Prospects For Determining Element Partitioning Between Silicate And Metallic Melts From Ab Initio Calculations

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General idea (to refine):

Partitioning of Ni, Co, Mn, Cr, REE, etc. between:

(Mg,Fe)O and/or (Mg,Fe)(Si,Fe)O3 and/or (Mg,Fe)2SiO4

&

Si, C, O, S, P, etc. – bearing Fe-rich melt

As a function of:

- Pressure & Temperature
- Fe amount in oxide/silicate melt
- Fe redox state
- Fe spin state
- Si, C, O, S, P amount in iron melt

1st approach:

get solubility of element X independently in two different melts as a function of different parameters (P, T, concentration of other elements, iron spin and redox state, etc.)

ratio yields partitioning

pros: "clean" thermodynamics, a lot of information about the melts

cons: fluctuation of thermodynamical parameters might be too large

2nd approach

put two melts in contact

atoms on the interface

monitor relative diffusion

pros: chemical reactions

cons: requires VERY LONG simulation times & sizes

Methodology:

computational methods

First-principles Molecular Dynamics

- Newtonian equations of motion of particles (i.e. atoms)
- Energy + forces computed using Density-Functional Theory
- Final aim: explore P-T-X conditions unreachable in experiments

Ensure overlap in some of P-T-X-mass conditions exist for double checks and confirmations

experimental methods

- Piston-cylinder / multianvil /diamond anvil cell experiments
- Final aim: explore mass-X conditions unreachable in calculations

WHAT IS THE DENSITY FUNCTIONAL THEORY

$$E[n(r)] = T_s[n(r)] + E_{ext}[n(r)] + E_{col}[n(r)] + E_{xc}[n(r)]$$

Kinetic energy of non-interacting electrons

Energy term due to exterior

Coulombian energy = $E_{ee} + E_{eN} + E_{NN}$

Exchange correlation energy

Electron spin:

Decrease energy

Increases

$$n(r) = N\int d^3r_2 \int d^3r_3 \ldots \int d^3r_N \psi^*(r, r_2, r_3, \ldots, r_N)\psi(r, r_2, r_3, \ldots, r_N)$$

computational methods

DENSITY FUNCTIONAL THEORY

Idea:
one determines ***the energy and the electron density***
(Kohn, Sham in the sixties: the one responsible for the chemical bonds) from which by proper integrations and derivations all the other physical properties are obtained.

INPUT

Structure: atomic types + atomic positions =
initial guess of the geometry

There is no experimental input !

What is it HARD to calculate ?

Transport properties: thermal conductivity, electrical conductivity of insulators, rheology, diffusion

Excited electronic states: optical spectra

Width of IR/Raman peaks, **Melting curves**, **Fluid properties**

PARTITIONING BETWEEN 2 FLUIDS / 2 SOLIDS / FLUID+MELT

What we can *easily* calculate ?

Electronic properties: orbital energies, chemical bonding, electrical conductivity

Structural properties: prediction of structures (under extreme conditions), phase diagrams, surfaces, interfaces, amorphous solids

Mechanical properties: elasticity, compressibility, thermal expansion

Dielectric properties: hybridizations, atomic dynamic charges, dielectric susceptibilities, polarization, non-linear optical coefficients, piezoelectric tensor

Spectroscopic properties: Raman spectra with peak position and intensity, IR peaks

Dynamical properties: phonons, lattice instabilities, prediction of structures, thermodynamic properties, phase diagrams, thermal expansion

experimental methods

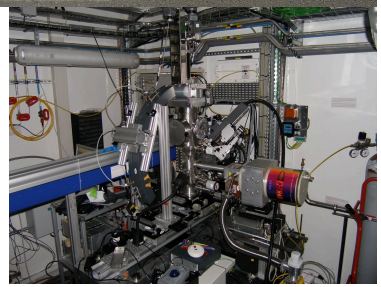
Get a diamond anvil cell

Get beamtime on a synchrotron

Load your cell. Put medium.

Go to synchrotron/ Come to BGI

Run your experiment



computational methods

Get an ab initio software package

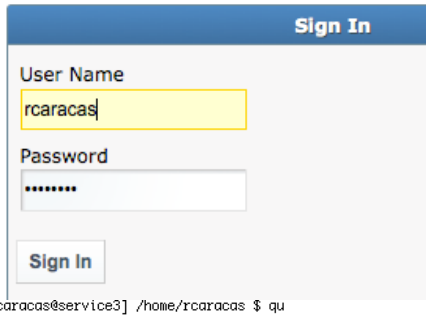
abinit.org

Get time on a supercomputer

Input your structure. Choose pseudos, XCs.

```
kptopt 1
ngkpt 6 6 6
ecut 16 pawecutdg 36
nstep 1000 ixc 7 nshiftk 1
natom 20 ntypat 3 znucl 26
typat    1 2  3  3  1  2  3
ecutsm 0.5 dilatmx 1.2
: vi fesio3.MxS1.inp
```

