Thermochemistry of magmatic degassing

Roberto Moretti

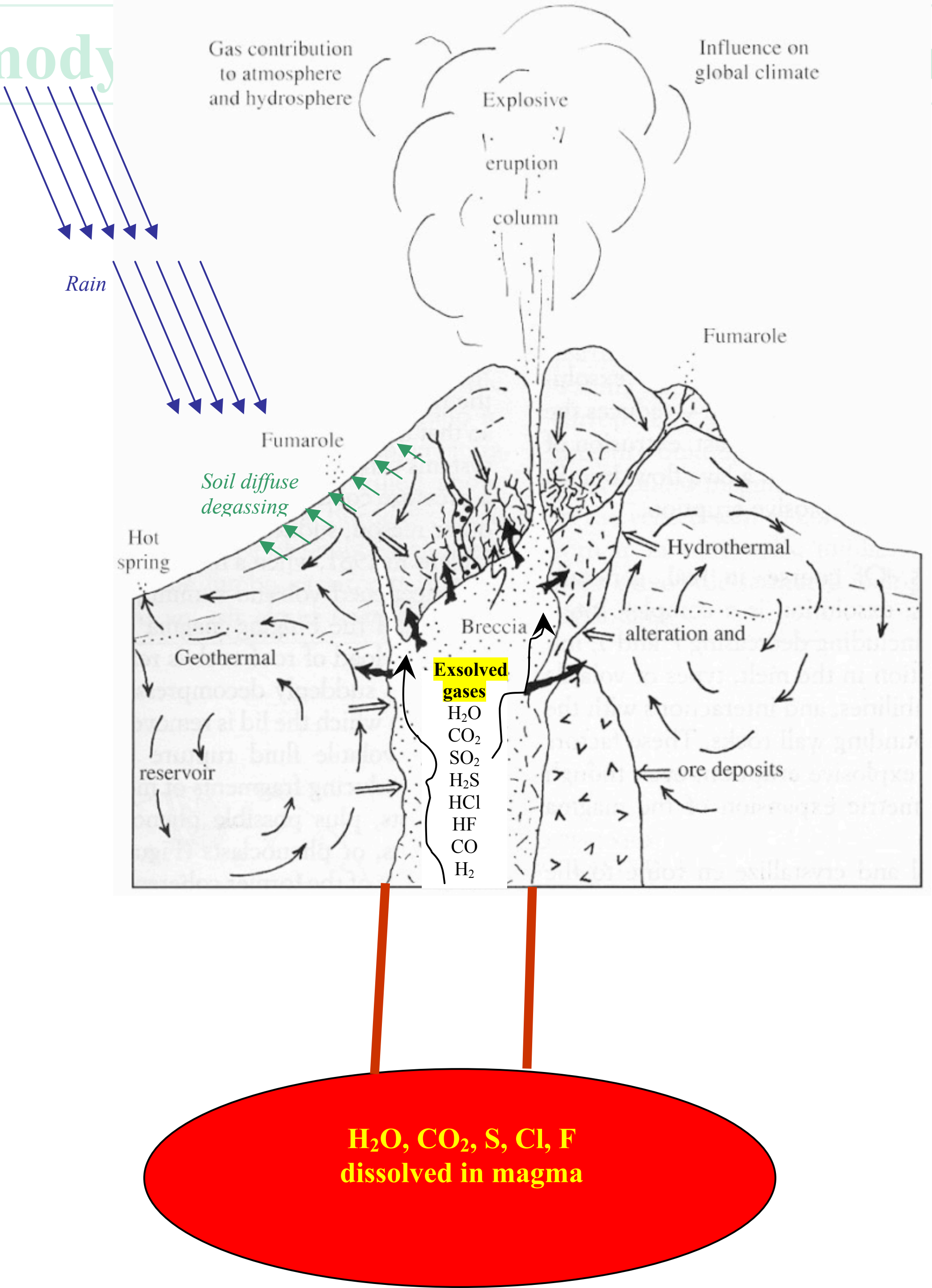
Université de Paris
Institute de Physique du Globe de Paris

Observatoire Volcanologique et Sismologique
De Guadeloupe
Institut de Physique du Globe de Paris

Andy Warhol, 1985

OUTLINE

- Introduction: the problem of volcanic degassing; measurements and sources
- « solubility » models (better if we talk about « saturation »)
- Mixing properties of silicate melts
- Polymeric modeling of the iron oxidation state and sulfur solubility and speciation


Gas contribution to atmosphere and hydrosphere
Explosive eruption column
Influence on global climate
Rain
Fumarole
Fumarole
Soil diffuse degassing
Hot spring
Hydrothermal alteration and ore deposits
Breccia
Geothermal reservoir
Exsolved gases
H_2O
CO_2
SO_2
H_2S
HCl
HF
CO
H_2
H_2O, CO_2, S, Cl, F dissolved in magma

Introduction: volcanic and hydrothermal gases

Volcanic

	t °C	H_2O	CO_2	SO_2	H_2S	HCl	HF	H_2	N_2	CH_4	CO
Erta Ale	1130	794000	104000	67800	6200	4200	tr	14900	1800	tr	4600
Klyuchevskoy	1100	977300	1200	900	20	14200	2500	5900	40	0.1	12
Mutnovsky	360	987000	5190	4020	1640	975	260	884	156	0.1	0.5
Mount Usu	690	993000	3600	320	180	340	60	2000	104	5.7	0.5
Ngauruhoe	640	960000	16050	10200	6800	2500	-	1420	1500	0.3	42
Papandayan	400	960000	29400	6750	2900	1250	33	140	550	0.6	0.3
Mt St Helens	540	985000	9130	730	1370	890		2440	470	0.2	13
Satsuma Iwo J,	880	973000	5100	8180	1640	5306	277	6070	80	4	17.2
Sierra Negra	280	311000	672000	12450	2700	275	21	3	1520	0.3	0.2
Showa Shinzan	800	980000	12000	430	4	530	240	6300	570	7.1	33
Tokachi	505	931000	11520	32570	21460	2760	345	120	224	0.1	1.1
Vulcano	620	861000	119000	6800	4800	4530	1010	1510	1068	0.1	110

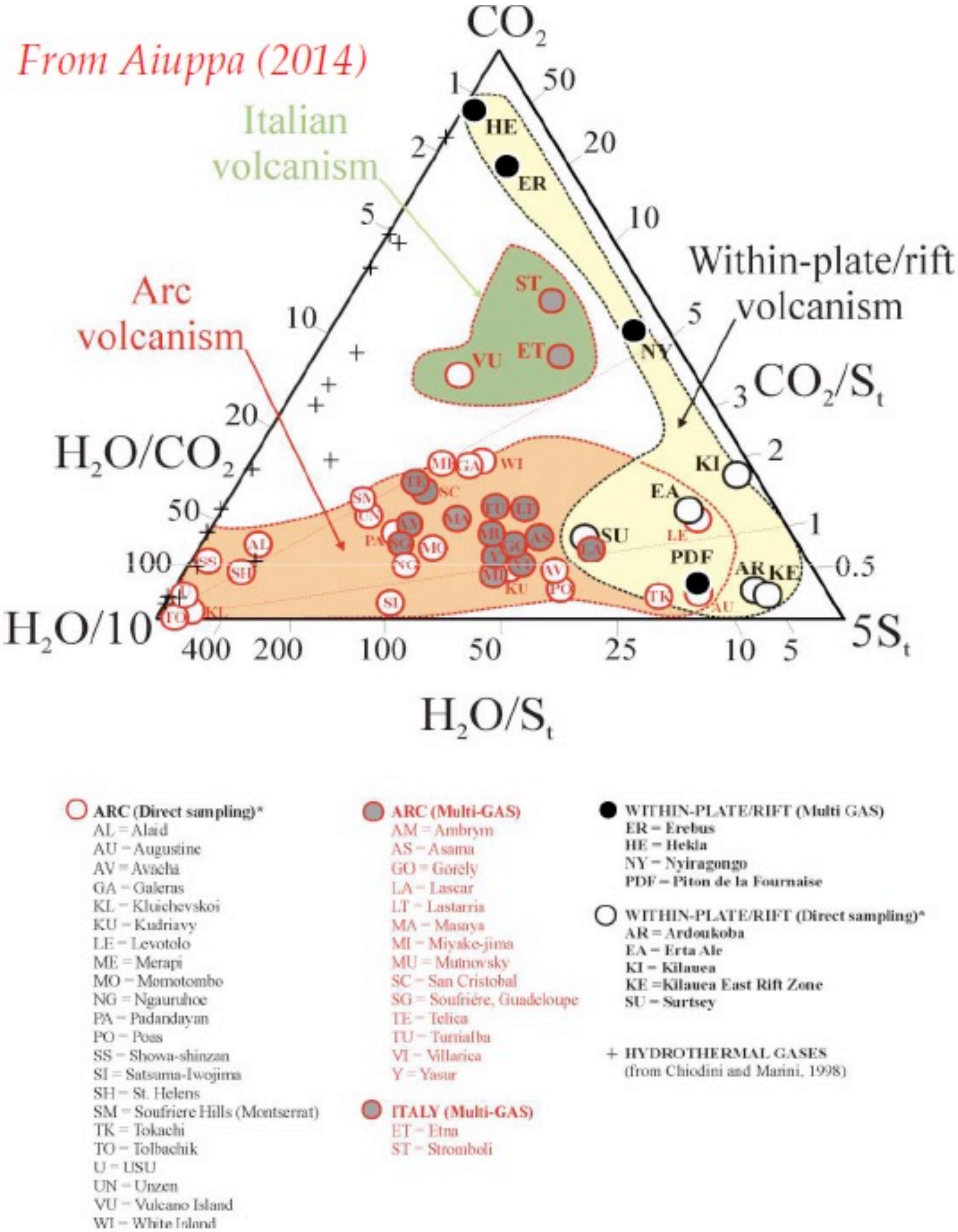
Hydrothermal

	t °C	H_2O	CO_2	SO_2	H_2S	HCl	HF	H_2	N_2	CH_4	CO
Solfatara-BG (2)	160	824529	173383	nd	1341	nd	nd	255.7	637	17.4	0.440
Vesuvio-FC1 (2)	99	982000	17750	nd	23	nd	nd	185	34.2	13.3	1.600
Pantelleria-F (2)	100	967900	23210	nd	tr	nd	nd	1220	6800	884.0	0.056
Vulcano-Vi (2)	99	936100	61200	nd	1478	nd	nd	654	509	66.0	0.056
Vulcano-Vsf (2)	98	906600	89970	nd	2309	nd	nd	108.7	867	115.8	0.100
Lipari-K1 (2)	96	852800	139700	nd	242	nd	nd	102	1820	5330.0	0.045
Ischia-DR (4)	99	997200	2655	nd	73	nd	nd	34.7	31.6	0.4	0.023
Tambora (5)	150	995500	3756	nd	389	nd	nd	268	46.2	4.5	0.045
Teide (6)	83	824300	174400	nd	171	nd	nd	492	660	3.9	0.290
Montserrat-L1 (9)	100	952000	43800	nd	3700	nd	nd	47	390	300.0	0.028
Kizildere (10)	94	638200	355000	nd	0	nd	nd	16.3	3740	2190.0	0.580
Larderello-Mr1 (2)	99	988700	10020	nd	352	nd	nd	380	119	434.0	0.011
Nisyros-1 (11)	98	985000	12460	nd	2340	nd	nd	120	54.1	72.7	0.067

Cold

	t °C	H_2O	CO_2	SO_2	H_2S	HCl	HF	H_2	N_2	CH_4	CO
Mefite	13	nd	980000	nd	3580	nd	nd	80.7	14300	2130.0	0.480
Selvena	15	nd	885000	nd	12500	nd	nd	5140	17000	80400.0	9.500
Amiata	7	nd	960700	nd	1750	nd	nd	0.955	23580	13980.0	0.148
Umbertide	9	nd	923000	nd	nd	nd	nd	2	74400	2520.0	0.120
Caldara	11	nd	974000	nd	13100	nd	nd	5	12600	206.0	0.270

From Aiuppa (2014)



Techniques

(i) **DIRECT SAMPLING AND ANALYSIS IN LAB** allows all major volcanogenic components (H_2O, CO_2, SO_2, HCl, ect.) to be simultaneously measured

Main problem: hazardous; time-consuming; Need to measure both:

- **intensive** parameters: **composition** = relative abundance of major species on air-free basis (direct sampling)
- **extensive** parameters: **fluxes =** mass of a given species emitted in unit time (e.g., tonnes per day)

(ii) **REMOTE SENSING; bulk (total) volcanic gas measurement from a distal location:**

Main problem**:** the atmosphere contains high and variable H_2O and CO_2 contents. Focus on SO_2

(iii) **MultiGAS**

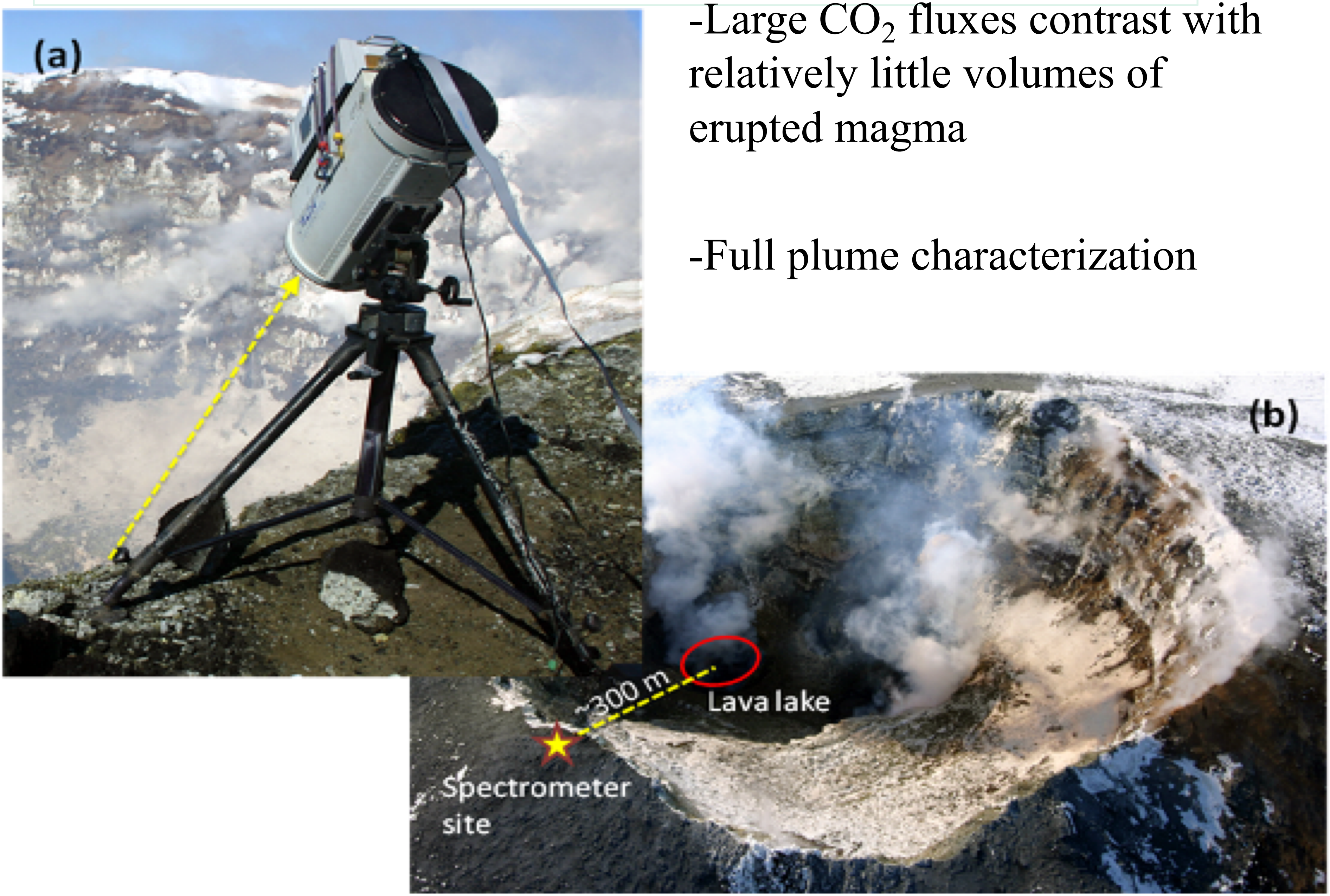
…..and also

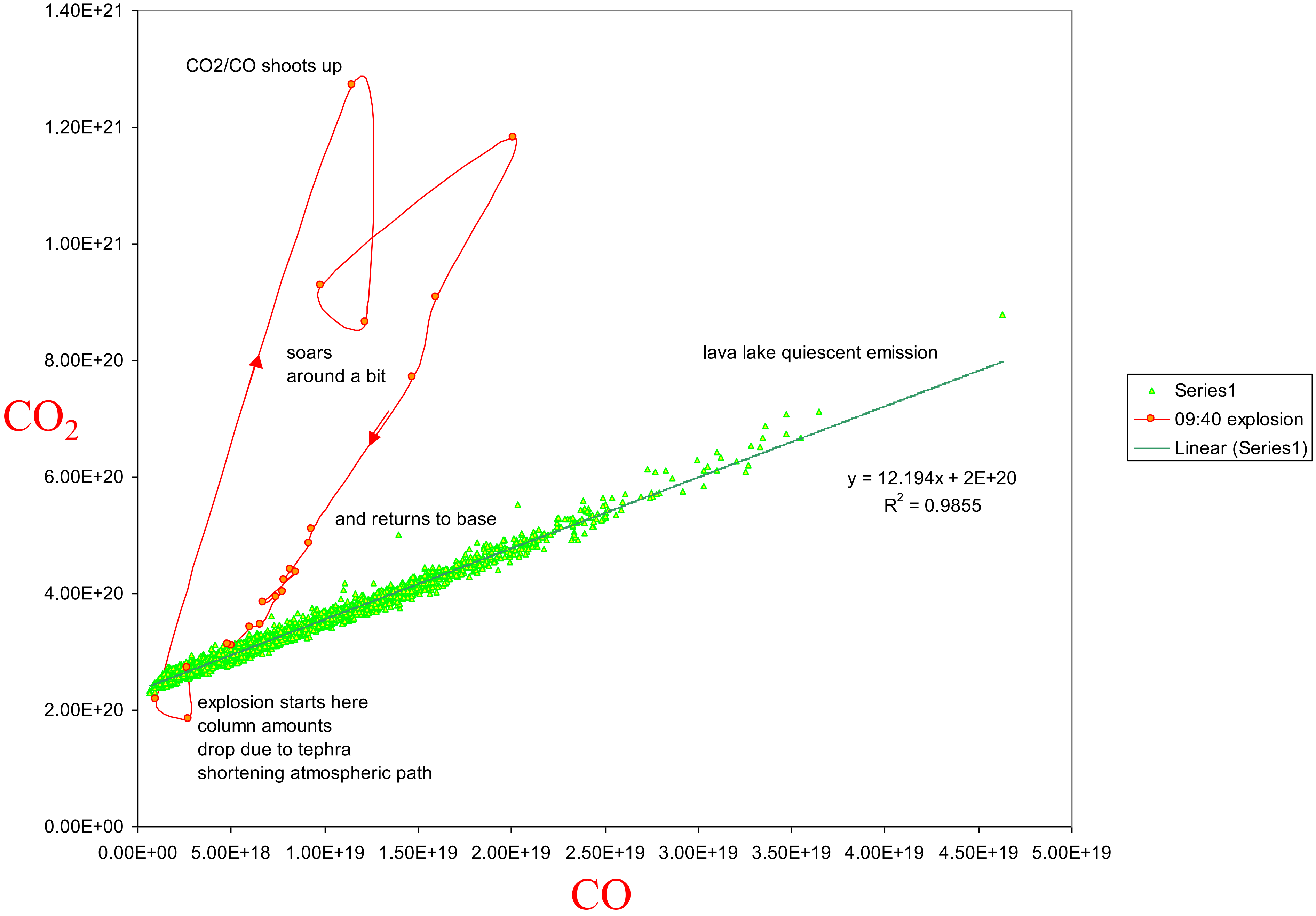
iv) **Soil Gas measurements** of hydrothermal areas

FTIR measurements of the emissions from the 2750 m. a.s.l. cone during the 2002 eruption of Mount Etna (Courtesy of Mike Burton, INGV Catania).

-Large CO_2 fluxes contrast with relatively little volumes of erupted magma

-Full plume characterization




CO2/CO shoots up
soars
around a bit
and returns to base
lava lake quiescent emission
explosion starts here
column amounts
drop due to tephra
shortening atmospheric path
y = 12.194x + 2E+20
R^2 = 0.9855
Series1
09:40 explosion
Linear (Series1)
CO_2
CO
1.40E+21
1.20E+21
1.00E+21
8.00E+20
6.00E+20
4.00E+20
2.00E+20
0.00E+00
0.00E+00
5.00E+18
1.00E+19
1.50E+19
2.00E+19
2.50E+19
3.00E+19
3.50E+19
4.00E+19
4.50E+19
5.00E+19

magnetite   hematite

MH $4\ Fe_3O_4 + O_2 = 6\ Fe_2O_3$

fayalite   magnetite   quartz

FMQ $3\ Fe_2SiO_4 + O_2 = 2\ Fe_3O_4 + 3\ SiO_2$

wustite   magnetite

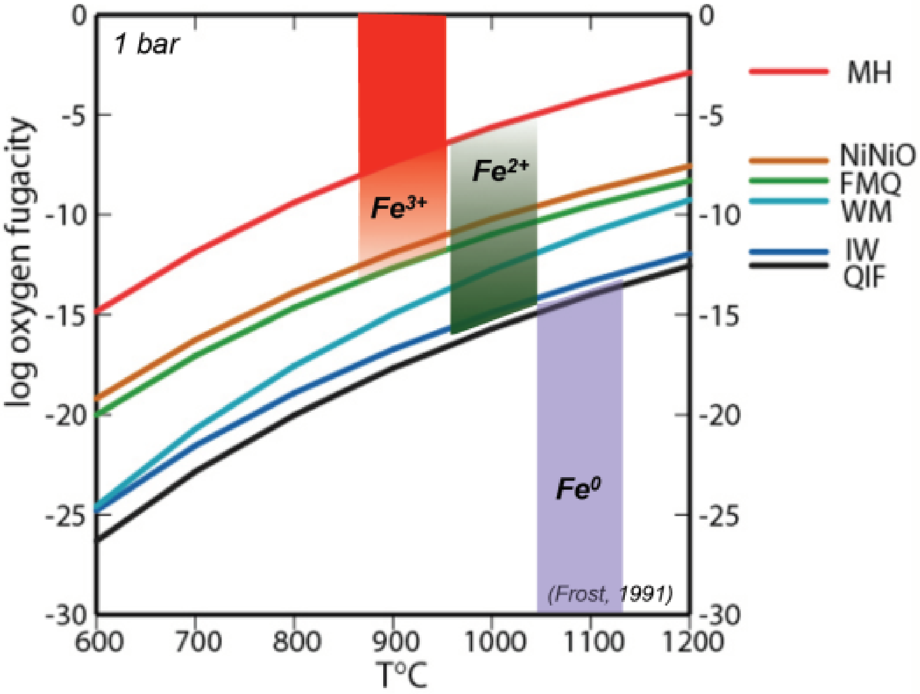
WM $3\ Fe_{1-x}O + O_2 \sim Fe_3O_4$

metal   wustite

IW $2(1-x)\ Fe + O_2 = 2\ Fe_{1-x}O$

metal   quartz   fayalite

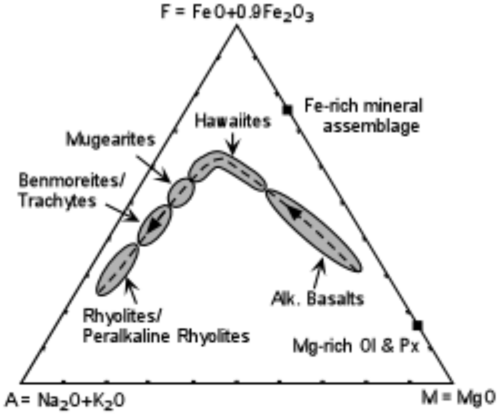
QIF $2\ Fe + SiO_2 + O_2 = Fe_2SiO_4$

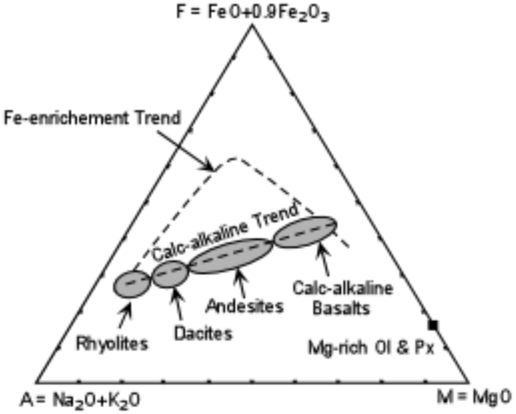


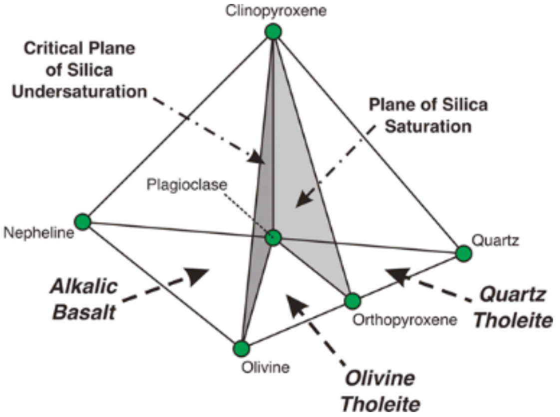
(Frost, 1991)

$$\log(fO_2) = A / T + B + C(P-1) / T$$

(P en bars, T en Kelvins)

