Solubility of sulfur in basaltic melts: the attempts towards accurate results

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Volatile components in igneous systems

H_2O
from 1000 ppm > ocean-floor basalts
to
many wt.% > some granitic melts

CO_2
from 10s of ppm
to
10s of thousands ppm
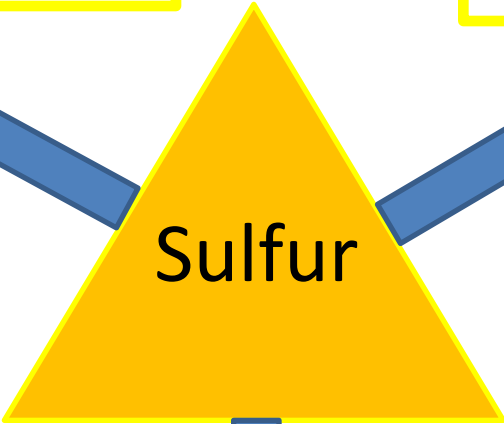
S
from < 100 ppm
to
many wt%

Cl, F
< 5000 ppm

« minor » elements may exceed CO_2 in subduction-zone magmas
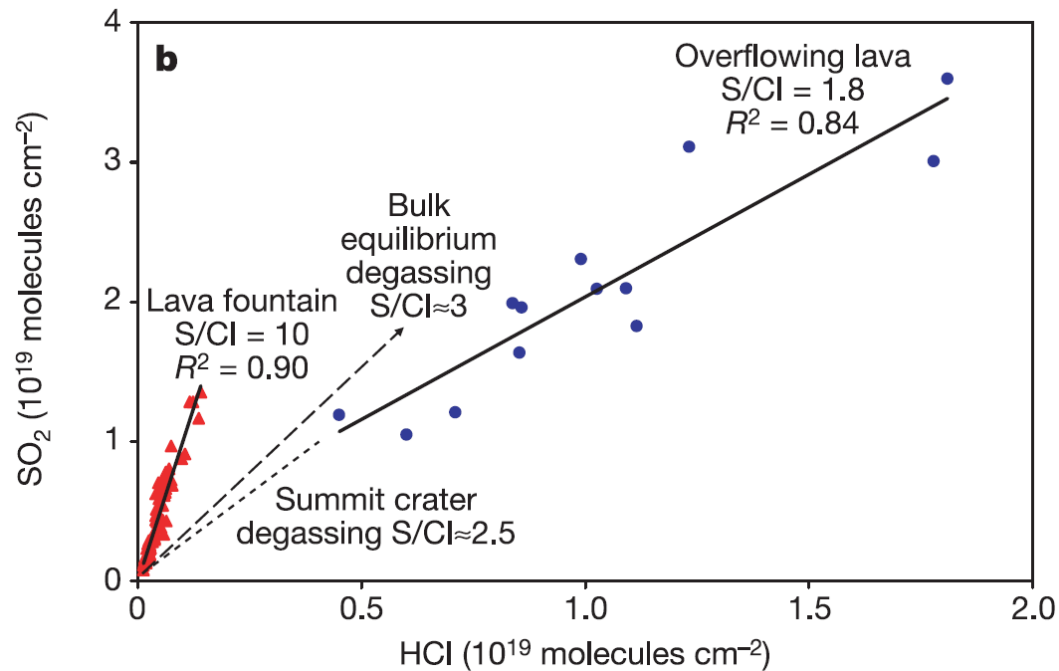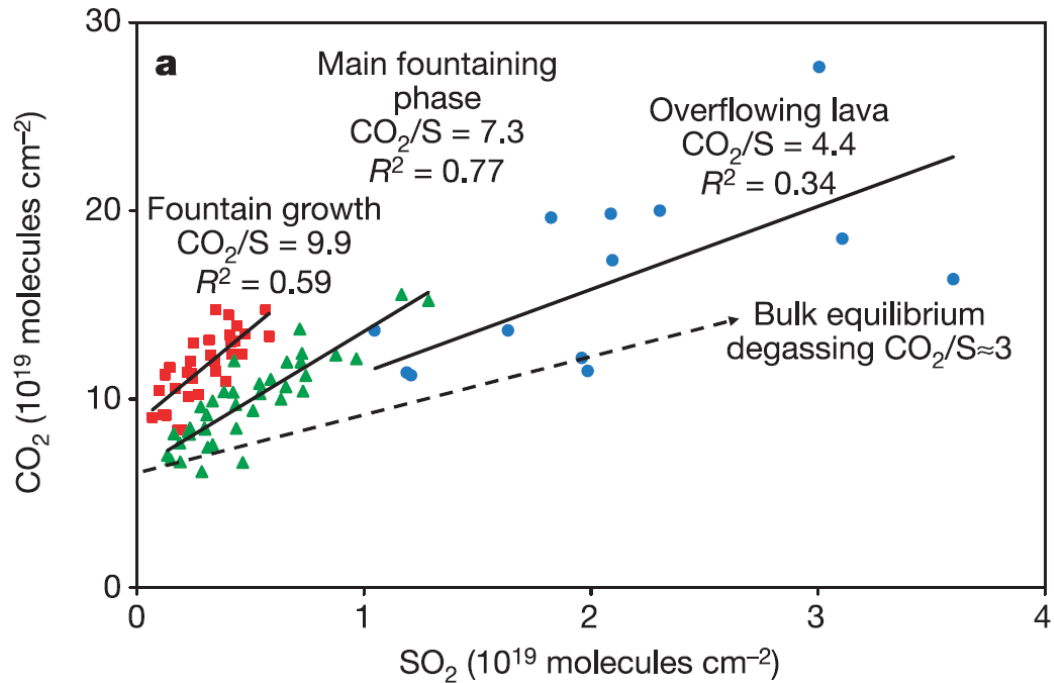
Formation of ore deposits
(es. volcanogenic massive sulfide, influence on PGE, Au, Ni, Cu transport)