Go to supercomputer



Run your experiment

```
[rcaracas@service3] /home/rcaracas $ qu

service0:

                                                                  Req'd  Req'd   Elap
Job ID          Username Queue    Jobname    SessID NDS TSK Memory Time  S Time
--------------- -------- -------- ---------- ------ --- --- ------ ----- - -----
1011554.service rcaracas long_hpt d30.d00Y.P  24139   2  16   16gb 120:0 R 86:16
1015159.service rcaracas long_hpt d35.d00Y.P   5509   2  16   16gb 120:0 R 60:36
1015626.service rcaracas long_hpt pv8_00GPa    8203   1   8 7813mb 120:0 R 39:48
1015627.service rcaracas long_hpt pv8_20GPa   27010   1   8 7813mb 120:0 R 39:39
1015628.service rcaracas long_hpt pv8_40GPa   32353   1   8 7813mb 120:0 R 39:38
1015629.service rcaracas long_hpt pv8_60GPa   30866   1   8 7813mb 120:0 R 39:38
1015630.service rcaracas long_hpt pv8_80GPa   26176   1   8 7813mb 120:0 R 39:04
1015631.service rcaracas long_hpt pv8_100GPa  29547   1   8 7813mb 120:0 R 38:48
1015632.service rcaracas long_hpt pv8_120GPa  24968   1   8 7813mb 120:0 R 38:45
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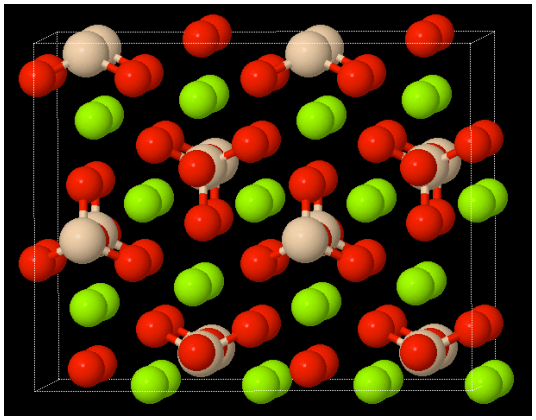
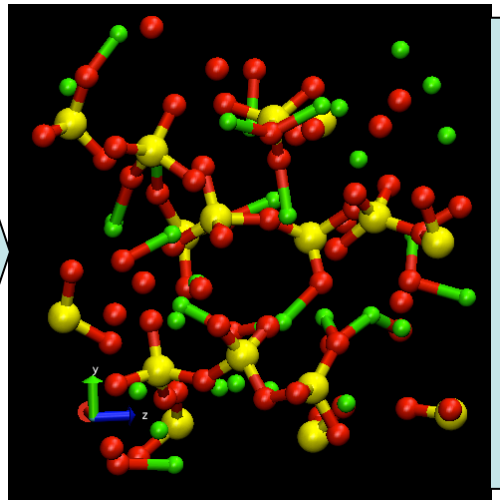
1st approach: PROCEDURE

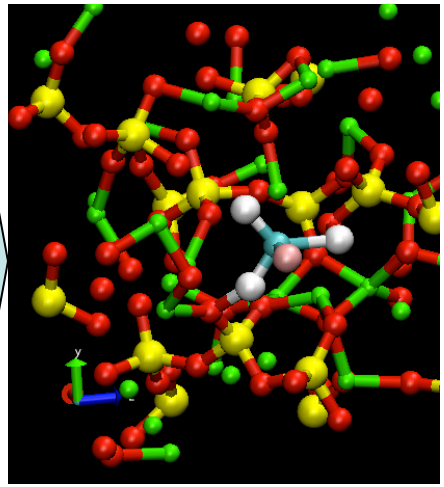
