SECONDA UNIVERSITÀ DEGLI STUDI DI NAPOLI

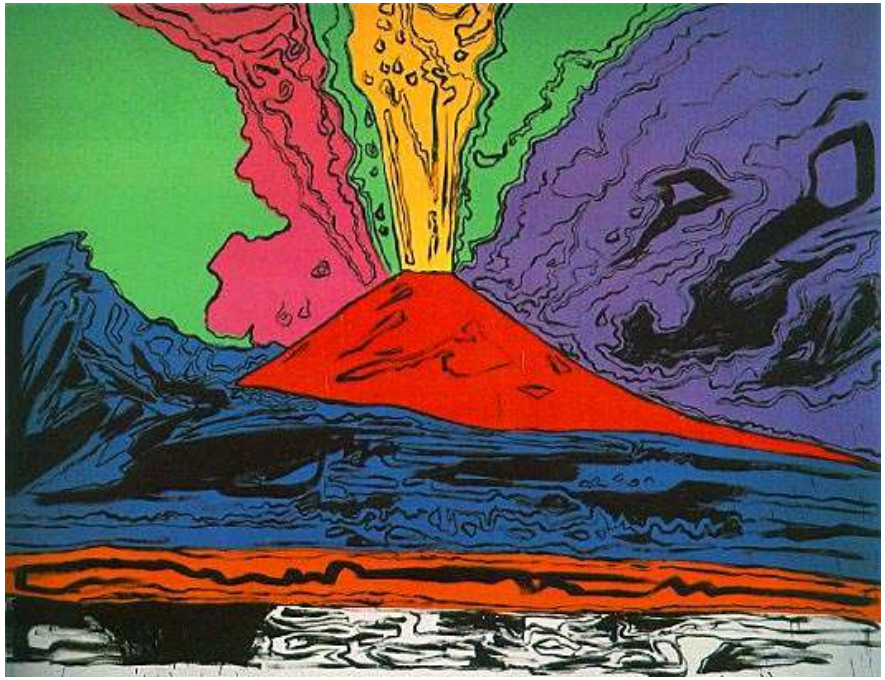
Istituto Nazionale di Geofisica e Vulcanologia

Gas-melt interactions in the C-H-O-S-(Cl)-silicate system

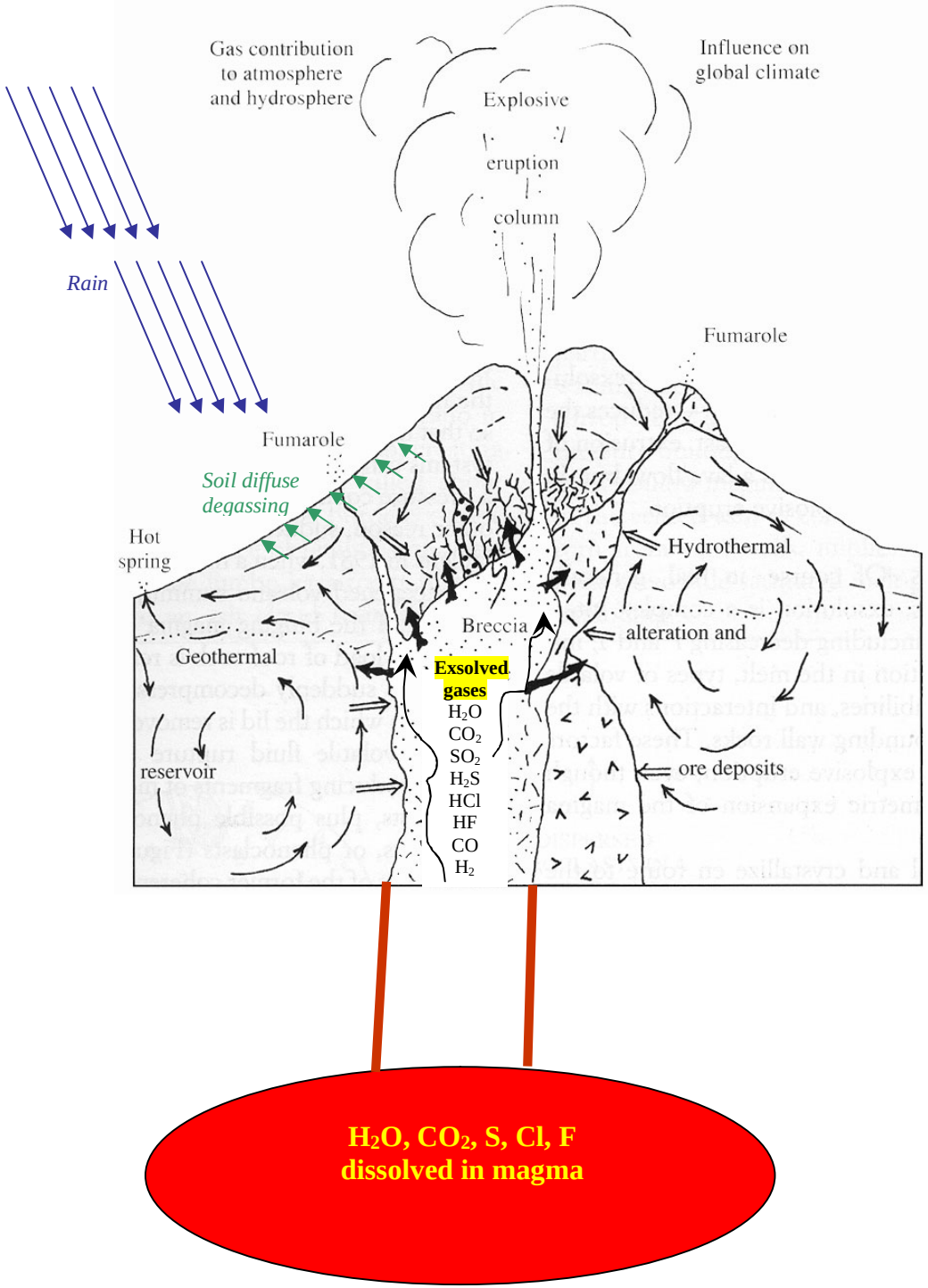
Roberto Moretti

Seconda Università di Napoli
Dip. Ingegneria Civile, Design, Edilizia, Ambiente
Via Roma 29 - 81031 Aversa (I)

INGV - Osservatorio Vesuviano
Via Diocleziano 328 - 80124 Napoli (I)



Andy Warhol, 1985


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

Major goals for volcanology:

- global evolution and degassing of magma bodies
- modeling and simulation of volcanic processes

Major goals for Civil Protection:

- impact of volcanic eruptions, volcanic and diffuse degassing
- pollution by volcanic gases

Major goals for industrial applications:

- glass, ceramics, steel, cement, metallurgy, …

Major goals for ore deposits and exploration geochemistry…

Volatile components in magmas

Analysis of volcanic gases

Direct sampling

Air borne IR-measurements

Satellite linked spectroscopic measurements

Analysis of volcanic glasses

Extraction methods, spectroscopy, electron and ion microprobe

The most abundant volatile components

H_2O CO_2 SO_2 HCl

Pinatubo Philippines (6/91)

89% H_2O
7% CO_2
3% SO_2
1% HCl

Mount St. Augustine: Alaska (7/79)

97% H_2O
2% CO_2
0.2% SO_2
0.4% HCl

Merapi Indonesia (79)

90% H_2O
7% CO_2
2% SO_2
1% HCl

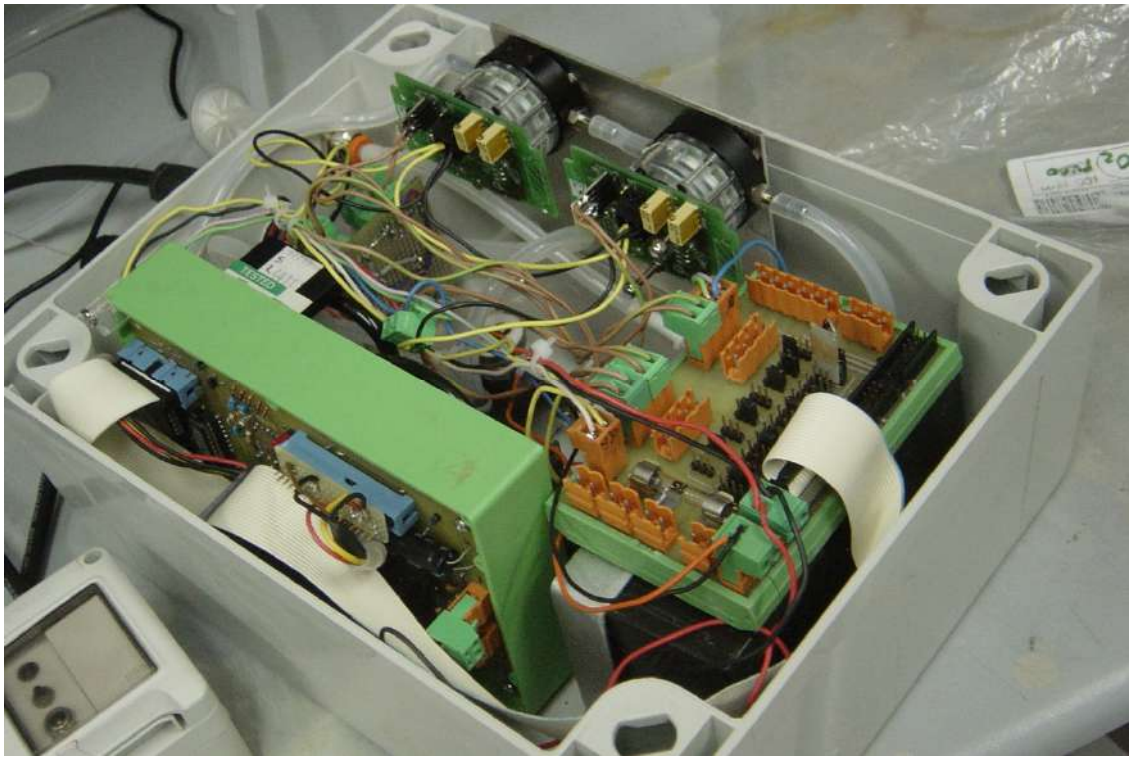
FTIR measurements of the emissions from the 2750 m. a.s.l. cone during the 2002 eruption of Mount Etna (Courtesy of Mike Burton, INGV Catania).

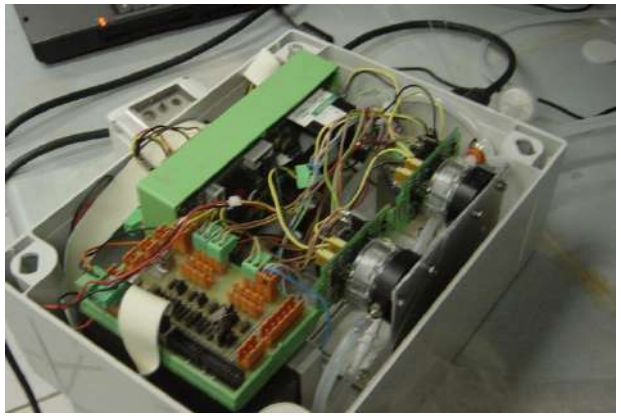
CO_2 / SO_2

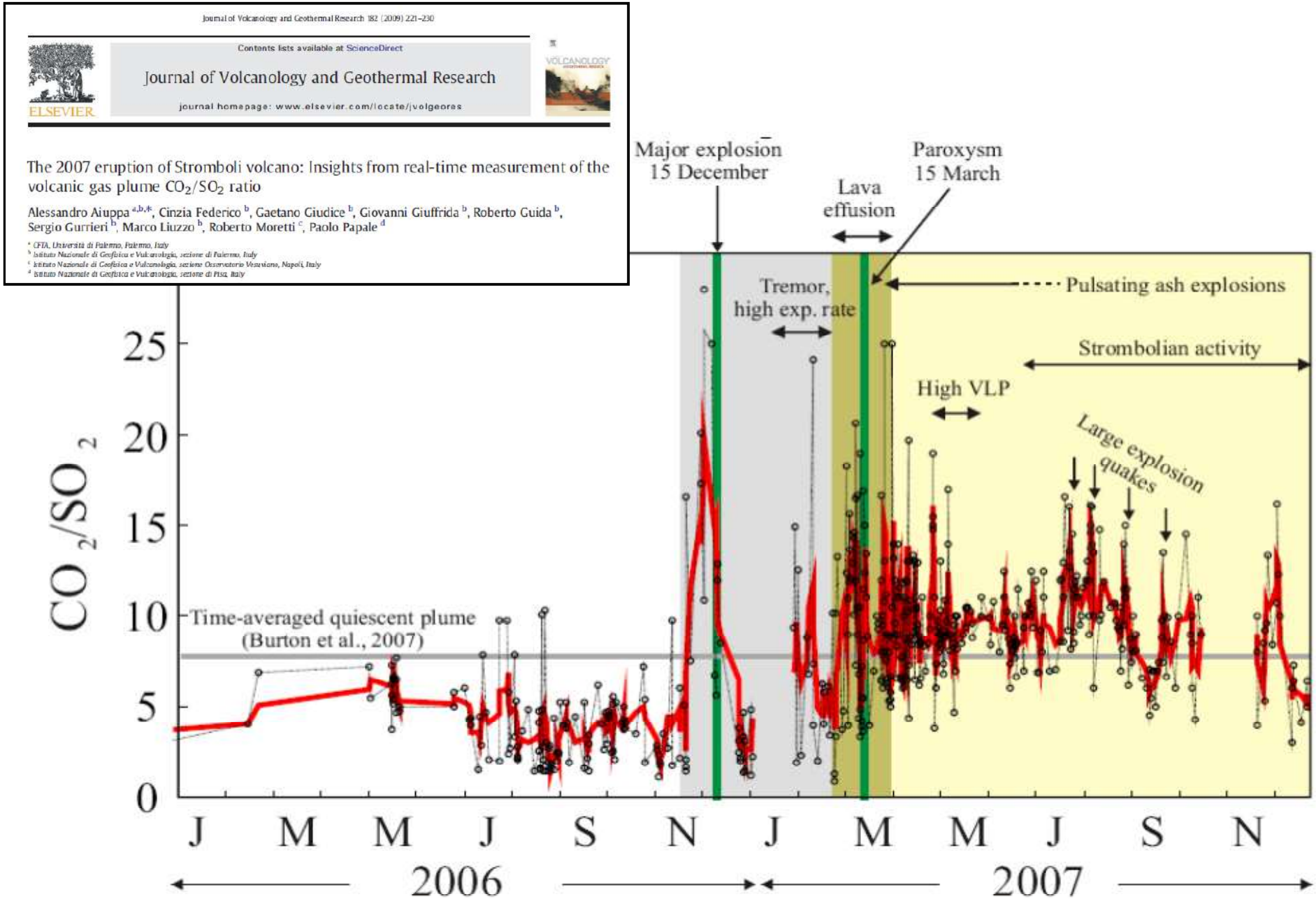
method

CO_2 : IR spectrometry SO_2 (HCl, H_2S): electrochemical sensor

Acquisition frequency: 1s; low power consumption;
High concentration = high accuracy
Future perspective: real time continuous monitoring

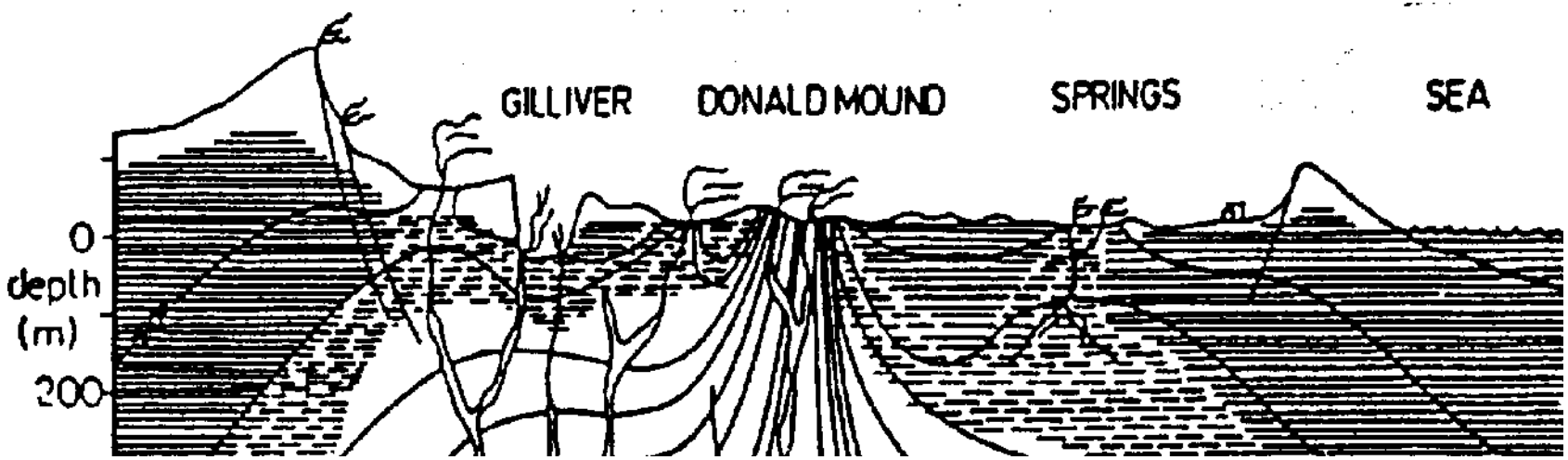




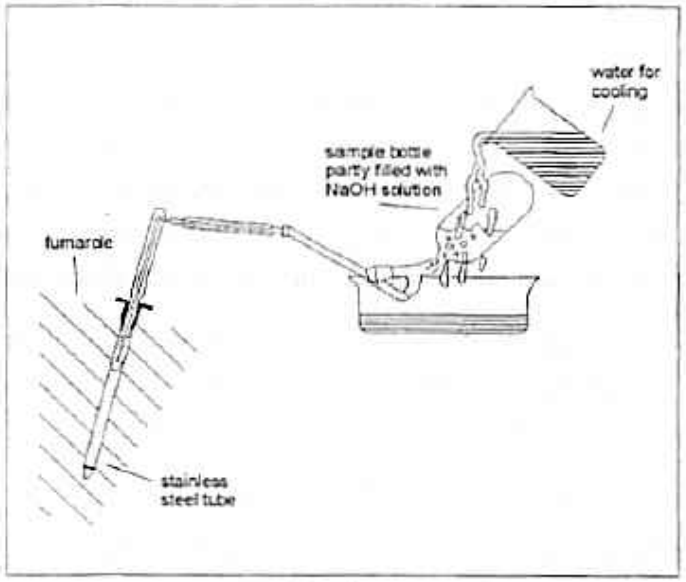


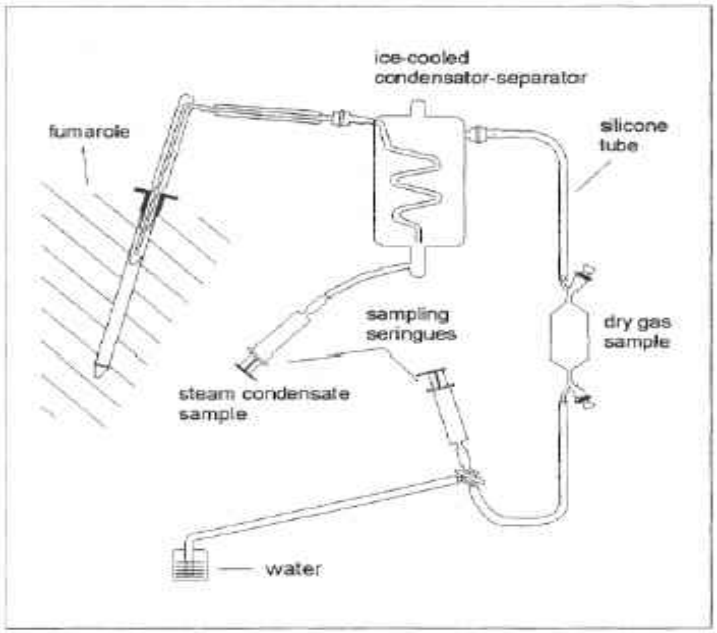
Aiuppa et al. (2009)

•***hydrothermal liquids*** hosted in the hydrothermal systems, which are frequently interposed between the magma batch stationing at depth and the surface.



Conceptual geochemical model of White Island [Giggenbach, 1987]

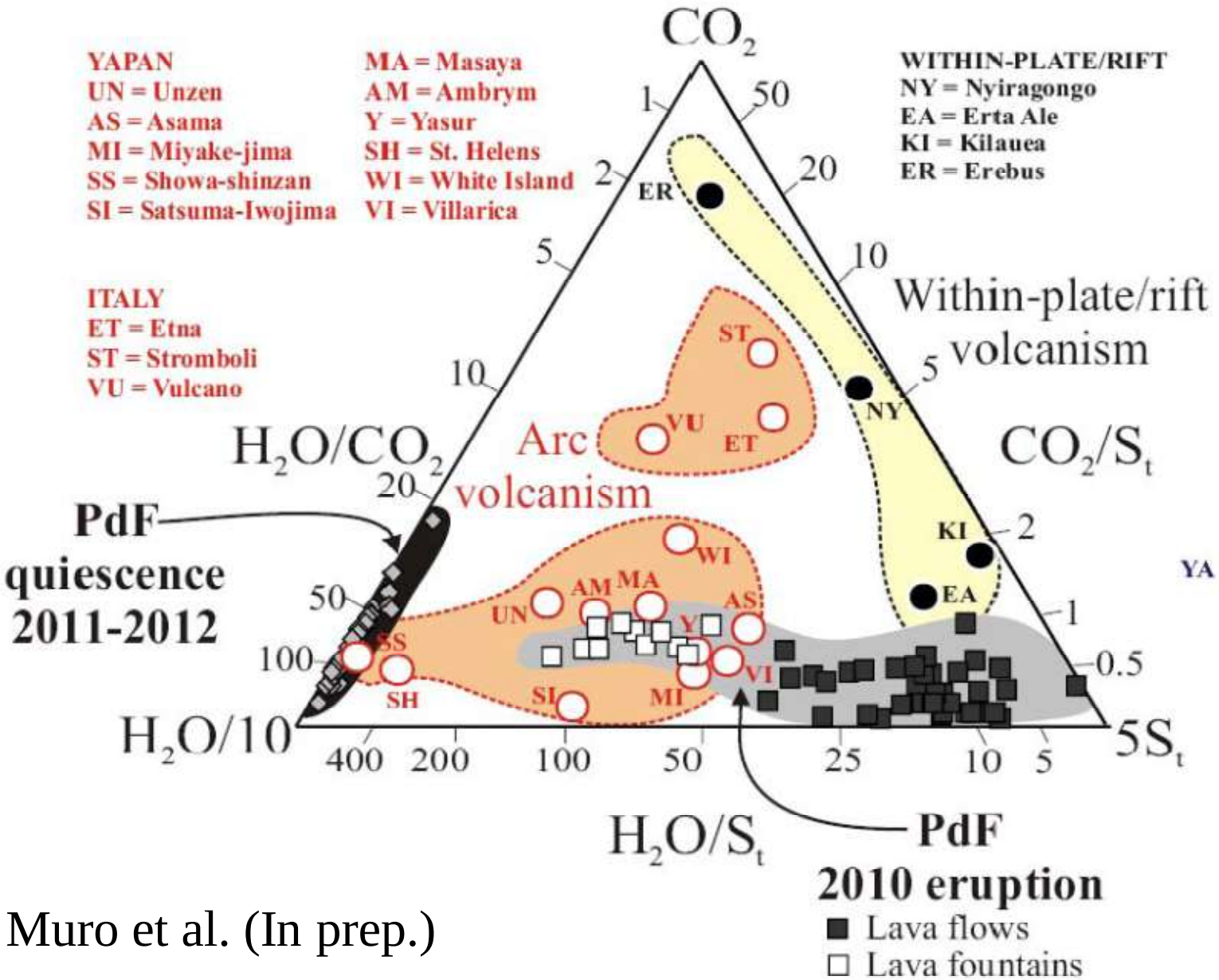

water for cooling
sample bottle partly filled with NaOH solution
fumarole
stainless steel tube


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

Average chemical composition of Bocca Grande fumarole during1998-2000 (the data are expressed in mmol/mol)

T °C	161
H_2O	843600
CO_2	154100
H_2S	1360
N_2	475
H_2	364
CH_4	23.2
He	1.27
CO	0.51
Ar	0.49
O_2	0.24

The absence of typical magmatic gases (i.e. SO2, HCl, HF) and the relatively high contents of CH4 suggest that Solfatara fluids were stored in an hydrothermal environment before discharging.



Di Muro et al. (In prep.)

Measuring <u>Initial</u> Magmatic Volatiles

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

- **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

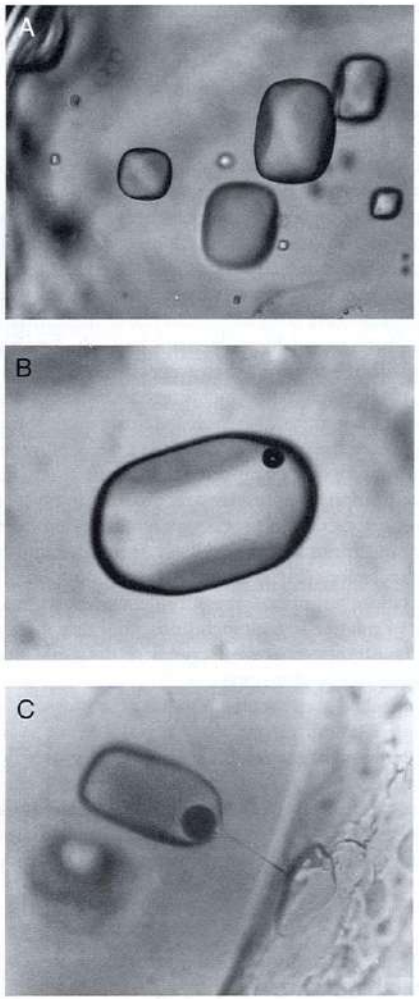
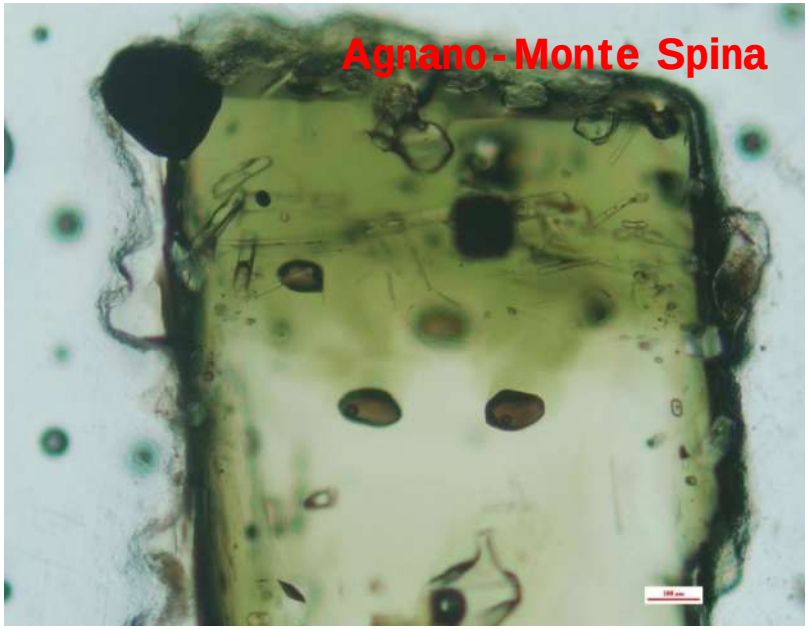
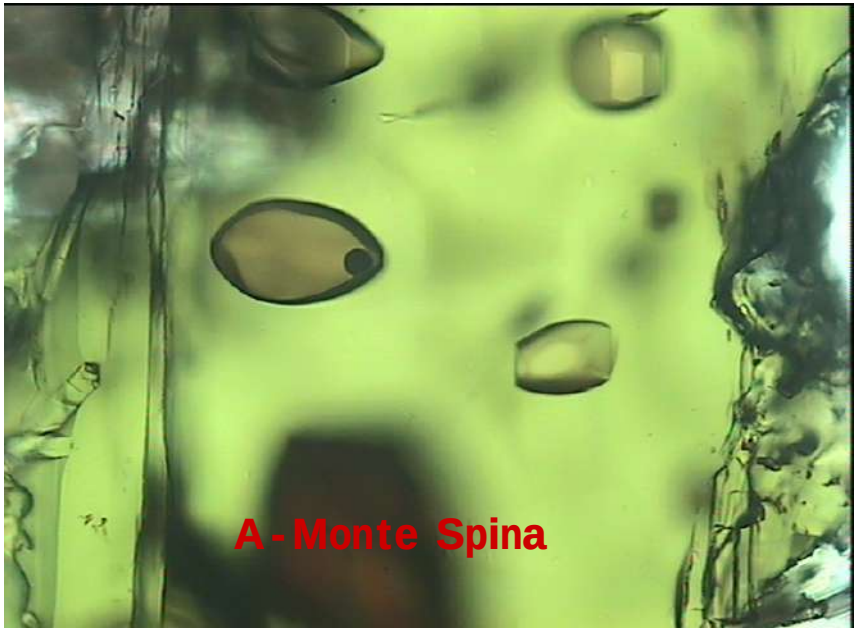


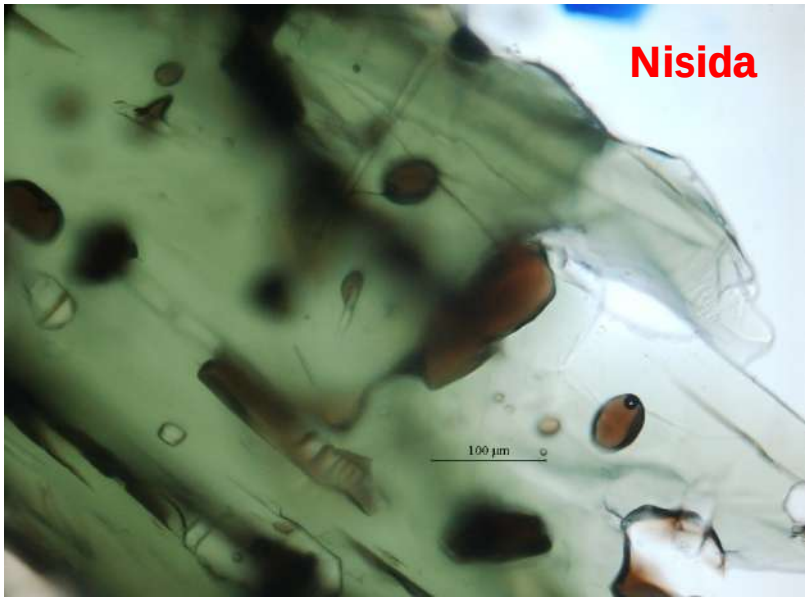
FIGURE 8 Glass (melt) inclusions in crystals from volcanic rocks. (A) A fragment of an ~3-mm quartz phenocryst from the rhyolitic Bishop Tuff containing inclusions of glass up to about 100 μm in diameter. (B) Close-up of a melt inclusion containing

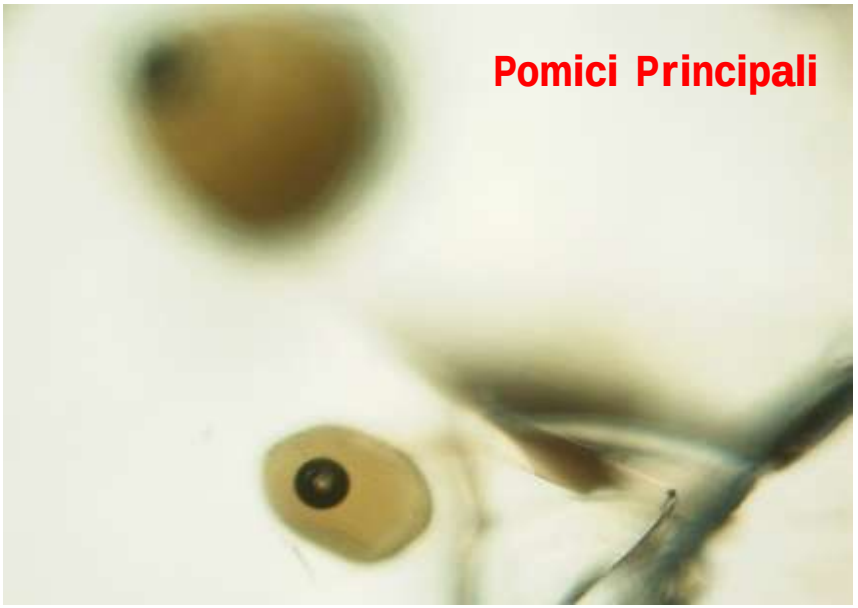
- **Can measure abundances in submarine glasses because little to no degassing invoked; magma cools on contact with seawater**
- **Melt inclusions, which are blobs of melt (glass) surrounded by crystal.**
- **Interpretation is that these blobs of melt do not lose volatiles because “armored” by solid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