Volcanic degassing
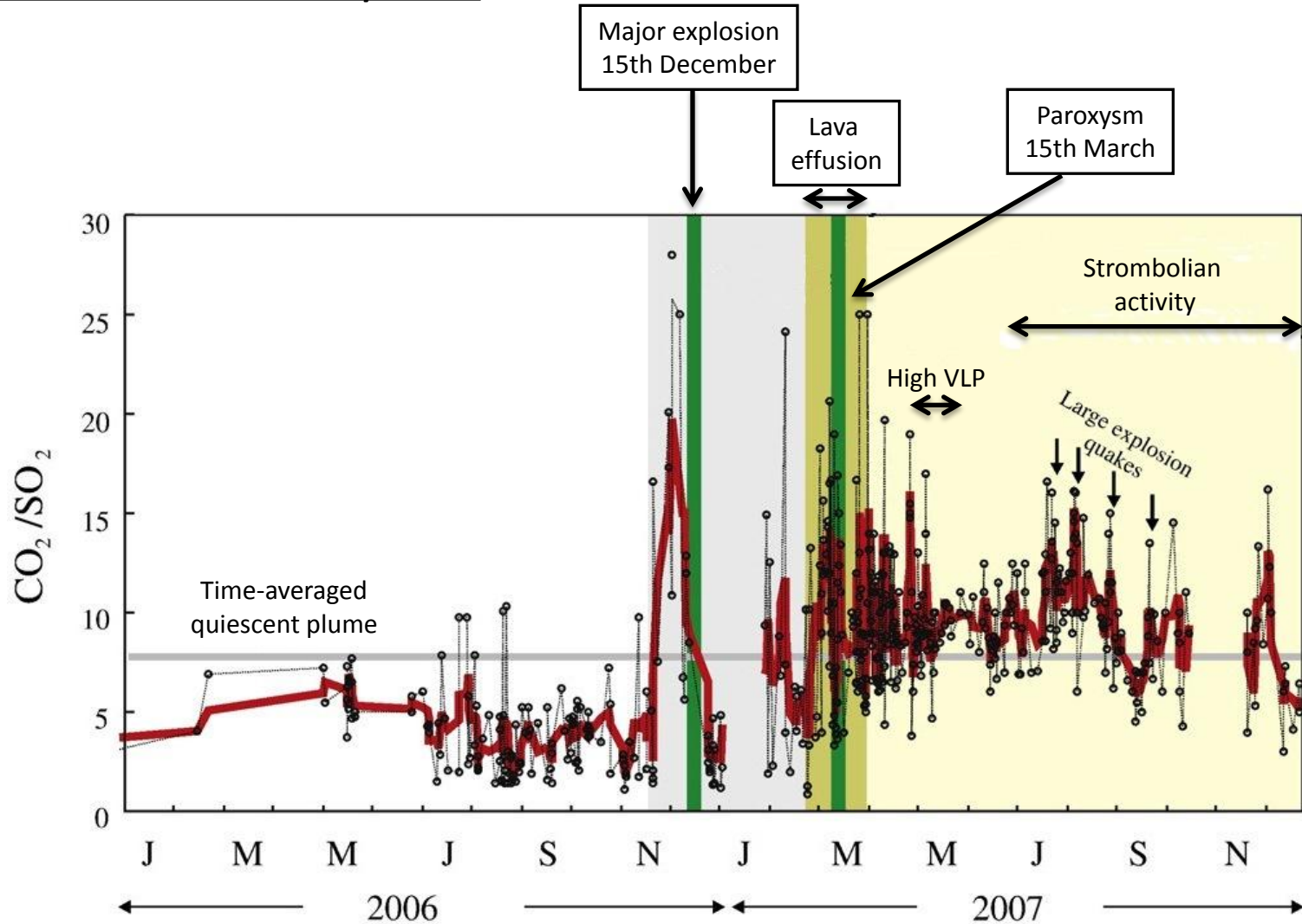(it is the third most abundant species emitted after H_2O and CO_2)
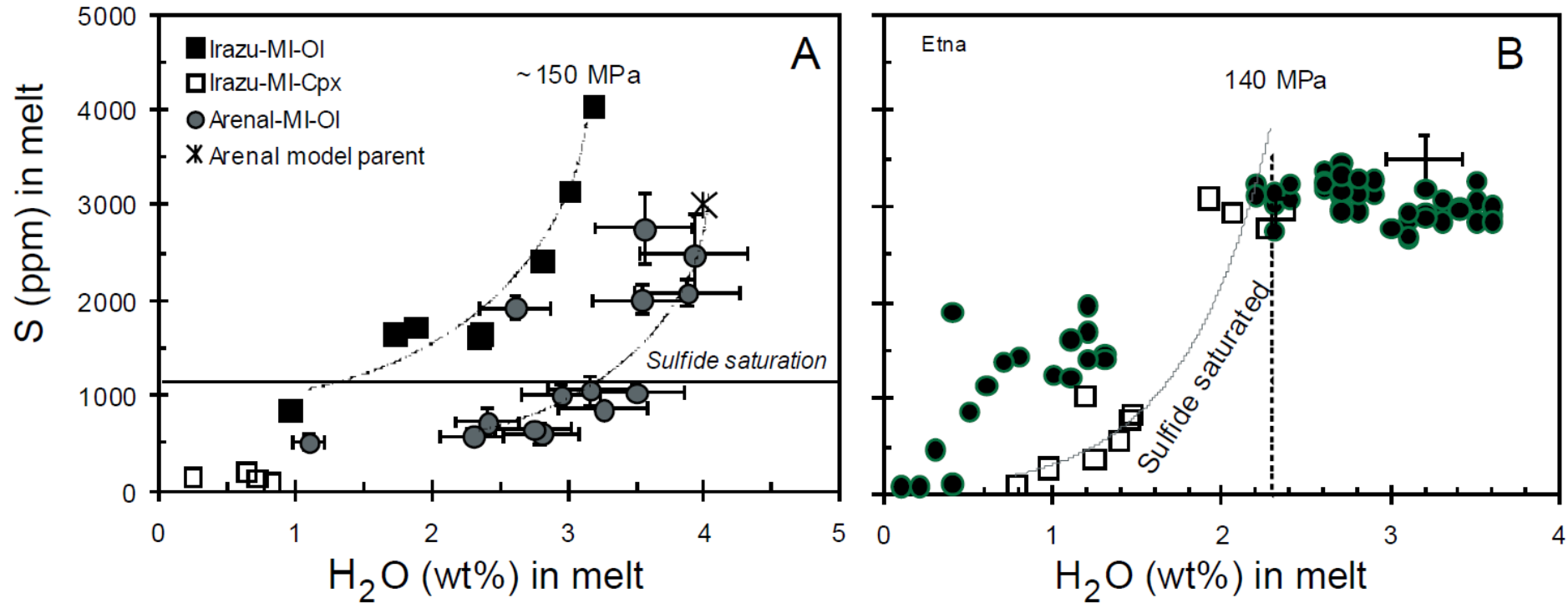
Sulfur