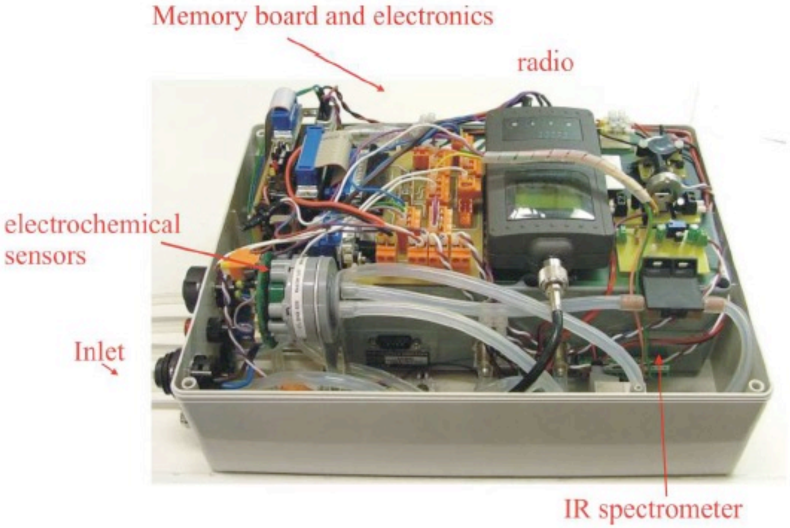






Multi-GAS measurements

[*Aiuppa et al, 2006, 2007, JGR, Geology*]



- *The* *Multi-GAS (Multi-component Gas Analyzer System)*, *a custom-made instrument for detection of H_2O, CO_2, SO_2, H_2 and H_2S concentrations in volcanic plumes;*
- *developed in Italy (INGV-Pa) and Japan (H. Shinohara) in the early 2000's;*

In-situ method: gas is pumped in the sensors and measured
(no remote sensing; interference from atmosphere reduced)

Sensors:
CO_2 (and H_2O): IR spectrometry
H_2S, SO_2: electrochemical sensors

Automatic and semi-real-time
1 measure every 2-9 seconds

Telemetry
Automatic datalogging and radio transfer to Palermo

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Steam and gas emission rate from La Soufriere volcano, Guadeloupe (Lesser Antilles): Implications for the magmatic supply during degassing unrest

Patrick Allard [a,*], Alessandro Aiuppa [b,c], François Beauducel [a], Damien Gaudin [d], Rossella Di Napoli [b], Sergio Calabrese [b], Francesco Parello [e], Olivier Crispi [e], Gilbert Hammouya [e], Giancarlo Tamburello [b]

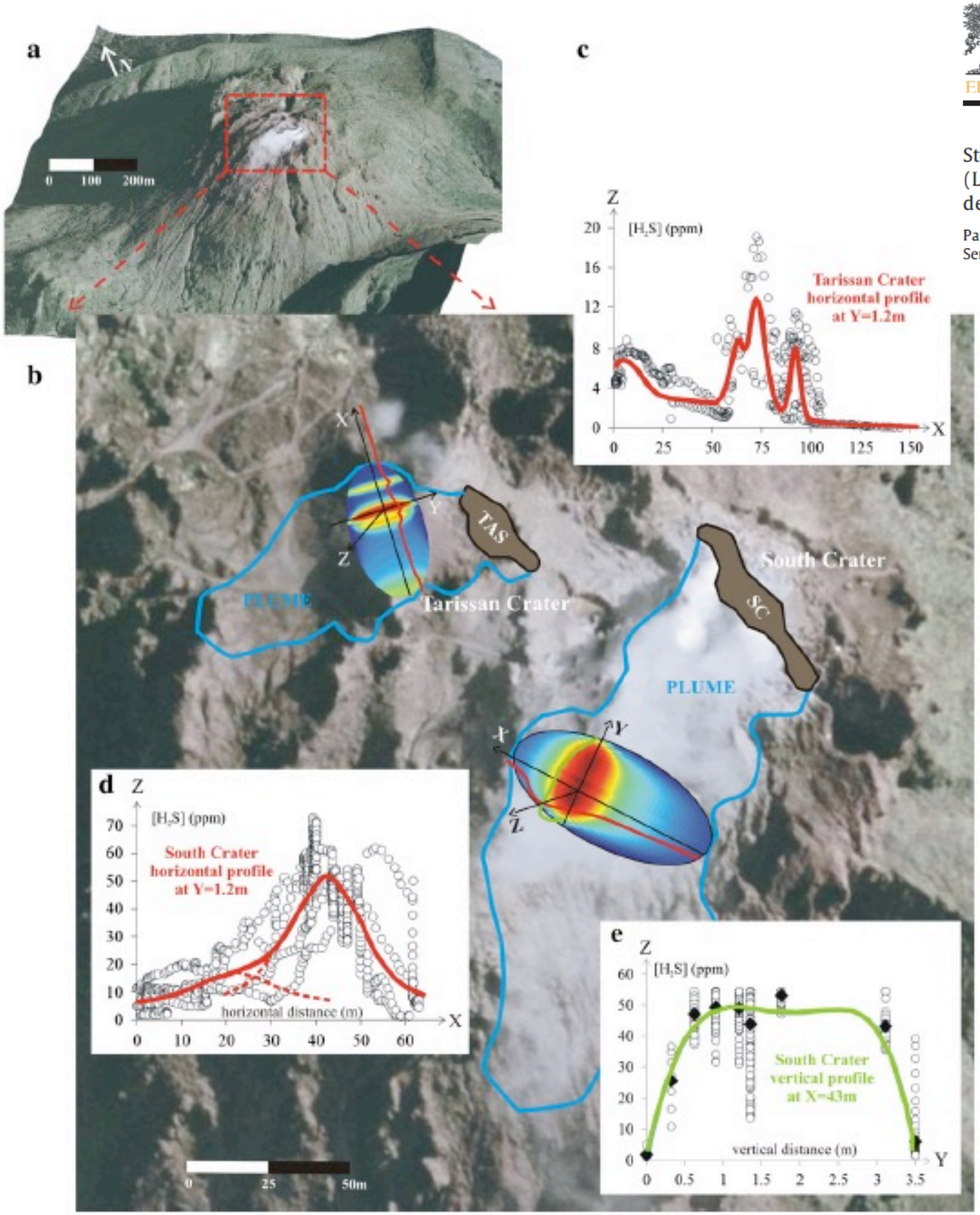
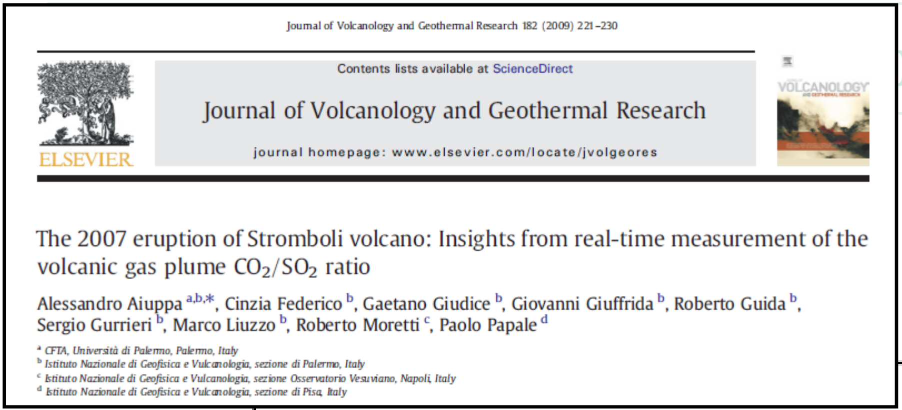


Fig. 5. Horizontal and vertical concentration profiles of H2S in SC and TAS volcanic plumes in March 2012. Maps show (a) the summit lava dome and (b) the area of SC and TAS craters and their plumes. Variations in H_2S concentration along X (horizontal distance) and Y (height above ground) in the ellipsoidal cross section of both plumes are depicted by the colour scale from blue (low values) to dark red (high values). These were calculated from the horizontal and vertical profiles shown in (c, d) and (e), and by combining Eqs. (1) and (2) (see text). (c) Horizontal H_2S concentration profile across TAS volcanic plume (1.2 m height above the ground); (d) cumulative horizontal H_2S concentration profile, obtained by summing the results of all MultiGAS traverses orthogonal to the SC plume; and (e) vertical profile (Y, in m) of H_2S concentrations (Z, in ppm) obtained in the core of SC plume (e.g., at horizontal distance X = 43 m from A, along the track A–D of Fig. 4).



Journal of Volcanology and Geothermal Research 182 (2009) 221–230

Contents lists available at ScienceDirect

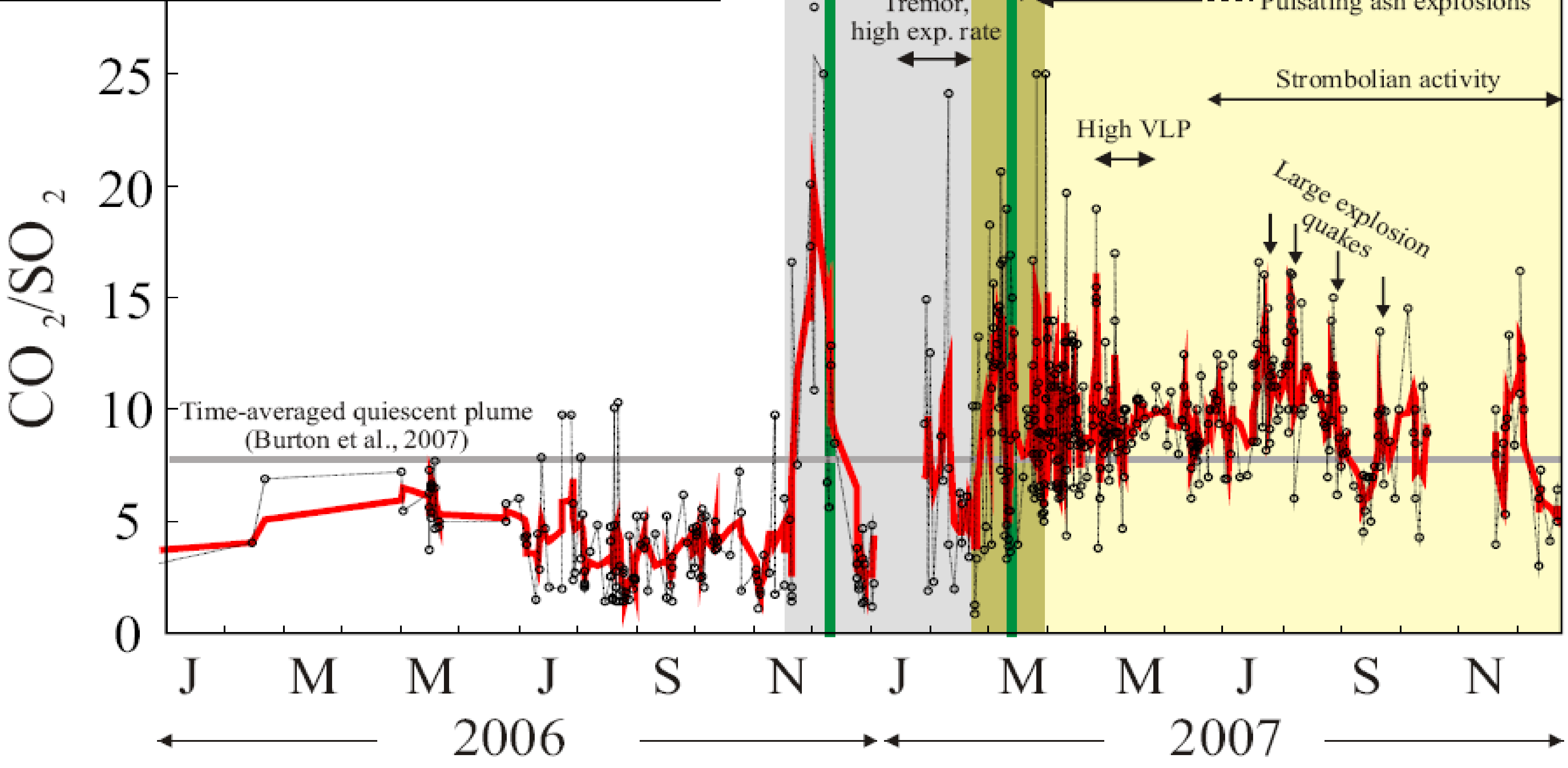
Journal of Volcanology and Geothermal Research

journal homepage: www.elsevier.com/locate/jvolgeores

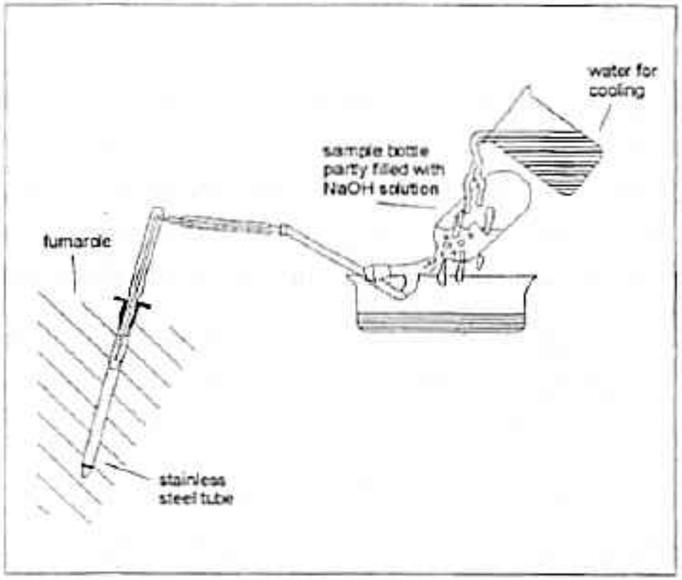
The 2007 eruption of Stromboli volcano: Insights from real-time measurement of the volcanic gas plume CO_2/SO_2 ratio

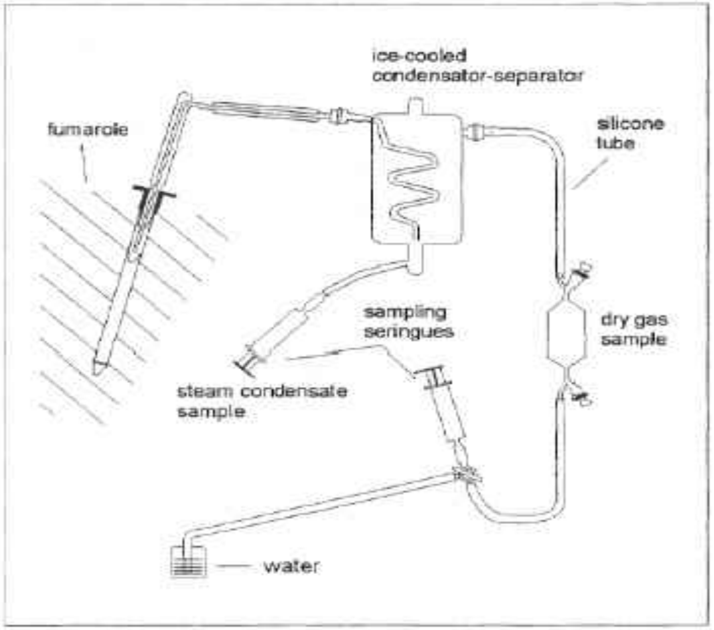
Alessandro Aiuppa [a,b,*], Cinzia Federico [b], Gaetano Giudice [b], Giovanni Giuffrida [b], Roberto Guida [b], Sergio Gurrieri [b], Marco Liuzzo [b], Roberto Moretti [c], Paolo Papale [d]

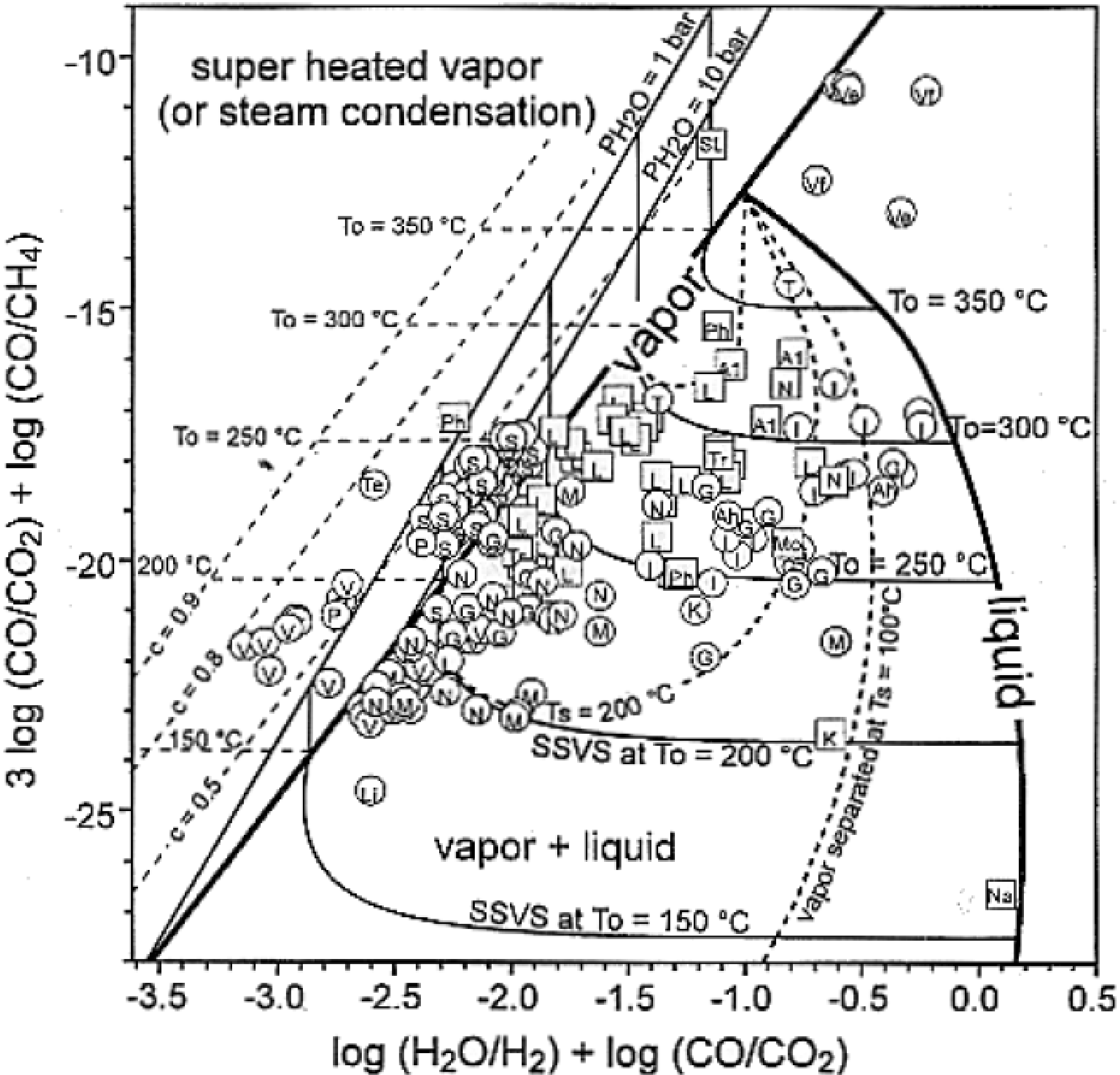
[a] CFTA, Università di Palermo, Palermo, Italy
[b] Istituto Nazionale di Geofisica e Vulcanologia, sezione di Palermo, Italy
[c] Istituto Nazionale di Geofisica e Vulcanologia, sezione Osservatorio Vesuviano, Napoli, Italy
[d] Istituto Nazionale di Geofisica e Vulcanologia, sezione di Pisa, Italy

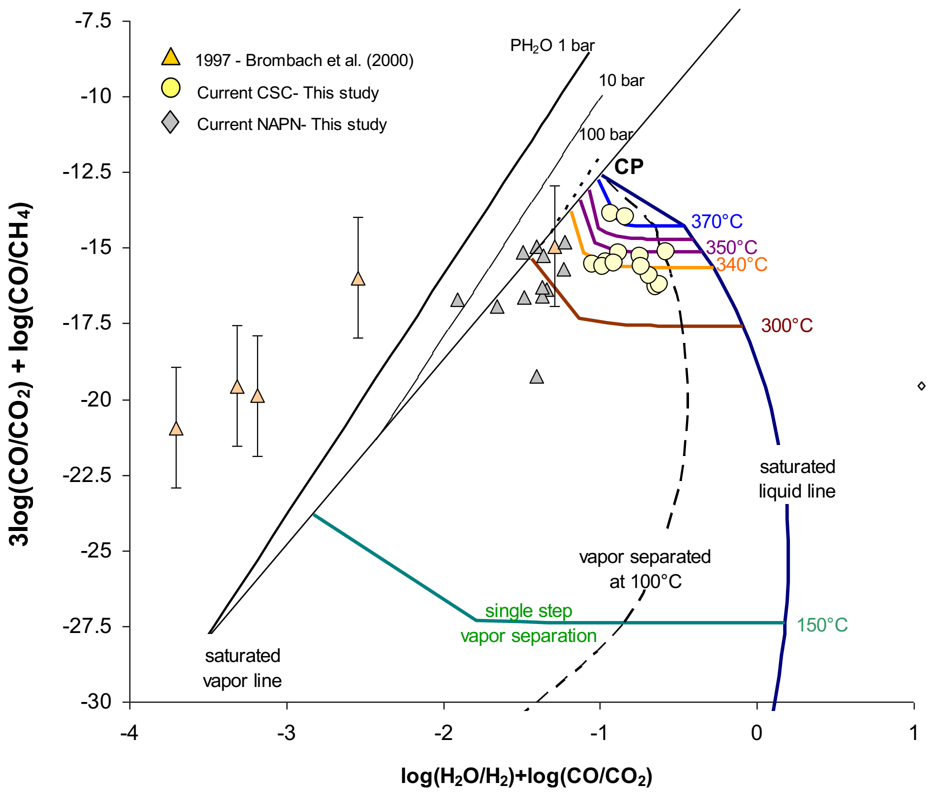


Aiuppa et al. (2009)

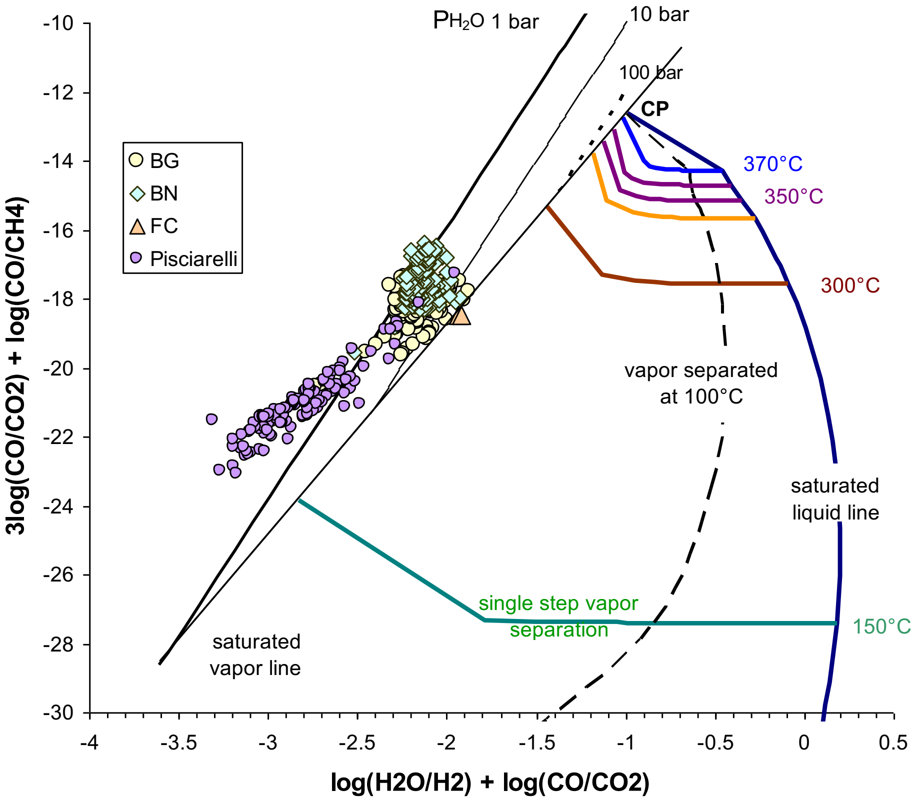

water for cooling
sample bottle partly filled with NaOH solution
fumarole
stainless steel tube


ice-cooled condensator-separator
fumarole
silicone tube
sampling seringues
dry gas sample
steam condensate sample
water


super heated vapor
(or steam condensation)
PH2O = 1 bar
PH2O = 10 bar
vapor
liquid
vapor + liquid
To = 350 °C
To = 300 °C
To = 250 °C
200 °C
150 °C
To=300 °C
Ts = 200 °C
SSVS at To = 200 °C
SSVS at To = 150 °C
Vapor separated at Ts = 100 °C
c = 0.9
c = 0.8
c = 0.5
SL
Ph
Te
Li
Na
K
Vf
Ve
-10
-15
-20
-25
-3.5
-3.0
-2.5
-2.0
-1.5
-1.0
-0.5
0.0
0.5
3 log (CO/CO2) + log (CO/CH4)
log (H2O/H2) + log (CO/CO2)