Campi Flegrei Melt/glass inclusions

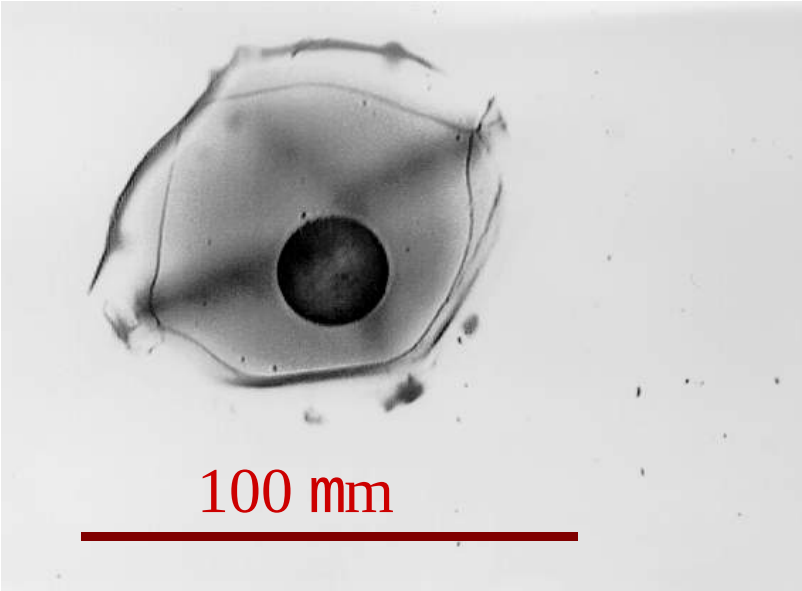


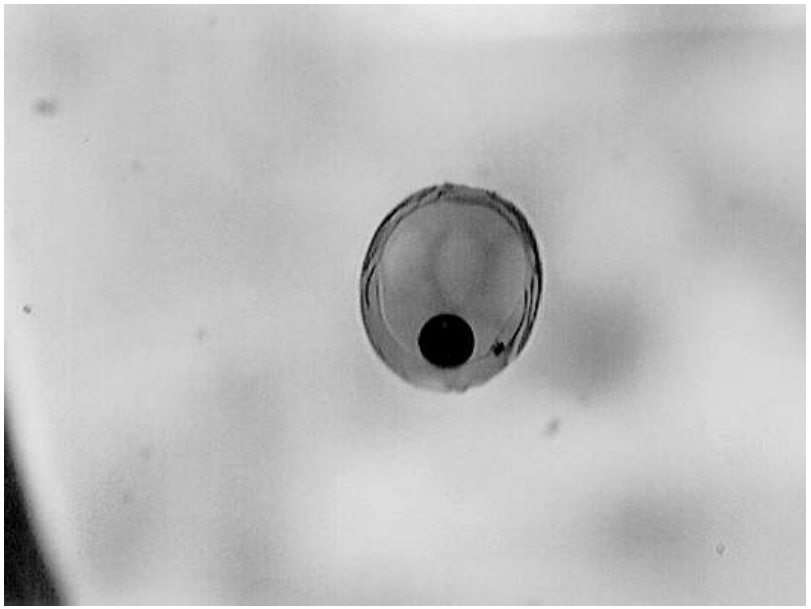


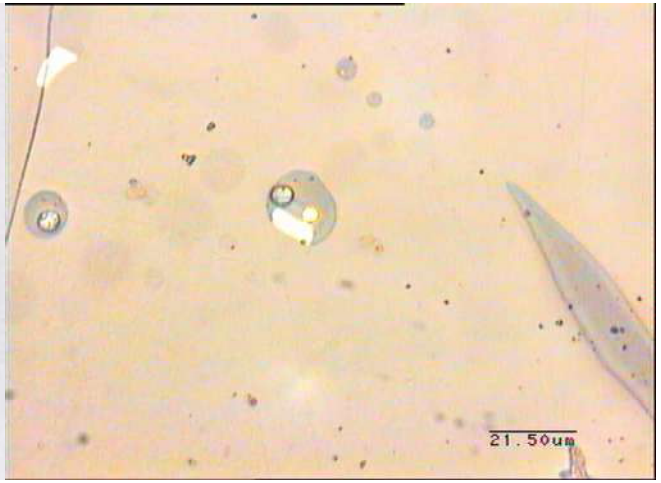




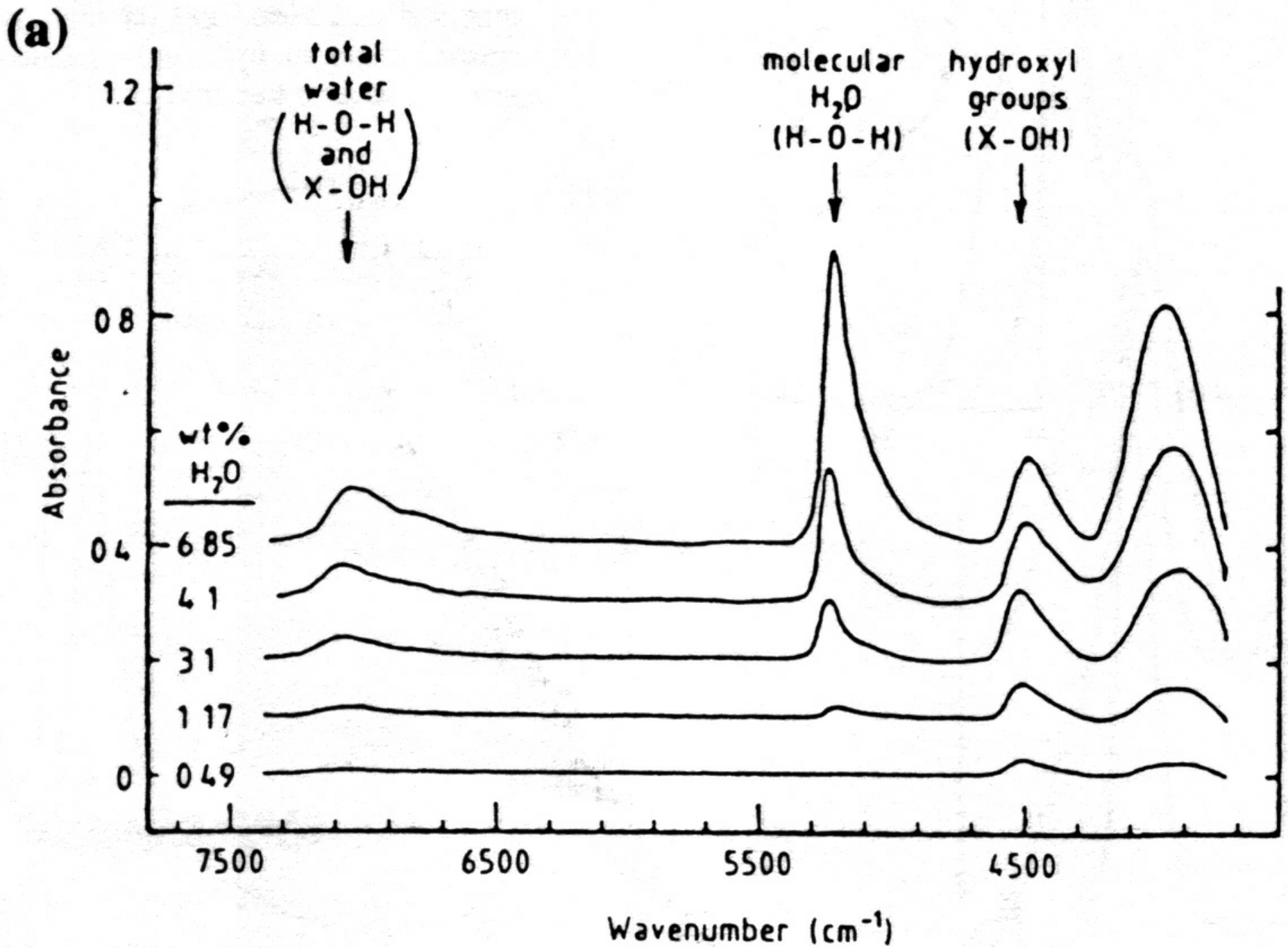
Stromboli MIs

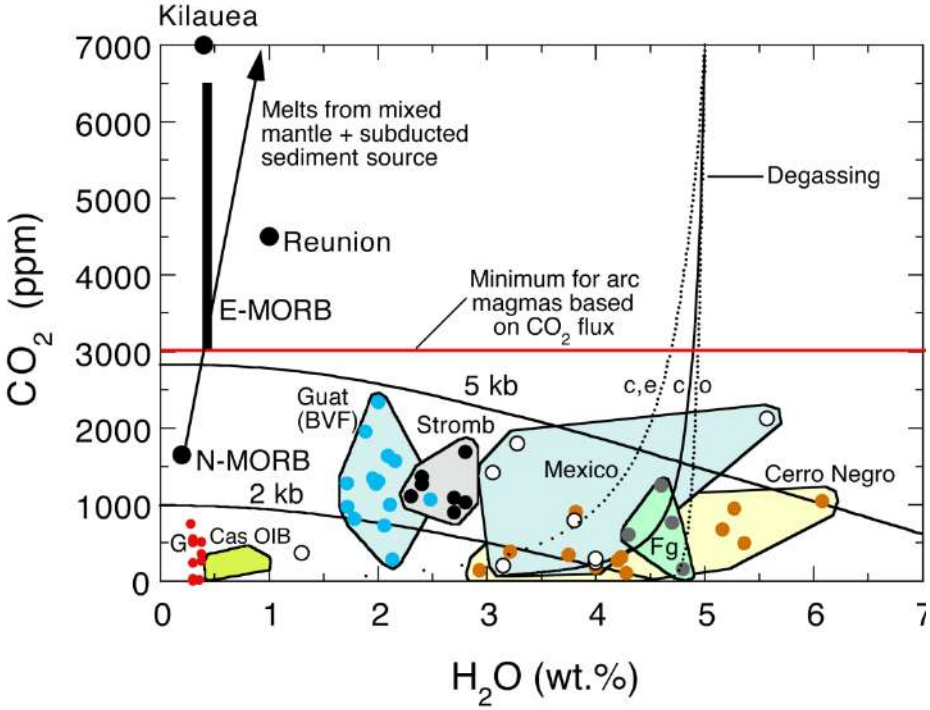






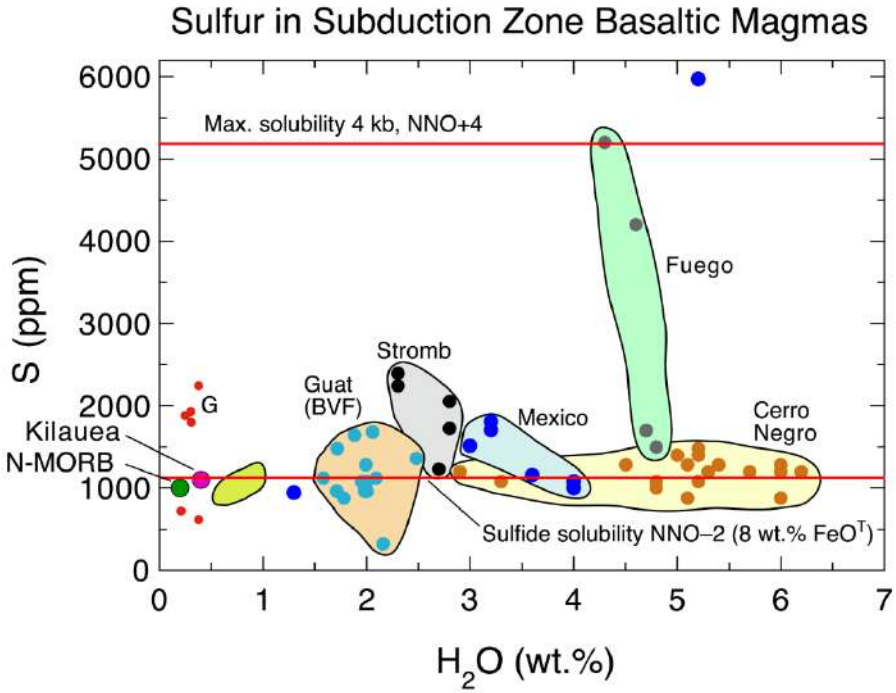
Etna MIs

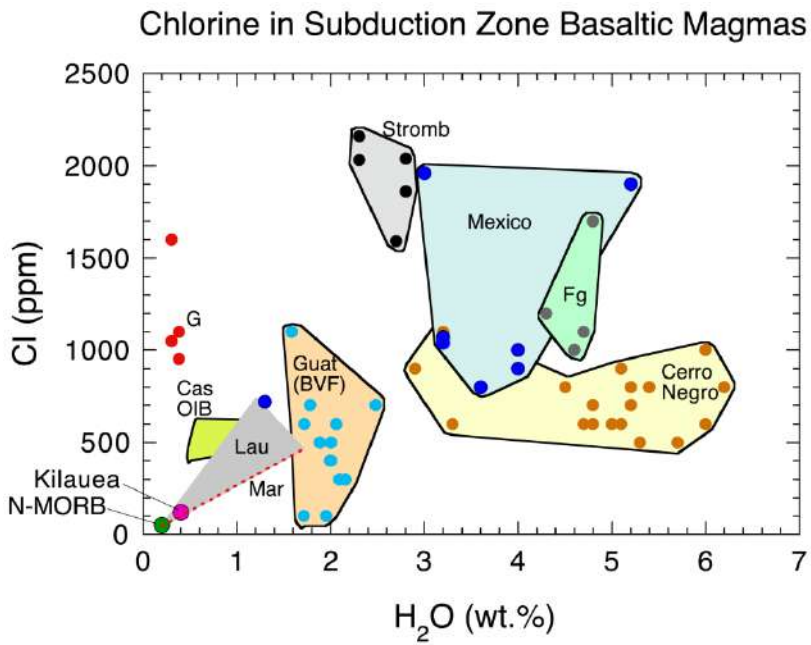

(a)
total water (H-O-H and X-OH)
molecular H_2O (H-O-H)
hydroxyl groups (X-OH)
Absorbance
1.2
0.8
0.4
0
wt% H_2O
6.85
4.1
3.1
1.17
0.49
7500
6500
5500
4500
Wavenumber (cm^{-1})



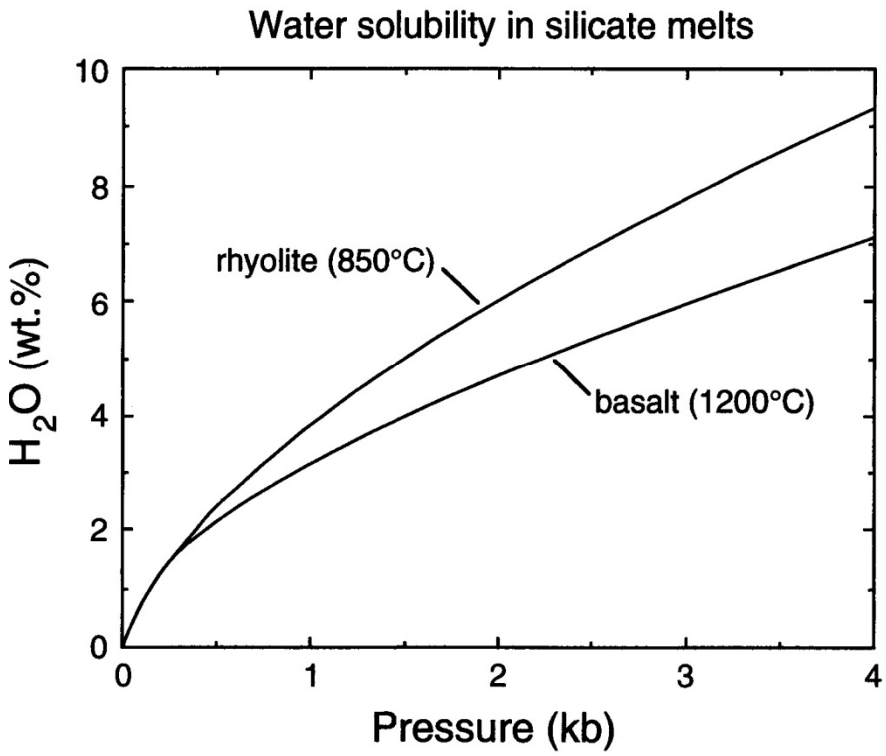
Basaltic magmas

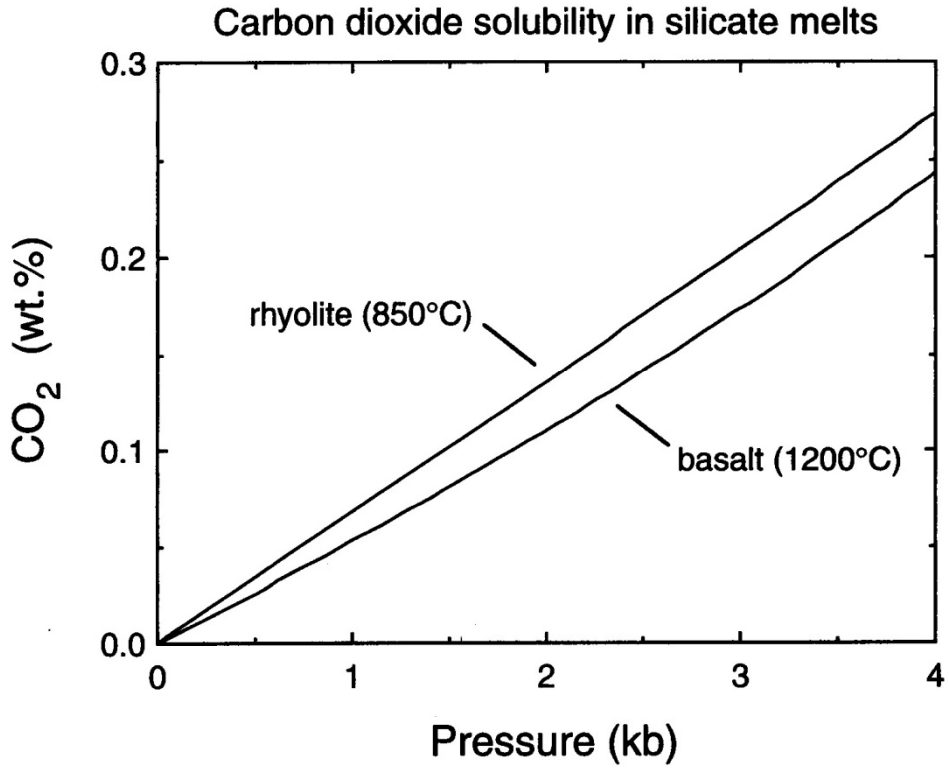
(Wallace, 2005)





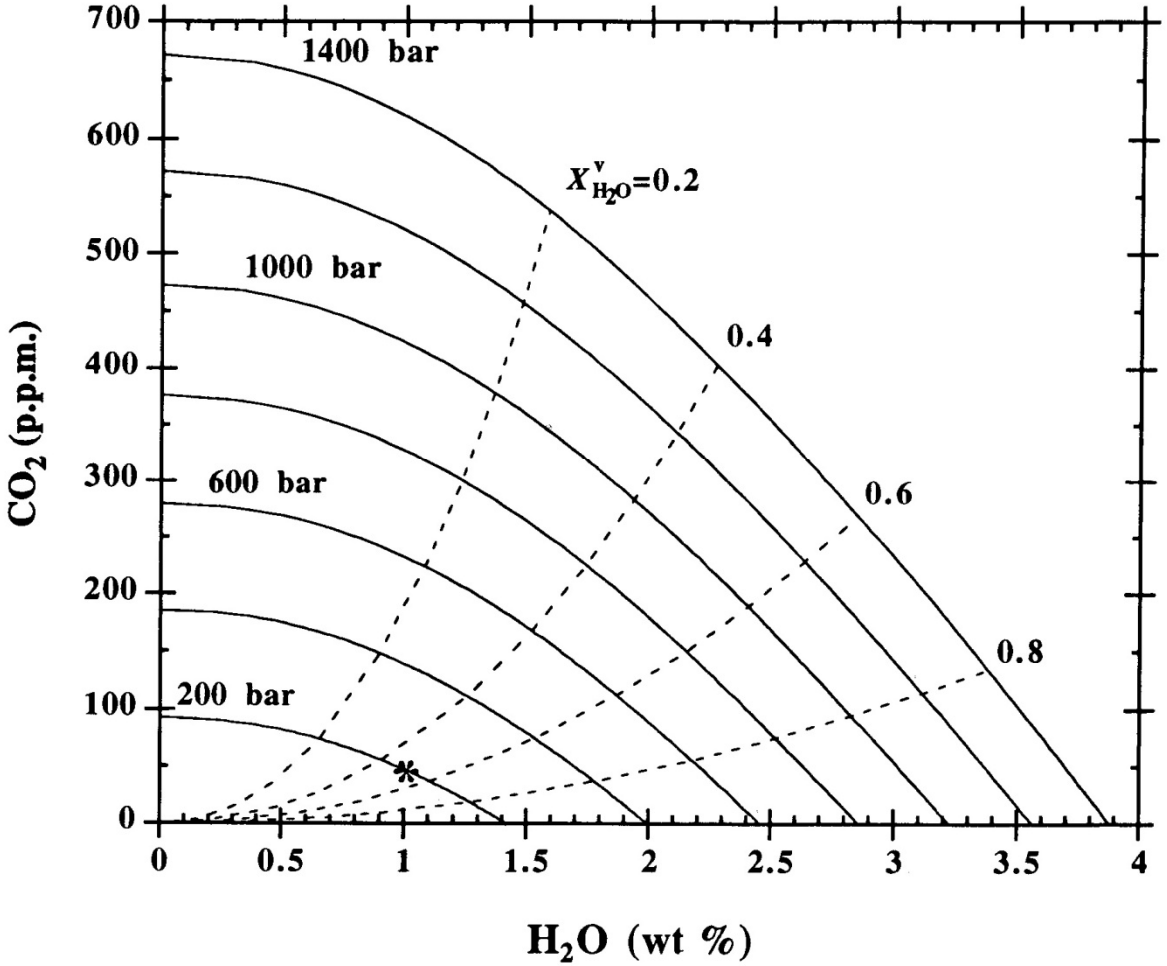
Understanding solubilities and saturation properties demands first experiments…then thermodynamics





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

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

- S solubility is more complicated because of multiple oxidation states
- Dissolved S occurs as either S^{2-} or S^{6+}

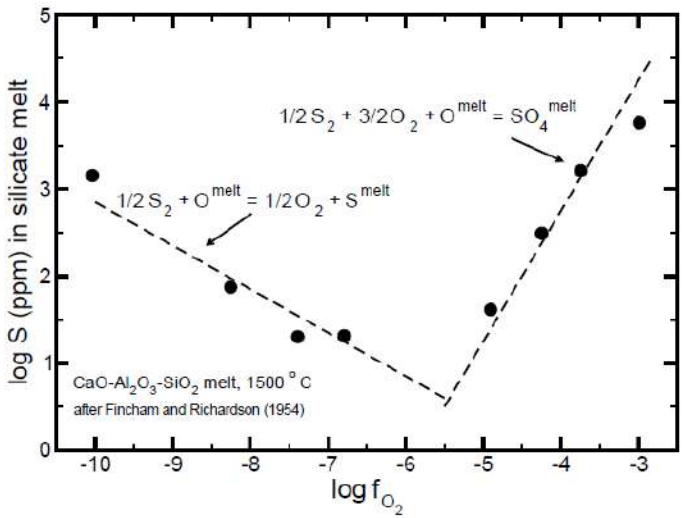
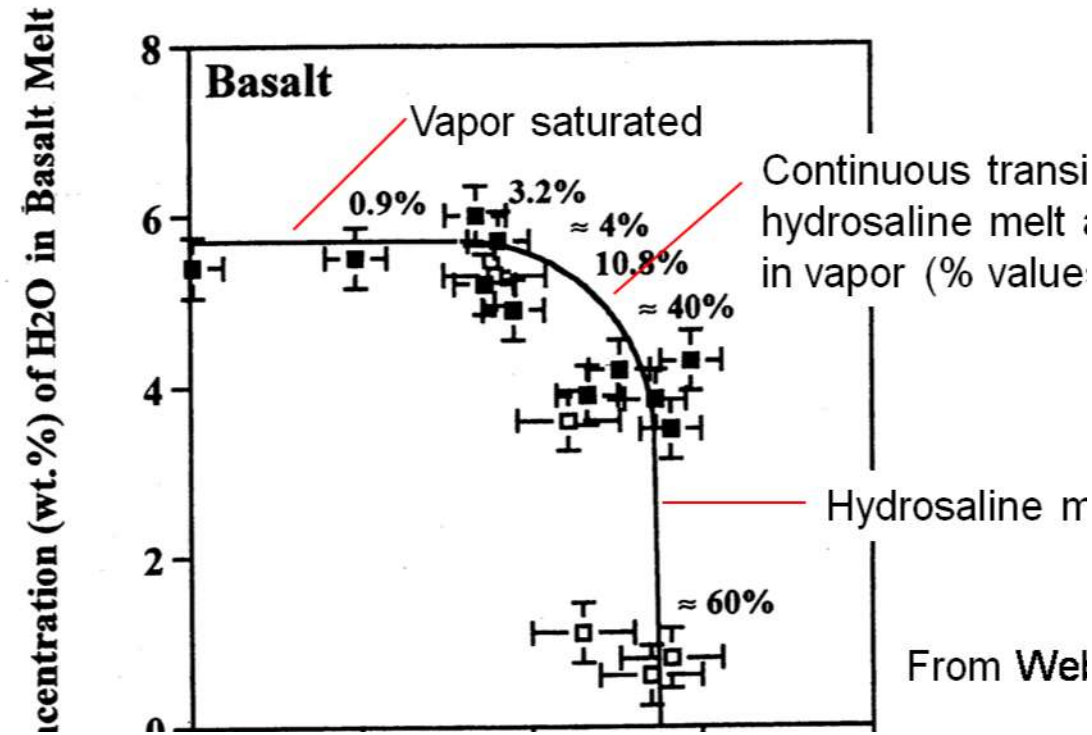


Figure 2. Solubility of sulfur in silicate melts at conditions of a fixed mole fraction of SO_2 in the input gas phase and varying f_{O_2} measured by Fincham and Richardson (1954) in a $CaO-Al_2O_3-SiO_2$ melt at 1 bar pressure. Please see text for further discussion of the reactions portrayed in these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

Baker and Moretti (2011)

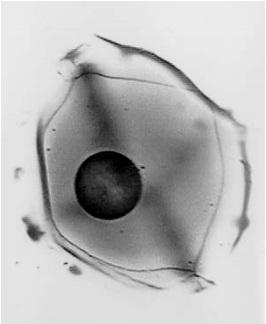
Jugo (2005)

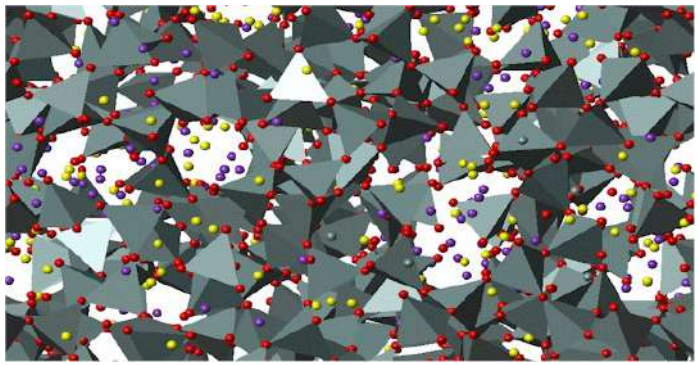
Chlorine Solubility



→ In real basalts there is less chlorine (luckly!) → saturation with brine is avoided!

The message: Integrated and synergetic approach





$$\ln f_i^{oL}(P,T) = \ln f_i^{oL}(P^o,T^o) + \int_{P^o}^{P} \frac{v_i^o}{RT} dP - \int_{T^o}^{T} \frac{1}{RT^2} \int_{P^o}^{P} \left[v_i^o - T\left(\frac{\partial v_i^o}{\partial T}\right)_P \right] dP dT$$

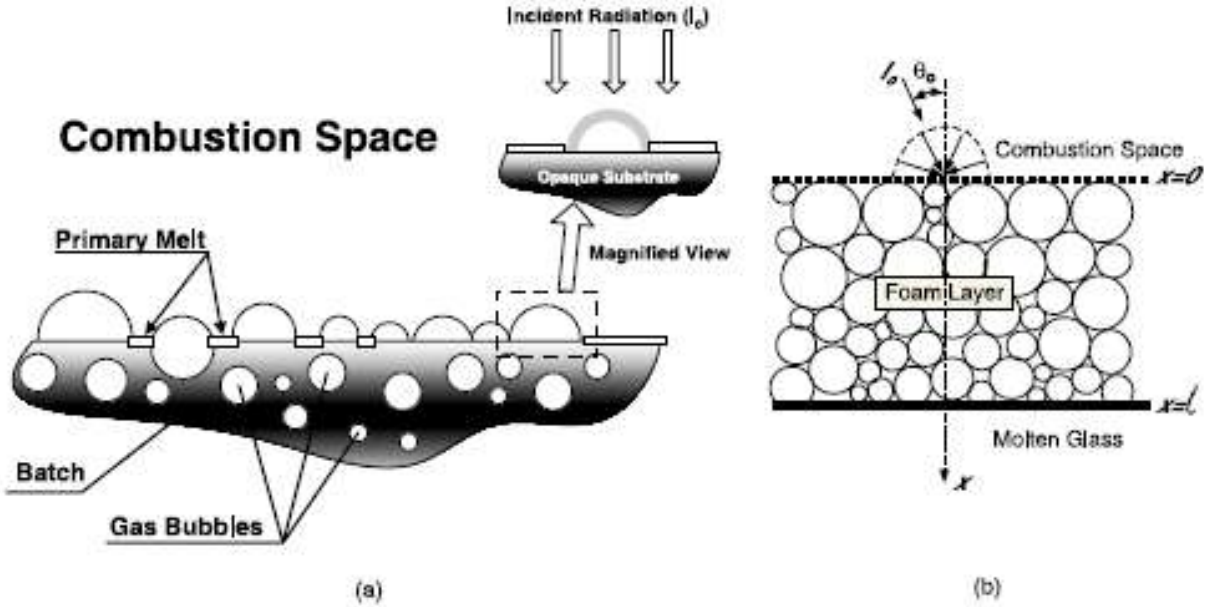


Fig. 2. (a) A layer of the primary foam formed on top of batch logs with a magnified view showing an idealized unit cell used for analysis of radiative transfer, and (b) an idealized layer of the secondary glass foam.

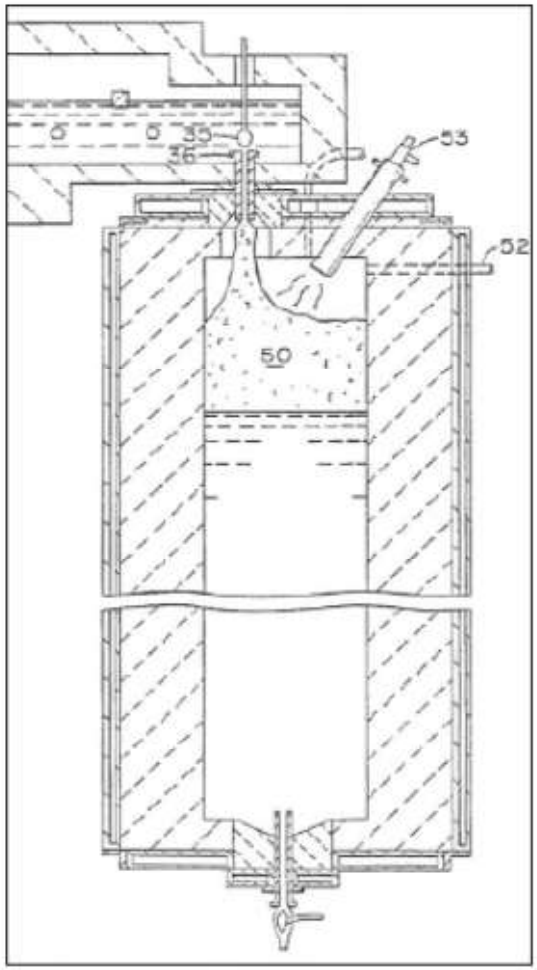


Fig. 2. Commercial vacuum-refining module [(35-36) is special valving arrangement, (52) is pressure maintenance tube, (50) is foam and (53) is gas burner].

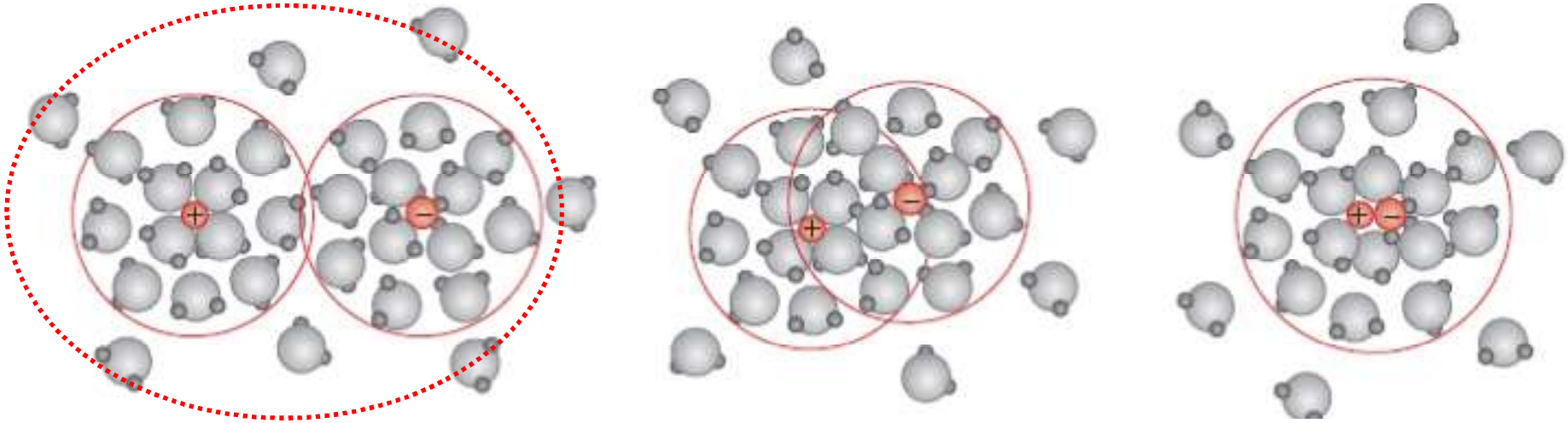
Fedorov and Pilon (2002; JNCS)

Silicate melts are not liquid water…

Outer sphere ion pair

Inner sphere ion pair

(complex)

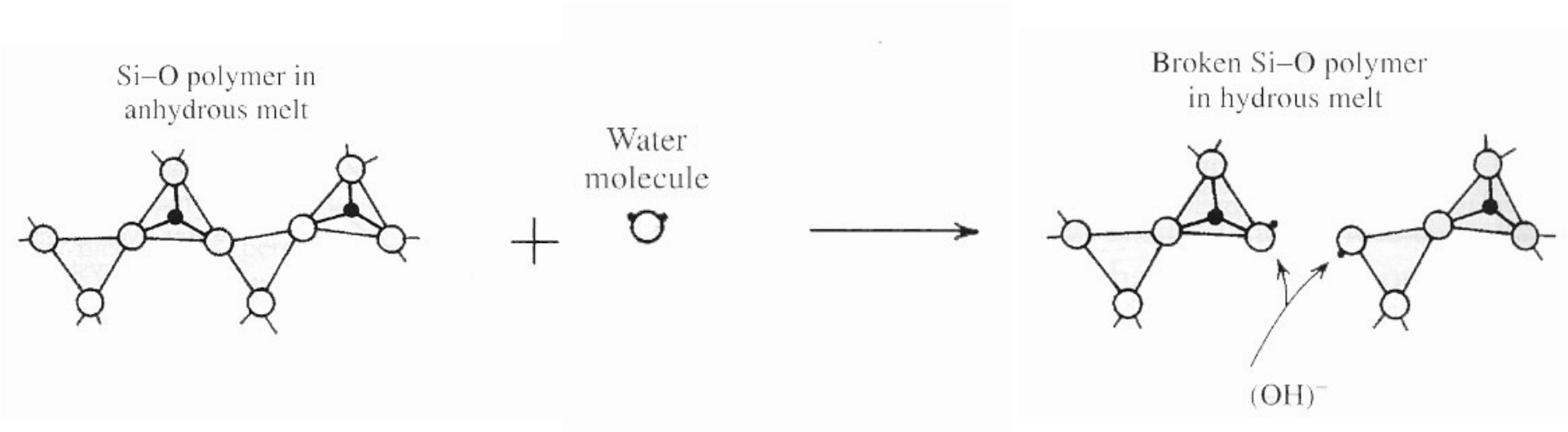


Intact solvation shells

Partial disruption of solvation shells

Disruption of solvation shells

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



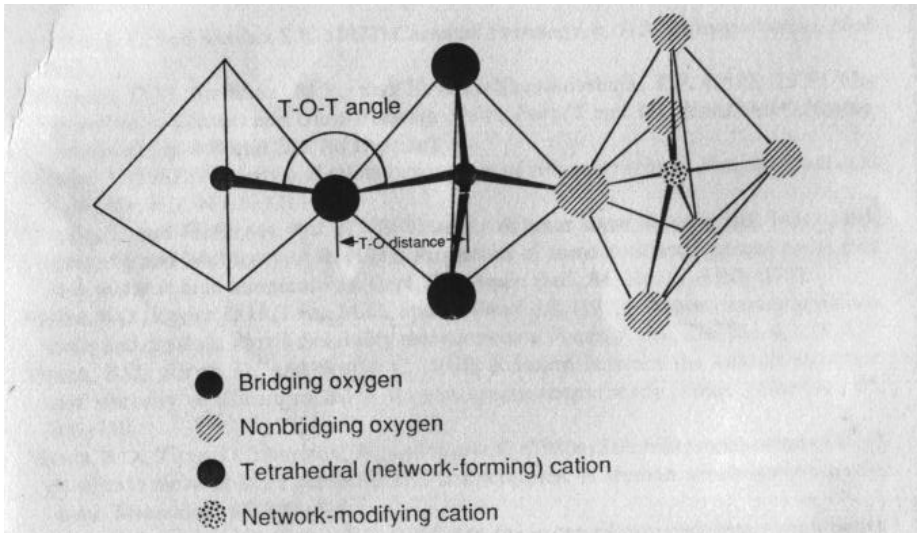


Fig. 1. Schematic representation of the geometric relationships of bridging and nonbridging oxygen and network-forming and network-modifying cations.