Global climate change

a

Main fountaining phase
$CO_2/S = 7.3$
$R^2 = 0.77$

Overflowing lava
$CO_2/S = 4.4$
$R^2 = 0.34$

Fountain growth
$CO_2/S = 9.9$
$R^2 = 0.59$

Bulk equilibrium degassing $CO_2/S \approx 3$

CO_2 (10^{19} molecules cm^{-2})

SO_2 (10^{19} molecules cm^{-2})

b

Overflowing lava
S/Cl = 1.8
$R^2 = 0.84$

Bulk equilibrium degassing S/Cl$\approx$3

Lava fountain
S/Cl = 10
$R^2 = 0.90$

Summit crater degassing S/Cl$\approx$2.5

SO_2 (10^{19} molecules cm^{-2})

HCl (10^{19} molecules cm^{-2})

Etna - 2000 lava fountains

(Allard et al. 2005, Nature)

Stromboli - 2007 eruption

Major explosion
15th December

Lava
effusion

Paroxysm
15th March

Strombolian
activity

High VLP

Large explosion
quakes

Time-averaged
quiescent plume

(Aiuppa et al. 2009, JVGR)
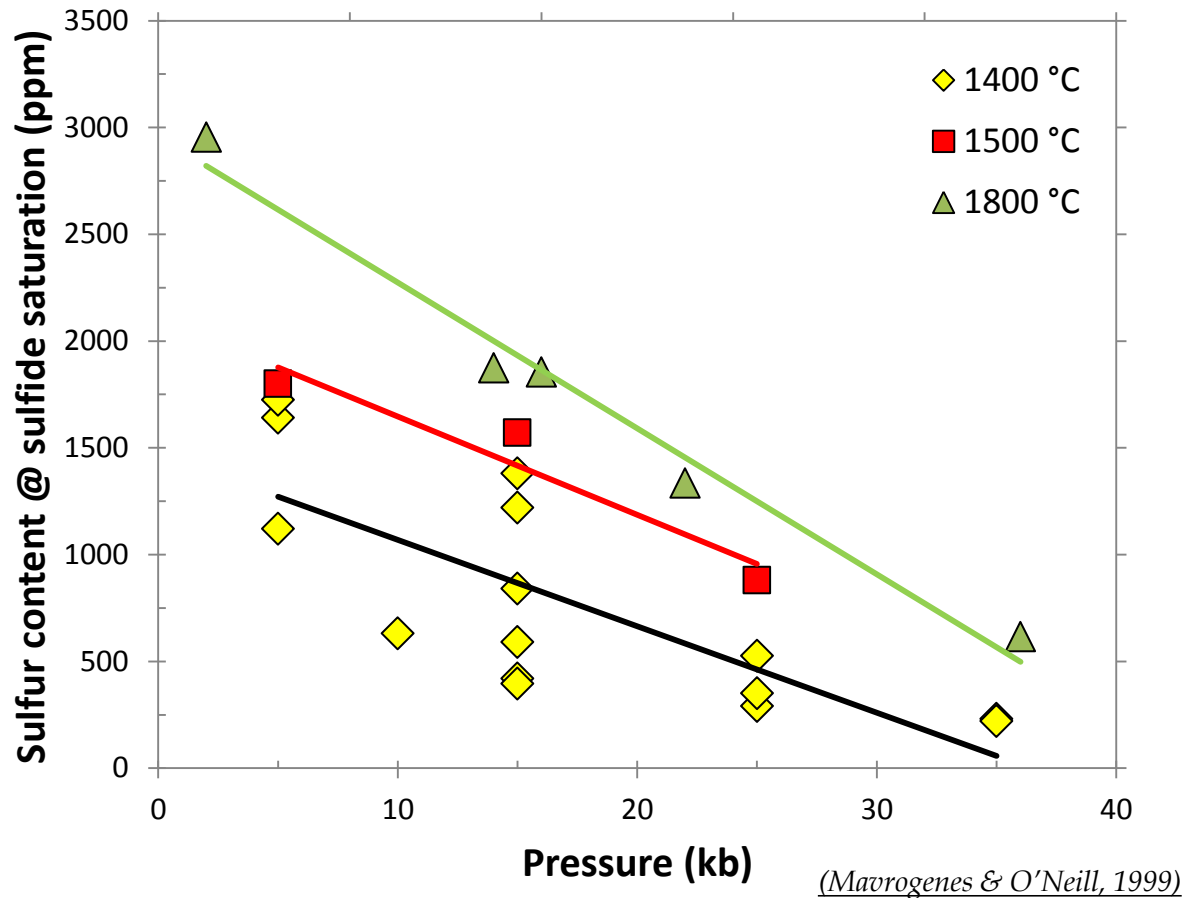
S-H₂O variation in basaltic melt inclusion and S-degassing paths

(Metrich & Wallace, 2008)

EXPERIMENTS

What do we have up to now?