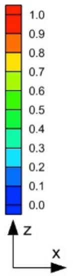
Soufrière de Guadeloupe (France)
outlet at 100°C

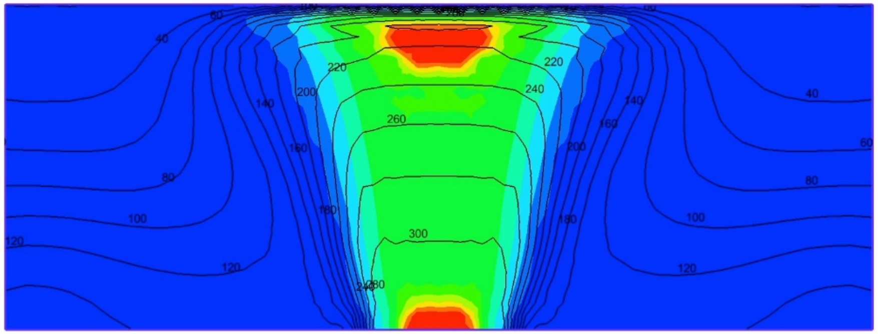


Solfatara (Campi Flegrei, Italy
outlet at 145-160°C

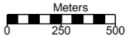
The thermo-fluid-dynamical modeling (H_2O + CO_2 fluid) of hydrothermal systems

Enthalpy assessment and P-T properties in input

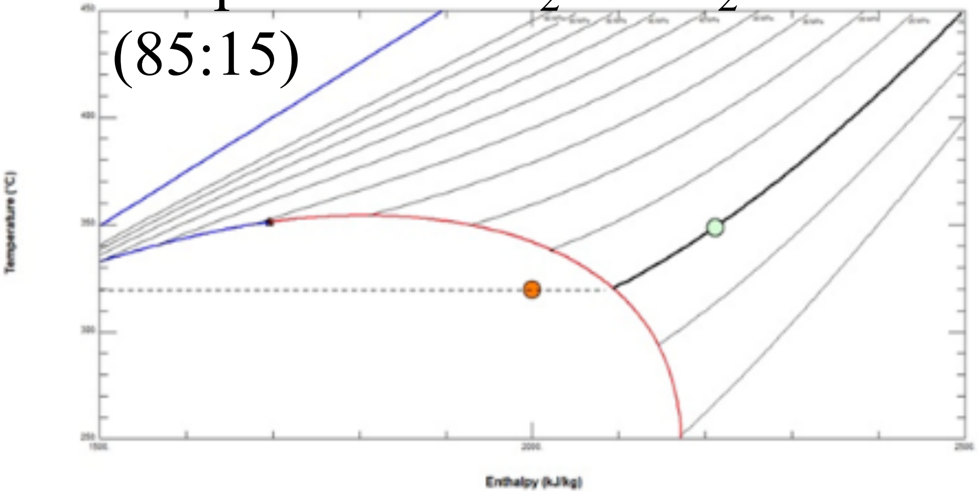


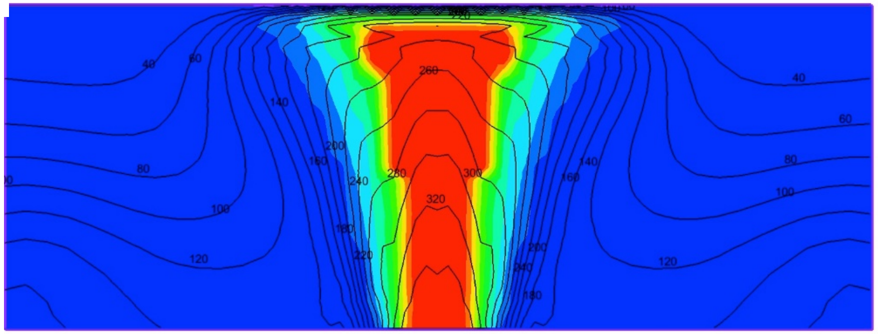


IDEAL MIXTURE



T-h plot of the H_2O-CO_2 mixture (85:15)





REAL GAS

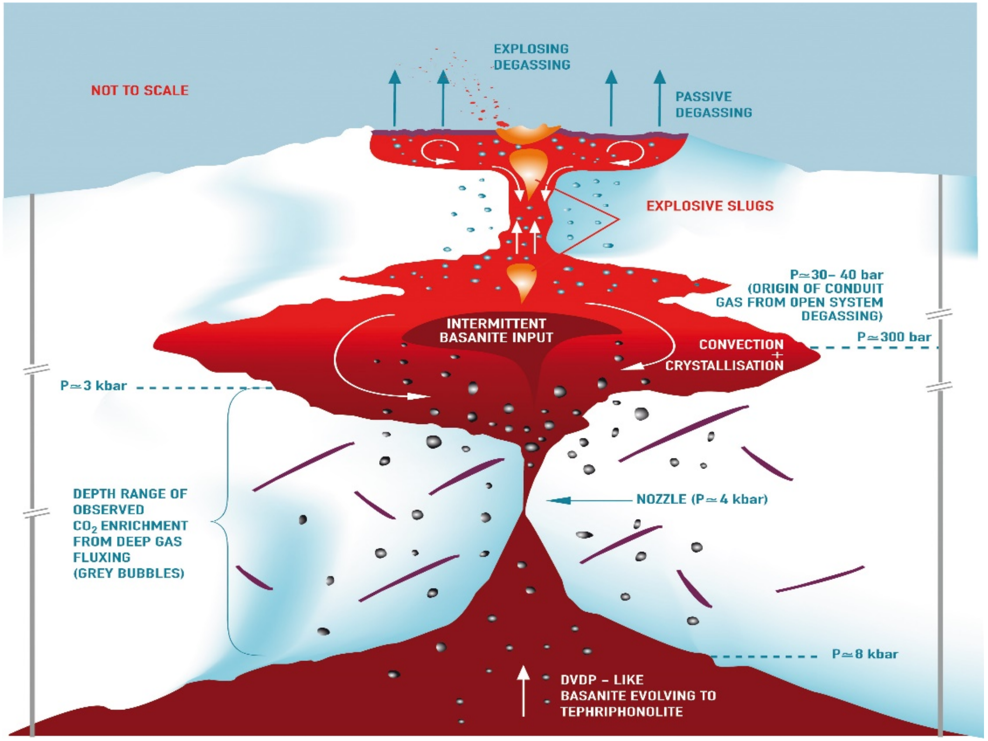
1 km

○ **Real gas** at 15 Mpa and 350°C → Single gas, h = 2220 J/g

● **Ideal mixture** → h = 2000 J/g, but at 15 MpaT is 320°C !!! → So it MUST be a two-phase (L+V) systetm

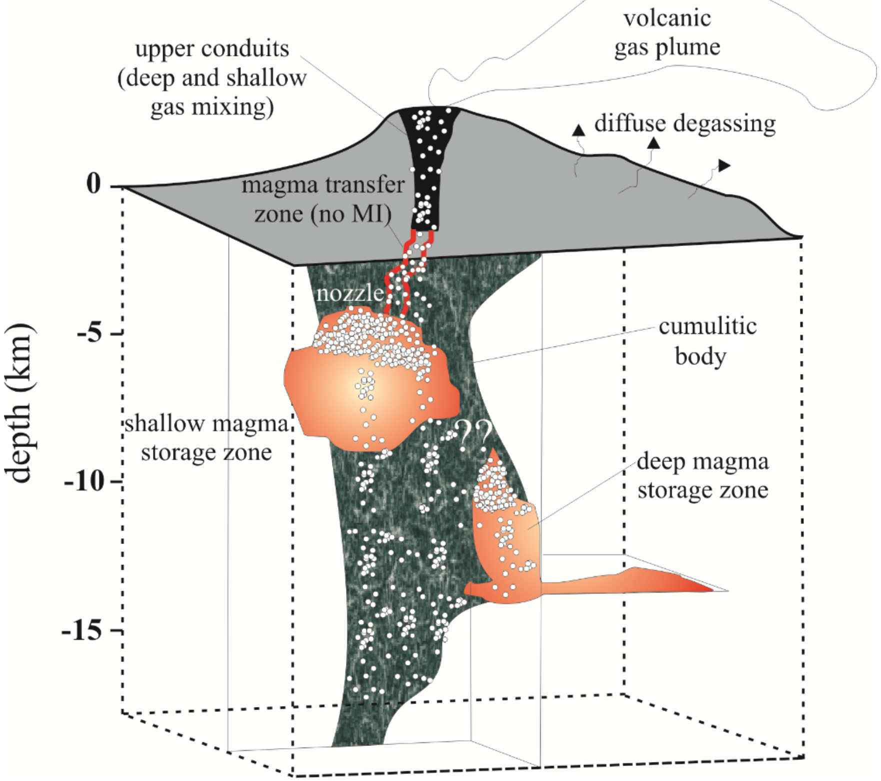
Troise et al. (2019, ESR)
Moretti et al. (submitted)

Erebus



Oppenheimer et al., 2011

Etna



Moretti et al., 2018

To draw, we look at magma…and its liquid phase: THE MELT

Measuring Initial Magmatic Volatiles

What is the challenge in accurately measuring/estimating amount of volatiles in magmas?

- **When gas samples taken at surface, they can become contaminated with atmosphere or other secondary sources (meteoric waters etc…)**
- **If magma saturated and bubbles formed, lost some of its volatile supply prior to eruption**

We can use “Phase Equilibria” or…

Glasses and Melt Inclusions

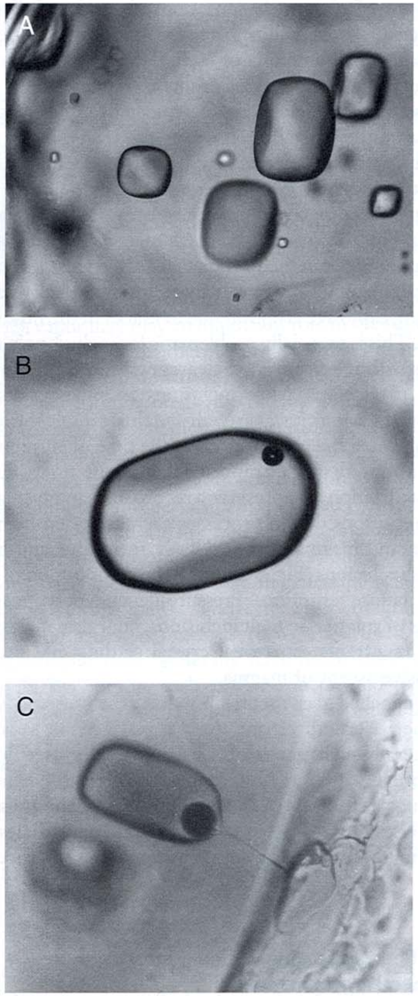
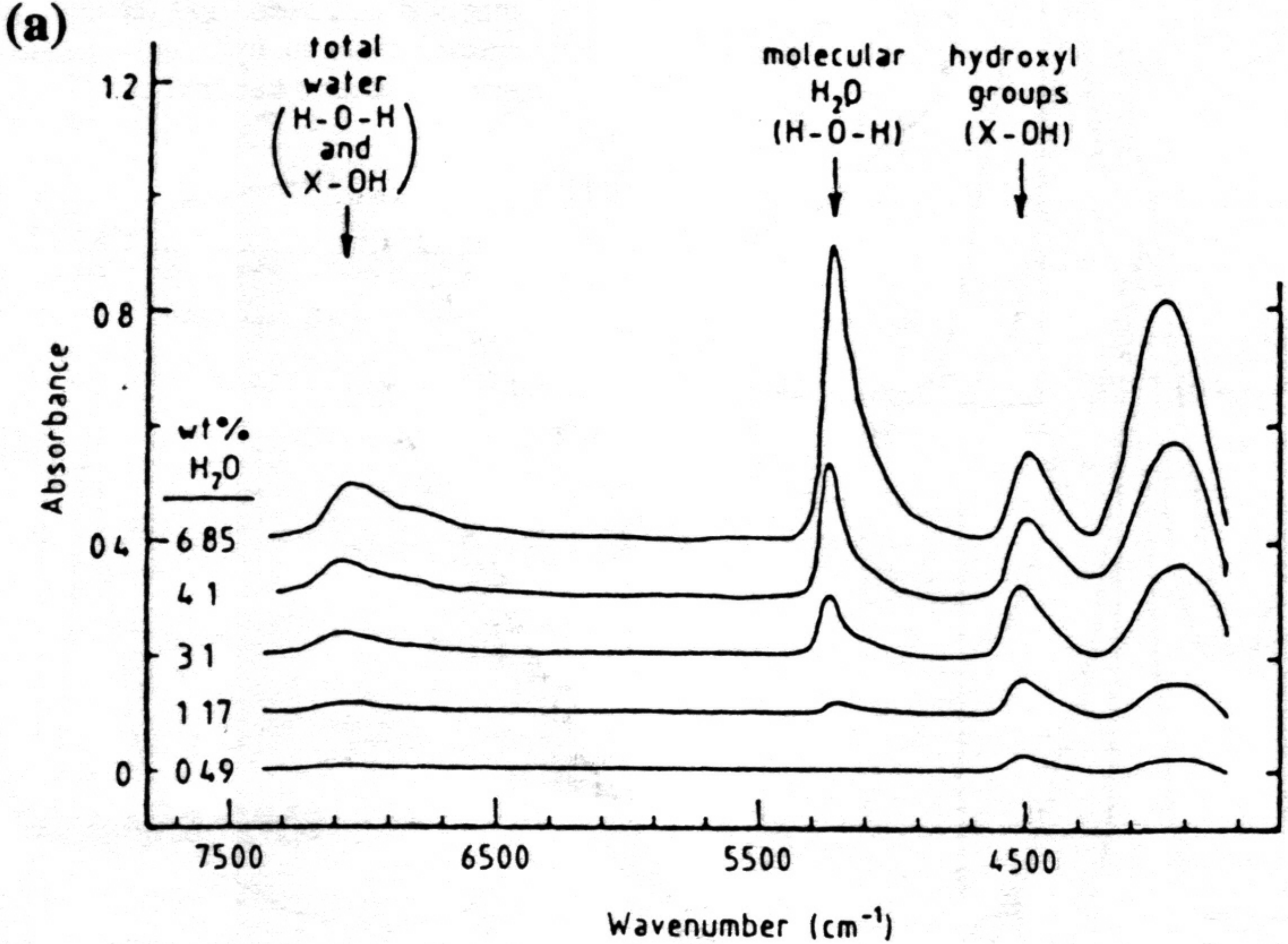
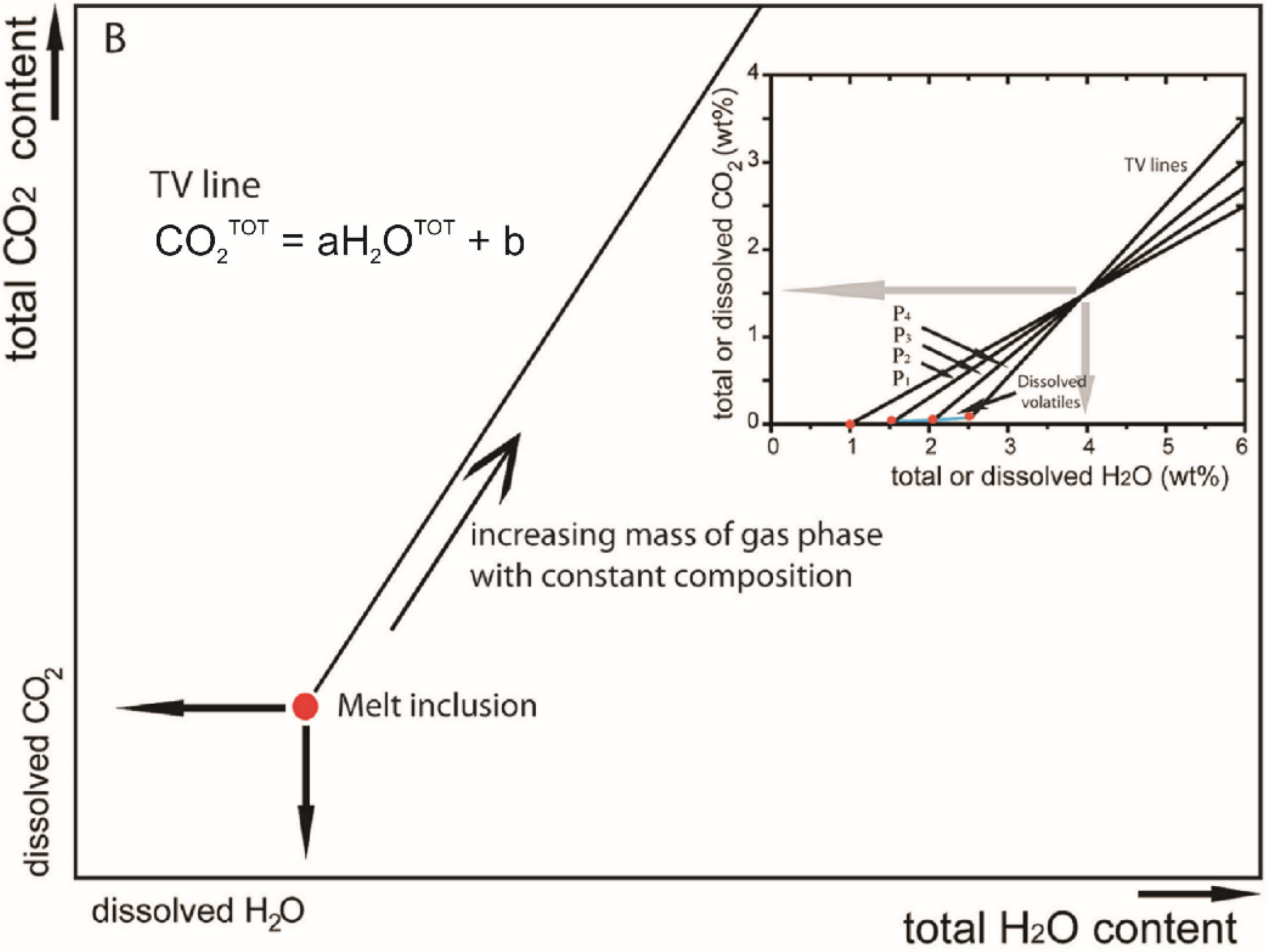


FIGURE 8 Glass (melt) inclusions in crystals from volcanic rocks. (A) A fragment of an ~3-mm quartz phenocryst from the rhyolitic Bishop Tuff containing inclusions of glass up to about 100 μm in diameter. (B) Close-up of a melt inclusion containing

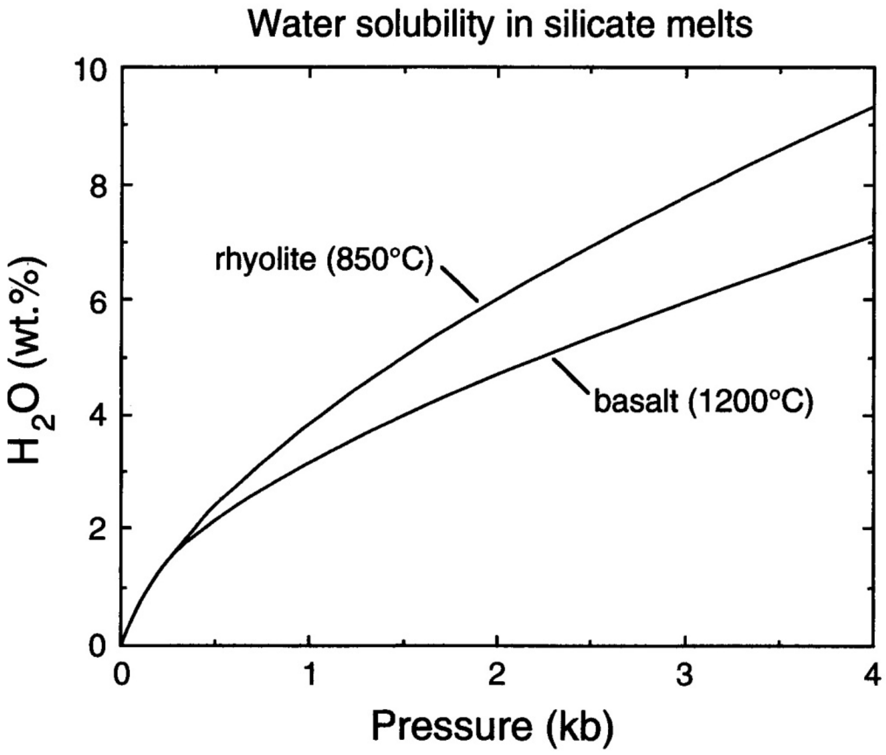
- **Can measure abundances in submarine glasses because little to no degassing invoked; magma cools on contact with seawater**
- **Melt inclusions, which are blobs of melt (glass) surrounded by crystal.**
- **Interpretation is that these blobs of melt do not lose volatiles because “armored” by solid crystal.**

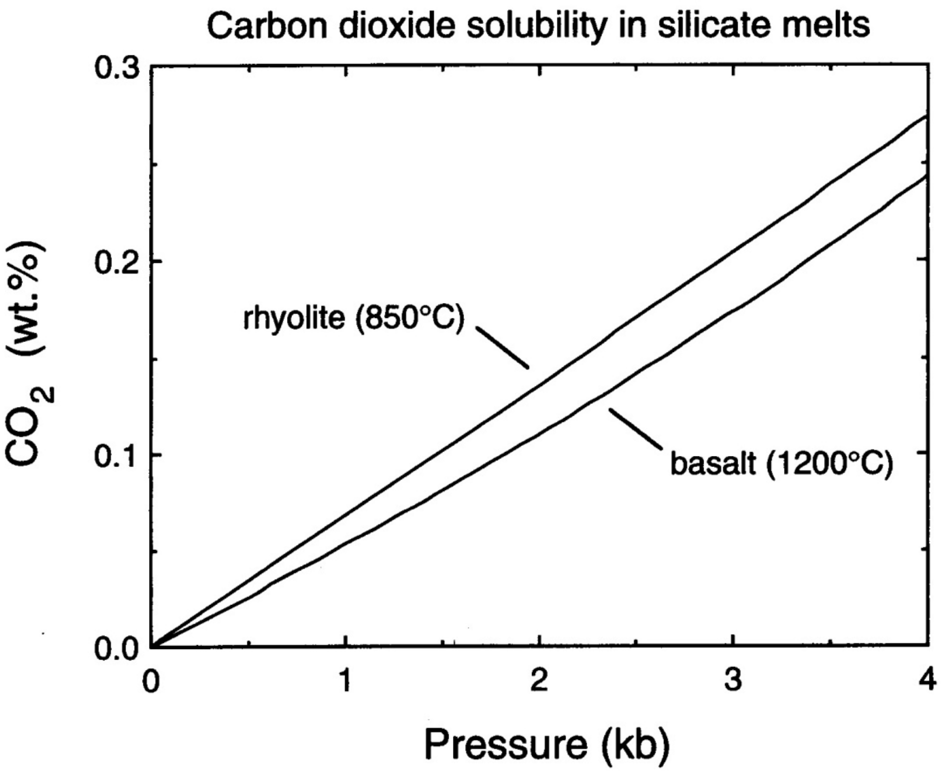

(a)
total water (H-O-H and X-OH)
molecular H_2O (H-O-H)
hydroxyl groups (X-OH)
1.2
0.8
0.4
0
Absorbance
wt% H_2O
6.85
4.1
3.1
1.17
0.49
7500
6500
5500
4500
Wavenumber (cm^{-1})


B
TV line
$CO_2^{TOT} = aH_2O^{TOT} + b$
increasing mass of gas phase with constant composition
Melt inclusion
total CO_2 content
dissolved CO_2
dissolved H_2O
total H_2O content
TV lines
P_4
P_3
P_2
P_1
Dissolved volatiles
total or dissolved CO_2 (wt%)
total or dissolved H_2O (wt%)
0
1
2
3
4
5
6

Then we need « solubility » models or to be more precise modeling of gas-melt interactions able to **precisely** calculate the saturation surface of the **H_2O-CO_2-H_2S-SO_2 (+ Cl, F) – silicate melt system** and see how magma degasses under **varying P and T**

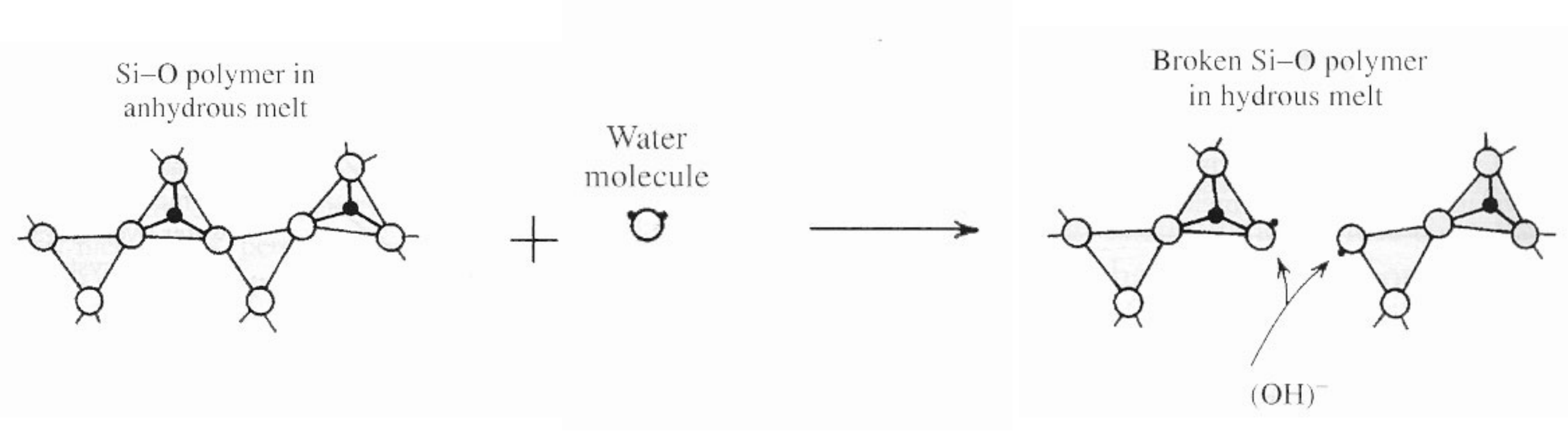
Understanding solubilities and saturation properties demands first experiments…then “thermodynamics”





- Solubilities are strongly pressure dependent
- Solubilities do not vary much with composition
- CO_2 has very low solubility compared to H_2O (~30x lower)

How was the solubility of water assessed ?