Mysen and Richet, 2005

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:

Acid + O^{2-} ⇔ 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:

Acid ⇔ 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)*

<u>This is the main redox couple in oxide melts.</u>

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-}.

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

$$SiO_4^{4-} + SiO_4^{4-} \Leftrightarrow Si_2O_7^{6-} + O^{2-}$$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Chemical Geology 174 (2001) 157–179

CHEMICAL GEOLOGY

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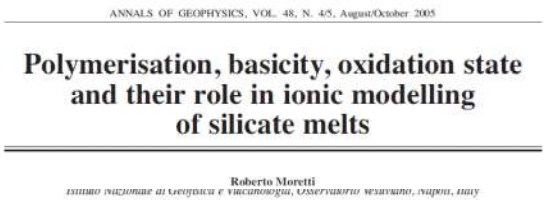
Oxidation state of iron in silicate glasses and melts: a thermochemical model

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


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

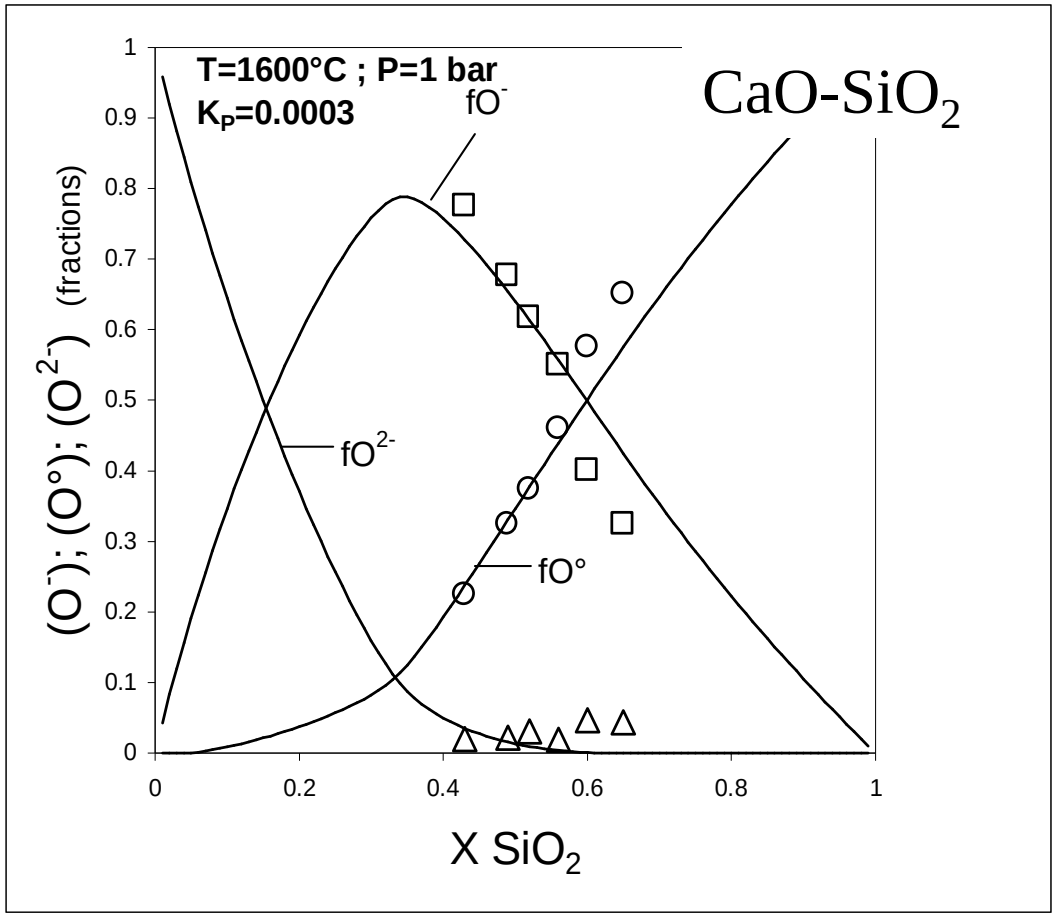
Polymerisation, basicity, oxidation state and their role in ionic modelling of silicate melts

Roberto Moretti

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

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

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



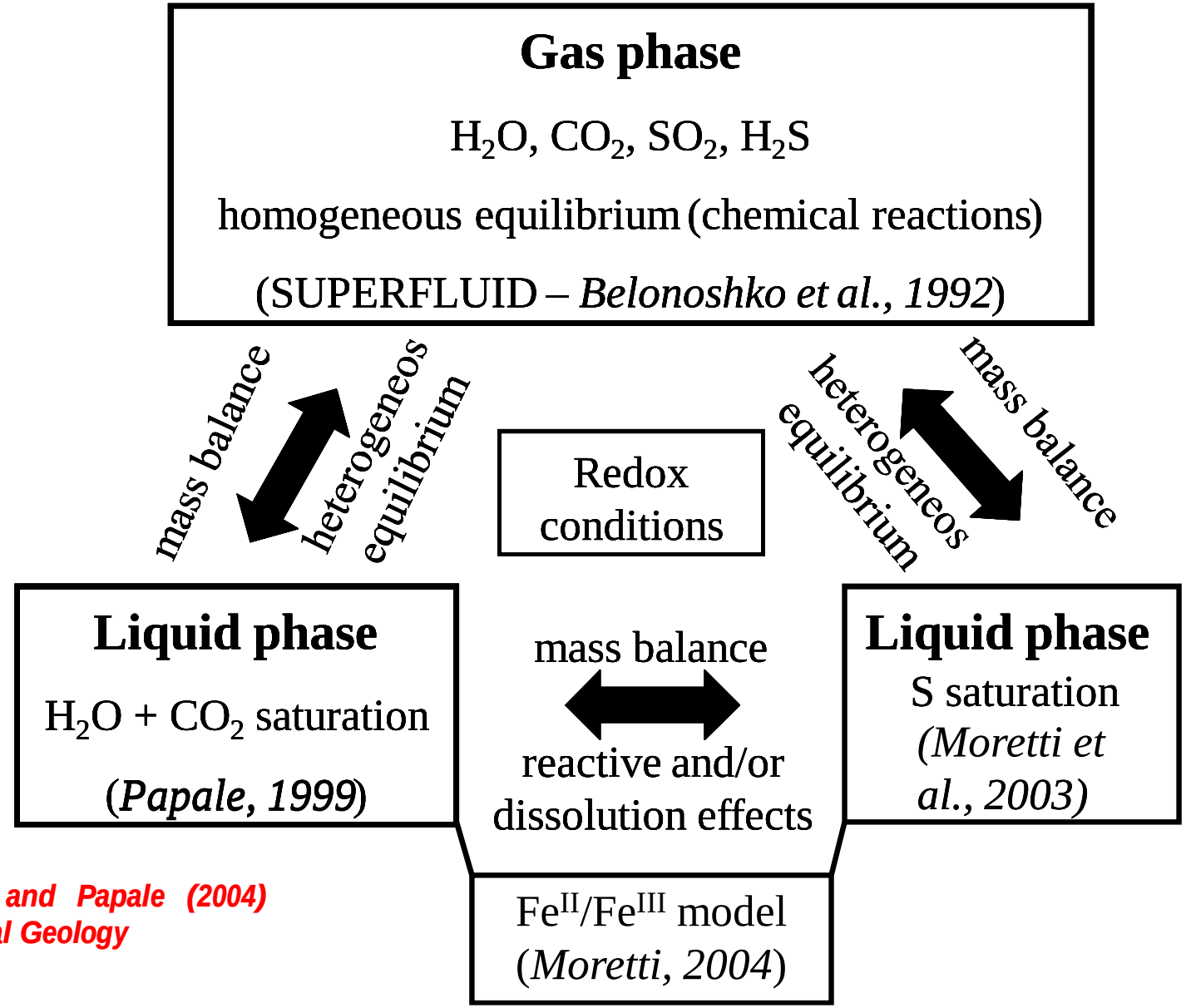
Ottonello and Moretti (2004) J. Phys. Chem. Solids

The message:

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

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

The H_2O-CO_2-H_2S-SO_2 saturation model



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

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

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

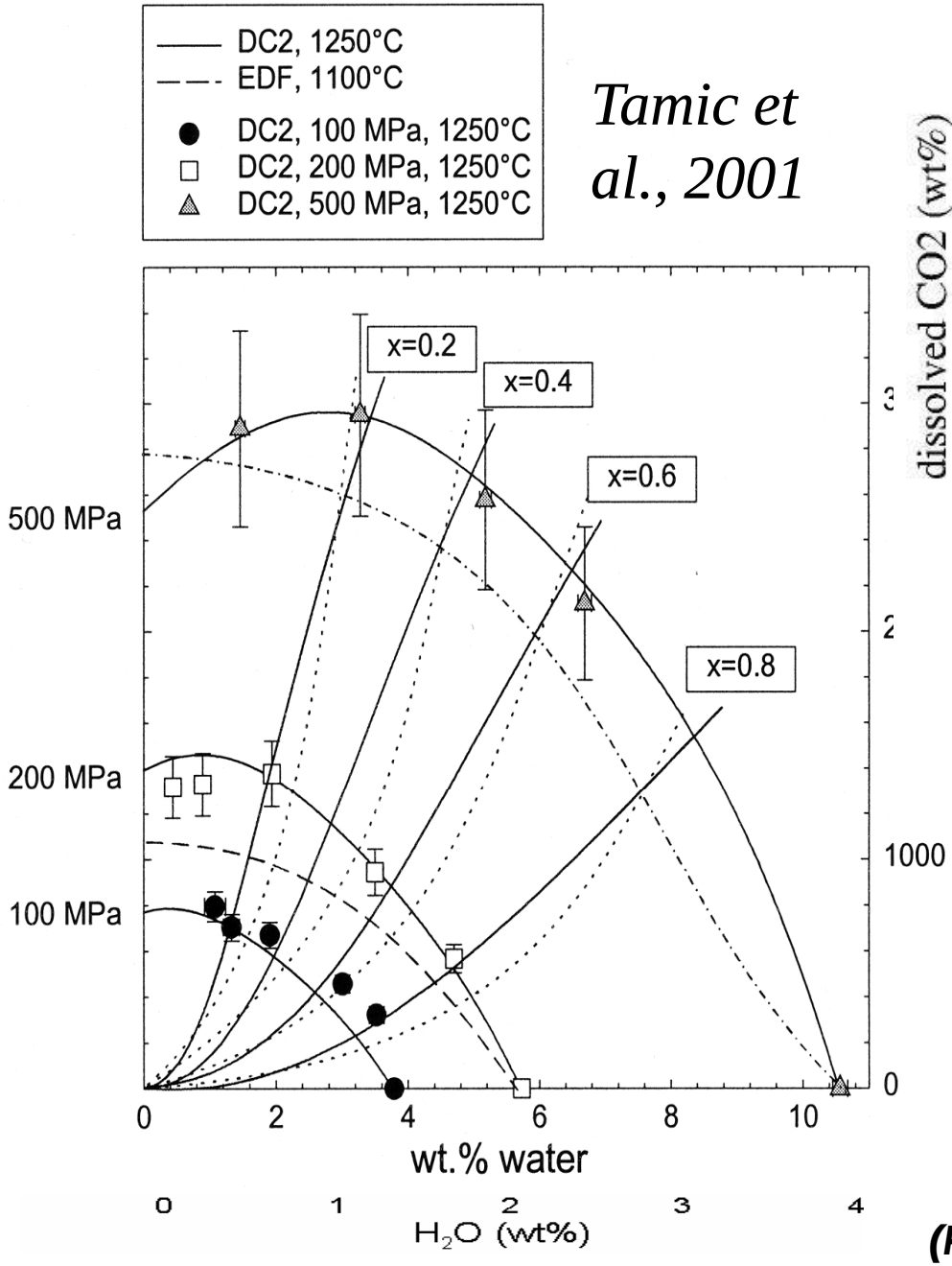
$$f^G_{H_2O} = f^L_{H_2O} \Rightarrow \phi_{H_2O} y_{H_2O} P = \gamma_{H_2O} x_{H_2O} f^{oL}_{H_2O}$$

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

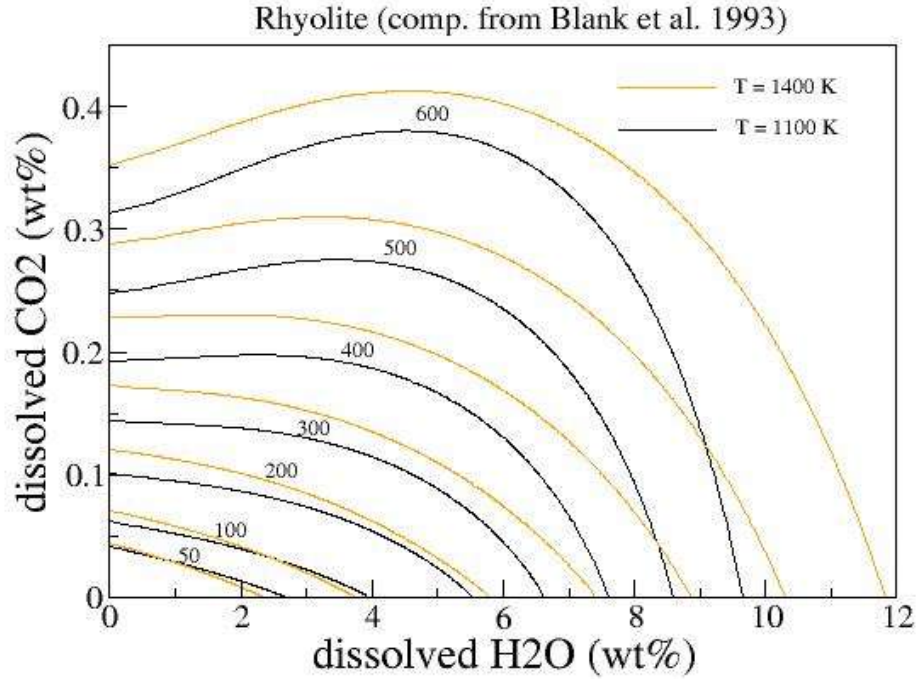
Mass balance equations

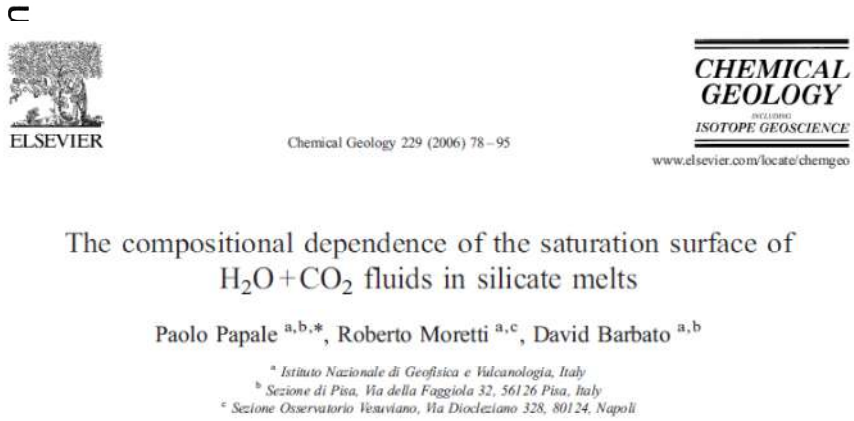
$$y_{H_2O} + y_{CO_2} = 1$$

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



Tamic et al., 2001

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Chemical Geology 229 (2006) 78 – 95

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

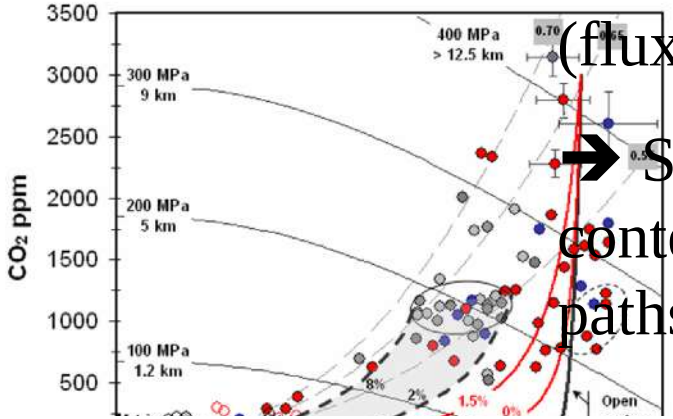
Paolo Papale [a,b,*], Roberto Moretti [a,c], David Barbato [a,b]

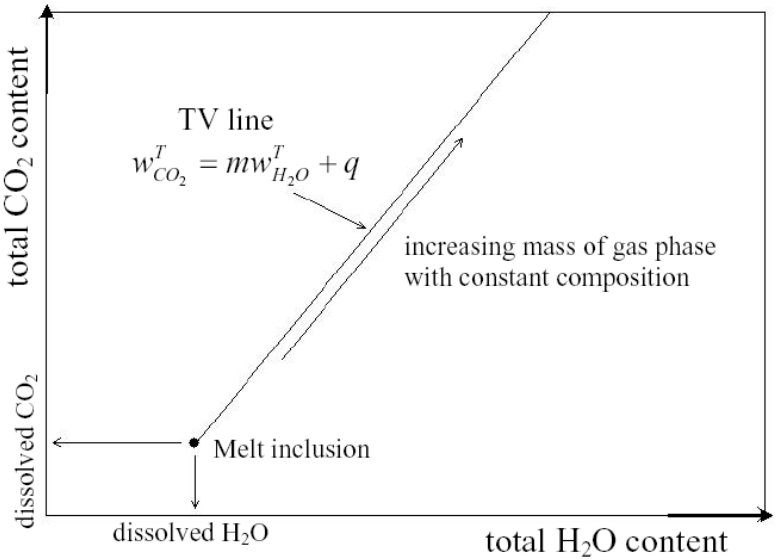
[a] Istituto Nazionale di Geofisica e Vulcanologia, Italy
[b] Sezione di Pisa, Via della Faggiola 32, 56126 Pisa, Italy
[c] Sezione Osservatorio Vesuviano, Via Diocleziano 328, 80124, Napoli

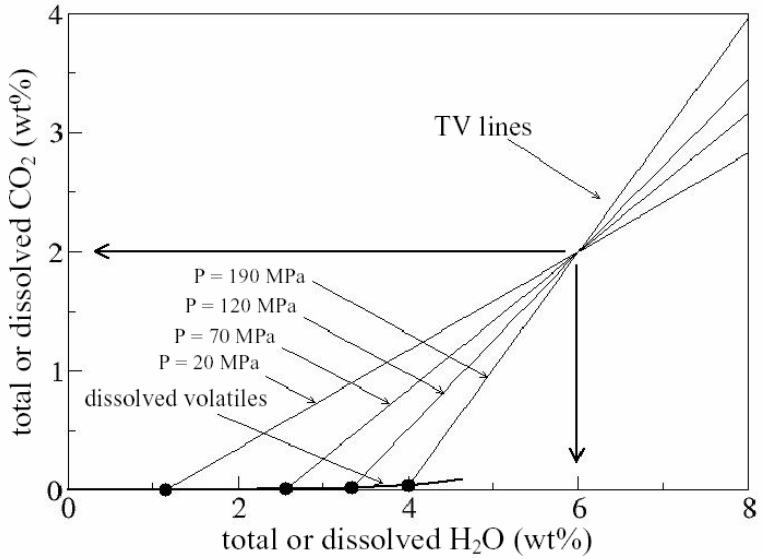
(Papale et al., 2006)

MIs show processes of CO_2 addition and dehydration (fluxing)

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



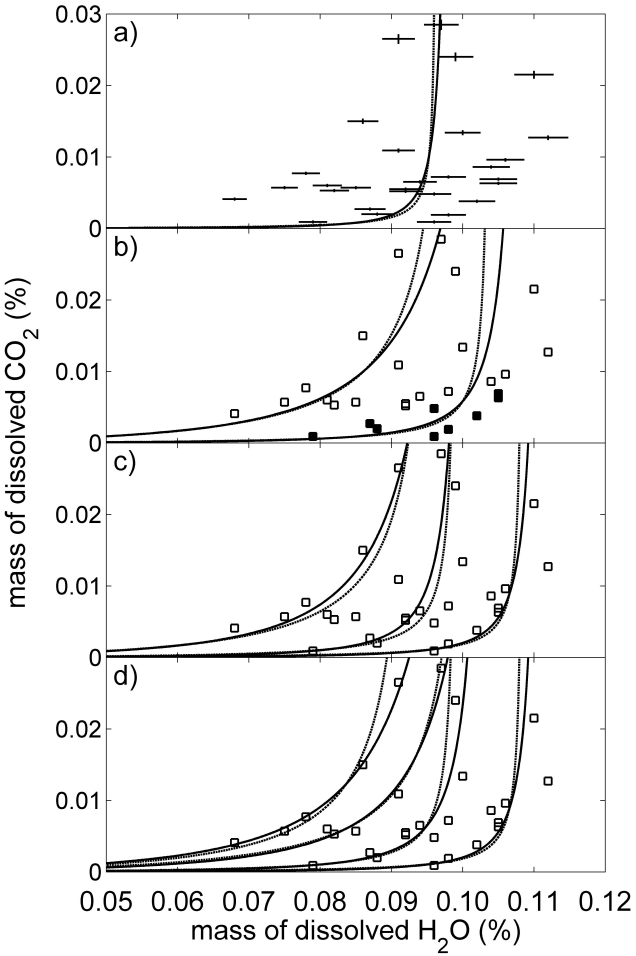




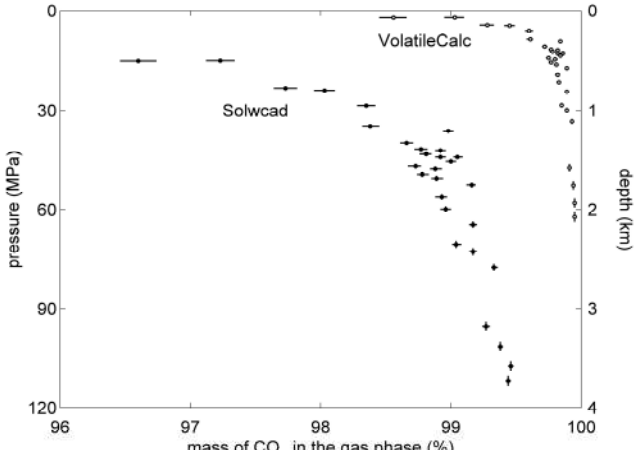
Papale, 2005

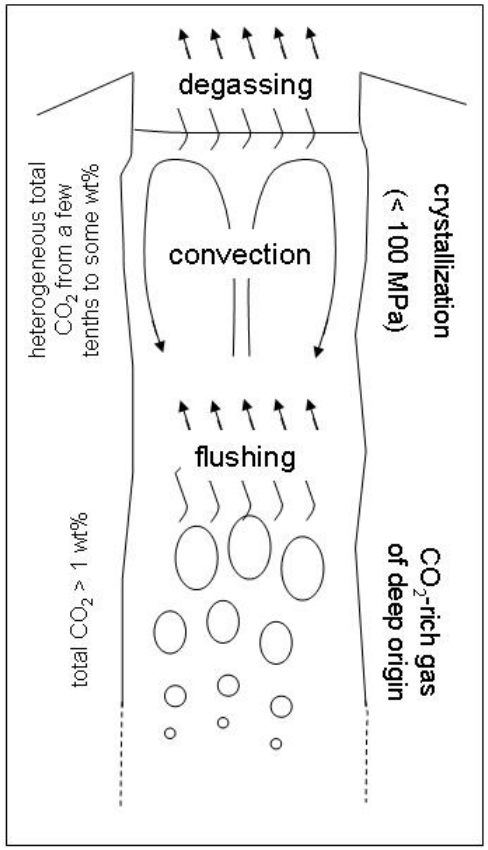
Barsanti et al. (2009, JGR)

KILAUEA



Sat.Mod.	N. of curves	wTH2O (wt%)	wTCO2 (wt%)
SWCD 1	0.100	0.50	
SWCD 2	0.110	0.80	
	0.114	3.80	
SWCD 3	0.111	0.50	
		0.102	0.80
		0.105	3.10
SWCD 4	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

Click Here for Full Article

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…

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

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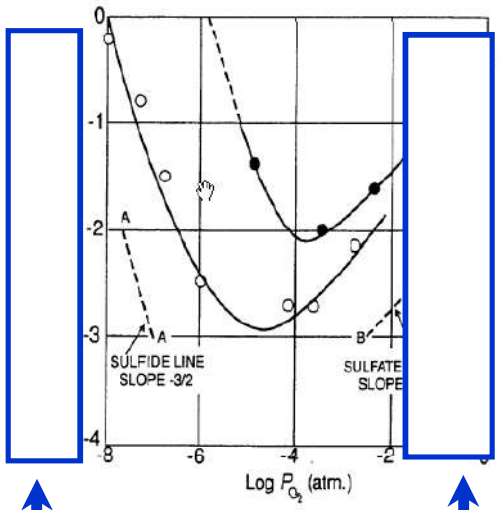
Geochimica et Cosmochimica Acta, Vol. 69, No. 4, pp. 801–823, 2005

0016-7037/05 $30.00 + .00

doi:10.1016/j.gca.2004.09.006

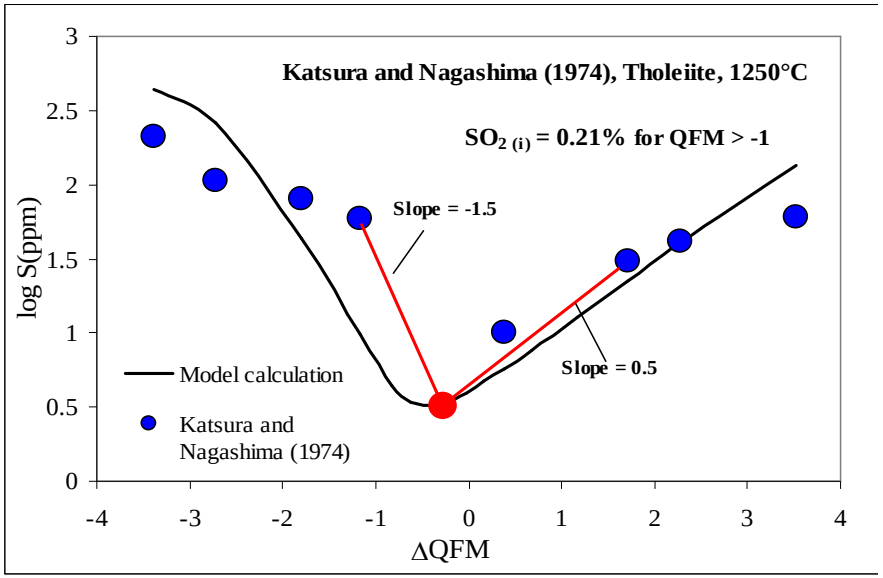
Solubility and speciation of sulfur in silicate melts: The Conjugated Toop-Samis-Flood-Grjotheim (CTSFG) model

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:

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

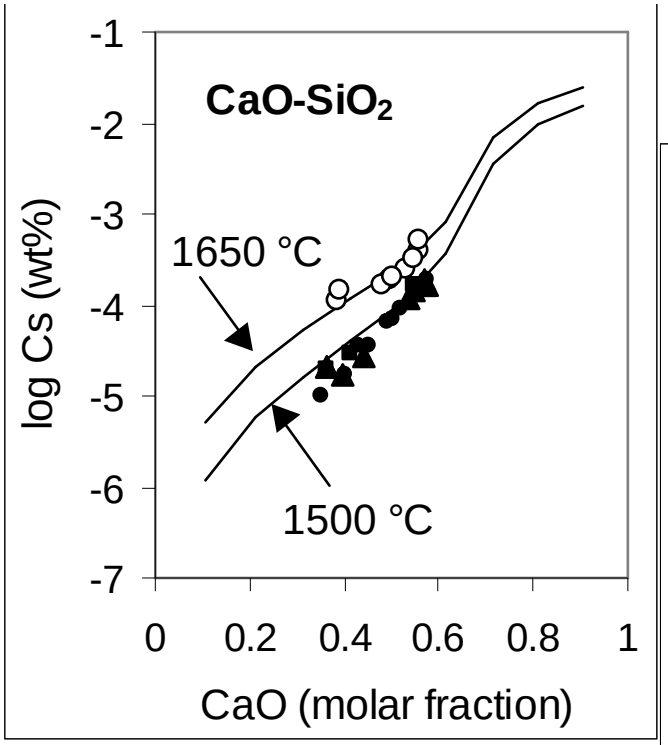
$$C_S = [S]\frac{f_{O_2}^{1/2}}{f_{S_2}^{1/2}} \longrightarrow SO_2^{gas} + O^{2-,silicate\ melt} \leftrightarrow \frac{3}{2}O_2^{gas} + S^{2-,silicate\ melt}$$

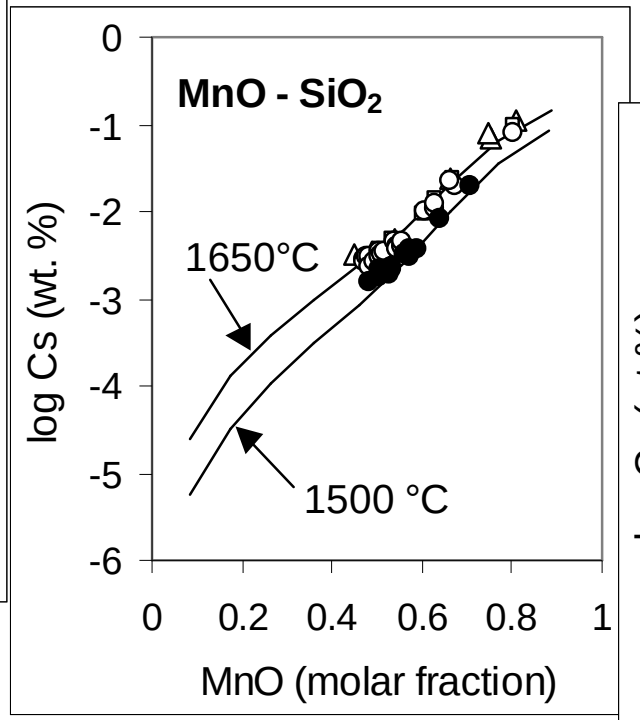
$$C_{S,c} = K'_{O\text{-}S,M}\left(O^{2-}\right)\left(\frac{f_{O_2}^{\circ}}{f_{S_2}^{\circ}}\right)^{\frac{1}{2}} M_S \sum_{mol} oxides \longleftarrow \ln K'_{O\text{-}S,M} = A'_{O\text{-}S,M} + \frac{B'_{O\text{-}S,M}}{T}$$

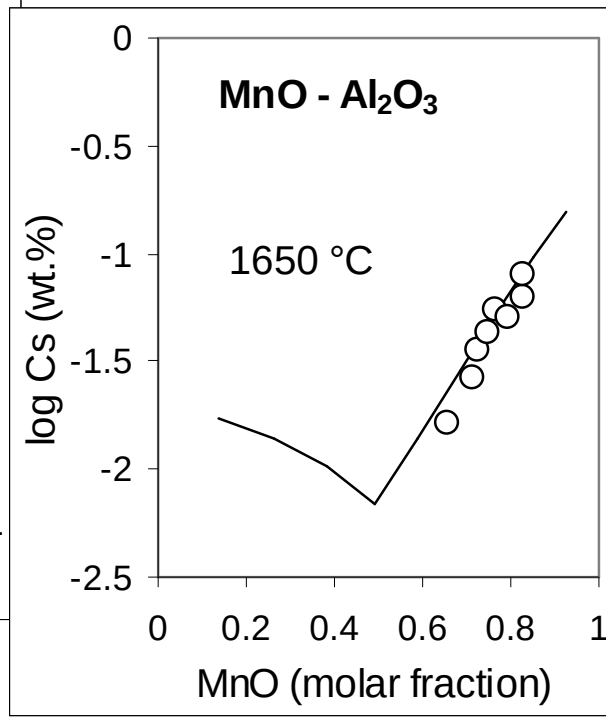
A Polymeric Approach to the Sulfide Capacity of Silicate Slags and Melts

