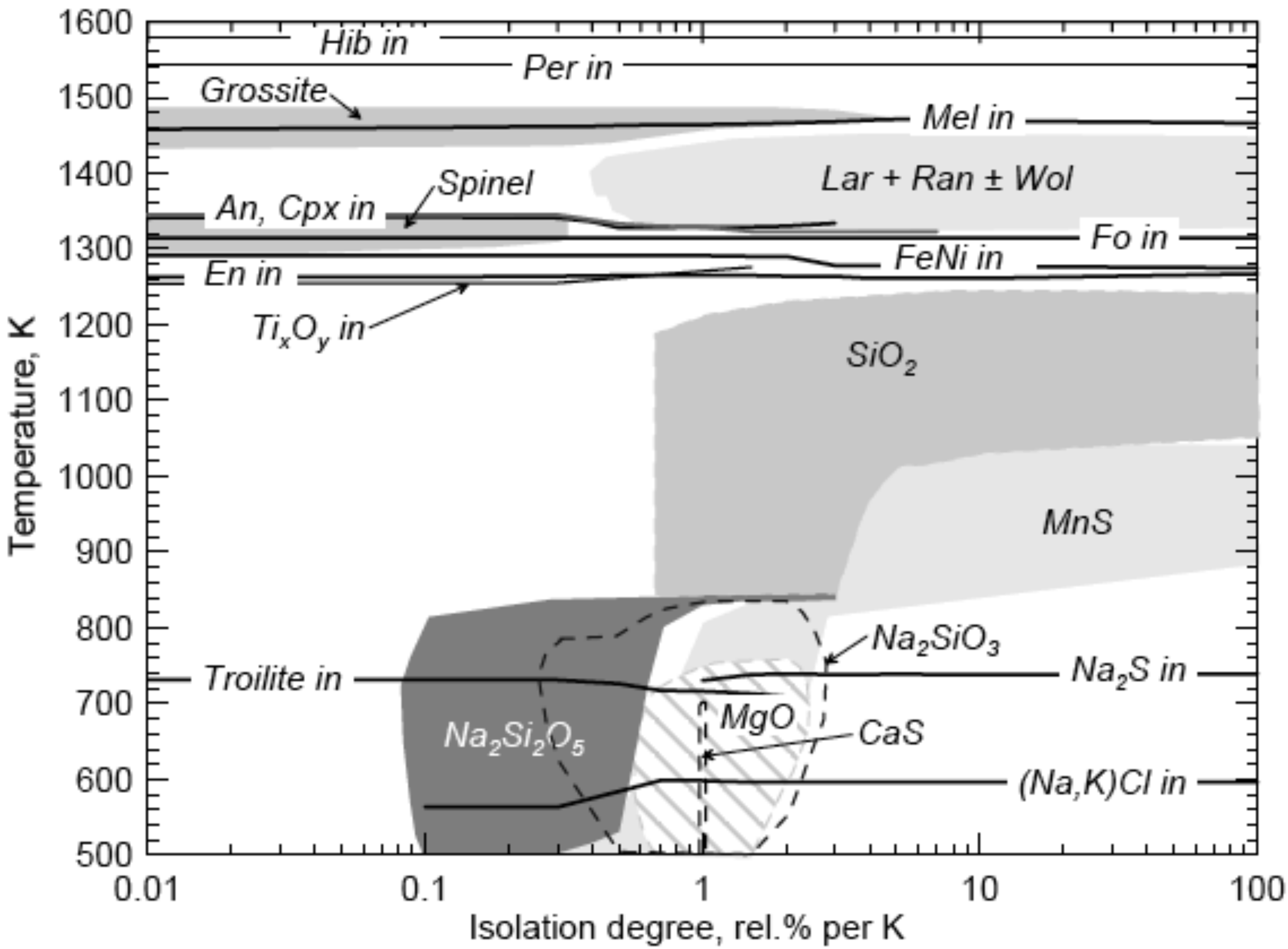
Condensation **W**ith **P**artial **I**solation model*

As condensation proceeds a specified fraction of the existing condensate is withdrawn from reactive contact with the residual gas so that:

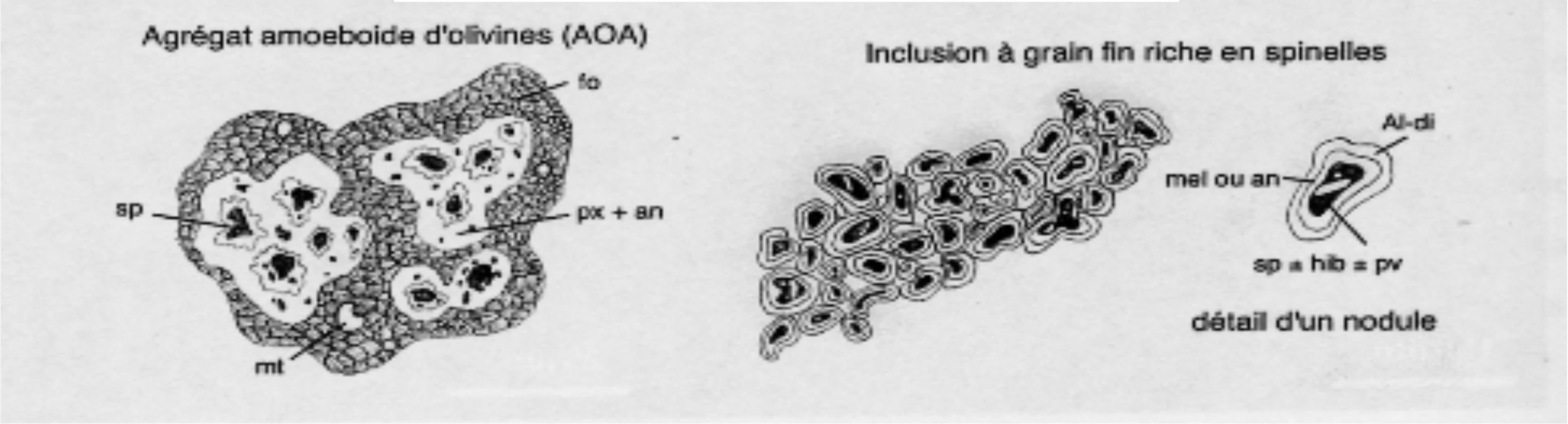
- System contains two categories of condensate – *Reactive solids* and *Inert solids*
- *Reactive solids* (M_r) are exposed to the residual gas and remain in complete equilibrium with it
- *Inert solids* (M_i) are isolated from the residual gas
- *Isolation degree* ξ is the relative amount (% per K) of reactive solids that is withdrawn from the reactive system at any given temperature interval
- *Isolation rate* (dM_i/dT) is the absolute amount of reactive solids, Δm_i (moles), that is withdrawn from the reactive system at any given temperature interval

* *Petaev M. I. and Wood J. A.* (1998) *MAPS* **33**, 1123-1137.

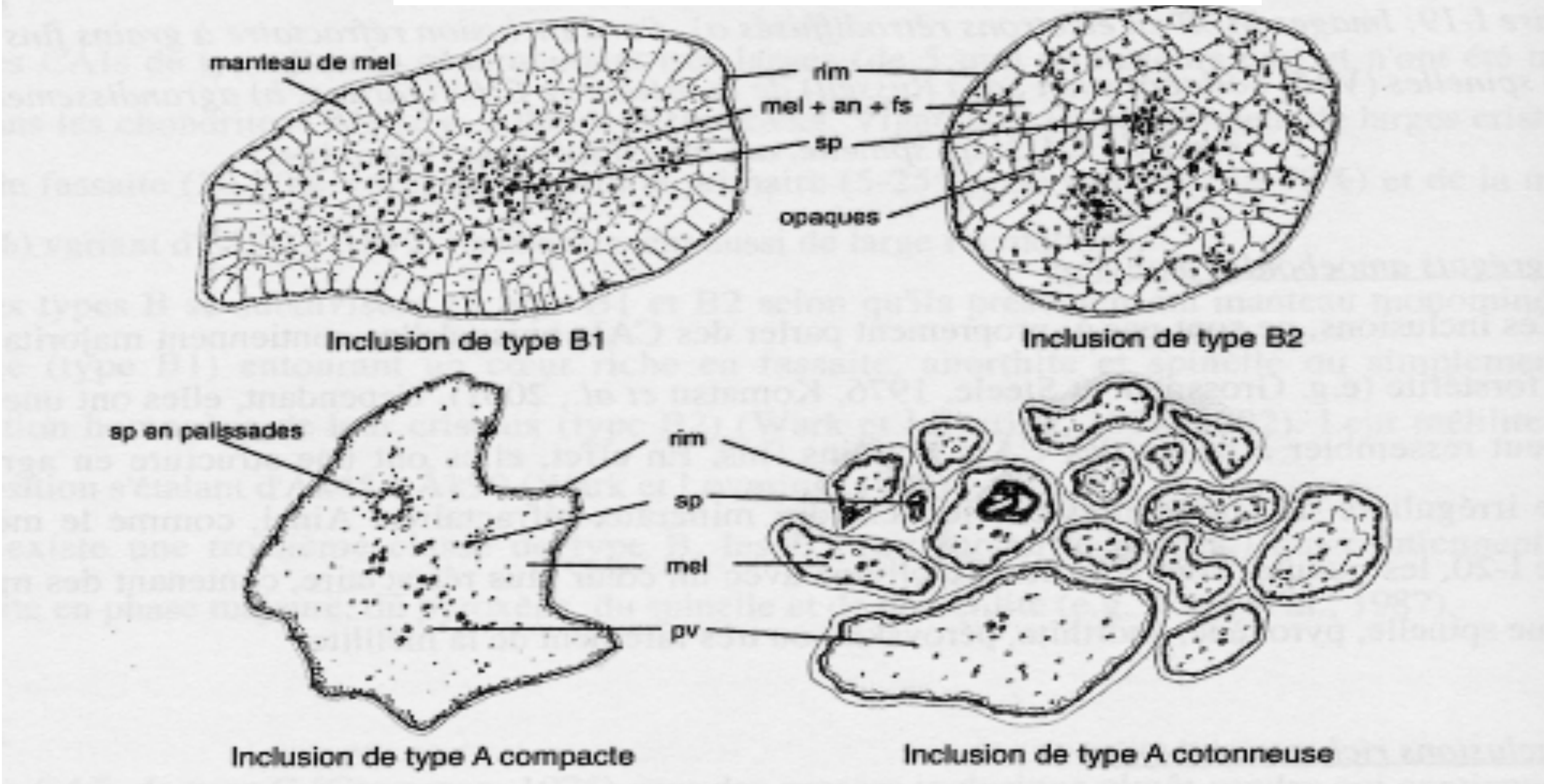
Condensation With Partial Isolation model



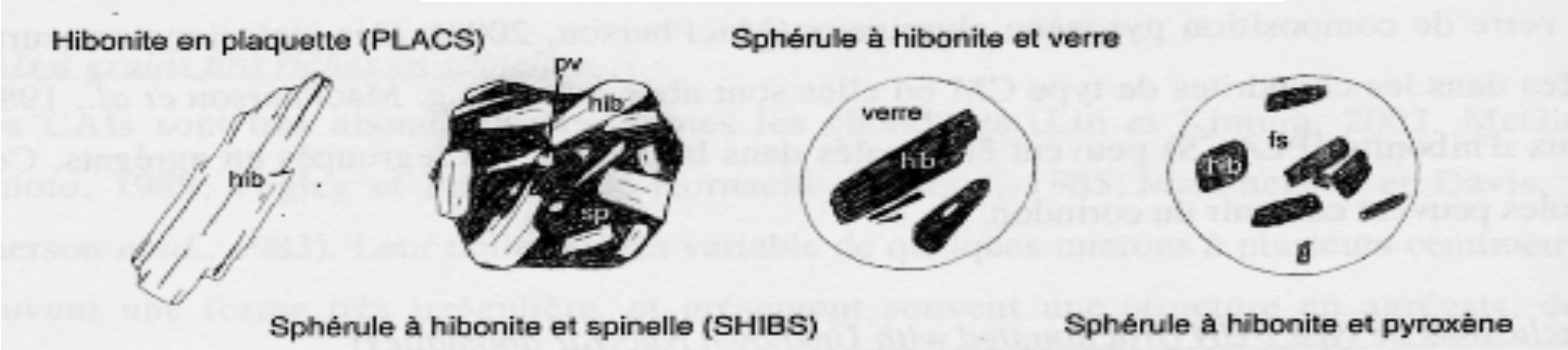
Fine-grained inclusions



Coarse-grained inclusions

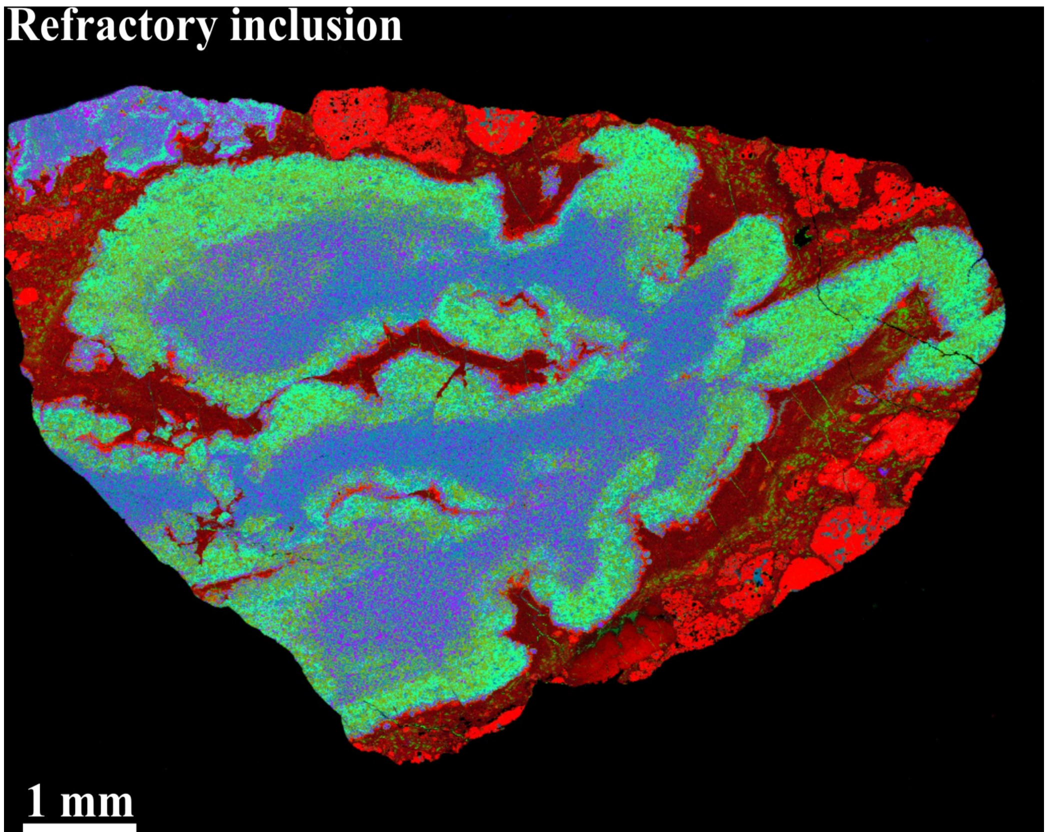


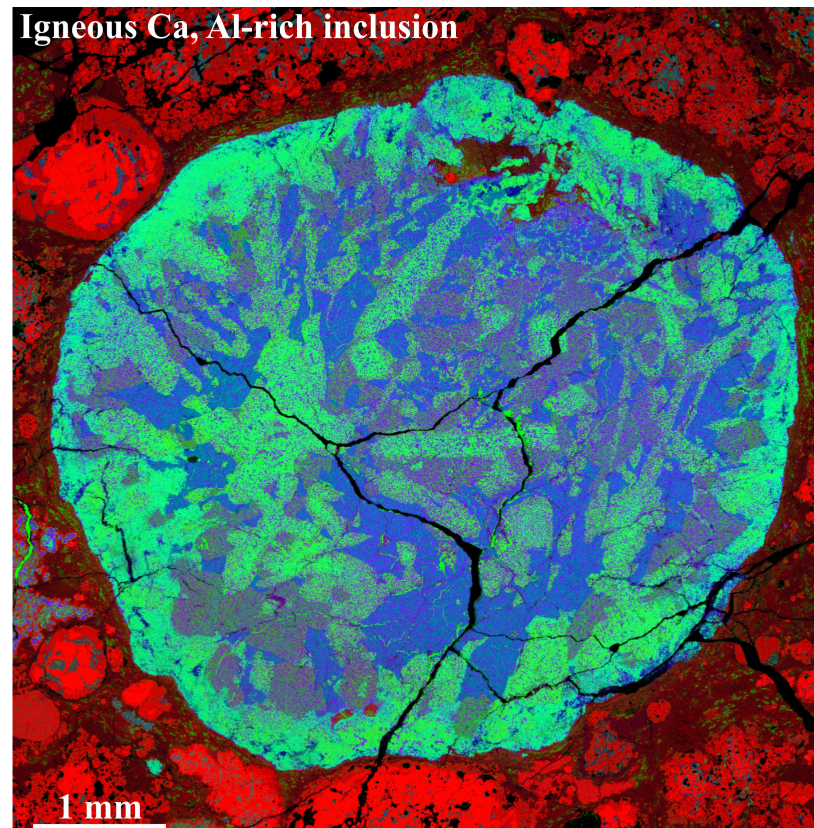
Hibonite-bearing inclusions



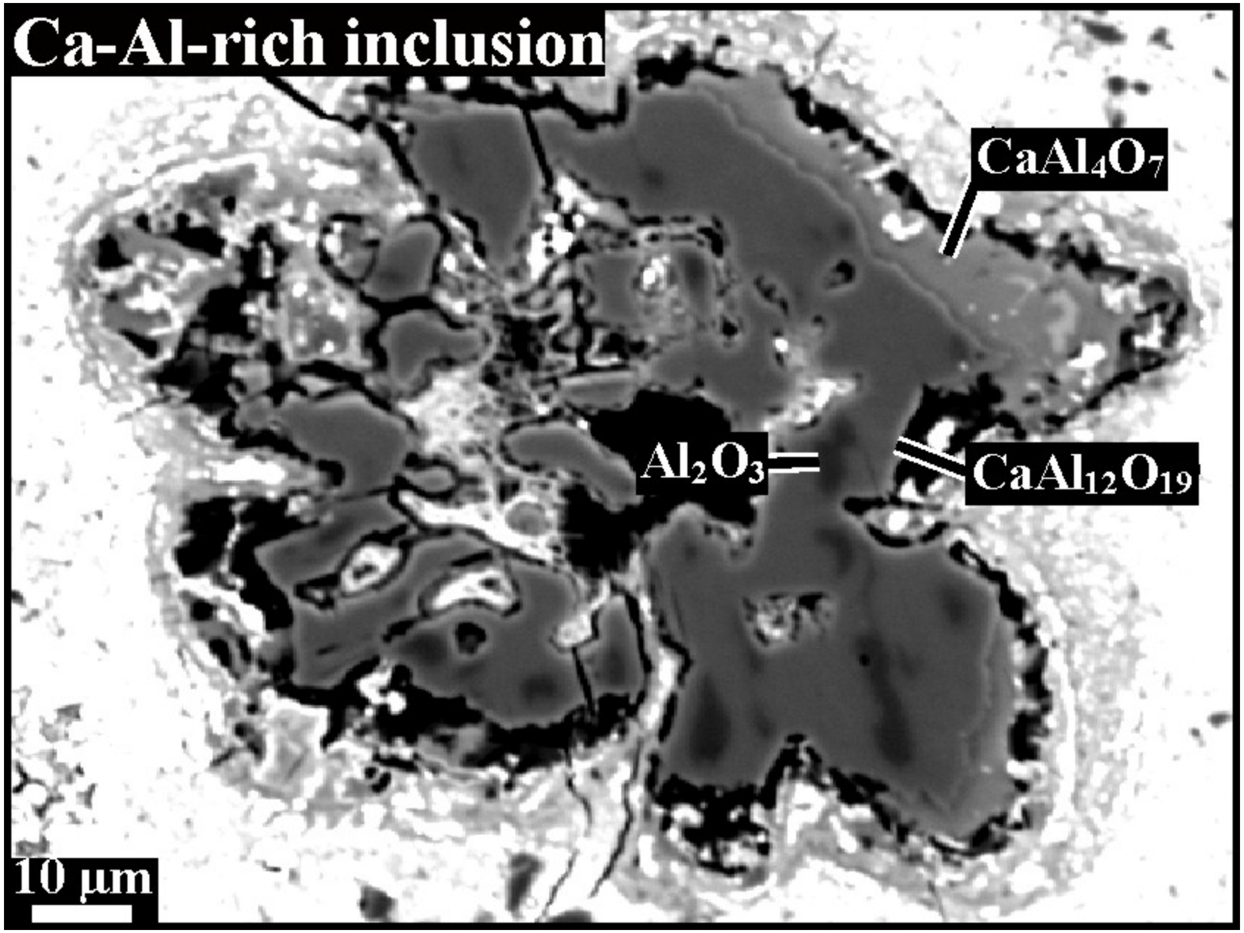
Calcium-aluminum-rich inclusions

- irregularly-shaped (unmelted?) & spheroidal (melted) CAIs; coexist within a chondrite
- irreg.-shaped, fine-grained, porous inclusions with characteristic volatility-controlled rare earth element (REE) patterns (Type II): *solid condensates*

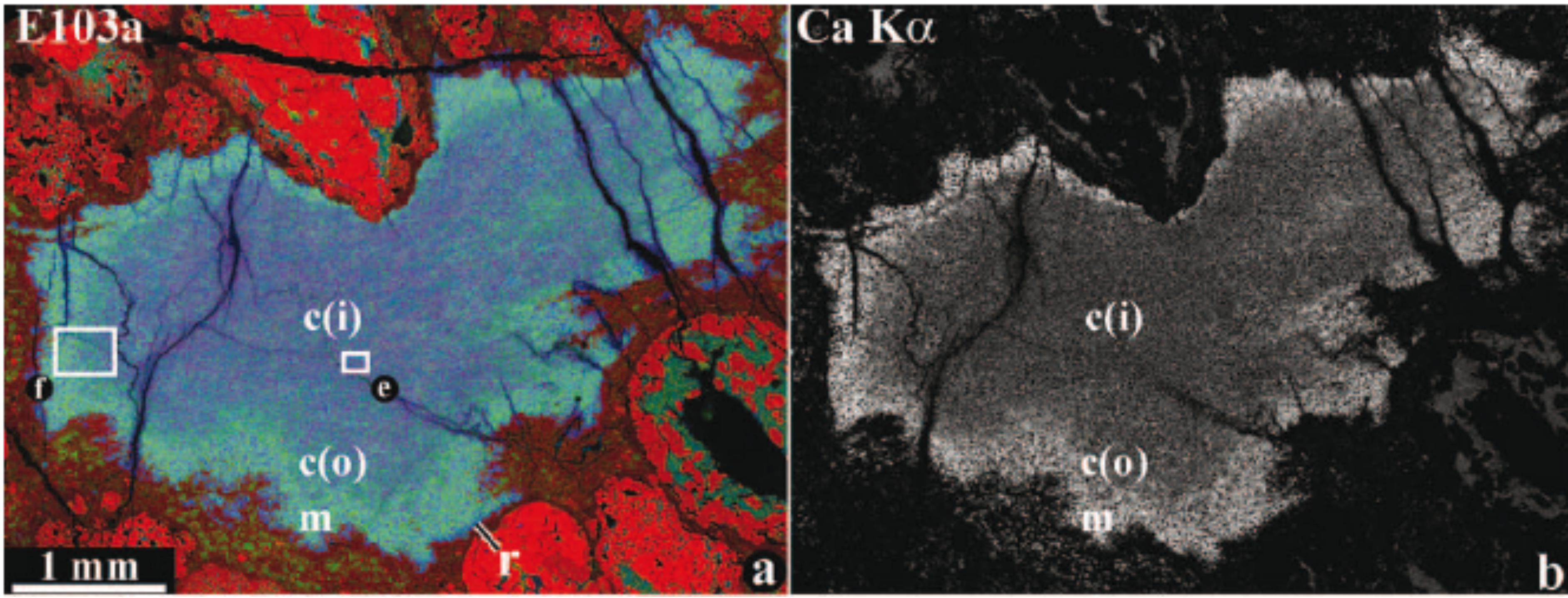




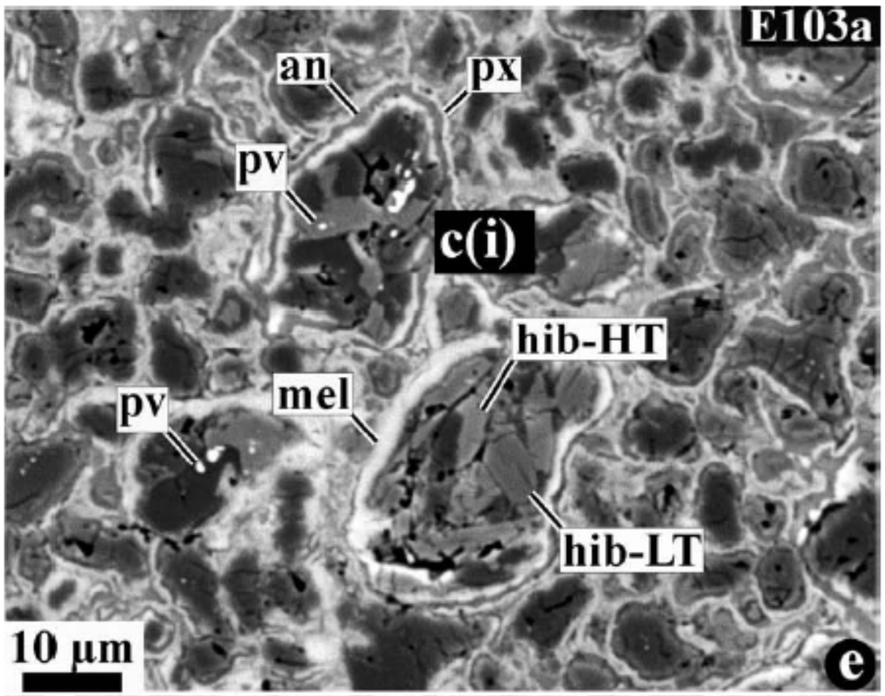
Corundum bearing fine-grained inclusions