example C-bearing forsterite melt,
do believe me nothing to do with Dan's talk !



Melt



Add
C
CO2
$MgCO_3$



We start with forsterite (Mg_2SiO_4) 128 atoms box

Overheat (5000K) => melt

Cool down (3000K) the melt

Play with chemistry:

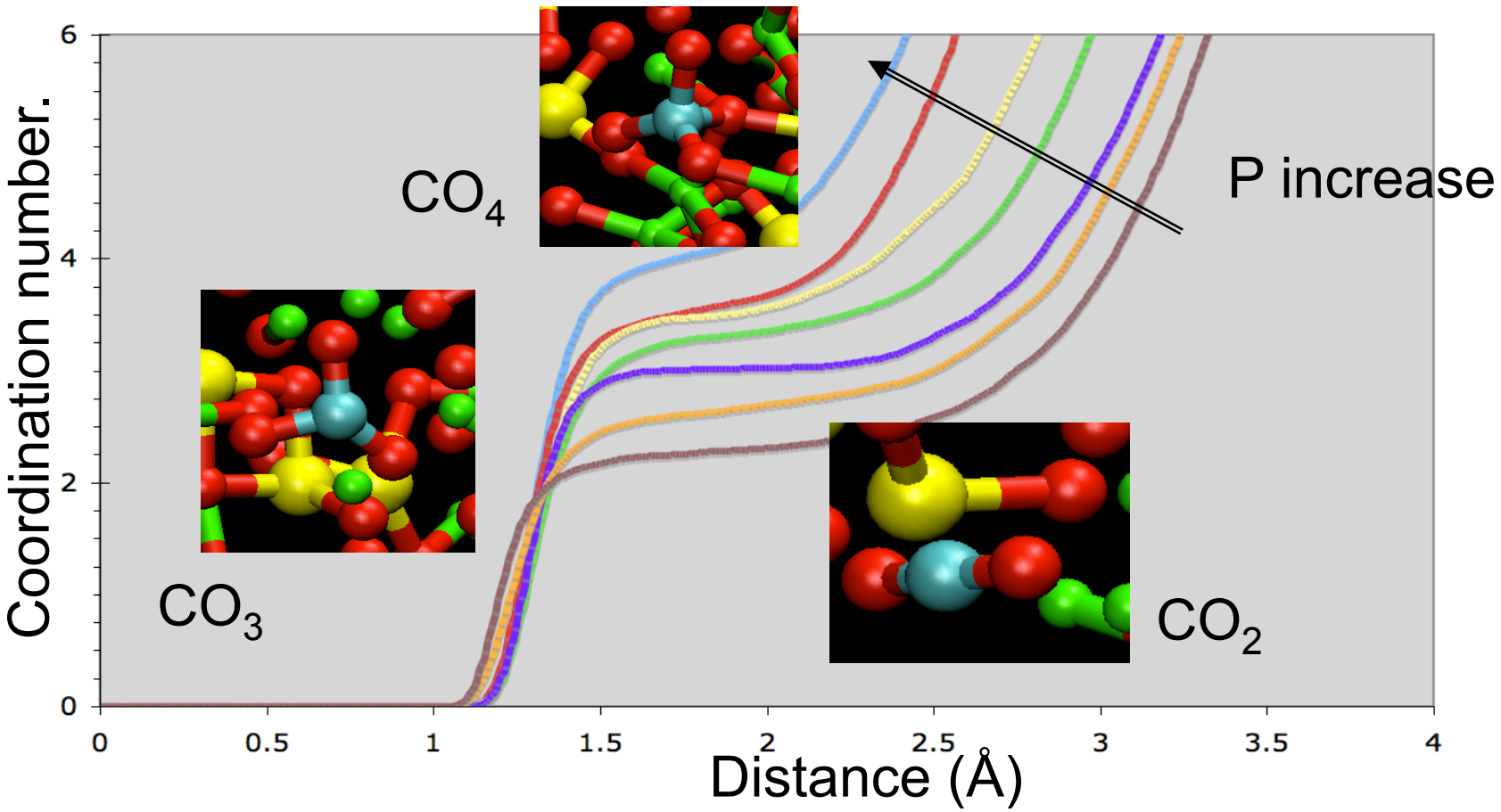
Add Ni, Co,

Replace

Mg ⇔ Fe,

Mg+Si ⇔ 2Fe

LIQUID STRUCTURE : CO_2-bearing

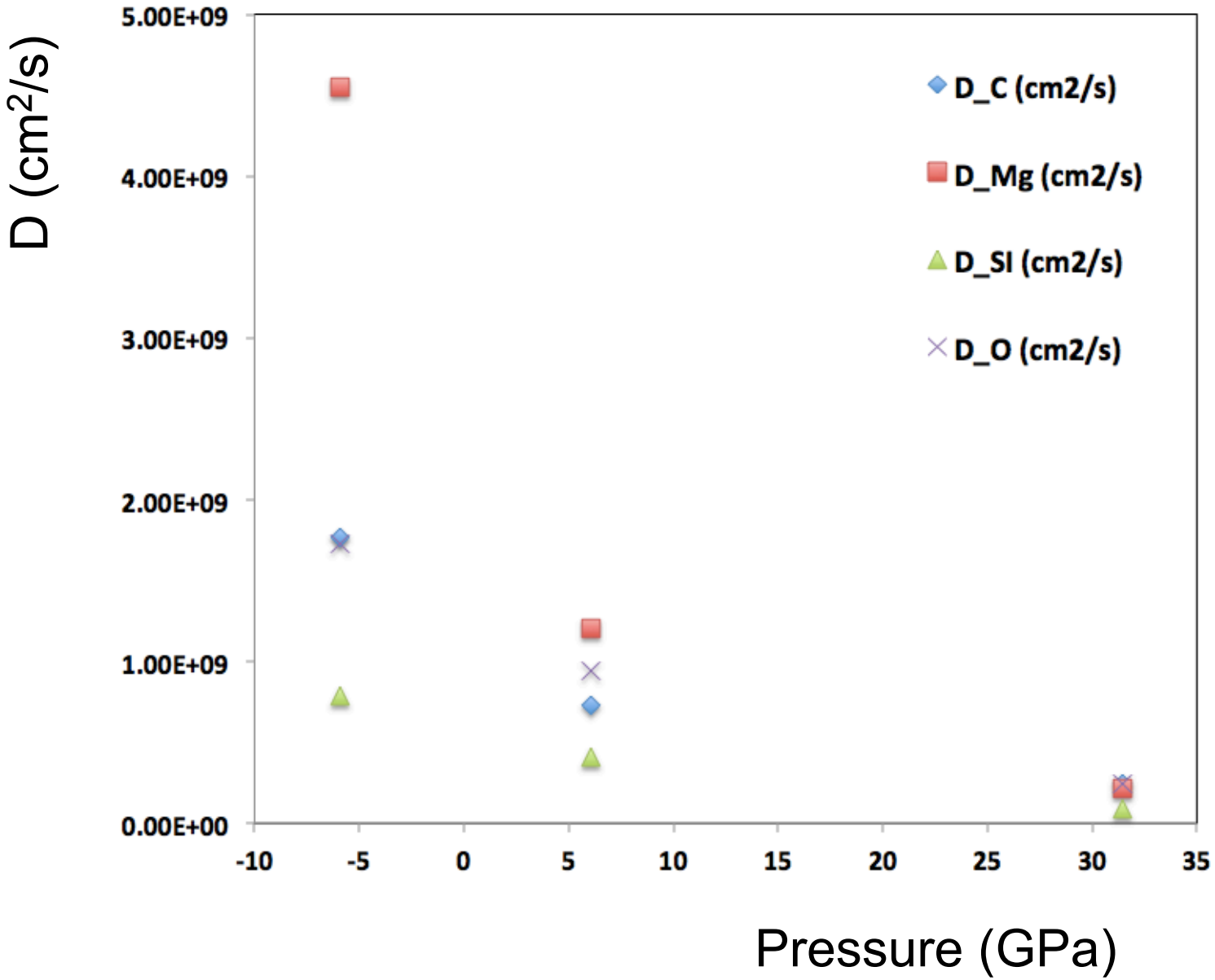


Enters as linear molecular CO_2

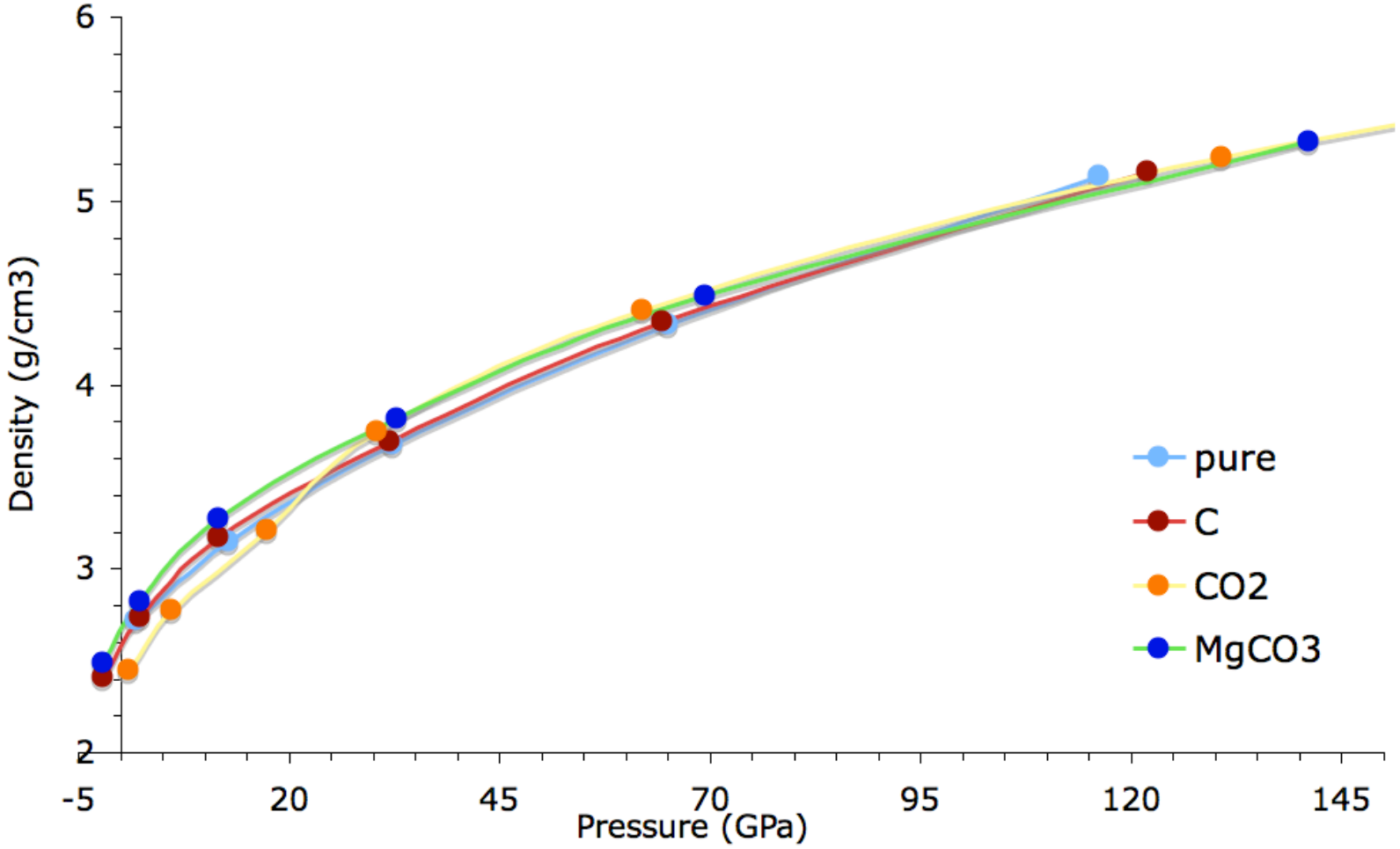
1. Low-pressure remains linear CO_2
2. Moderate pressure starts to form CO_3 groups
3. Ultra-high pressure forms CO_4

At all lower mantle pressures remains CO_3