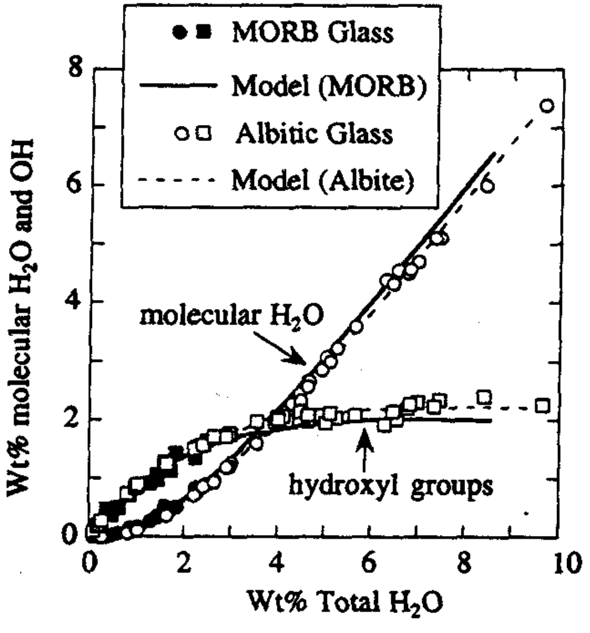
Silver and Stolper (1989) and Stolper (1989) considers the reactio

$$H_2O_{(m)} + O^{2-}_{(m)} = 2\ OH^-_{(m)} \tag{1}$$

$$-2 \ln (X_{OH,m})^2 + \ln [X_{H2O,m}(1- X_{OH,m} - X_{H2O,m})] = A' + B'\ X_{OH,m} + C'\ X_{H2O,m} \tag{2}$$

A', B', C' from *fitting* of IR data on H_2O speciation

Question: is (2) a true thermodynamic equilibrium constant ?



For the reactive solubility of CO_2 in melts (Fine and Stolper, 1989)

$$CO_{2(fluid)} + O^{2-}_{(m)} = CO_3{}^{2-}_{(m)} \qquad (1)$$

Basalts: CO2 as carbonate ion only

Rhyolites: CO2 as molecular CO2 only

Then, it is considered that:

$$K = X_{CO_3{}^{2-},m} / (f_{CO_2} X_{O^{2-},m}) \qquad (2)$$

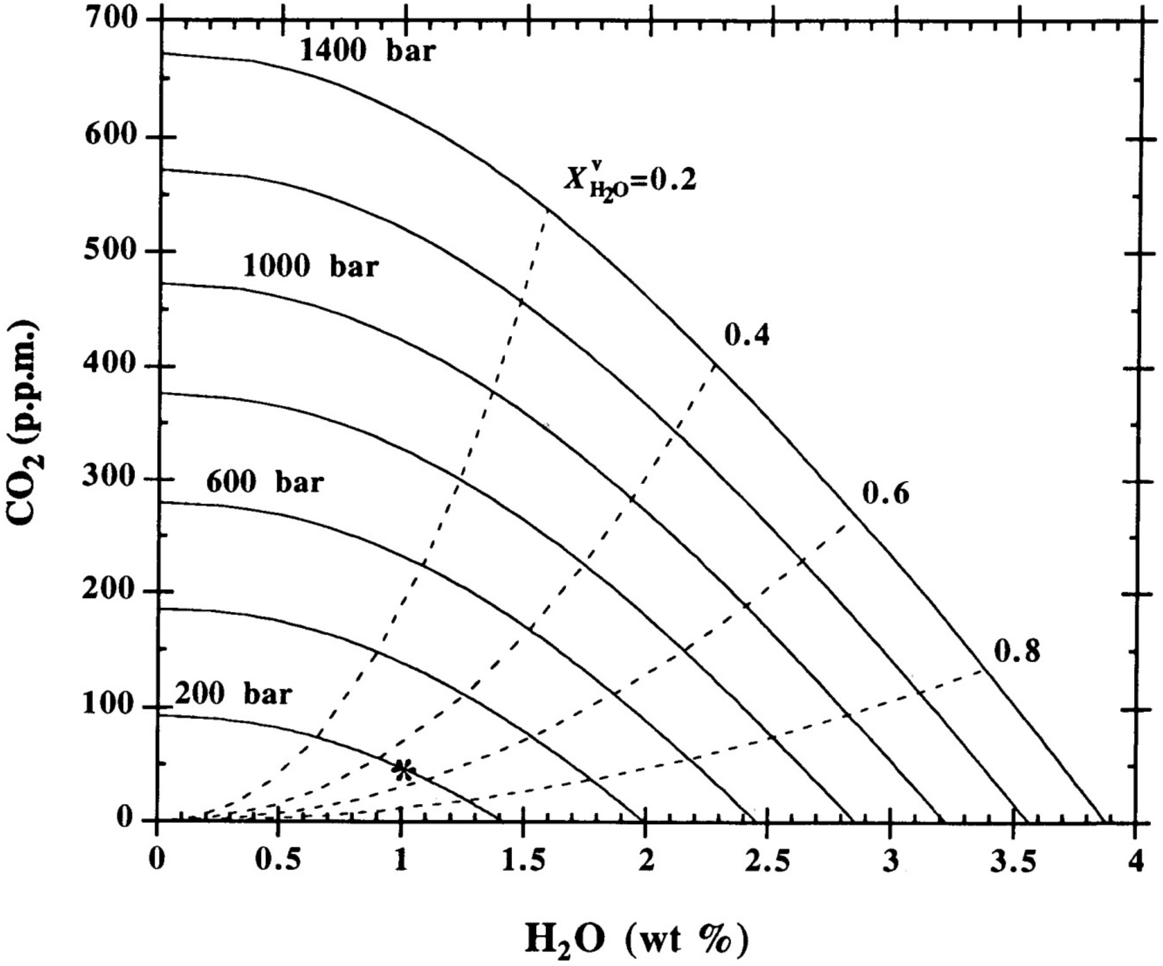
$$K = K° \exp[(-\Delta V°(P-P°)/RT) - (\Delta H°/R)(1/T - 1/T°)] \qquad (3)$$

Surprisingly, $X_{O2-,m}$ is given as:

$$X_{O2-,m} = 1 - X_{CO_3{}^{2-},m} \quad !!! \qquad (4)$$

(but what about $2\,O^{-}_{(m)} = O°_{(m)} + O^{2-}_{(m)}$????)

Solubilities with more than 1 volatile component present



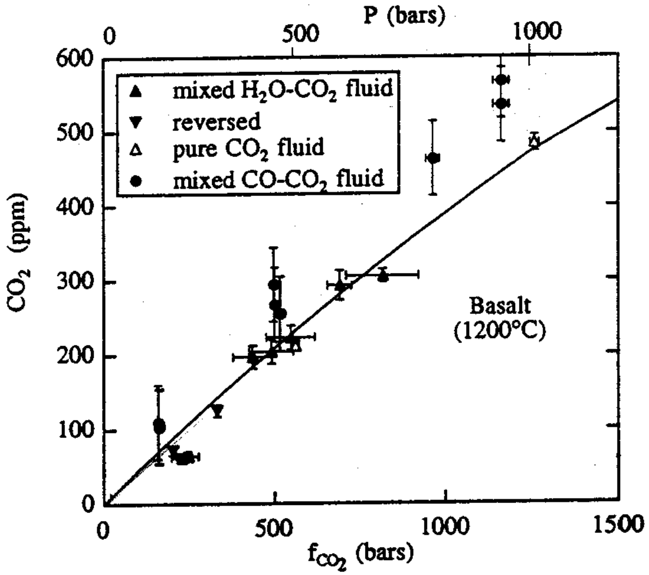
Solid lines show solubility at different constant total pressures

Dashed lines show the vapor composition in equilibrium with melts of different H_2O & CO_2

From Dixon & Stolper (1995)

- In natural systems, melts are saturated with a multicomponent vapor phase
- H_2O and CO_2 contribute the largest partial pressures, so people often focus on these when comparing pressure & volatile solubility

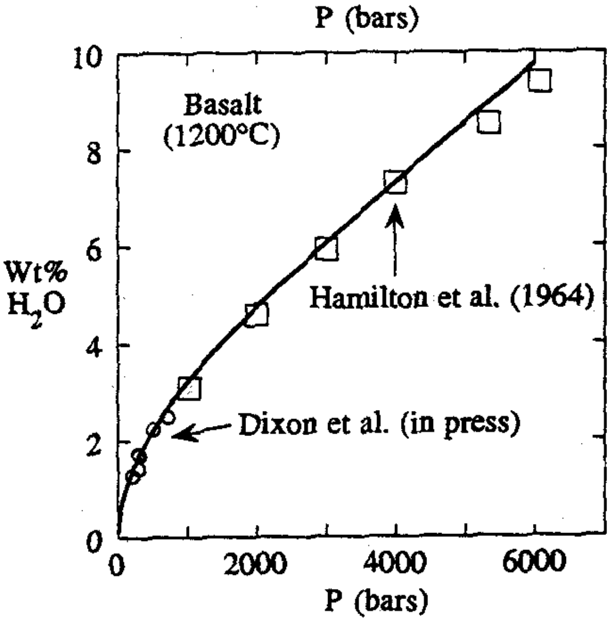
Let us consider ideal gas ($P_{TOT} = P_{H2O} + P_{CO2}$) and let us forget speciation phenomena in the melt phase (very simple



$P_{CO2} = K_{H,CO2}\ C_{CO2}$

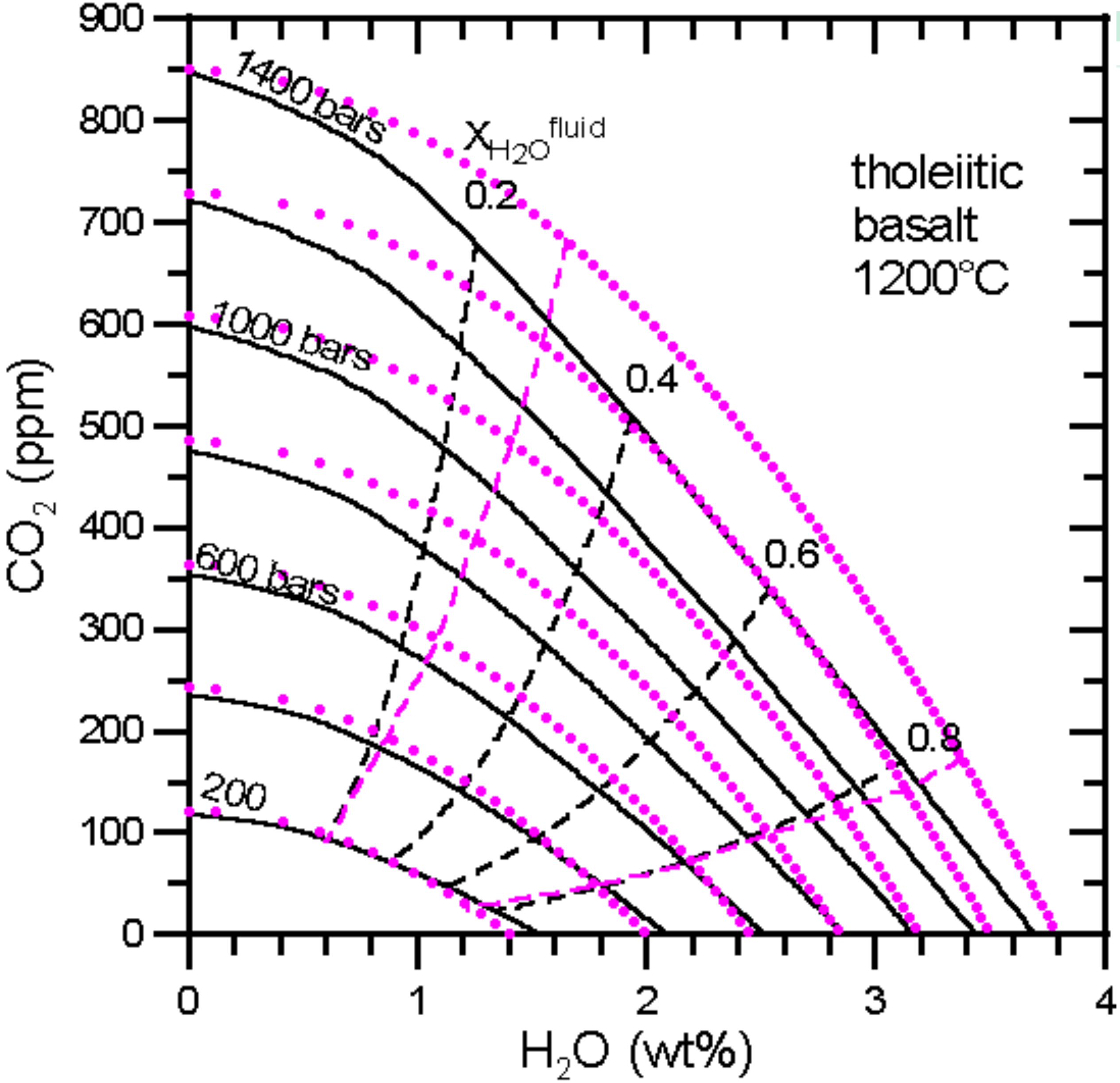
with

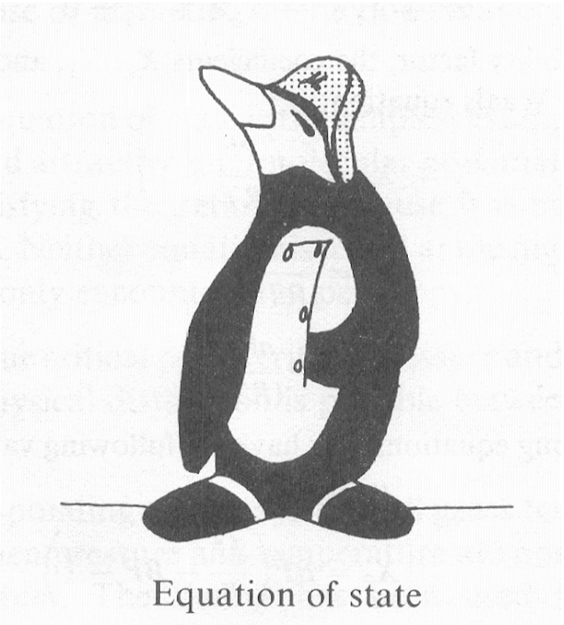
$K_{H,CO2} = 1.647$ bar/ppm



$P_{H2O} = 103.57\ W_{H2O}^{\ 1.9532}$

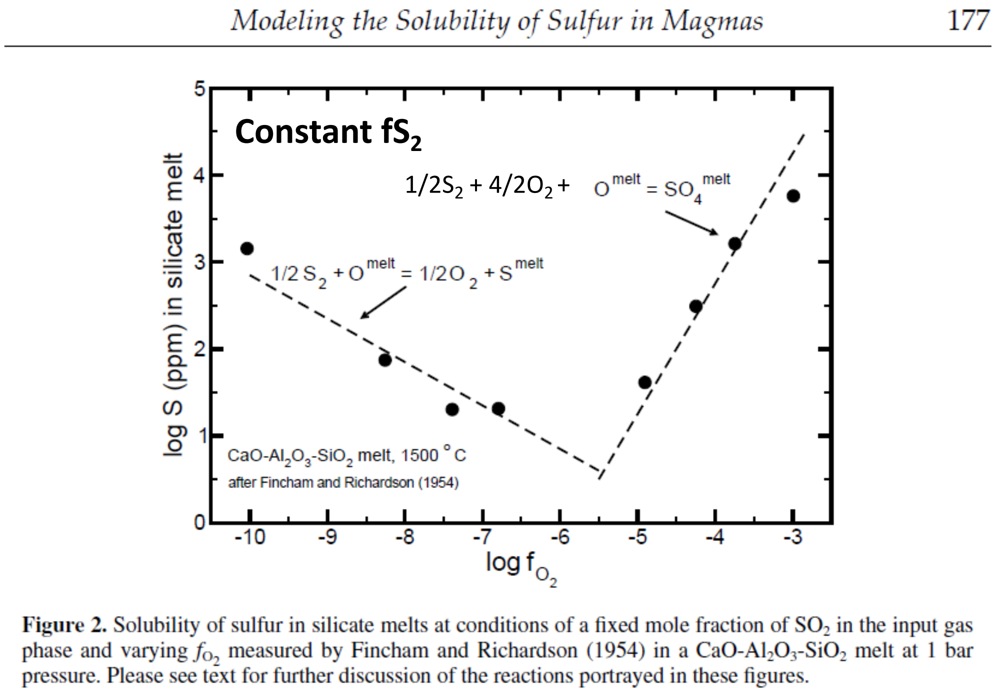
Look at violet points and lines in the next slide !




Equation of state

The penguin is unhappy and wants more accurate equations for both liquid and gas phases !

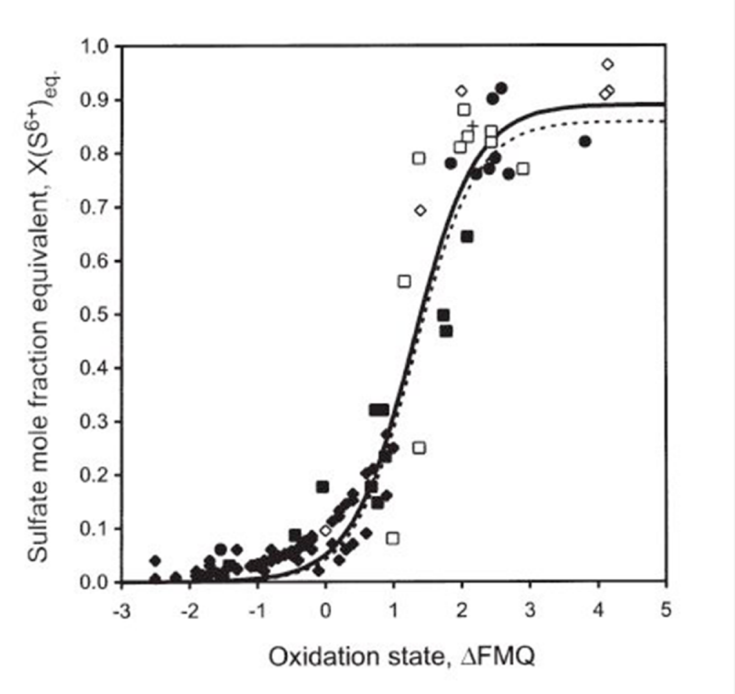
- S solubility is more complicated because of multiple oxidation states
- Dissolved S occurs as either S^{2-} or S^{6+}
- Solubility is limited by sat'n with pyrrhotite, Fe-S melt, anhydrite, or $CaSO_4$ melt
- S in vapor phase occurs primarily as H_2S and SO_2



Modeling the Solubility of Sulfur in Magmas 177

Figure 2. Solubility of sulfur in silicate melts at conditions of a fixed mole fraction of SO_2 in the input gas phase and varying f_{O_2} measured by Fincham and Richardson (1954) in a $CaO\text{-}Al_2O_3\text{-}SiO_2$ melt at 1 bar pressure. Please see text for further discussion of the reactions portrayed in these figures.

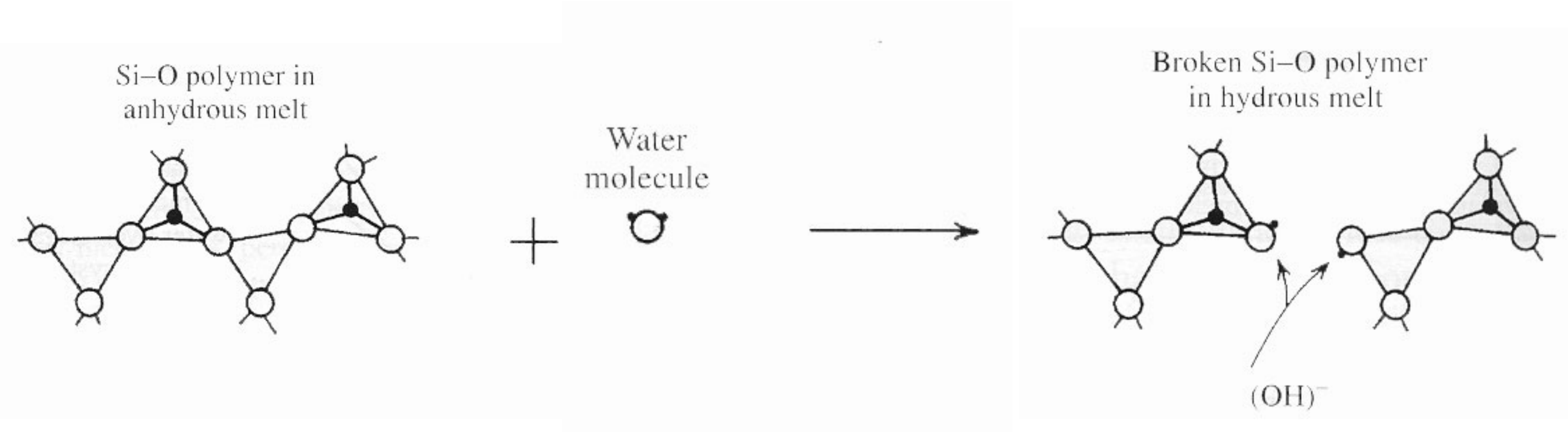
Baker and Moretti (2011)



Jugo (2005)

So, we also need to describe RedOx properties

Depolymerization of Silicate Melts to accommodate volatiles (e.g. water)



Question: how much we need to know about structure ?

Answer: the amount of knowledge enough to describe speciation (e.g., same as in aqueous solution) and write reactions

Comment 1: this implies consistent choices for the thermodynamic state of reference

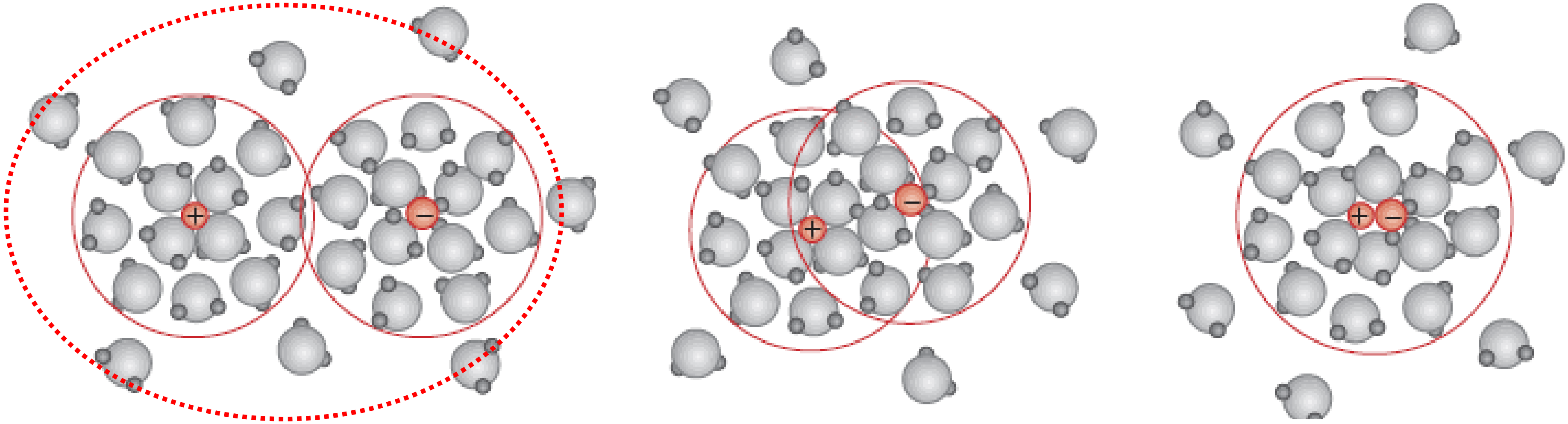
Comment 2: it also implies the choice of a well performing model for **melt mixing properties**

Silicate melts are not liquid water…

Outer sphere ion pair

Inner sphere ion pair

(complex)



Intact solvation shells

Partial disruption of solvation shells

Disruption of solvation shells

How deep need we to go with connections between structure and chemical thermodynamics ?

The “thermochemical knowledge” of a melt system does not seem to require the microstructural “complexity” that can be revealed by many spectroscopic investigations: the structural “characterization” exceeding that required for the **description of acid-base properties (e.g, in the Lux-Flood notation for oxide systems)** may be not useful.