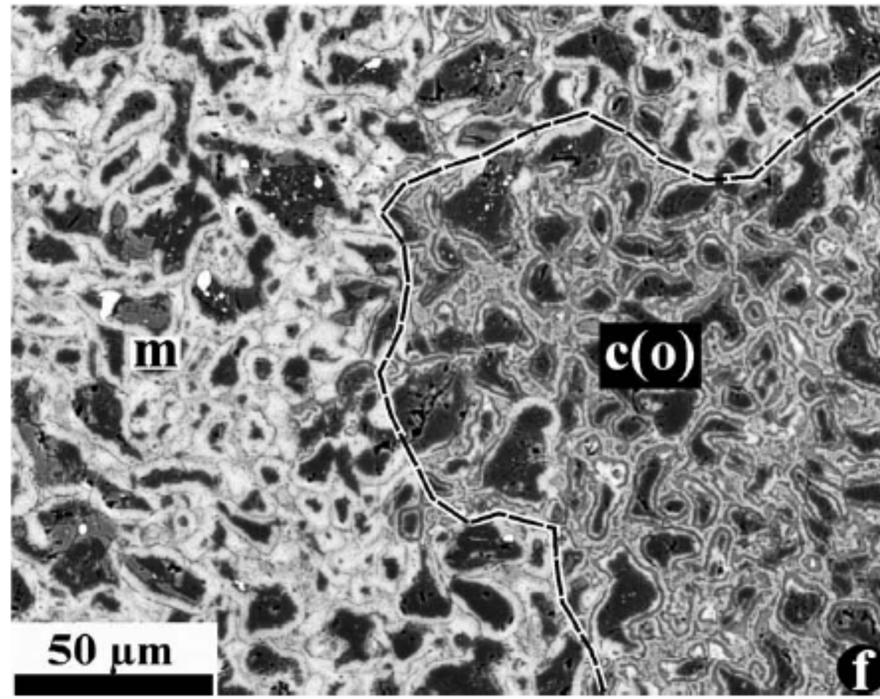


Fine-grained spinel-rich CAI

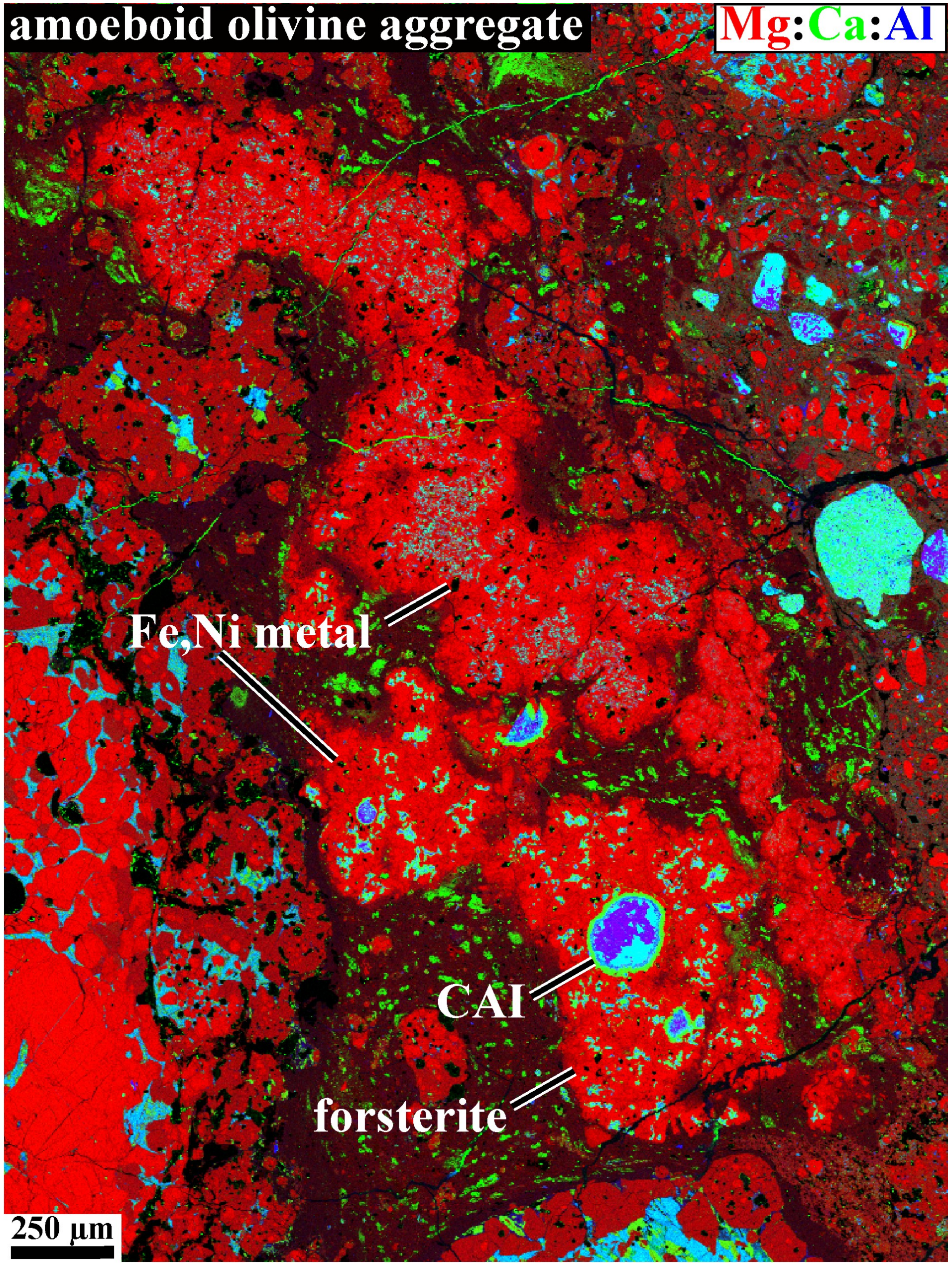


Fine-grained spinel-rich CAI

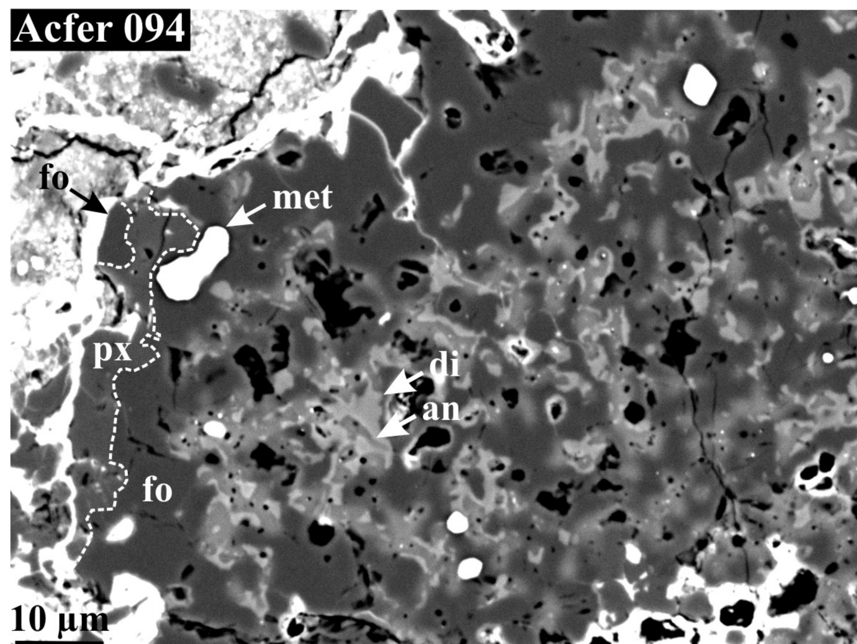




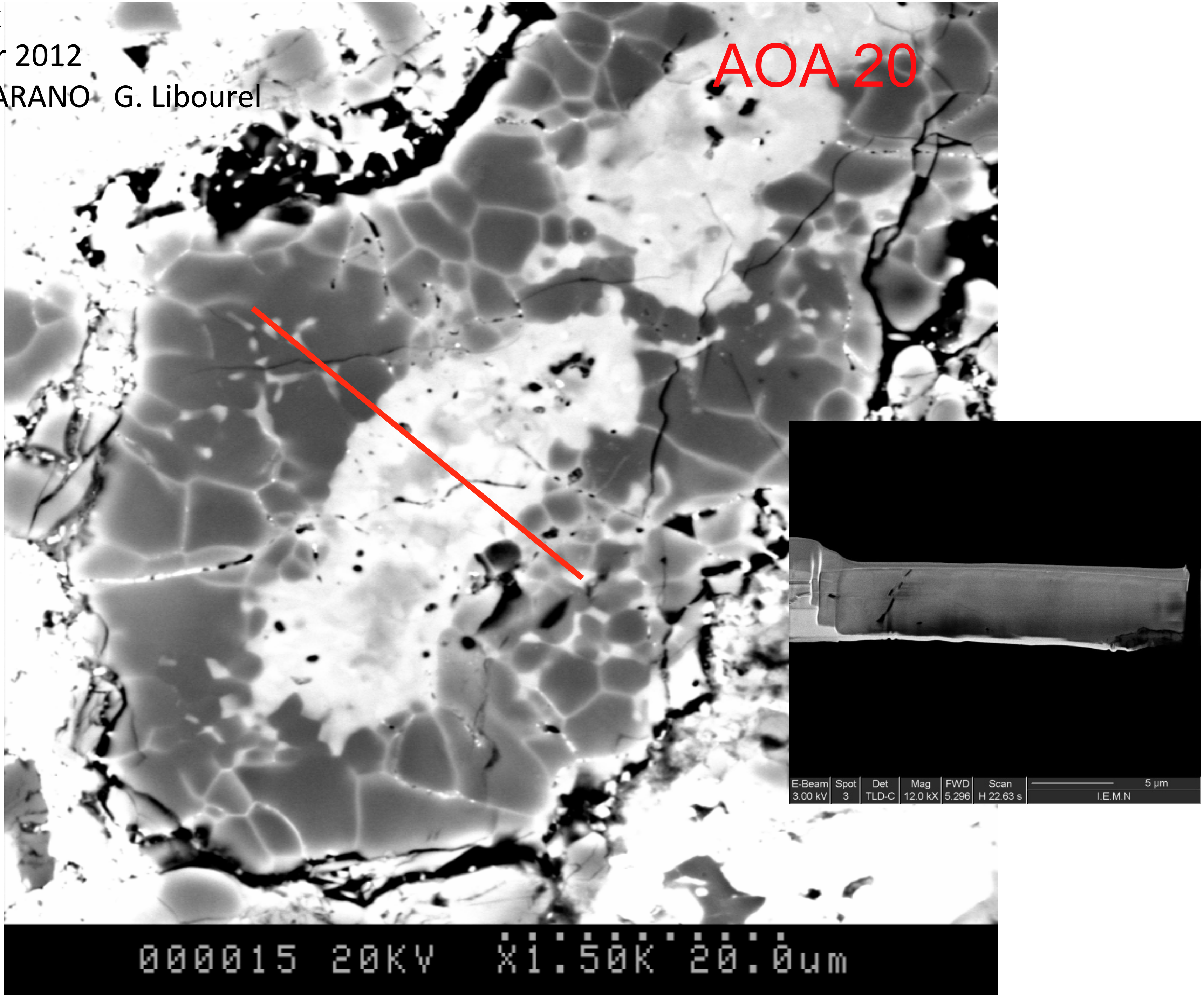
Amoeboid olivine aggregates (AOAs)

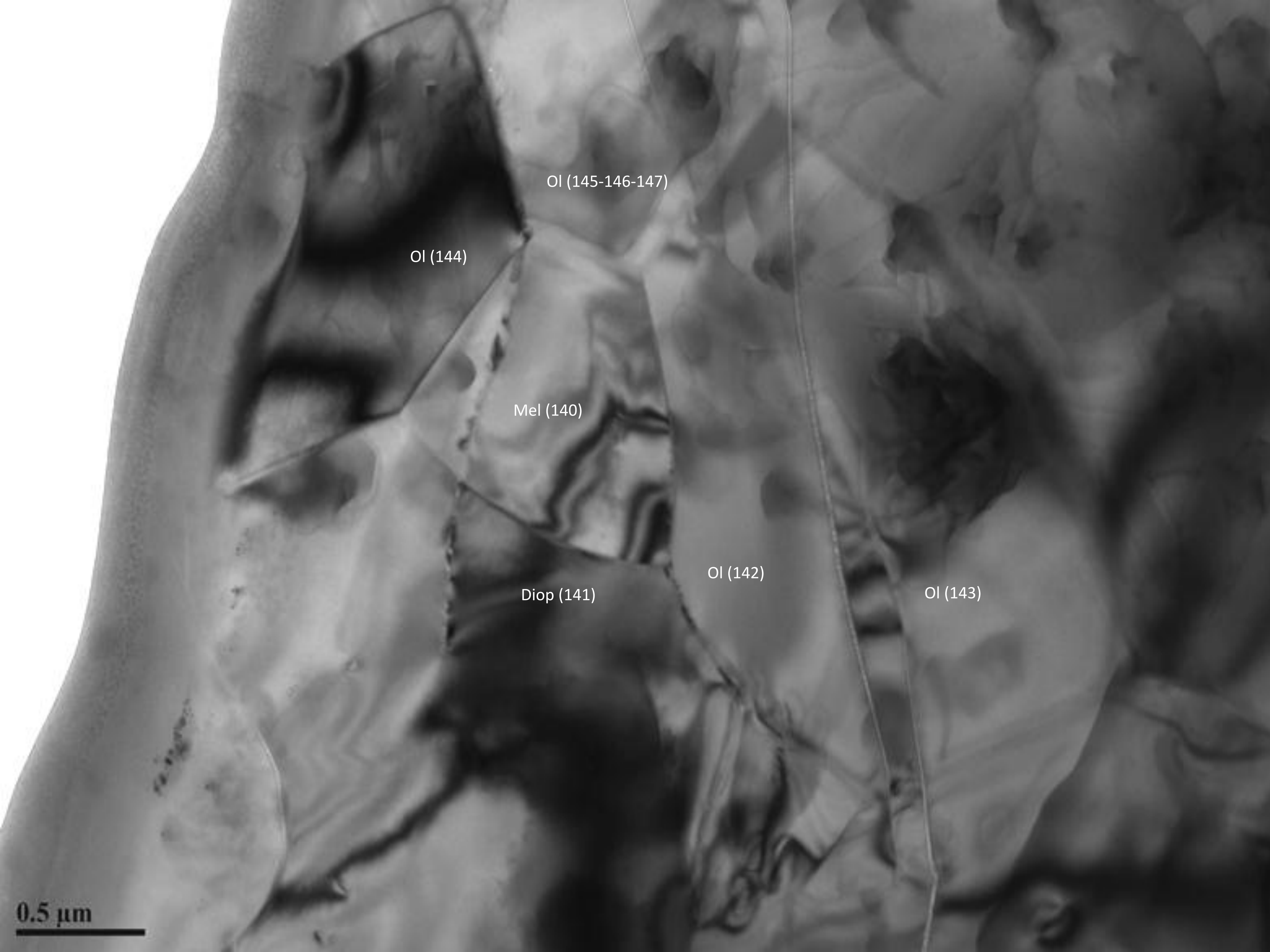


- aggregates of CAIs, forsterite (Mg_2SiO_4), and metallic Fe-Ni
- minor component: 0.1-5 vol.%; 10 µm to 5 mm in size
- fine-grained: 5-20 µm; porous; irregularly shaped
- condensed from gas of solar composition at 1350-1450 K

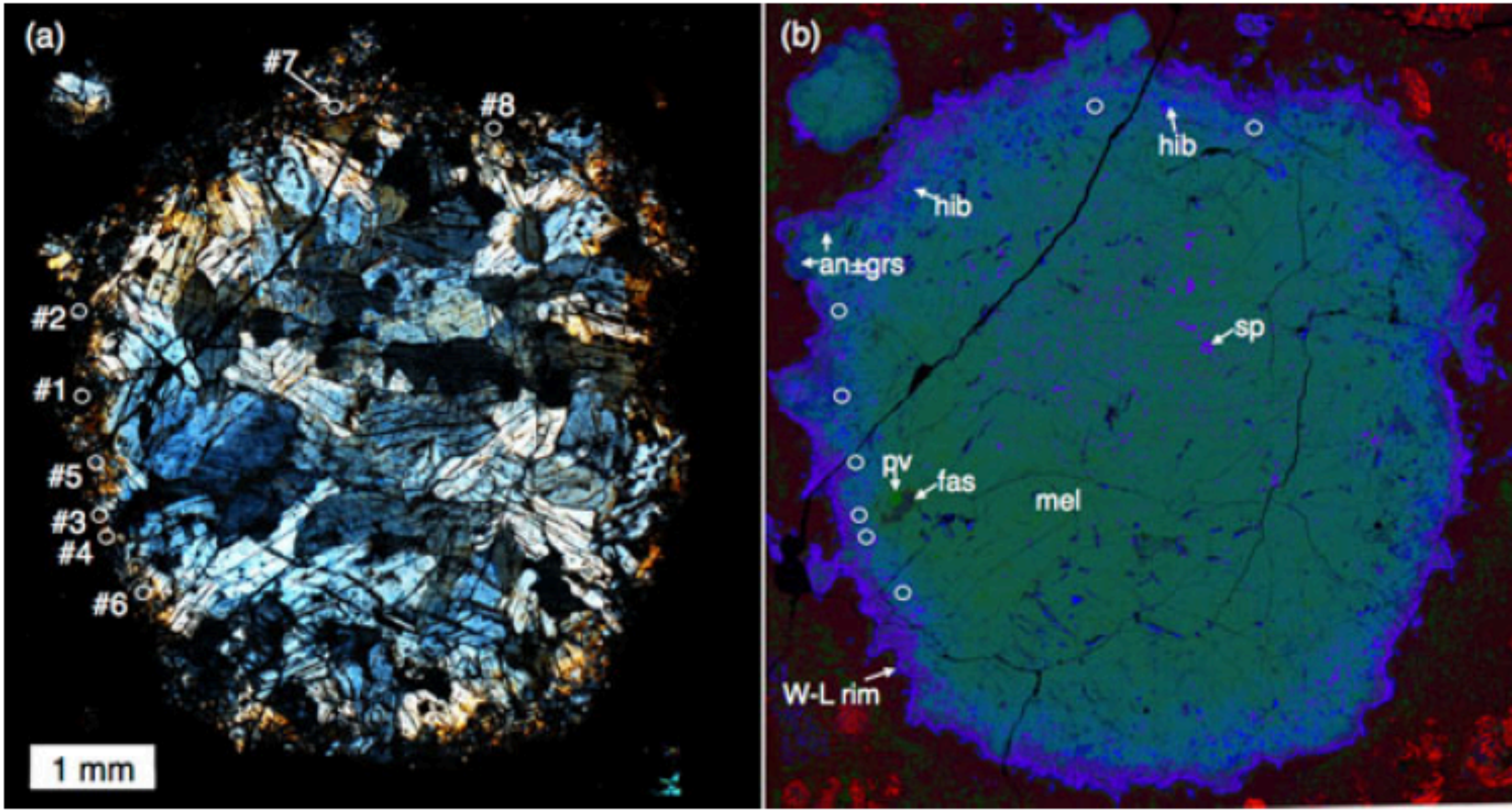


H. Leroux
26 janvier 2012
AOA VIGARANO G. Libourel




Ol (145-146-147)
Ol (144)
Mel (140)
Ol (142)
Ol (143)
Diop (141)
0.5 µm

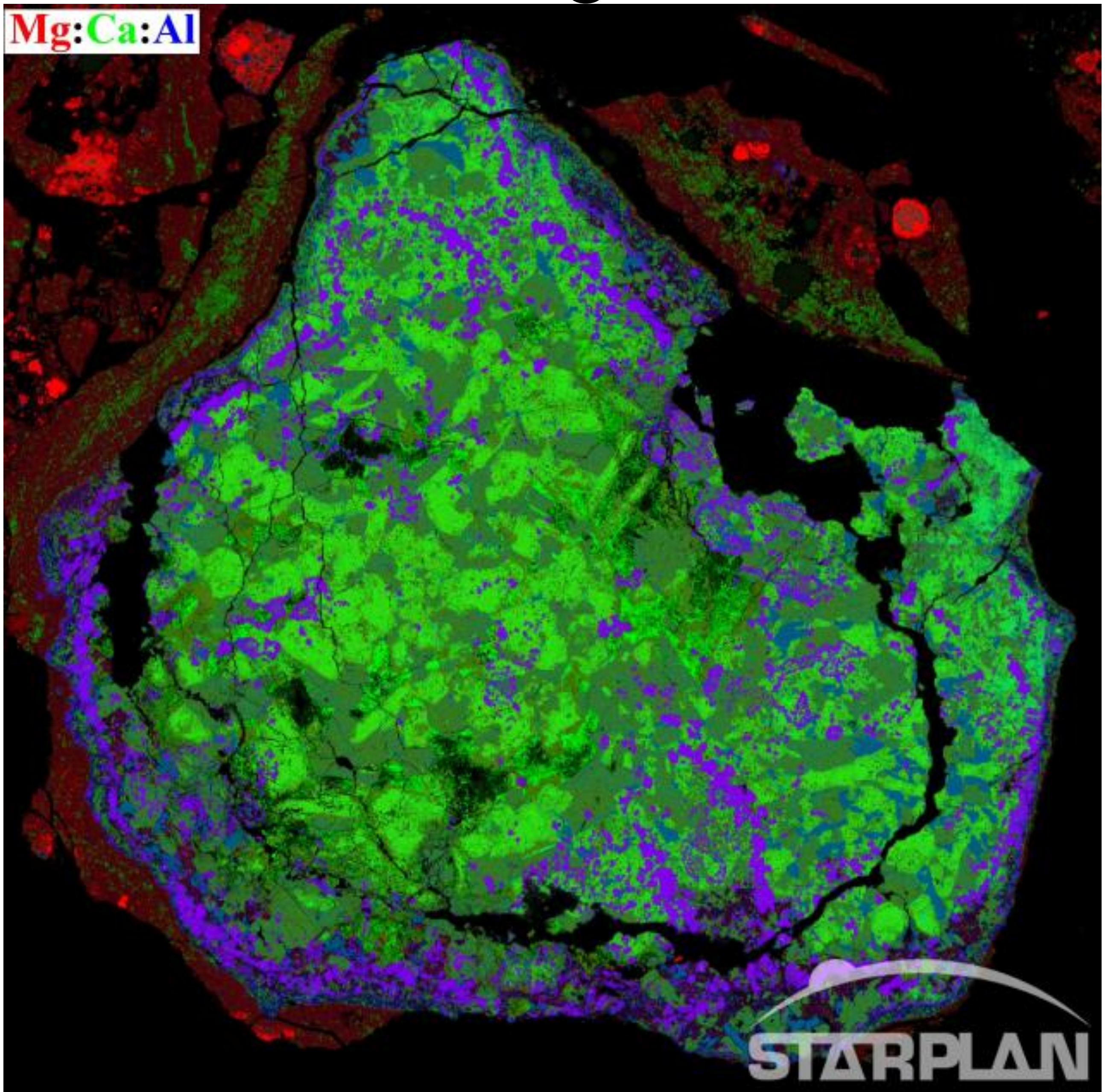
Corse-grained inclusions



Type A CAI ON01 of the Allende carbonaceous chondrite (Park et al. 2012)

Compact Type A

Corse-grained inclusions



Type B1 CAI Efremovka CV

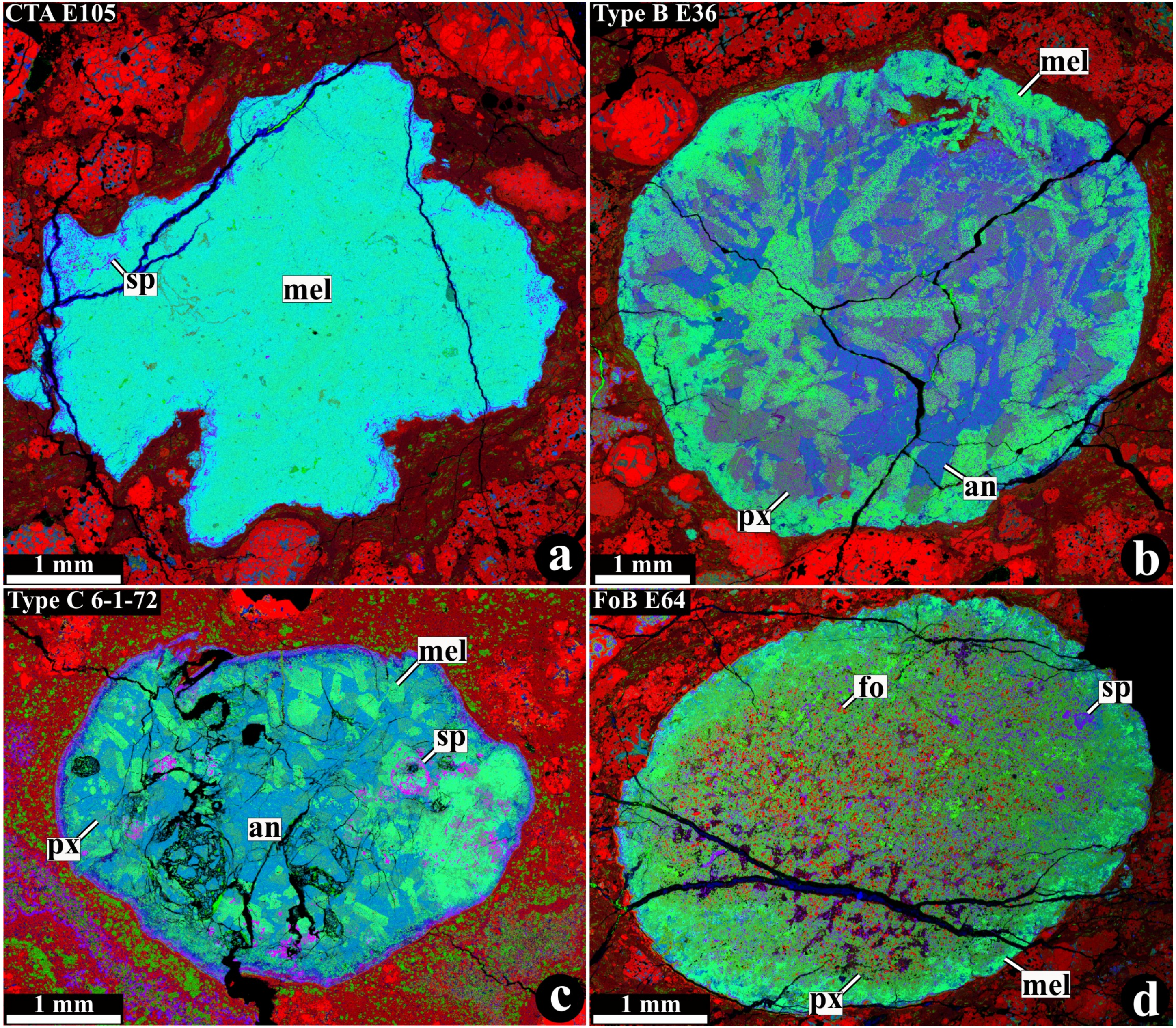
Igneous CAIs: Compact Type A, Type B, Type C

mel+sp

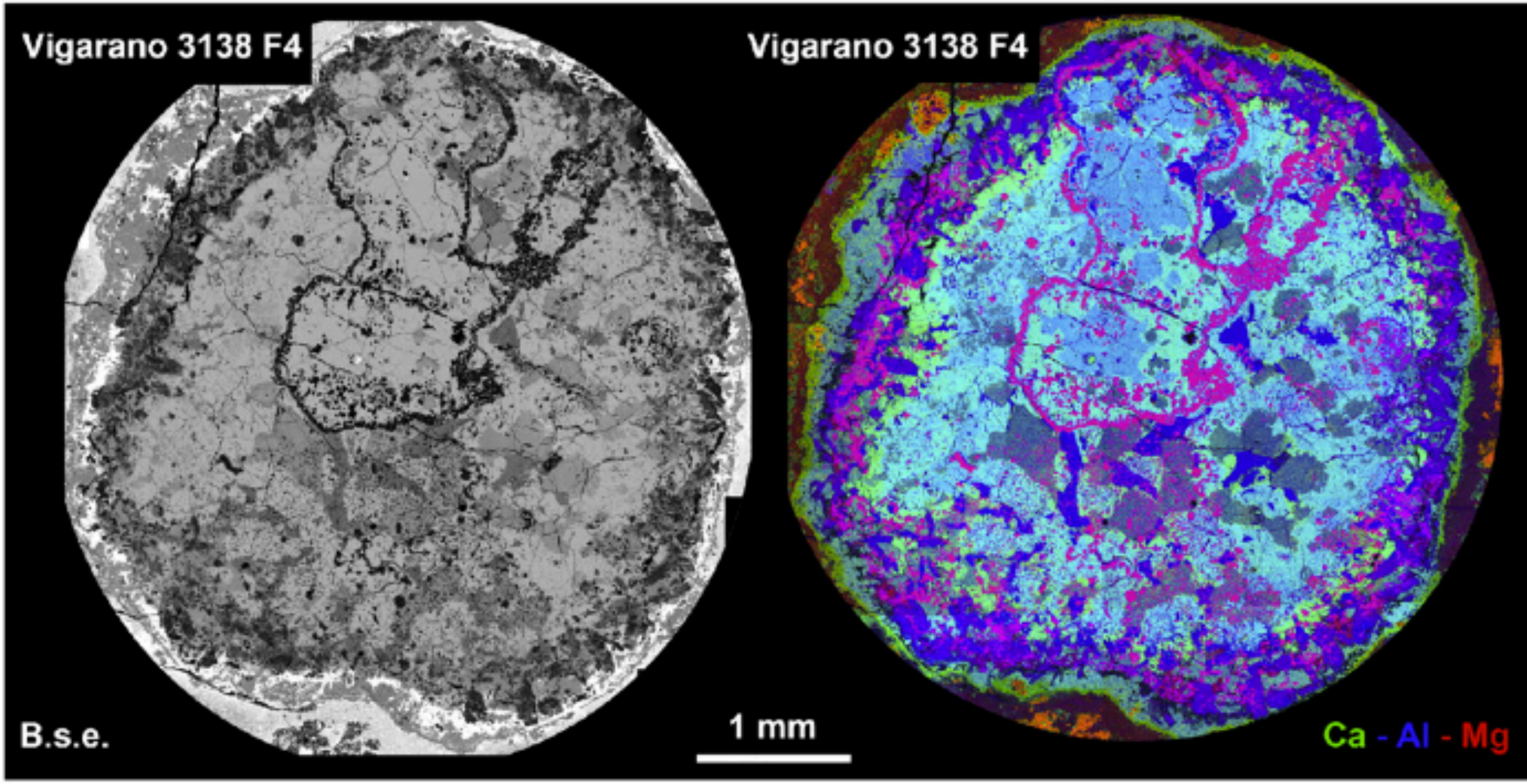
mel+px+an +sp

an+px+sp ±mel

mel+px+an +fo+sp



Complex Igneous CAIs



MacPherson et al. 2012

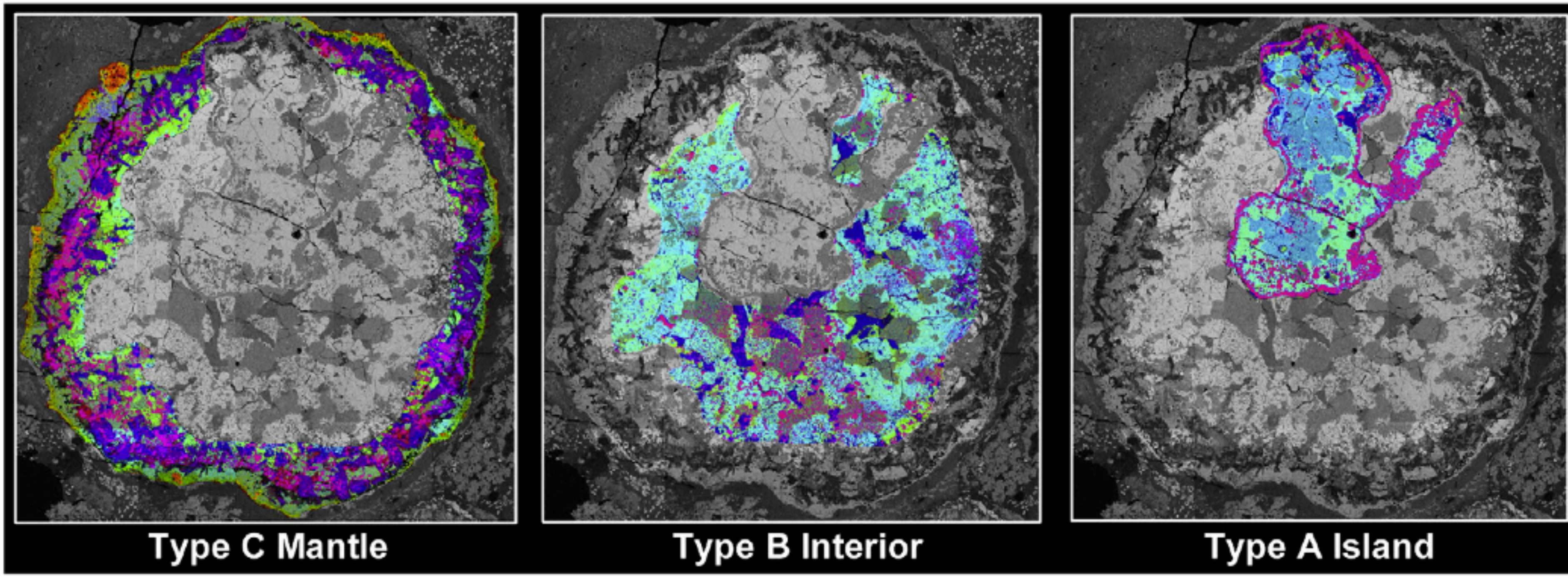
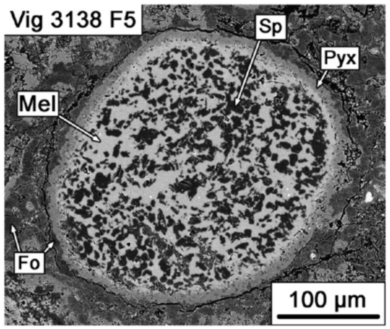
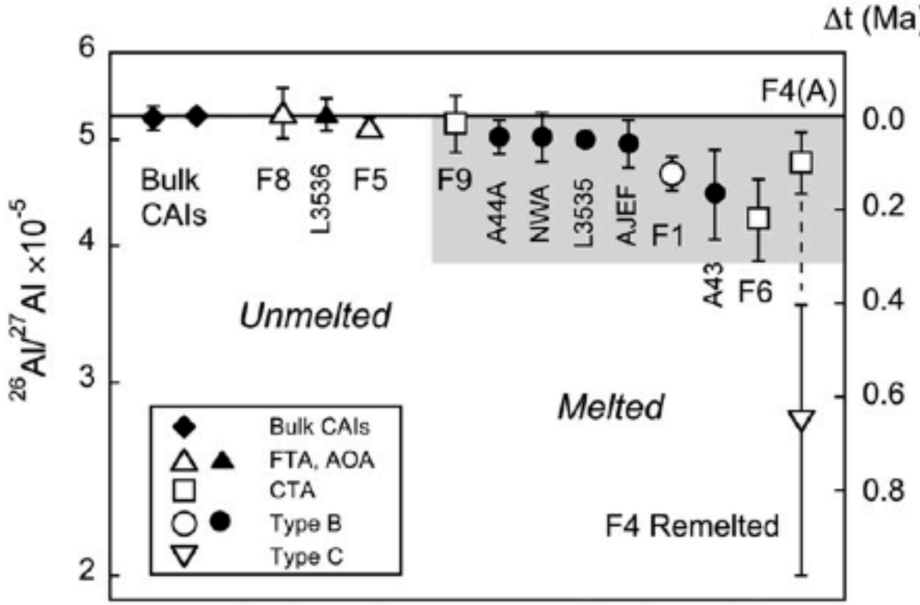
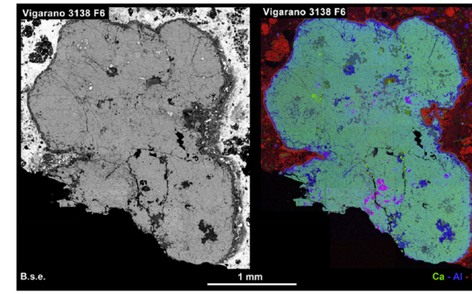


Fig. 2. False-color X-ray element maps of the three lithologic units in Vigarano 3138 F4, superimposed onto back-scattered electron images. Colors as in Fig. 1.