ROBERTO MORETTI and GIULIO OTTONELLO

METALLURGICAL AND MATERIALS TRANSACTIONS B

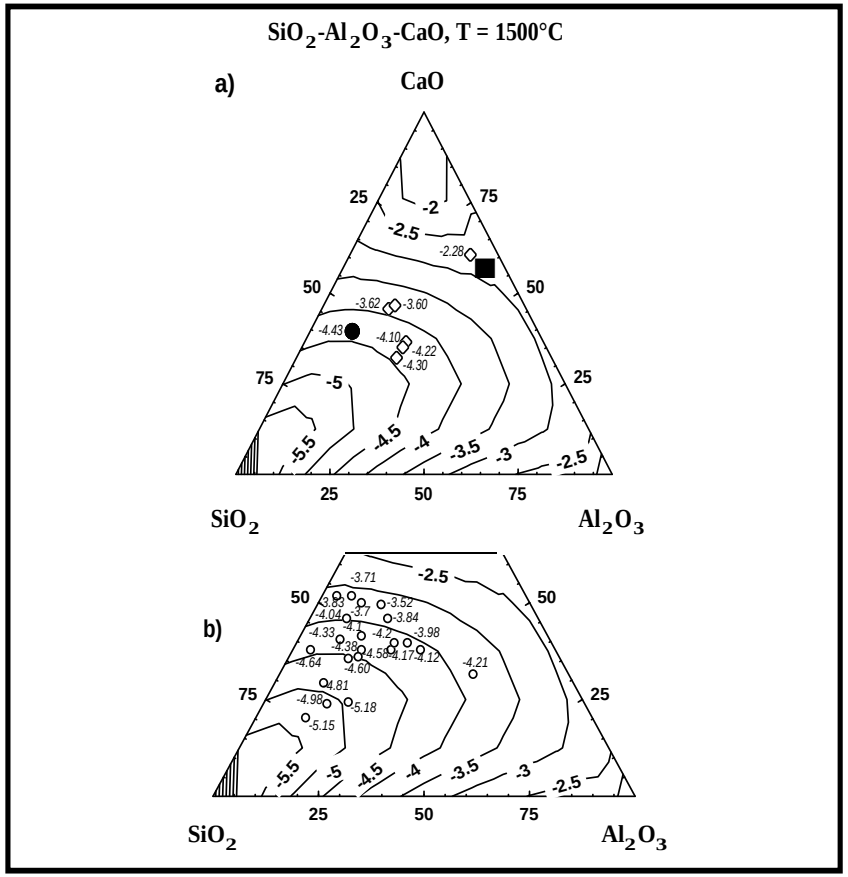






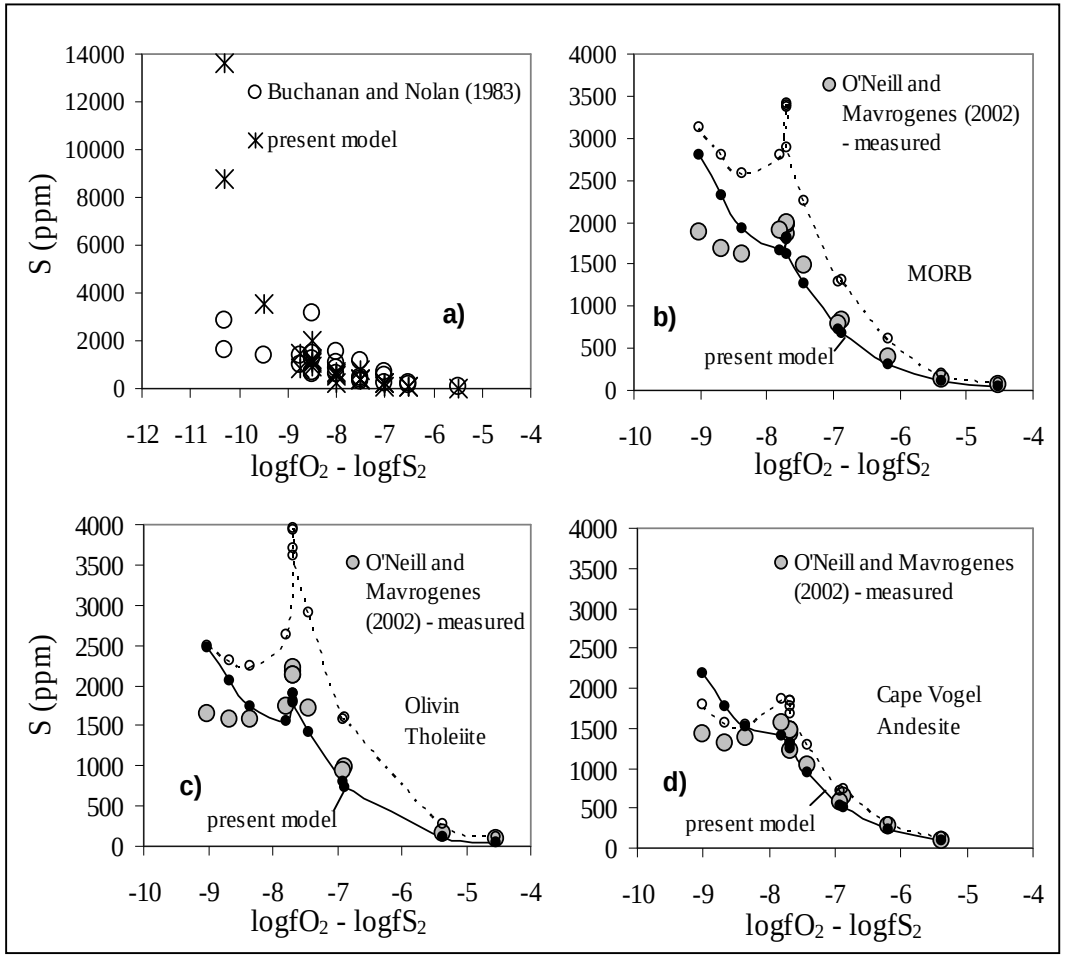
Moretti and Ottonello, 2003 MMTB

Simple metallurgical slags (log Cs contouring)



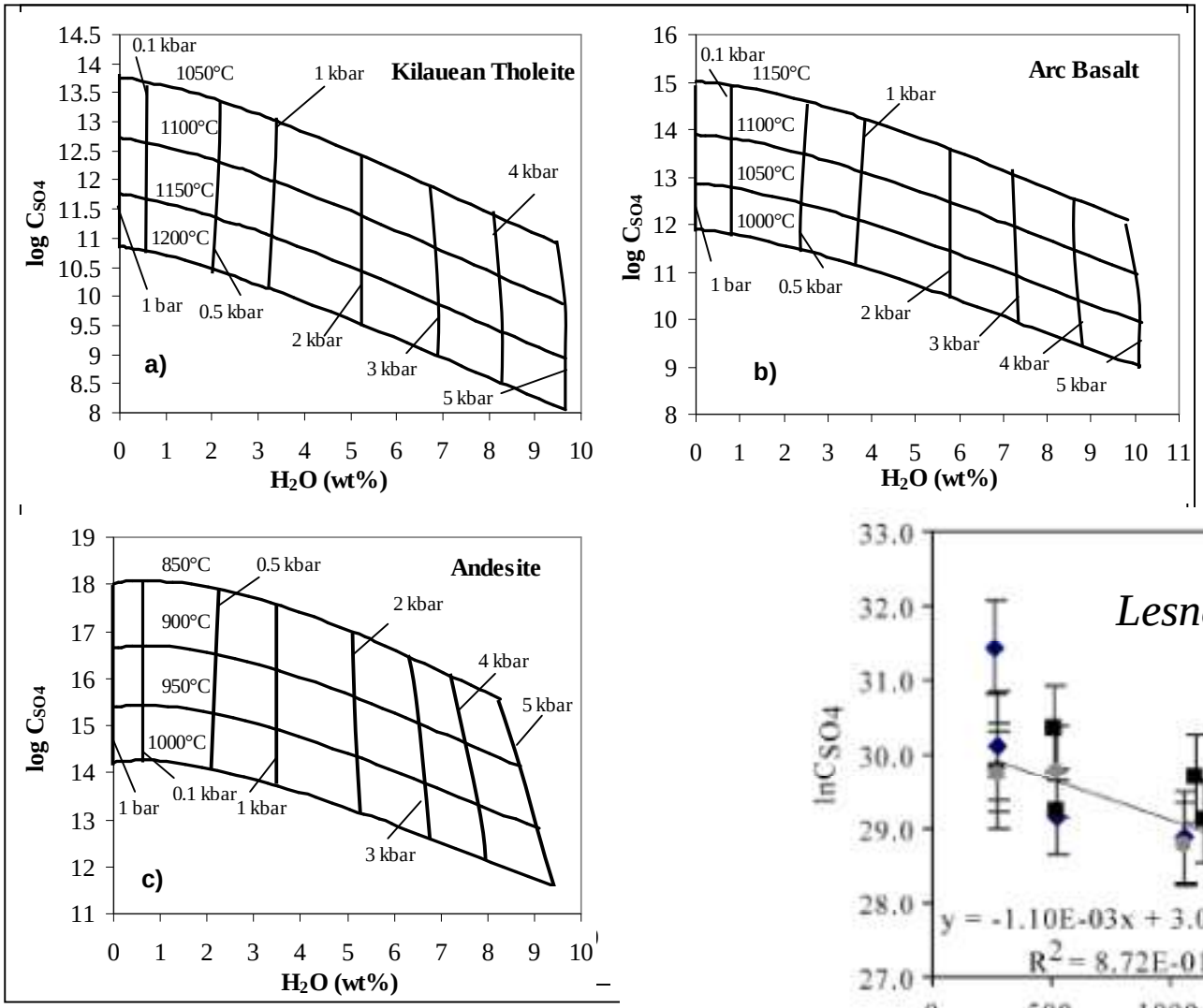
Moretti and Ottonello (2003), Metall. Mat. Trans. B

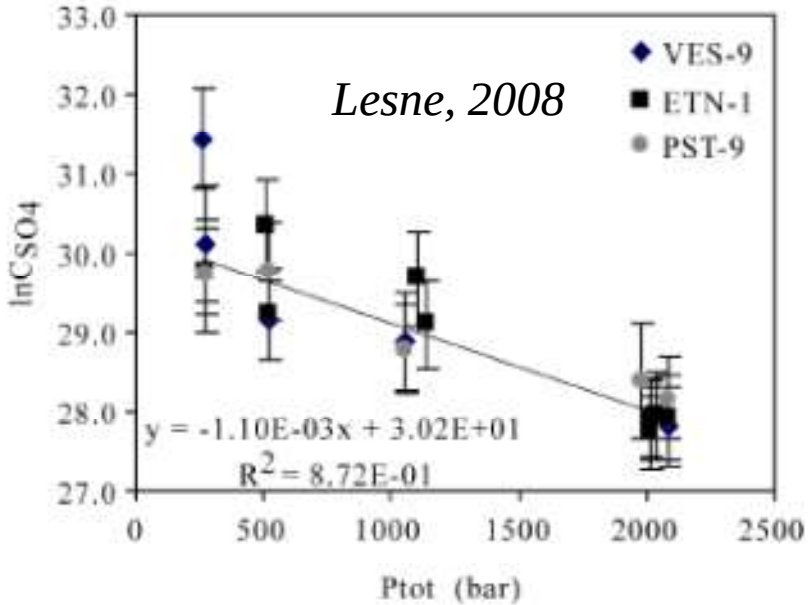
Natural-like melts (sulfur content)



Moretti and Ottonello (2005)

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





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

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

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

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

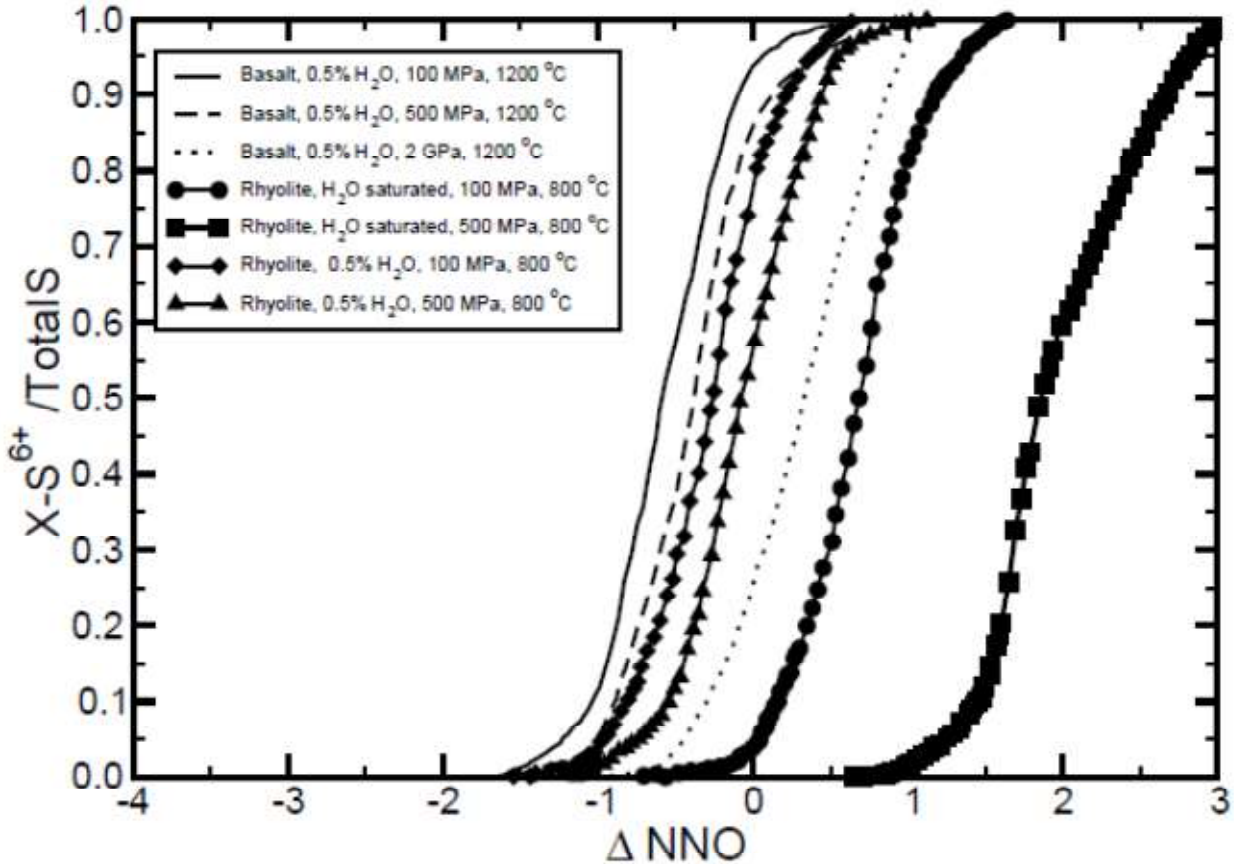
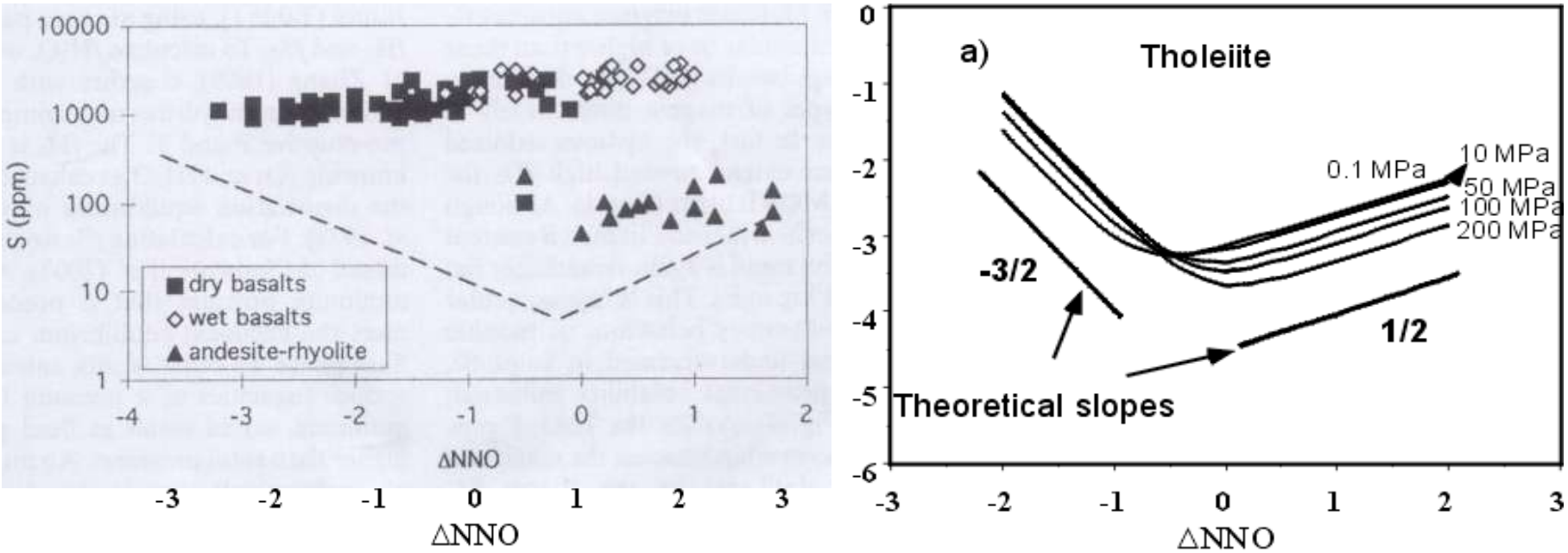


Figure 13. Comparison of the calculated molar ratio of S^{6+}/Total S (X-S^{6+}/Total S) in melts as a function of ΔNNO for basaltic and rhyolitic melts at different temperatures, pressures and water concentrations in the melt. Drawn after Moretti and Baker (2008). Note how unlike in Figure 8, the curves 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)

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.

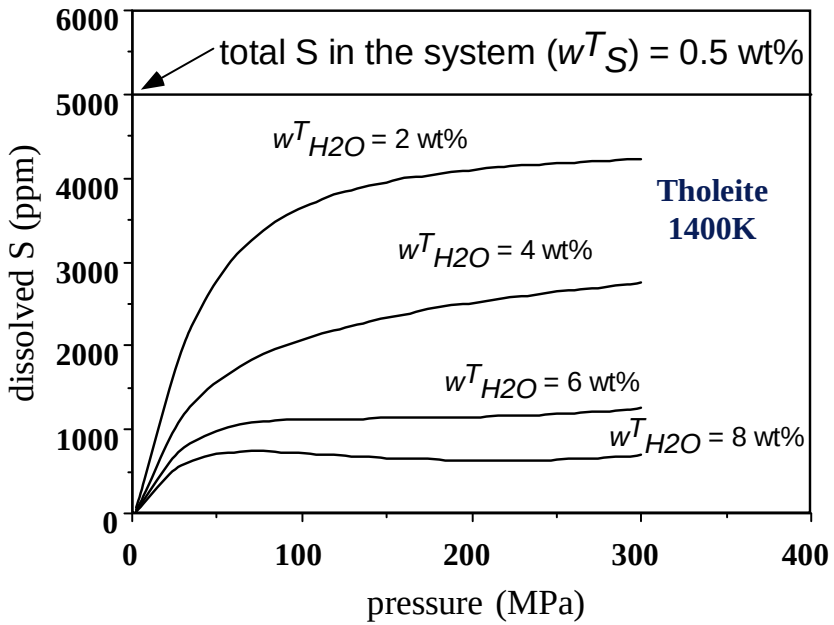
A Model for the Saturation of C–O–H–S Fluids in Silicate Melts

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

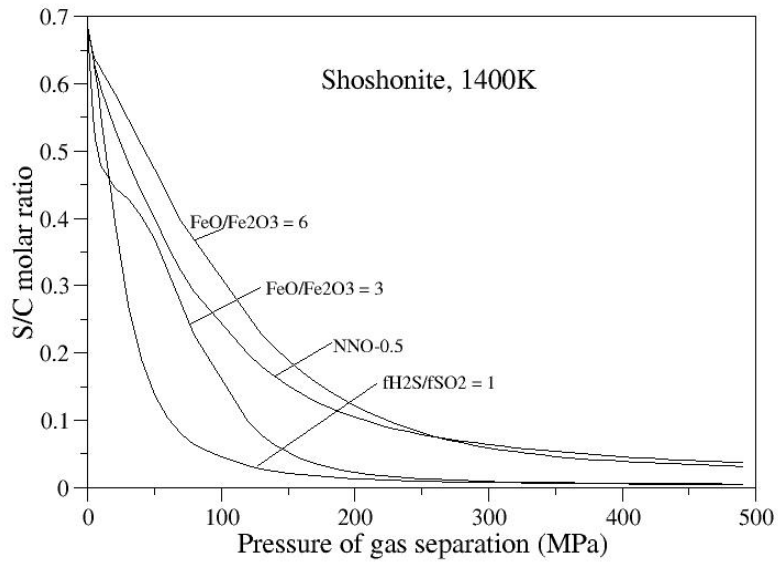
Volatile mixed "solubility"



(applicable to glass inclusions)

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

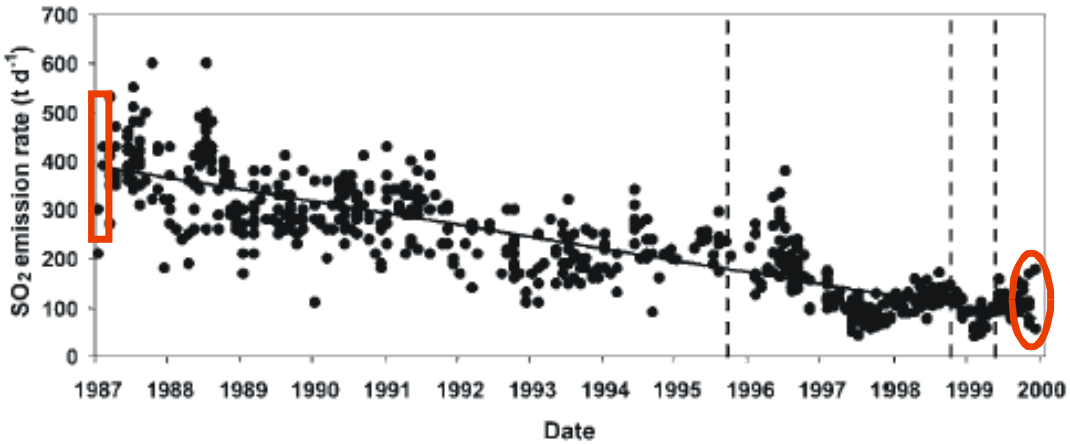
Single-step volatile separation

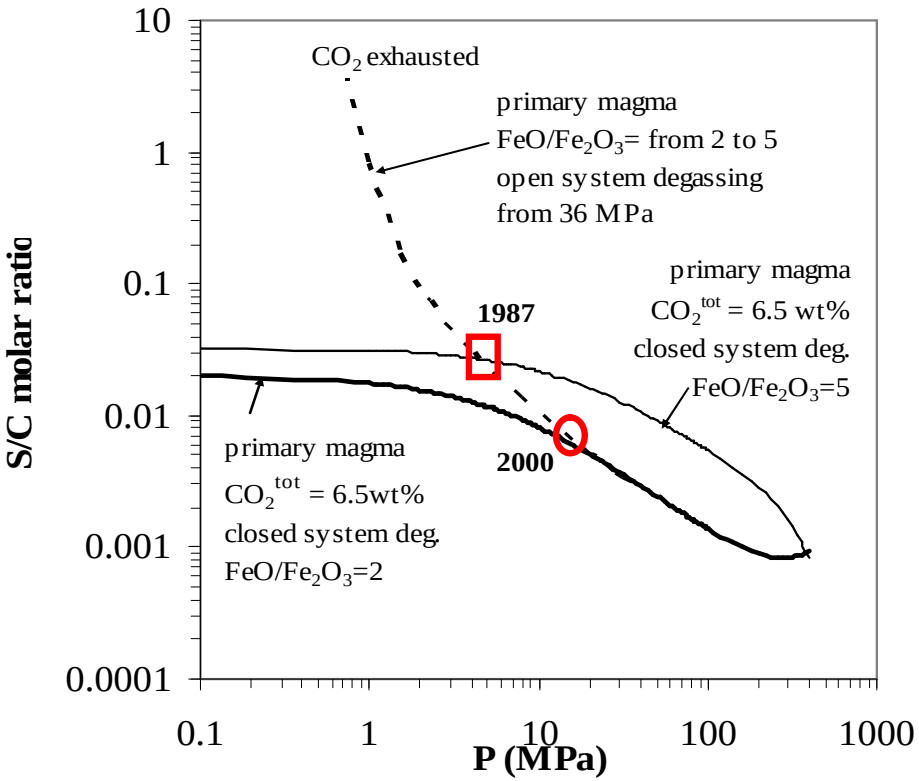


(applicable to the geochemical sensing of volcanoes)

The Kilauea example…

Summit SO_2 emission rates (1987-2000; Elias et al., 1998, Gerlach et al., 2002).



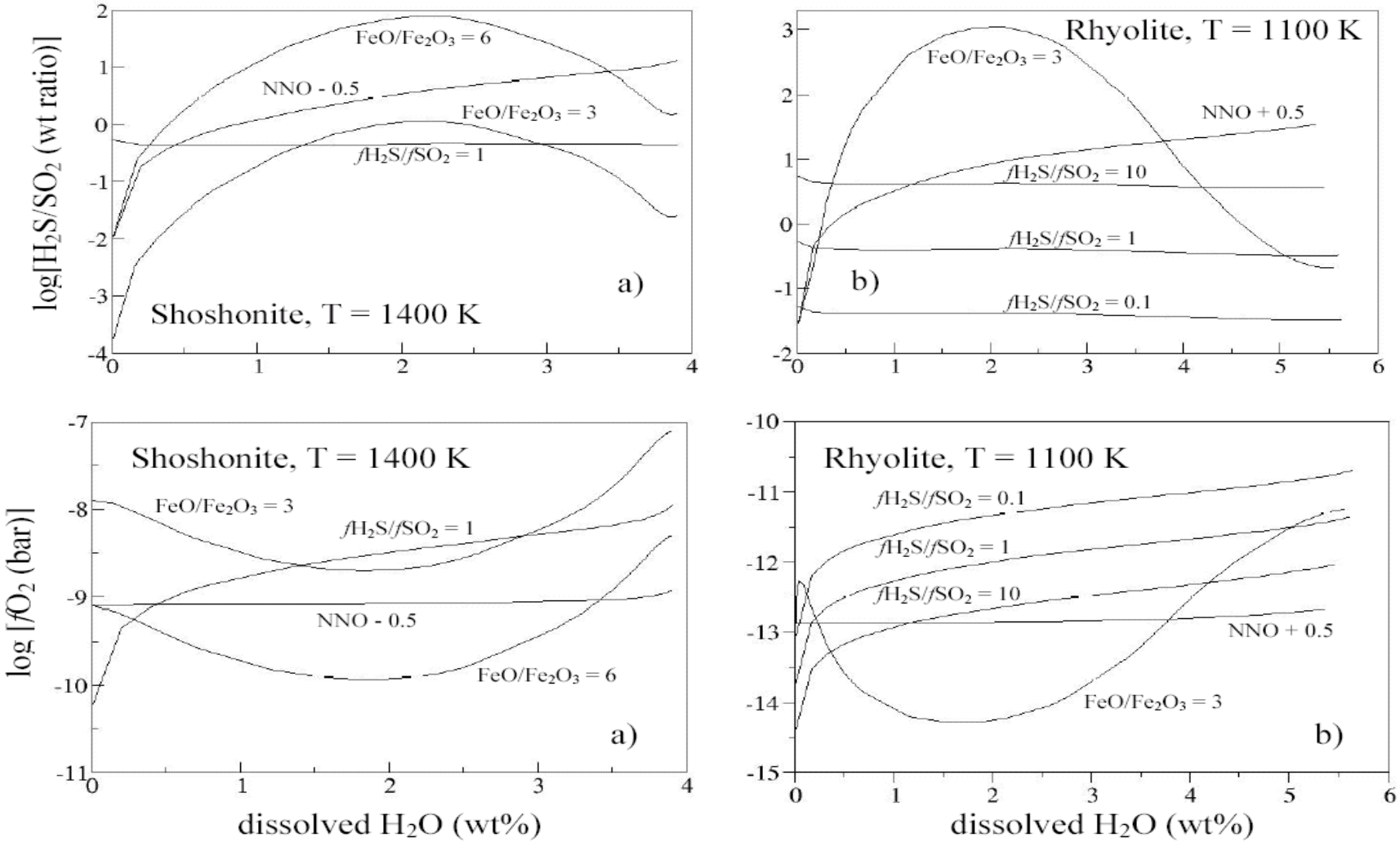


By assuming a CO_2 flux of 9000 tons/day, constant through years (Gerlach, 2002), the following S/C molar <u>average</u> ratios can be computed:

year 1987: S/C = 0.03

year 2000: S/C = 0.0075

→ From 1987 to 2000: downward migration of 7 Mpa (about 300 m.) of the main degassing surface (i.e., fresh magma arrival?) and onset of more oxidized conditions



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Chemical Geology 213 (2004) 265–280

CHEMICAL GEOLOGY
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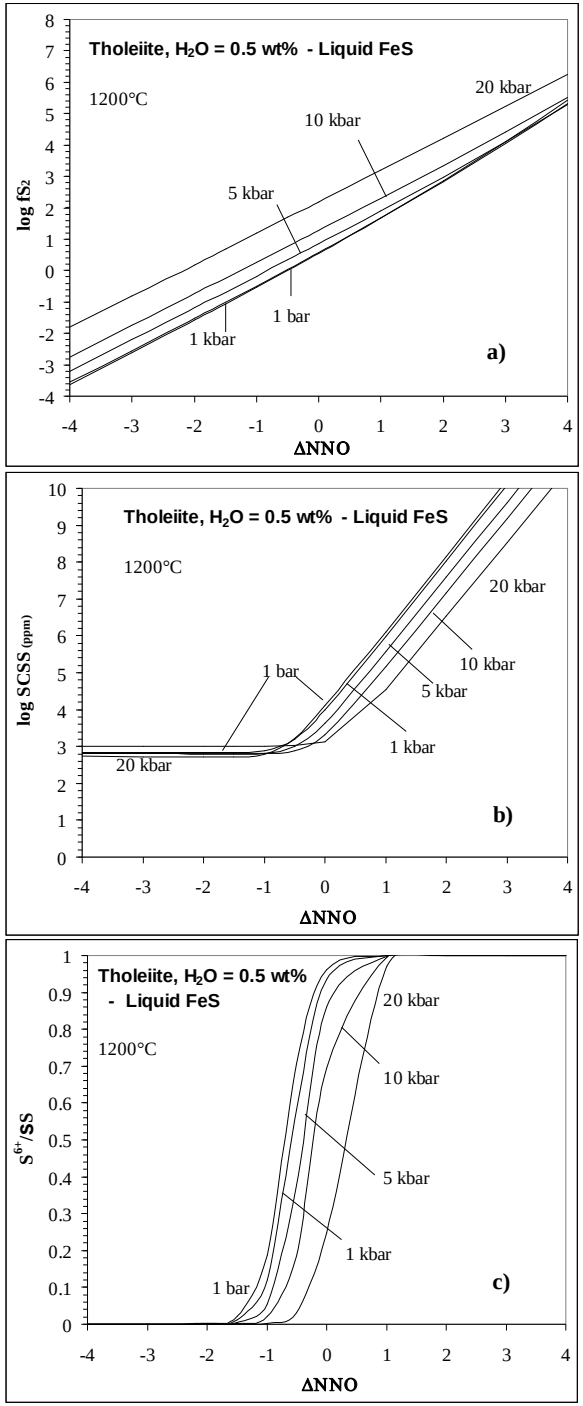
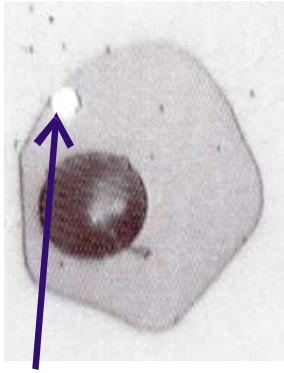
On the oxidation state and volatile behavior in multicomponent gas–melt equilibria

Roberto Moretti[a,*], Paolo Papale[b]

Moretti and Papale (2004) Chem. Geol.