Back to basics

In silicate melts acid-base properties are expressed in terms of Lux-Flood formalism:

$\text{Acid} + O^{2-} \Leftrightarrow \text{Base}$ (1)

(Ottonello et al., 2001; Moretti, 2005; Moretti and Ottonello; 2003; Ottonello, 1997: "Principles of Geochemistry"; Flood and Forland, 1947; Fraser, 1975; 1977).

In oxide systems, "reaction" 1 is the analogous of the Bronsted-Lowry one in aqueous solutions:

$\text{Acid} \Leftrightarrow \text{Base} + H^{+}$ *(2)*

In aqueous solutions the electrode of reference is the "normal hydrogen electrode", whereas in silicate melts the reference electrode is the "normal oxygen electrode" (Ottonello et al., 2001), i.e.:

$1/2O_2 + 2e^{-} \Leftrightarrow O^{2-}$ *(3)*

This is the main redox couple in oxide melts.

O^{2-} ? Virtual or real ?

Journal of Non-Crystalline Solids 357 (2011) 170–180

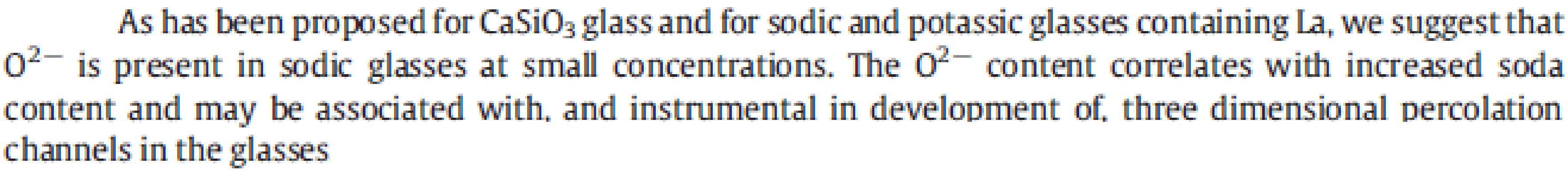
Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Bridging, non-bridging and free (O^{2-}) oxygen in Na_2O-SiO_2 glasses: An X-ray Photoelectron Spectroscopic (XPS) and Nuclear Magnetic Resonance (NMR) study

H.W. Nesbitt [a,*], G.M. Bancroft [b], G.S. Henderson [c], R. Ho [a], K.N. Dalby [a], Y. Huang [b], Z. Yan [b]



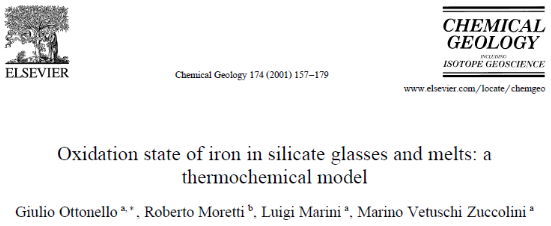
As has been proposed for $CaSiO_3$ glass and for sodic and potassic glasses containing La, we suggest that O^{2-} is present in sodic glasses at small concentrations. The O^{2-} content correlates with increased soda content and may be associated with, and instrumental in development of, three dimensional percolation channels in the glasses

Polymeric nature of anion matrix: Toop-Samis model

In polymeric models for silicate melts, it is postulated that, at each composition, for given P-T values, the melt is characterized by an equilibrium distribution of several ionic species of oxygen, metal cations and ionic polymers of monomeric units SiO_4^{4-}.

$$2O_m^{-} \Leftrightarrow O_m^{0} + O_m^{2-}$$

$$SiO_4^{4-} + SiO_4^{4-} \Leftrightarrow Si_2O_7^{6-} + O^{2-}$$



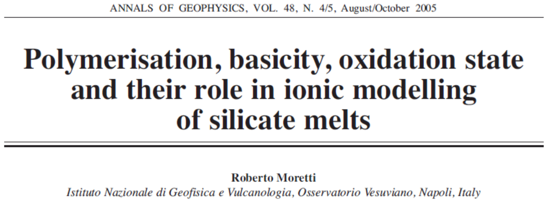
ELSEVIER

Chemical Geology 174 (2001) 157–179

CHEMICAL GEOLOGY
INCLUDING ISOTOPE GEOSCIENCE
www.elsevier.com/locate/chemgeo

Oxidation state of iron in silicate glasses and melts: a thermochemical model

Giulio Ottonello [a,*], Roberto Moretti [b], Luigi Marini [a], Marino Vetuschi Zuccolini [a]



ANNALS OF GEOPHYSICS, VOL. 48, N. 4/5, August/October 2005

Polymerisation, basicity, oxidation state and their role in ionic modelling of silicate melts

Roberto Moretti

Istituto Nazionale di Geofisica e Vulcanologia, Osservatorio Vesuviano, Napoli, Italy

$$K_{58} = \frac{(O^{\circ})(O^{2-})}{(O^{-})^2}$$

$$\Delta G_{mixing} = [(O^{-})/2]RT\ln K_{polym}$$

Theory: the polymeric model

On the basis of simple mass balances we can link the three oxygen species to the melt composition and therefore to the melt compositions

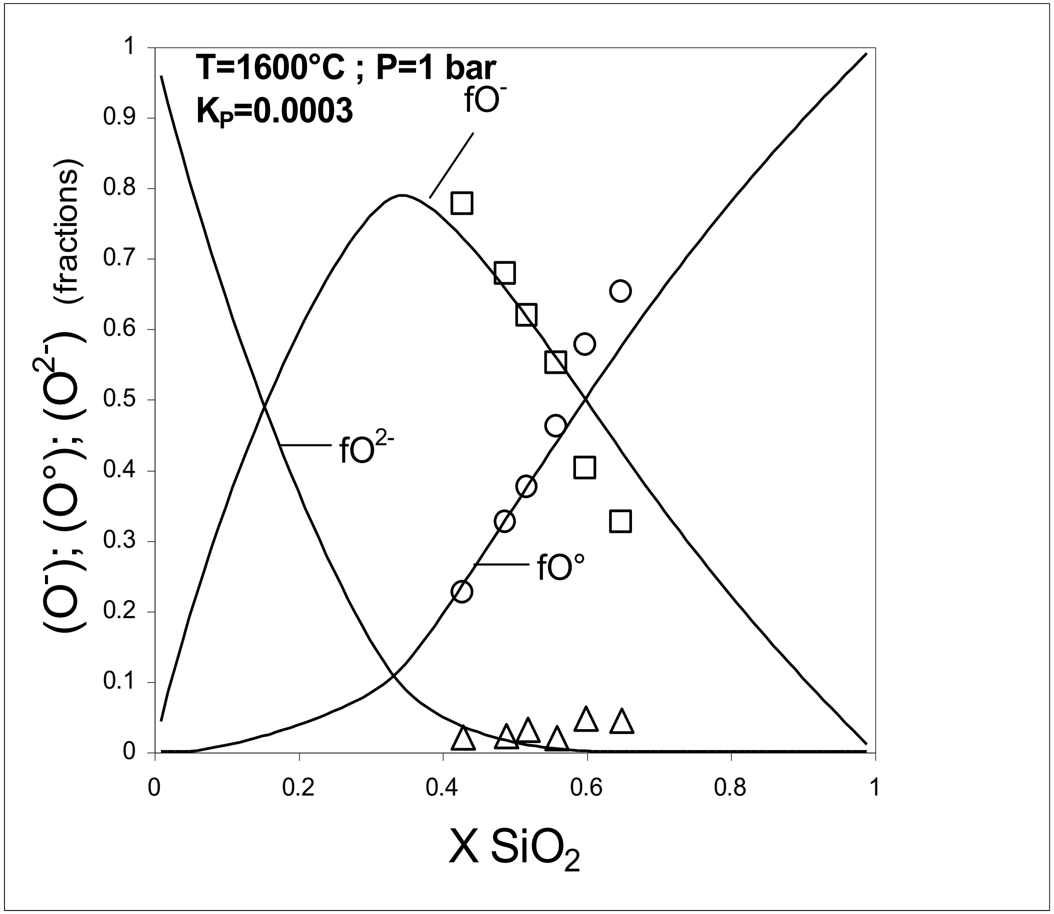
$$\left(O^{0}\right)=\frac{4N_{SiO_2}-\left(O^{-}\right)}{2}$$

$$\left(O^{2-}\right)=\left(1-N_{SiO_2}\right)-\frac{\left(O^{-}\right)}{2}$$

$$\left(O^{-}\right)^{2}\left(4K_2-1\right)+\left(O^{-}\right)\left(2+2N_{SiO_2}\right)+8N_{SiO_2}\left(N_{SiO_2}-1\right)=0$$

$Kp=(O^{\circ})(O^{2-})/(O^{-})^{2}$

CaO-SiO_2



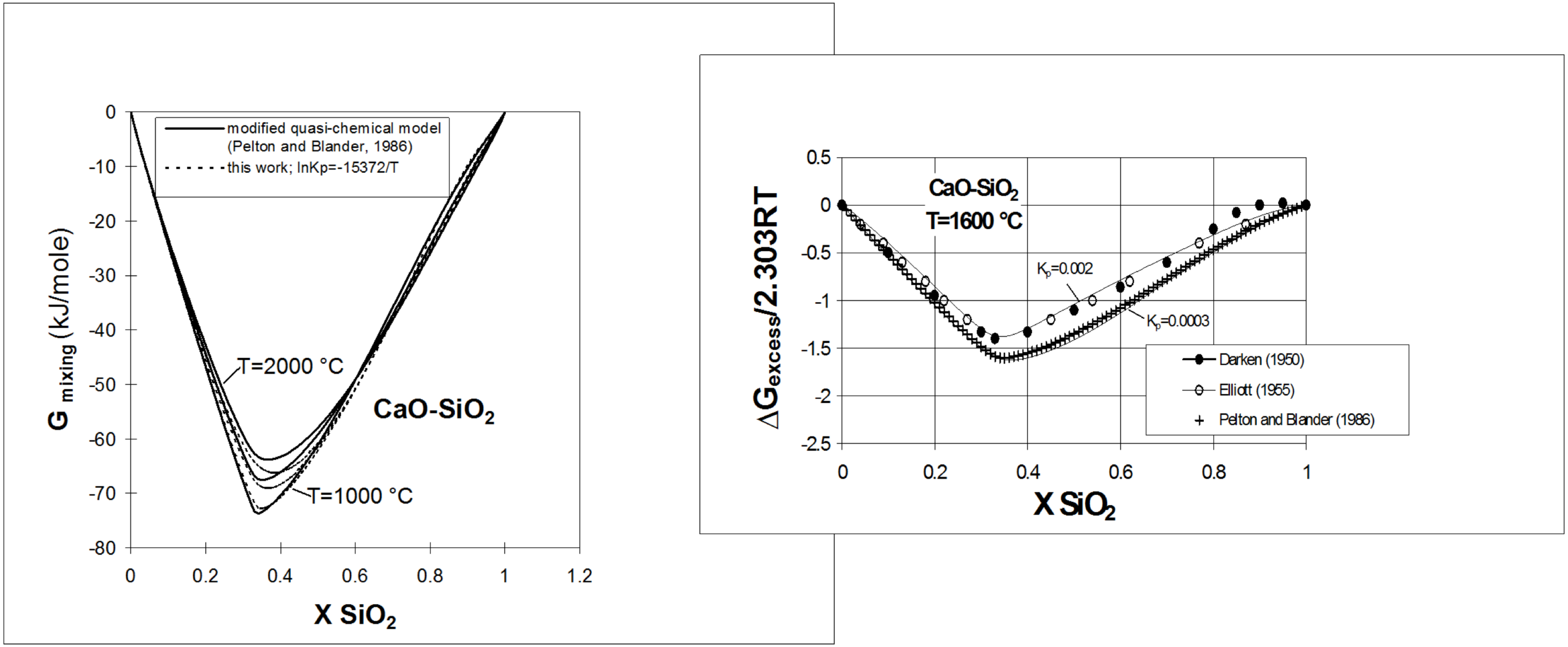
Ottonello (2001)

Ottonello and Moretti (2004)

Join	lnKp = A/T+B		R^2	T range	Notes
	A	B	C	(°C)	
K_2O - SiO_2	-31708	0	-	1127-1527	(1)
	-29540	0	-	1223	(2)
	-36967	0	0.9922	1500-1800	(3)
Na_2O- SiO_2	-23336	0	0.9995	1000-1800	(3)
CaO - SiO_2	-15372	0	0.9958	1000-2000	(4)
	-14807	0	0.9943	1000-2000	(2)
MgO - SiO_2	-9809.5	0	0.9955	1400-2000	(3)
ZnO - SiO_2	-6460.1	0	-	1400-2000	(3)
MnO - SiO_2	-6183.8	0	0.9596	1000-2000	(3)
	-5649.1	0	-	1600	(1)
PbO - SiO_2	-5330.0	0	0.5825	1000-1800	(3)
	-4098.1	0	-	1273	(5)
FeO - SiO_2	-3600.0	0	0.9973	1000-2000	(4)
Fe_2O_3 - SiO_2	7569.5	- 7.2752	0.9350	1000-2000	(5)
TiO_2 - SiO_2	4667.3	-3.2092	0.9107	1500-1900	(3)
ZrO_2 - SiO_2	2685.9	- 6.382	0.9658	1400-2000	(3)
NiO - SiO_2	1507.7	- 1.7772	0.9825	1500-2000	(3)
Al_2O_3 - $SiO_2$0		- 1.4059	-	1000 – 2000	(3)
B_2O_3 - SiO_2 0		- 1.0660	-	1000 – 2000	(3)

(1) Ottonello (2003); (2) Ottonello and Moretti (2003), based on experiments of Eliezer et al. (1978); (3) Ottonello and Moretti (2003), based on the Modified Quasi Chemical parameterization of Pelton et al. (1995); (4) Ottonello (2001); (5) Ottonello et al. (2001)

Ottonello and Moretti (2004)



Ottonello et al., 2001

Toop-Samis model embodies ideal and excess Gibbs free energy contributions to the Gibbs free energy of the liquid MO-SiO_2 mixture in a single term

$$\Delta G_{\text{mixing}} = -\frac{\left(O^-\right)}{2} RT \ln K$$

➔ the amount of Gibbs free energy necessary to open a liquid solvus at high SiO_2 content can be seen as an elastic energy contribution which, for a chain of $\overline{v}_{Si}$ monomers extending to a distance x may be expressed (e.g. Bates and Fredrickson, 1999)

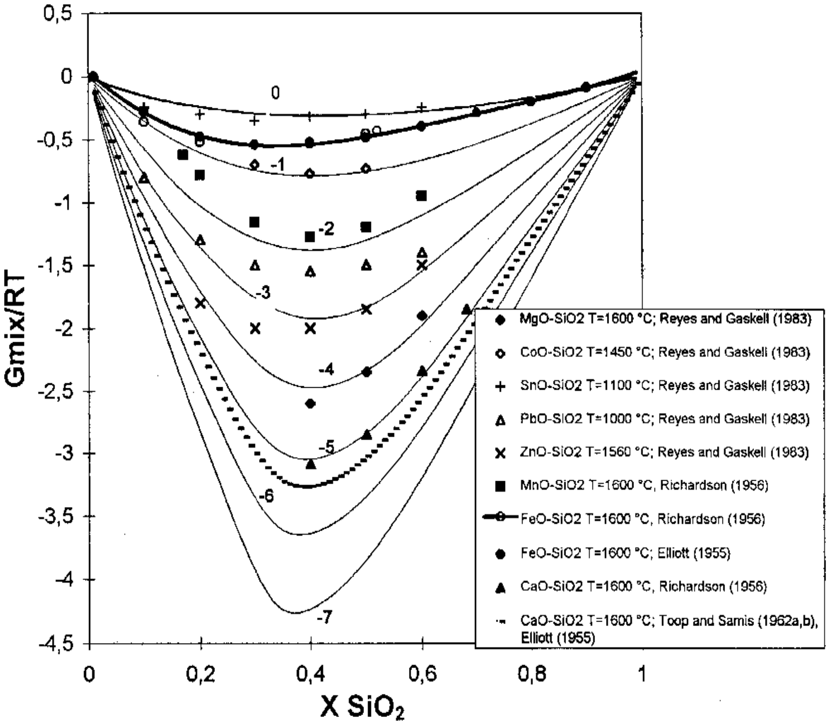
$$G_{\text{strain}} = \frac{3RT}{2\overline{v}_{Si}} \left(\frac{x}{a}\right)^2 .$$

$$\frac{x}{a} = \chi_1 \cdot N_{SiO_2} + \chi_2 \cdot N^2_{SiO_2} + \chi_3 \cdot N^3_{SiO_2} + \chi_4 \cdot N^4_{SiO_2} + \ldots$$

Extended as: $\ln K_P = N'_{A^{\nu+}} + \ln K_{P,A-F} + N'_{B^{o+}} + \ln K_{P,B-F} + \ldots.$

$$N'_{A^{\nu+}} = \frac{\nu^+_A n_A}{\nu^+_A n_A + \nu^+_B n_B + \ldots}$$

A « crude » approximation…



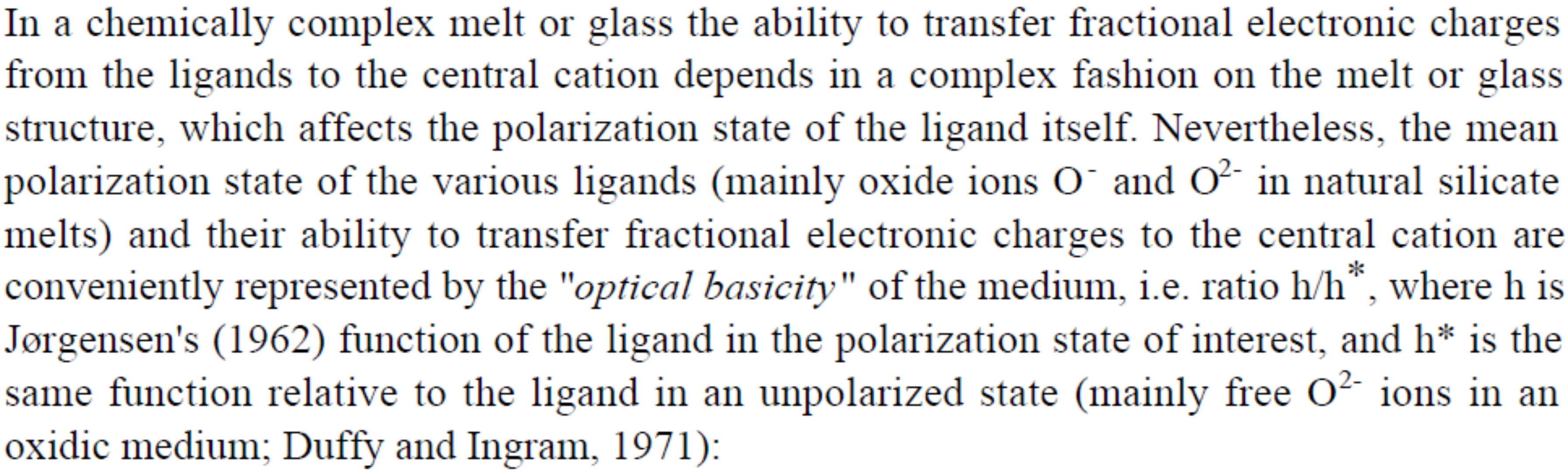
Modifiers - Formers

$$\Delta G^{\text{mixing}} = \frac{(O^-)}{2} RT \ln K_{\text{polym.}}$$

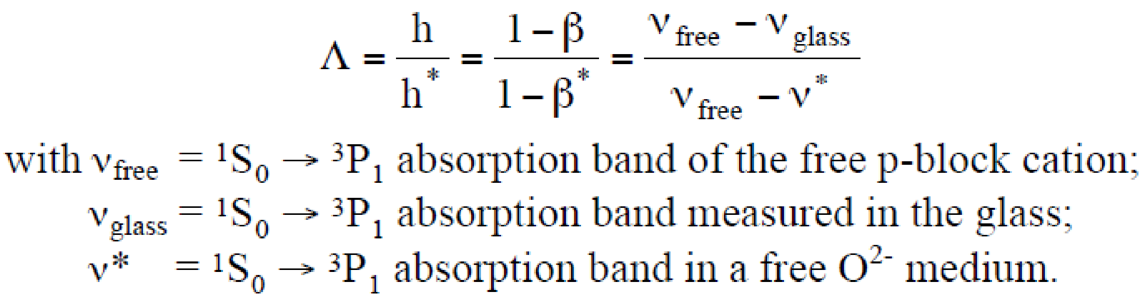
$$K_{\text{polym}} = \exp\left[4.662\times\left(\sum_i X_{M_i^{\nu+}}\gamma_{M_i^{\nu+}} - \sum_j X_{T_j^{\eta+}}\gamma_{T_j^{\eta+}}\right) - 1.1445\right]$$

Ottonello et al., Chem. Geol. (2001)

Even simple interaction parameters along limiting binaries cannot be reduced to fitting coefficients of mathematical minimization routines, but must be formally linked to the intrinsic atomistic properties of the interacting ions and molecules



In a chemically complex melt or glass the ability to transfer fractional electronic charges from the ligands to the central cation depends in a complex fashion on the melt or glass structure, which affects the polarization state of the ligand itself. Nevertheless, the mean polarization state of the various ligands (mainly oxide ions O^- and O^{2-} in natural silicate melts) and their ability to transfer fractional electronic charges to the central cation are conveniently represented by the "*optical basicity*" of the medium, i.e. ratio h/h^*, where h is Jørgensen's (1962) function of the ligand in the polarization state of interest, and h^* is the same function relative to the ligand in an unpolarized state (mainly free O^{2-} ions in an oxidic medium; Duffy and Ingram, 1971):



$$\Lambda = \frac{h}{h^*} = \frac{1-\beta}{1-\beta^*} = \frac{\nu_{free} - \nu_{glass}}{\nu_{free} - \nu^*}$$

with $\nu_{free} = {}^1S_0 \rightarrow {}^3P_1$ absorption band of the free p-block cation;

$\nu_{glass} = {}^1S_0 \rightarrow {}^3P_1$ absorption band measured in the glass;

$\nu^* = {}^1S_0 \rightarrow {}^3P_1$ absorption band in a free O^{2-} medium.

The reciprocal of optical basicity Λ of a cation (i.e. "*basicity moderating parameter*" γ of Duffy and Ingram, 1973) represents the tendency of an oxide forming metal M to reduce the localized donor properties of oxide ions, and is related to the optical basicity of the medium by:

$$\gamma_M = \frac{Z_M \times r_M}{|Z_O| \times \Lambda_{MO}}$$

where Z_M = formal oxidation number of cation in MO

Z_O = formal oxidation number of oxide ion in MO

r_M = stoichiometric ratio between number of cations and number of total oxide ions in the medium.

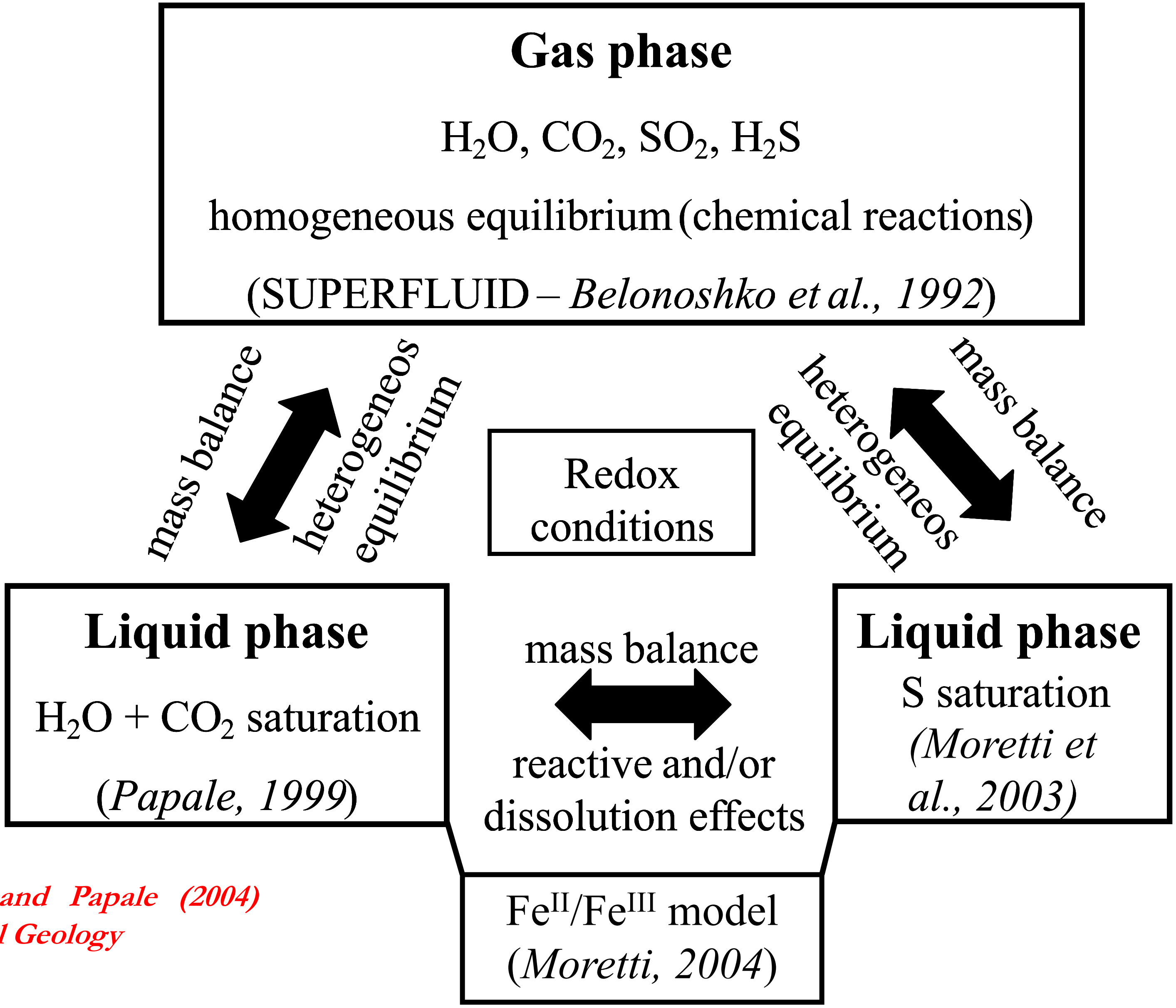
Table I. Optical basicity Λ and basicity moderating parameter of the central cation γ according to various sources. Pauling's and Sanderson's electronegativities (Pauling, 1932, 1960; Sanderson, 1967) are also listed. Λ, γ, χ_S: adimensional; χ_P: eV (from Ottonello *et al.*, 2001).