DIFFUSION COEFFICIENTS



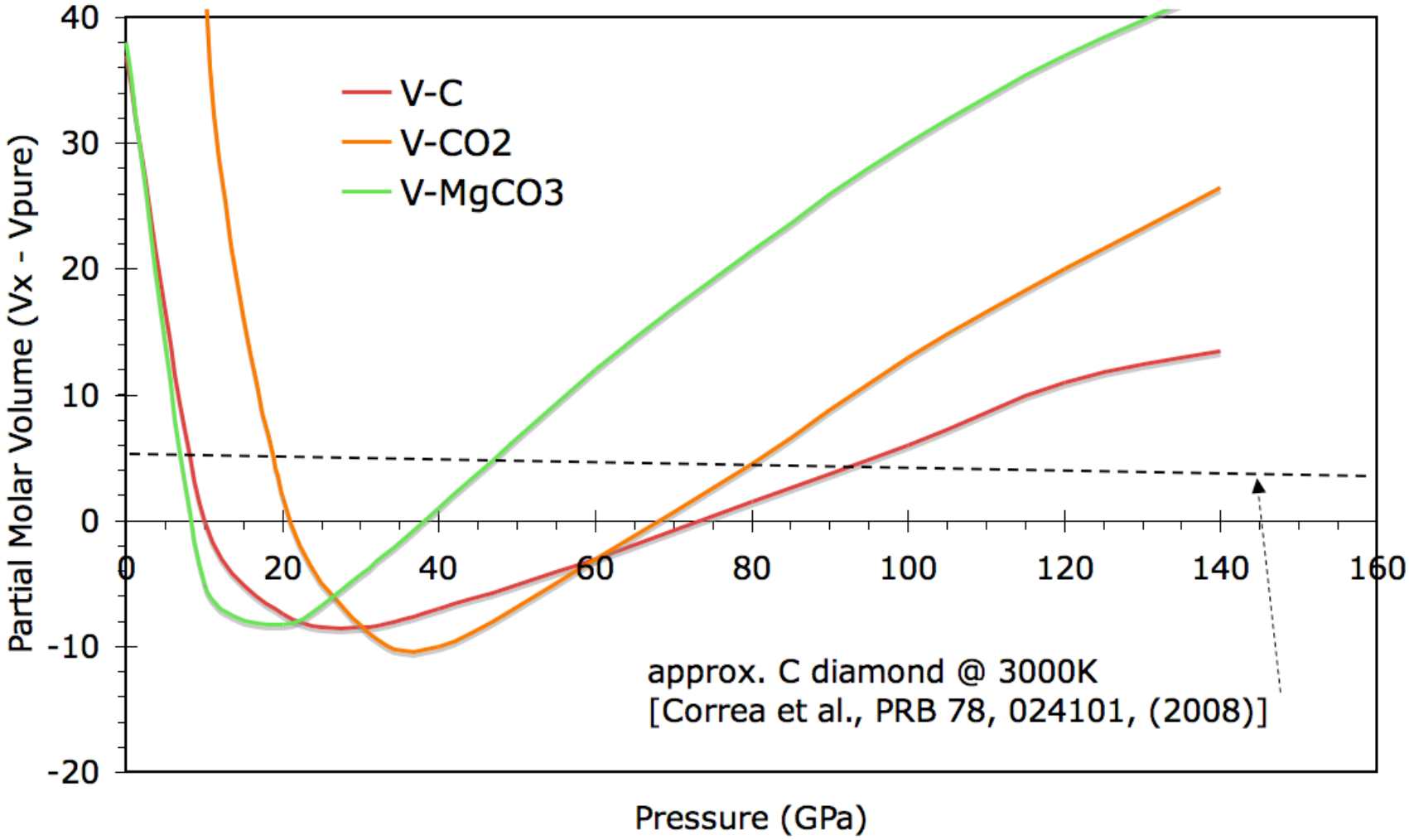
EQUATION OF STATE



Similar EOS

Density crossing at high pressures

PARTIAL MOLAR VOLUME OF C-BEARING SPECIES



Exsolved (e.g. volcanic degassing) → Dissolved in the melt → Exsolved (maybe going into diamonds, core, carbonates? ~ fO_2)

1st melt (for example Fe-bearing oxide/silicate with Ni)
Partial molar volume

=>

Partial pressure

=>

Activity concentration and solubility

2nd melt (for example Si,O-bearing iron with Ni)
Partial molar volume

=>

Partial pressure

=>

Activity concentration and solubility

Ratios give partitioning coefficient