Not all CAIs formed at "time zero",







MacPherson et al. 2012

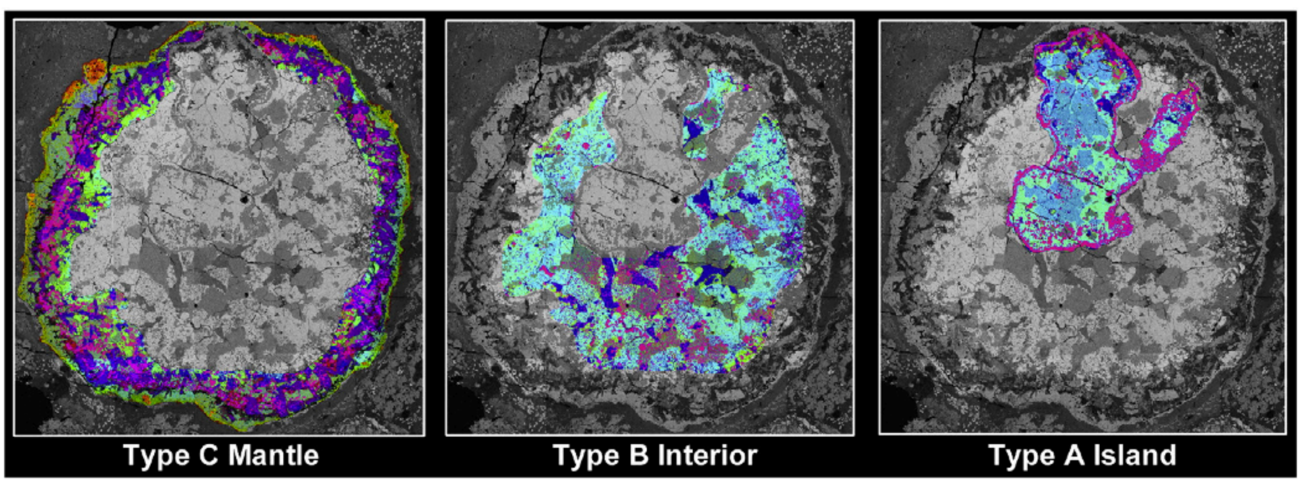
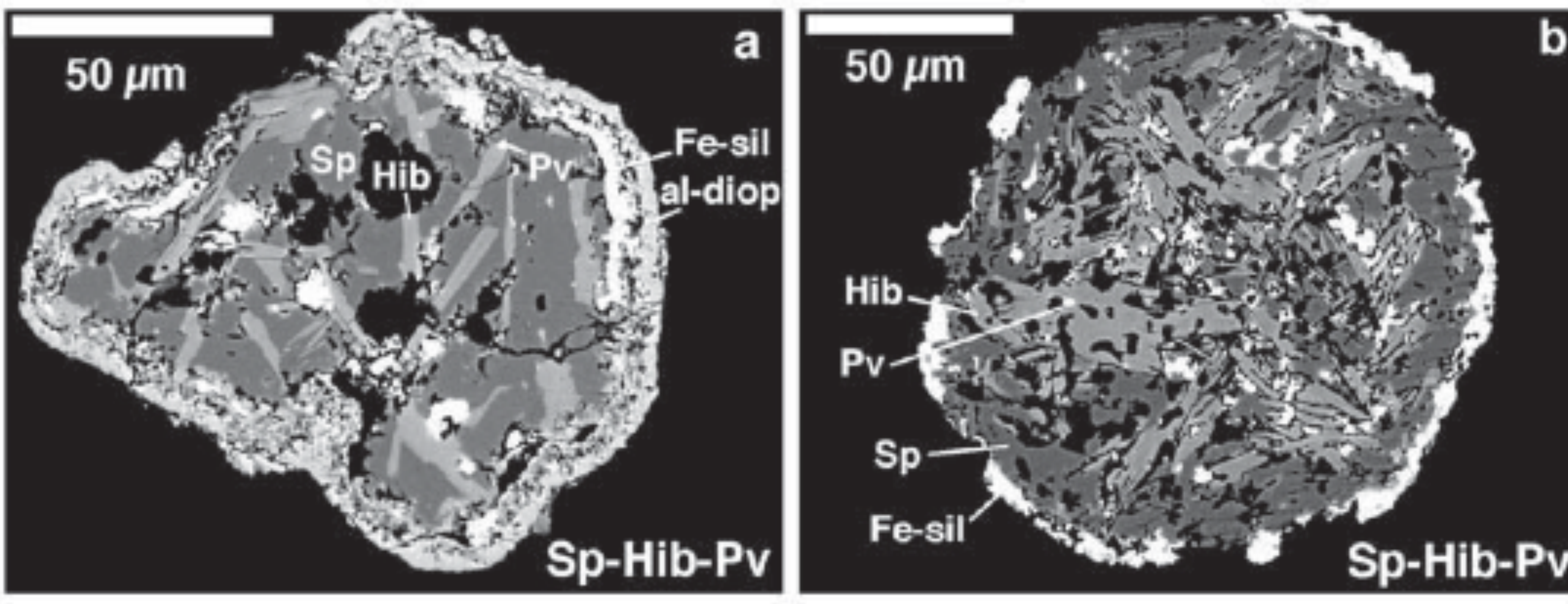
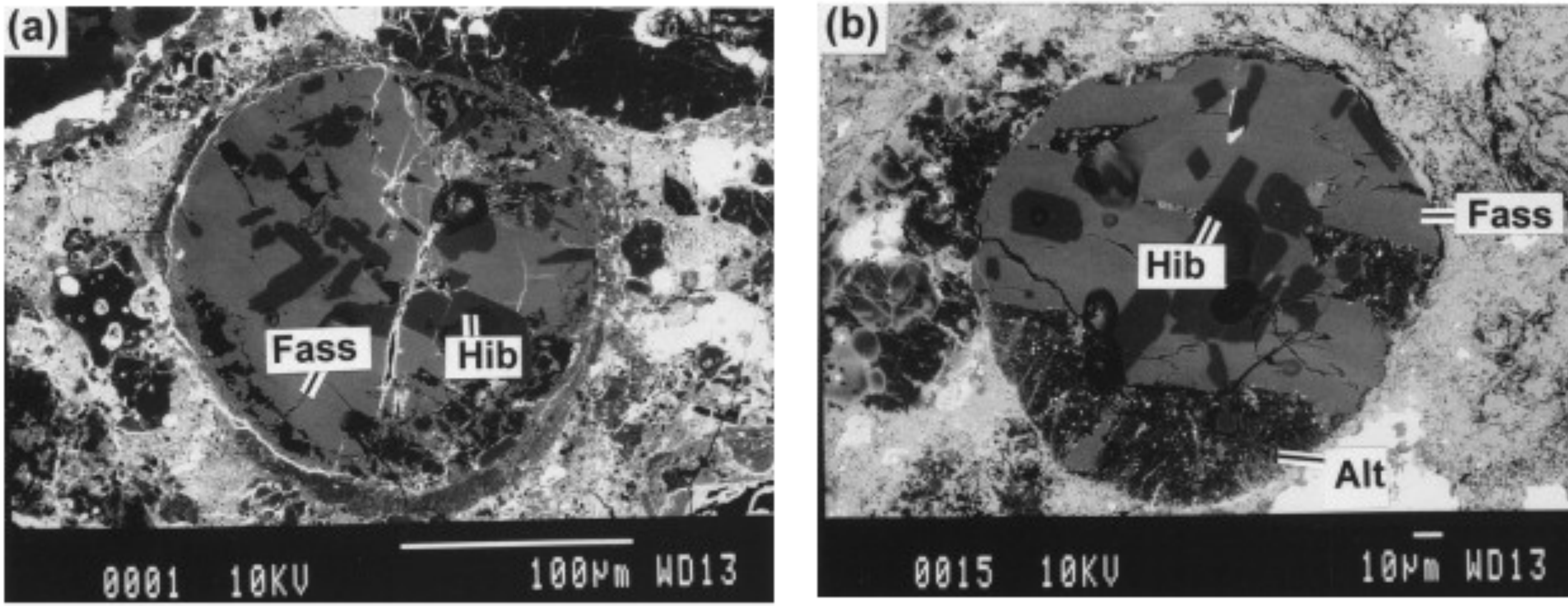


Fig. 2. False-color X-ray element maps of the three lithologic units in Vigarano 3138 F4, superimposed onto back-scattered electron images. Colors as in Fig. 1.

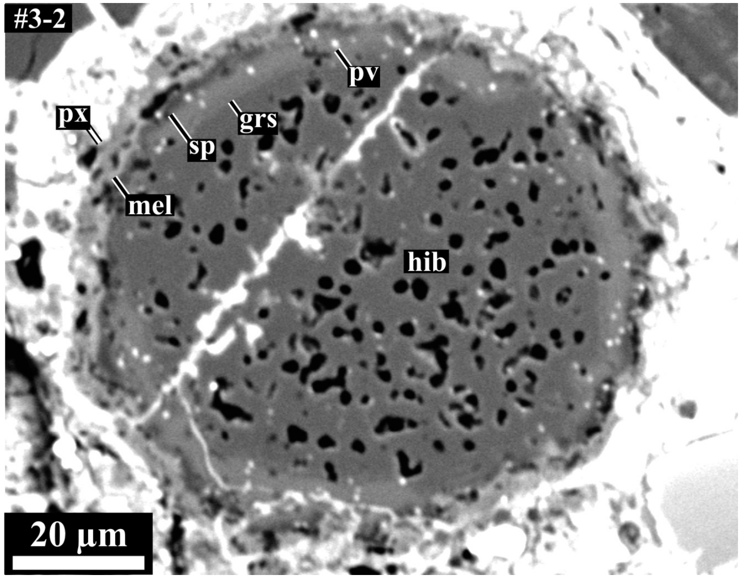
SHIBS Inclusions

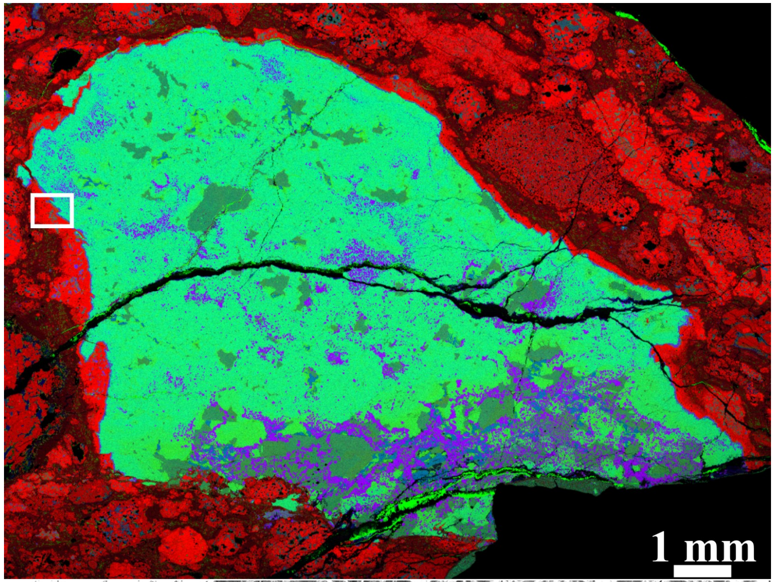


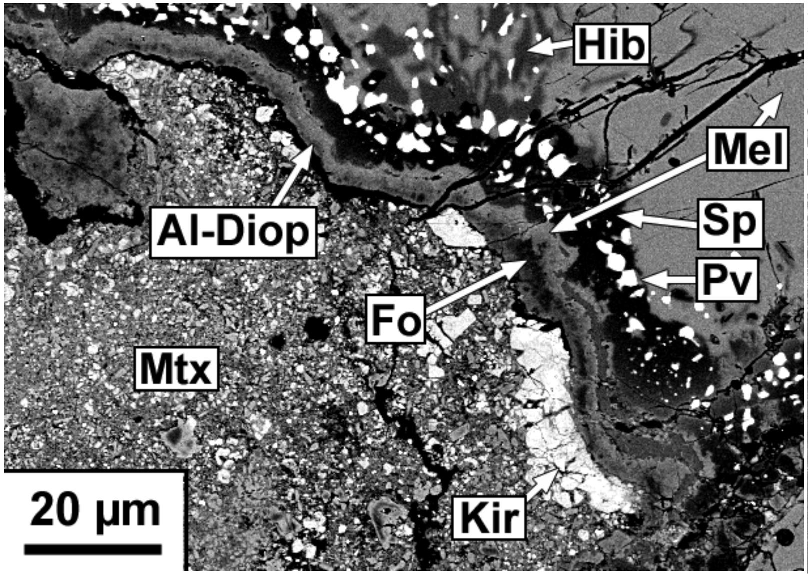
Hibonite spherules

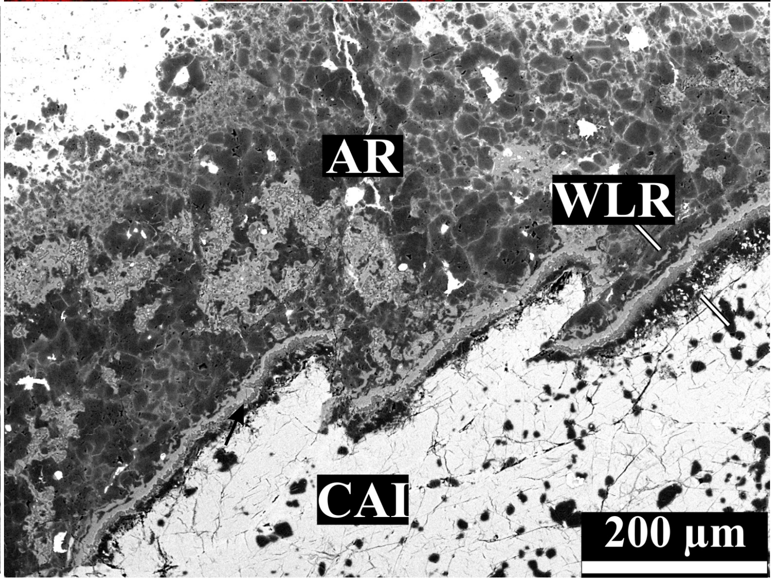


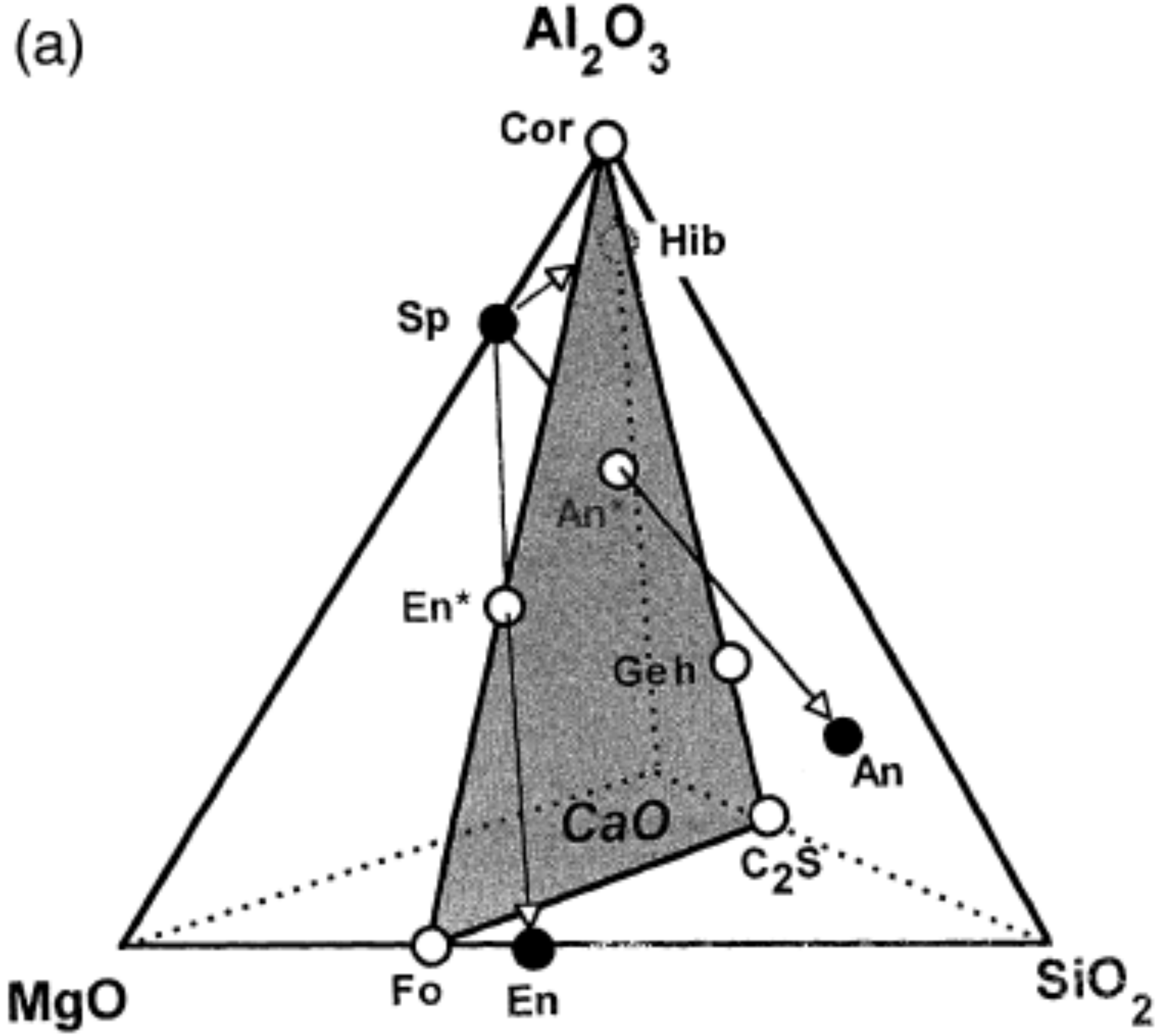
Wark-lovering rims



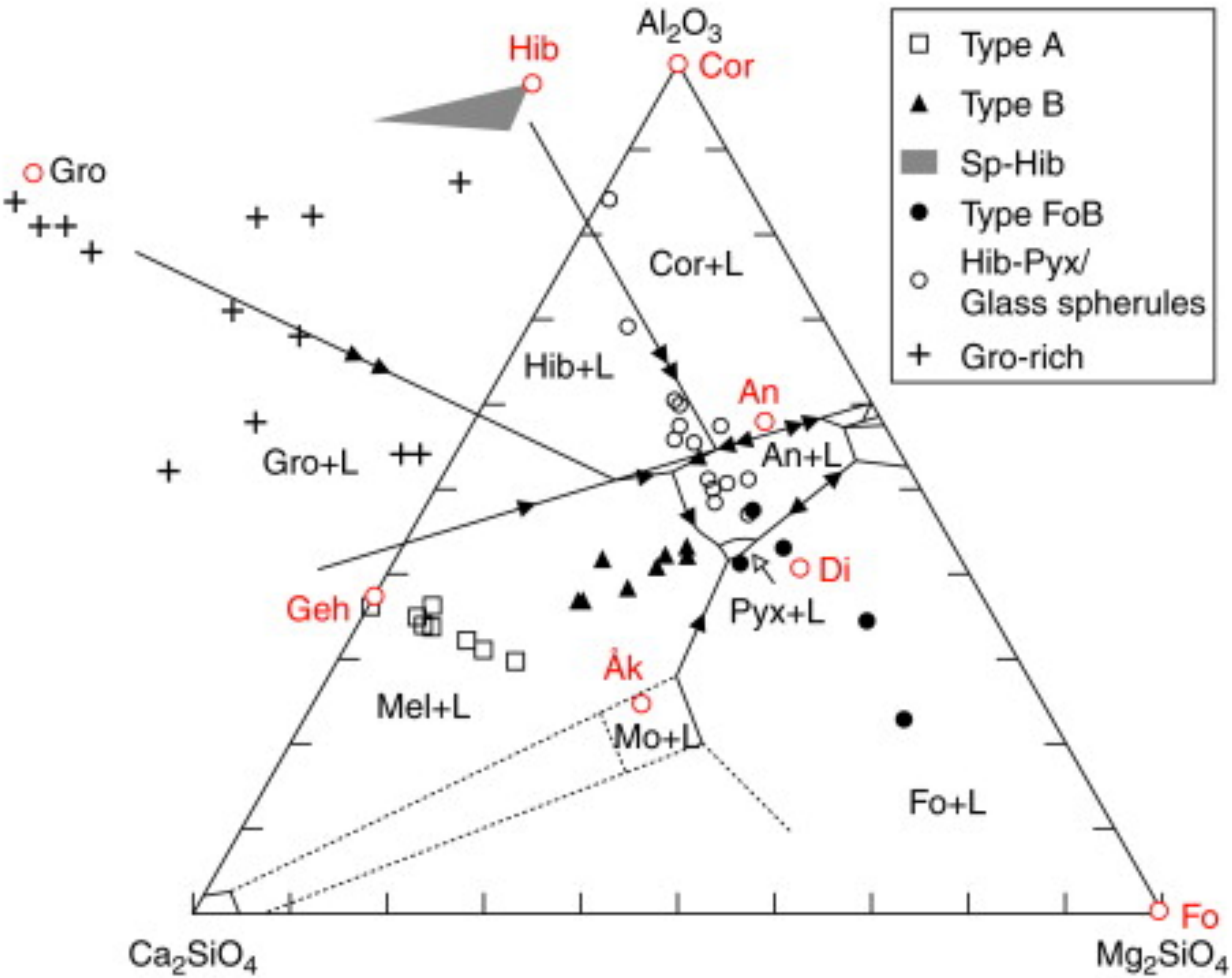




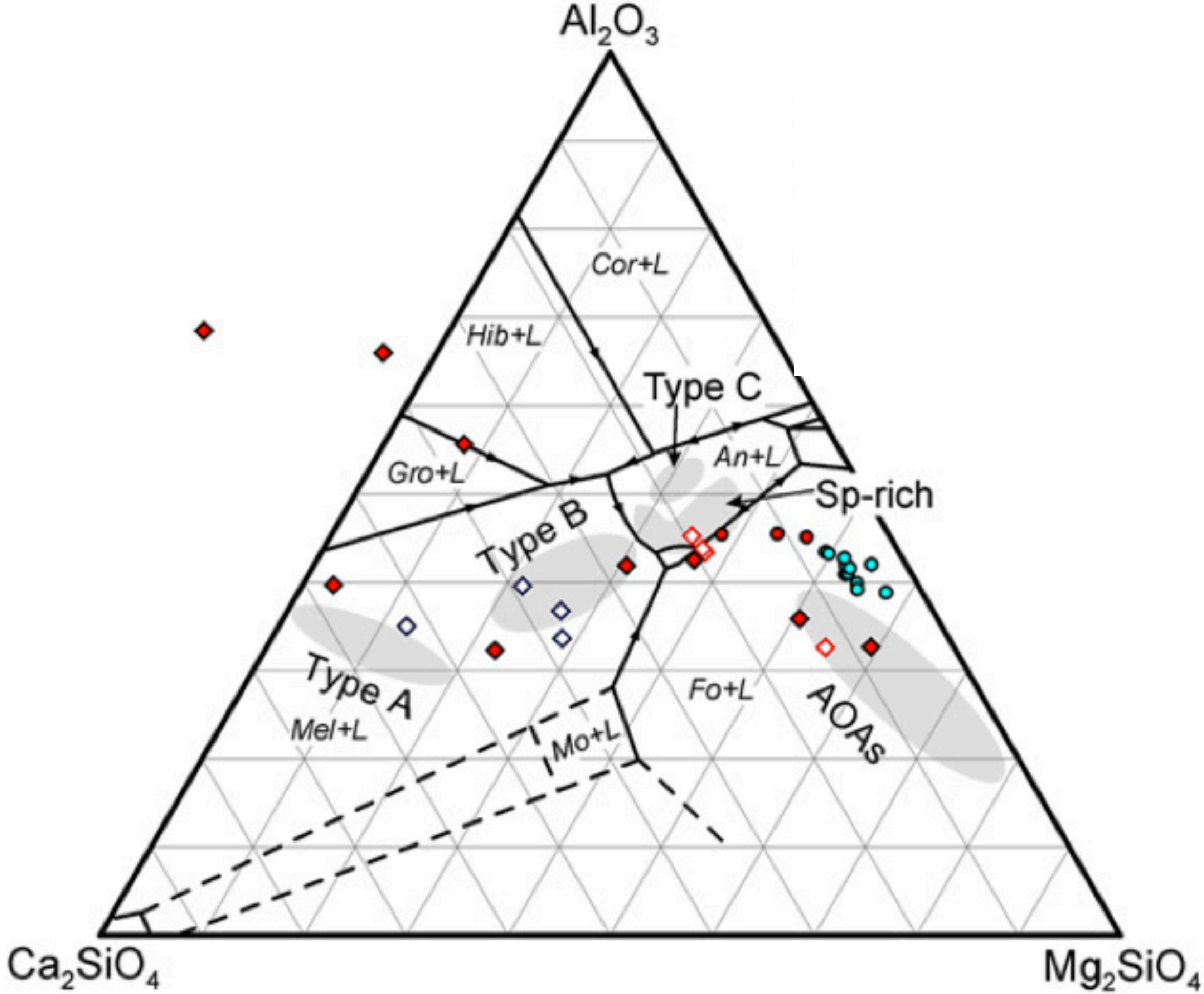




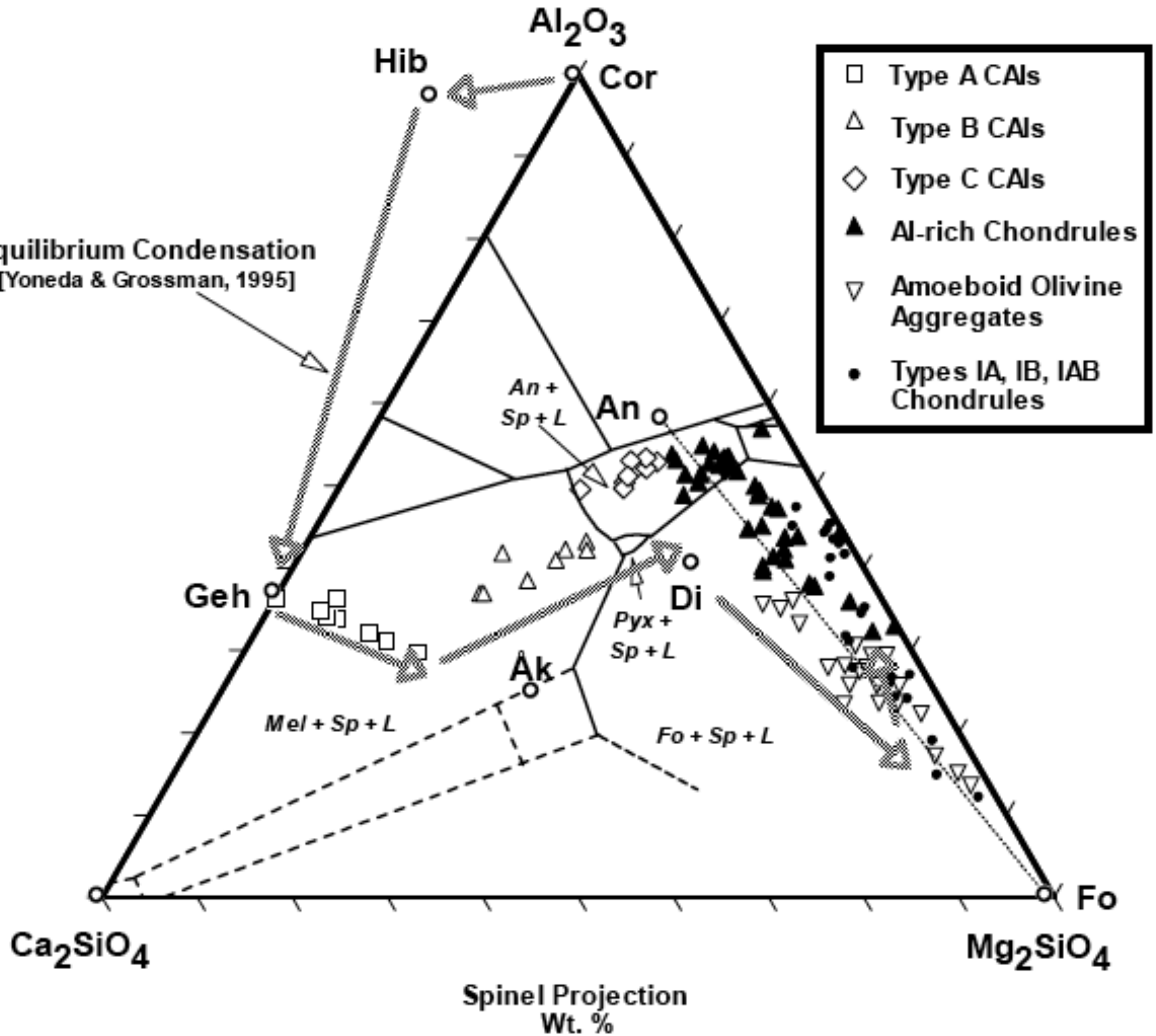
(a)
Al2O3
Cor
Hib
Sp
An*
En*
Geh
An
CaO
C2S
MgO
Fo
En
SiO2



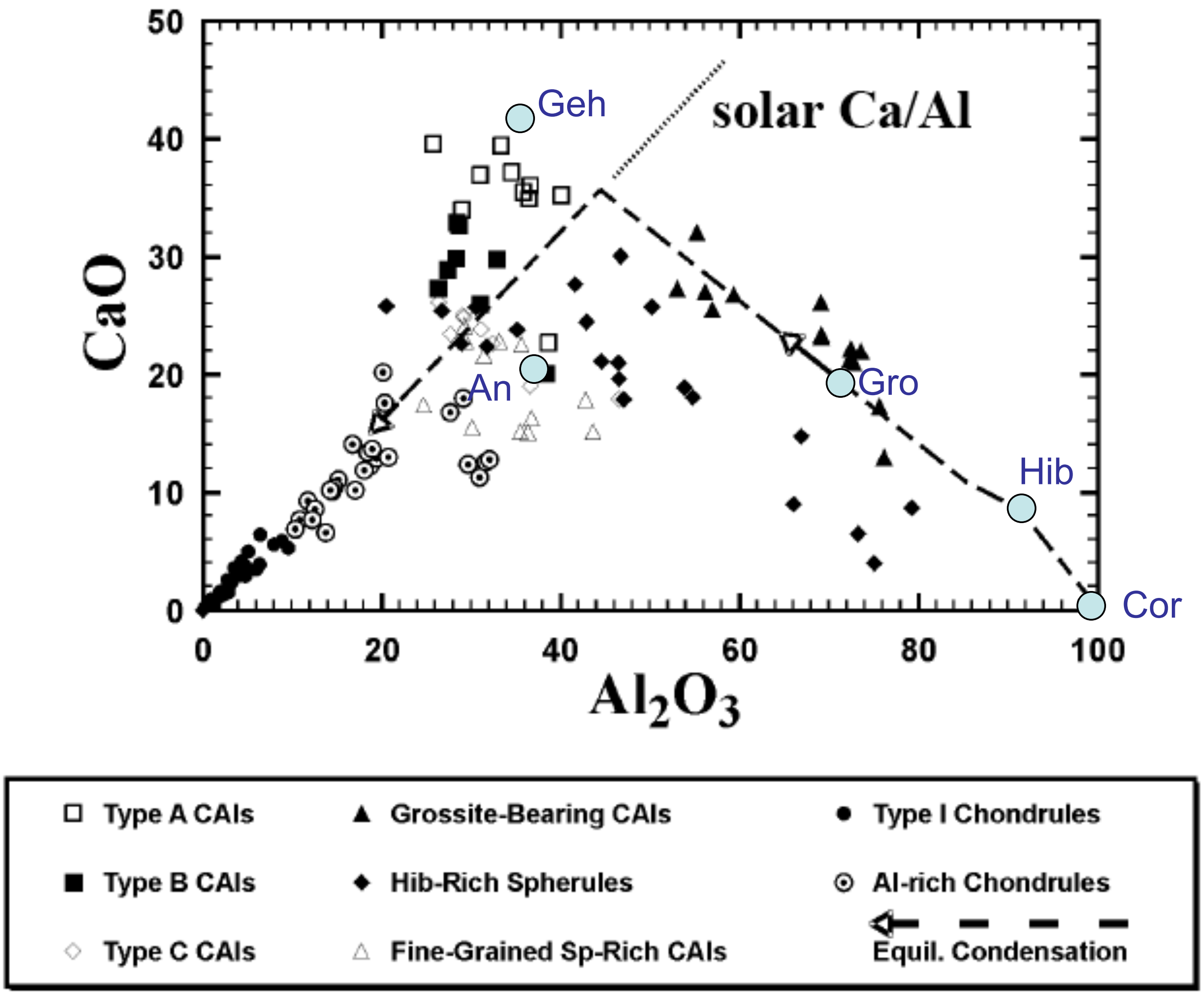
Al2O3
Hib
Cor
Gro
Type A
Type B
Sp-Hib
Type FoB
Hib-Pyx/
Glass spherules
Gro-rich
Cor+L
Hib+L
An
An+L
Gro+L
Di
Geh
Pyx+L
Åk
Mel+L
Mo+L
Fo+L
Fo
Ca2SiO4
Mg2SiO4