Oxide	Λ						γ		χ_P	χ_S
	(1)	(2)	(3)	(4)	(5)	(6)	(6)	(7)		
H_2O			0.40			0.39	2.56	2.50	2.15	3.55
Li_2O						1.00	1.00		1.0	0.74
B_2O_3			0.42			0.42	2.38		2.0	2.84
Na_2O		1.15	1.15	1.15	1.15	1.15	0.87	0.87	0.9	0.70
MgO	0.78	0.78	0.78	0.78	0.78	0.78	1.28	1.28	1.2	1.99
Al_2O_3	0.60	0.60	0.60	0.61	0.59	0.59	1.69	1.67	1.5	2.25
SiO_2	0.48	0.46	0.48	0.48	0.48	0.48	2.09	2.09	1.8	2.62
TiO_2		0.65		0.61	0.61	0.58	1.72	1.54	1.6	1.60
Cr_2O_3	0.70					0.58	1.72		1.6	1.88
MnO	0.94-1.03	0.98		0.90	0.59	0.59	1.69	1.69	1.5	2.07
FeO	0.86-1.08	1.03	1.00	1.03	0.51	0.48	2.09	1.354	1.8	2.10
Fe_2O_3	0.73-0.81	0.77		1.21	0.48	0.48	2.09	2.09	1.8	2.10
CoO						0.51	1.96	1.96	1.7	2.10
NiO						0.48	2.09	2.09	1.8	2.10
Cu_2O						0.43	2.30	2.30	1.9	2.60
ZnO		0.82-0.98				0.58	1.72	1.72	1.6	2.84
SrO	1.10					1.03	0.97		1.0	1.00
SnO						0.48	2.09	2.09	1.8	3.10
BaO	1.15	1.15		1.15	1.15	1.12	0.89		0.9	0.78
PbO						0.48	2.09	2.09	1.8	3.08

(1) Duffy (1992); (2) Young *et al.* (1992); (3) Duffy and Ingram (1974a,b); (4) Sosinsky and Sommerville (1986); (5) Gaskell (1982); (6) Ottonello *et al.* (2001); eq. (4.19) (note that $\Lambda = \gamma^{-1}$); (7) Ottonello *et al.* (2001); obtained by non linear minimization of FeO thermodynamic activity data in multicomponent melts.

depolymerizing role of water has been overrated with respect to its actual acid-based properties in melts.

The H_2O-CO_2-H_2S-SO_2 saturation model



Gas phase

H_2O, CO_2, SO_2, H_2S

homogeneous equilibrium (chemical reactions)

(SUPERFLUID – *Belonoshko et al., 1992*)

mass balance

heterogeneos equilibrium

Redox conditions

heterogeneos equilibrium

mass balance

Liquid phase

$H_2O + CO_2$ saturation

(*Papale, 1999*)

mass balance

reactive and/or dissolution effects

Liquid phase

S saturation

(*Moretti et al., 2003*)

Fe^{II}/Fe^{III} model

(*Moretti, 2004*)

Moretti and Papale (2004)
Chemical Geology

Theory of the revised and extended H_2O-CO_2 saturation model (Papale, Moretti & Barbato, 2006)

- Fully non-ideal
- Fluid phase of any composition in the system H_2O+CO_2
- Liquid phase of any composition from two/three components to natural (12 components)

Equilibrium equations

$$P^G = P^L = P$$

$$T^G = T^L = T$$

$$f^G_{H_2O} = f^L_{H_2O} \Rightarrow \phi_{H_2O} y_{H_2O} P = \gamma_{H_2O} x_{H_2O} f^{oL}_{H_2O}$$

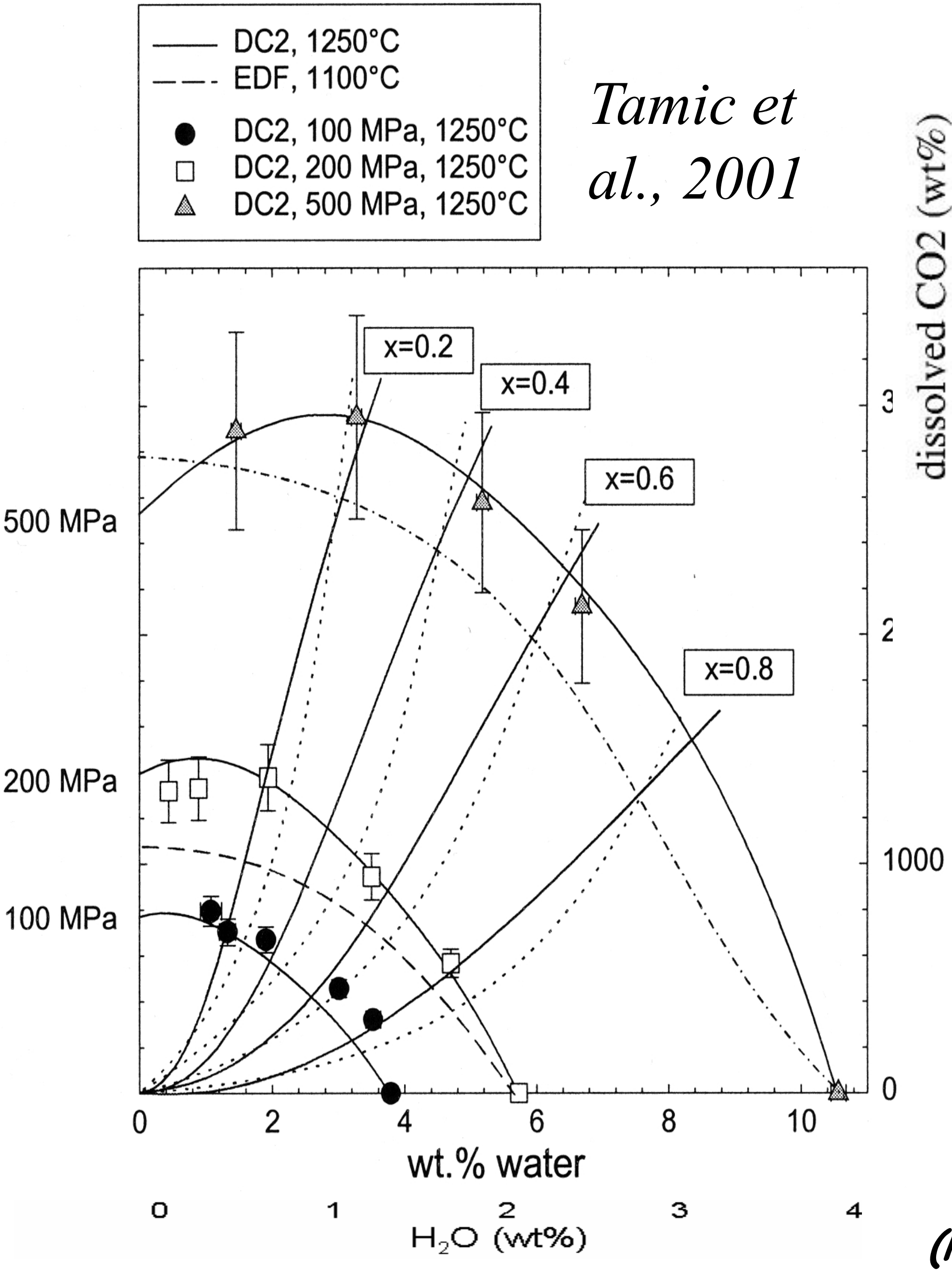
$$f^G_{CO_2} = f^L_{CO_2} \Rightarrow \phi_{CO_2} y_{CO_2} P = \gamma_{CO_2} x_{CO_2} f^{oL}_{CO_2}$$

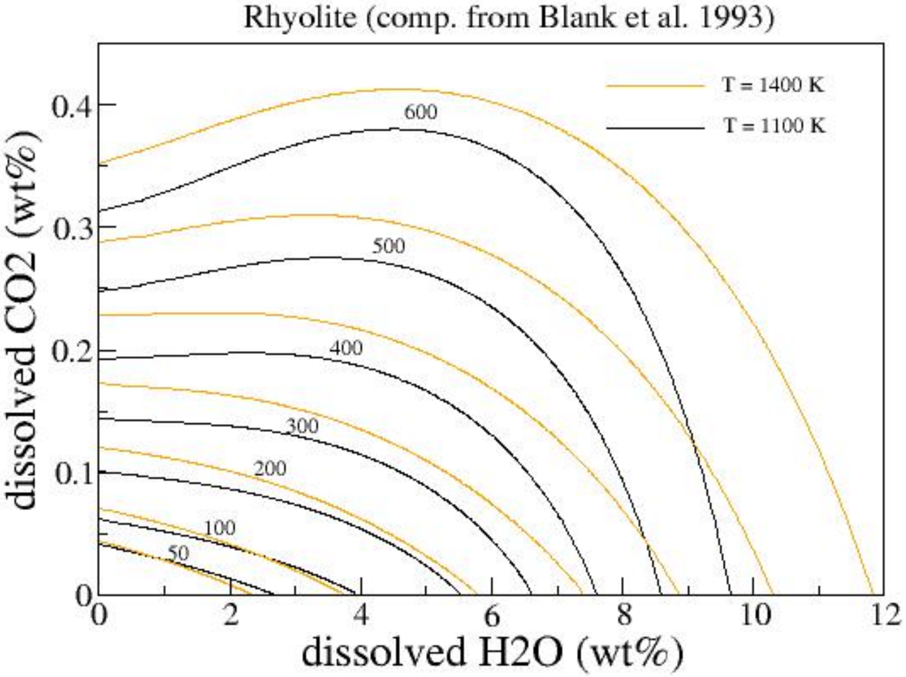
Mass balance equations

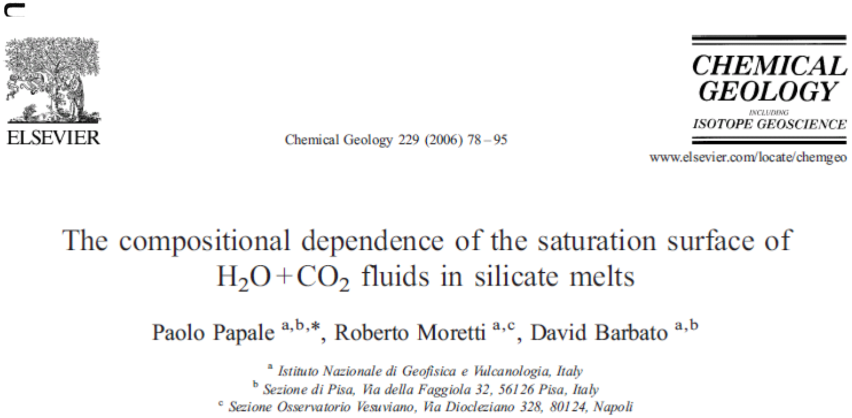
$$y_{H_2O} + y_{CO_2} = 1$$

$$\frac{x^T_{H_2O} - x_{H_2O}}{y_{H_2O} - x_{H_2O}} = \frac{x^T_{CO_2} - x_{CO_2}}{y_{CO_2} - x_{CO_2}}$$

Tamic et al., 2001






ELSEVIER

Chemical Geology 229 (2006) 78 – 95

CHEMICAL GEOLOGY
INCLUDING
ISOTOPE GEOSCIENCE

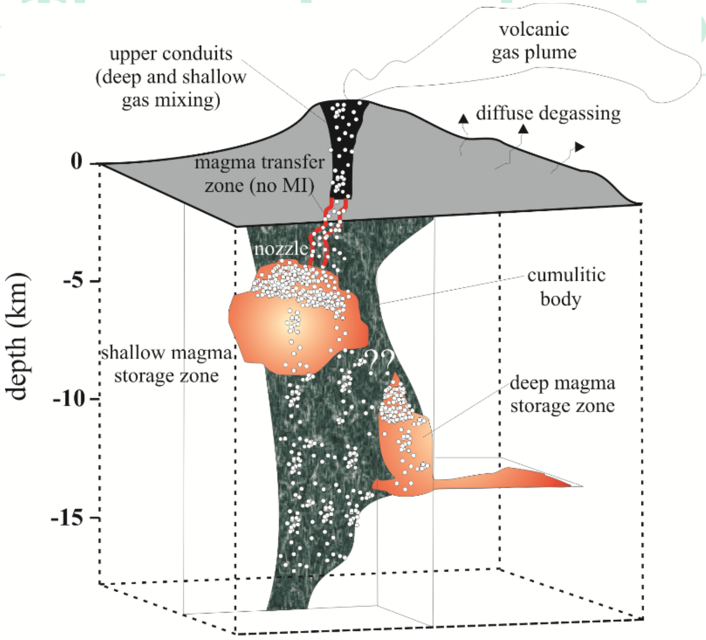
www.elsevier.com/locate/chemgeo

The compositional dependence of the saturation surface of $H_2O + CO_2$ fluids in silicate melts

Paolo Papale [a,b,*], Roberto Moretti [a,c], David Barbato [a,b]

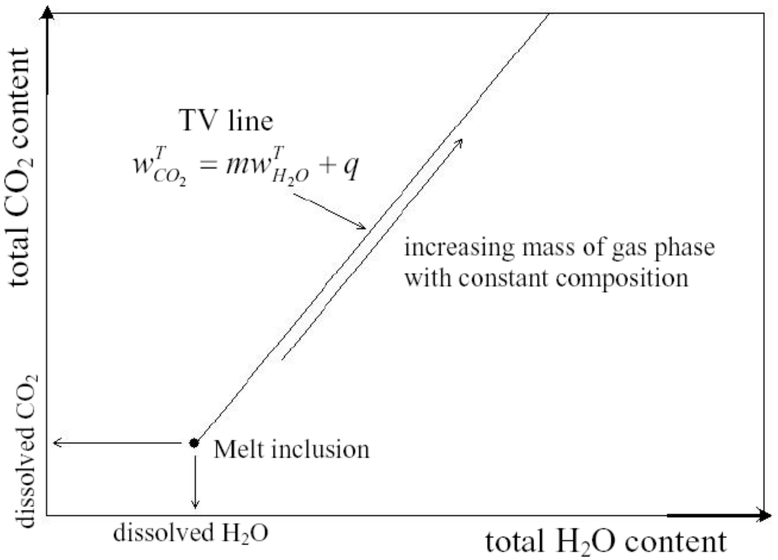
[a] Istituto Nazionale di Geofisica e Vulcanologia, Italy
[b] Sezione di Pisa, Via della Faggiola 32, 56126 Pisa, Italy
[c] Sezione Osservatorio Vesuviano, Via Diocleziano 328, 80124, Napoli

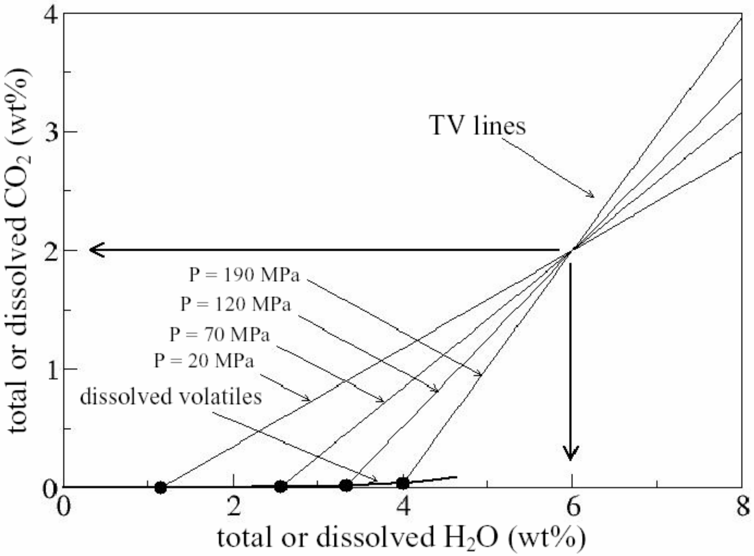
(Papale et al., 2006)



MIs show processes of CO_2 addition and dehydration (fluxing)

➔ Shift in total/initial volatile content → many degassing paths

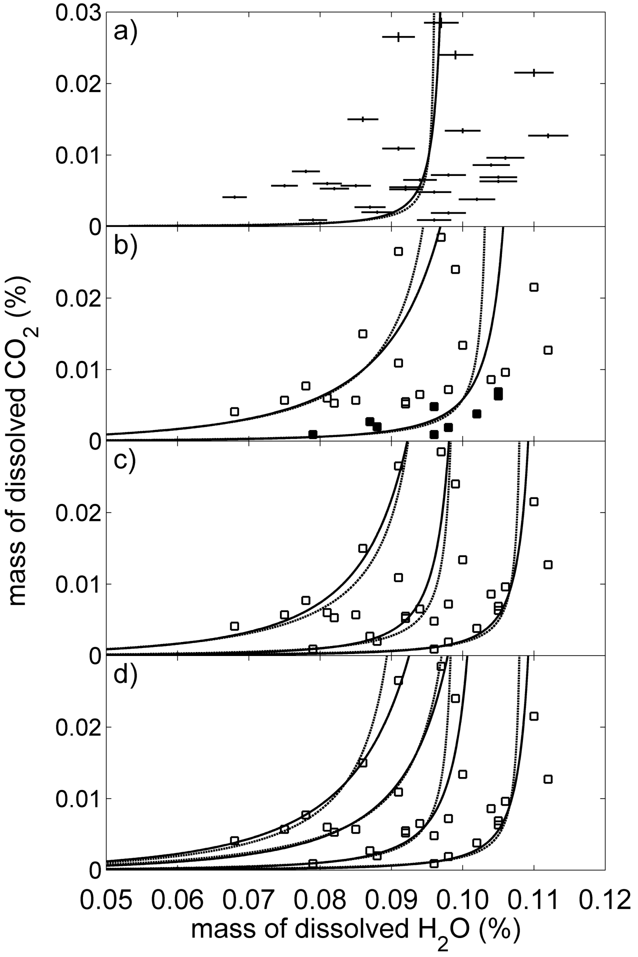




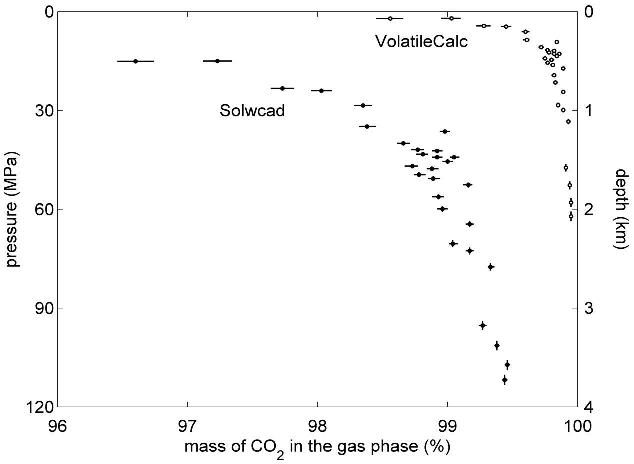
Papale, 2005

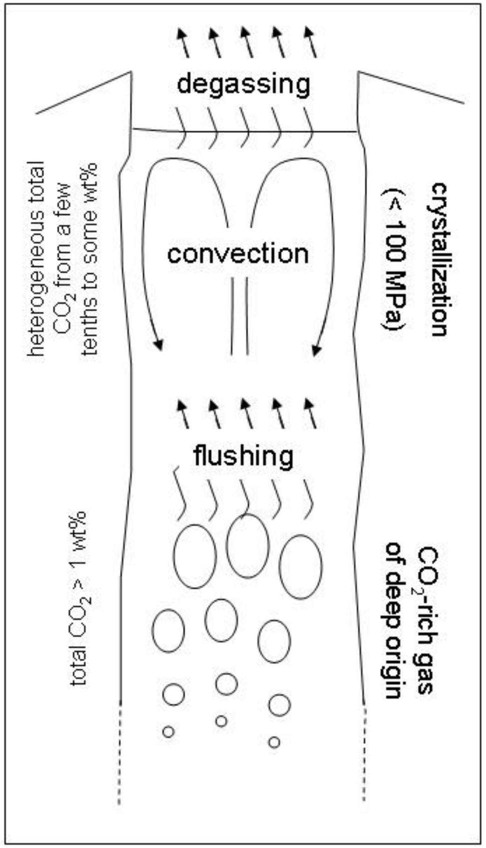
Barsanti et al. (2009, JGR)

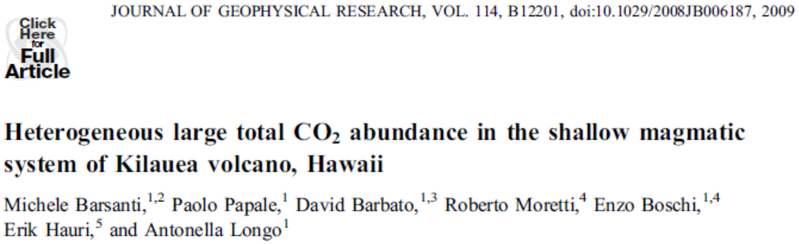
KILAUEA



Sat.Mod.	N. of curves	wTH2O (wt%)	wTCO2 (wt%)
SWCD1	0.100	0.50	
SWCD2	0.110	0.80	
	0.114	3.80	
SWCD3	0.111	0.50	
		0.102	0.80
		0.105	3.10
SWCD4	0.112	0.54	
		0.105	0.96
		0.110	2.82
	0.112	4.38	







JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 114, B12201, doi:10.1029/2008JB006187, 2009

Heterogeneous large total CO_2 abundance in the shallow magmatic system of Kilauea volcano, Hawaii

Michele Barsanti,[1,2] Paolo Papale,[1] David Barbato,[1,3] Roberto Moretti,[4] Enzo Boschi,[1,4] Erik Hauri,[5] and Antonella Longo[1]

…shifting degassing paths…

$$Fe^{2+} + 1/4\ O_2 \Leftrightarrow Fe^{3+} + 1/2\ O^{2-},$$

$$K_{3/2} = (a_{Fe^{3+}}/a_{Fe^{2+}})\ (a_{O^{2-}})^{1/2}/f_{O_2}{}^{1/4},$$

$$\log\ (Fe^{3+}/Fe^{2+}) = \log K_{3/2} + 1/4 \log\ f_{O_2} - 1/2 \log a_{O^{2-}} = A - 1/2 \log a_{O^{2-}}$$

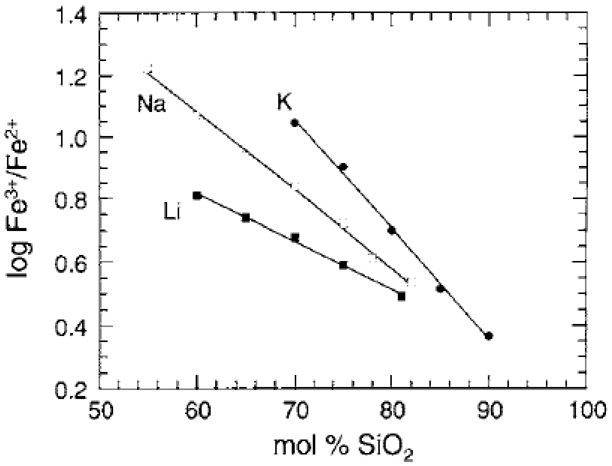
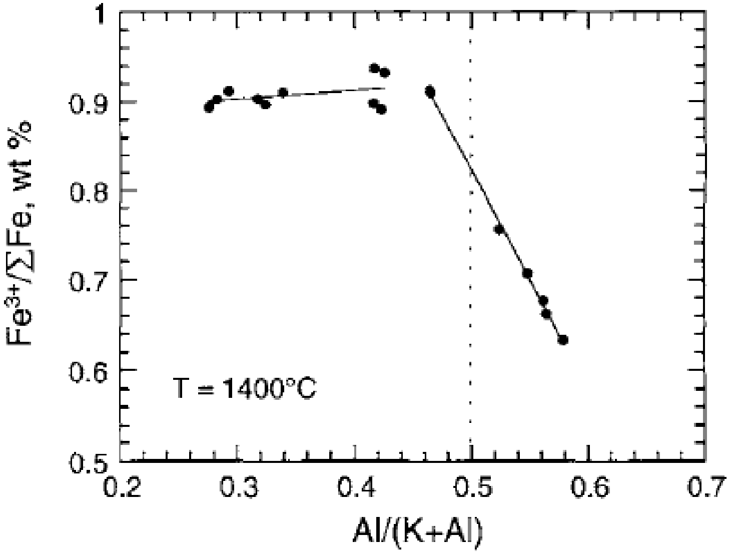


Figure 10.12. Iron redox ratio of alkali silicate melts at 1400°C in air against SiO_2 concentration [Paul and Douglas, 1965]. Total iron content of 0.41 wt %.

variations of $a_{O^{2-}}$ with composition!???!