S solubility in _reducing and anhydrous_ basaltic melts
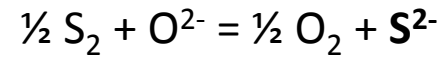

(Mavrogenes & O'Neill, 1999)

S solubility decreases ↓ with P

S solubility increases ↑ with T

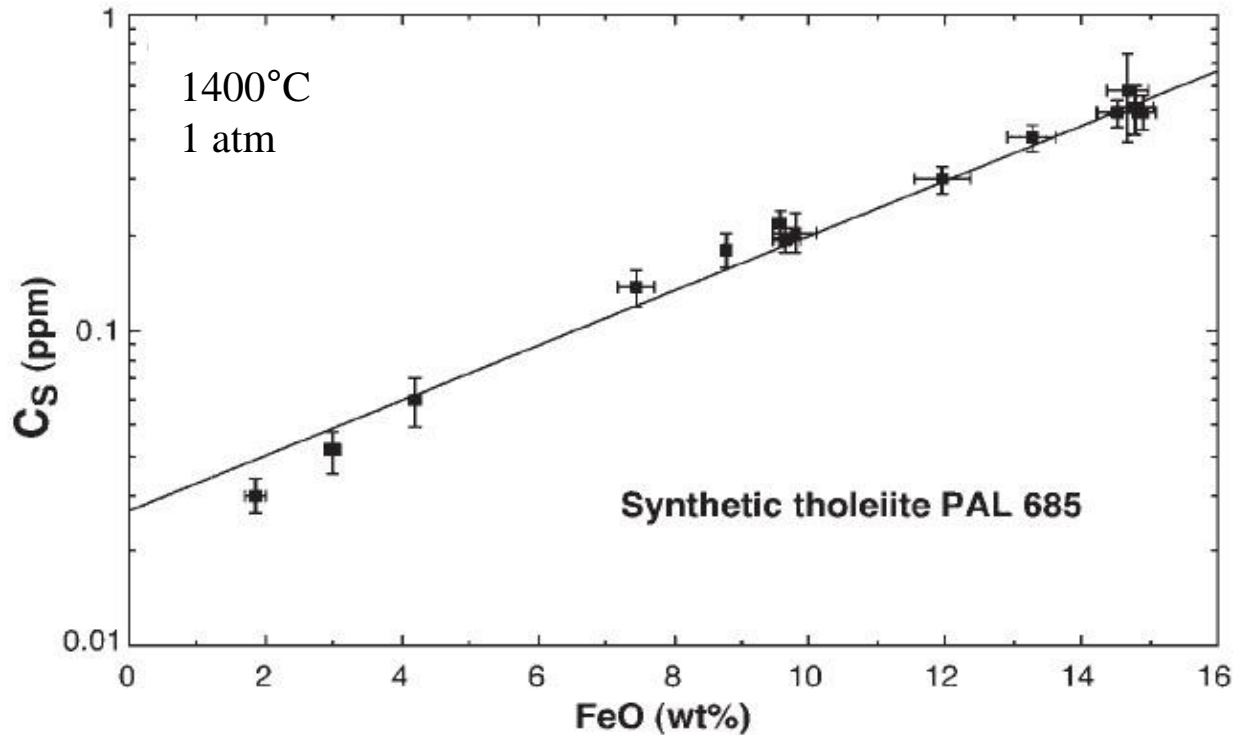# S solubility in _reducing and anhydrous_ basaltic melts

$$\tfrac{1}{2}\, S_2 + O^{2-} = \tfrac{1}{2}\, O_2 + \mathbf{S^{2-}}$$

O'Neill & Mavrogenes, 2002

$$[S]\ \mu\ (fS_2\ /\ fO_2)^{1/2}$$

CMAS
log fS_2 = -1.9

CMAS
log fO_2 = -10.3

S solubility in _**reducing and anhydrous**_ basaltic melts
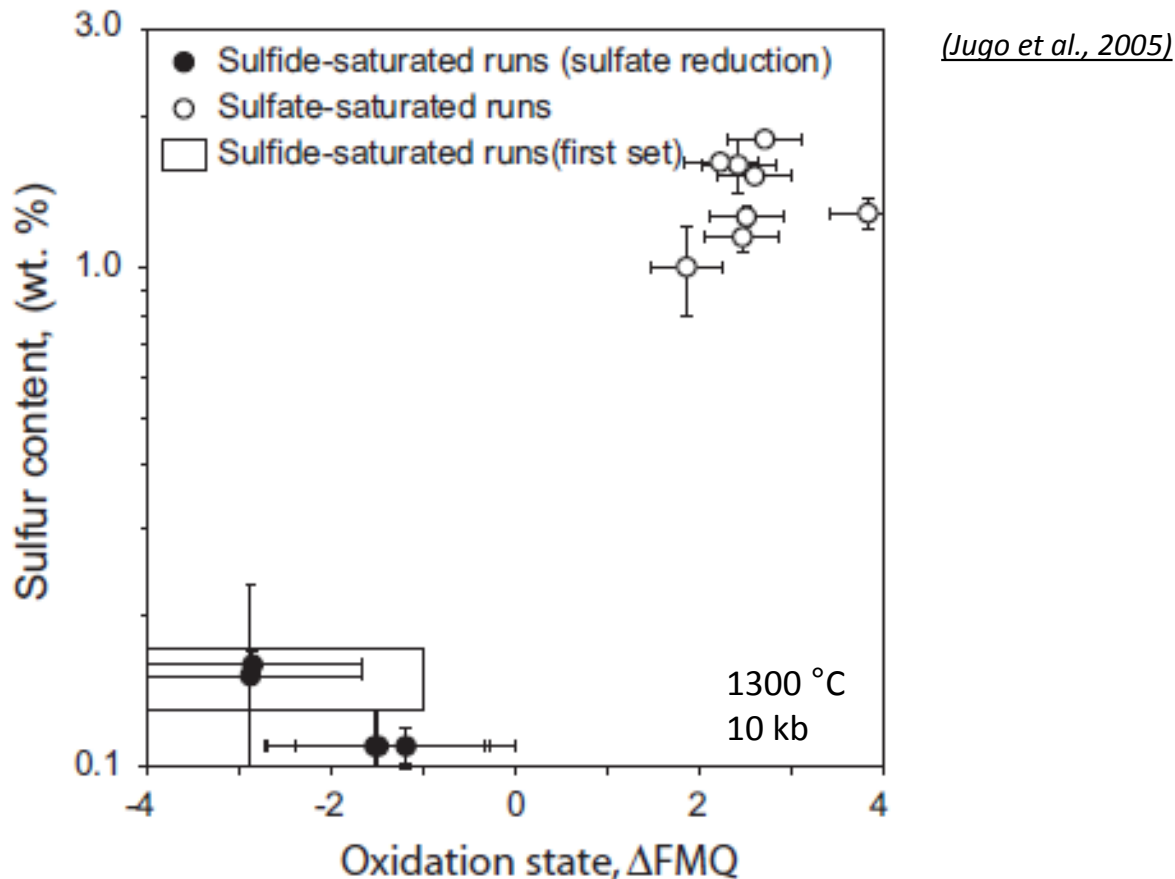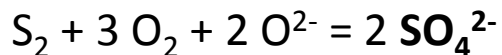