Al2O3
Cor+L
Hib+L
Type C
An+L
Sp-rich
Gro+L
Type B
Type A
Fo+L
AOAs
Mel+L
Mo+L
Ca2SiO4
Mg2SiO4

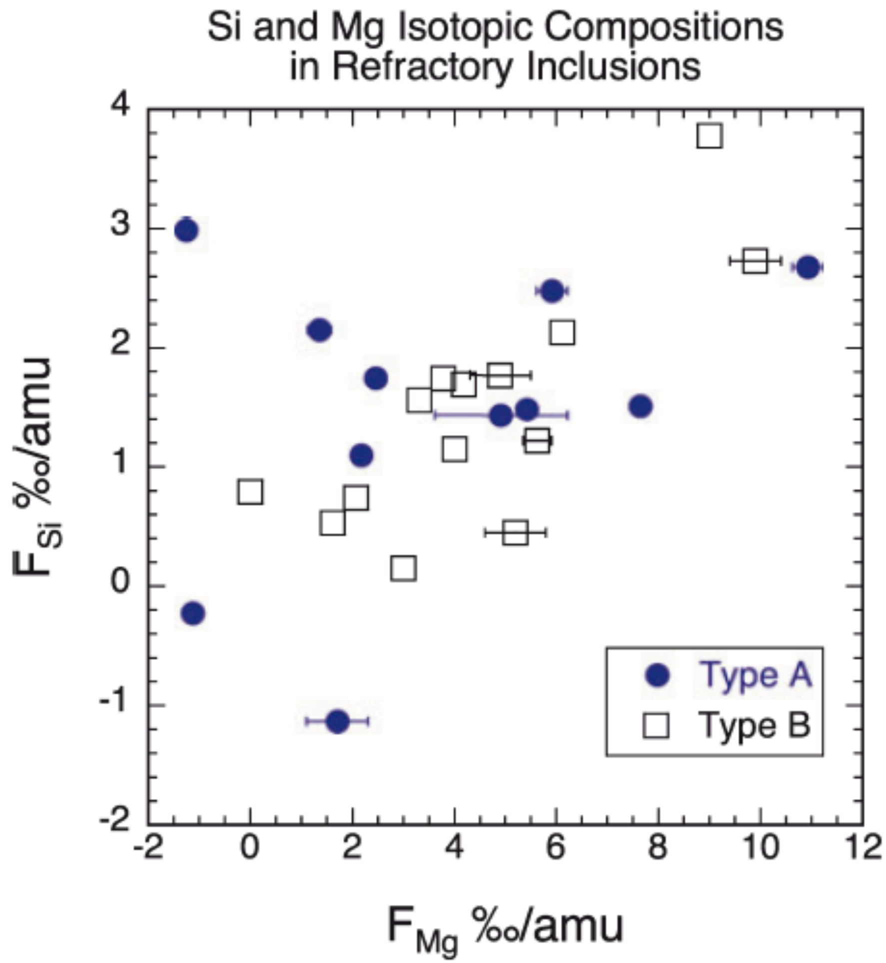


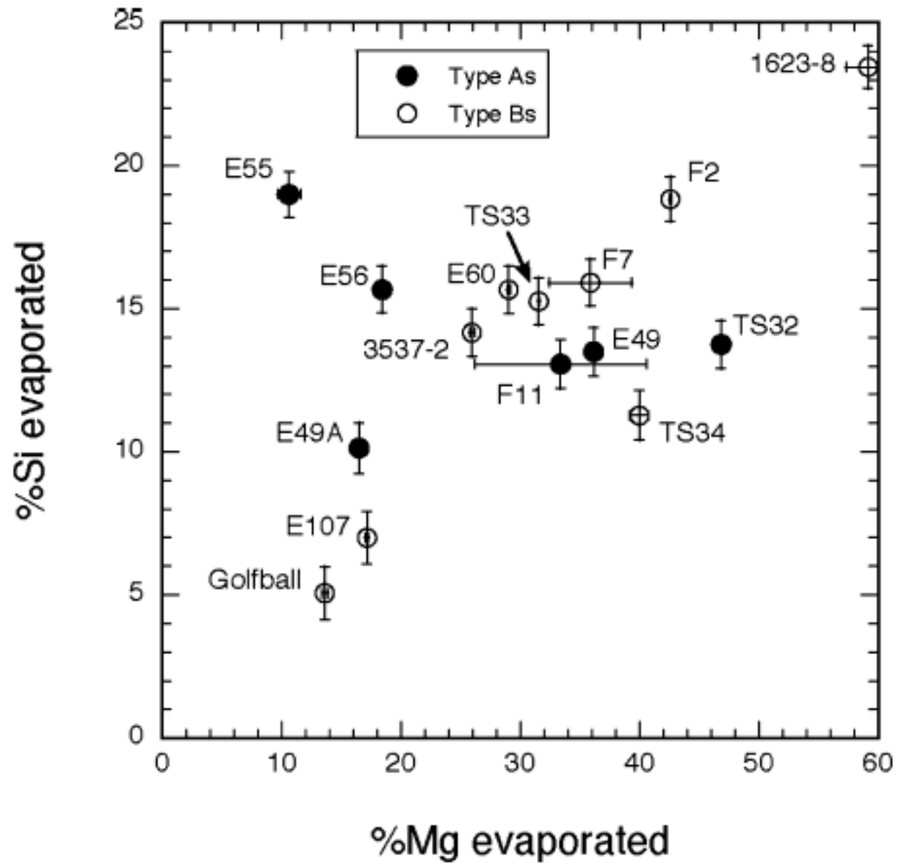
Al2O3
Cor
Hib
Type A CAIs
Type B CAIs
Type C CAIs
Al-rich Chondrules
Amoeboid Olivine Aggregates
Types IA, IB, IAB Chondrules
Equilibrium Condensation
[Yoneda & Grossman, 1995]
An + Sp + L
An
Geh
Di
Pyx + Sp + L
Ak
Mel + Sp + L
Fo + Sp + L
Fo
Ca2SiO4
Mg2SiO4
Spinel Projection
Wt. %



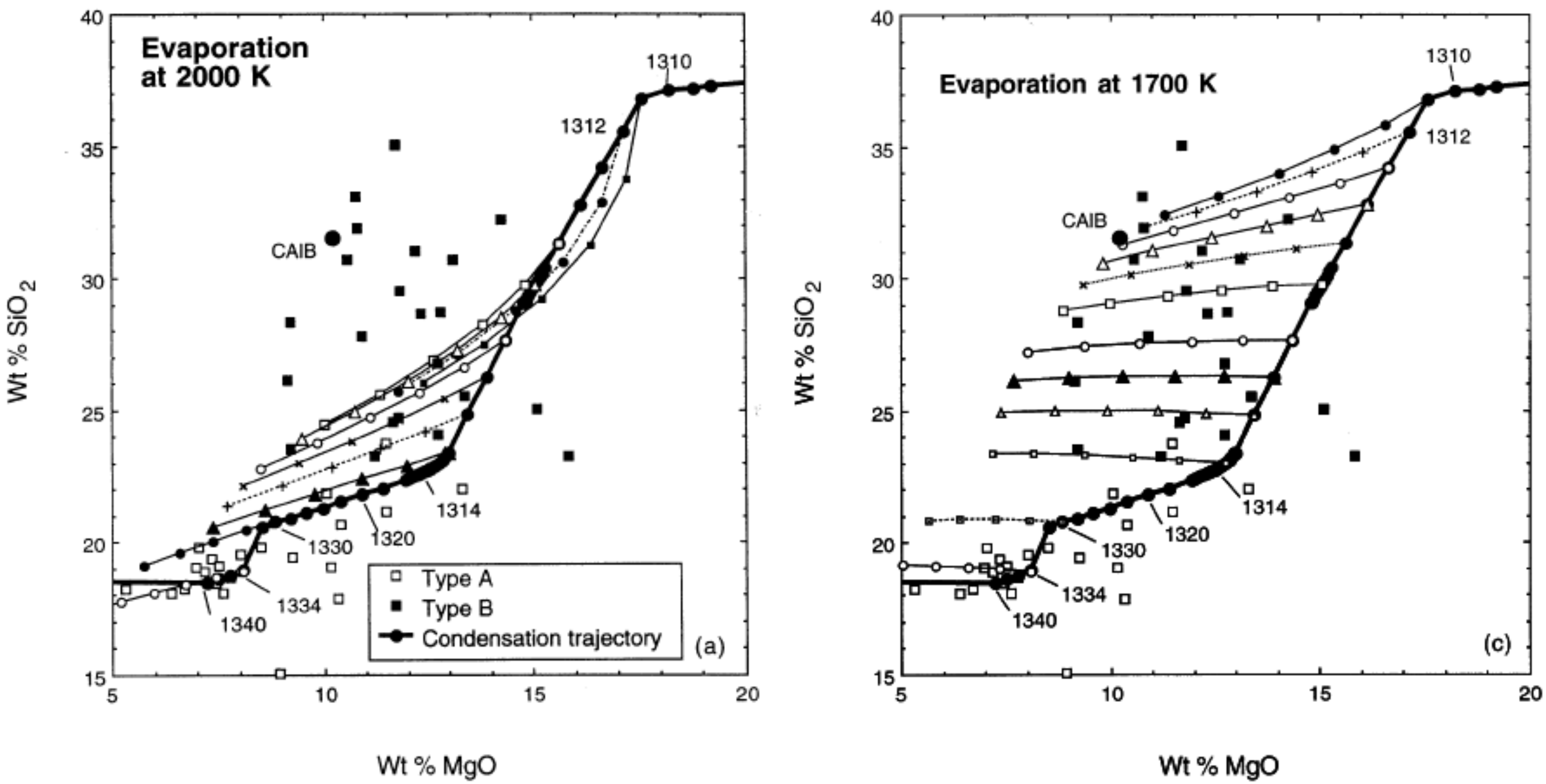
solar Ca/Al
Geh
An
Gro
Hib
Cor
CaO
Al_2O_3
0
10
20
30
40
50
0
20
40
60
80
100
Type A CAIs
Type B CAIs
Type C CAIs
Grossite-Bearing CAIs
Hib-Rich Spherules
Fine-Grained Sp-Rich CAIs
Type I Chondrules
Al-rich Chondrules
Equil. Condensation

Grossman et al. (2000)

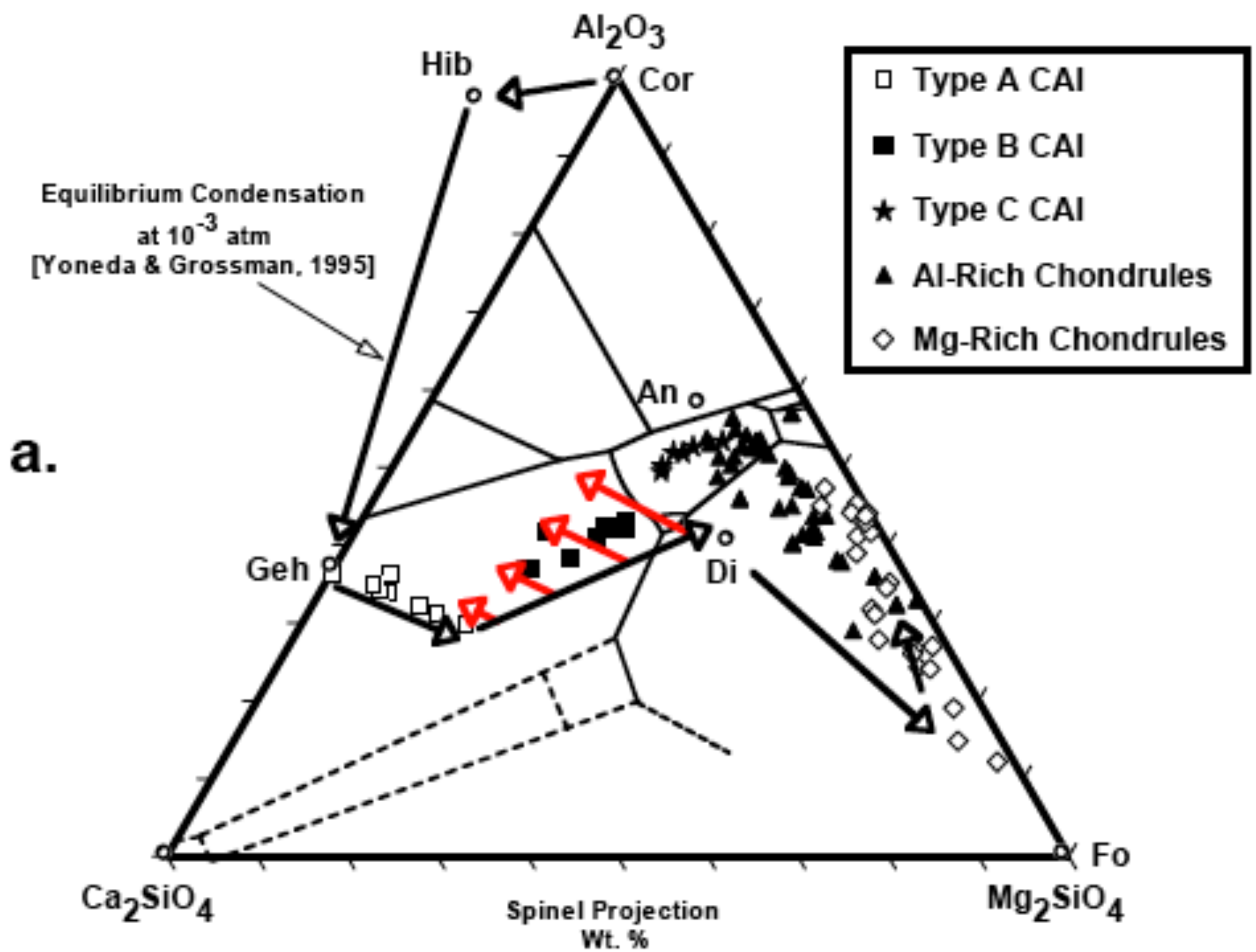




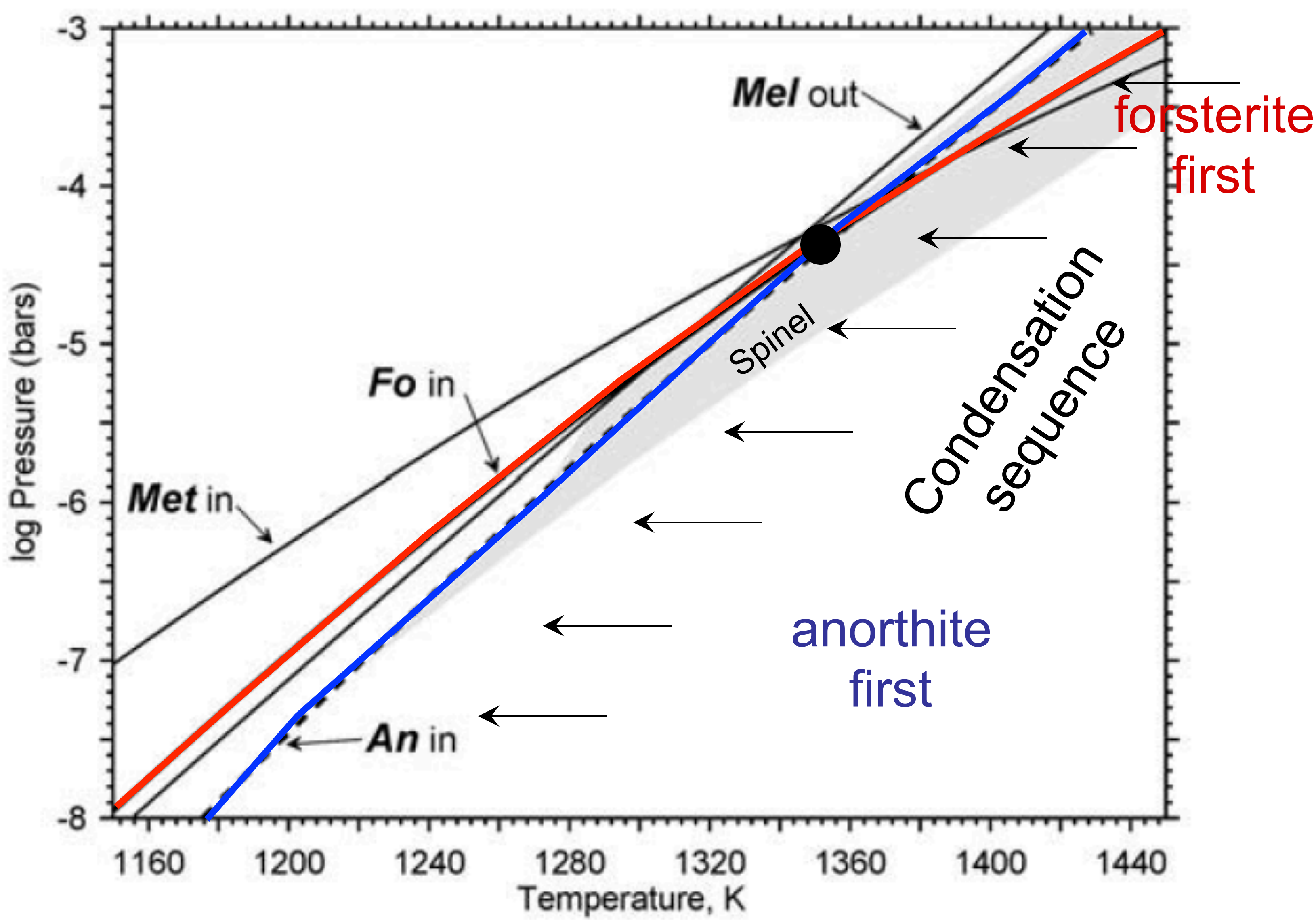
- Bulk compositions of igneous CAIs are depleted in Si & Mg compared to the calculated compositions of condensates
- Such depletions can be explained by non-equilibrium evaporation into H_2 gas at 1700 K from melt droplets with compositions on a condensation trajectory



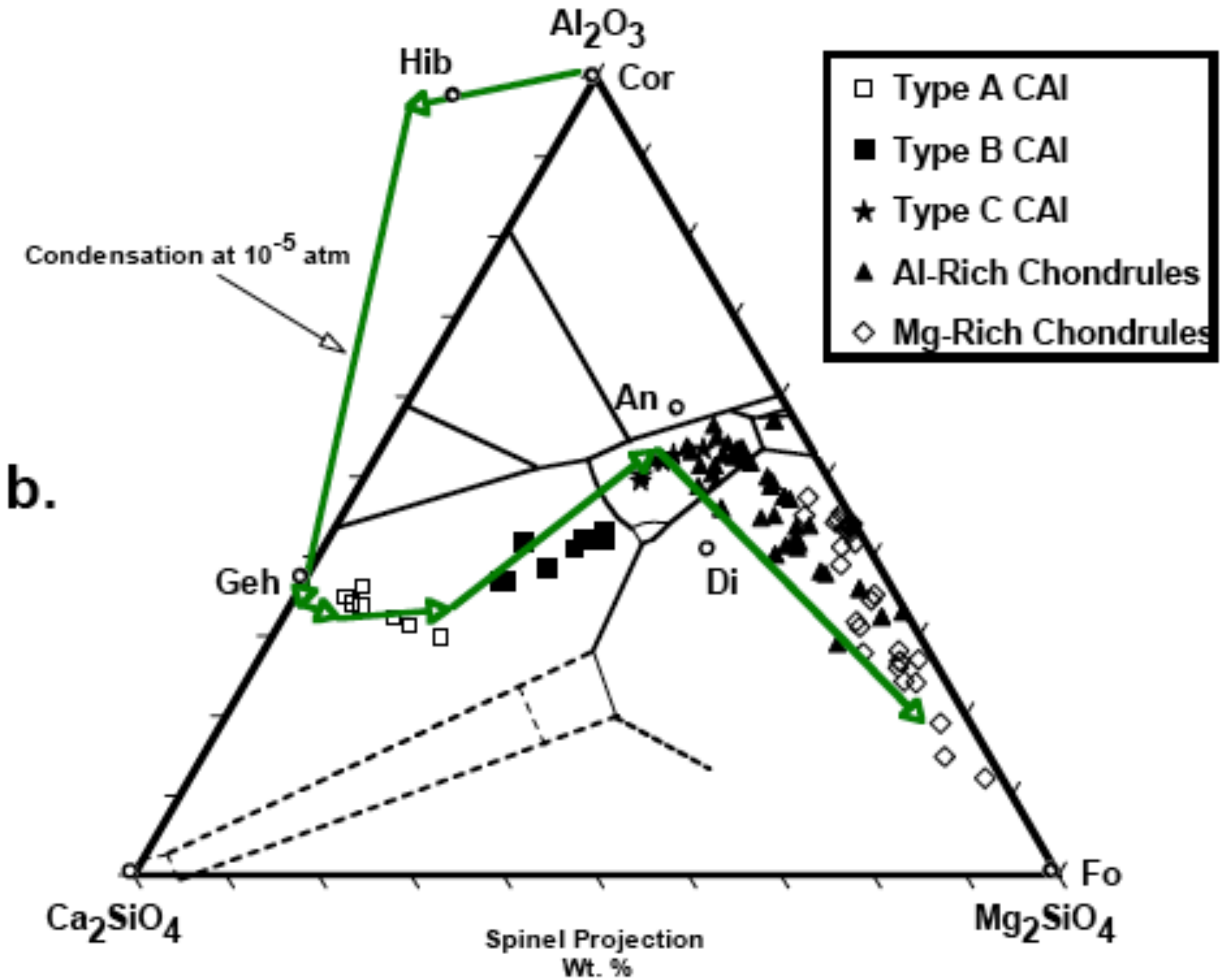
Grossman et al. (2000)



Grossman et al. (2000)



(Krot et al. 2004; Petaev & Wood, 1998

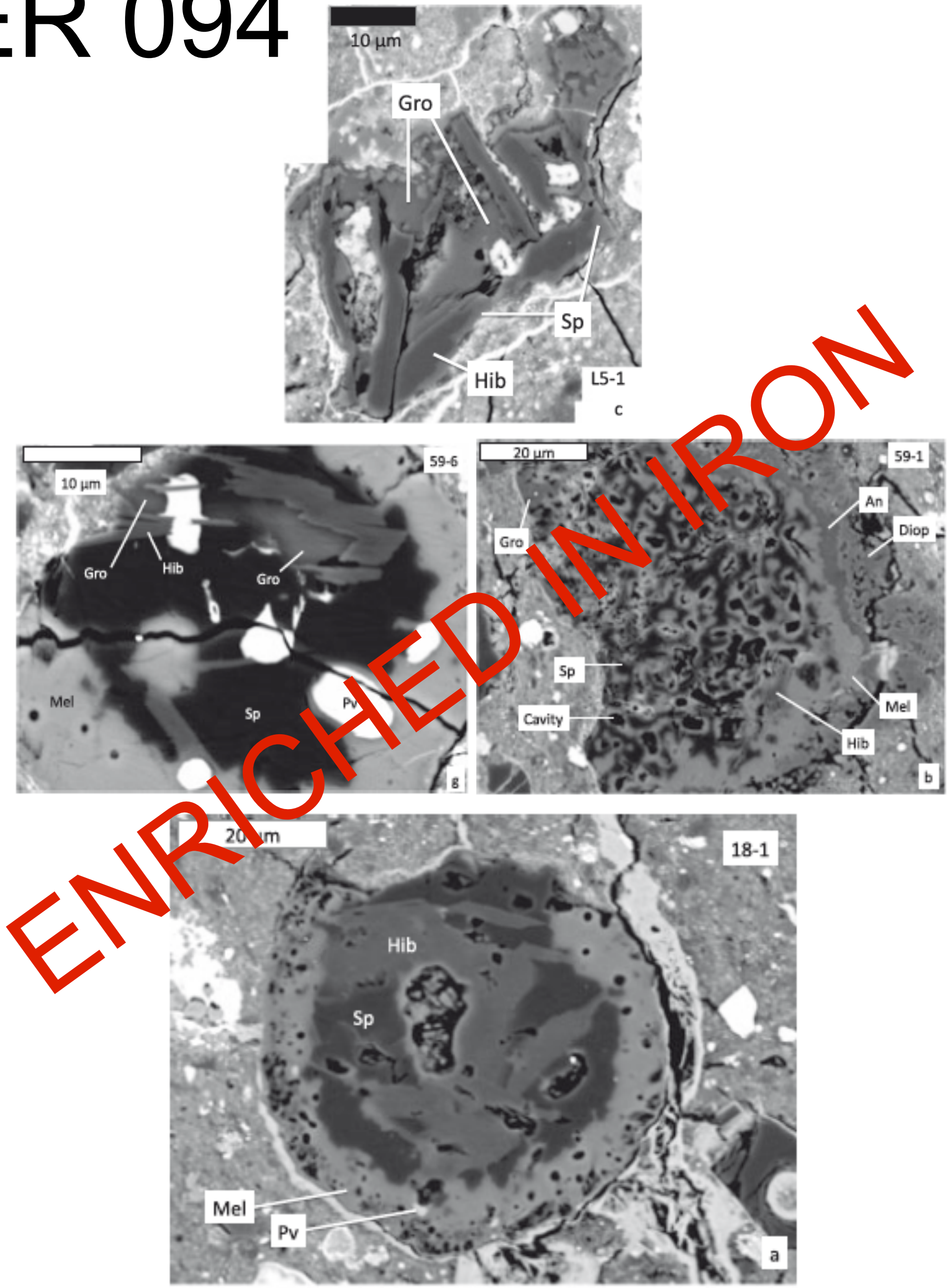

b.
Al_2O_3
Hib
Cor
Condensation at 10^{-5} atm
An
Geh
Di
Ca_2SiO_4
Mg_2SiO_4
Fo
Spinel Projection
Wt. %
Type A CAI
Type B CAI
Type C CAI
Al-Rich Chondrules
Mg-Rich Chondrules

CAIs in ACFER 094

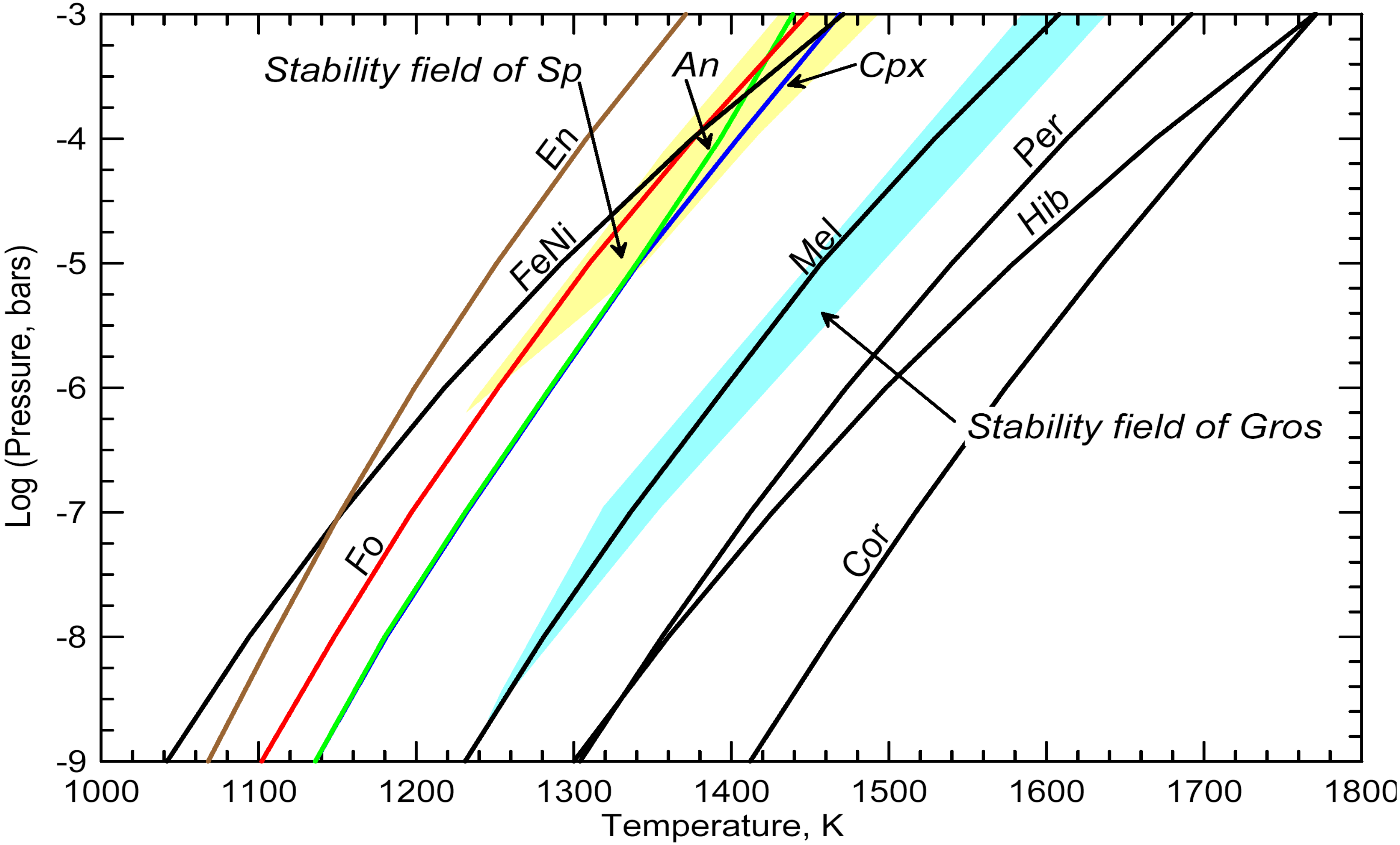
Table 1. Mineralogy of refractory inclusions found in thin section USNM 7233-1.

Mineralogy	No. of objects	% of objects
Sp + Mel ± Pv	65	22.5
Sp + Pv	47	16.3
Sp	28	9.7
An + Pyx	28	9.7
Hib + Sp + Mel ± Pv	20	7.0
Sp + An + Diop	17	5.9
Sp + Pyx	11	3.8
Sp + An	10	3.5
Sp + Mel + Tpyx	8	2.8
Hib + Gro + Sp + Mel ± Pv	8	2.8
Mel + An + Sp	8	2.8
Mel + An + Pyx	7	2.4
Hib ± Sp ± Pv	6	2.1
Gro + Sp + Mel + Pv	5	1.7
Mel + An	5	1.7
Sp + Mel + Diop + An	2	0.7
Mel + Pv + An	2	0.7
Gro + Pv + Sp	2	0.7
Tpyx + Diop + pv	2	0.7
Cor + Hib	1	0.3
Hib + Sp + Fo	1	0.3
Hib + Mel	1	0.3
Sp + Tpyx + An	1	0.3
Sp + Mel + Diop + Pv	1	0.3
Sp + Mel + Fo + FeS + Diop	1	0.3
Mel + Pv	1	0.3
Mel + Diop + Fo	1	0.3

Sp = spinel; Mel = melilite; Pv = perovskite; An = anorthite; Pyx = pyroxene; Hib = hibonite; Diop = diopside; Tpyx = Ti-bearing pyroxene; Gro = grossite; Cor = corundum; Fo = forsterite. "Pyx" indicates that some members of the group contain diopside and others contain Tpyx.