Figure 10.16 - Iron redox ratio against K/(K+Al) for potassium aluminosilicates at constant 78 mol % SiO_2 [Dickenson and Hess, 1981]. Experiments made in air at 1400°C with a total of 2 wt % FeO.



Empirical efforts….

$$\ln(x_{Fe_2O_3}/x_{FeO}) = a \ln f_{O_2} + b/T + c + \sum d_i x_i$$

$$\ln(x_{Fe_2O_3}/x_{FeO}) = a \ln f_{O_2} + b/T + c + \sum d_i x_i$$
$$+ e\,[1 - T_0/T - \ln T/T_0] + f\,P/T + g\,(T-T_0)P/T + hP^2/T$$

$$\ln(x_{Fe^{3+}}/x_{Fe^{2+}}) = a \ln f_{O_2} + b/T + c + d(\mathrm{Al}/(\mathrm{Al}+\mathrm{Si}) + e(\mathrm{Fe}^{3+}/\mathrm{Fe}^{3+}+\mathrm{Si}) + \sum f_i x_i$$

……..

Back to basics: amphoteric behavior of trivalent iron

$$\mathbf{FeO + 1/4O_2 \Leftrightarrow FeO_{1.5}}$$

In the above reaction the redox potential is expressed by the oxygen fugacity . But how does the electron transfer take place?

$$\begin{array}{l}
\mathrm{Fe}^{3+}_{\mathrm{melt}} + e^{-} \Leftrightarrow \mathrm{Fe}^{2+}_{\mathrm{melt}} \qquad + \\
\frac{1}{2}\mathrm{O}^{2-}_{\mathrm{melt}} \Leftrightarrow \frac{1}{4}\mathrm{O}_{2,\mathrm{melt}} + e^{-} \qquad = \\
\hline
\mathrm{Fe}^{3+}_{\mathrm{melt}} + \frac{1}{2}\mathrm{O}^{2-}_{\mathrm{melt}} \Leftrightarrow \mathrm{Fe}^{2+}_{\mathrm{melt}} + \frac{1}{4}\mathrm{O}_{2,\mathrm{melt}}
\end{array}$$

$$\begin{array}{l}
\mathrm{FeO}^{-}_{2,\mathrm{melt}} + e^{-} \Leftrightarrow \mathrm{Fe}^{2+}_{\mathrm{melt}} + 2\mathrm{O}^{2-}_{\mathrm{melt}} \qquad + \\
\frac{1}{2}\mathrm{O}^{-}_{2,\mathrm{melt}} \Leftrightarrow e^{-} + \frac{1}{4}\mathrm{O}_{2,\mathrm{melt}} \qquad = \\
\hline
\mathrm{FeO}^{-}_{2,\mathrm{melt}} \Leftrightarrow \mathrm{Fe}^{2+}_{\mathrm{melt}} + \frac{3}{2}\mathrm{O}^{2-}_{\mathrm{melt}} + \frac{1}{4}\mathrm{O}_{2,\mathrm{melt}}
\end{array}$$

That's the way electron transfer operates. It is not evident from the equilibrium involving macroscopic components: to get that you must adopt the ionic notation.

Iron redox model

The message:

1. Silicate melts are polymerized liquids
2. Polymeric units are highly reactive

Polymerization and redox state are intimately interrelated. This melt affects properties, including oxidation state, volatile solubility *et cetera.*

$$\left(\frac{Fe^{II}}{Fe^{III}}\right) = \frac{n_{Fe^{II}}}{n_{Fe^{III}}} = \frac{[Fe^{2+}]\sum cations}{[FeO_2^-]\sum anions + [Fe^{3+}]\sum cations}$$

$$\left(\frac{Fe^{II}}{Fe^{III}}\right) = \boxed{\frac{1}{K_1 f_{O_2}^{1/4}}} \times \boxed{\frac{a_{O^{2-}}^{1/2} K_4 \sum cations}{K_2^{1/2} a_{O^{2-}}^2 \sum anions + K_3^{1/2} \sum cations}}$$

Ratio of activities
($a_{FeO}/a_{FeO1.5}$)

Ratio of activity coefficients
($\gamma_{FeO1.5}/\gamma_{FeO}$)

S solubility: the Conjugated-Toop-Samis (CTSFG) model

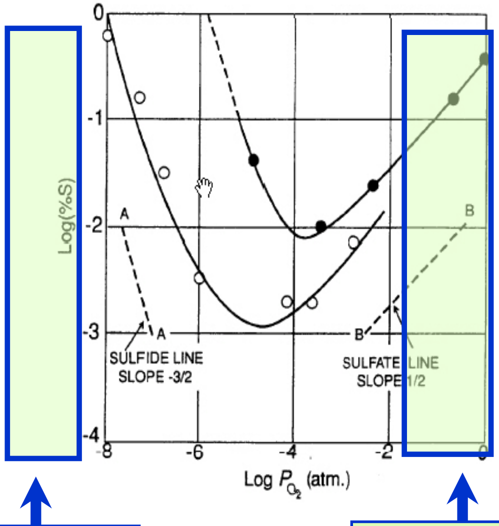
Geochimica et Cosmochimica Acta, Vol. 69, No. 4, pp. 801–823, 2005
Copyright © 2005 Elsevier Ltd
Printed in the USA. All rights reserved
0016-7037/05 $30.00 + .00

ELSEVIER

doi:10.1016/j.gca.2004.09.006

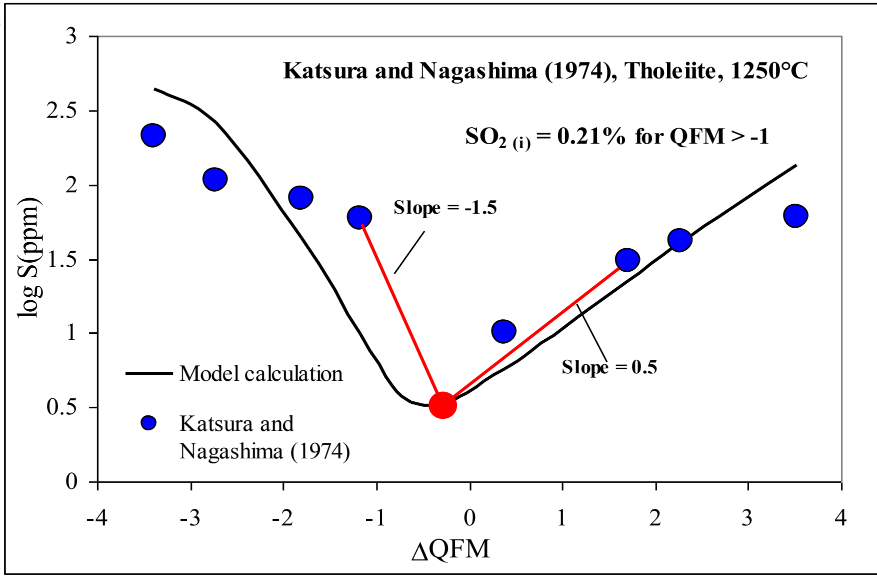
Solubility and speciation of sulfur in silicate melts: The Conjugated Toop-Samis-Flood-Grjotheim (CTSFG) model

ROBERTO MORETTI[1],* and GIULIO OTTONELLO[2]



S as sulphide

S as sulphate



Moretti and Ottonello (2005 GCA)

Sulfide equilibrium:

$$O^{2-}(L) + \frac{1}{2}S_2(G) \Leftrightarrow \frac{1}{2}O_2(G) + S^{2-}(L)$$

Sulfate equilibrium:

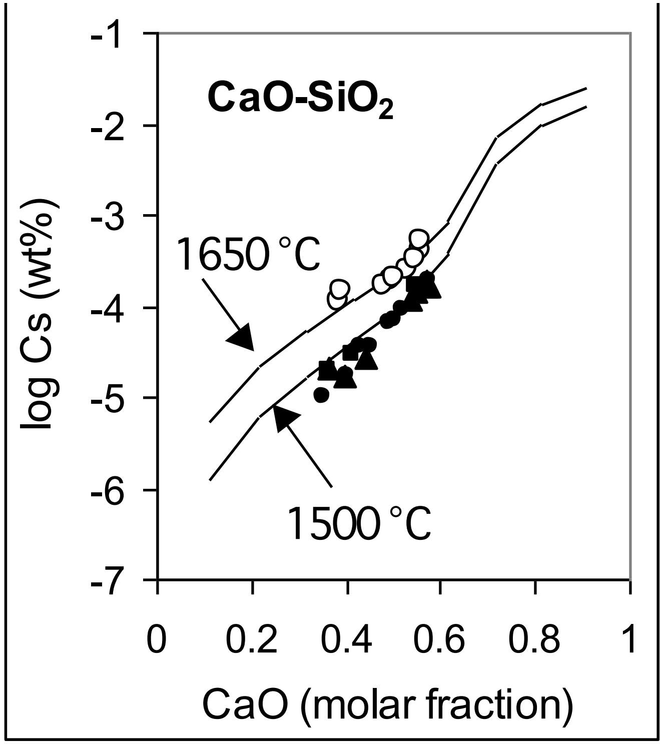
$$O^{2-}(L) + \frac{1}{2}S_2(G) + \frac{3}{2}O_2(G) \Leftrightarrow SO_4^{2-}(L)$$

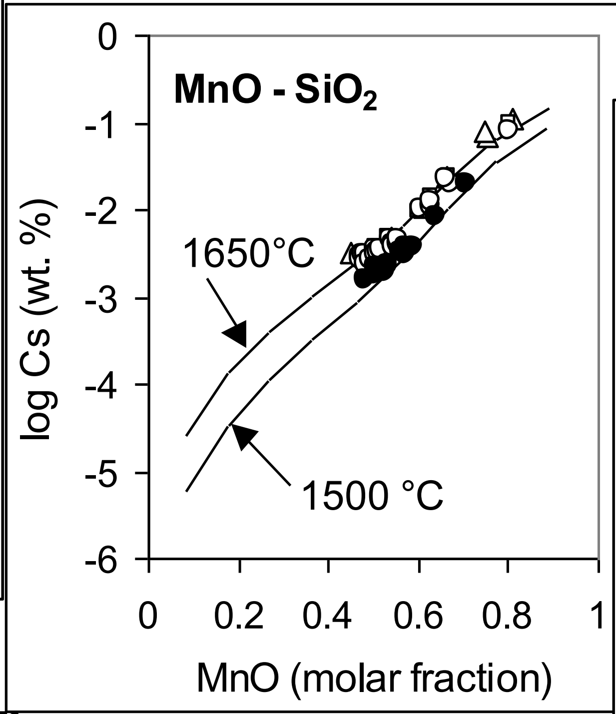
$$\begin{tikzcd}
C_S = [S]\dfrac{f_{O_2}^{1/2}}{f_{S_2}^{1/2}} \arrow[r] \arrow[d] & SO_2^{gas} + O^{2-,silicate\ melt} \leftrightarrow \dfrac{3}{2}O_2^{gas} + S^{2-,silicate\ melt} \arrow[d] \\
C_{S,c} = K'_{O\text{-}S,M}\left(O^{2-}\right)\left(\dfrac{f^{\circ}_{O_2}}{f^{\circ}_{S_2}}\right)^{\frac{1}{2}} M_S \sum_{mol} oxides & \ln K'_{O\text{-}S,M} = A'_{O\text{-}S,M} + \dfrac{B'_{O\text{-}S,M}}{T} \arrow[l]
\end{tikzcd}$$

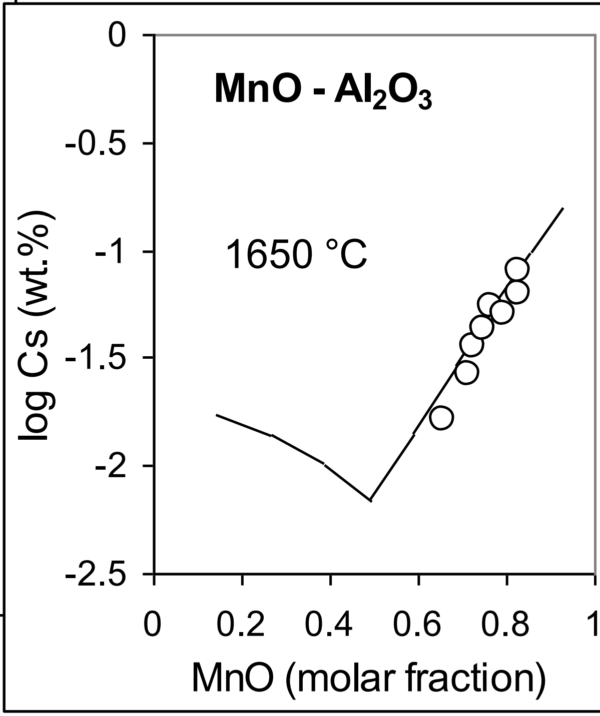
A Polymeric Approach to the Sulfide Capacity of Silicate Slags and Melts

ROBERTO MORETTI and GIULIO OTTONELLO

METALLURGICAL AND MATERIALS TRANSACTIONS B







Moretti and Ottonello, 2003 MMTB

Theory of the S solubility model (CTSFG)

$$C_{S^{2-}} = [S]_{wt\%} \left(\frac{f_{O_2}}{f_{S_2}} \right)^{1/2}$$

$$C_{SO_4^{2-}} = [S]_{wt\%} f_{O_2}^{-3/2} f_{S_2}^{-1/2}$$

The model computes $C^{anneal.}$ (entropies of annealing). $k_{MO\text{-}(S2\text{-},SO42\text{-})}$ constants are from independent thermodynamic compilations when available.

Gas-liquid reactions: **Flood and Grjotheim** (1952) thermochemical cycle:

$$\ln k_{S^{2-},SO_4^{2-}} = \sum_{i=1}^{N_{OX}} N_i^{\nu+} \ln C^{anneal} k_{MO-(S^{2-},SO_4^{2-}),i}$$

$$N_i^{\nu+} = \frac{\nu_i^+ n_i}{\sum_{i=1}^{N_{OX}} \nu_i^+ n_i}$$

where $N_i^{\nu+}$ represent *electrically equivalent fractions*, and n_i are mole fractions computed over the appropriate matrix, either **cationic** or **anionic** (**Temkin model** of fused salts)

Fincham and Richardson (1954):

$$2O^{-} \Leftrightarrow O^{0} + O^{2-}$$

And Toop-Samis approach

S solubility at P: considering volumes for systems in which they have never been determined !

$$\ln K'^{\,P-T}_{O-S,M} = \boxed{A'_{O-S,M} + B'_{O-S,M}}/T - \frac{1}{RT}\int_1^P \left(\Delta V_m + \Delta V_g\right)dP$$

1-bar lnK

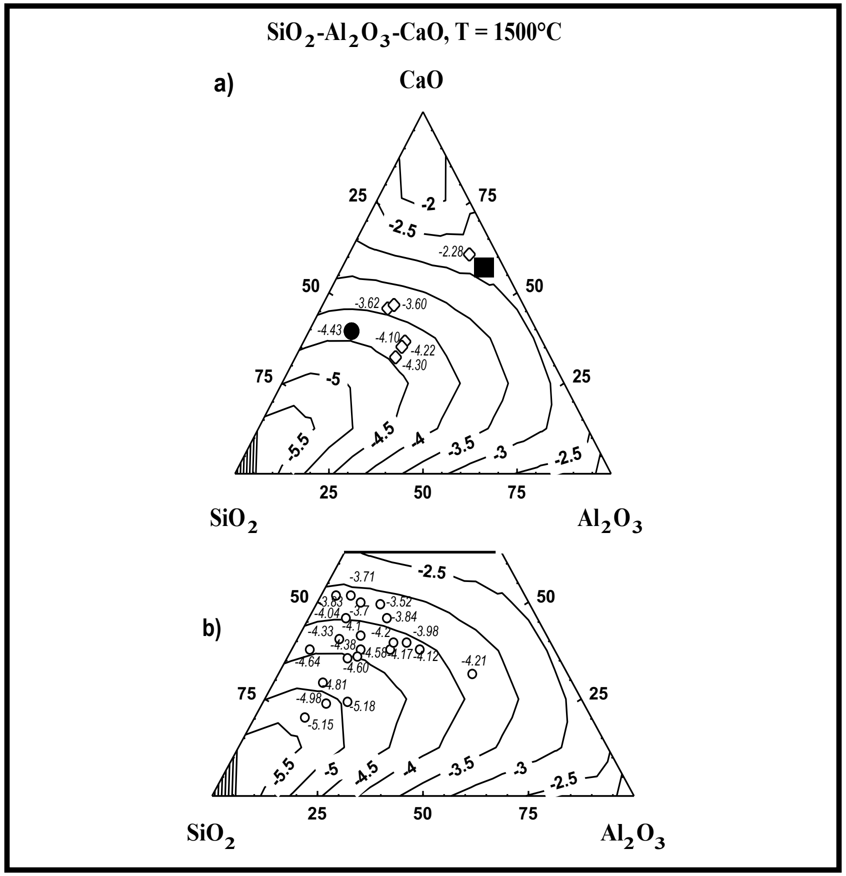
$$V_{M_{2/\upsilon^+}SO_4} = V_{M_{2/\upsilon^+}O} + V_{SO_3}$$

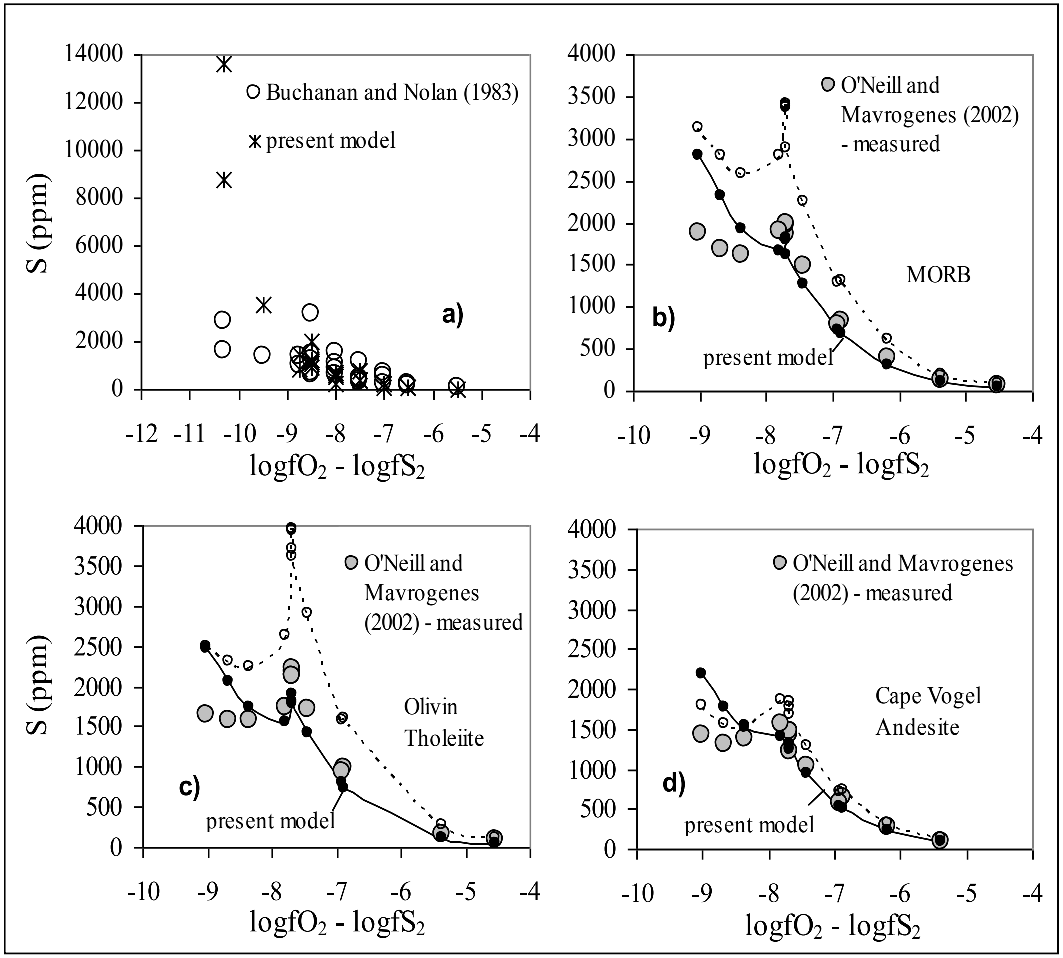
Our value for the (partial) molar volume of V_{SO_3} is ***57.71 cm³/mol*** *at 1673K… must be checked experimentally (no data at present)*

$$\Delta V_{SO_4\text{-}S_2} = V_{M_{2/\upsilon^+}SO_4} - V_{M_{2/\upsilon^+}S} = 41 \ \ (\mathrm{cm}^3/\mathrm{mol})$$

Simple metallurgical slags (log Cs contouring)

Natural-like melts (sulfur content)

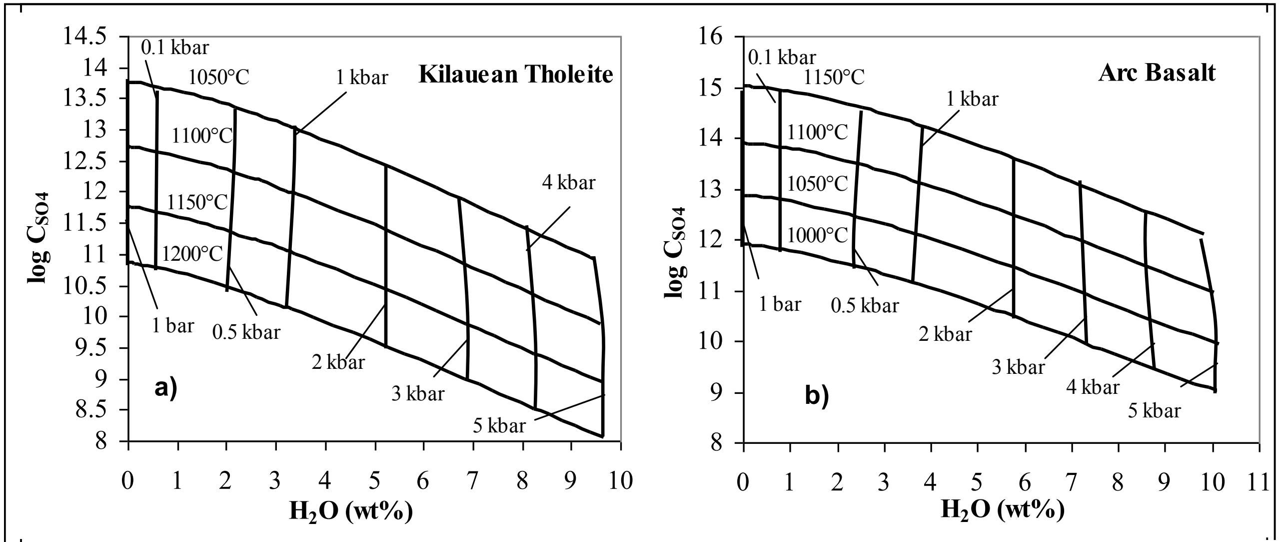


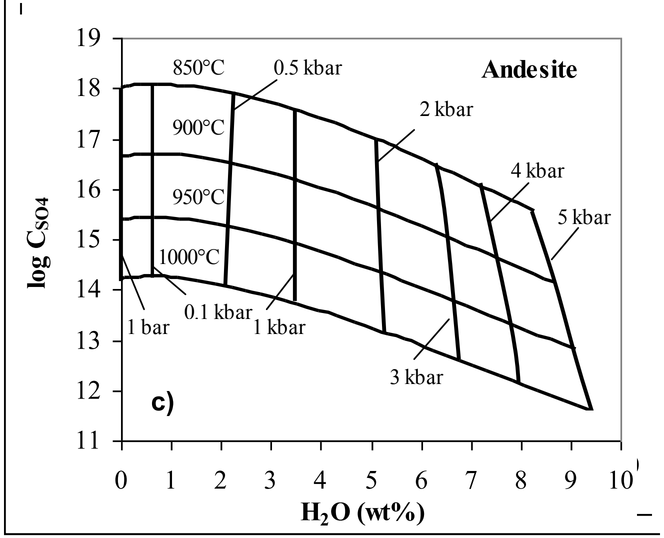


Moretti and Ottonello (2003), Metall. Mat. Trans. B

Moretti and Ottonello (2005)

The CTSFG solubility model: features of the sulfide and sulfate capacity surfaces





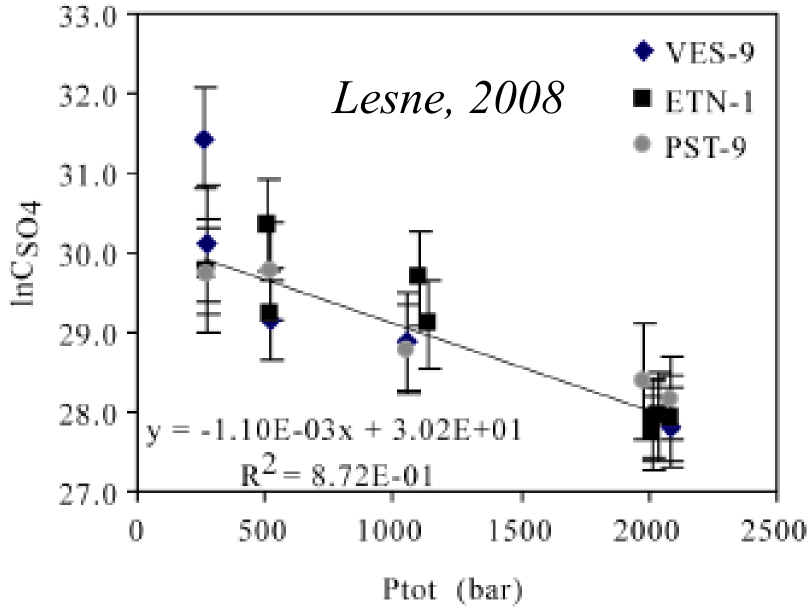


Figure III.10: ln C_{SO4} calculated as explained in the text, versus total pressure.