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



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

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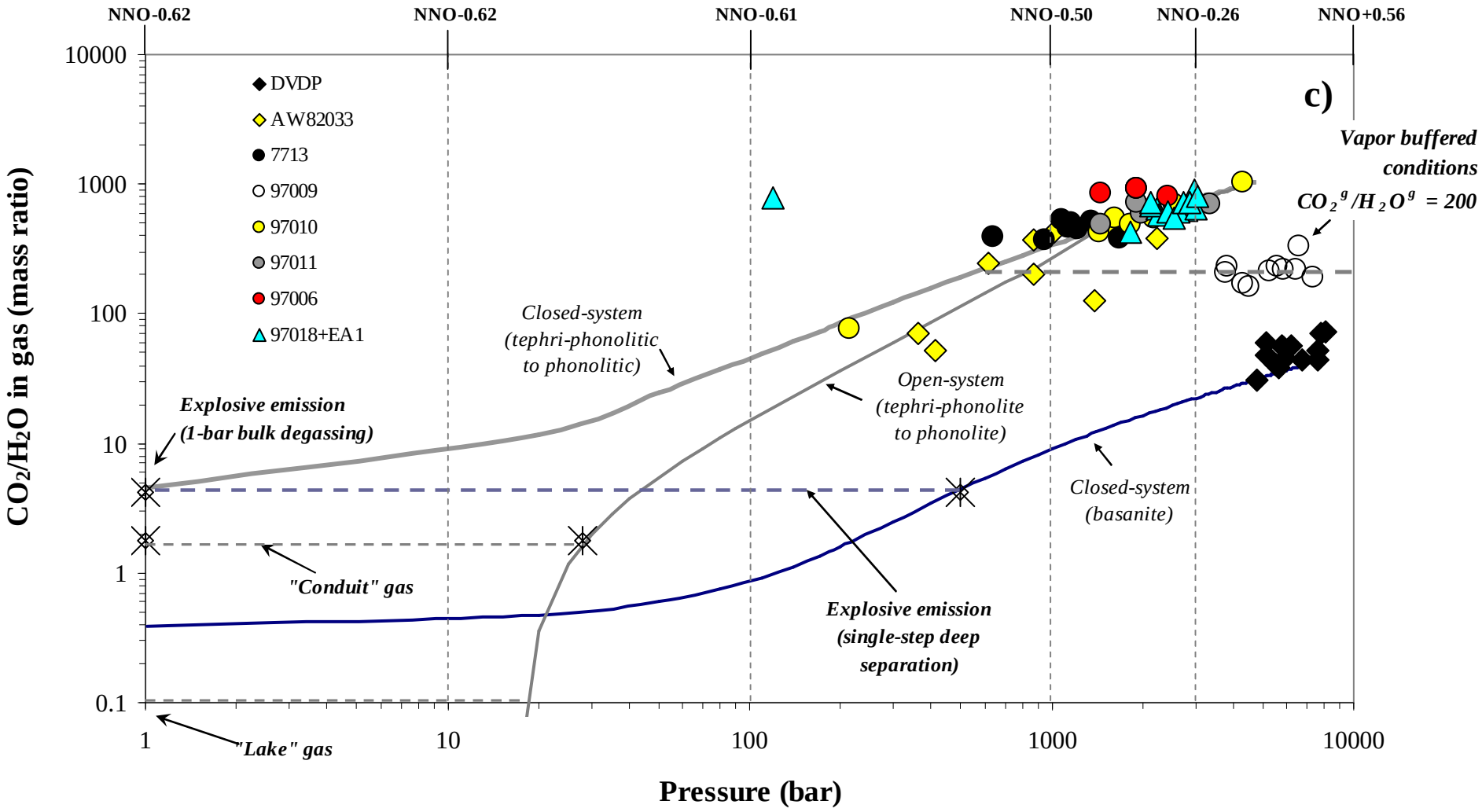
Modeling the interplay of fO_2 and fS_2 along the FeS-silicate melt equilibrium

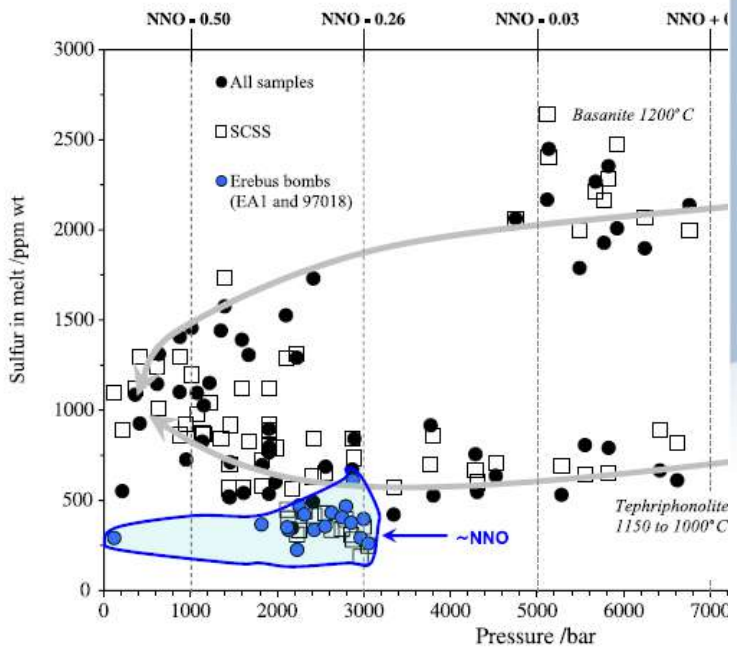
Roberto Moretti [a,*], Don R. Baker [b,c]

Open-conduit conditions (e.g., Erebus)



Oppenheimer et al. (2011)

Modelled CO_2^{gas}/H_2O^{gas} mass ratios



$$[S]_{wt.\%,SCSS} = [S]_{wt.\%,sulfide} +$$

Earth and Planetary Science Letters 306 (2011) 261–271

Contents lists available at ScienceDirect

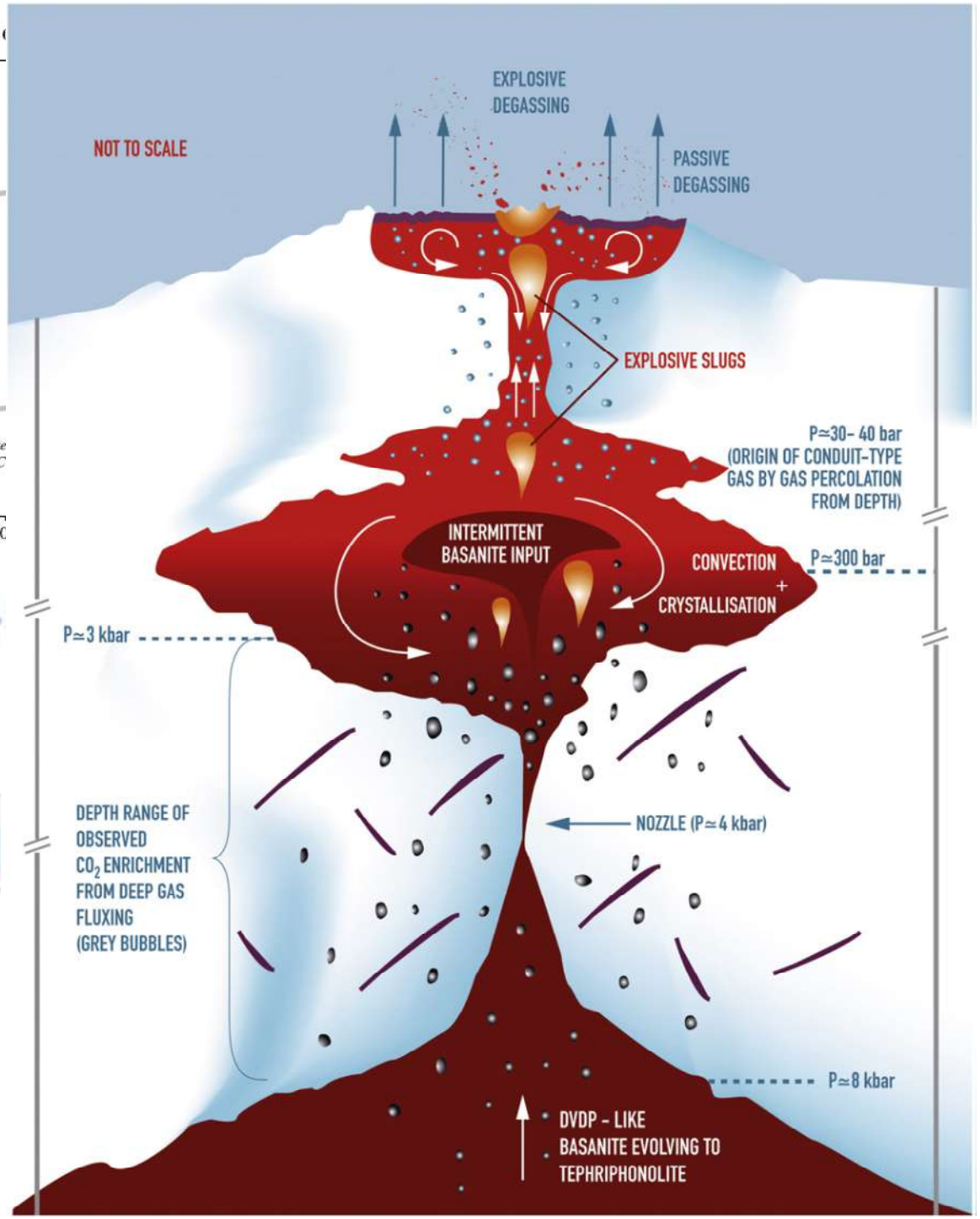
Earth and Planetary Science Letters

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

Mantle to surface degassing of alkalic magmas at Erebus volcano, Antarctica

Clive Oppenheimer [a,b,c,*], Roberto Moretti [d,e], Philip R. Kyle [f], Al Eschenbacher [f], Jacob B. Lowenstern [g], Richard L. Hervig [h], Nelia W. Dunbar [i]

Oppenheimer et al. (2011)



Montserrat – Soufrière Hills

Geochemistry Geophysics Geosystems G3
AN ELECTRONIC JOURNAL OF THE EARTH SCIENCES
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Article
Volume 11, Number 4
24 April 2010
Q04005, doi:10.1029/2009GC002781
ISSN: 1525-2027

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Excess volatiles supplied by mingling of mafic magma at an andesite arc volcano

M. Edmonds
COMET, National Centre for Earth Observation, Earth Sciences Department, University of Cambridge, Cambridge CB2 3EQ, UK (me2014@cam.ac.uk)

A. Aiuppa
Dipartimento CFTA, Università di Palermo, Via archirafi 36, I-90123 Palermo, Italy

M. Humphreys
Earth Sciences Department, University of Cambridge, Cambridge CB2 3EQ, UK

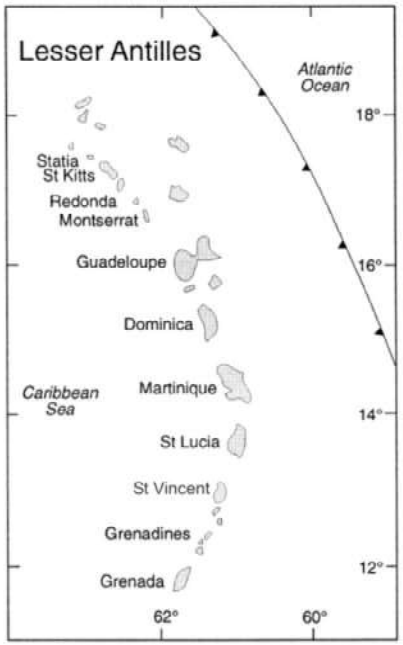
R. Moretti
Osservatorio Vesuviano, Istituto Nazionale di Geofisica e Vulcanologia, Via Diocleziano, 328, I-80124 Naples, Italy

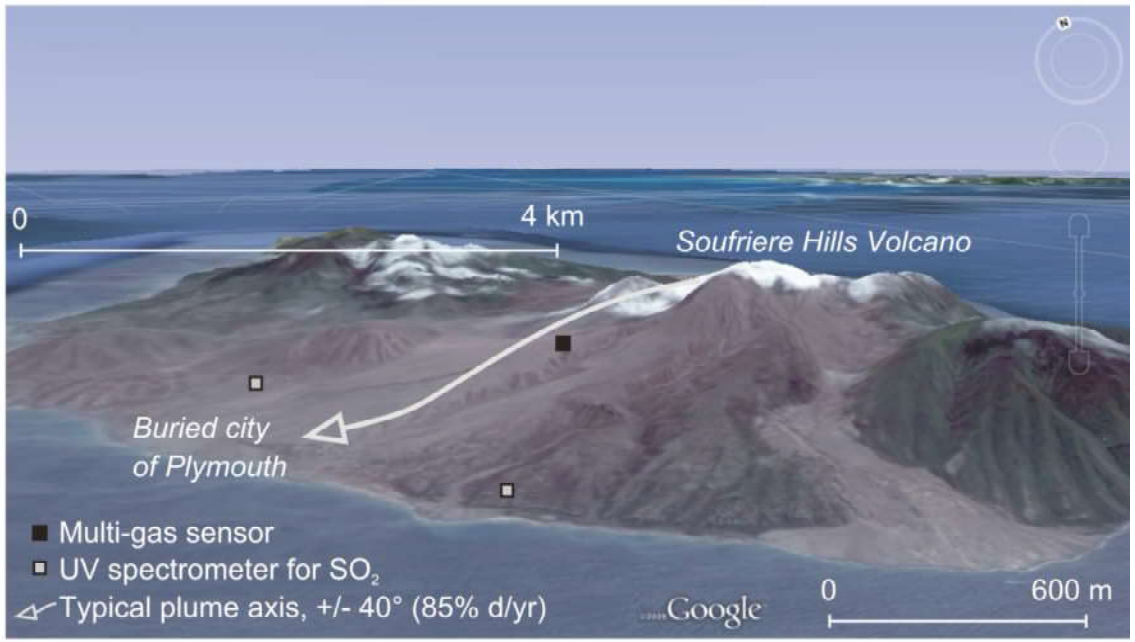
G. Giudice
Sezione di Palermo, Istituto Nazionale di Geofisica e Vulcanologia, Via Ugo La Malfa, 153, I-90146 Palermo, Italy

R. S. Martin
Earth Sciences Department, University of Cambridge, Cambridge CB2 3EQ, UK

R. A. Herd
School of Environmental Sciences, University of East Anglia, Norwich, NR4 7TJ, UK

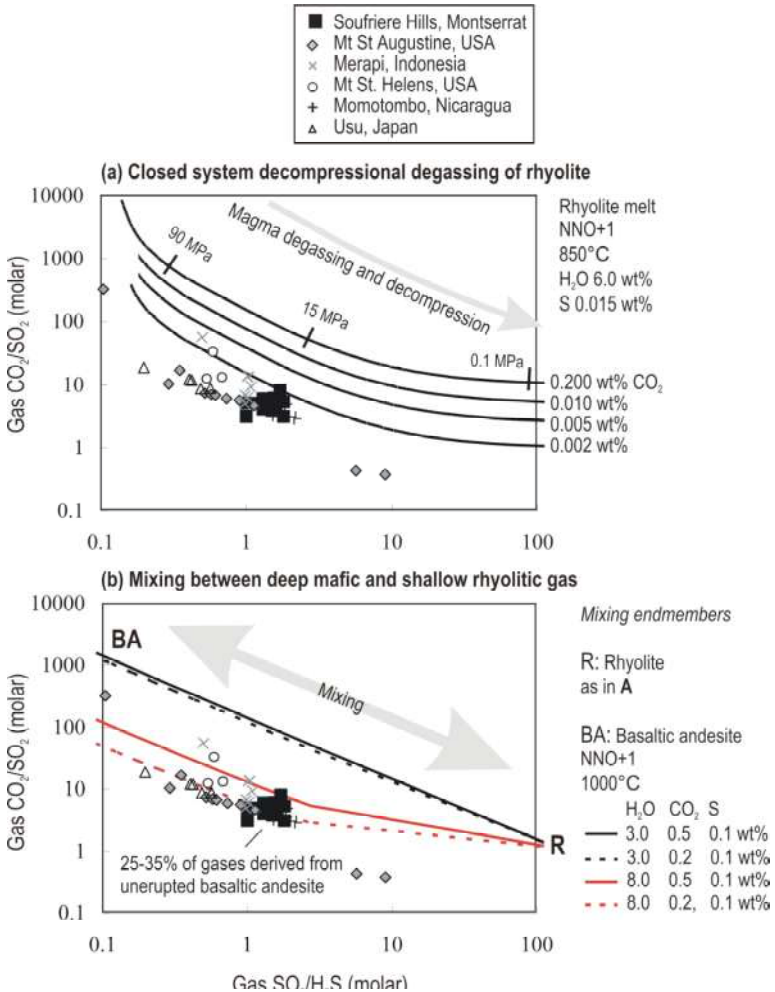
T. Christopher
Montserrat Volcano Observatory, Montserrat, West Indies

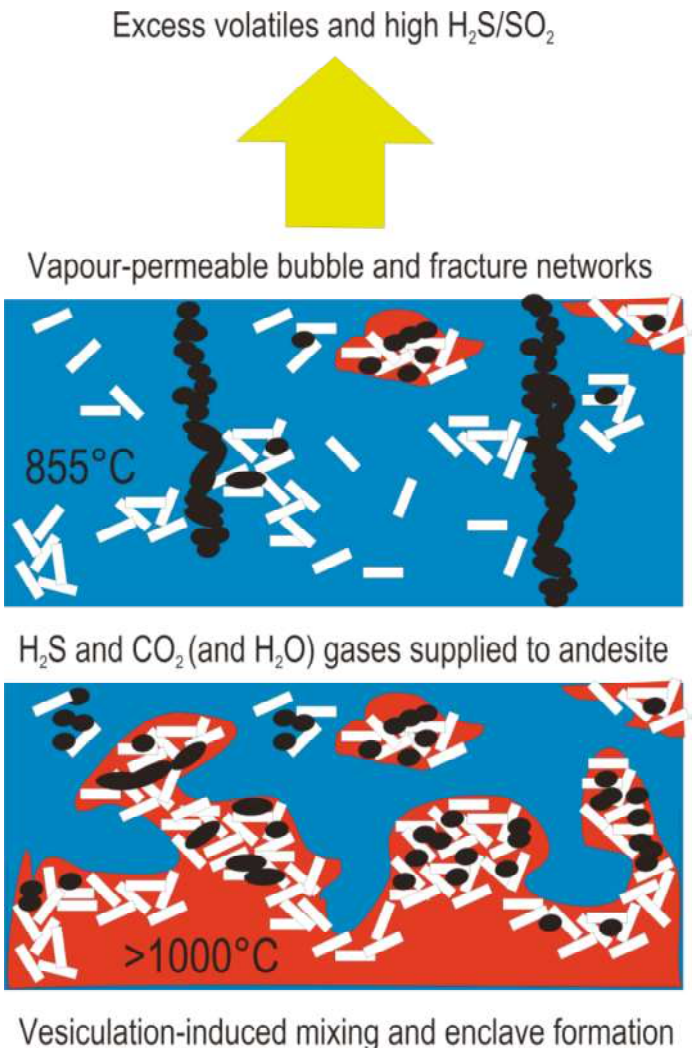




Problem: mafic enclaves ←→ excess volatiles ←→ high plume SO_2/H_2S

Edmonds et al. (2008)



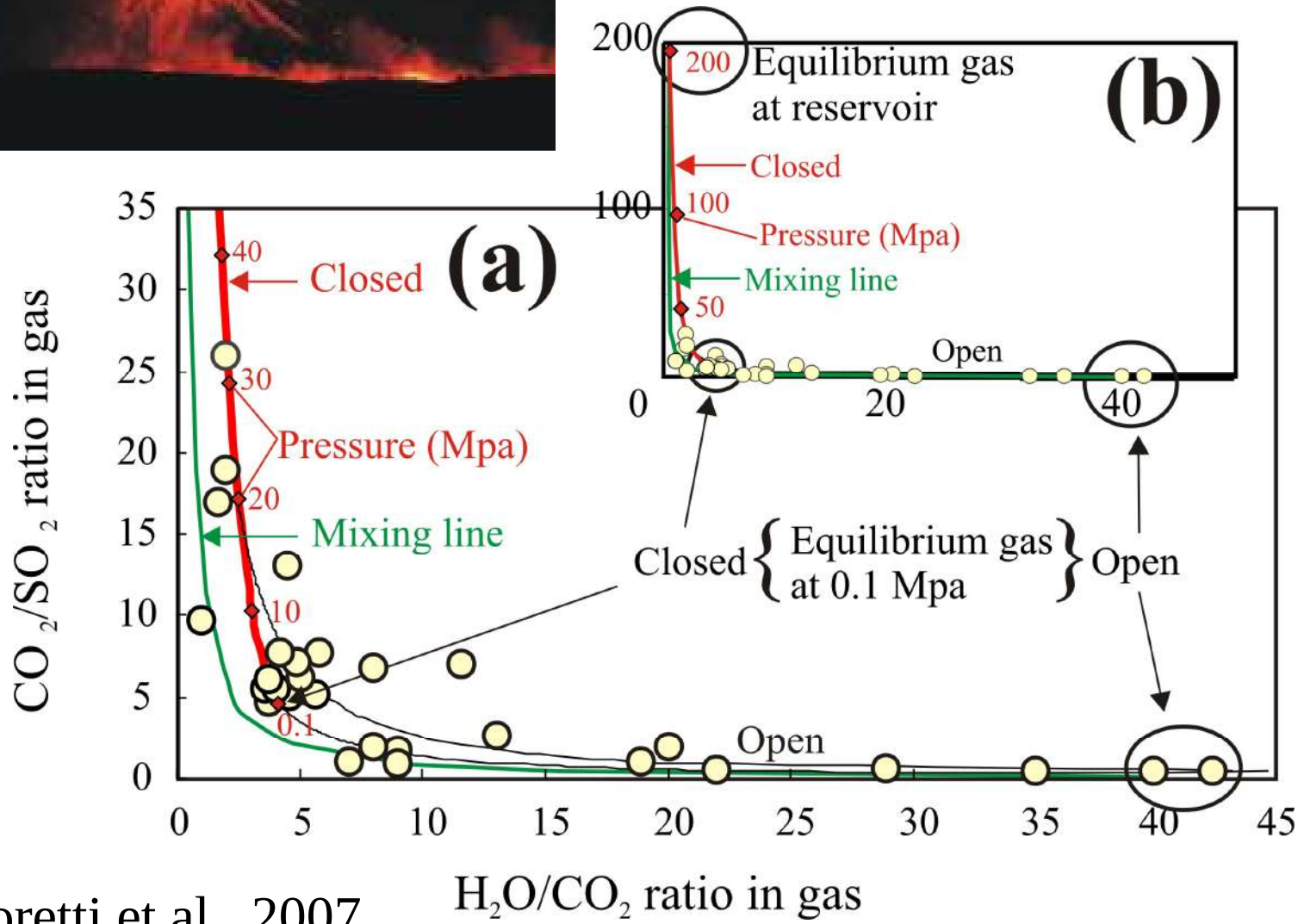


"….volatiles are supplied from a quenching, vesiculating mafic magma against a cooler, more crystalline andesitic magma in the crust "

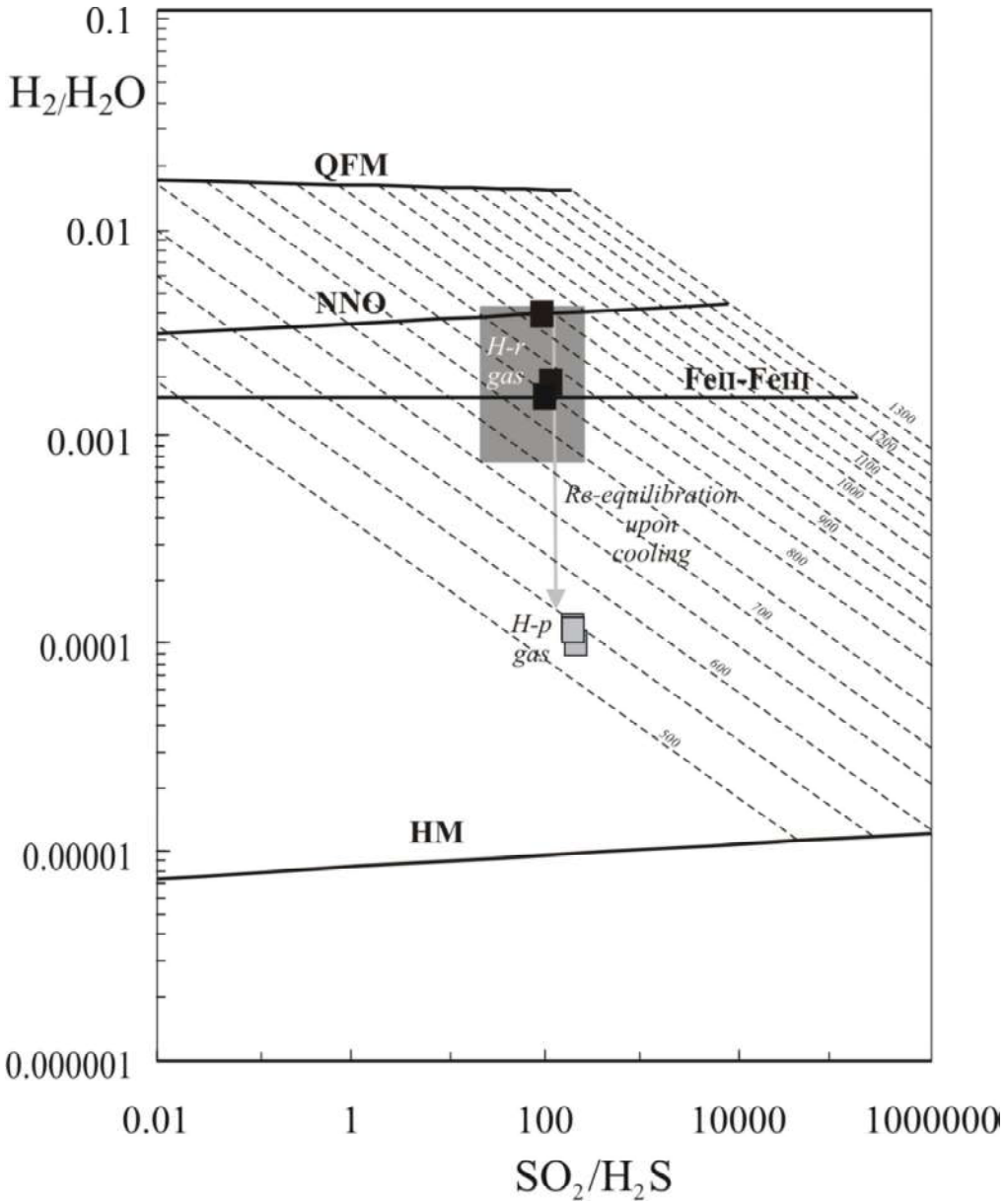
Open-conduit conditions (e.g., Etna…)

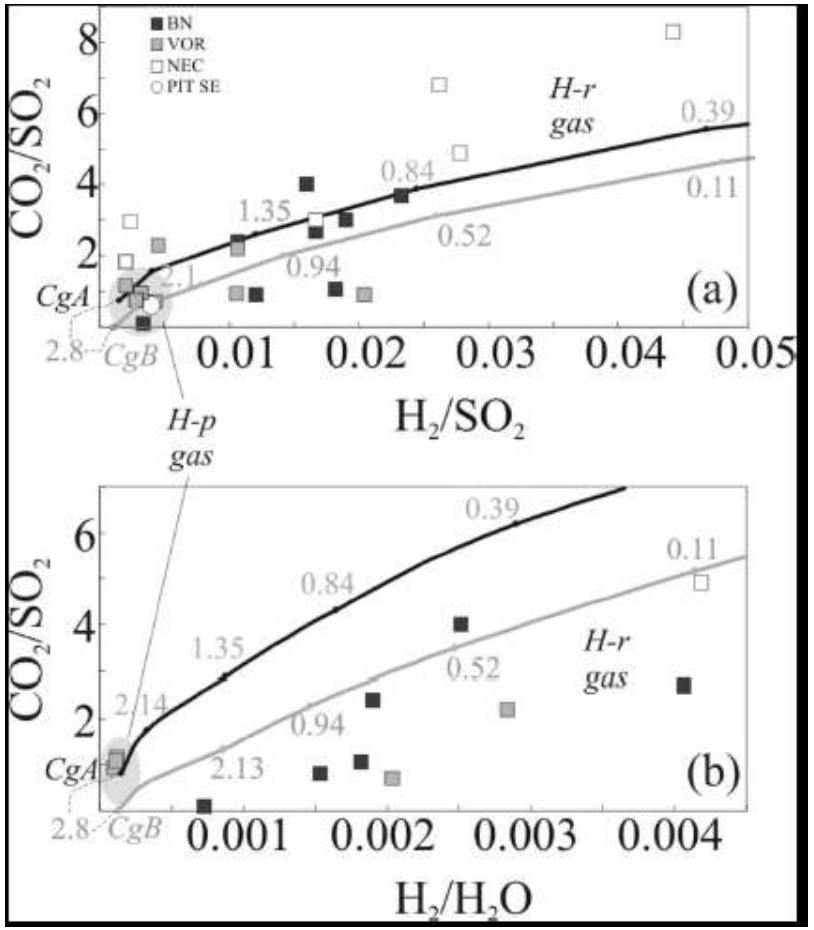
Aiuppa, Moretti et al., 2007

Open-conduit conditions (e.g., Etna…)



Aiuppa, Moretti et al., 2007

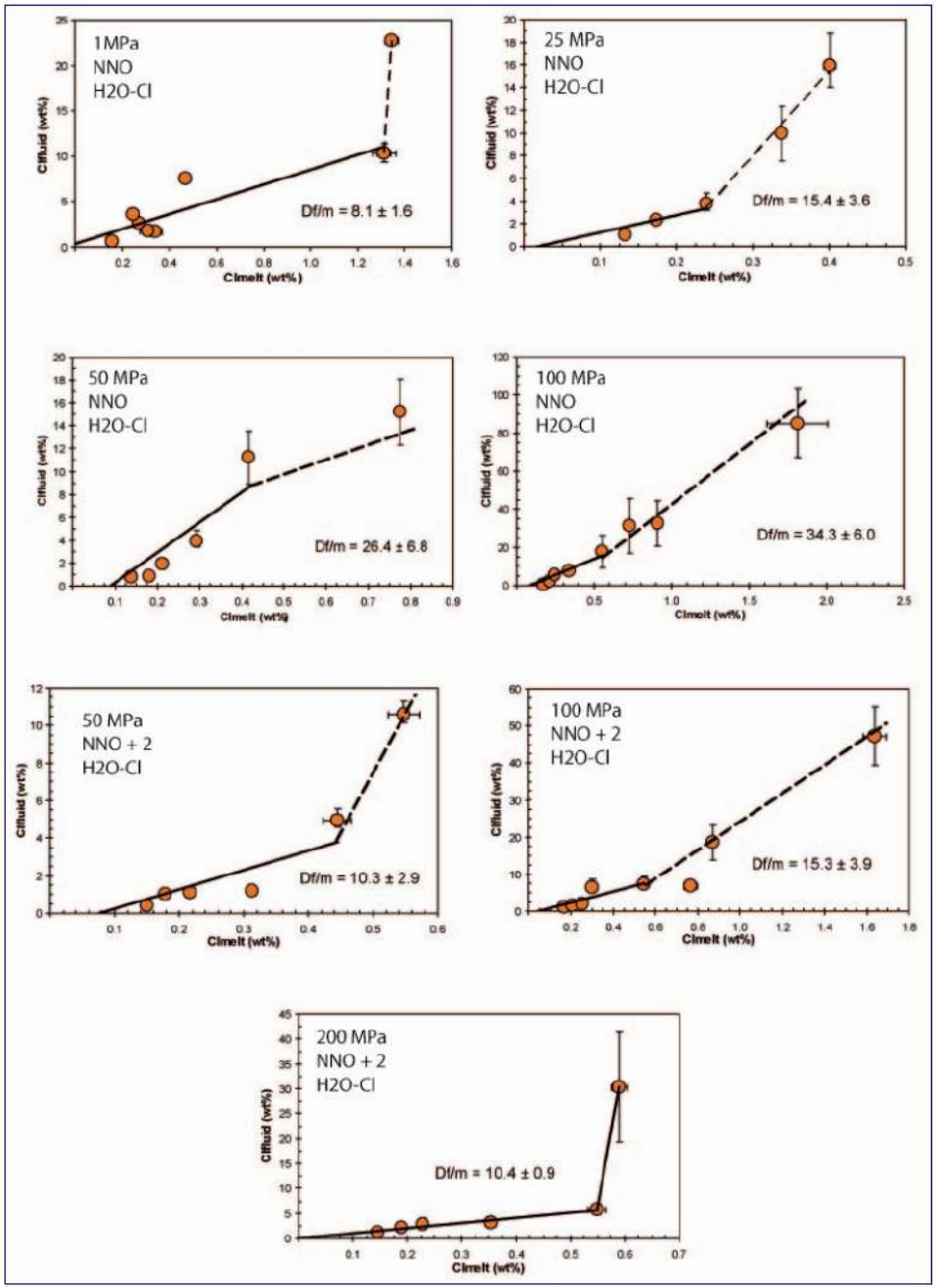




Aiuppa, Shinohara, Giudice, Liuzzo, Moretti (2011, JGR)

Partition coefficents (H_2O-Cl exps)

Alletti et al, 2009



In the ionic-polymeric approach we set the following equilibria:

$$\frac{1}{2}H_2O_{(gas)} + Cl^-_{(melt)} \Leftrightarrow HCl_{(gas)} + \frac{1}{2}O^{2-}_{(melt)}$$

which can be also derived from:

$$\frac{1}{4}O_{2(gas)} + Cl^-_{(melt)} \Leftrightarrow \frac{1}{2}Cl_{2(gas)} + \frac{1}{2}O^{2-}_{(melt)}$$

Hirosumi and Morita (2000; for chlorine)

by considering the following dissociations and redox couples:

$$\frac{1}{2}H_2O_{(gas)} \Leftrightarrow \frac{1}{2}H_{2\,(melt)} + \frac{1}{4}O_{2\,(melt)}$$ [Water dissociation]

$$HCl_{(gas)} \Leftrightarrow \frac{1}{2}H_{2\,(gas)} + \frac{1}{2}Cl_{2\,(melt)}$$ [Hydrogen chloride dissociation]

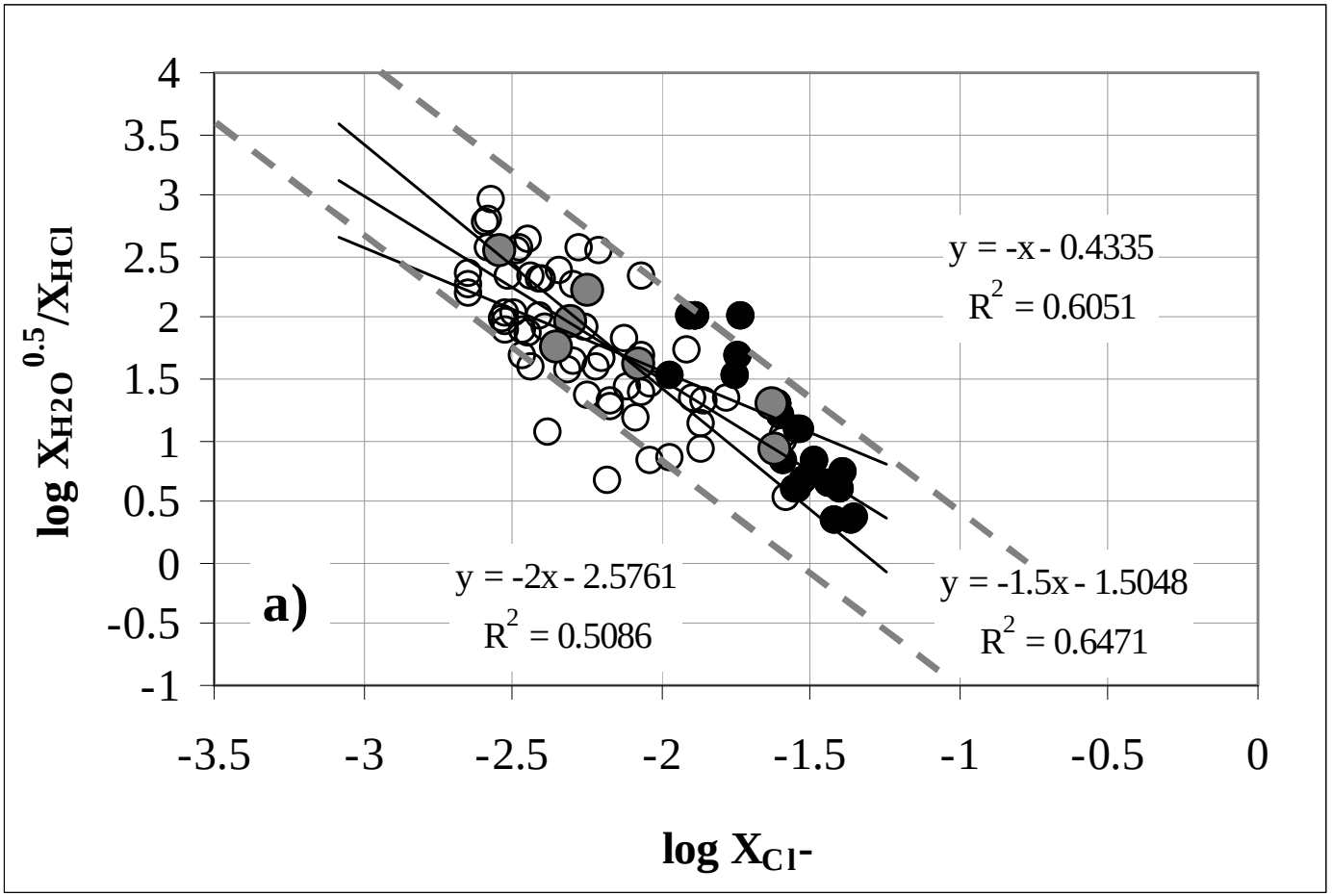
$$\frac{1}{2}Cl_2 + e^- \Leftrightarrow Cl^-$$ [Chlorine electrode]

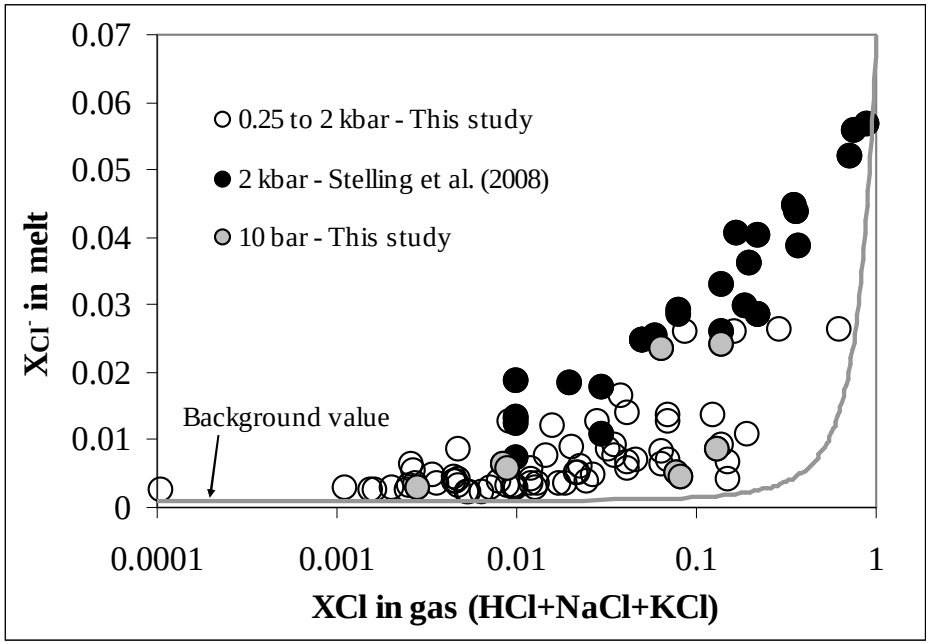
$$\frac{1}{4}O_2 + e^- \Leftrightarrow O^{2-}$$ [Oxygen electrode]

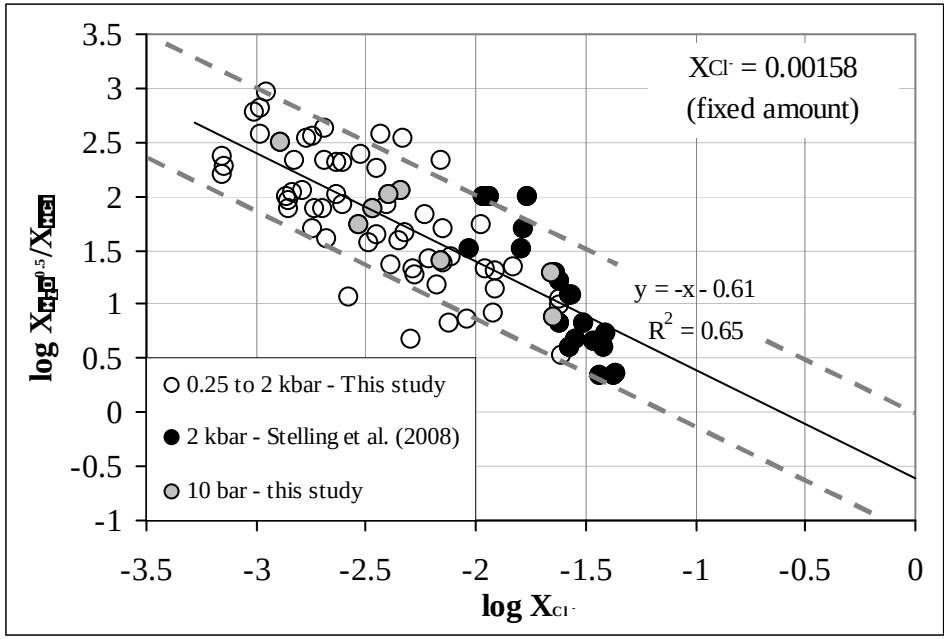
Moretti et al., in prep.