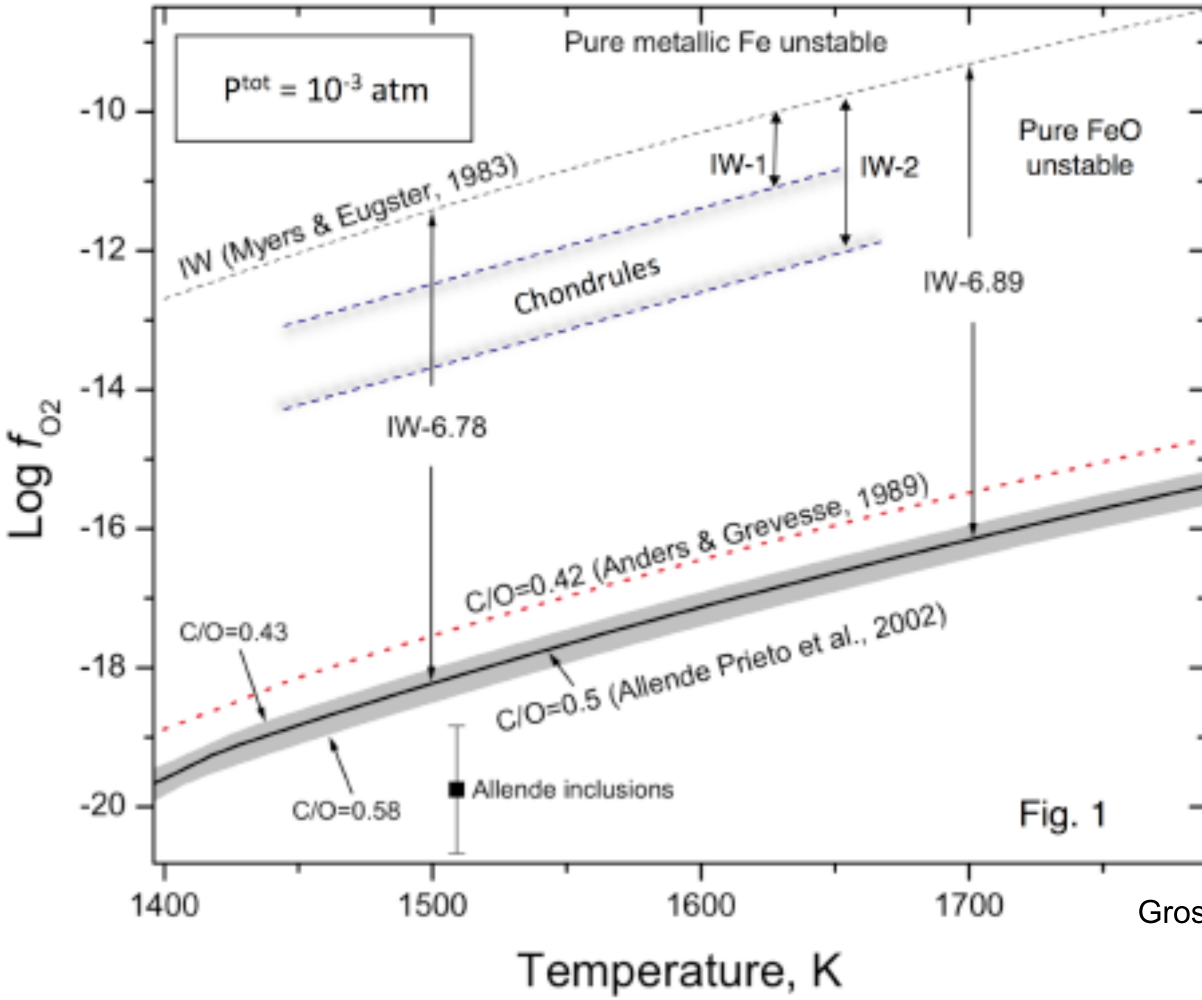
Simon & Grossman. 2012



There are no known nebular conditions under which the refractory phases found in Acfer 094 could acquire FeO enrichments to the observed levels !!!!

Simon & Grossman. 2012

Redox of the solar gas

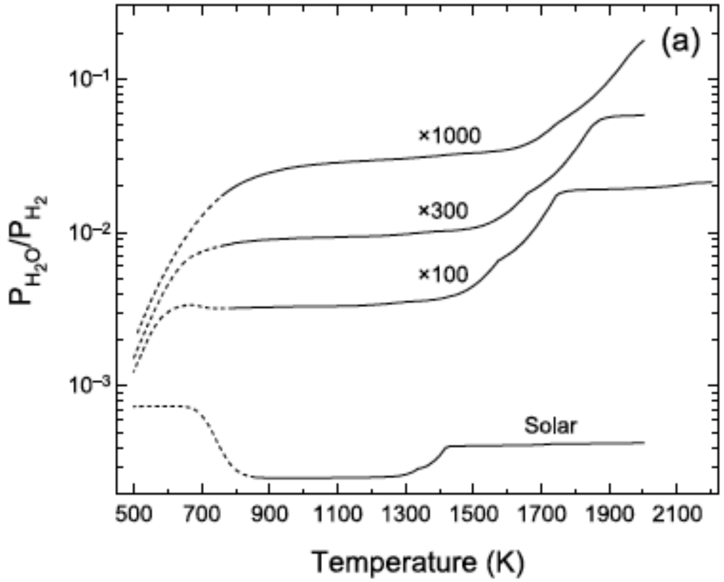


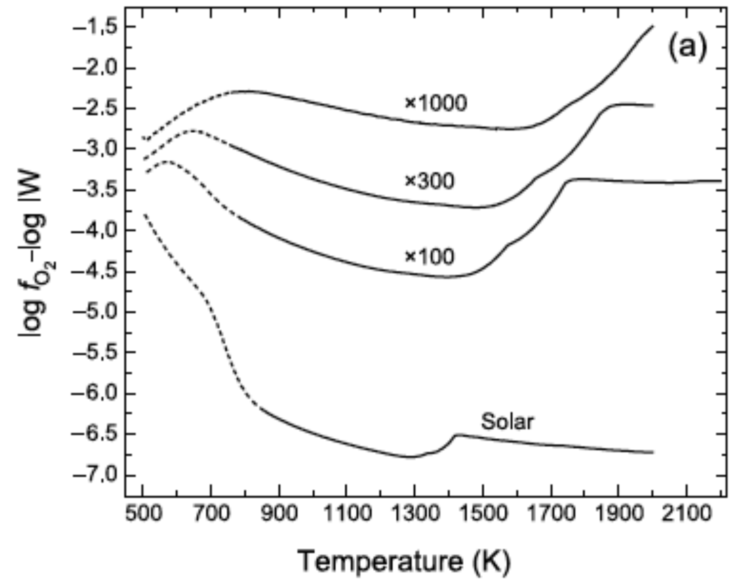
Grossman et al. 2011

In the high-temperature interval where reaction kinetics are most favorable, the fO2 of a gas of solar composition lies so far below IW that only vanishingly small concentrations of FeO would be expected in silicates that equilibrate with metallic Ni-Fe.

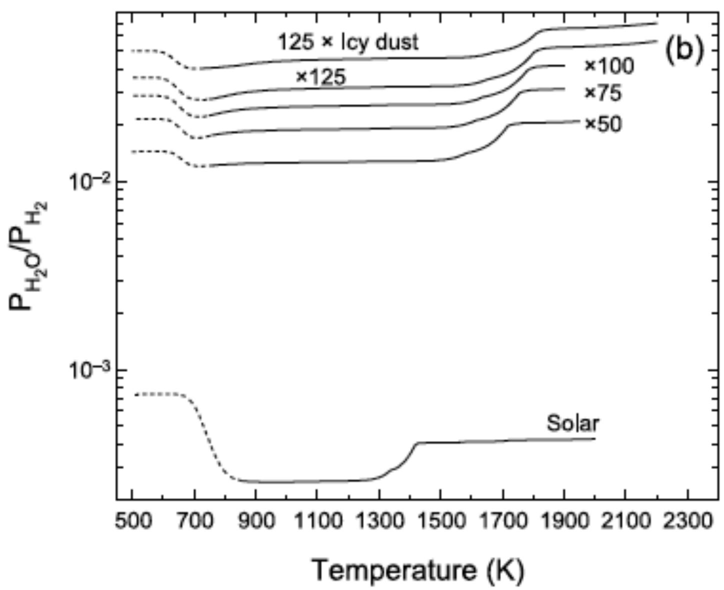
Enhancing fO_2 at fixed total pressure

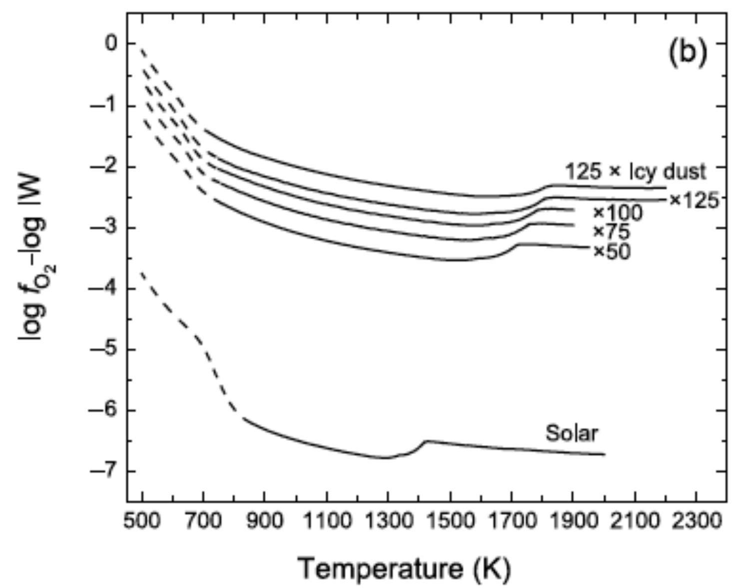
CI dust enrichment





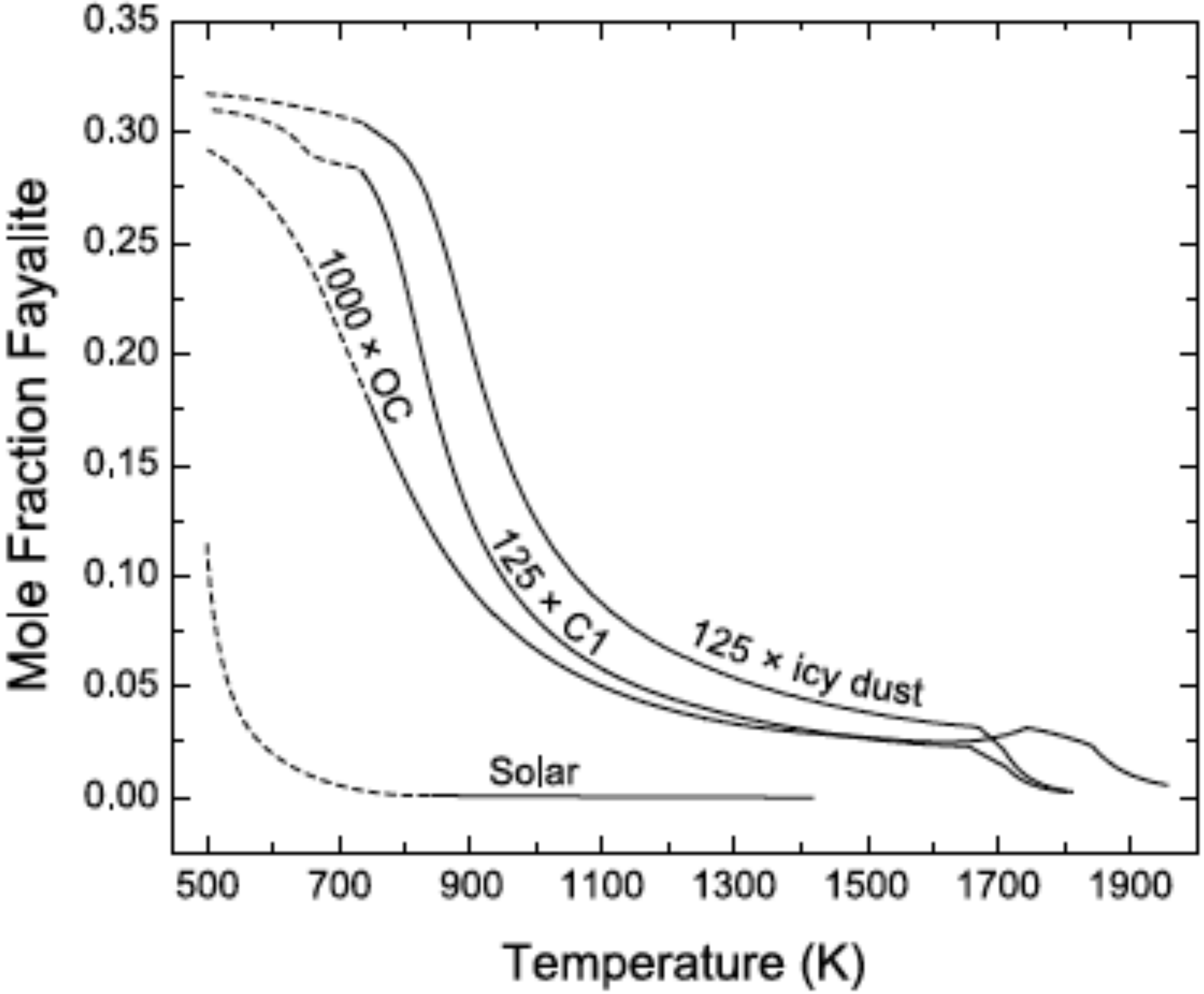
Ice enrichment





Fedkin & Grossman 2011

FeO enrichment in silicates



Fedkin & Grossman 2011

Origin of oxidized iron in the solar system

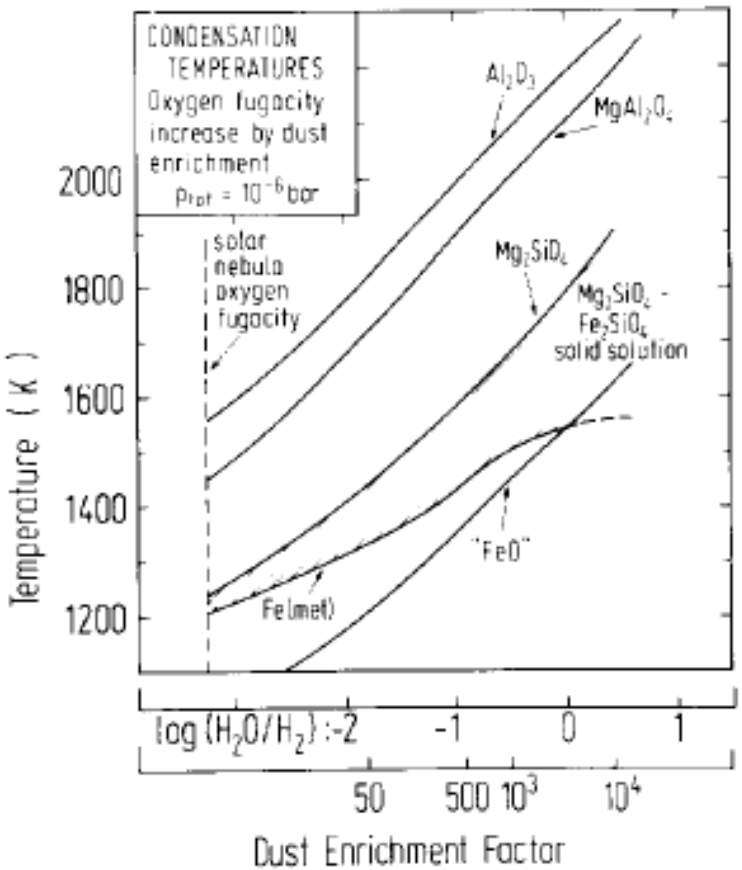


Fig. 8. Increasing the dust/gas ratio as a means to increase oxygen fugacity would simultaneously increase the partial pressures of all other elements. The results of such calculation are shown here. The forsterite-fayalite solid-solution field is shifted to higher temperatures, suggesting that olivine in Allende may never have experienced an environment as reducing as that of the solar nebula.

Palme & Fegley 1990

Evaluation of the redox of the solar gas

Elligham diagram

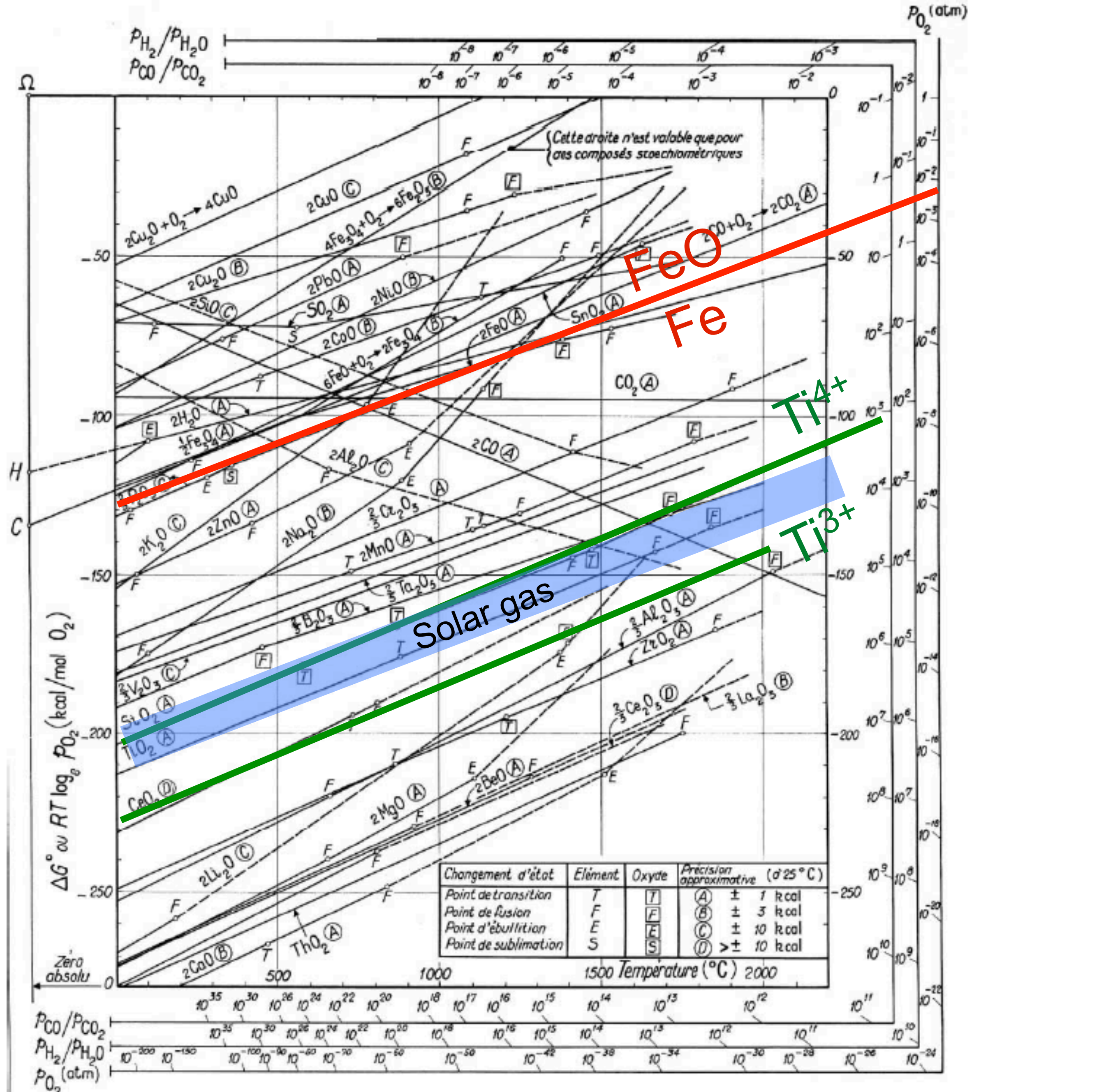
$$(SiO_2) \rightarrow [Si] + 2\,[O]$$

$$\Delta G_1 = 0$$

$$\lg \frac{a_{[Si]} \cdot a_{[O]}^2}{a_{(SiO_2)}} = -\frac{\Delta G_1^0}{2{,}3\,RT}$$

$$\lg K_1 = -\frac{\Delta G_1^0}{2{,}3\,RT}$$

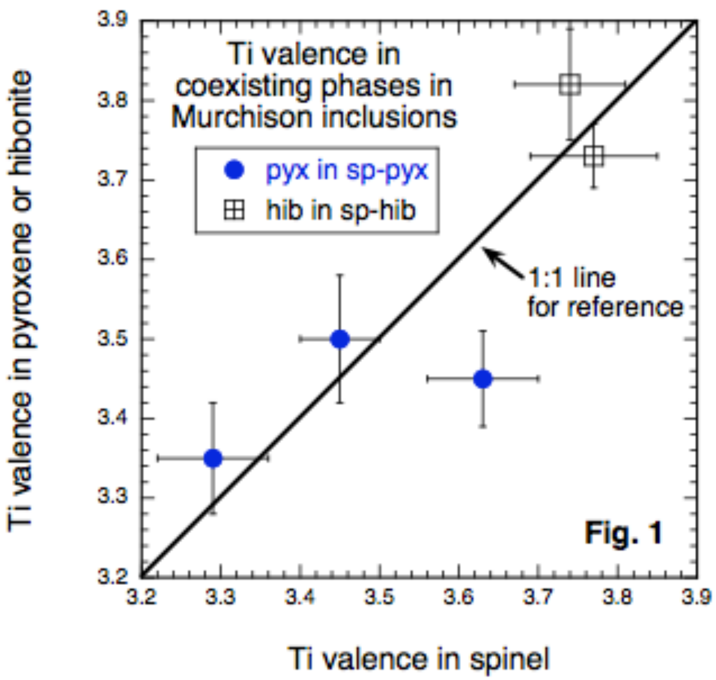
$$\frac{a_{[Si]} \cdot a_{[O]}^2}{a_{(SiO_2)}} = K_1$$

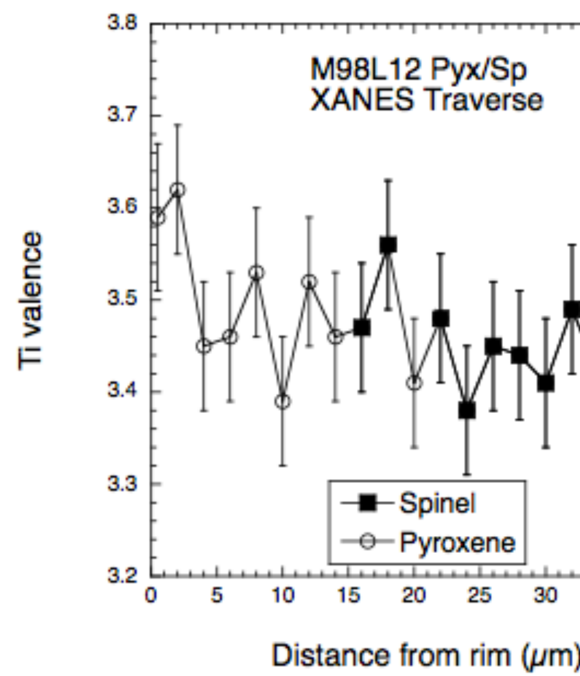


Ti^{3+}/Ti^{4+} ratio in refractory phases

Table 1. Ti valence by XANES. Sp: spinel; Px: pyroxene; Hb: hibonite; Pv: perovskite; Mel: melilite.

Sample	Mineral.	Spinel	Pyroxene	Hibonite
M98L1	Sp-Pv-Px	3.63±0.07	3.45±0.06	-
M98L4	Hb-Sp-Pv-Mel	3.74±0.07	-	3.82±0.07
M98L5	Hb-Sp-Pv	3.77±0.08	-	3.73±0.04
M98L6	Hibonite	-	-	3.43±0.16
M98L10	Sp-Px	3.35±0.07	3.27±0.07	-
M98L12	Sp-Px	3.45±0.05	3.50±0.08	-





Simon et al. 2009, 2011

Ti^{3+}/Ti^{4+} ratio in hibonite

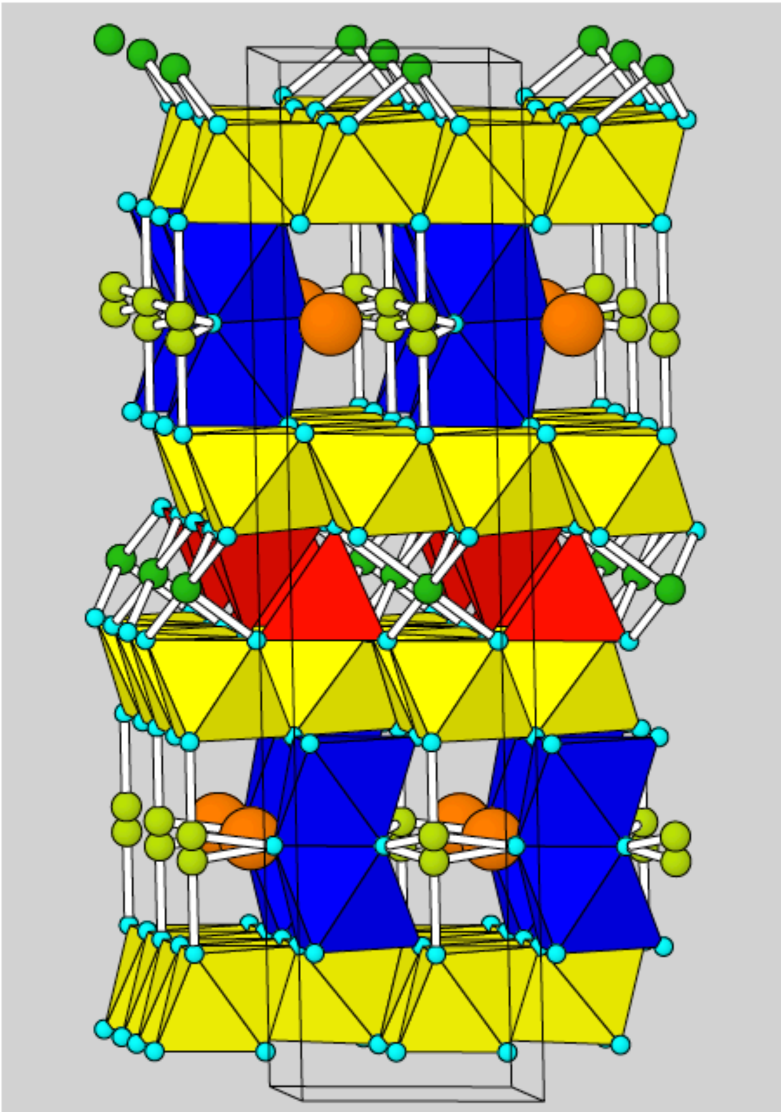


Figure 1. The hibonite structure (Bermanec et al. 1996). Orange spheres = Ca sites; dark green spheres = M1 octahedral sites; light green spheres = M2 trigonal bipyramidal sites; red tetrahedra = M3 sites; blue octahedra = M4 sites; yellow octahedra = M5 sites.

Ti3+/Ti4+ ratio can be used to estimate the oxygen fugacity,

$$M^{3+} = Al^{3+},\ M^{2+} + M^{4+} = 2Al^{3+},\ 2M^{2+} + M^{5+} = 3Al^{3+}$$

Beckett et al. (1988)

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ScienceDirect
Geochimica et Cosmochimica Acta 75 (2011) 937–949
Geochimica et Cosmochimica Acta
www.elsevier.com/locate/gca

Valence state of titanium in the Wark–Lovering rim of a Leoville CAI as a record of progressive oxidation in the early Solar Nebula

Kathryn A. Dyl [a,*], Justin I. Simon [b,c], Edward D. Young [a,d]

[a] Department of Earth and Space Sciences, UCLA, Los Angeles, CA 90095, United States
[b] Center for Isotope Geochemistry, UC Berkeley, Berkeley, CA 94720, United States
[c] Berkeley Geochronology Center, Berkeley, CA 94709, United States
[d] Institute of Geophysics and Planetary Physics, UCLA, Los Angeles, CA 90095, United States

Received 15 October 2009; accepted in revised form 23 September 2010; available online 31 October 2010

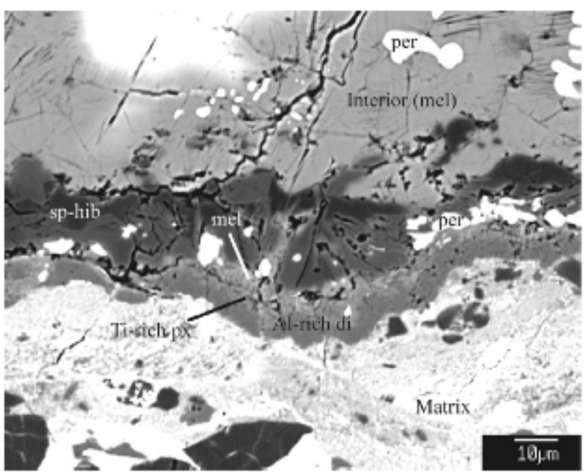
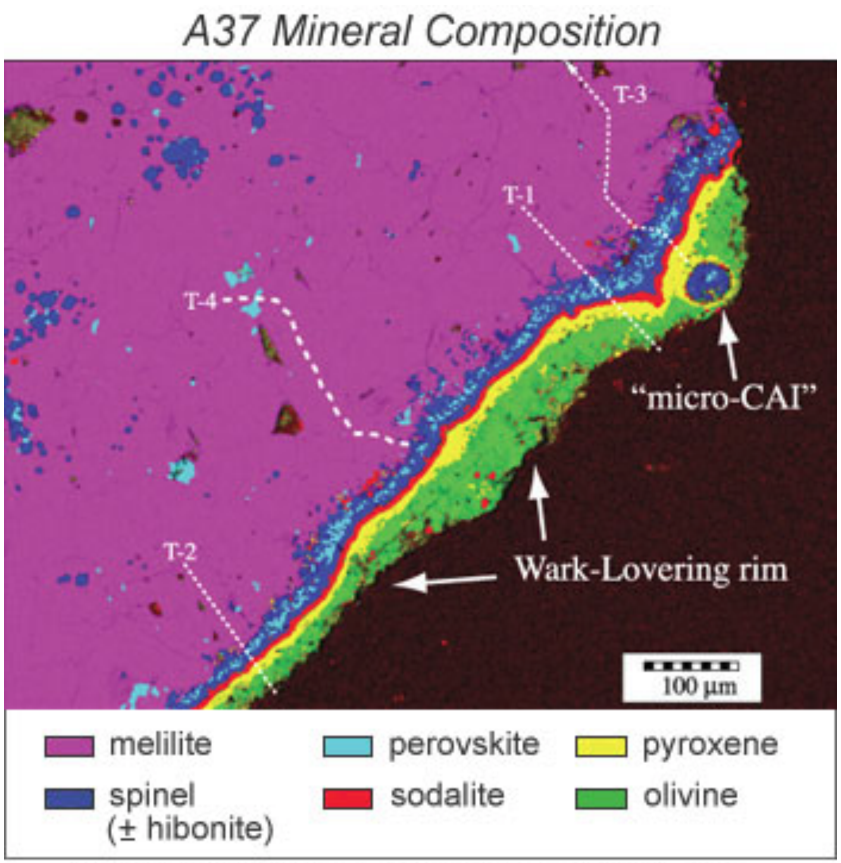


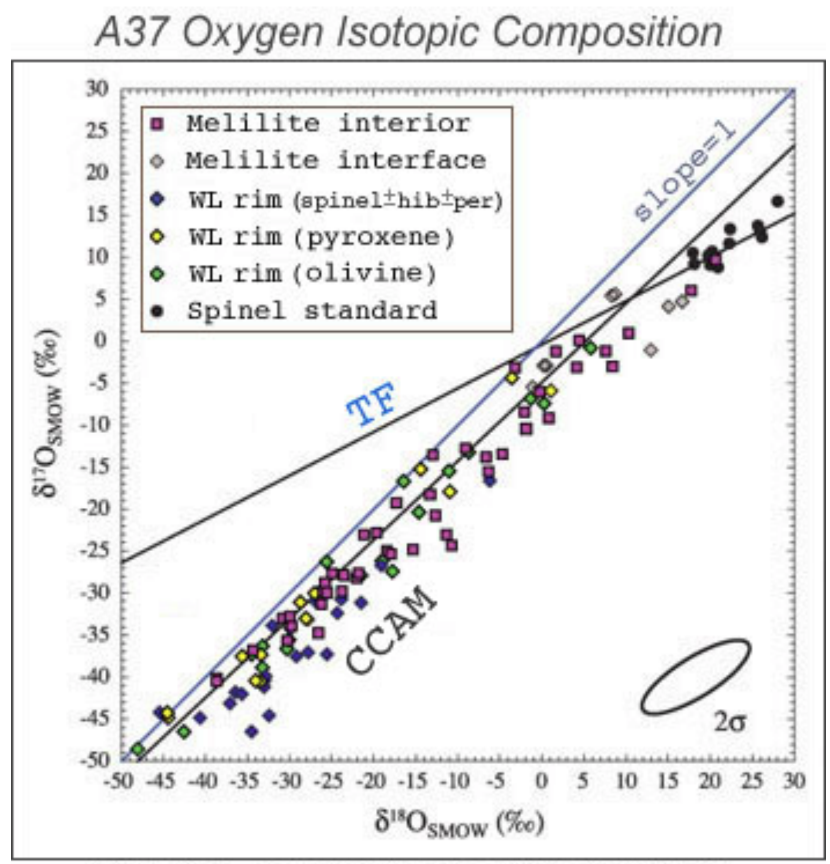
Fig. 1. BSE image of Leoville 144A Wark–Lovering rim. Bands of spinel + hibonite ± perovskite (sp–hib, pv), melilite (mel), Al-Ti diopside (Ti-rich px), and Al-diopside (Al-di) are observed.