1400°C
1 atm

Synthetic tholeiite PAL 685
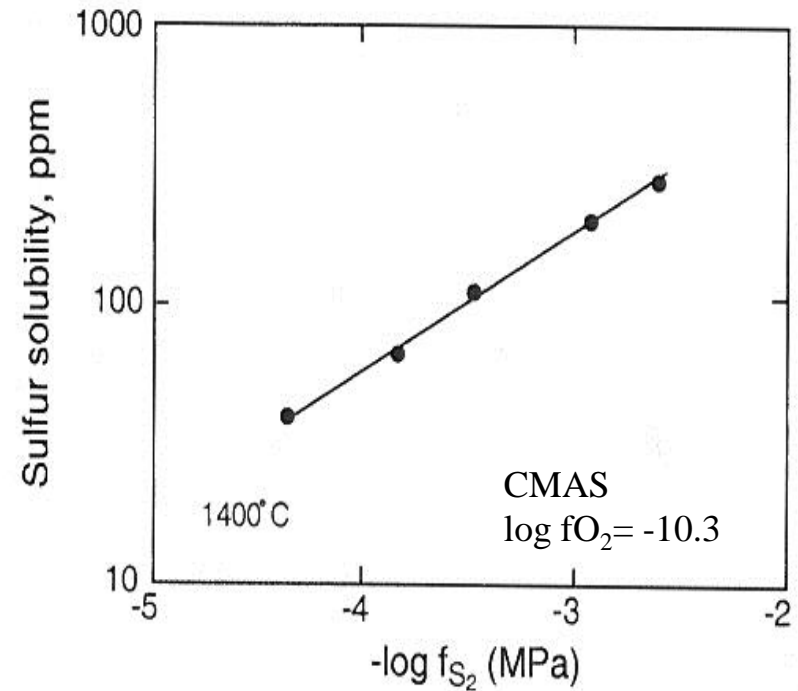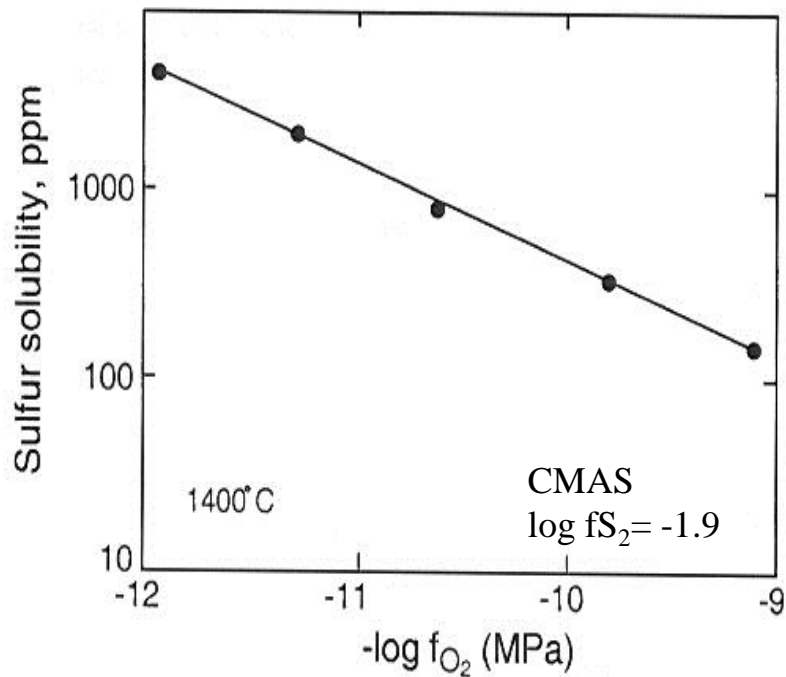
(O'Neill & Mavrogenes, 2002)

$Cs = ([S_{ppm}].(fO_2/fS_2)^{0.5})$

The effect of FeO on Cs increases as FeO ⬆

S solubility in **oxidizing and anhydrous** basaltic melts

$$S_2 + 3\,O_2 + 2\,O^{2-} = 2\,SO_4^{2-}$$

(Jugo et al., 2005)

Sulfur solubility increases ↑ under oxidizing conditions

Sulfur solubility in **hydrous** basaltic melts???

Liu et al., 2007

Moune et al., 2009

Beerman et al., 2011

Sulfur solubility in **hydrous** basaltic melts???

