Trace elements in silicate melts at high pressure

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**PLANETARY DIFFERENTIATION DURING PLANETARY MELTING**

Does pressure affect the geochemical affinity of elements with silicate melts?

→ **compatible/incompatible:** crust formation $^{176}\text{Lu}/^{176}\text{Hf}$, $^{146}\text{Sm}/^{142}\text{Nd}$, $^{182}\text{Hf}/^{182}\text{W}$

→ **lithophile/volatile:** atmosphere formation $^{129}\text{I}/^{129}\text{Xe}$

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**Table of Elements**

- **Os** siderophile
- **Cu** chalcophile
- **Rb** lithophile
- **N** atmophile

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**Diagram**

Planetary differentiation

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**Periodic Table**

- Elements are classified into categories: incompatible, compatible, lithophile, and volatile.

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**Notes**

- $^{176}\text{Lu}/^{176}\text{Hf}$, $^{146}\text{Sm}/^{142}\text{Nd}$, $^{182}\text{Hf}/^{182}\text{W}$ indicate isotopic ratios used to study crust formation.

- $^{129}\text{I}/^{129}\text{Xe}$ indicates isotopic ratios used to study atmosphere formation.
Exploring silicate melt structure at high P-T conditions

Informations:
1) First coordination shell: interatomic distance, nature of neighbouring atoms, coordination number, oxidation state
2) mid-range order (XRD), second coordination shell (XRD, XAS)

X-ray diffraction:
All elements contribute to signal

X-ray absorption spectroscopy:
Chemically selective, model dependent

Drewitt et al., PRB 2013.
Wilke et al., Chem. Geol. 2006.
Trace and minor elements in magmas: experimental approaches

X-ray diffraction:
All elements contribute to signal
Restrictions: only very heavy elements
Fe-free compositions

Elements: Lu, Nd, Xe

X-ray absorption spectroscopy:
Chemically selective, model dependent
Restrictions: 11 keV < energy < 30 keV

Elements: W, Nb, Br, Kr

Major oxide components in silicate melts:

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>FeO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>granite</td>
<td>76%</td>
<td>13%</td>
<td>2%</td>
<td>0.5%</td>
<td>2.5%</td>
<td>3%</td>
<td>2%</td>
<td></td>
</tr>
<tr>
<td>haplogranite</td>
<td>68%</td>
<td>11%</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4%</td>
<td>3%</td>
<td>15%</td>
</tr>
<tr>
<td>basalt</td>
<td>50%</td>
<td>15%</td>
<td>8%</td>
<td>8%</td>
<td>13%</td>
<td>2%</td>
<td>2%</td>
<td></td>
</tr>
</tbody>
</table>

Drewitt et al., PRB 2013.
Probing trace elements in melts at high P-T conditions using XRD

Window between 1.8-2.5 Å: where many key trace elements are expected

Requirement of a sufficiently large q-range:
high-energy angle dispersive XRD in DACs or energy dispersive XRD in large volume presses

Molten haplogranite in RH-DAC
Or ambient P-T glass

Ideal but impossible now at high P
Best at high P
Possible at high P
Insufficient resolution

Sanloup and de Grouchy, in Magmas under pressure 2018.
Probing trace elements in melts at high P-T conditions using XRD

**Angle-dispersive x-ray diffraction and DACs:**
correction for diamonds Bragg peaks is significant at high energies

33 keV, MAR555
60 keV, Perkin-Elmer
Probing trace elements in melts at high P-T conditions using XRD

Energy-dispersive x-ray diffraction and large-volume press

Anorthite-diopside melt + Lutetium

APS, HPCAT, 16BM-B

NB: some elements may have strong fluorescence peaks that need to be removed
Exploring silicate melt structure at high P-T conditions

**Resistive heating DACs:**

Optimizing sample volume
Large opening DACs, e.g. Boelher-Almax anvils
Need hydrated glasses to lower melting T

**Paris-Edinburgh press:**

Same cell-assembly used for XRD and XAS (provided by the APS)

High stability at high T, large vertical access

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![Diagram showing the structure of the Paris-Edinburgh press with labeled parts and dimensions.](image)
X-ray absorption spectroscopy at high P-T conditions

Requires nanocrystalline diamond capsules or anvils
PRIUS programme, GRC Ehime University (Pr. Irifune)

Br-dopped (0.4 at%) dacitic melt

Using polycrystalline diamond capsules (Almax)