EFFECT OF Fe SPIN STATE

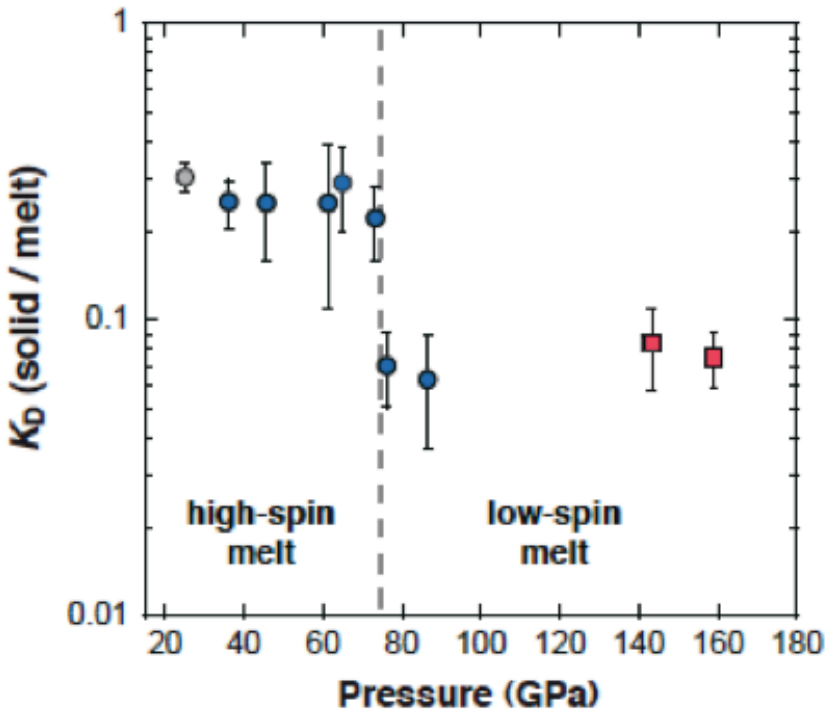


Figure 1. Change in Fe-Mg distribution coefficient and calculated density profiles. KD = (Fepv/Mgpv) / (Femelt/Mgmelt) between perovskite (blue) [or postperovskite (red)] and melt dramatically drops above 76 GPa, likely due to the effect of spin crossover of iron in silicate melt. After Nomura et al., 2011

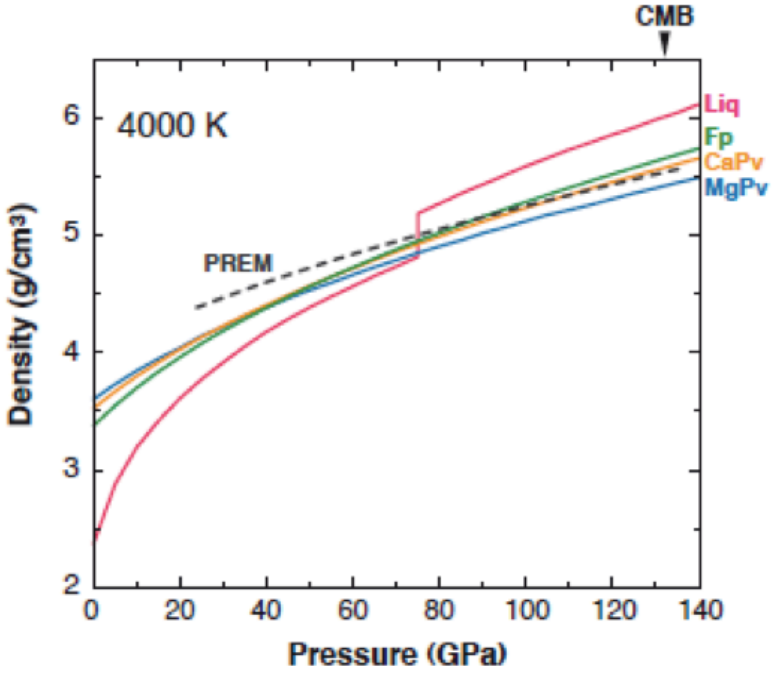
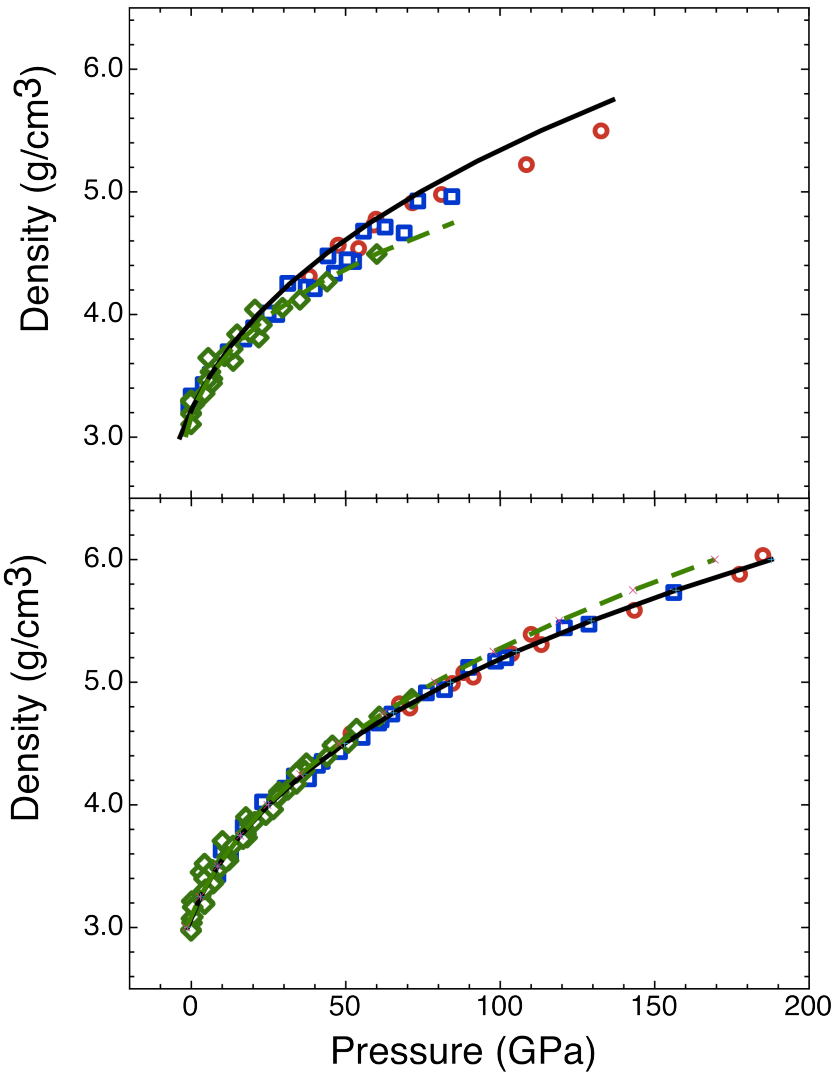
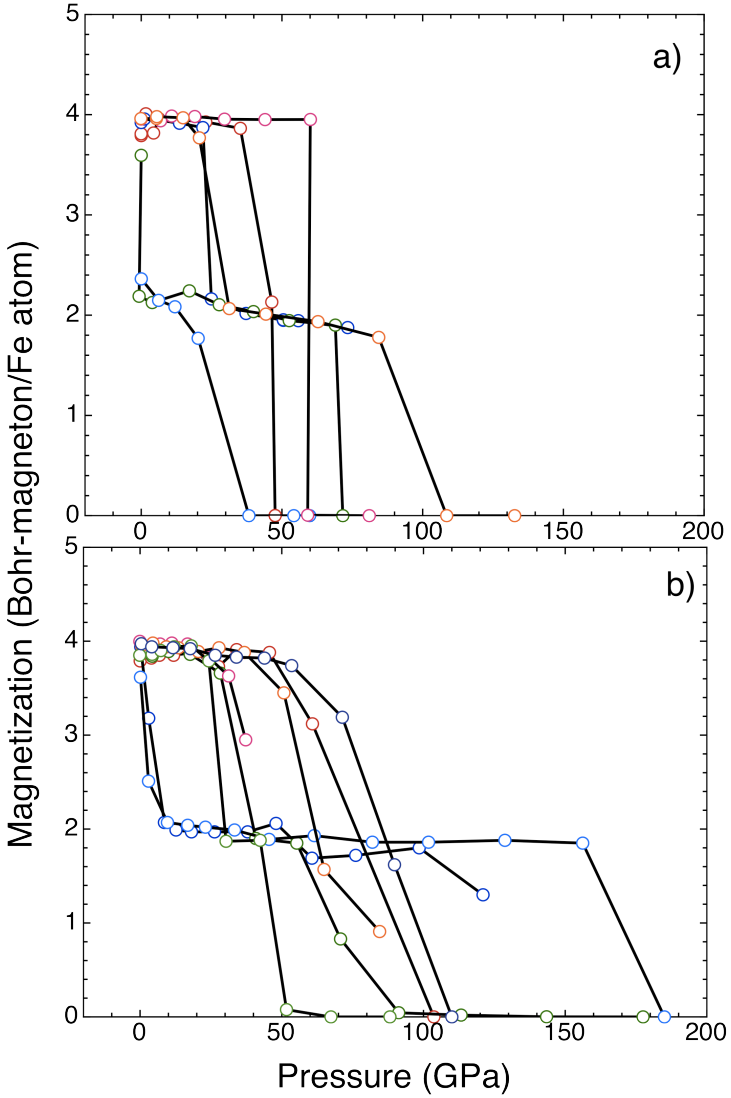


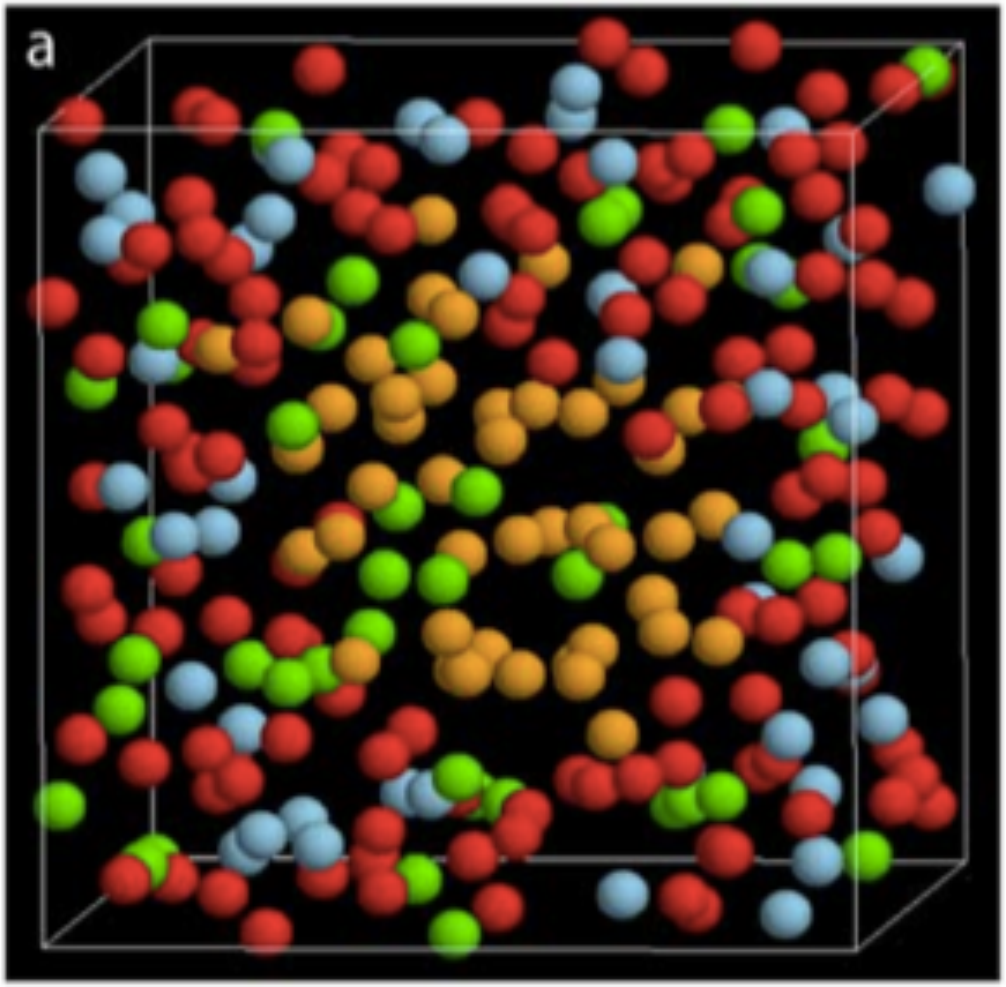
Figure 2. Density of (Mg,Fe)SiO3 liquid coexisting with (Mg0.92Fe0.08)SiO3 perovskite is calculated at 4,000 