Liu et al., 2007

Moune et al., 2009

Beerman et al., 2011

S solubility in _**hydrous**_ _basaltic melts_

No P effect

Small effect of H_2O

Strong influence of melt composition

(Liu et al., 2007)

T = 1250 °C

Legend: Dry Basalt, Dry Andesite, Hydrous-Basalt, Hydrous-Andesite, Basalt+FeO

Limits:
- Only 2 hydrous experiments for basaltic composition
- Very high pressure experiments to reproduce the storage system for basaltic magmas
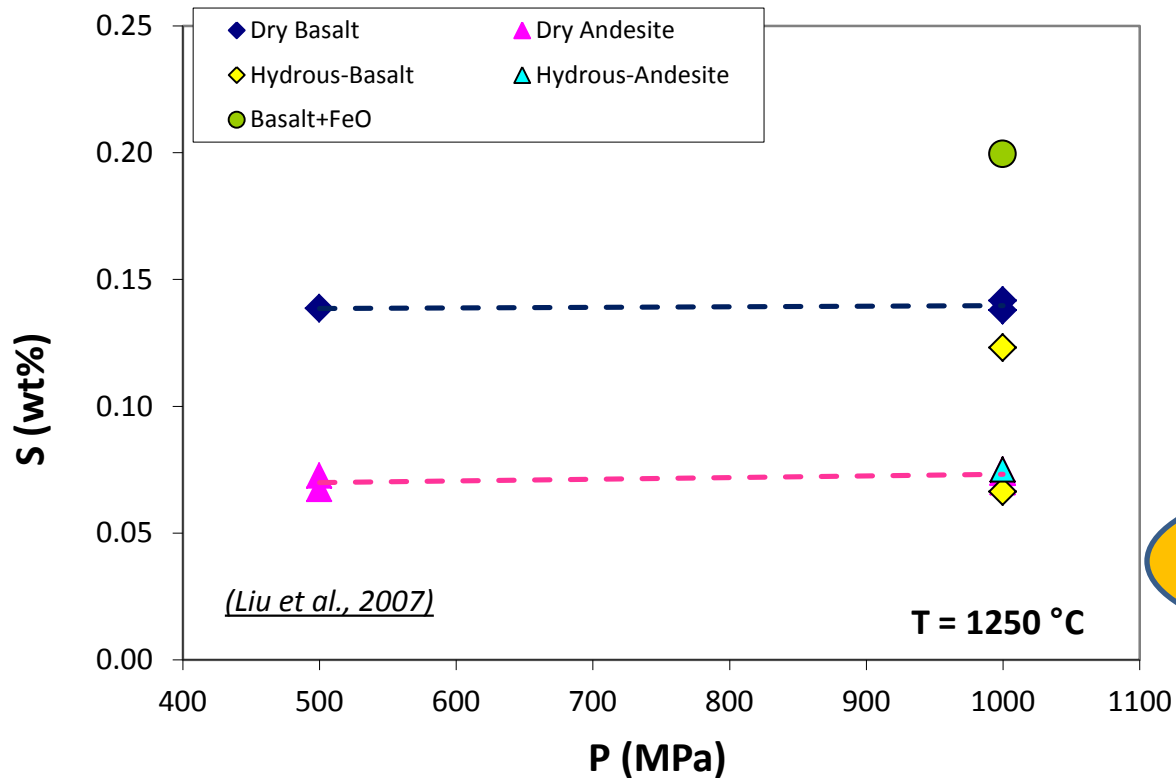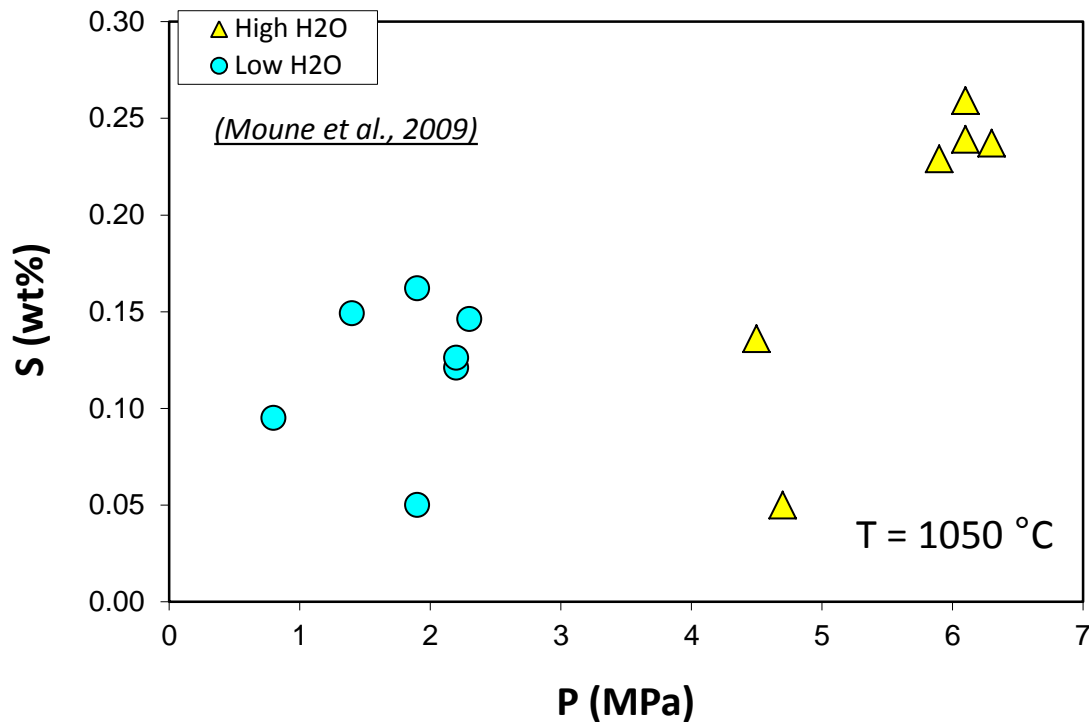- Too reduced conditions (FMQ-2)

Sulfur solubility in **hydrous** basaltic melts???