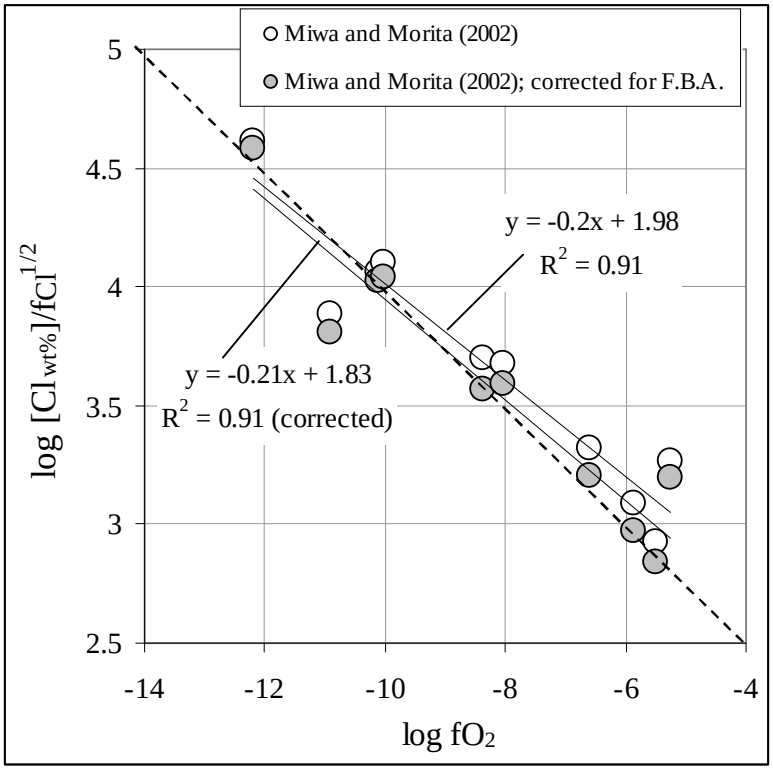
$$\tfrac{1}{2}H_2O(gas) + Cl^-(melt) \Leftrightarrow HCl(gas) + \tfrac{1}{2}O^{2-}(melt)$$

$$\log \frac{X_{H_2O,gas}^{1/2}}{X_{HCl,gas}} = -\log K_3^* - \log X_{Cl^-}^{melt}$$









$$D^* = \frac{X_{HCl}}{X_{Cl^-}^{2}} = X_{H2O}^{1/2} \cdot 10^{2.5761}$$

Moretti et al., in progress

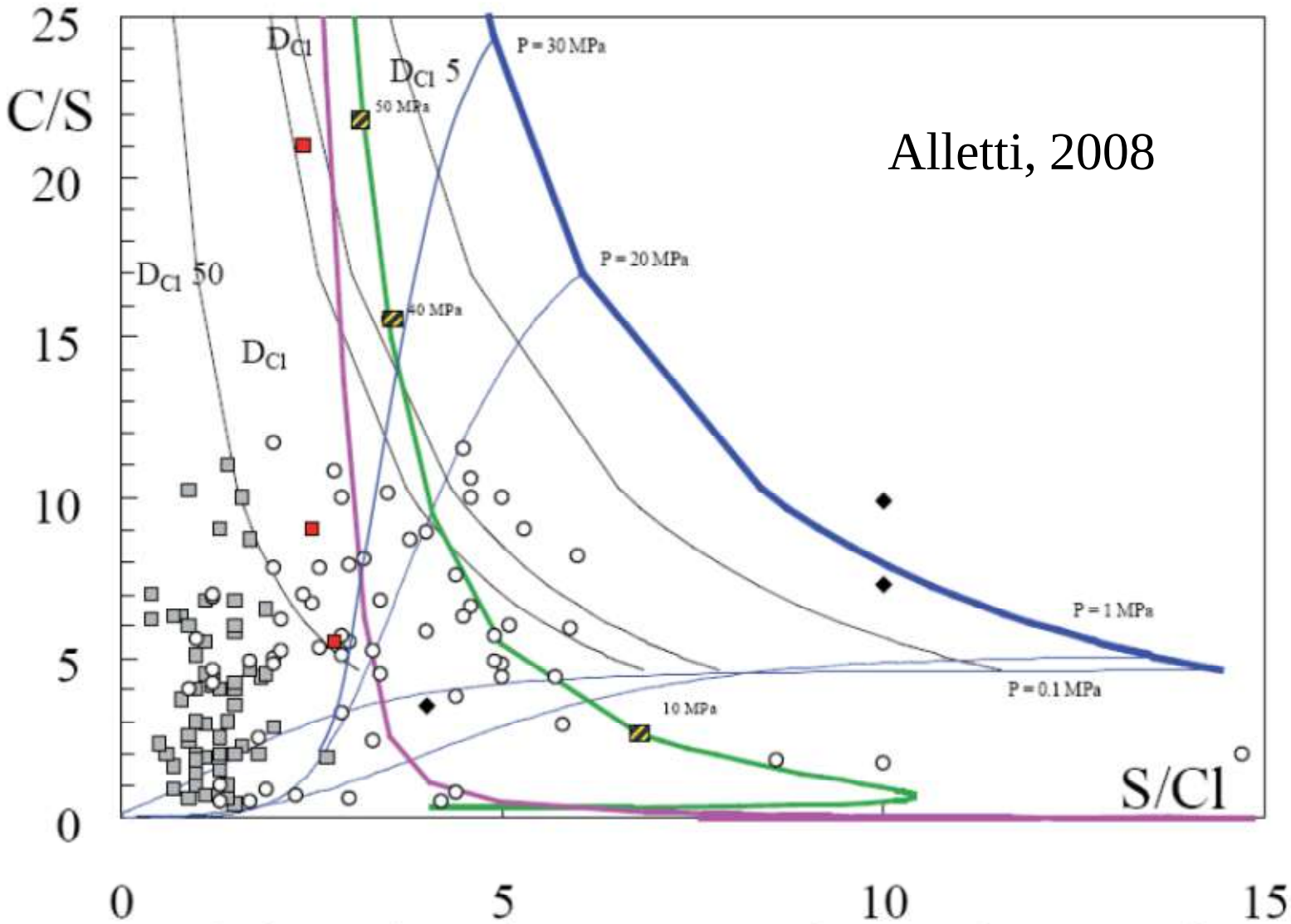
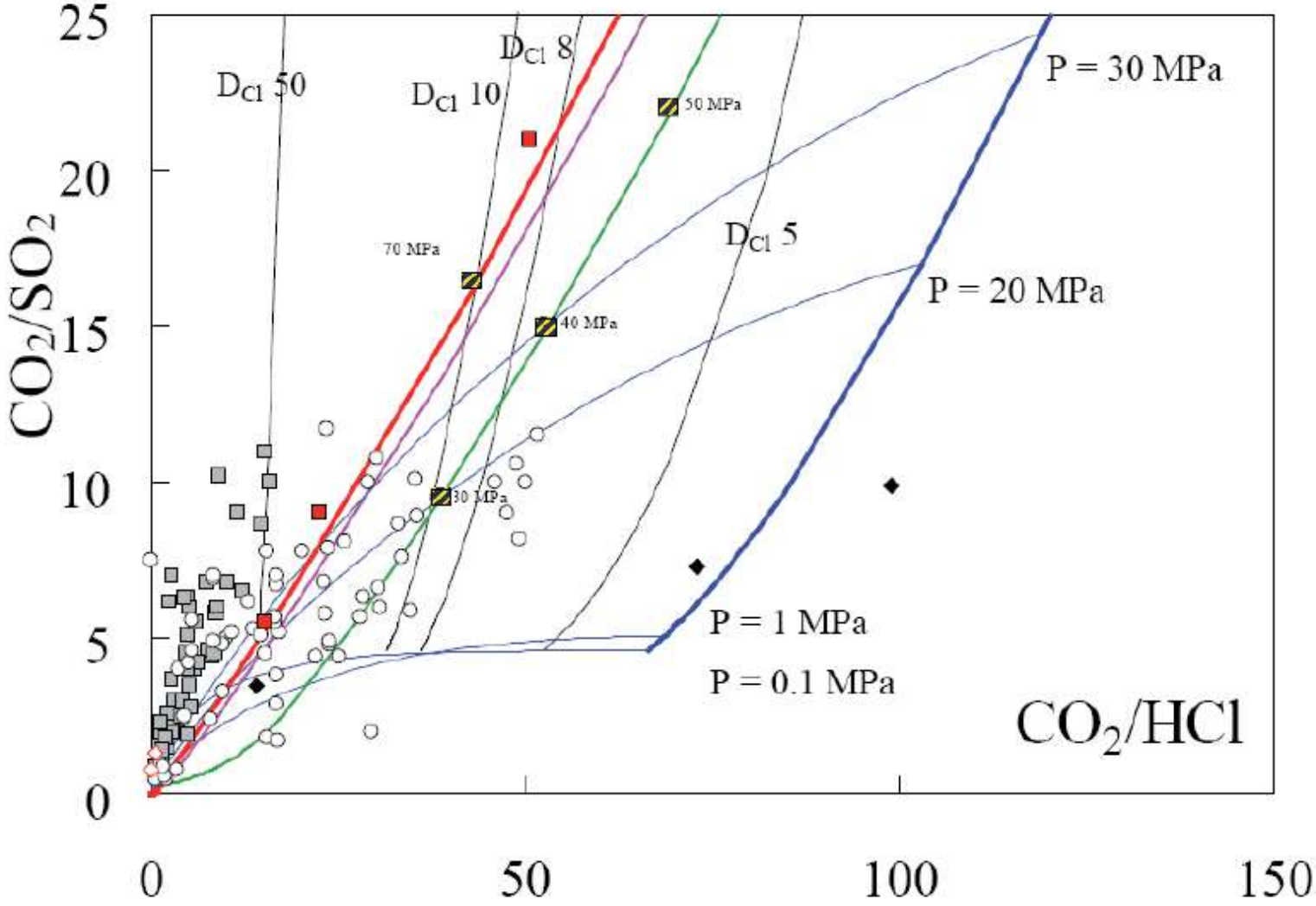


Fig. 30: SO_2/HCl vs. CO_2/SO_2 molar ratios in Etna's volcanic gas plume, contrasted against model results for the magmatic gas phase (symbols as in Fig. 25).

Alletti, 2008



Gas fluxing determines the detected K-enrichment by stripping K to the gas phase as KCl.

=> the measured K variability reflects the **K-gain**, by some portions of the magmatic system, that **superimposes to the normal trend of fractional crystallization**.

By considering KCl and HCl as the most important gas species, the following chemical reactions can be written:

$$HCl_{gas} + 1/2K_2O_{melt} \Leftrightarrow KCl_{melt} + 1/2H_2O_{gas} \qquad (1)$$

$$KCl_{melt} \Leftrightarrow KCl_{gas} \qquad (2)$$

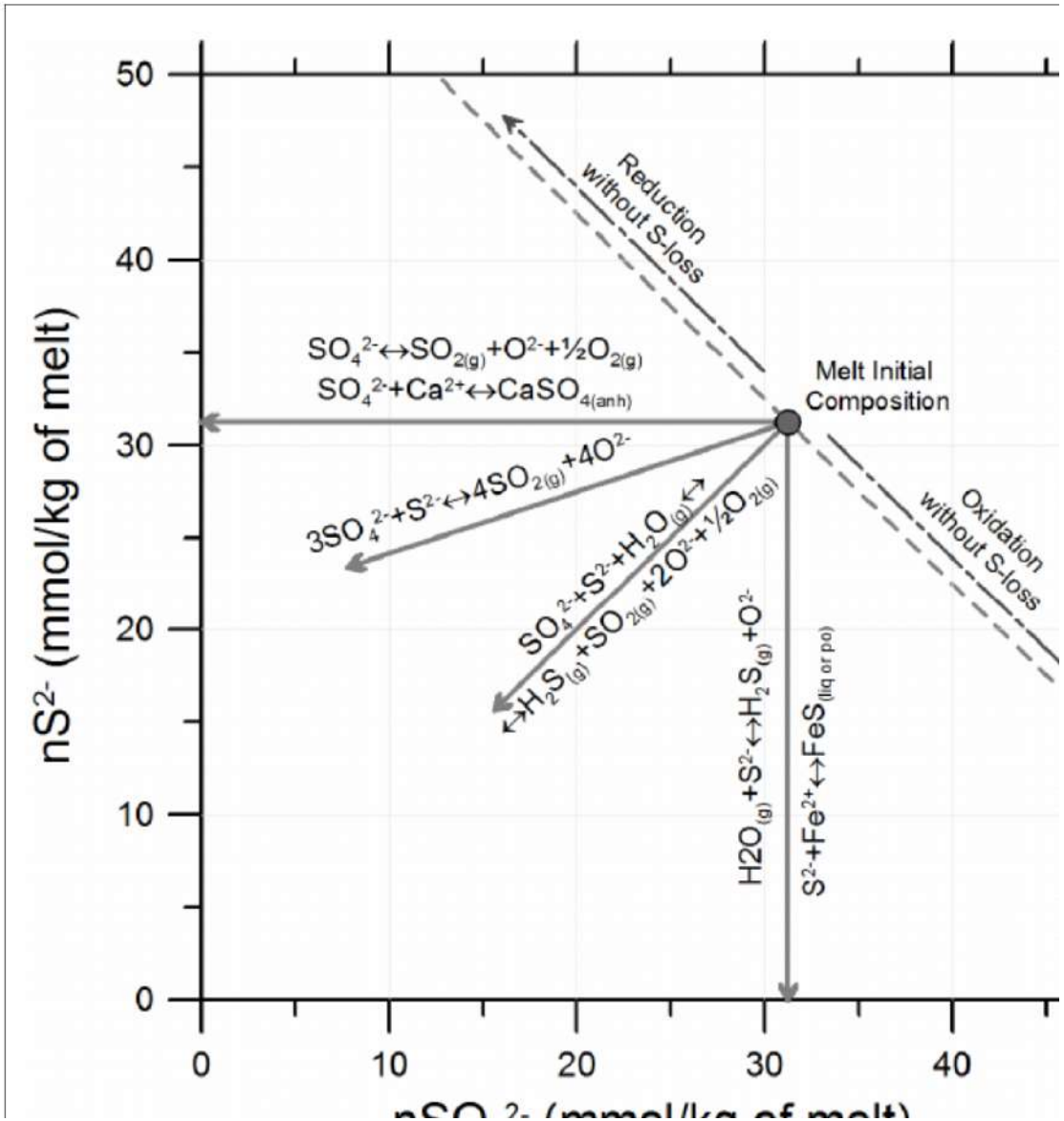
From their equilibrium constants:

$$\log a_{KCl_{melt}} = \log a_{KCl_{gas}} - \log K_2 = \log \frac{a_{HCl_{gas}}}{a_{H_2O_{gas}}^{1/2}} + \log a_{K_2O_{melt}} + \log K_1$$

Moretti et al. JPet (accepted)

If K_2O=const ➔ $\frac{a_{HCl_{gas}}}{a_{H_2O_{gas}}^{1/2}}$ increases due to CO_2-fluxing and dehydration

➔ $a_{KCl_{melt}}$ increases, hence $X_{KCl_{melt}}$ increases



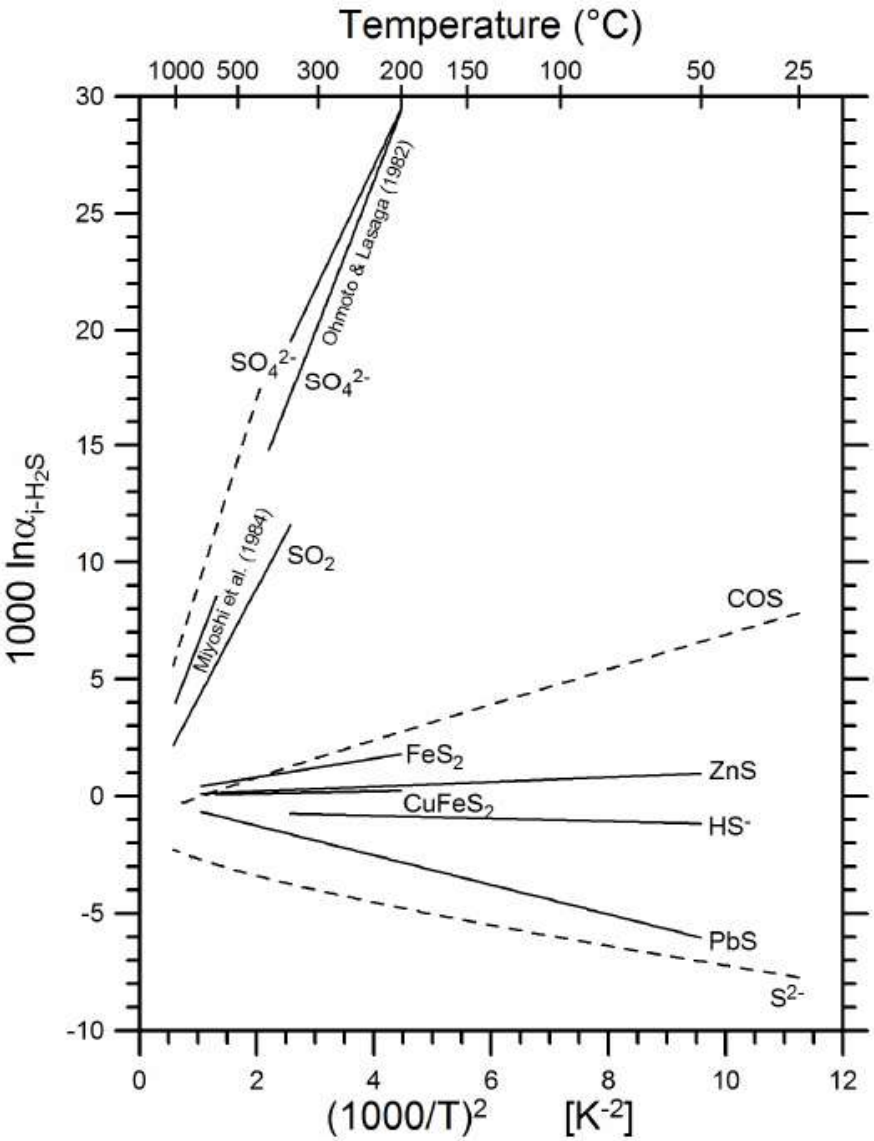
S-species and reactions involved in the <u>full tracking</u> of volcanic degassing…

High reactivity

↓

many degassing paths

Marini, Moretti & Accornero (2011) RiMG 73



Ohmoto-Rye, 1979

$$\delta^{34}S_{\Sigma S} = \delta^{34}S_{SO_2} \cdot y_{SO_{2(g)}} + \delta^{34}S_{H_2S} \cdot \left(1 - y_{SO_{2(g)}}\right),$$

$$y_{SO_{2(g)}} = X_{SO_{2(g)}} \Big/ \left(X_{SO_{2(g)}} + X_{H_2S_{(g)}}\right).$$

$$1000 \ln \alpha_{SO_2-H_2S} = \delta^{34}S_{SO_2} - \delta^{34}S_{H_2S}$$

Degassing…

$$\delta^{34}S_{\Sigma S,f} = \delta^{34}S_{\Sigma S,i} - (1 - F) \cdot 1000 \ln \alpha_{gas-melt}$$ (closed s.)

$$\delta^{34}S_{\Sigma S,f} = \delta^{34}S_{\Sigma S,i} + 1000 \cdot \left(F^{\alpha_{gas-melt}-1} - 1\right)$$

$$F = C_{\Sigma S,melt,f} / C_{\Sigma S,melt,i}$$

Marini et al.
(2011)

Nordstrom and Munoz, 1986

Degassing…

$$1000\ln\alpha_{gas-melt} \cong \delta^{34}S_{\Sigma S,gas} - \delta^{34}S_{\Sigma S,melt} =$$

$$= \left[Y_{SO_2}\cdot\delta^{34}S_{SO_2} + \left(1 - Y_{SO_2}\right)\cdot\delta^{34}S_{H_2S}\right] - \left[Y_{SO_4^{2-}}\cdot\delta^{34}S_{SO_4^{2-}} + \left(1 - Y_{SO_4^{2-}}\right)\cdot\delta^{34}S_{S^{2-}}\right] =$$

$$= Y_{SO_2}\cdot 1000\ln\alpha_{SO_2-H_2S} + Y_{SO_4^{2-}}\cdot 1000\ln\alpha_{S^{2-}-SO_4^{2-}} + 1000\ln\alpha_{H_2S-S^{2-}}$$

where $Y_{SO_4^{2-}}$ and Y_{SO_2} are defined as:

$$Y_{SO_4^{2-}} = X_{SO_4^{2-}}/(X_{SO_4^{2-}} + X_{S^{2-}})\,;\; Y_{SO_2} = X_{SO_2}/(X_{SO_2} + X_{H_2S})$$

$$1000\ln\alpha_{SO_2-H_2S} = -0.42\cdot\left(10^3/T\right)^3 + 4.367\cdot\left(10^3/T\right)^2 - 0.105\cdot\left(10^3/T\right) - 0.41$$

$$1000\ln\alpha_{H_2S-S^{2-}} = 1.1\cdot\left(10^3/T\right)^2 - 0.19\,.$$

Taylor, 1986

We MUST know <u>how $Y_{SO_4^{2-}}$ and $Y_{S^{2-}}$ are related to P, T and composition</u>

Sulfide separation…

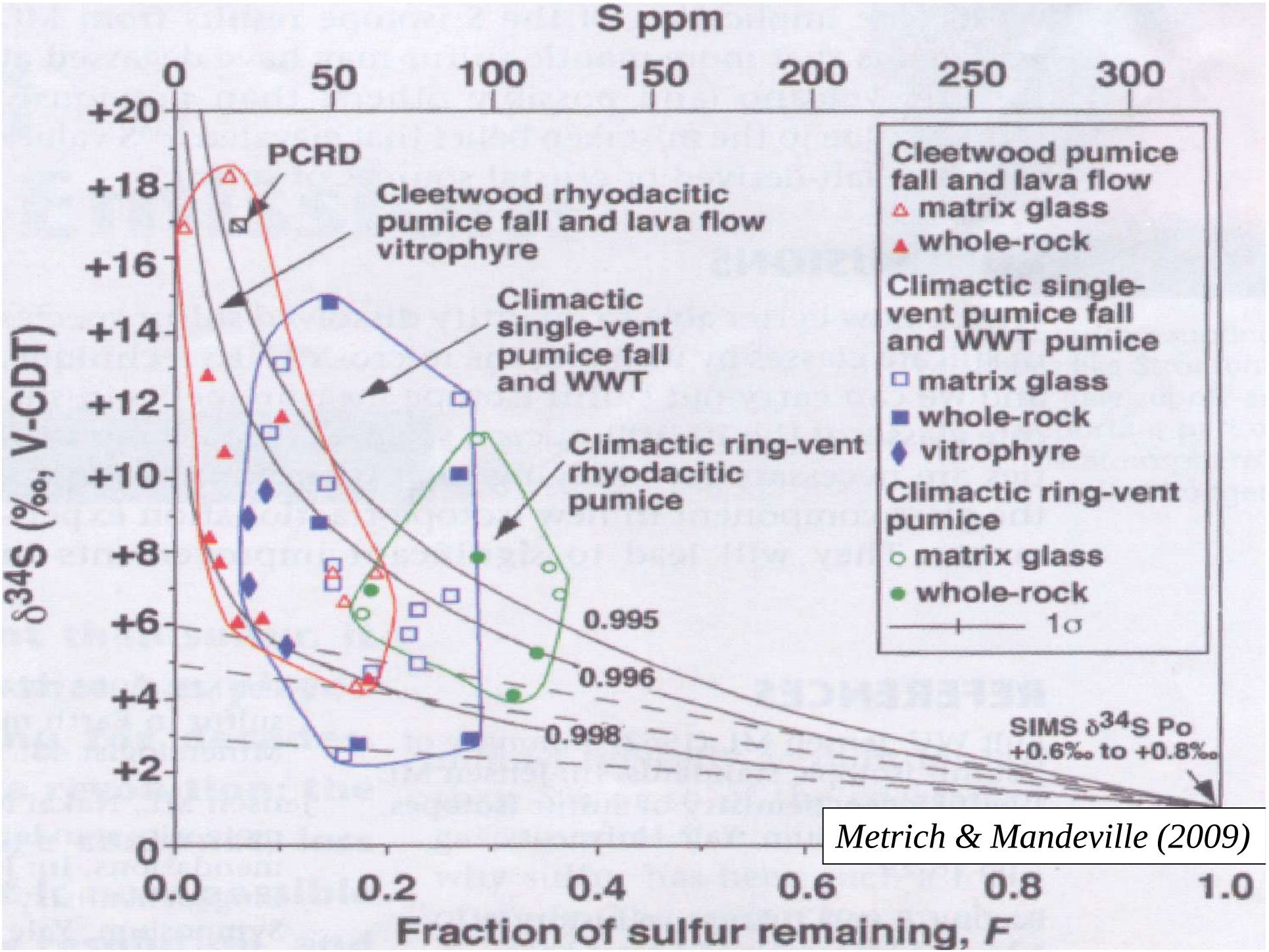
$$1000\ln\alpha_{FeS-melt} \cong \delta^{34}S_{FeS} - \delta^{34}S_{\Sigma S,melt} =$$
$$= \delta^{34}S_{FeS} - \left[Y_{SO_4^{2-}} \cdot \delta^{34}S_{SO_4^{2-}} + \left(1 - Y_{SO_4^{2-}}\right) \cdot \delta^{34}S_{S^{2-}}\right] =$$
$$= Y_{SO_4^{2-}} \cdot 1000\ln\alpha_{S^{2-}-SO_4^{2-}} + 1000\ln\alpha_{FeS-H_2S} + 1000\ln\alpha_{H_2S-S^{2-}}$$

Set by taking pyrrhotite…

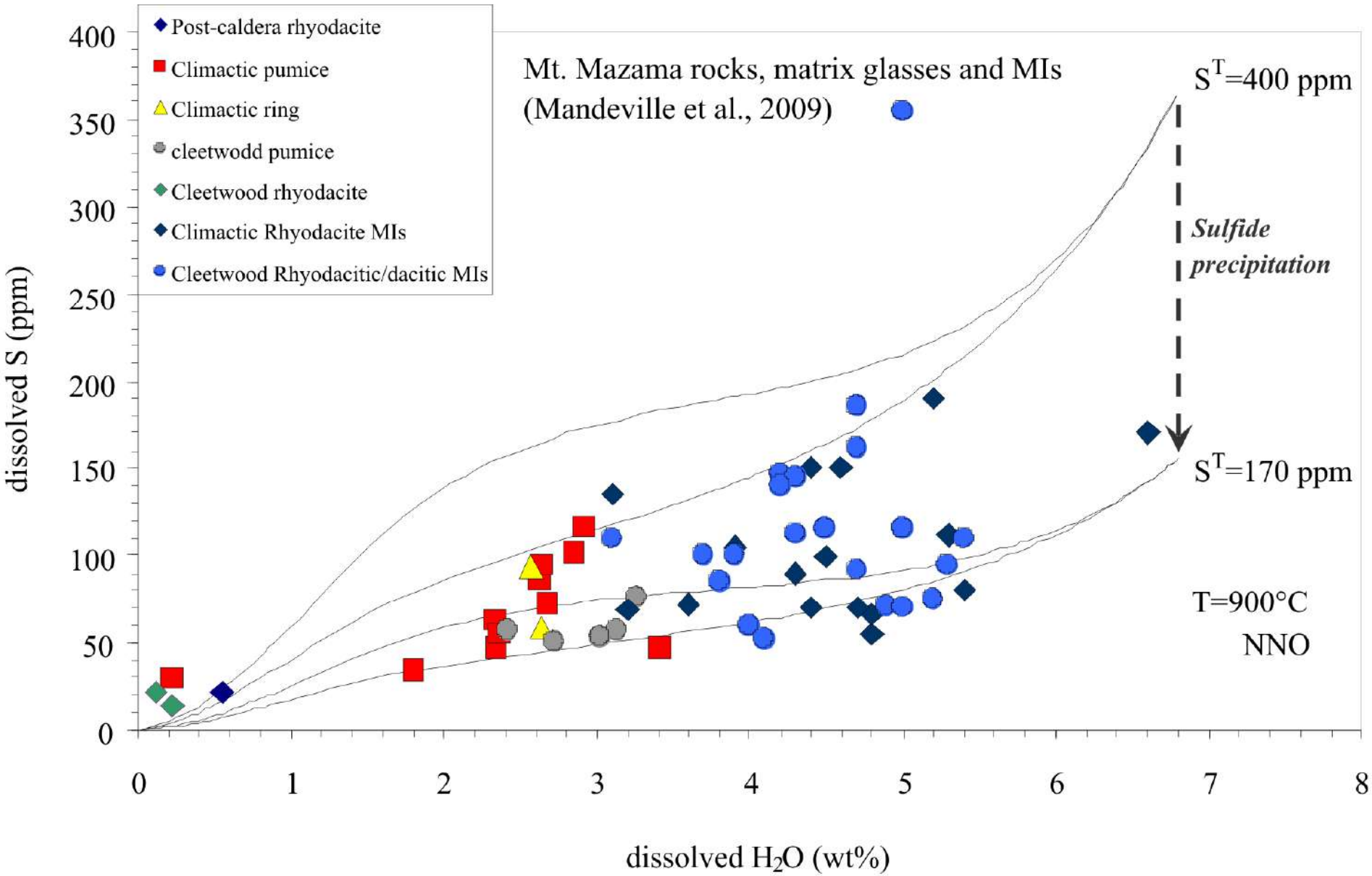
Considered to be valid for FeS liquids (…it also approximates FeOS liquids)

$$1000\ln\alpha_{FeS-H_2S} = 0.10 \cdot \left(10^3 / T\right)^2$$ Ohmoto and Rye, 1979