K using newly obtained Fe Mg partitioning data. Those of (Mg0.86Fe0.14)O ferropericlase, Ca-perovskite, and PREM are also shown for comparison. After Nomura et al., 2011

Fe spin state in MgSiO3 glasses



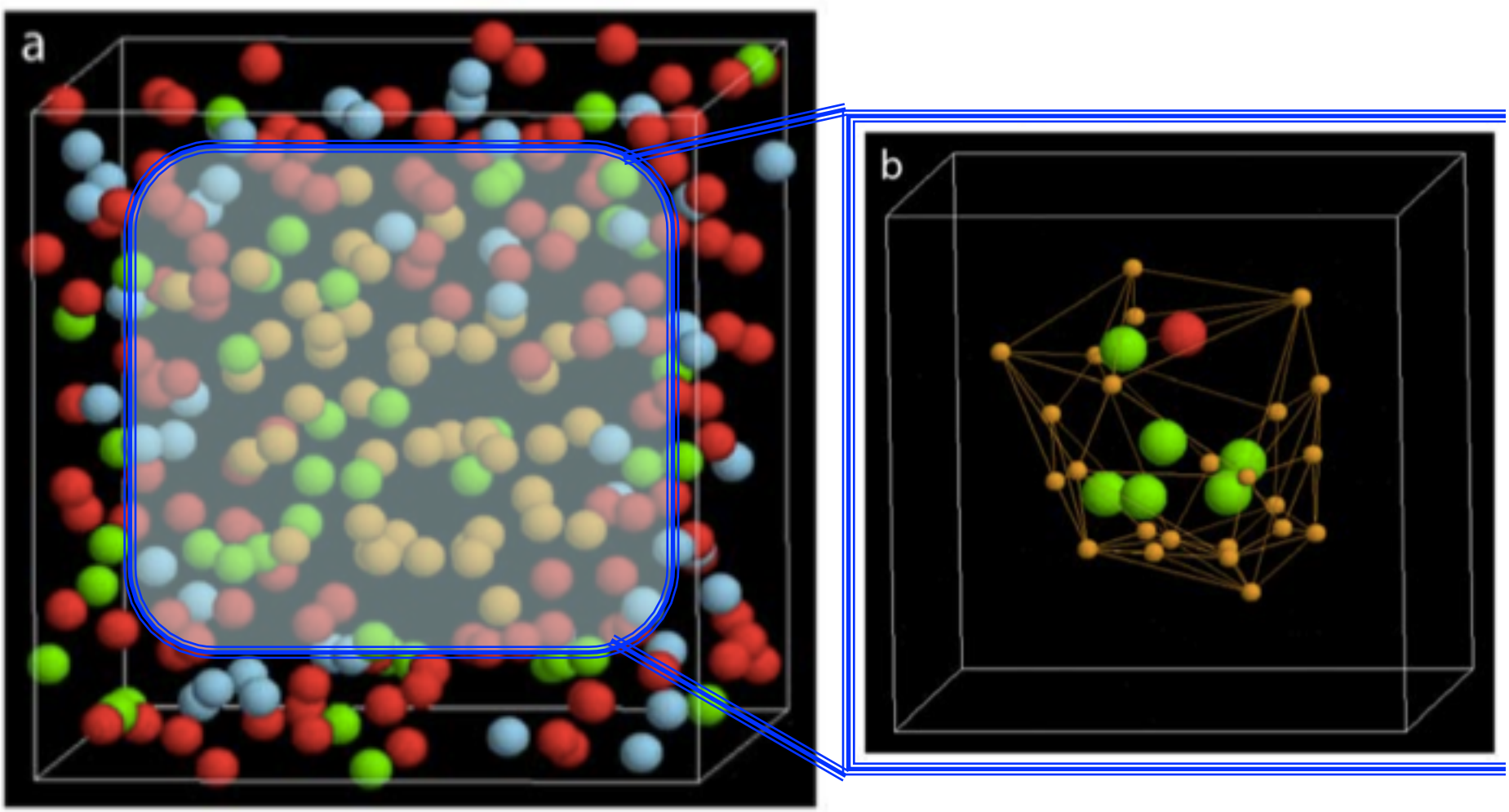


2nd approach: PROCEDURE



Zhang and Guo, GRL, 2012

2nd approach: PROCEDURE – 2 melts



Zhang and Guo, GRL, 2012

2nd approach: PROCEDURE – 2 melts

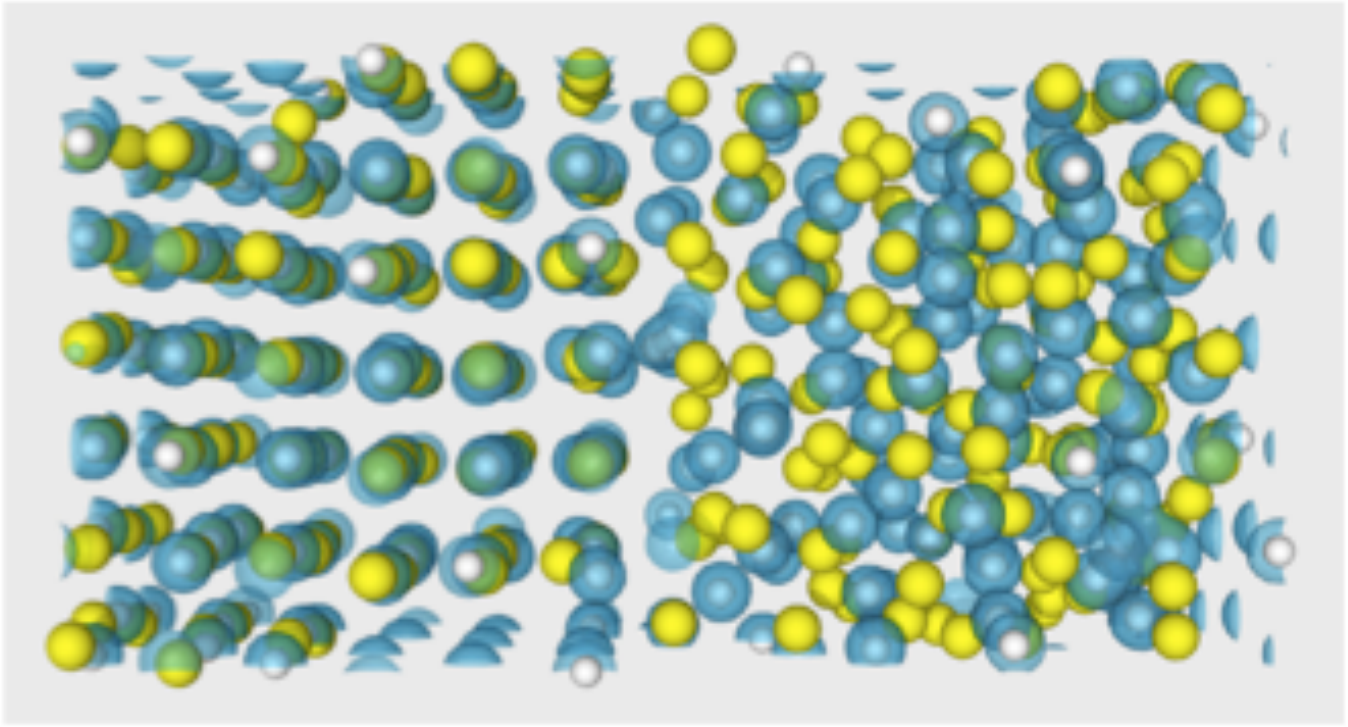


Figure 2. The melting curve is determined using the two-phase simulation technique: in a large simulation box we put in contact melt (right half) with solid (left half) at the same temperature. The simulation performed at constant temperature and pressure sees the boundary between the two phases moved towards the thermodynamically stable one. Repeating this procedure at different pressures and temperatures allows us to bracket the melting curve.

PERSPECTIVES:

First choose 1 Ni, Co, Mn, Cr, REE, etc. between:

One of (Mg,Fe)O and/or (Mg,Fe)(Si,Fe)O3 and/or (Mg,Fe)2SiO4

&

Two of Si, C, O – bearing Fe-rich melt

As a function of:

- Pressure & Temperature
- Fe amount in oxide/silicate melt
- Fe redox state + spin state
- Si, C, O amount in iron melt

Using two independent melts + thermodynamics
Using two melts in contact