Liu et al., 2007

Moune et al., 2009

Beerman et al., 2011

S solubility in _**hydrous**_ basaltic melts

H$_2$O can have a positive effect on the solubility of S

Limit: • Too low temperature to represent basaltic **melts.**
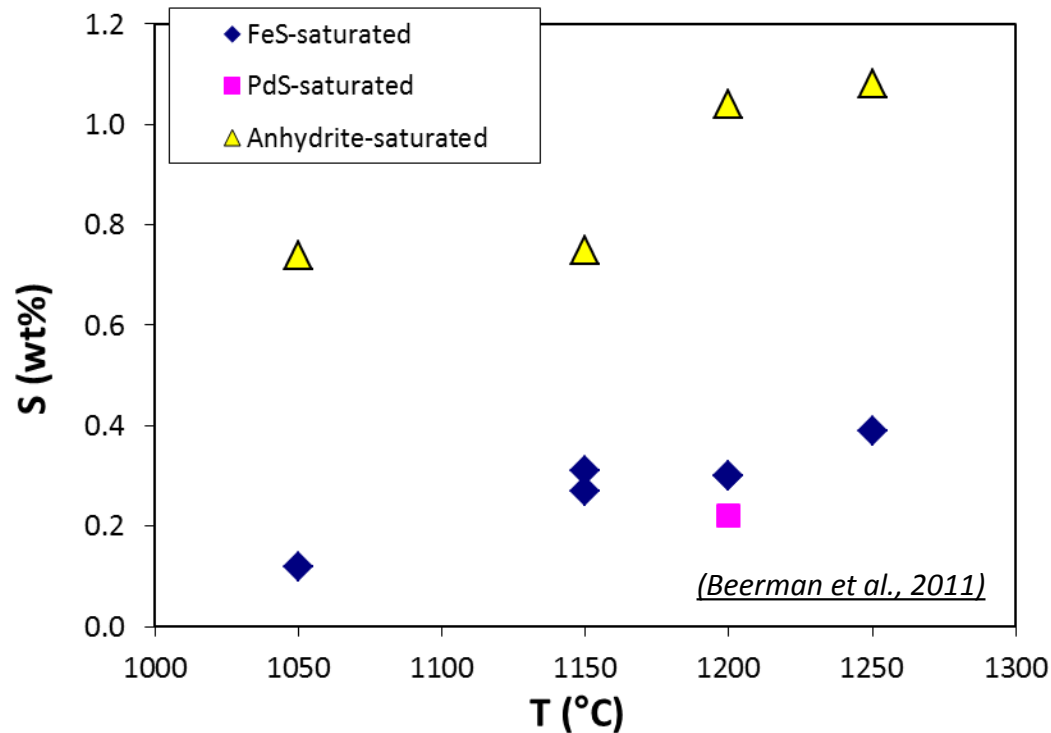   **Sulfur solubility is reasonably underestimated**

Sulfur solubility in *hydrous* basaltic melts???

Liu et al., 2007

Moune et al., 2009

Beerman et al., 2011

S solubility in **hydrous** basaltic melts

FeS-saturated
PdS-saturated
Anhydrite-saturated

(Beerman et al., 2011)

Sulfur solubility increases ↑ with T

Limits:
- Only the sulfide saturated experiments approach typical basaltic redox conditions
- The experiments are performed only at 200 MPa
- The effect of CO_2 is not considered

S solubility in *hydrous* basaltic melts

(Beerman et al., 2011)
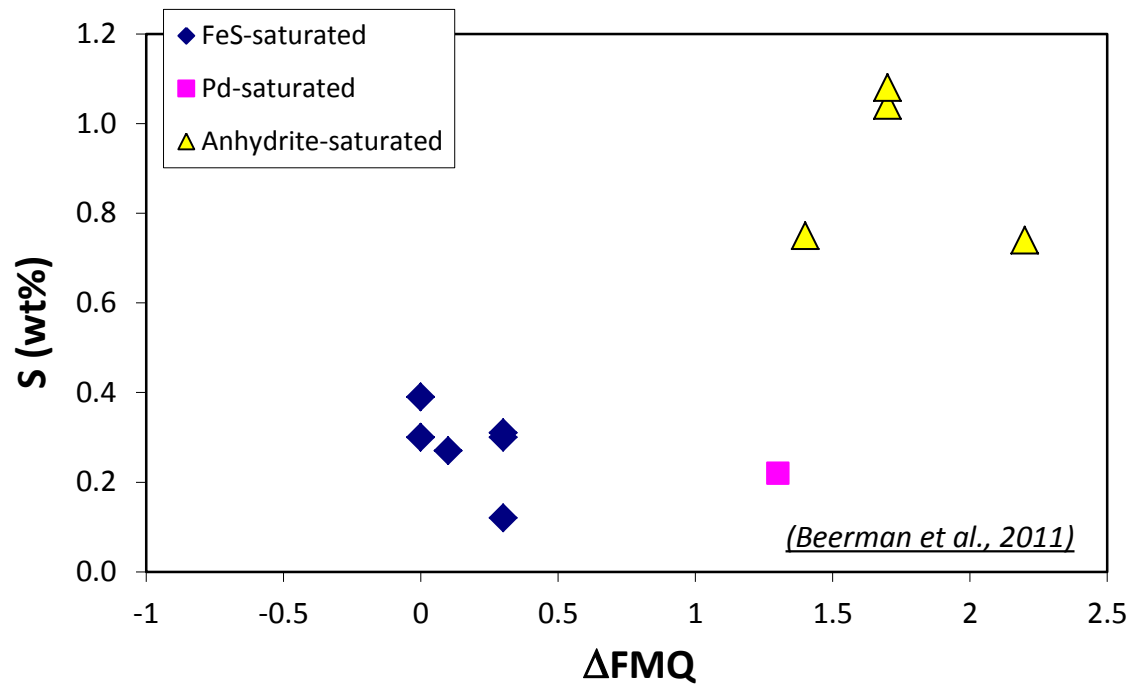
Strongly affected by fO_2

Limits:
- Only the sulfide saturated experiments approach typical basaltic redox conditions
- The experiments are performed only at 200 MPa
- The effect of CO_2 is not considered

Solubility of sulfur in hydrous basaltic melts

Starting material: natural basaltic pumice (PST9)

3 types of experiments:

1) Fe pre-saturation of platinum capsules @ T= 1200 - 1250 °C, P=1 atm, log fO_2 ≈ -8.2 (~NNO-0.5). Experiments performed in a 1 atm-furnace with $CO-CO_2$ gas mixture.