Using nanocrystalline diamond capsules (Ehime)

Cochain et al. Chem Geol 2015
X-ray absorption spectroscopy using a Paris-Edinburgh press

Long collection times (3 hours) ⇒ Need high stability cell-assembly and large vertical gap to optimise signal/noise ratio

Nanocrystalline diamond capsules ⇒ Need to raise T above 1000 °C for P increase

Use of Pt-Rh or graphite caps:
Possibility to buffer the redox state (also talc powder outside caps)

Lu-O coordination change in basalts: from 6 to 8 at 4-5 GPa

An-D: Fe-free basalt analogue
HPG: Fe-free granite analogue

Fit of the Lu-O contribution:

⇒ Lu-O coordination change in basalts: from 6 to 8 at 4-5 GPa

de Grouchy et al, EPSL 2017

G(r)

G(r)

Distance, r (Å)

Distance, r (Å)
Changes of environment of Lu, Nd in melts at high P: summary

- Lu-O: CN changes from 6 to 8 at \(\sim 4-5\) GPa
- Coincides with change of P-dependence in crystal/melt partitioning
- Nd-O: CN changes from 6 to 8 at \(\sim 1-2\) GPa

\(\Rightarrow\) \(D_{\text{Lu}}/D_{\text{Hf}}\sim 1\) above 5 GPa: Lu and Hf should not be fractionated in high P basalts

\(\Rightarrow\) Decoupling of Lu/Hf and Nd/Sm systems for high P melts
Reactivity of xenon and krypton in magmas

X-ray diffraction @ 60 keV, PetralII (Hambourg)

Haplogranite melt

\[ \text{Xe-O} = 2.1 \pm 0.1 \text{ Å} \]

⇒ similar distance in crystals, but different CN

Leroy et al. EPSL 2018
Reactivity of xenon and krypton in magmas

EXAFS, ESRF (BM23)
Glass and molten feldspar (sanidine) doped with Xe:Kr gas

Xe edge

Kr edge

Crépisson et al. Chem Geol 2018
Reactivity of xenon and krypton in magmas

EXAFS, ESRF (BM23)
Glass and molten feldspar (sanidine) doped with Xe:Kr gas

Kr-O = 2.5±0.1 Å

⇒ Kr also gets oxidized under pressure

Crépisson et al. Chem Geol 2018
Basalt +0.6 wt% W

- Current debate on change from $W^{6+}$ to $W^{4+}$ with pressure

$\Rightarrow$ Reduction of W in the melt around 2-3 GPa
$\Rightarrow$ Not preserved in the quenched glass

Cochain et al. *In prep.*
Tungsten – Effect of oxidation state on partitioning

High pressure residues have high [W]

Fonseca et al. EPSL 2014
Righter&Shearer, GCA 2003

This work, nanoSIMS
Trace elements in melts: perspectives opened by the EBS

**X-ray diffraction:**
Currently limited to upper mantle studies for trace elements

**EBS:**
Much shorter collection times at high energy (>60 keV)
Better focusing at high energy
⇒ compatible with laser heating DAC

**X-ray absorption spectroscopy:**
Chemically selective, model dependent
Restrictions: 11 keV < energy < 30 keV

**EBS:**
Higher energies accessible at high P-T
Real ‘trace’ elements studies instead of 1% concentrations, i.e. <0.1 at%

⇒ Eventually also using LH-DACs
⇒ Opens applications to the whole terrestrial P-T range
(i.e. deep mantle reservoirs, core formation) with natural concentrations
Thanks for provision of beamtime:
APS HPCAT 16BM-B, ESRF BM23, Diamond I15

Contributed to this work:

for synchrotron experiments:
D. Daisenberg\textsuperscript{1}, I. Kantor\textsuperscript{2}, Y. Kono\textsuperscript{3}, Z. Konopkova\textsuperscript{4}, K. Glazyrin\textsuperscript{4}, A. Rosa\textsuperscript{2}

for nano-SIMS analysis:
M. Roskosz\textsuperscript{5}

\textsuperscript{1}Diamond Light Source, \textsuperscript{2}ESRF,
\textsuperscript{3}HPCAT, Carnegie Institution of Washington now at Ehime University,
\textsuperscript{4}DESY, \textsuperscript{5}Museum National d’Histoire Naturelle

Work funded by the European Research Council
“Magmas at depth: an Experimental Study at Extreme Conditions”