$$[S]_{wt\%,tot} = [S]_{wt\%,sulfide} + [S]_{wt\%,sulfate} = C_{S^{6+}} fO_2^{3/2} fS_2^{1/2}$$

Reviews in Mineralogy & Geochemistry
Vol. 73 pp. 167-213, 2011

Modeling the Solubility of Sulfur in Magmas: A 50-Year Old Geochemical Challenge

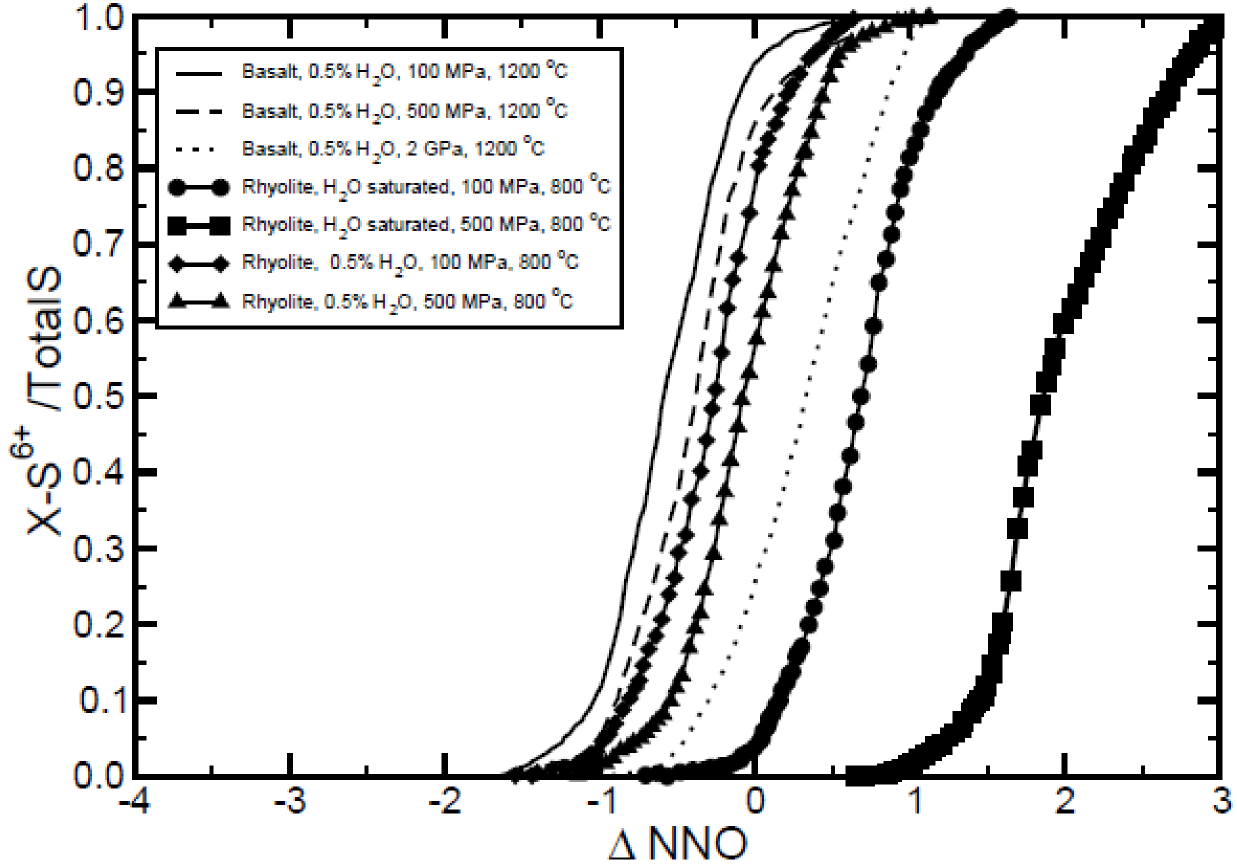
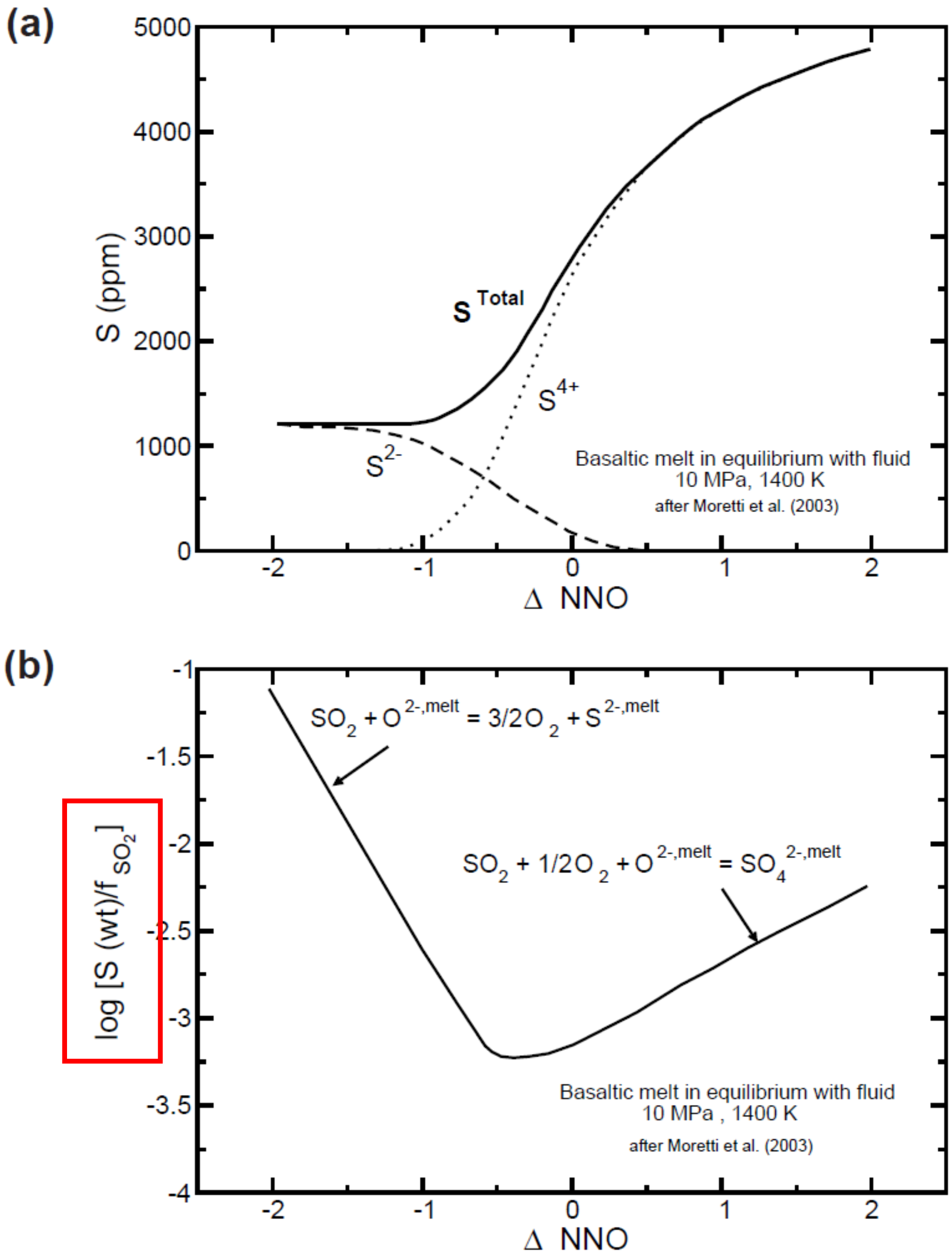


Figure 13. Comparison of the calculated molar ratio of S^{6+}/Total S (X-S^{6+}/Total S) in melts as a function of ΔNNO for basaltic and rhyolitic melts at different temperatures, pressures and water concentrations in the melt. Drawn after Moretti and Baker (2008). Note how unlike in Figure 8, the curves are functions of the intensive thermodynamic variables describing the melt, e.g., pressure, temperature and composition. Please see the text for further discussion.

Baker and Moretti (2011)



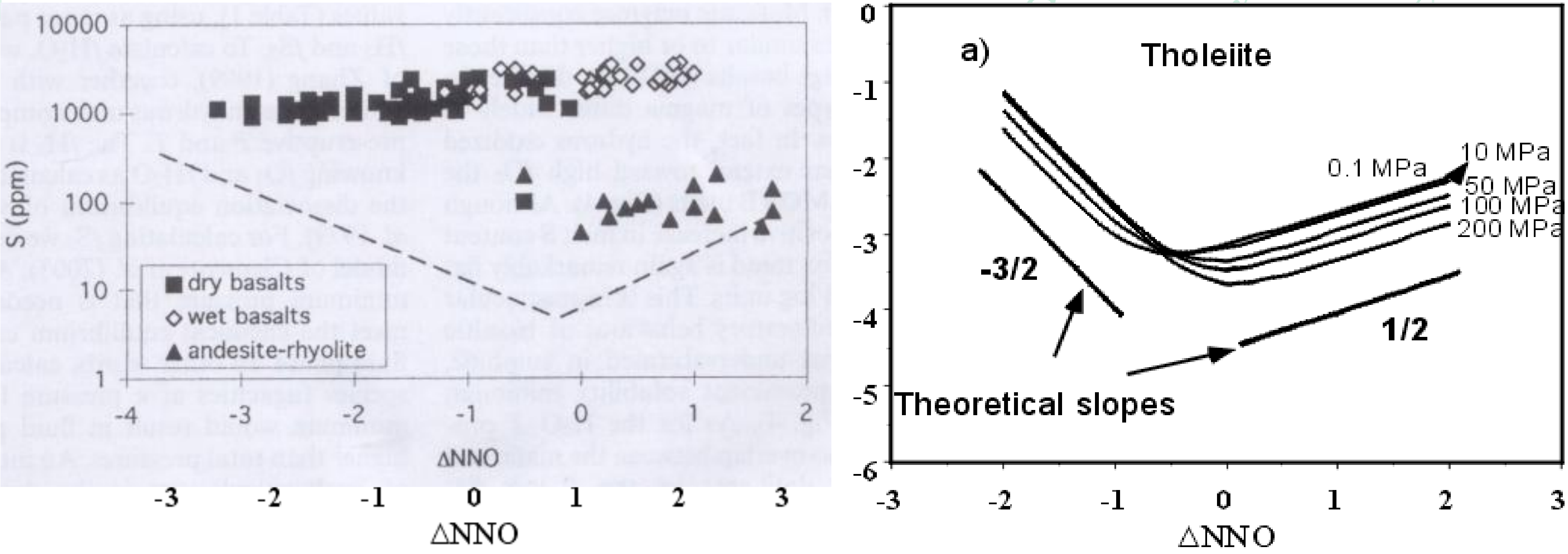
<= Non linear behavior

<= Linear (stoichiometric) behavior

Moretti et al. (2003)

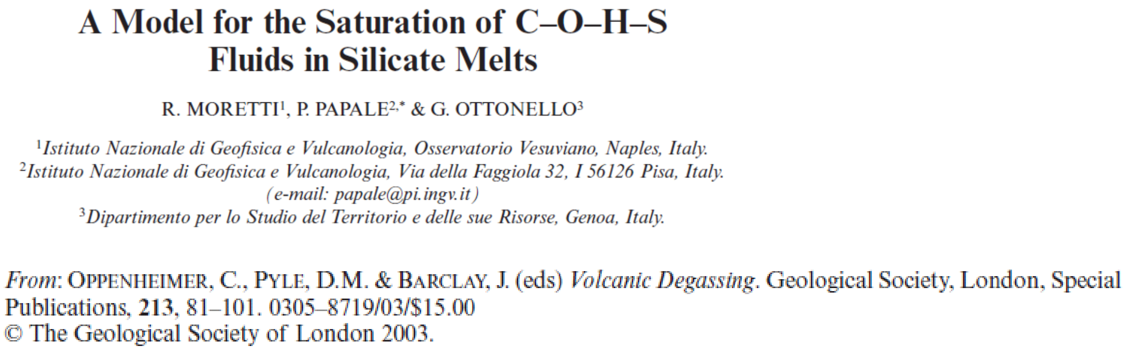
Baker & Moretti (2011)

Tholeite, 1400K . H_2O^{tot}=3%wt; CO_2^{tot}=1%wt; S^{tot}=0.5%wt



Moretti et al. (2003) Geol. Soc. Spec. Publ. 213

Mass partitioning in Nature is non-linear. The expected linearity required by theory (stoichiometry in this case) is embodied, not cancelled. Models must account for it.



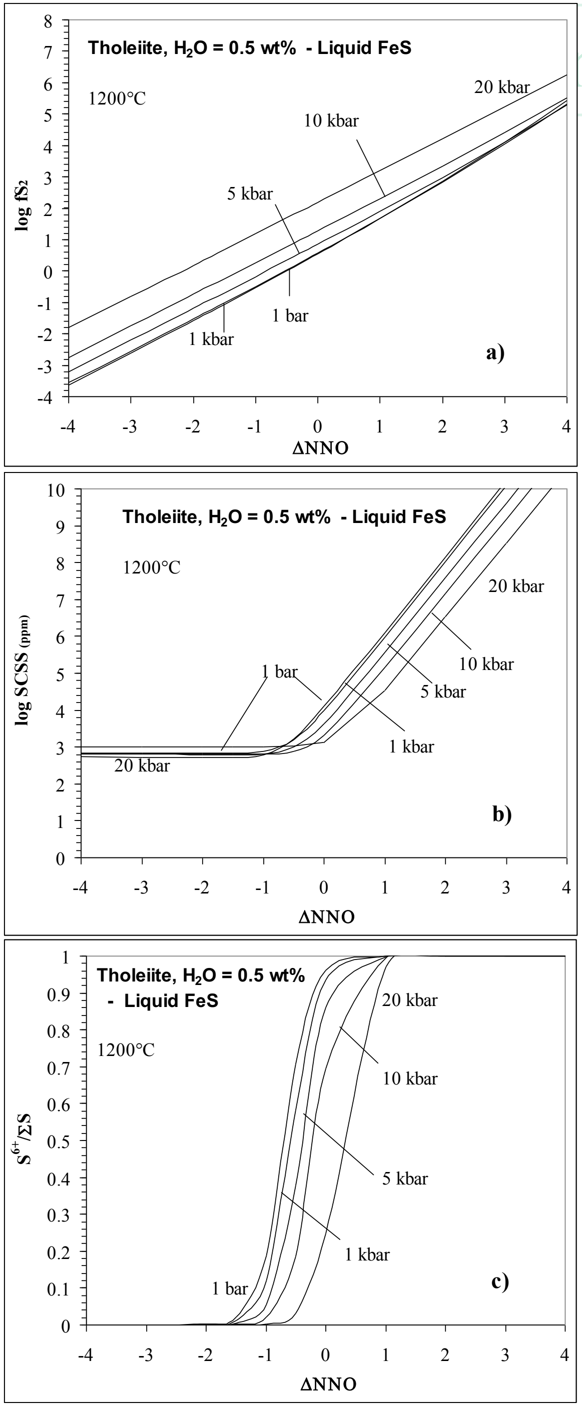
A Model for the Saturation of C–O–H–S Fluids in Silicate Melts

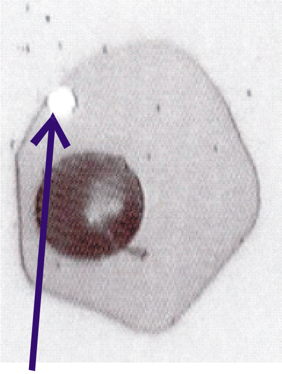
R. MORETTI[1], P. PAPALE[2,*] & G. OTTONELLO[3]

[1]Istituto Nazionale di Geofisica e Vulcanologia, Osservatorio Vesuviano, Naples, Italy.
[2]Istituto Nazionale di Geofisica e Vulcanologia, Via della Faggiola 32, I 56126 Pisa, Italy.
(e-mail: papale@pi.ingv.it)
[3]Dipartimento per lo Studio del Territorio e delle sue Risorse, Genoa, Italy.

From: OPPENHEIMER, C., PYLE, D.M. & BARCLAY, J. (eds) *Volcanic Degassing*. Geological Society, London, Special Publications, **213**, 81–101. 0305–8719/03/$15.00

$FeS_{(po)} + 1/2O_2 \Leftrightarrow FeO + 1/2S_2$



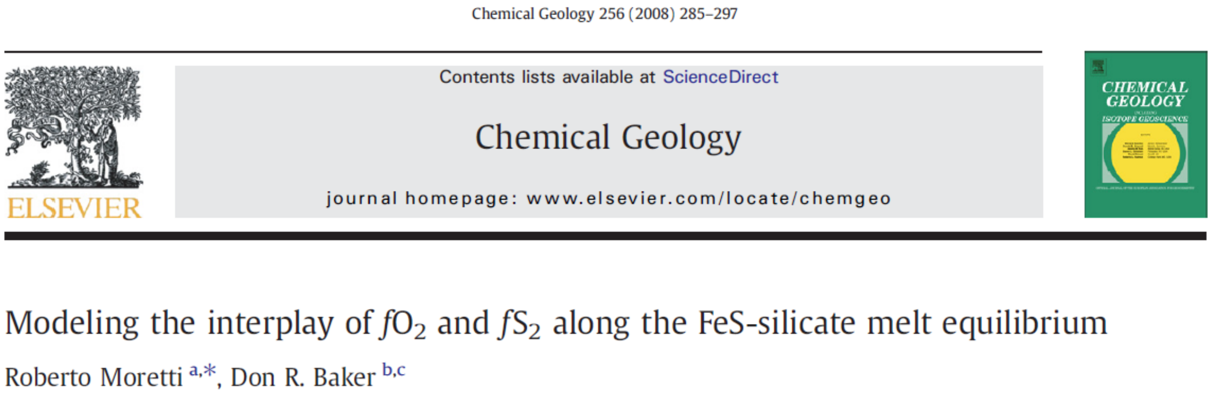


Sulfide globule

$$\overline{H}^0_{i,P_r,T,\mathrm{melt}} = \overline{H}^0_{i,P_r,T_r,\mathrm{crystal}} + \int_{T_r}^{T_f} C_{P,i,\mathrm{crystal}}\,\mathrm{d}T + \Delta\overline{H}_{i,\mathrm{fusion}} + \int_{T_r}^{T} C_{P,i,\mathrm{melt}}\,\mathrm{d}T$$

$$\overline{S}^0_{i,P_r,T,\mathrm{melt}} = \overline{S}^0_{i,P_r,T_r,\mathrm{crystal}} + \int_{T_r}^{T_f} C_{P,i,\mathrm{crystal}}\,\frac{\mathrm{d}T}{T} + \Delta\overline{S}_{i,\mathrm{fusion}} + \int_{T_r}^{T} C_{P,i,\mathrm{melt}}\,\frac{\mathrm{d}T}{T}$$

Moretti and Baker (2008, Chemical Geology)



Chemical Geology 256 (2008) 285–297

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Modeling the interplay of fO_2 and fS_2 along the FeS-silicate melt equilibrium

Roberto Moretti [a,*], Don R. Baker [b,c]

Fe-S mutual interactions

We can also study the mutual redox exchanges between more redox couples (when existing…) such as Fe, Ni, S and so on… But even when studying mutual interactions, O^{2-} and therefore oxygen species via Toop-Samis equilibrium, intervene through the normal oxygen electrode (see Moretti and Ottonello, 2003 JNCS). For example, if you consider Fe and S redox equilibria you should write the following ionic equilibria:

$$8Fe^{3+}_{melt} + S^{2-}_{melt} + 4O^{2-}_{melt} \Leftrightarrow 8Fe^{2+}_{melt} + SO^{2-}_{4,melt}$$

$$SO^{2-}_{4,melt} + 8Fe^{2+}_{melt} + 12O^{2-}_{melt} \Leftrightarrow S^{2-}_{melt} + 8FeO^{-}_{2,melt}$$

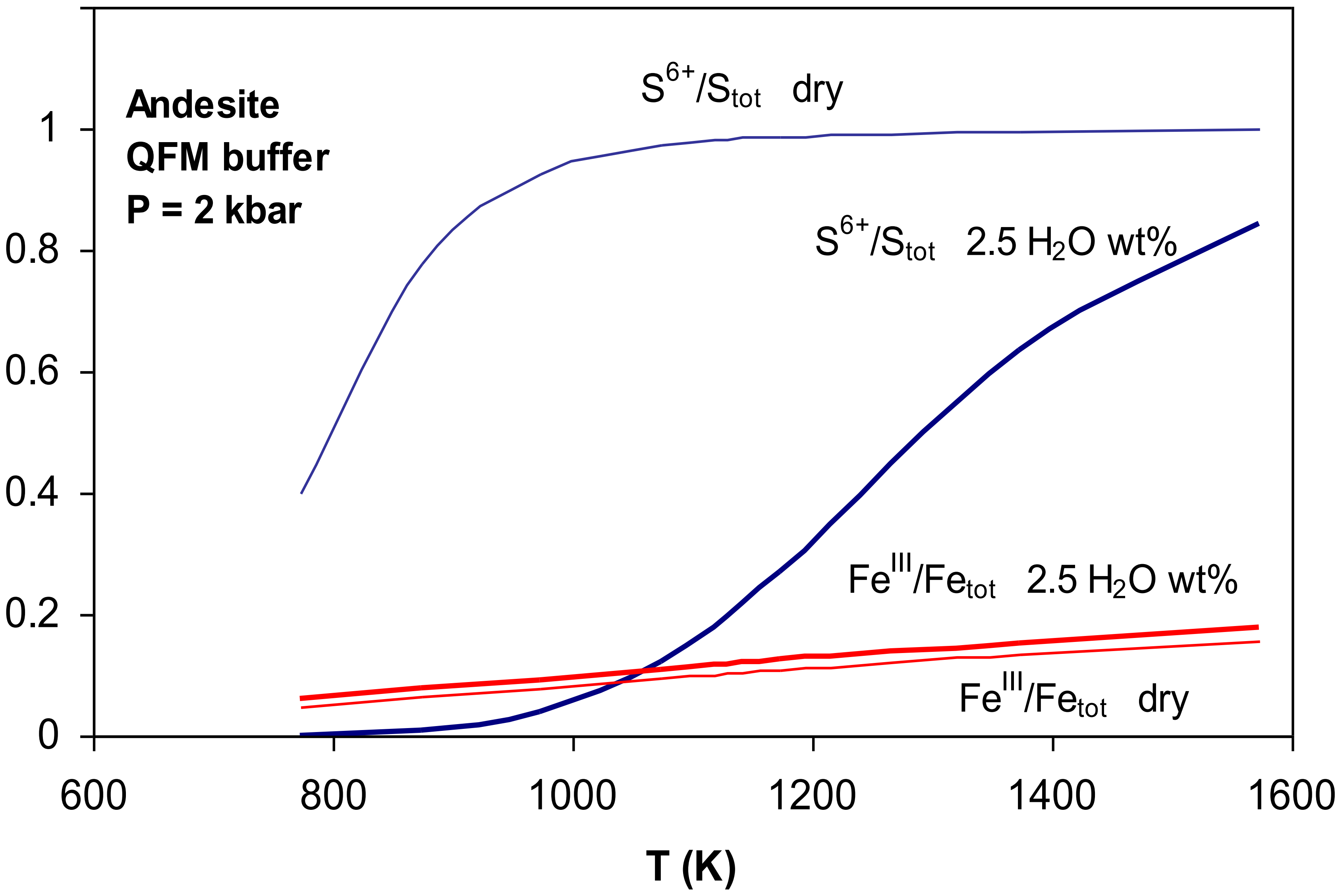
If you write:

$$SO^{2-}_{4,melt} + 8FeO \Leftrightarrow S^{2-}_{melt} + 4Fe_2O_{3,melt}$$

so that O^{2-} cancel out, you make a very huge mistake, since you are mixing different notations, confusing species with components and therefore mixing up standard states!

Remind that the basis of redox reactions in melts is the "normal oxygen electrode"

Fe-S mutual interactions



Remember, it is the following connection:

acid-base properties => polymerization

polymerization => redox state

redox state => solubilities

solubilities => acid-base properties, and so on…

That promotes our full understanding of the role of bulk composition on the partioning of volatiles in magmatic systems

Some observations and caveats…

We usually do not perceive the problem of the chemical syntax as long as we interpret our own data and a **few** more

➔ Thus we tend to adopt the detected structural scenario and turn it into the chemical syntax

→ we do not provide a thermodynamically coherent frame for acid-base e redox properties solving for speciation issues in melts/glasses and describing the ongoing chemistry

→ in general, too many structural attributions to the same REACTIVE species ($Fe^{III}O_2^-$, $Fe^{III}O_4^-$, $Fe^{III}O_5^-$ …) or no attribution at all (undifferentiated Fe^{3+} for all three-valent iron complexes)

→ inconsistent notations in the same reaction mechanisms → different standard states mixed-up