…<u>as for degassing: depends on fO_2 conditions for FeS saturation!</u>

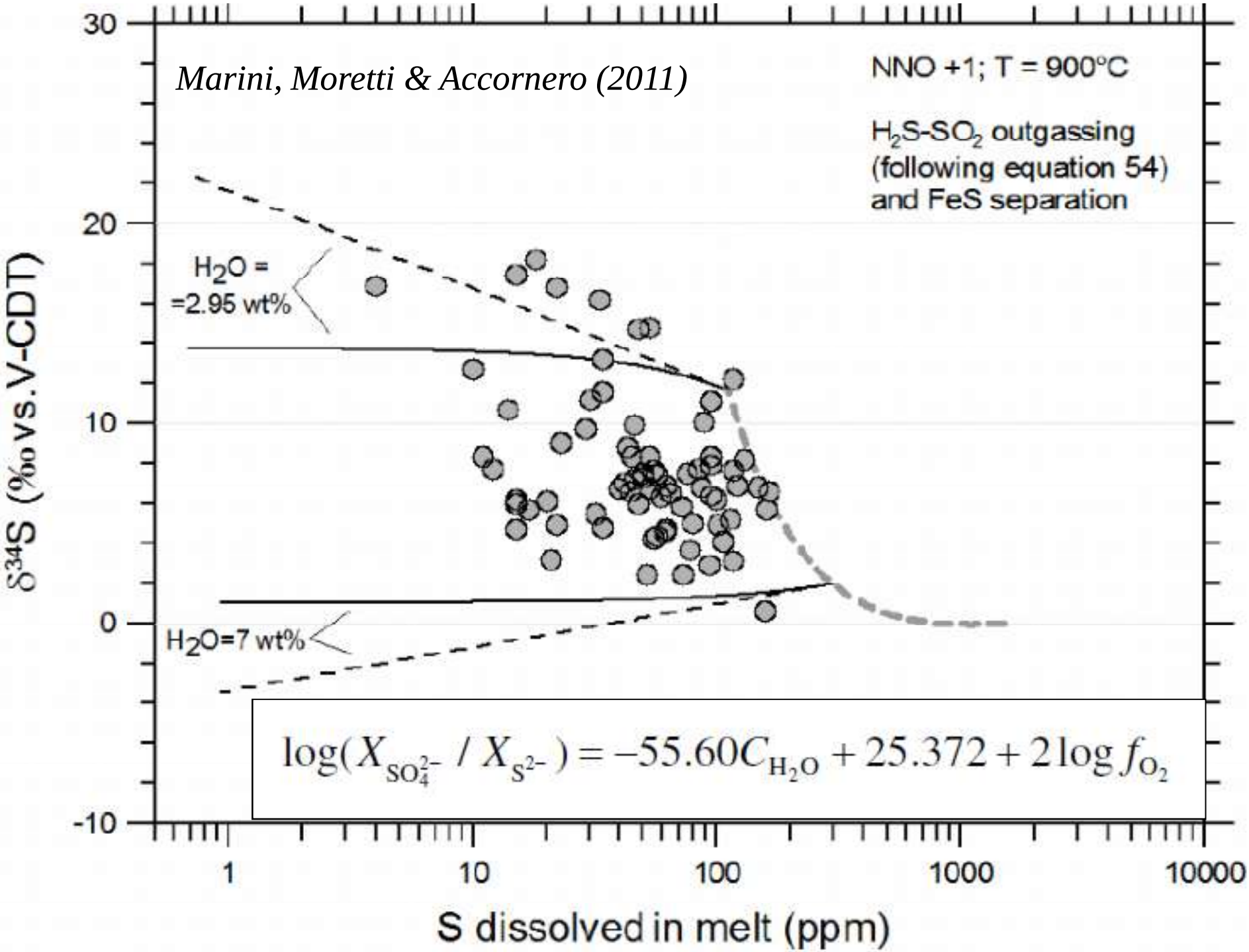


Metrich & Mandeville (2009)

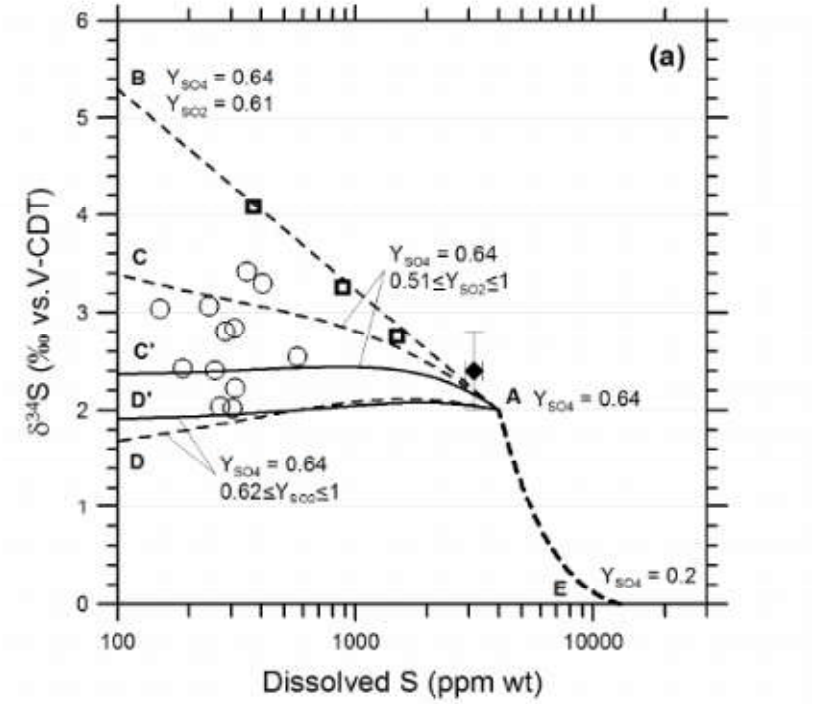


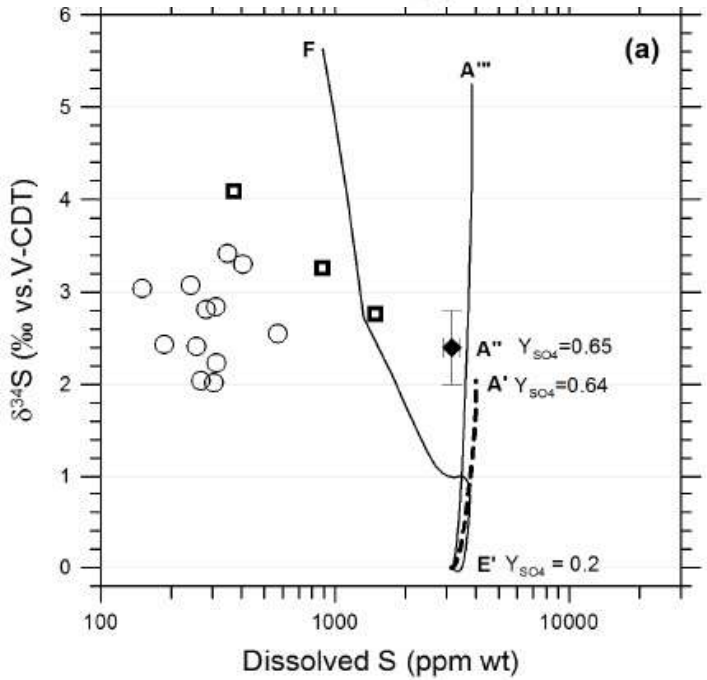
$$\log(X_{SO_4^{2-}} / X_{S^{2-}}) = -55.60 C_{H_2O} + 25.372 + 2\log f_{O_2}$$

Marini, Moretti & Accornero (2011)



$$\log(X_{SO_4^{2-}} / X_{S^{2-}}) = -55.60 C_{H_2O} + 25.372 + 2\log f_{O_2}$$





$$m_{XX}\ (wt\%) = -0.0075\ P(bar) + 30$$

Reviews in Mineralogy & Geochemistry
Vol. 73 pp. 423-492, 2011

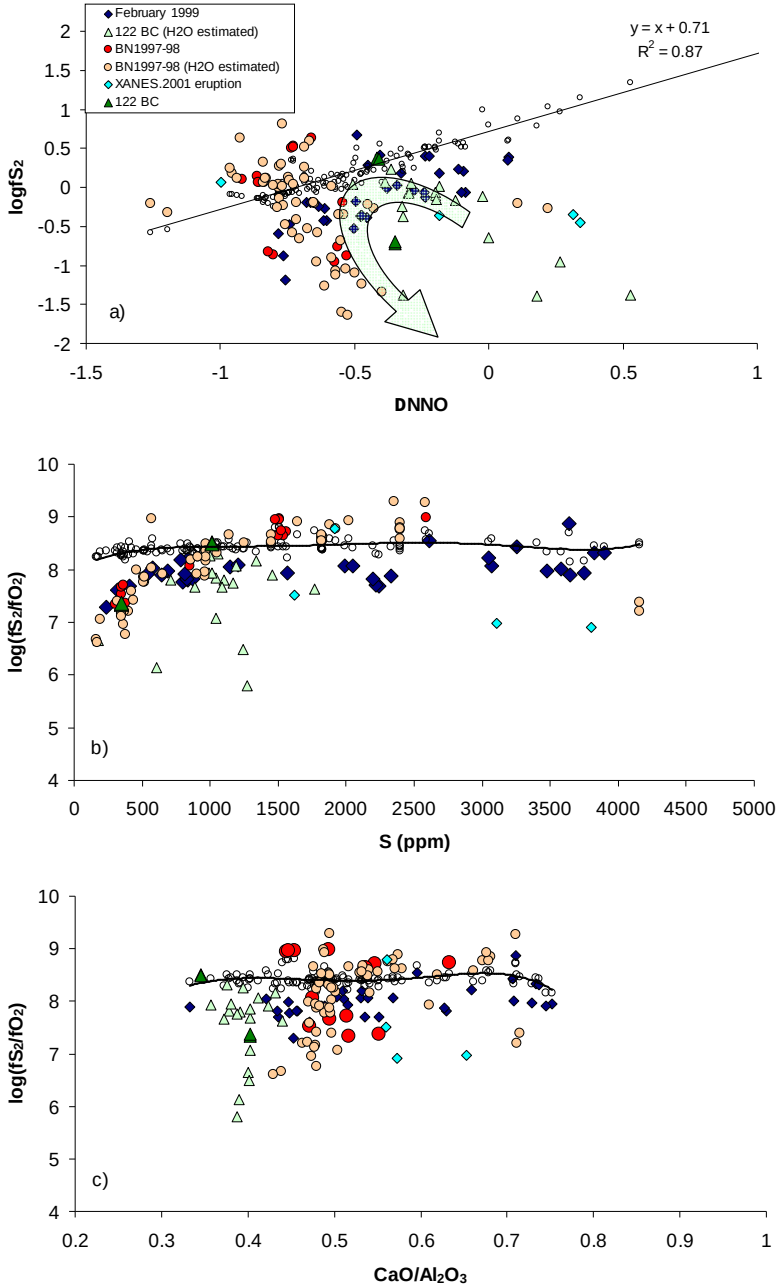
Sulfur Isotopes in Magmatic-Hydrothermal Systems, Melts, and Magmas

Luigi Marini
Laboratory of Geochemistry, Dip.Te.Ris
University of Genova, Corso Europa 26, I-16132 Genova, Italy
and
Institute of Geosciences and Georesources, CNR
Area della Ricerca, Via G. Moruzzi 1, I-56124 Pisa, Italy
lmarini@dipteris.unige.it

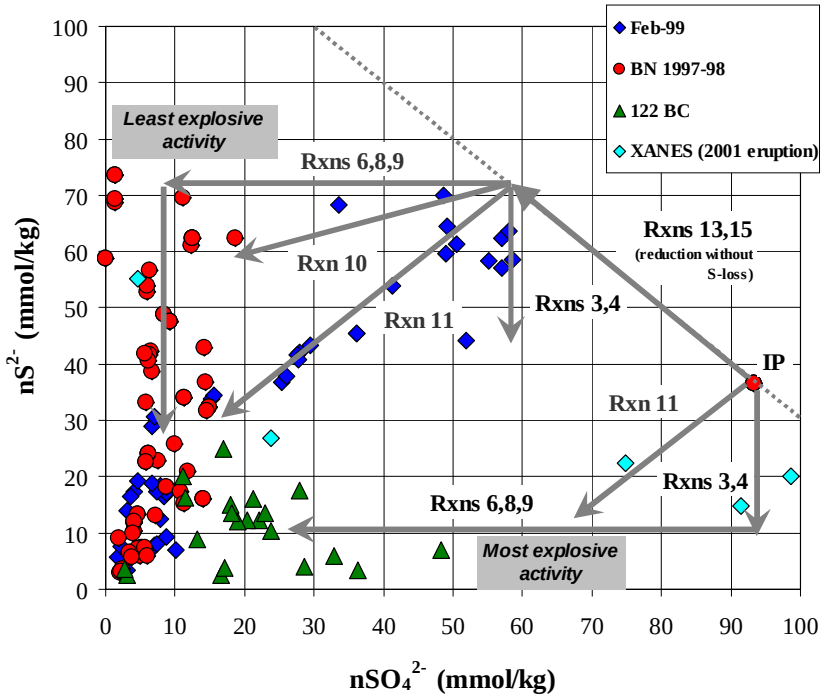
Roberto Moretti
Dipartimento di Ingegneria Civile, Seconda Università degli Studi di Napoli
Real Casa Santa dell'Annunziata
Via Roma 29, I-81031 Aversa (CE), Italy
and
Istituto Nazionale di Geofisica e Vulcanologia, sezione di Napoli 'Osservatorio Vesuviano'
Via Diocleziano 328, I-80124 Naples, Italy
roberto.moretti@unina2.it

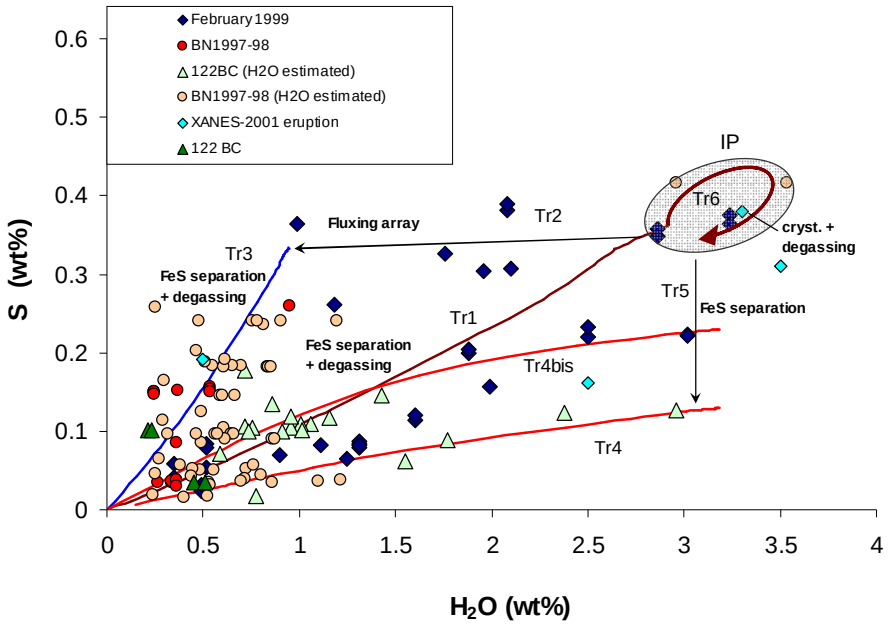
Marina Accornero
D'Appolonia S.p.A, Via S.Nazaro 19, I-16145 Genova, Italy
marina.accornero@dappolonia.it

Marini, Moretti & Accornero (2011)

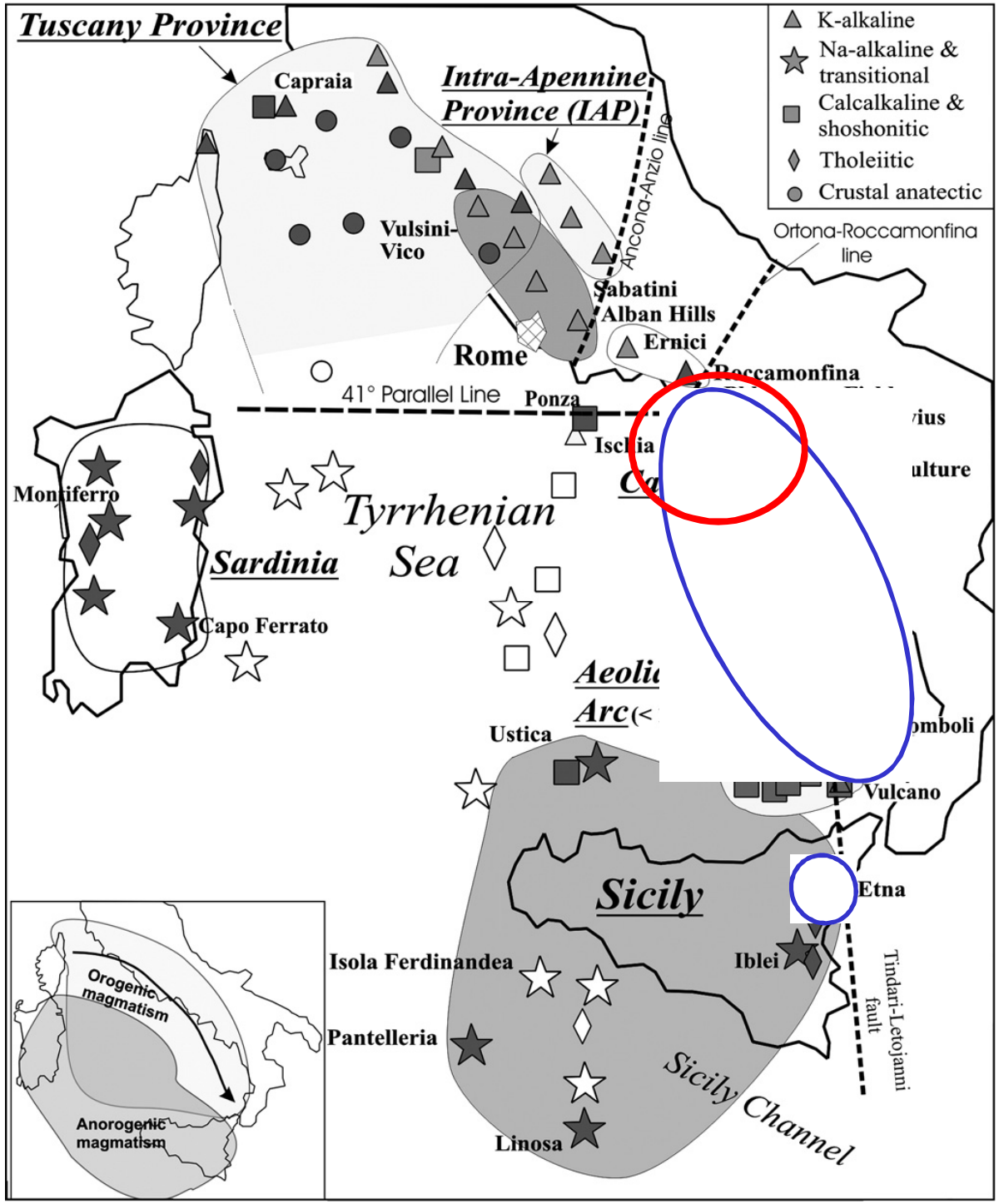


Etna



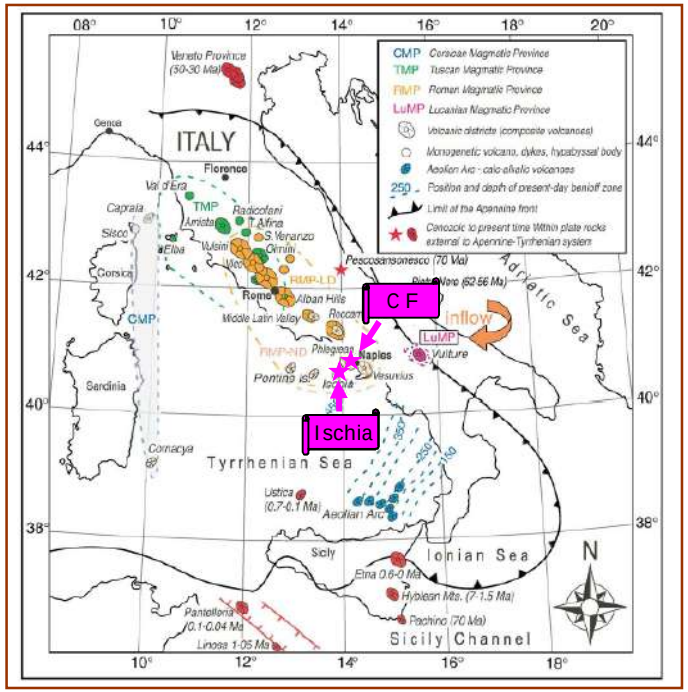


Moretti et al., in prep.

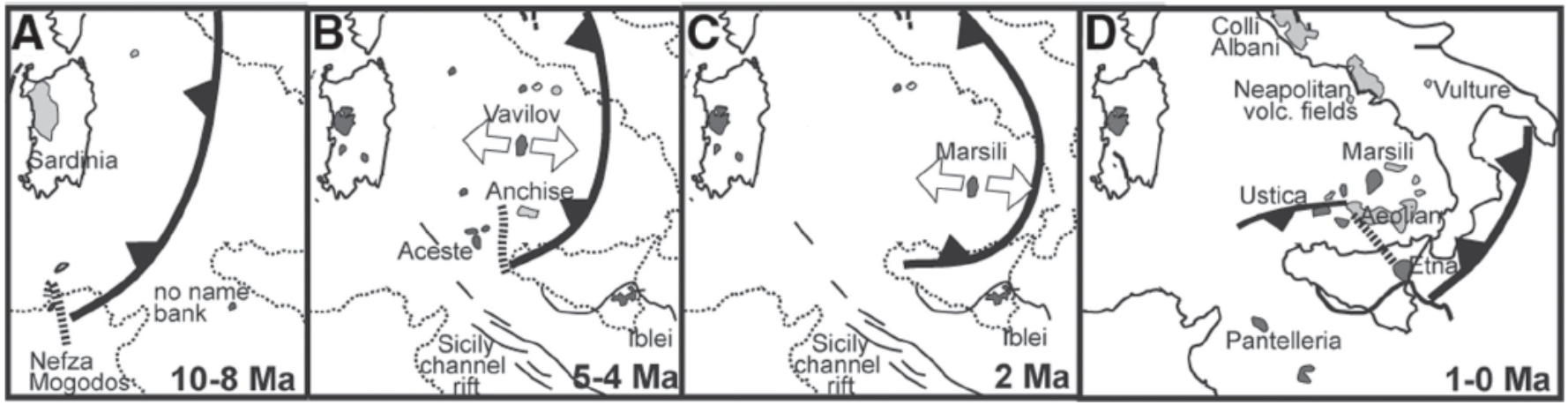

Tuscany Province
Capraia
Intra-Apennine Province (IAP)
Ancona-Anzio line
Vulsini-Vico
Sabatini
Alban Hills
Ernici
Rome
Ortona-Roccamonfina line
41° Parallel Line
Ponza
Ischia
Monteferro
Tyrrhenian Sea
Sardinia
Capo Ferrato
Ustica
Vulcano
Etna
Sicily
Isola Ferdinandea
Pantelleria
Iblei
Linosa
Sicily Channel
Tindari-Letojanni fault
K-alkaline
Na-alkaline & transitional
Calcalkaline & shoshonitic
Tholeiitic
Crustal anatectic
Orogenic magmatism
Anorogenic magmatism

The magmatism of the **Neapolitan area (Phlegraean district** = Ischia + Procida + Campi Flegrei and **Somma-Vesuvius)** is related to the NW subducting Ionian plate

The Plio-Quaternary Italian magmatism is related to the complex geodynamics of the Mediterranean basin induced by convergence between African and Eurasian plates



Faccenna et al., 2004

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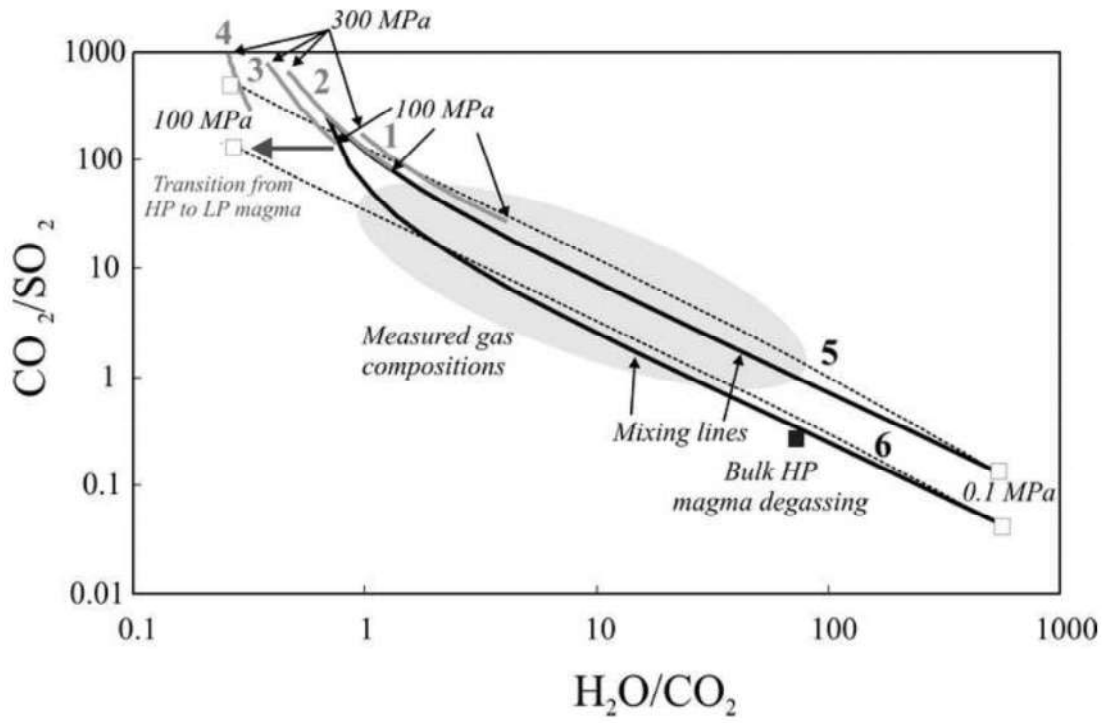
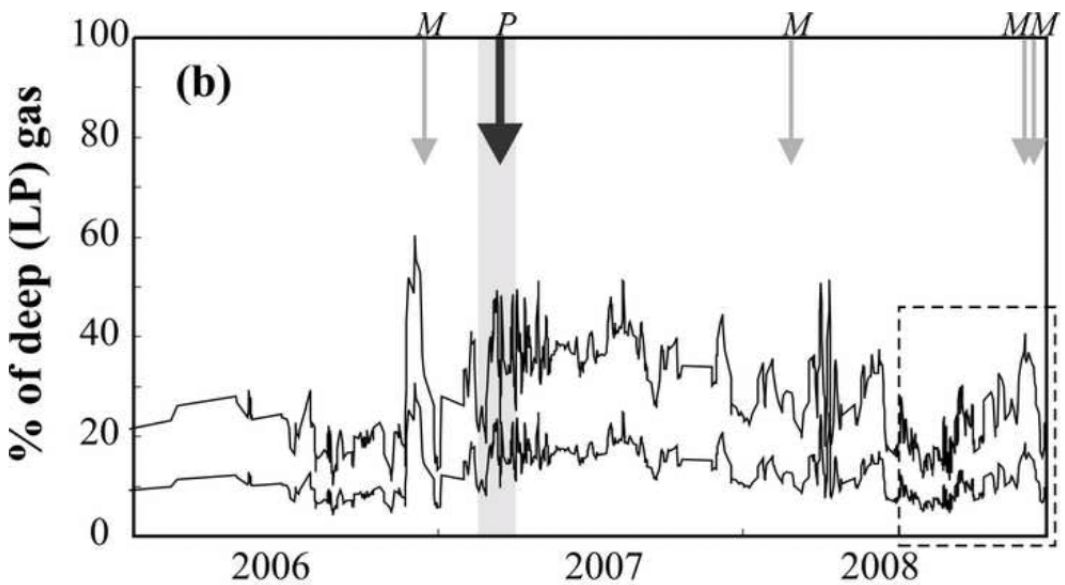
VULCANOLOGIA






Earth and Planetary Science Letters 295 (2010) 195–204

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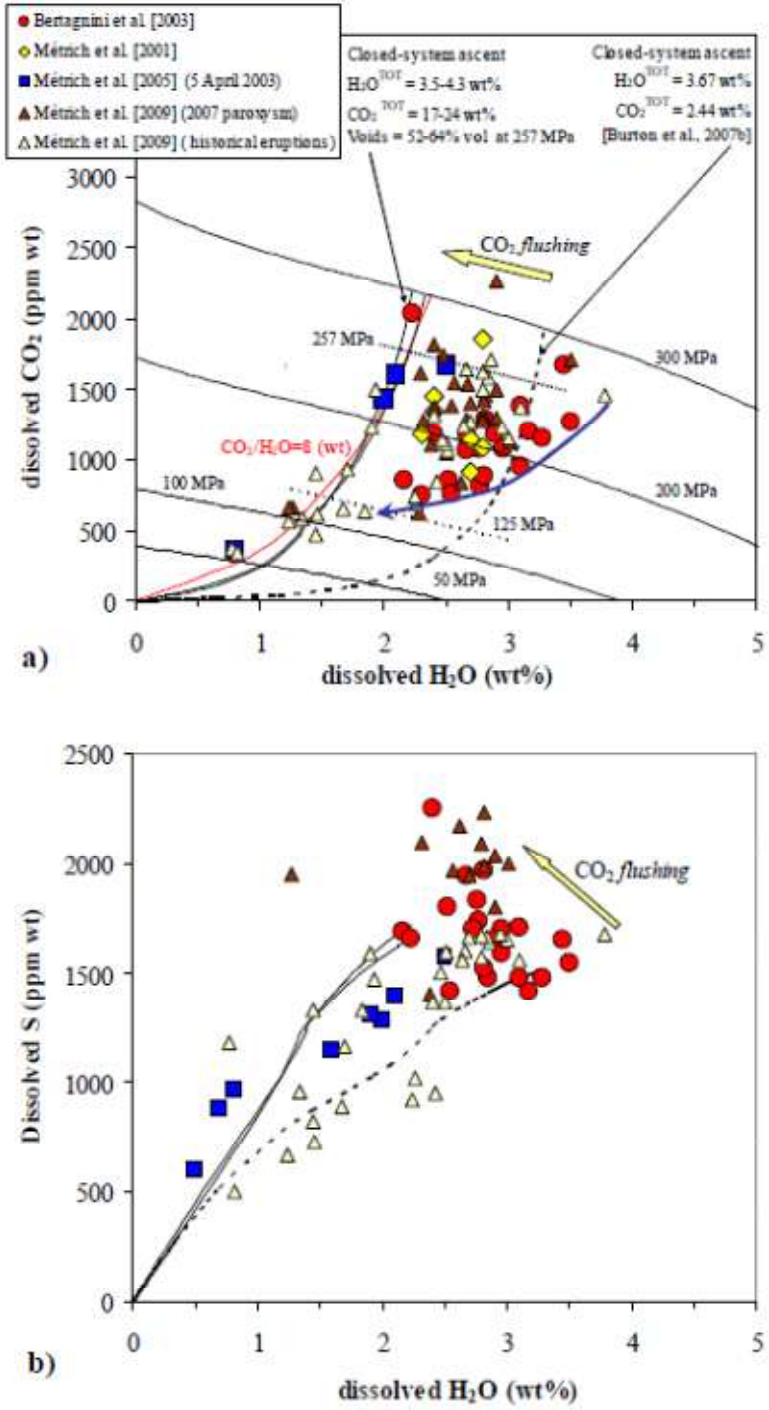
journal homepage: www.elsevier.com/locate/epsl

A model of degassing for Stromboli volcano

A. Aiuppa [a,b,*], A. Bertagnini [c], N. Métrich [c,d], R. Moretti [e], A. Di Muro [f], M. Liuzzo [b], G. Tamburello [a]

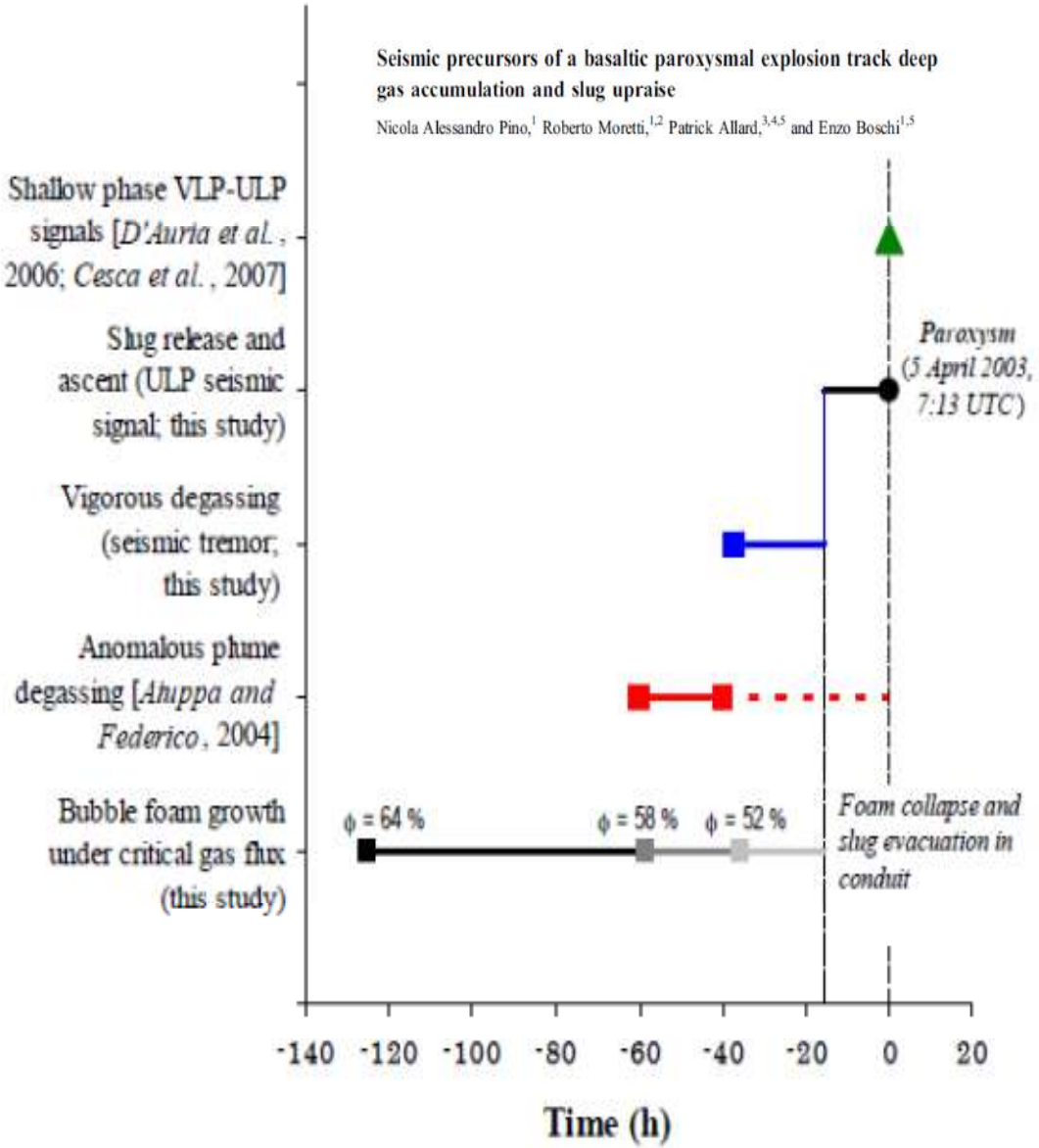
Aiuppa,Bertagnini, Metrich, Moretti, Di Muro, Liuzzo, Tamburello (2010)