. . . and the comments of Simon et al., 2012

Type A CAI



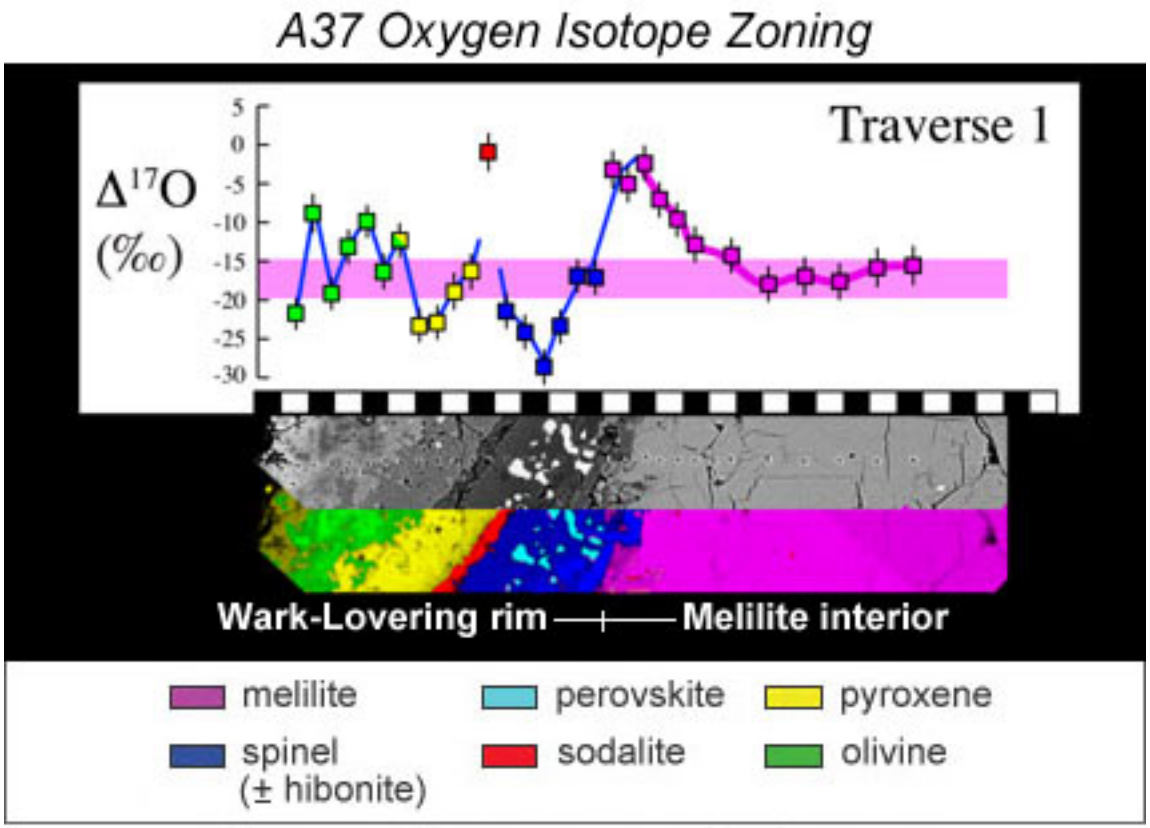
(From Simon, *etal.* (2011) *Science*, v. 331, p.1175-1178.)



(From Simon, *etal.* (2011) *Science*, v. 331, p.1175-1178.)

Minerals from a CAI and its prominent rim have a wide range of oxygen isotopic composition, suggesting formation in more than one reservoir.

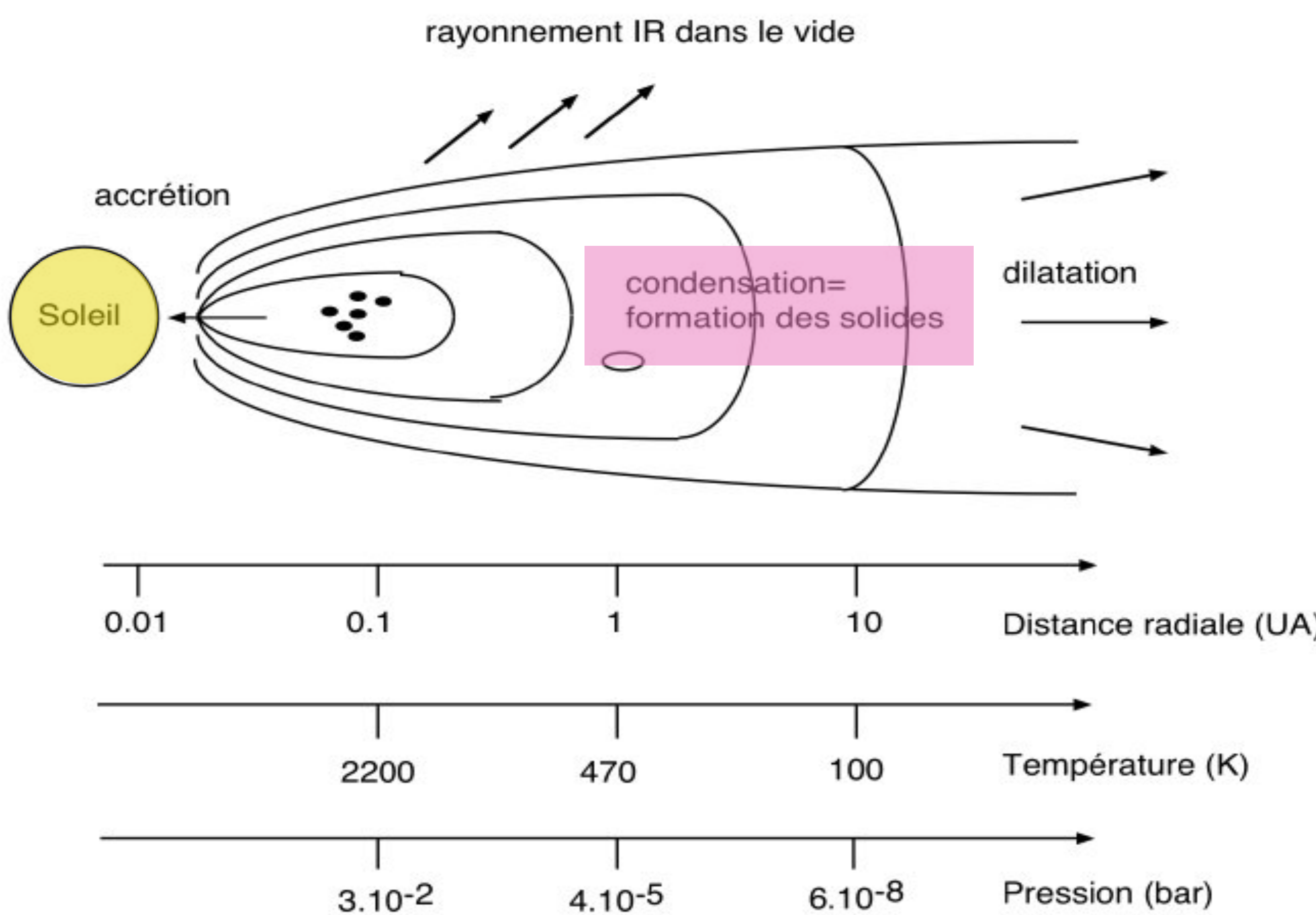
Oxygen Isotopic Zoning



(From Simon, *etal.* (2011) *Science*, v. 331, p.1175-1178.)

- Melilite interior has high ^{16}O (low $\Delta^{17}O$)
- $\Delta^{17}O$ increases (so ^{16}O decreases) towards the rim
- Spinel-rich region of Wark-Lovering rim has extremely low $\Delta^{17}O$
- Most of the rim oscillates around the value of the CAI interior
- These data clearly indicate exposure of the CAI and its rim to environments that varied in oxygen isotopic composition
- Implies extensive migration throughout the solar nebula

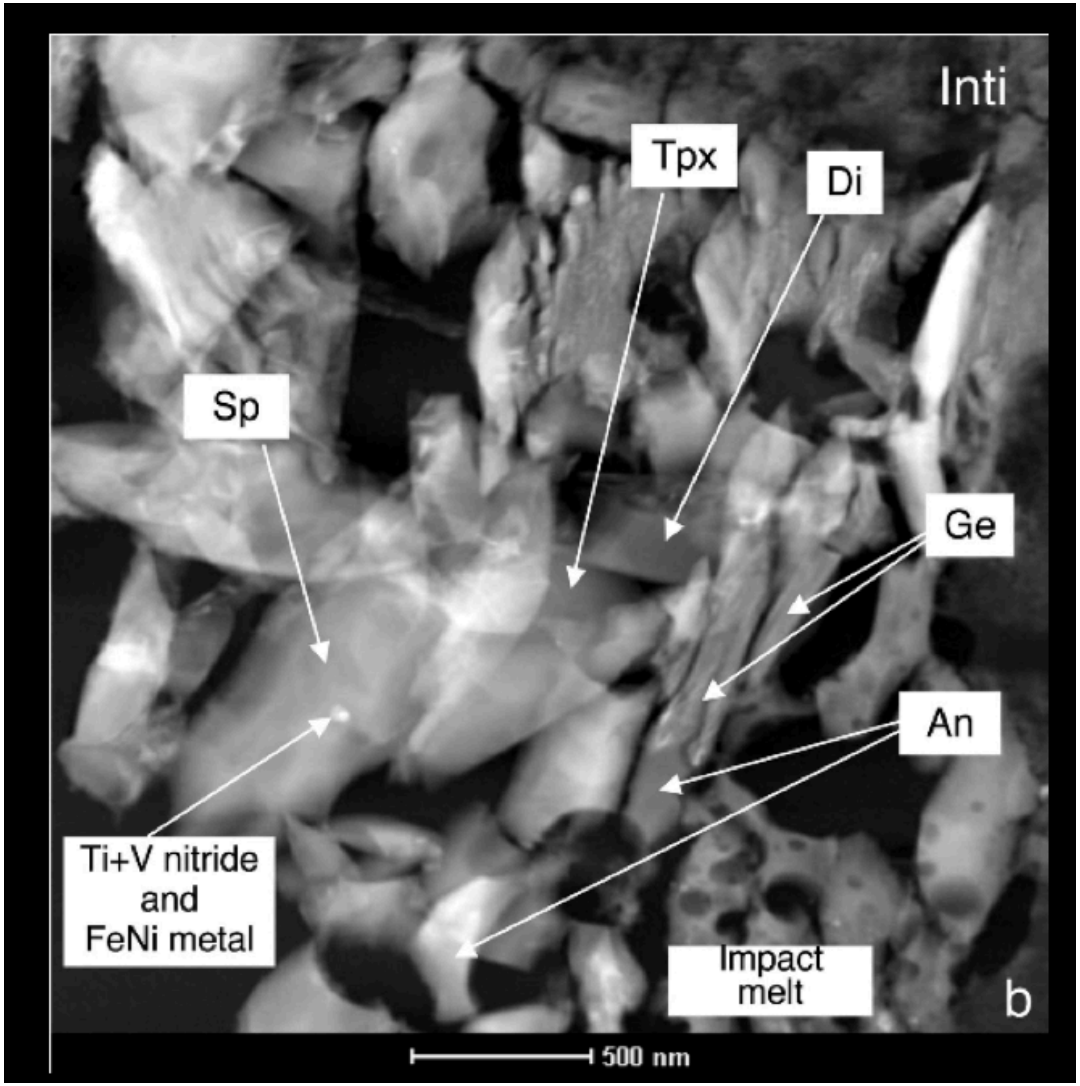
CAI formation



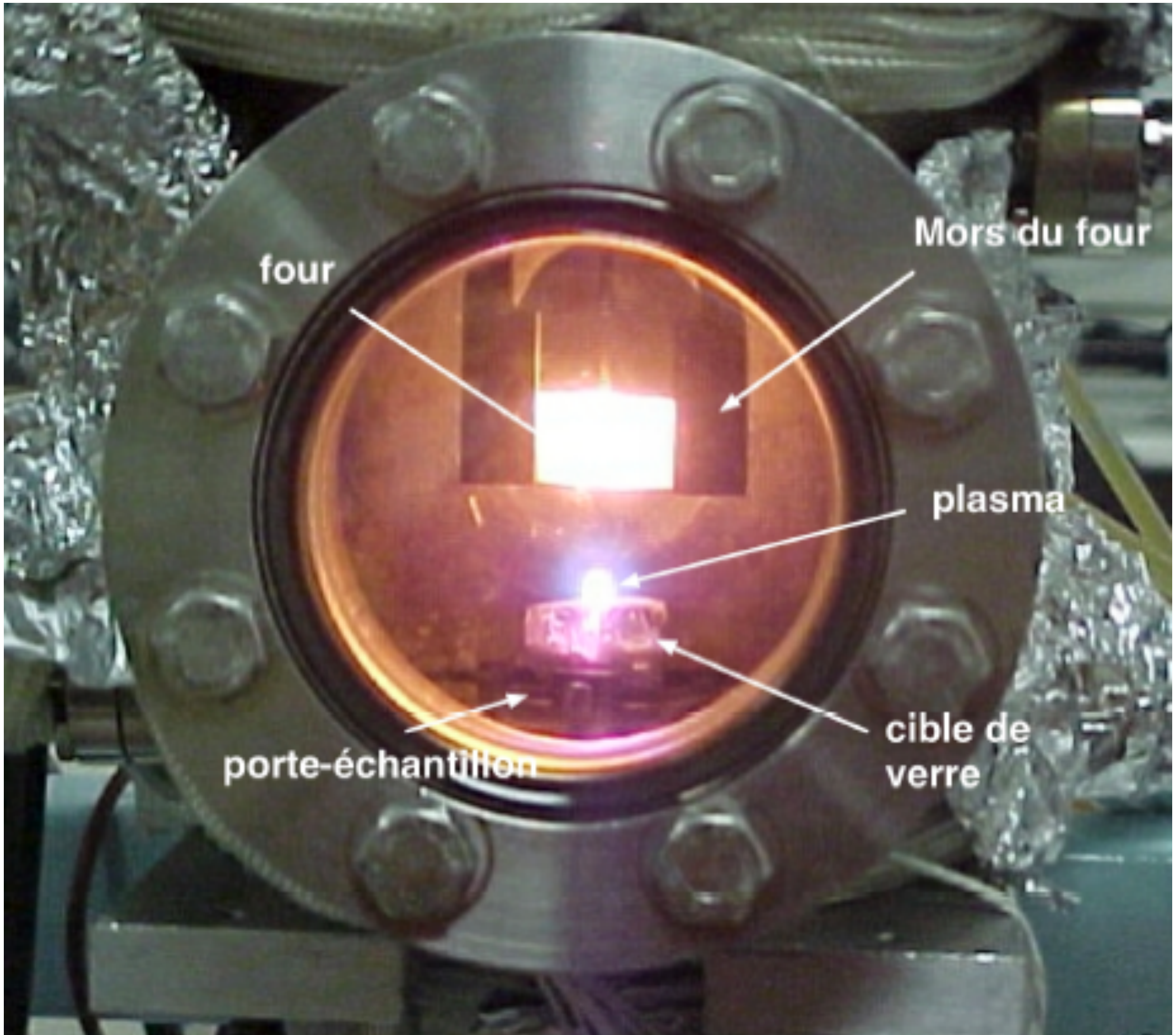
(Larimer & Grosmmann, 1977, etc

See E. Taillifet poster

Occurrence of CAI in Wild 2 comet



High temperature condensation of a solar gas : *Nebulotron*



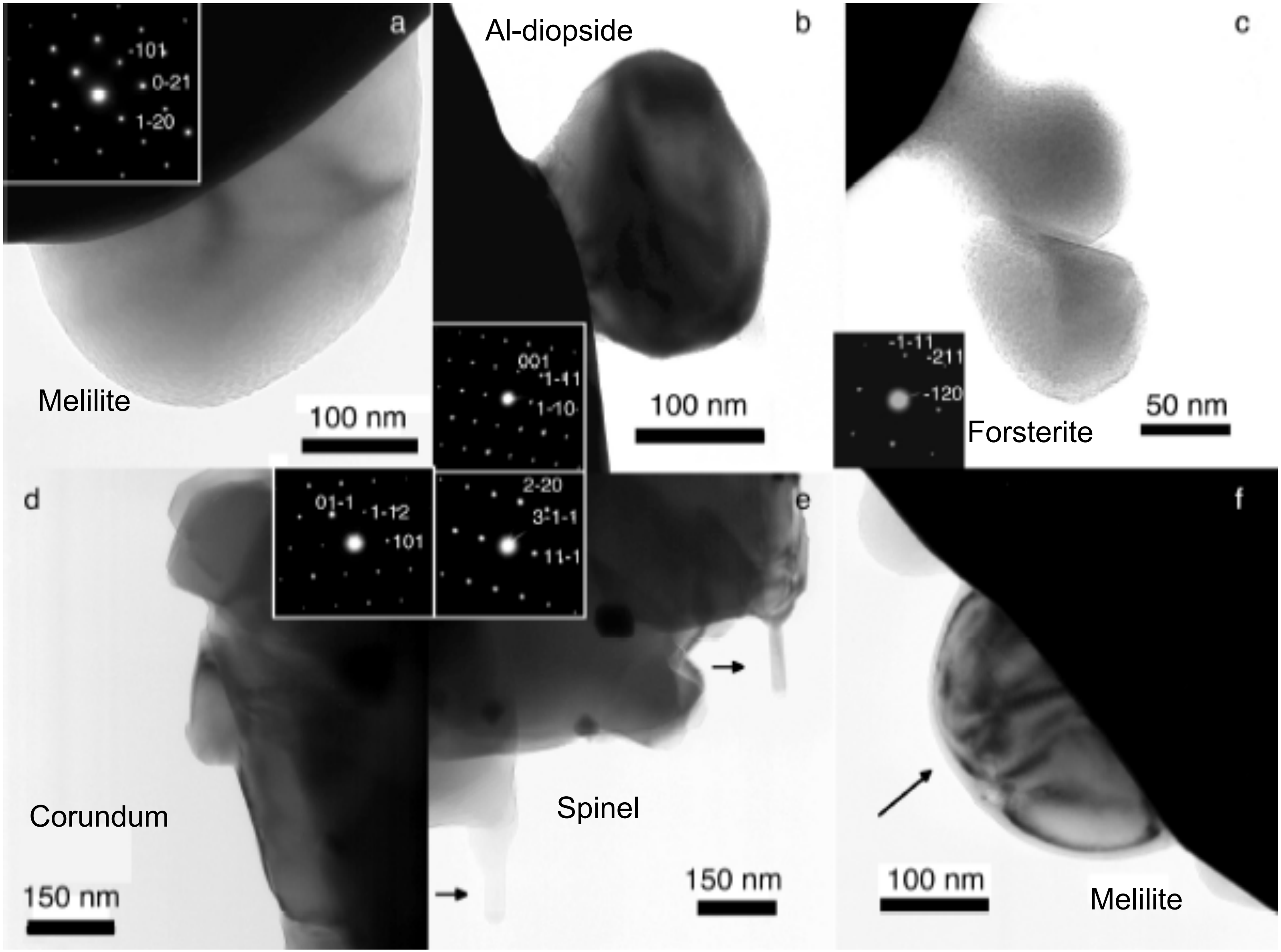
<u>Goals :</u>

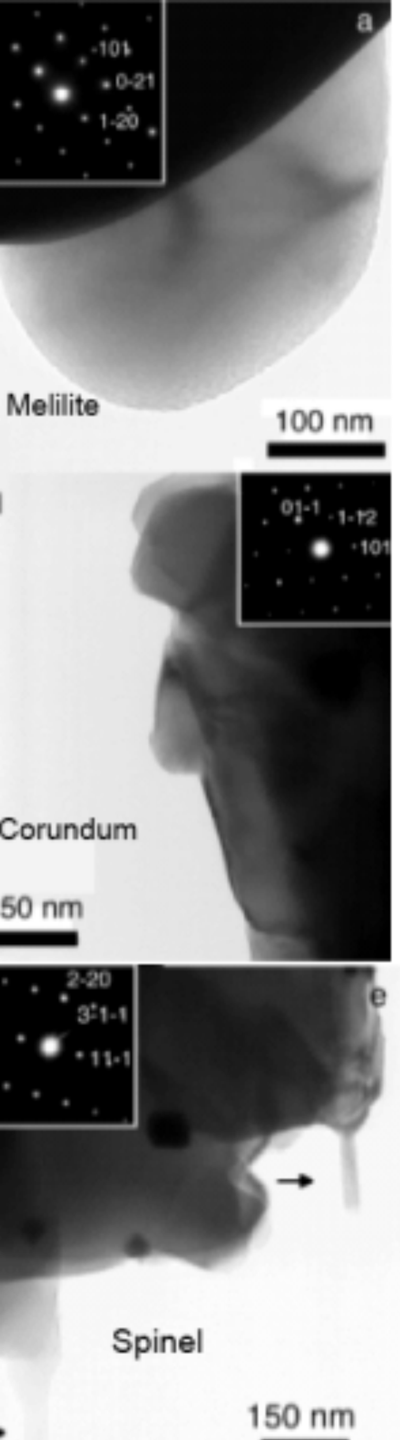
- ✓ Equilibirum or non equilibrium condensation
- ✓ condensation of refactory gases
- ✓ P, T, t controlled

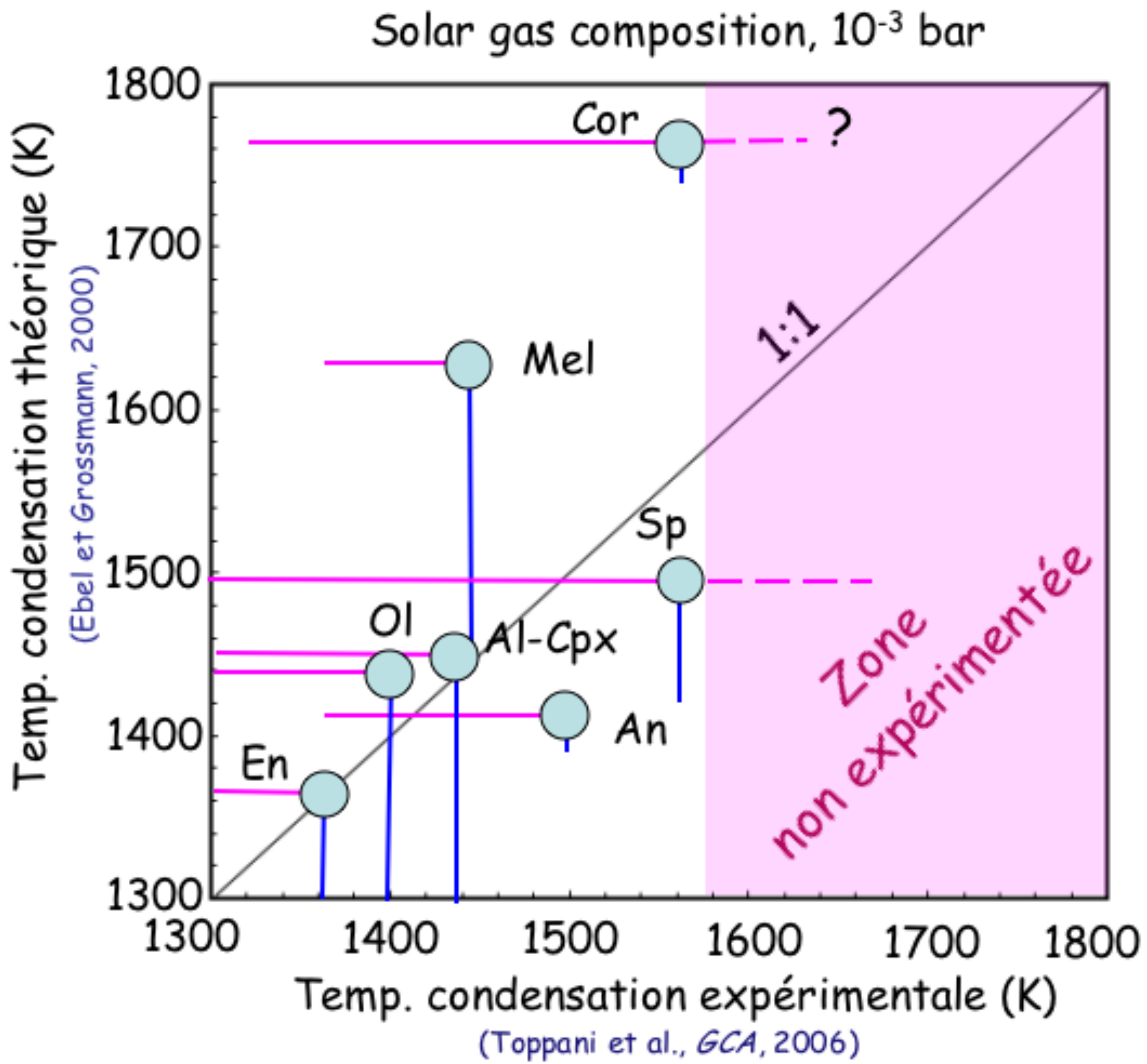
Stellar environments :

An experimental exploration

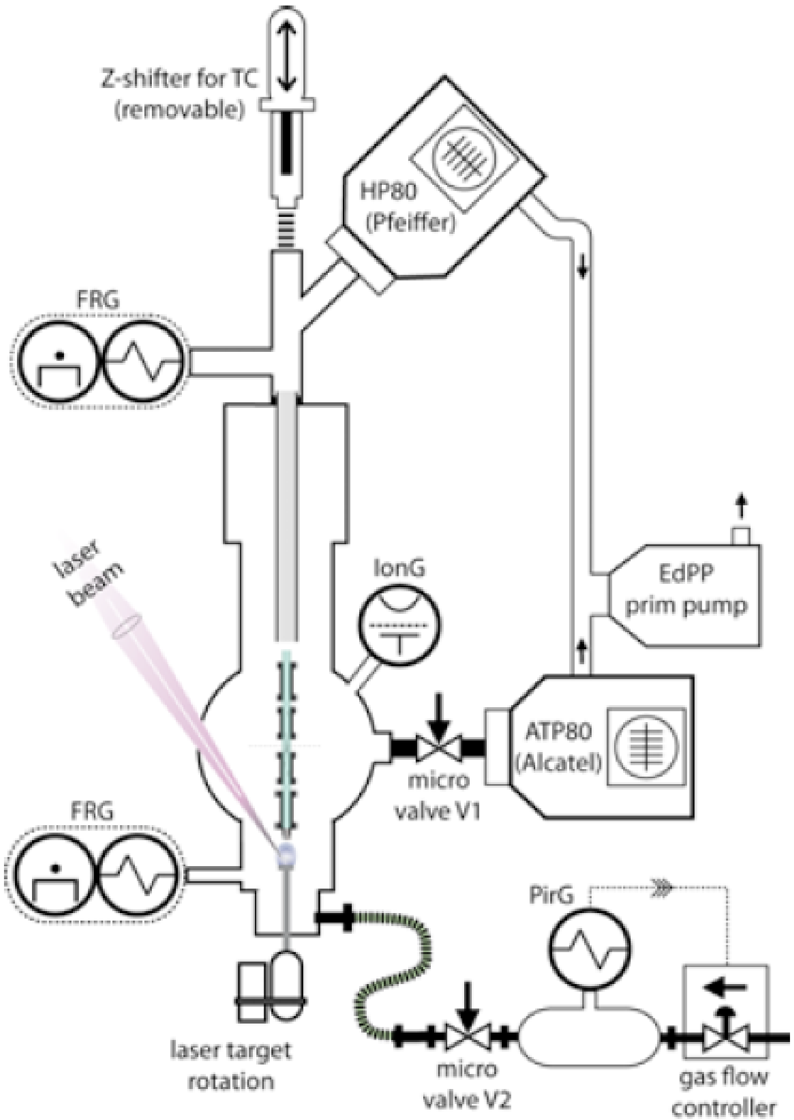
High temperature condensates from a solar gas composition.