   This represents the crucial first step in order to minimize Fe loss from the silicate melt during solubility experiments at high pressure.

2) fS_2 calibration @ T= 1200 °C, P=1 atm, log ≈ NNO. Experiments performed in a 1 atm-furnace with $CO-CO_2-SO_2$ gas mixture.

   Sulfur solubility is strongly dependent on fO_2 and fS_2 (besides of T and melt composition). The calibration of fS_2 in equilibrium with sulfide melts @ 1 atm will help us to recalculate fugacities of S-bearing species in equilibrium with the silicate melt in the high pressure experiments.

3) Sulfur solubility experiments @ T=1200 °C, P= 200 – 20 MPa, log fO_2 ≈ NNO, slightly H_2O under-saturated, in a second step with CO_2 present.

   These experiments represent the final aim of the study, the attainment of data under well controlled conditions being the only way to calibrate fluid-melt saturation models.
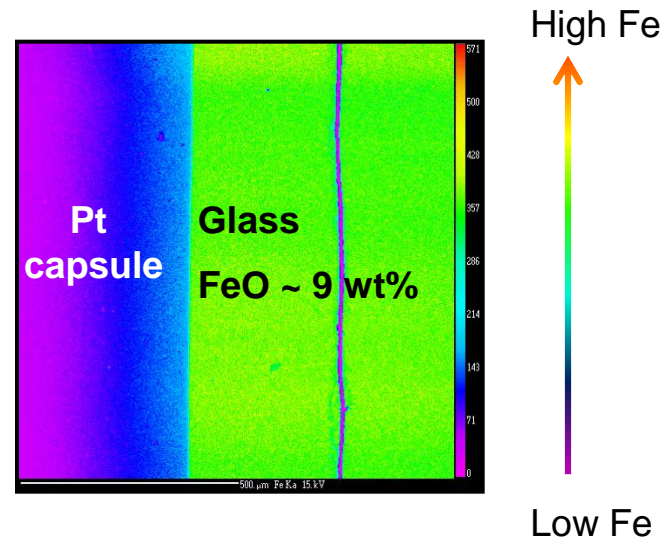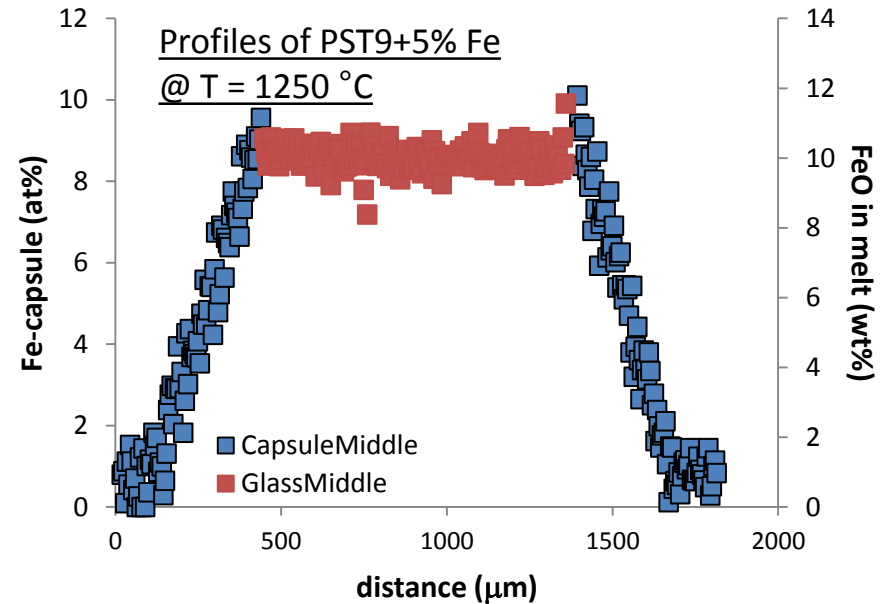
Preliminary results of Fe-presaturation experiments

3 compositions has been tested:
1) PST9 only
2) PST9+5%Fe
3) PST9+13%Fe

PST9+5% Fe gives at present the best response:
a) Fe is absorbed up to 8-9 % in the Pt-Fe alloy
b) 5% Fe added in the basalt does not significately change the melt composition in the final melt

Profiles of PST9+5% Fe @ T = 1250 °C

- CapsuleMiddle
- GlassMiddle

Fe-capsule (at%)

FeO in melt (wt%)

distance (µm)

High Fe

Pt capsule

Glass
FeO ~ 9 wt%

Low Fe

Next steps: 1) S solibility experiments @ high P using the pre-saturated capsules

to compare with

2) S solibility experiments @ high P syn-enriching the melt with ~ 5wt% Fe

THANK YOU!

- *"A full recalibration involving the Conjugated-Toop-Samis-Flood-Grjotheim model would be advantageous but it **requires the availability of high precision experiments reporting full chemical analyses of coexisting phase and as constrained as possible fO_2 and particularly fS_2 values**."*

  Moretti & Baker, 2008

- *" Modeling the composition of gas released at surface requires **a robust thermodynamic treatment and good estimates of the pressure-related behavior of sulfur** and other volatile components. "*

  Metrich & Mandeville, 2010

- *"The improvement of models requires **additional experimental data, particularly in the critical fO_2 range near the NNO buffer** where the speciation of dissolved sulfur changes from S^{2-} to S^{6+} with increasing fO_2."*

  Baker & Moretti, 2011

- *"Dedicated experiments are required at S concentrations sufficiently low to prohibit saturation in S-bearing solid phases, over a range of pressures and at fO_2 sufficient to maintain most S in the reduced state."*

  Witham et al., 2012