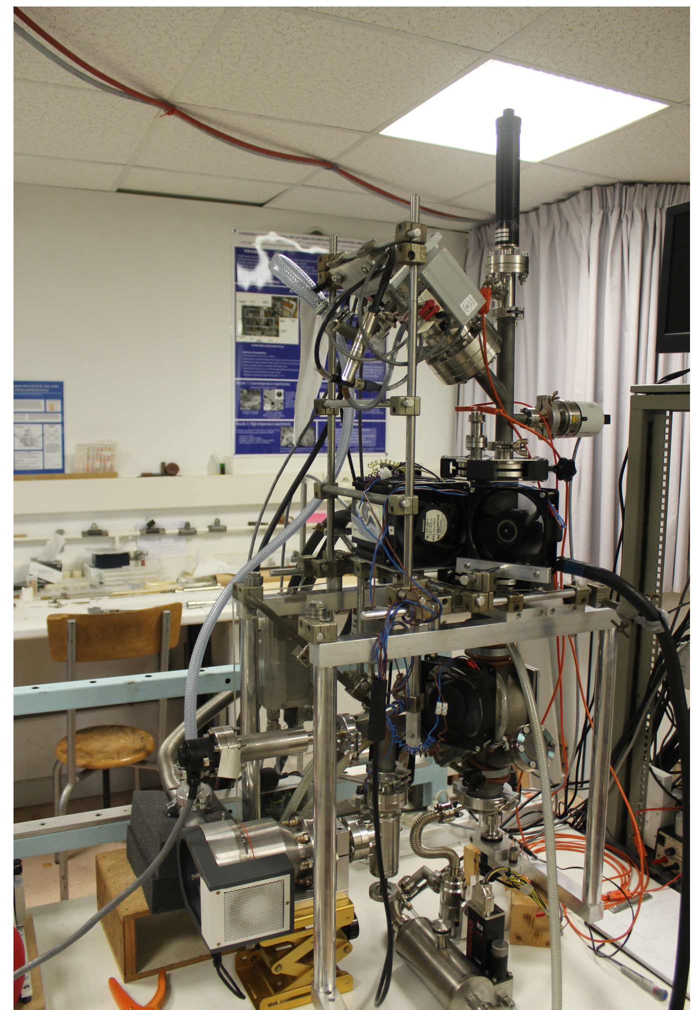

a
Melilite
100 nm
Corundum
50 nm
e
Spinel
150 nm


Solar gas composition, 10-3 bar
Temp. condensation théorique (K)
(Ebel et Grossmann, 2000)
Temp. condensation expérimentale (K)
(Toppani et al., GCA, 2006)
Cor
?
Mel
1:1
Sp
Ol
Al-Cpx
An
En
Zone
non expérimentée
1300
1400
1500
1600
1700
1800

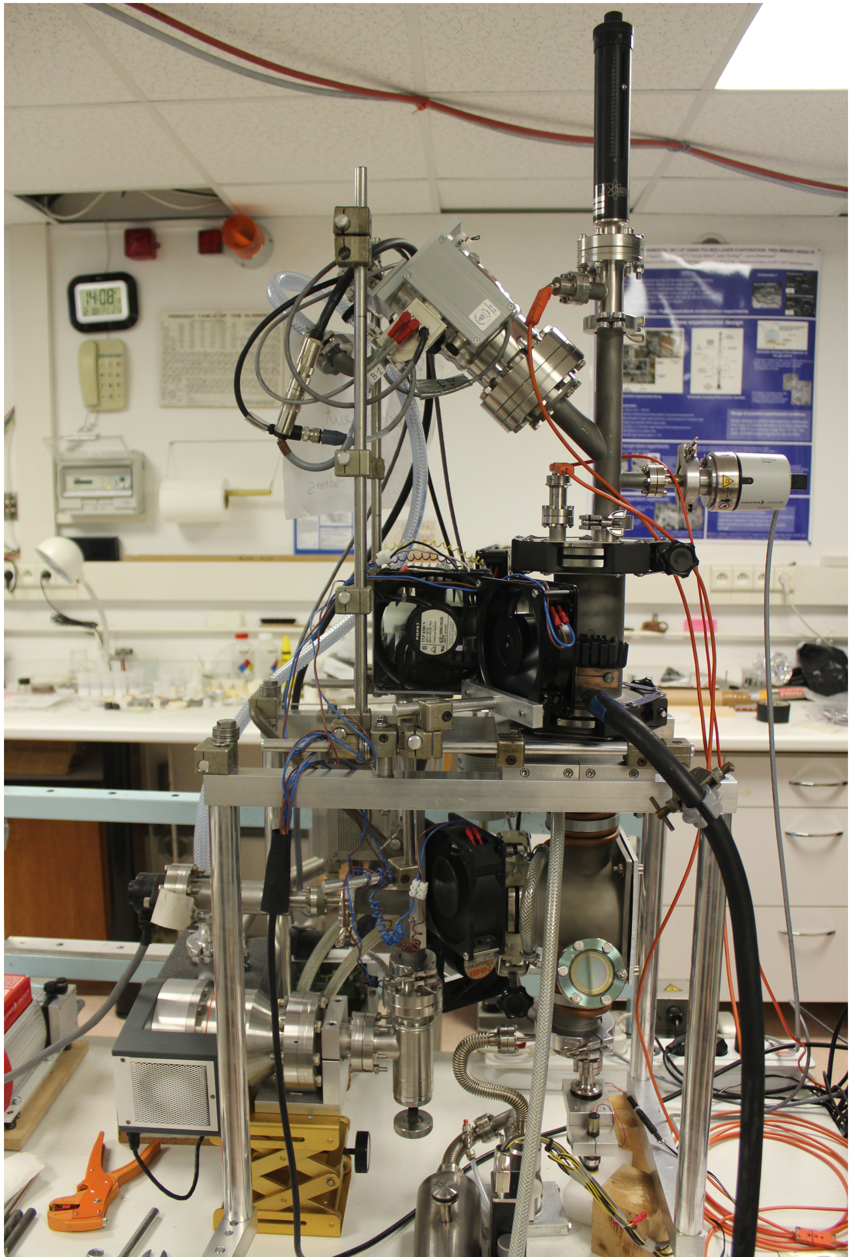
New generation of Nebulotron (VI)

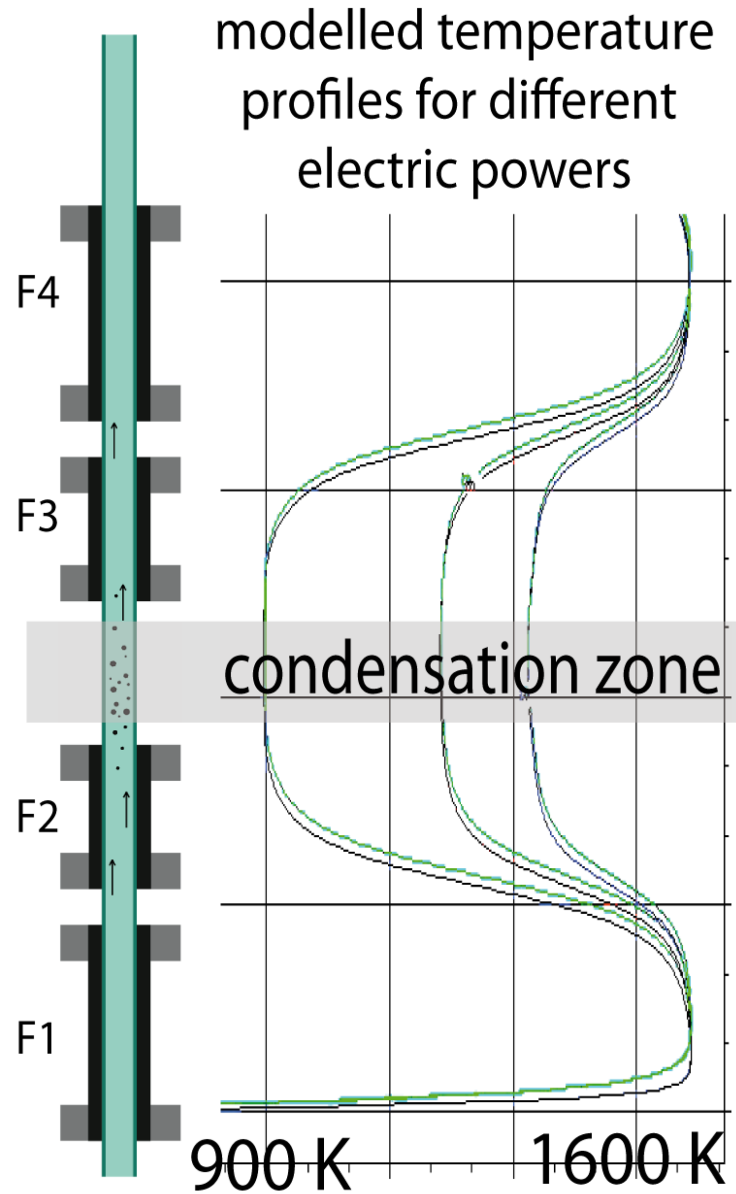


Kropf *et al.*, 2010
Marrocchi *et al.*, 2010, 2011



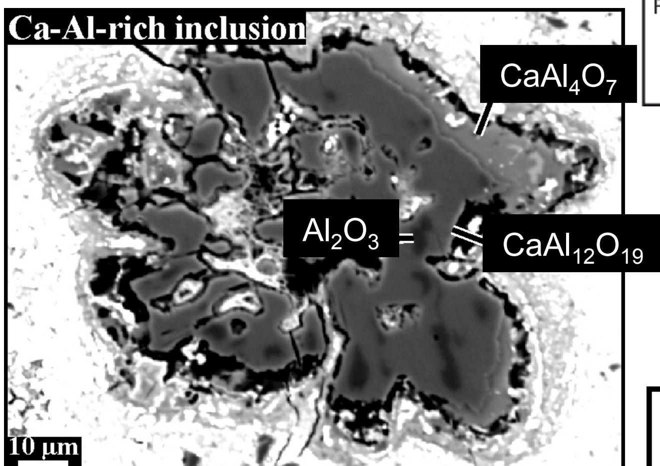
New generation of Nebulotron (VI)



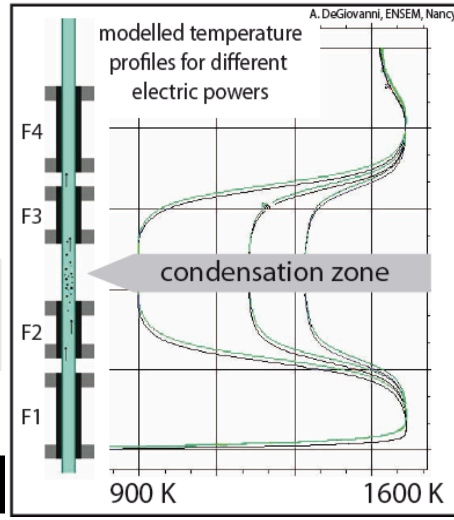


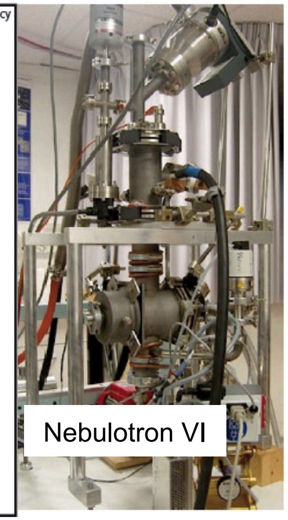
Condensation of the first solid in the solar system

Refractory inclusions (CAI) in chondrites



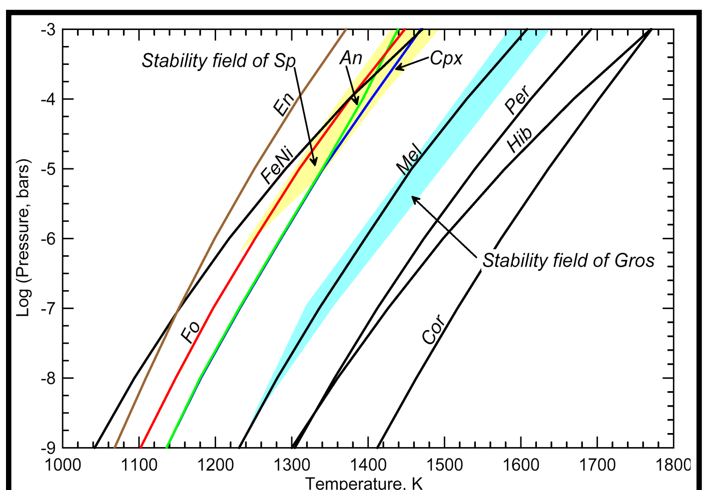
Primordial sequence of condensation
Solar and others stellar environments
Kinetics & condition of formation (P, T, fO_2)





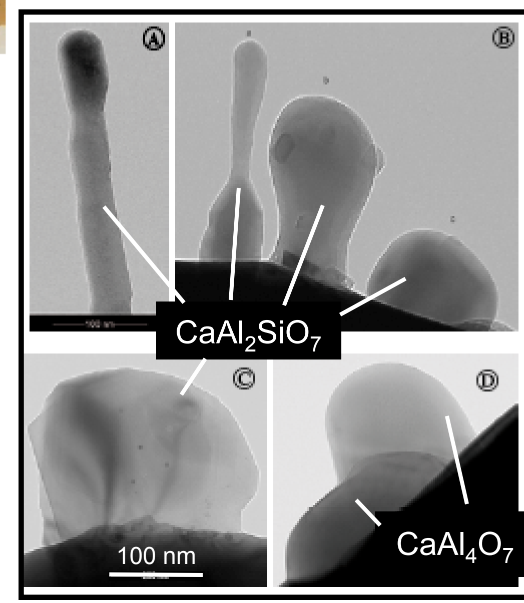
Analysis of condensates: post-mortem (TEM) or in-situ (SAXS, WAXS at ESRF)

Calculated stability fields of phases condensing from a solar gas



Experimental condensates from a solar gas,

$P_{tot} = 2*10^{-4}$ mbar; $T_{cond} = 1473$ K



Constraints on the origin of refractory inclusions

- formed early, possibly within 10^5 years of Sun formation
- formed in the high-temperature nebular region(s) (>1350 K), probably in the inner part of the disk
- formed under reduced (solar) conditions (e.g., Ti^{3+})
- preserved volatility-controlled REE patterns → CAIs or their precursors formed by evaporation-condensation processes; some were subsequently melted & cooled at 1-100 K/hr
- CAI melts experienced volatilization (experienced mass-dependent fractionation of Mg, Si, O isotopes) → low total pressure (<10^{-4} bar)
- were subsequently isolated (physically or kinetically) from hot nebular gas

Calcium-Aluminum-rich Inclusions WORLD

Gehlinite
$Ca_2Al_2SiO_7$

Spinel
$MgAl_2O_4$

Fassaite
$CaAl_2Si_2O_6$

Anorthite
$CaAl_2Si_2O_8$

Grossite
$CaAl_4O_7$

Ca-titanate
$Ca_4Ti_3O_{10}$

Melilite

Perovskite
$CaTiO_3$

Akermanite
$Ca_2MgSi_2O_7$

Krotite
$CaAl_2O_4$

Corundum
Al_2O_3

Hibonite
$CaAl_{12}O_{19}$

Dmisteinbergite
$CaAl_2Si_2O_8$

Diopside
$CaMgSi_2O_6$

Forsterite
Mg_2SiO_4

Condensation calculations

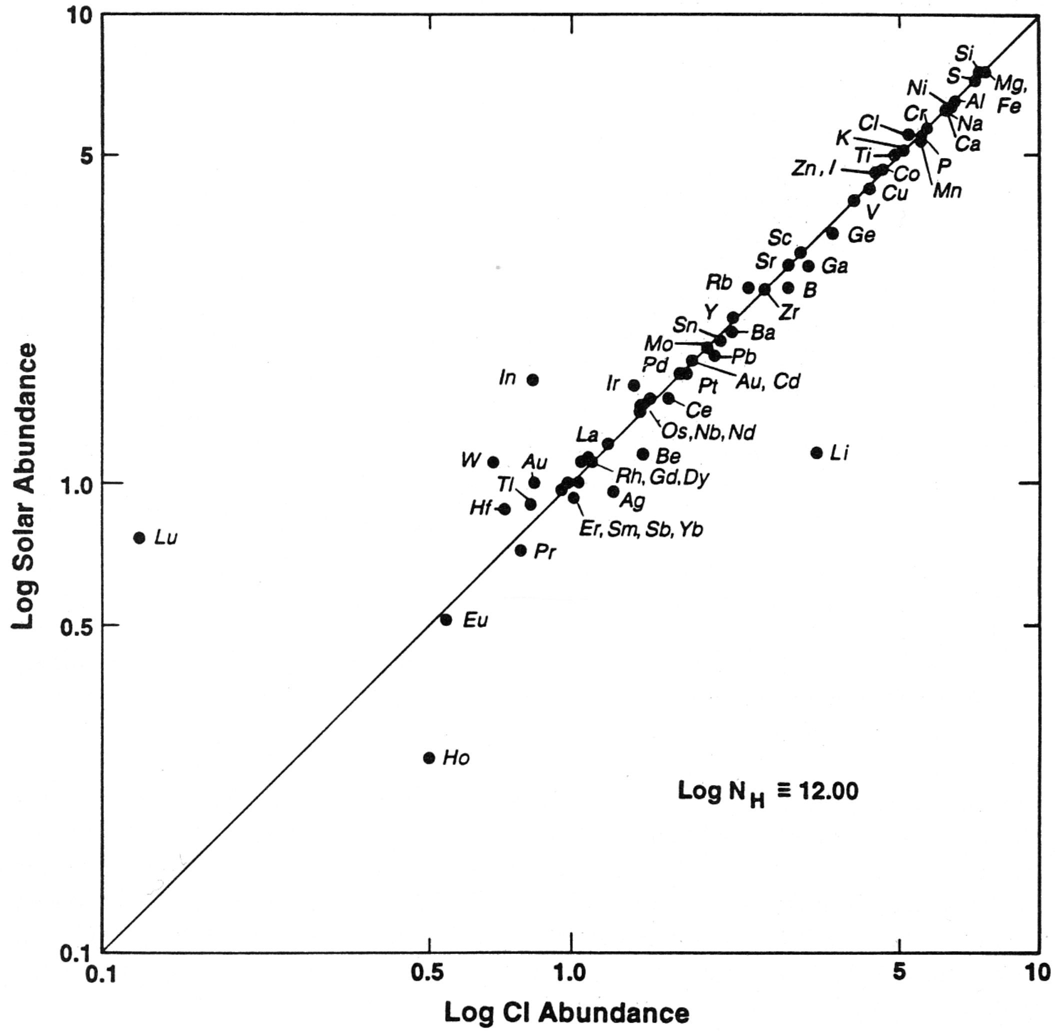
- How do they work?
  - starting composition: Solar composition, analysis of photosphere (spectroscopy) & chondrites (chemical analysis)

Table 1. First ionization potential, photospheric and solar atmosphere abundances above quiet regions[4]

Element		Ionization potential (eV)	Photospheric abundance	Log₁₀ solar abundance above typical quiet regions	
			$\log_{10}$	$3 \times 10^4 \le T \le 8 \times 10^5$ K	$\sim 1.4 \times 10^6$ K
1	H	13.6	12.00	12.00	12.00
2	He	24.6	10.93	10.93	10.93
6	C	11.3	8.52	8.52	8.52
7	N	14.5	7.92	7.92	7.92
8	O	13.6	8.83	8.83	8.83
10	Ne	21.6	8.11	8.11	8.11
11	Na	5.1	6.32	6.62	6.92
12	Mg	7.6	7.58	7.88	8.18
13	Al	6.0	6.49	6.79	7.09
14	Si	8.2	7.56	7.86	8.16
16	S	10.4	7.33	7.33	7.33
18	Ar	15.8	6.59	6.59	6.59
20	Ca	6.1	6.35	6.65	6.95
26	Fe	7.9	7.50	7.80	8.10
28	Ni	7.6	6.25	6.55	6.85

Starting composition

- Solar photosphere and meteorites have approximately the same (relative) abundances of condensable elements



Condensation calculations: HowTo

- Calculation of gas phase chemistry
  - basic thermodynamic data (c_p-functions, S^0_{298}, ΔH^0_{298}) are available from various sources (NIST-JANAF tables, CODATA, Robie *et al*., 1984, …)

- example: which are the stable components of "Si"
  - three gaseous components: Si(g), SiO(g) & SiO_2(g)

$$Si(g) + 0.5\ O_2 = SiO(g) \qquad (1)$$

$$Si(g) + O_2 = SiO_2(g) \qquad (2)$$

What are the proportions of the components in the gas?

- two equations, two unknowns (e. g. SiO, SiO_2)
  - third is then known: $n(Si) = n(Si_{tot}) - n(SiO) - n(SiO_2)$

Condensation calculations: HowTo

- Calculation of gas phase chemistry
  - three gaseous components: Si(g), SiO(g) & SiO_2(g)

Si(g) + 0.5 O_2 = SiO(g) (1)

Si(g) + O_2 = SiO_2(g) (2)

(1):

$$K_1 = \frac{p_{SiO}}{p_{Si} \times \sqrt{p_{O_2}}} \text{ with } \ln(K_1) = \frac{-\Delta G_{R(1)}}{R \times T}$$

re-aranging gives

$$\frac{-\Delta G_{R(1)}}{R \times T} + 0.5 \times \ln(p_{O_2}) = \ln \frac{p_{SiO}}{p_{Si}}$$

➡ $\Delta G_R(T,p)$ can be taken from thermodynamic databases

Condensation calculations: HowTo

- Calculation of gas phase chemistry
  - three gaseous components: Si(g), SiO(g) & SiO_2(g)

    Si(g) + 0.5 O_2 = SiO(g) (1)

    Si(g) + O_2 = SiO_2(g) (2)

    (2):

$$K_2 = \frac{p_{SiO_2}}{p_{Si} \times p_{O_2}} \text{ with } \ln(K_2) = \frac{-\Delta G_{R(2)}}{R \times T}$$

re-aranging gives

$$\frac{-\Delta G_{R(2)}}{R \times T} + \ln(p_{O_2}) = \ln \frac{p_{SiO_2}}{p_{Si}}$$

➔ $\Delta G_R(T,p)$ can be taken from thermodynamic databases

What are the proportions of the components in the gas?

- two equations, two unknowns (e. g. SiO, SiO_2)
  - third is then known: $n(\text{Si}) = n(\text{Si}_{tot}) - n(\text{SiO}) - n(\text{SiO}_2)$
  - proportions can be calculated from tabulated (or calculated) ΔG_R data (for calculating K_R's)

Gas-solid condensation (example forsterite condensation)

- 2 Mg(g) + SiO(g) + 3/2 O_2 = Mg_2SiO_4(s)

$$K_3 = \frac{a_{fo}}{p_{Mg}^2 \times p_{SiO} \times p_{O_2}^{\frac{3}{2}}} \text{ with } \ln(K_3) = \frac{-\Delta G_{R(3)}}{R \times T}$$

re-aranging gives

$$\frac{-\Delta G_{R(3)}}{R \times T} + \tfrac{3}{2}\ln(p_{O_2}) = \ln\frac{a_{fo}}{p_{SiO} \times p_{Mg}}$$

Oxygen fugacity buffered in a Solar gas

- gas is dominated by H & He (>99%)
  - C/O ratio of 0.5 (determines f_{O2}):
    - all C is bond to O as CO
    - rest (50%) of O is bond to H as H_2O
    - ratio H_2O/H_2 buffers f_{O2} in early Solar System

      reaction: $H + O_2 = H_2O$

➡ Solar nebula was VERY reducing

$\log f(O_2) \approx$ Fe/FeO-buffer – 6.5

Gas phase → condensates

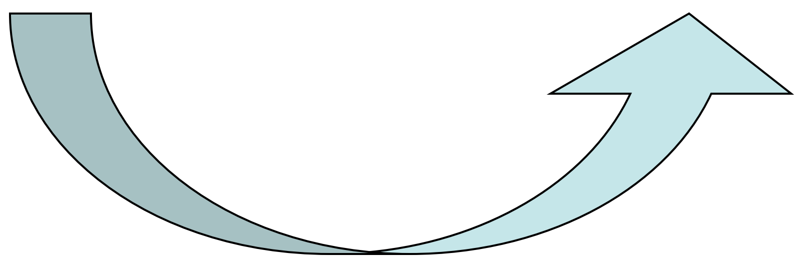
- the pressure (H_2 + He) in the inner Solar System was approximately 10^{-3} to 10^{-6} bar
- condensation accompanied by drastic volume reduction
  - very pressure sensitive

gas *forsterite*

- Reaction: $2\ Mg(g) + SiO(g) + 3/2\ O_2 = Mg_2SiO_4$ $T \approx 1400K$

ideal gas ($p = 10^{-5}$ bar)
cube: $V = 37.4 \times 37.4 \times 37.4$ m

mineral grains
$V = 3.5 \times 3.5 \times 3.5$ cm



➡ *condensation = volume reduction (!)*
➡ *condensation = oxidation reaction (in many cases)*

Gas phase → condensates

- condensation temperatures increase
  - with increasing pressure
  - with increasing oxygen fugacity

- principle of *Henri Le Chatelier* (1850–1936)

> ***If, to a system at equilibrium, a stress be applied, the system will react so as to relieve the stress.***

“Full condensation code”

- e. g. Ebel and Grossman (2000):
  - 24 elements
    - 324 gas species
    - 84 pure minerals
    - 8 complex solid solutions (e. g. metal alloys, pyroxene)
    - silicate melt

- requires simultaneous solution of >400 non-linear equations
  - numerical solution (requires approximations, e. g. Newton-Ralphson method)

Condensation calculations

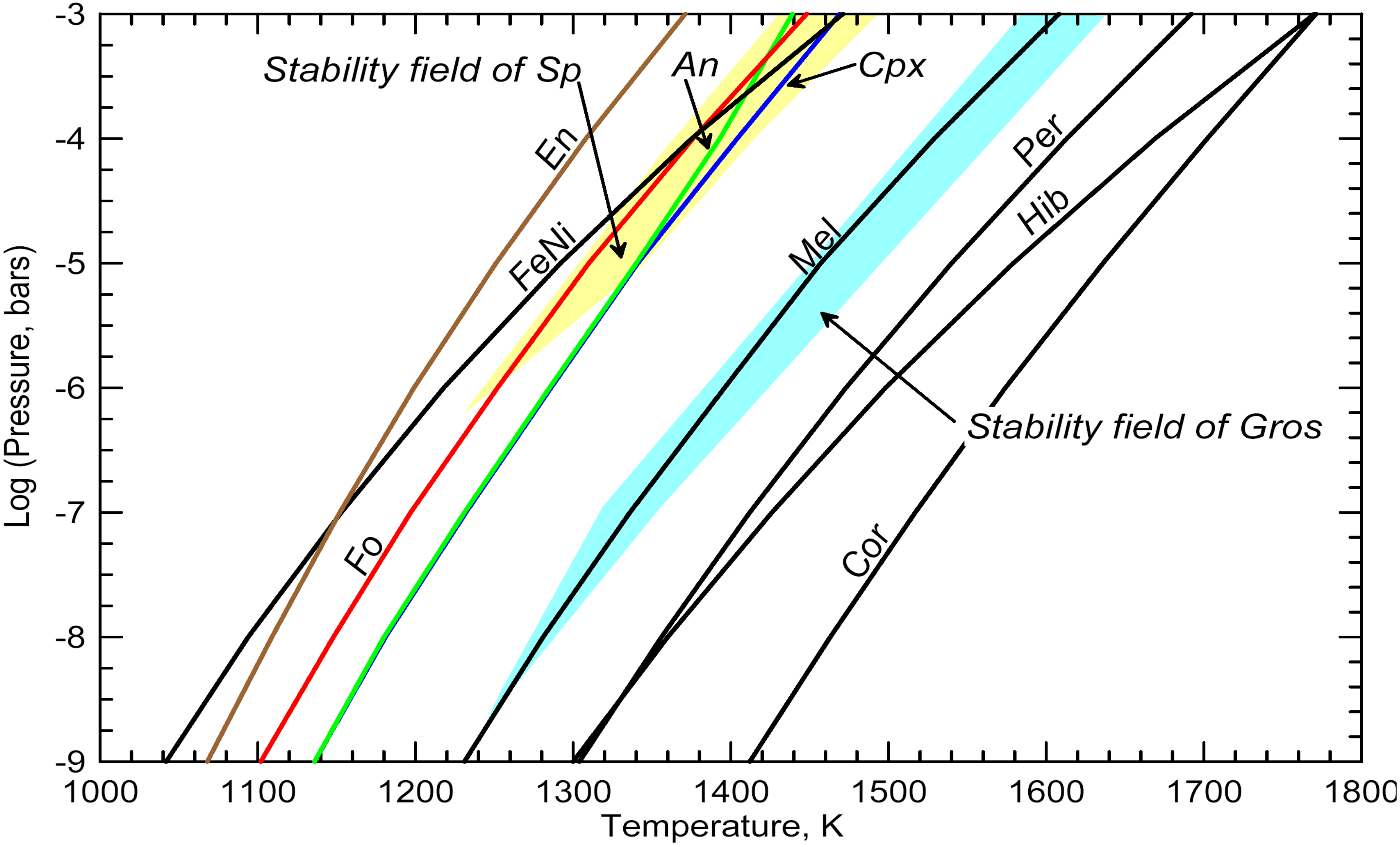
- condensation temperatures increase with increasing pressure

Table 3. Temperatures of appearance and disappearance of stable condensates at several representative total pressures in the pressure regime where liquids are not stable.

Condensate \ P^{tot} (atm)	1×10^{-6}		1×10^{-5}		1×10^{-4}		1×10^{-3}		1×10^{-2}	
	In	Out	In	Out	In	Out	In	Out	In	Out
Corundum	1571	1481	1633	1558	1699	1643	1770	1740		
Hibonite	1485	1292	1562	1350	1647	1421	1743	1500	1846	1590
Perovskite	1471	1257	1537	1317	1609	1380	1688	1448	1775	1523
$CaAl_2O_4$									1724	1711
Melilite ss									1711	1505
Corundum										
Spinel ss									1591	1481
Plagioclase ss										
Rankinite										
Fassaite ss									1524	
Spinel ss										
Forsterite									1525	
Plagioclase ss									1488	
Sphene										
Enstatite									1435	
Spinel ss	1161		1196		1217		1221		1219	
Ti_3O_5							1386	1361	1454	1358
Ti_4O_7			1252	1217	1324	1216	1361	1217	1358	1220
Sphene	1222		1217		1216		1217		1220	
Metal	1214		1287		1370		1464		1574	

increasing pressure → increasing condensation temperature

from Ebel and Grossman (2000) *Geochim. Cosmochim. Acta*



Petaev et al., 2005

Condensation calculations

- minerals that occur in CAIs condense at high temperatures

MAJOR ELEMENT CONDENSATION TEMPERATURES

Ideal Formula	Mineral Name	Solar System Composition (K)	Photospheric Composition (K)
Al_2O_3	Corundum	1677	1665
$CaAl_{12}O_{19}$	Hibonite	1659	1647
$CaAl_4O_7$	Grossite	1542	1531
$Ca_2Al_2SiO_7$	Gehlenite	1529	1519
$CaTiO_3$	Perovskite	1593	1584
$Ca_4Ti_3O_{10}$	Ca titanate	1578	1567
$Ca_3Ti_2O_7$	Ca titanate	1539	1529
$Ca_4Ti_3O_{10}$	Ca titanate	1512	1502
$CaTiO_3$	Perovskite	1441	1429
$MgAl_2O_4$	Spinel	1397	1387
$CaAl_2Si_2O_8$	Anorthite	1387	1378
Mg_2SiO_4	Forsterite	1354	1346
$MgSiO_3$	Enstatite	1316	1308
$CaMgSi_2O_6$	Diopside	1347	1339
Fe	Fe alloy	1357	1351
Fe_3P	Schreibersite	1248	1245
FeS	Troilite	704	693
Fe_3O_4	Magnetite	371	365
H_2O	Water ice	182	181

NOTE.—At 10^{-4} bar total pressure.

CAI minerals (Corundum through Diopside)

➡ minerals rich in Ca, Al and Ti (CAIs)

from Lodders (2003) *Astrophys. Journal*

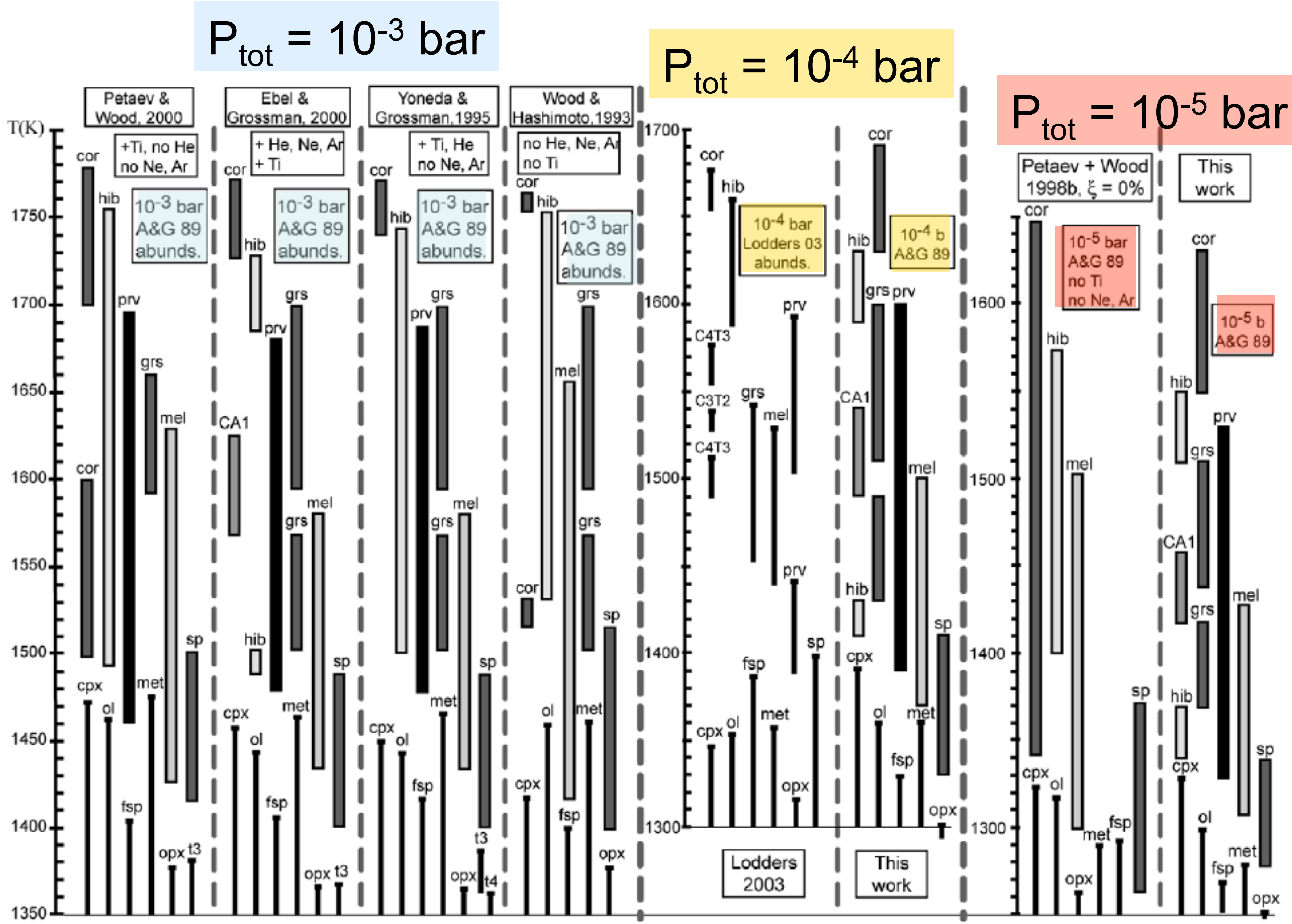
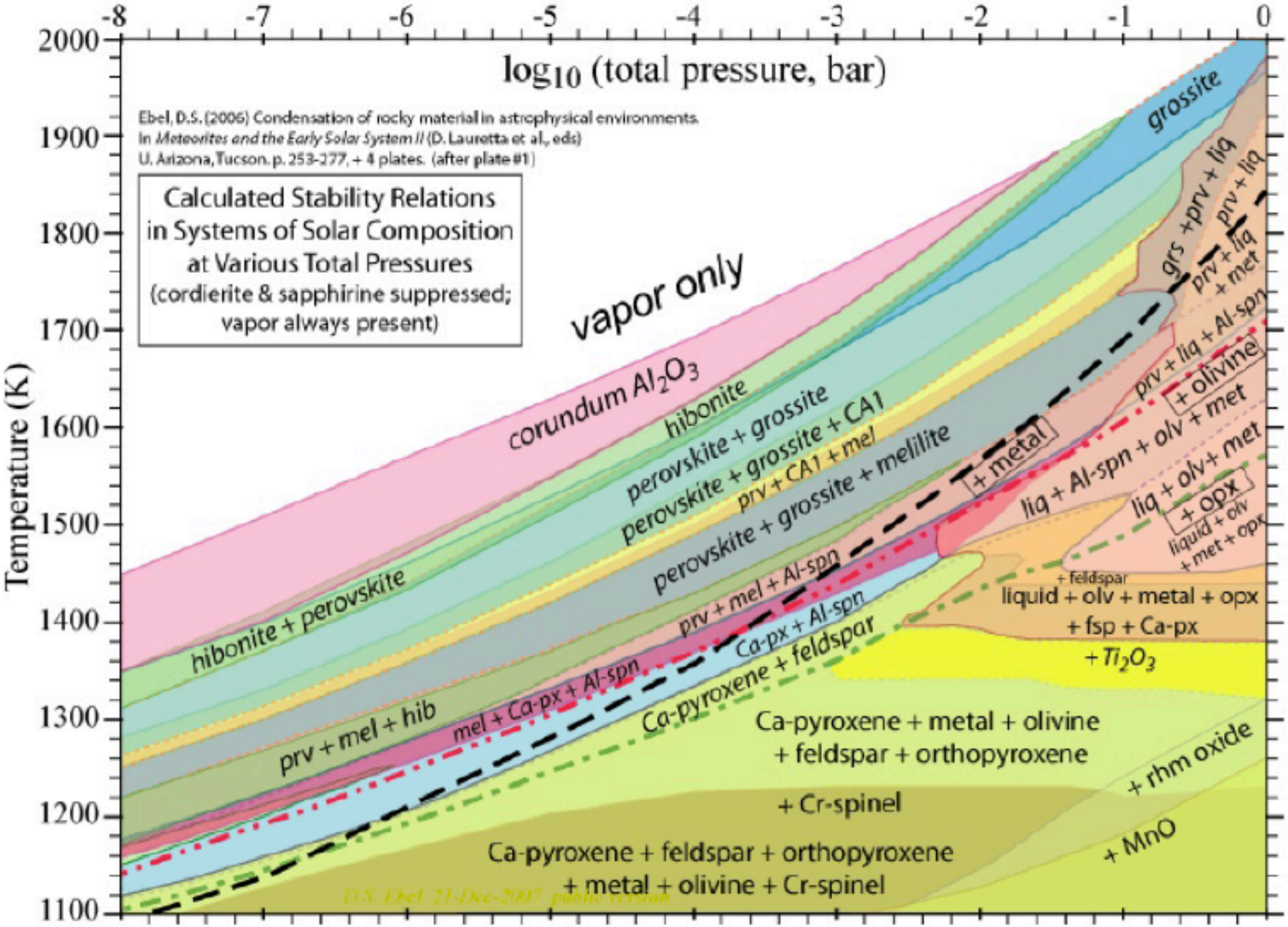
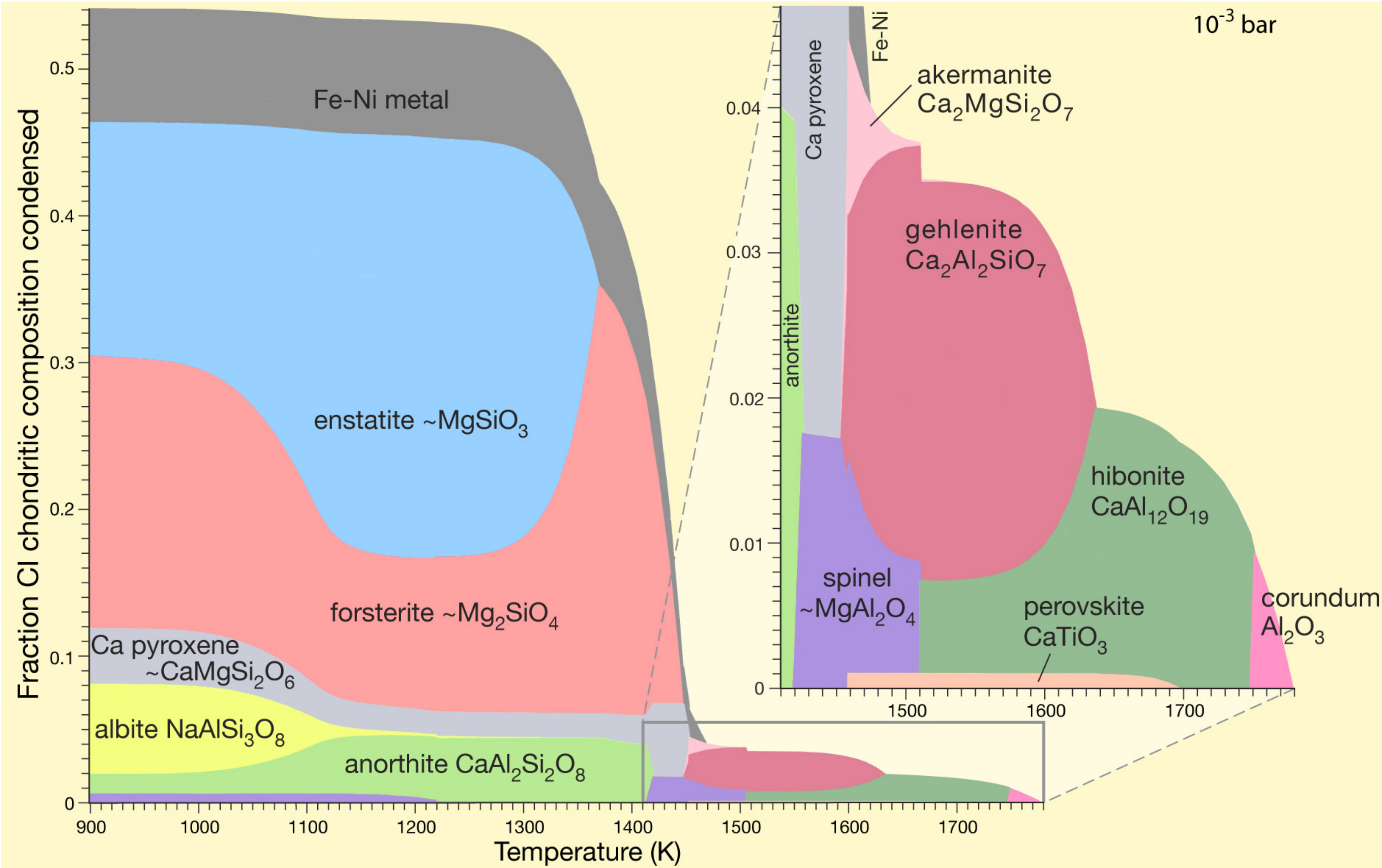


Fig. 1. Comparison of published results for vapor of solar composition (see section 3.1.2). Mineral abbreviations are t3 = Ti_3O_5, t4 = Ti_4O_7, C4T3 = $Ca_4Ti_3O_{10}$, C3T2 = $Ca_3Ti_2O_7$, sp = Al-spinel, cpx = Ca-pyroxene, and as listed in Table 1.


log10 (total pressure, bar)
-8
-7
-6
-5
-4
-3
-2
-1
0
Temperature (K)
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
Ebel, D.S. (2006) Condensation of rocky material in astrophysical environments.
In Meteorites and the Early Solar System II (D. Lauretta et al., eds)
U. Arizona, Tucson. p. 253-277, + 4 plates. (after plate #1)
Calculated Stability Relations
in Systems of Solar Composition
at Various Total Pressures
(cordierite & sapphirine suppressed;
vapor always present)
vapor only
corundum Al2O3
hibonite
hibonite + perovskite
perovskite + grossite
perovskite + grossite + CA1
prv + CA1 + mel
perovskite + grossite + melilite
perovskite + grossite + Al-spn
prv + mel + hib
mel + Ca-px + Al-spn
prv + mel + Al-spn
Ca-px + Al-spn
Ca-pyroxene + feldspar
grossite
grs + prv + liq
prv + liq
prv + liq + met
prv + liq + Al-spn
+ olivine
+ metal
liq + Al-spn + olv + met
liq + olv + met
+ opx
liquid + olv + met + opx
+ feldspar
liquid + olv + metal + opx
+ fsp + Ca-px
+ Ti2O3
Ca-pyroxene + metal + olivine
+ feldspar + orthopyroxene
+ rhm oxide
+ Cr-spinel
+ MnO
Ca-pyroxene + feldspar + orthopyroxene
+ metal + olivine + Cr-spinel
D.S. Ebel 21-Dec-2007 public version



Courtesy of A. Davis

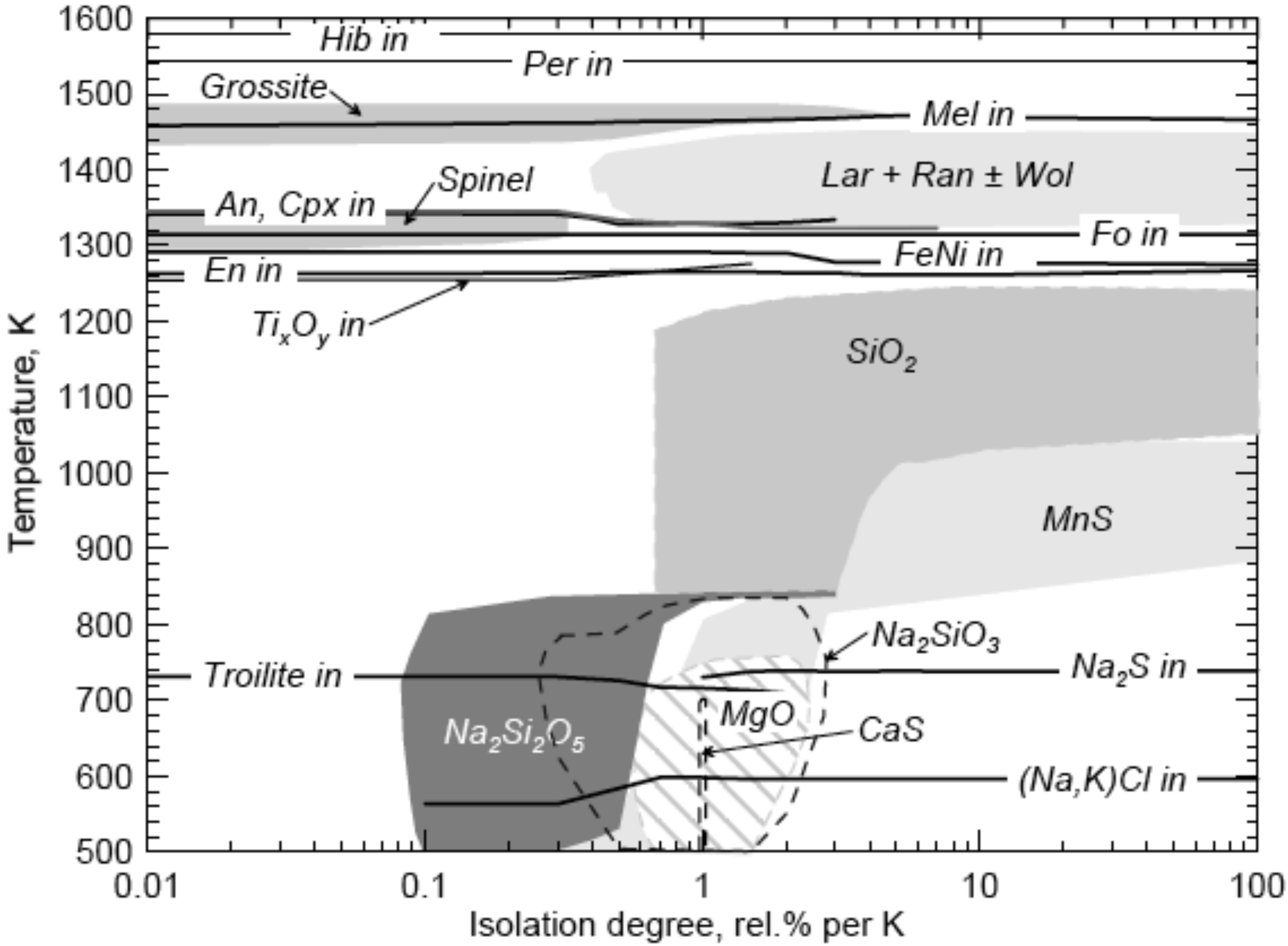
Condensation **W**ith **P**artial **I**solation model*

As condensation proceeds a specified fraction of the existing condensate is withdrawn from reactive contact with the residual gas so that:

- System contains two categories of condensate – *Reactive solids* and *Inert solids*
- *Reactive solids* (M_r) are exposed to the residual gas and remain in complete equilibrium with it
- *Inert solids* (M_i) are isolated from the residual gas
- *Isolation degree* ξ is the relative amount (% per K) of reactive solids that is withdrawn from the reactive system at any given temperature interval
- *Isolation rate* (dM_i/dT) is the absolute amount of reactive solids, Δm_i (moles), that is withdrawn from the reactive system at any given temperature interval

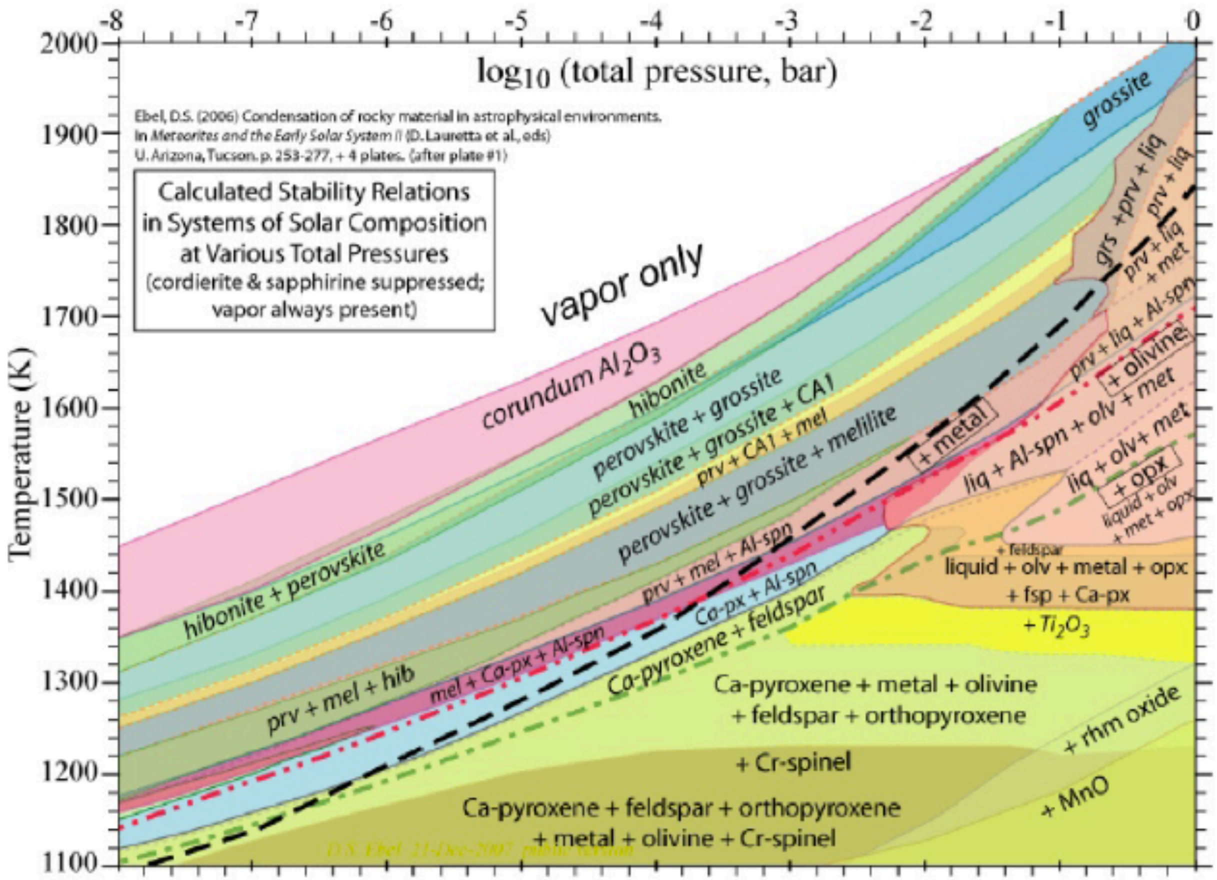
* *Petaev M. I. and Wood J. A.* (1998) *MAPS* **33**, 1123-1137.

Condensation With Partial Isolation model



The condensation calculations have been further improved by e.g. Lodders 2003 or Ebel 2006

Mineral	Abbreviation	Chemical Formula
corundum	cor	Al_2O_3
hibonite	hib	$CaAl_{12}O_{19}$
grossite	grs	$CaAl_4O_7$
Ca-monoaluminate	CA1	$CaAl_2O_4$
perovskite	prv	$CaTiO_3$
melilite	mel	$Ca_2(Al_2, MgSi)SiO_7$
Al-spinel	Al-spn	Al-rich $(Fe,Mg,Cr,Al,Ti)_3O_4$
Cr-spinel	Cr-spn	Cr-rich $(Fe,Mg,Cr,Al,Ti)_3O_4$
olivine	olv	$(Mg_2, Fe_2, MgCa)SiO_4$
metal alloy	met	Fe,Ni,Co,Cr,Si
feldspar	fsp	$(CaAl, NaSi, KSi)AlSi_2O_8$
Ca-pyroxene	Ca-px	$Ca(Mg,Fe,Ti^{4+},Al,Si)_2O_6$
orthopyroxene	opx	$MgSiO_3$-$FeSiO_3$
rhombohedral oxide	rhm oxide	$(Mg,Fe^{2+},Ti^{4+},Mn)_2O_3$
pyrophanite	—	$MnTiO_3$
whitlockite	wt	$Ca_3(PO_4)_2$
troilite	—	FeS
oldhamite	—	CaS
osbornite	—	TiN
graphite	—	C
cohenite	—	Fe_3C
Suppressed:		
cordierite	—	$Mg_2Al_4Si_5O_{18}$
sapphirine	—	$Mg_4Al_8Si_2O_{20}$



Equilibrium stability relations of vapor, minerals and silicate liquid as a function of temperature (T) and total pressure (P) in a system with solar bulk composition.

Condensation temperatures are **always** a function of

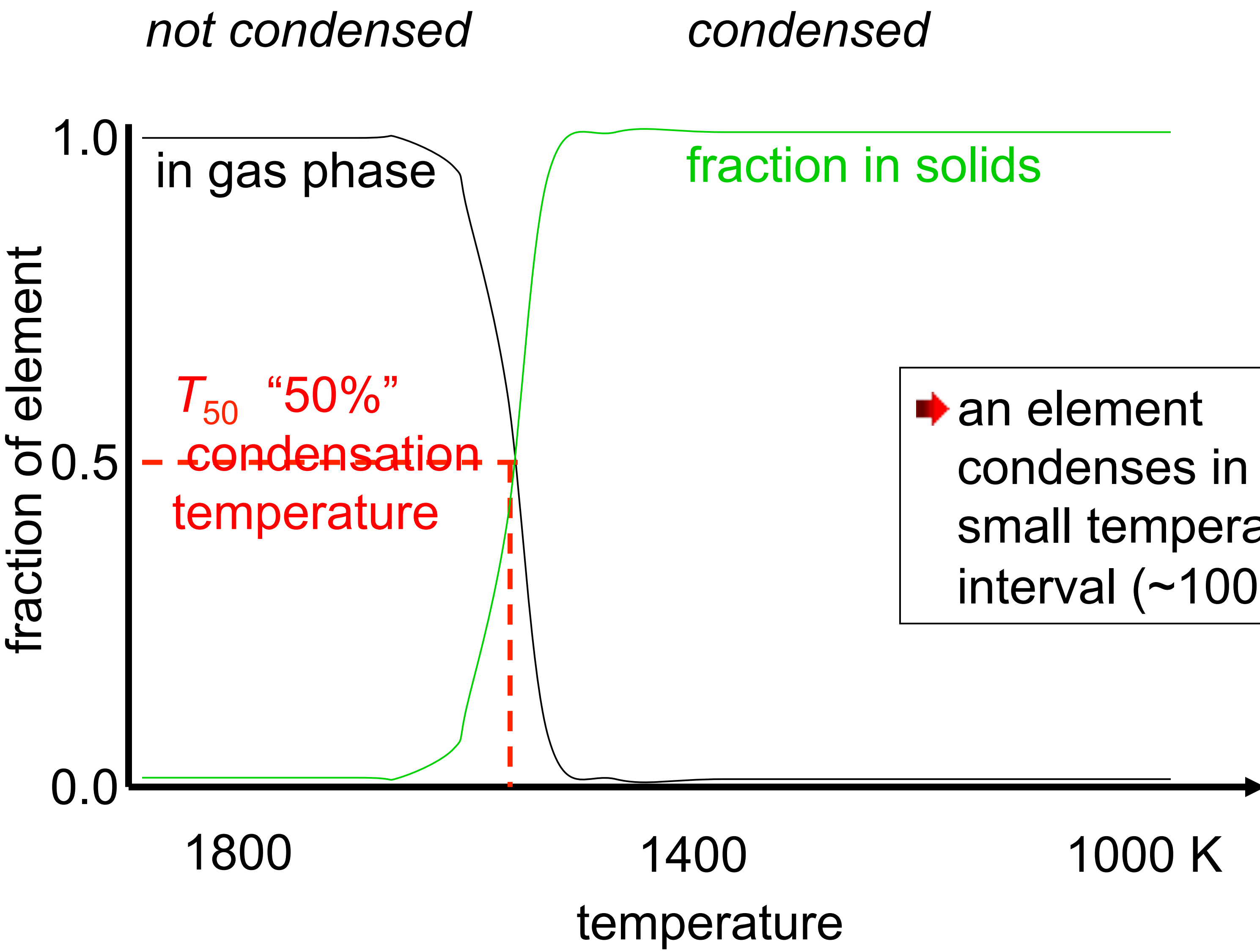
- pressure
- oxygen fugacity
- thermodynamic data used

Condensation temperatures can be given for
- minerals (*in-out*)
- elements ($T_{50\%}$)

EQUILIBRIUM CONDENSATION TEMPERATURES FOR A SOLAR-SYSTEM COMPOSITION GAS

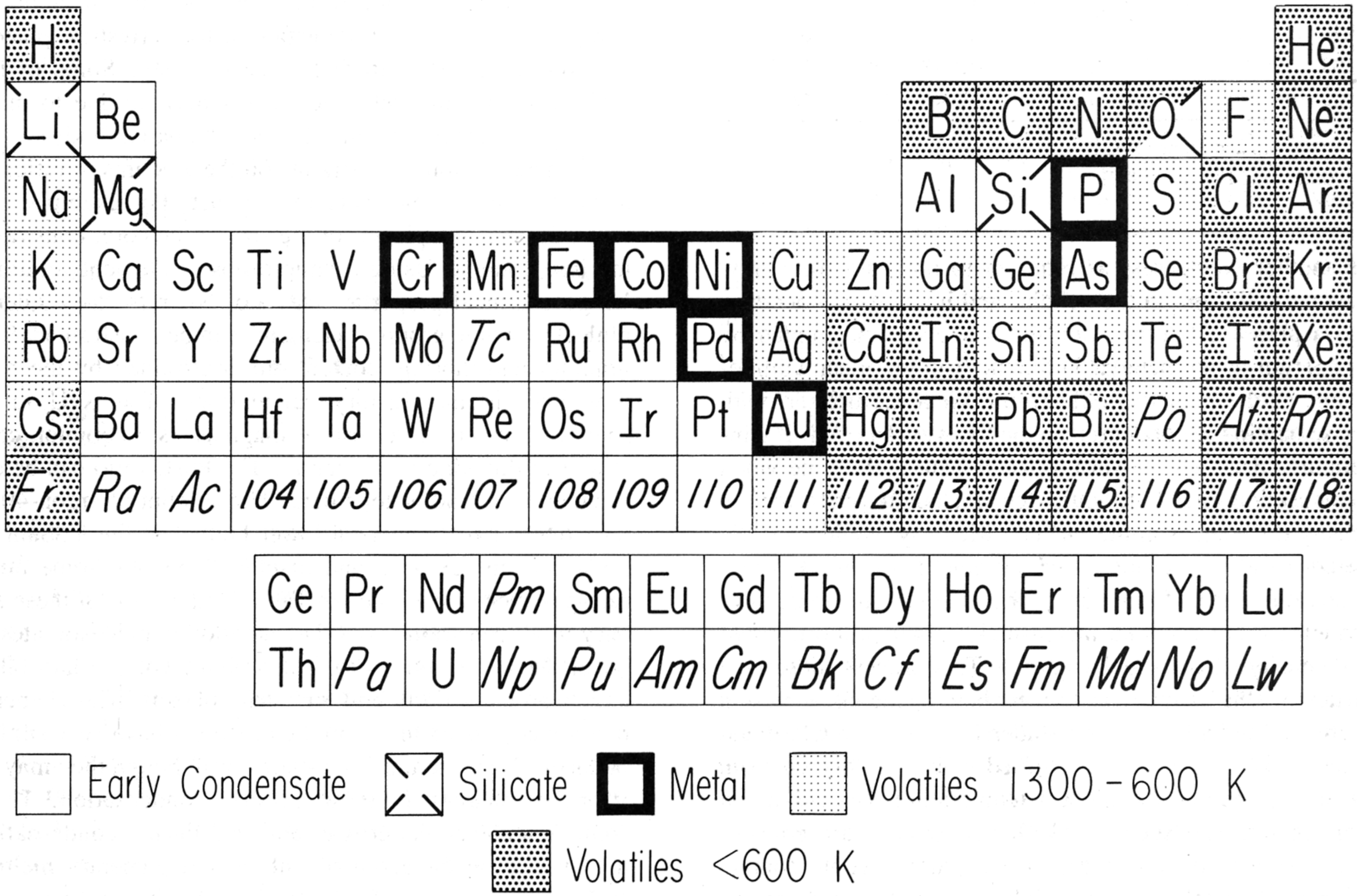
Element (1)	T_C (K) (2)	Initial Phase {Dissolving Species} (3)	50% T_C (K) (4)	Major Phase(s) or Host(s) (5)
H	182	H_2O ice	...	...
He	<3	He ice	...	...
Li		{Li_4SiO_4, Li_2SiO_3}	1142	Forsterite + enstatite
Be		{$BeCa_2Si_2O_7$}	1452	Melilite
B		{$CaB_2Si_2O_8$}	908	Feldspar
C	78	$CH_4{\cdot}7H_2O$	40	$CH_4{\cdot}7H_2O$ + CH_4 ice
N	131	$NH_3{\cdot}H_2O$	123	$NH_3{\cdot}H_2O$
O	182	Water ice[a]	180	rock + water ice
F	739	$Ca_5[PO_4]_3F$	734	F apatite
Ne	9.3	Ne ice	9.1	Ne ice
Na		{$NaAlSi_3O_8$}	958	Feldspar
Mg	1397	Spinel		
	1354	Forsterite[b]	1336	Forsterite
Al	1677	Al_2O_3	1653	Hibonite
Si	1529	Gehlenite		
	1354	Forsterite[b]	1310	Forsterite + enstatite
P	1248	Fe_3P	1229	Schreibersite
S	704	FeS	664	Troilite
Cl	954	$Na_4[Al_3Si_3O_{12}]Cl$	948	Sodalite
Ar	48	$Ar{\cdot}6H_2O$	47	$Ar{\cdot}6H_2O$
K		{$KAlSi_3O_8$}	1006	Feldspar
Ca	1659	$CaAl_{12}O_{19}$	1517	Hibonite + gehlenite
Sc		{Sc_2O_3}	1659	Hibonite
Ti	1593	$CaTiO_3$	1582	Titanate
V		{VO, V_2O_3}	1429	Titanate
Cr		{Cr}	1296	Fe alloy
Mn		{Mn_2SiO_4, $MnSiO_3$}	1158	Forsterite + enstatite
Fe	1357[c]	Fe metal[c]	1334	Fe alloy
Co		{Co}	1352	Fe alloy
Ni		{Ni}	1353	Fe alloy
Cu		{Cu}	1037	Fe alloy

Concept of the "50% *condensation temperature*"



➡ an element condenses in a very small temperature interval (~100 K)

Cosmochemical element classification



Condensation behavior of the elements. Short-lived radioactive elements are shown in italics (after Morgan and Anders, 1980).