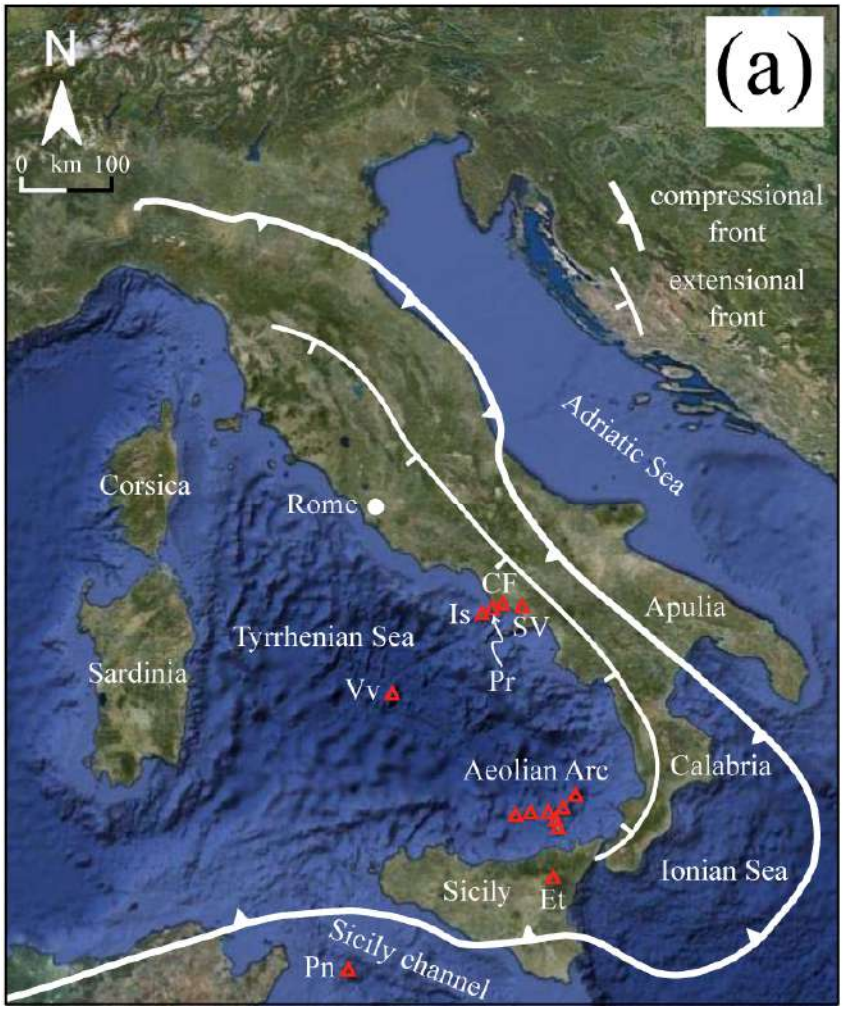
JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 116, B02312, doi:10.1029/2009JB000826, 2011

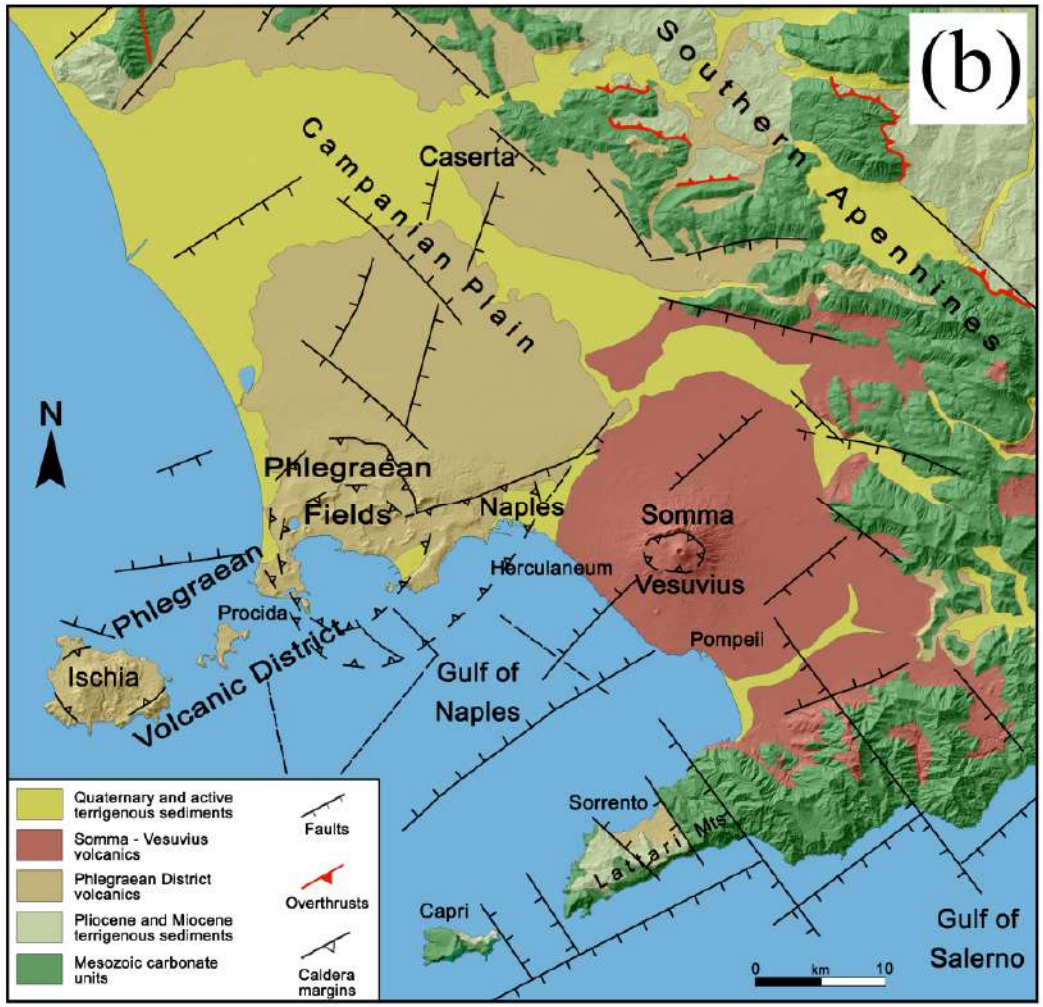
Seismic precursors of a basaltic paroxysmal explosion track deep gas accumulation and slug upraise

Nicola Alessandro Pino,[1] Roberto Moretti,[1,2] Patrick Allard,[3,4,5] and Enzo Boschi[1,5]



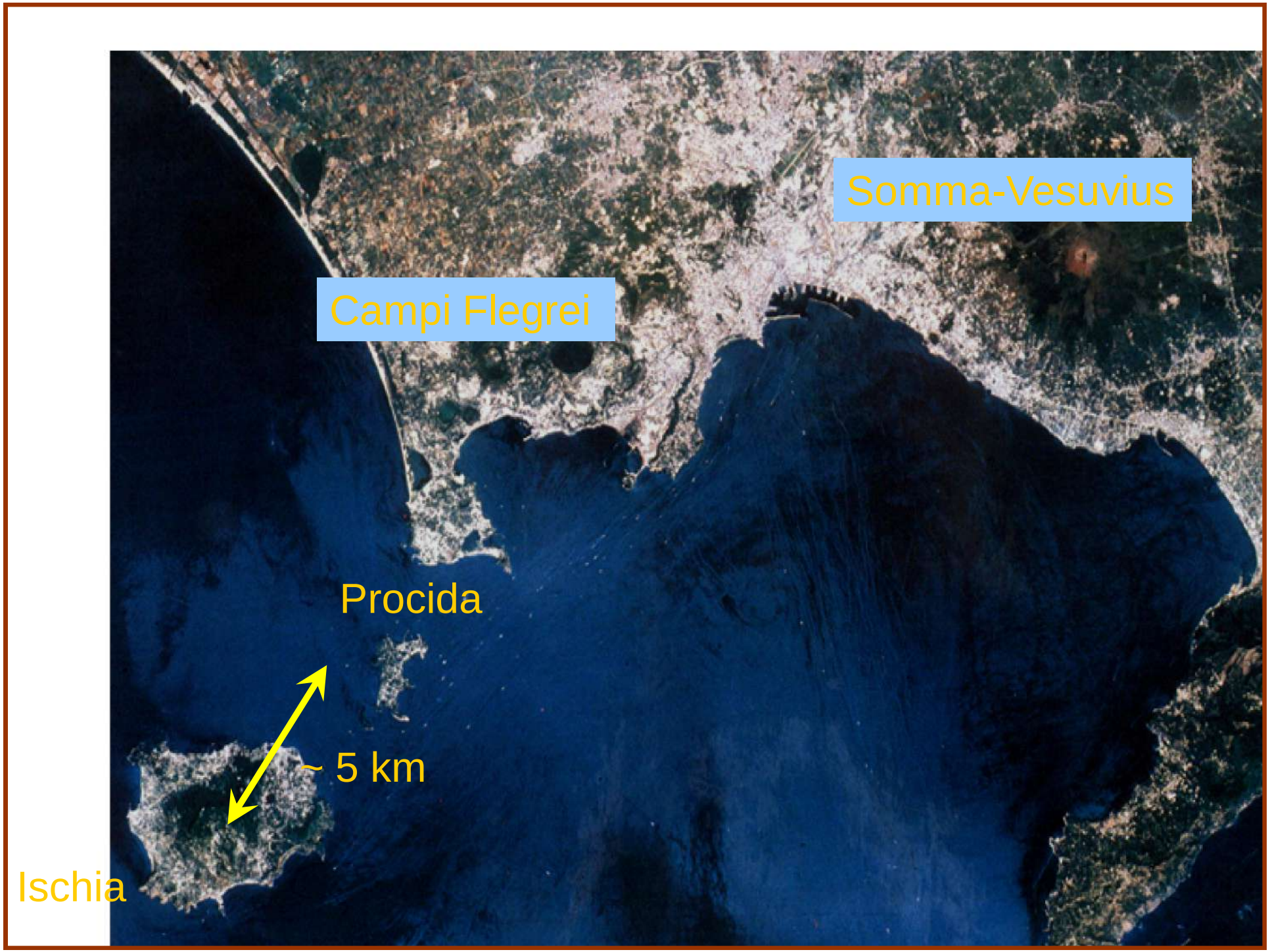
Pino, Moretti, Allard, Boschi (2011, JGR)

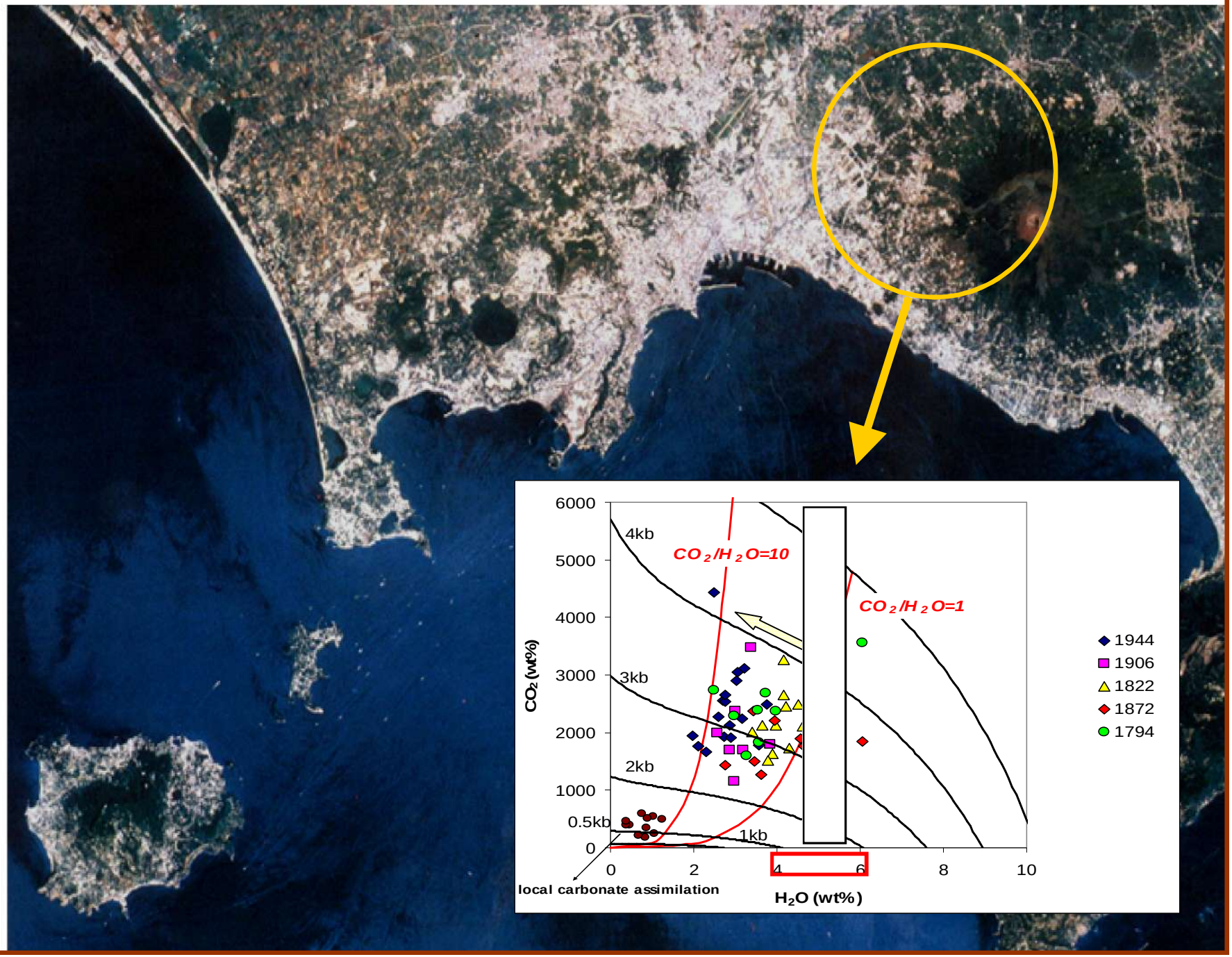


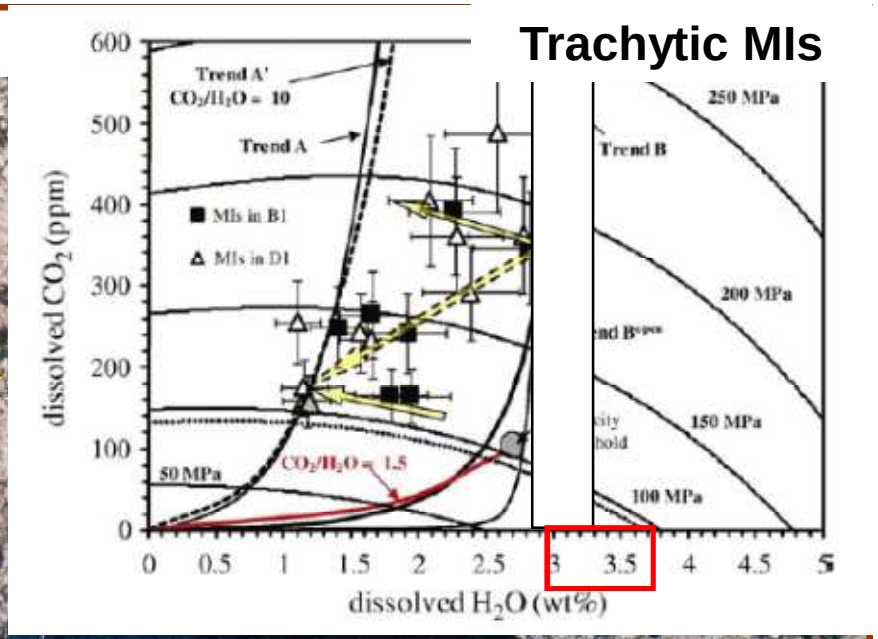


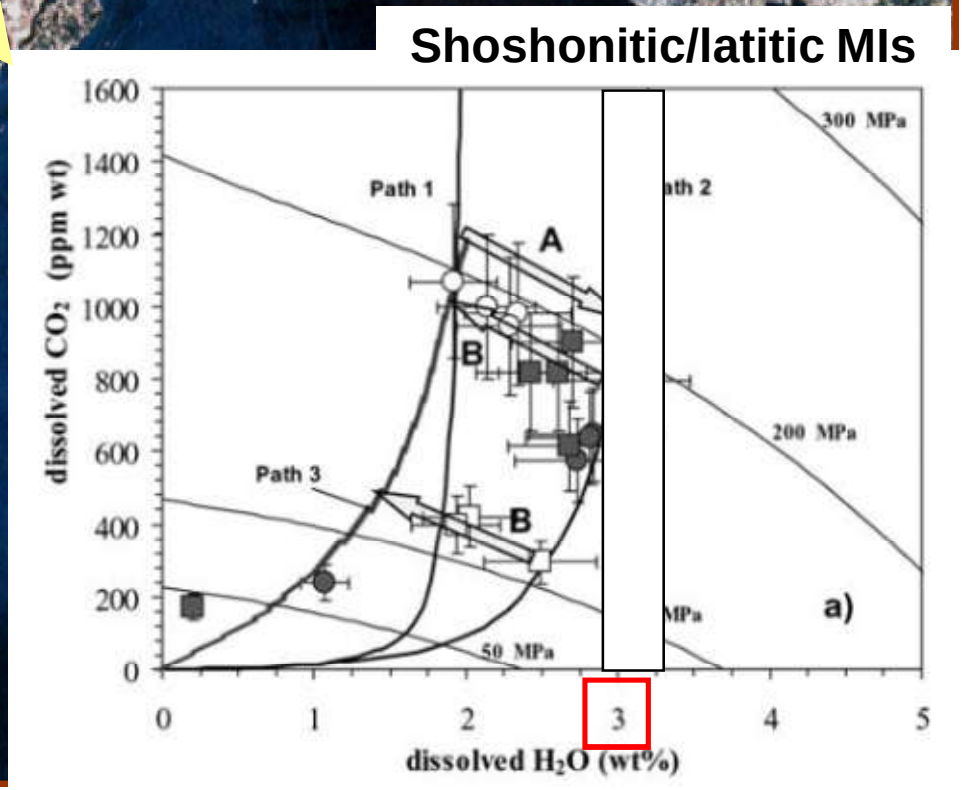
Panel a): traces of the subduction-related compression and extension fronts along the Apennines chain (modified after Acocella and Funiciello, 2006); Is = Ischia; Pr = Procida; CF = Campi Flegrei; SV = Somma-Vesuvius; Vv = Vavilov; Et = Etna; Pn = Pantelleria.

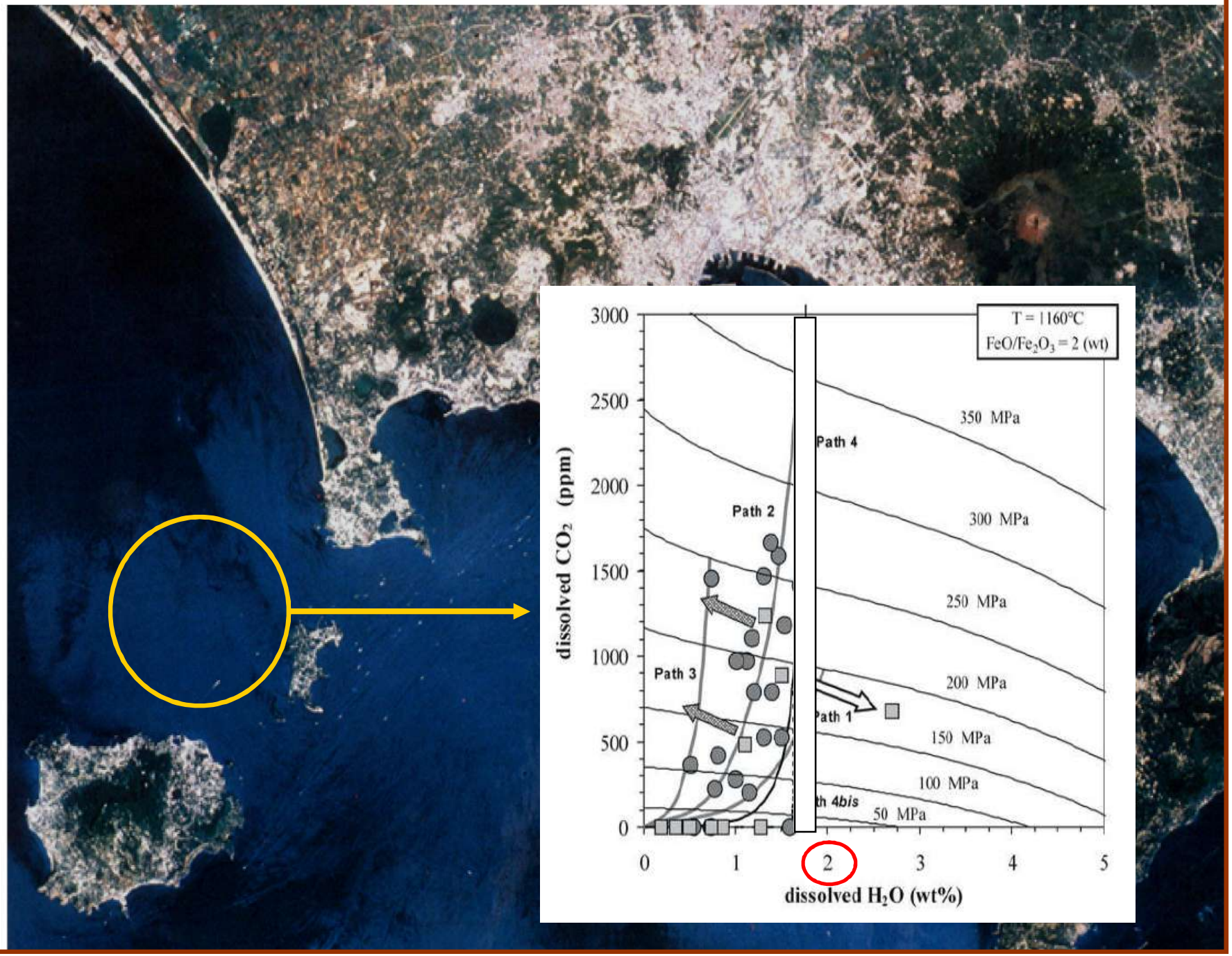
Panel b): structural sketch map of the Campanian Plain and surrounding Apennines (modified after Orsi et al., 2003).

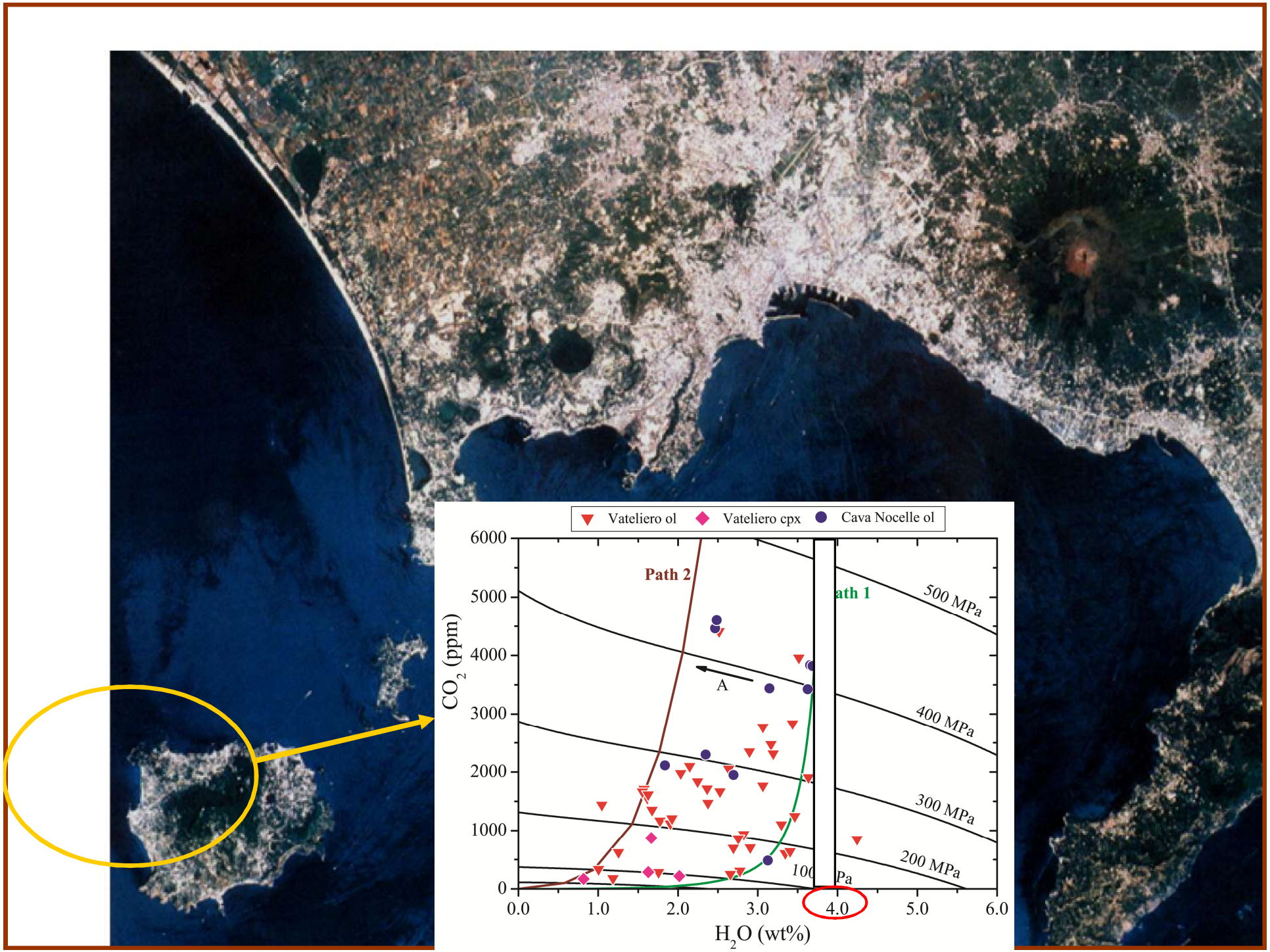

Somma-Vesuvius
Campi Flegrei
Procida
~ 5 km
Ischia

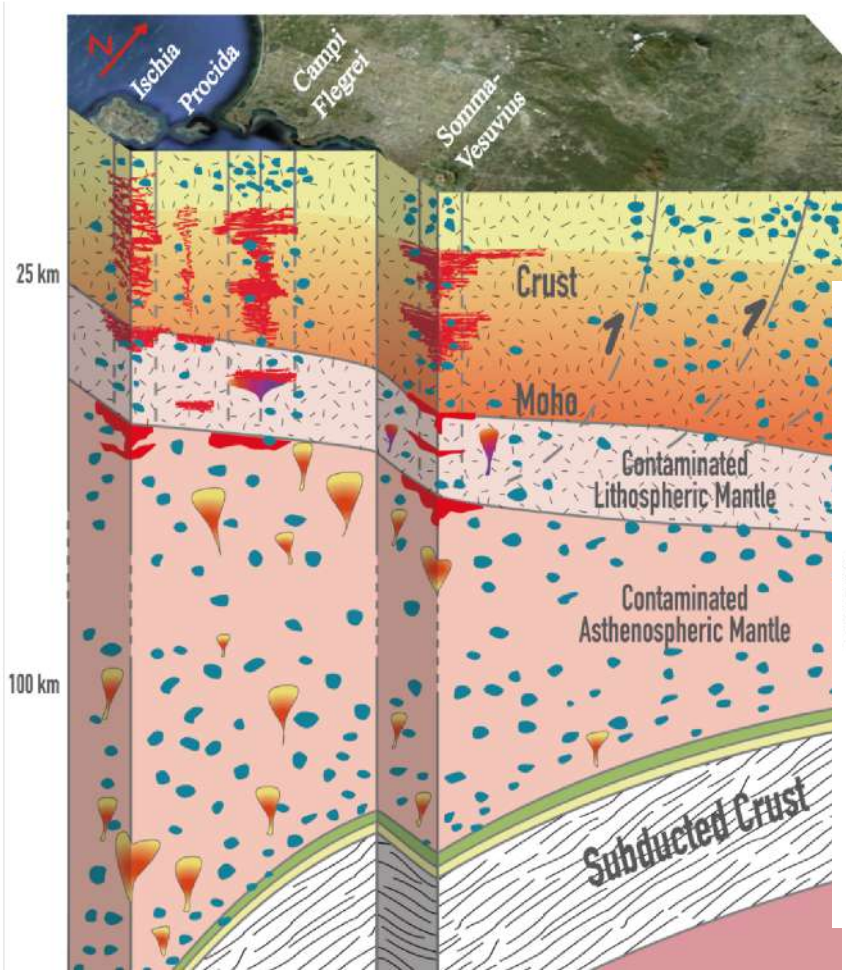

6000
5000
4000
3000
2000
1000
0.5kb
0
4kb
3kb
2kb
1kb
CO2/H2O=10
CO2/H2O=1
CO2 (wt%)
0
2
4
6
8
10
H2O (wt%)
local carbonate assimilation
1944
1906
1822
1872
1794


Trachytic MIs
Trend A'
CO_2/H_2O = 10
Trend A
MIs in B1
MIs in D1
CO_2/H_2O = 1.5
50 MPa
Trend B
250 MPa
200 MPa
150 MPa
100 MPa
dissolved CO_2 (ppm)
dissolved H_2O (wt%)

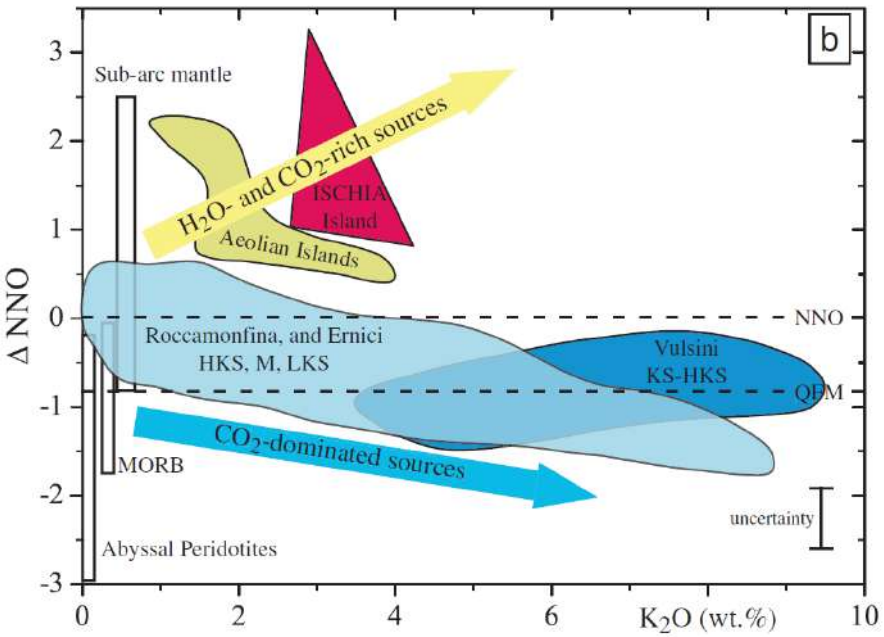

Shoshonitic/latitic MIs
Path 1
Path 2
Path 3
A
B
B
300 MPa
200 MPa
50 MPa
a)
dissolved CO_2 (ppm wt)
dissolved H_2O (wt%)


T = 1160°C
FeO/Fe2O3 = 2 (wt)
350 MPa
300 MPa
250 MPa
200 MPa
150 MPa
100 MPa
50 MPa
Path 1
Path 2
Path 3
Path 4
Path 4bis
dissolved CO2 (ppm)
dissolved H2O (wt%)
0
500
1000
1500
2000
2500
3000
0
1
2
3
4
5


Vateliero ol
Vateliero cpx
Cava Nocelle ol
Path 2
ath 1
A
500 MPa
400 MPa
300 MPa
200 MPa
100 Pa
CO_2 (ppm)
H_2O (wt%)
0
1000
2000
3000
4000
5000
6000
0.0
1.0
2.0
3.0
4.0
5.0
6.0



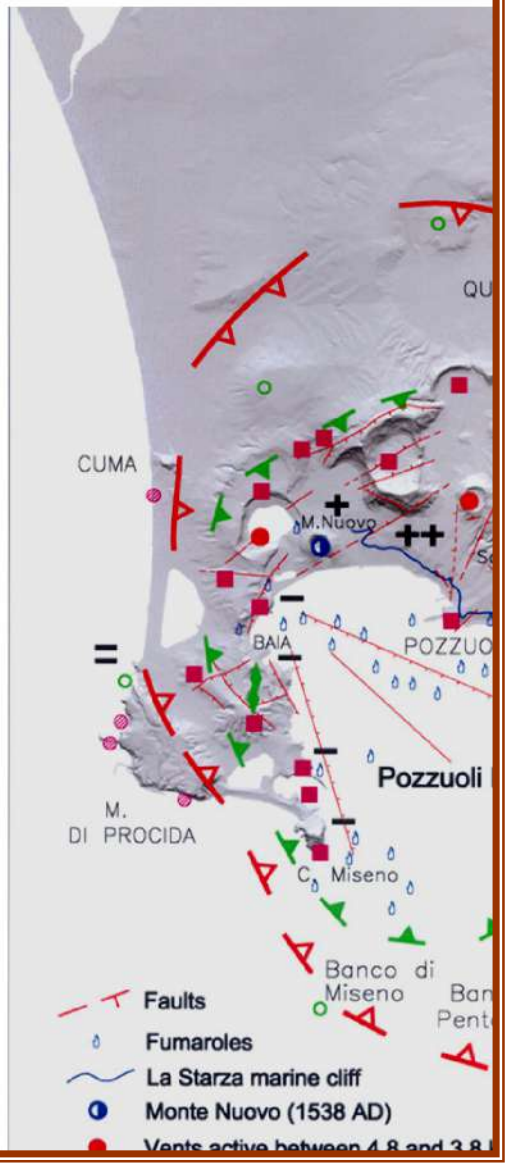
Moretti et al., 2012 (accepted in J.Pet.)



D'Antonio et al., 2012 (under review in Contrib. Min. Pet.)

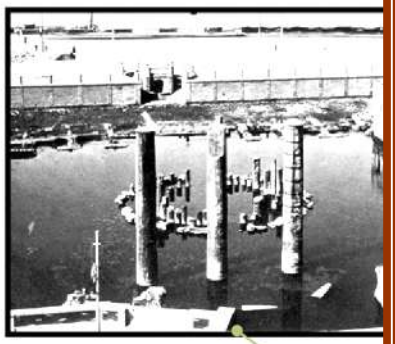
Campi Flegrei caldera

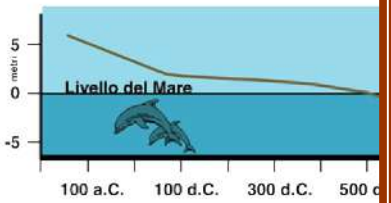
Structural map

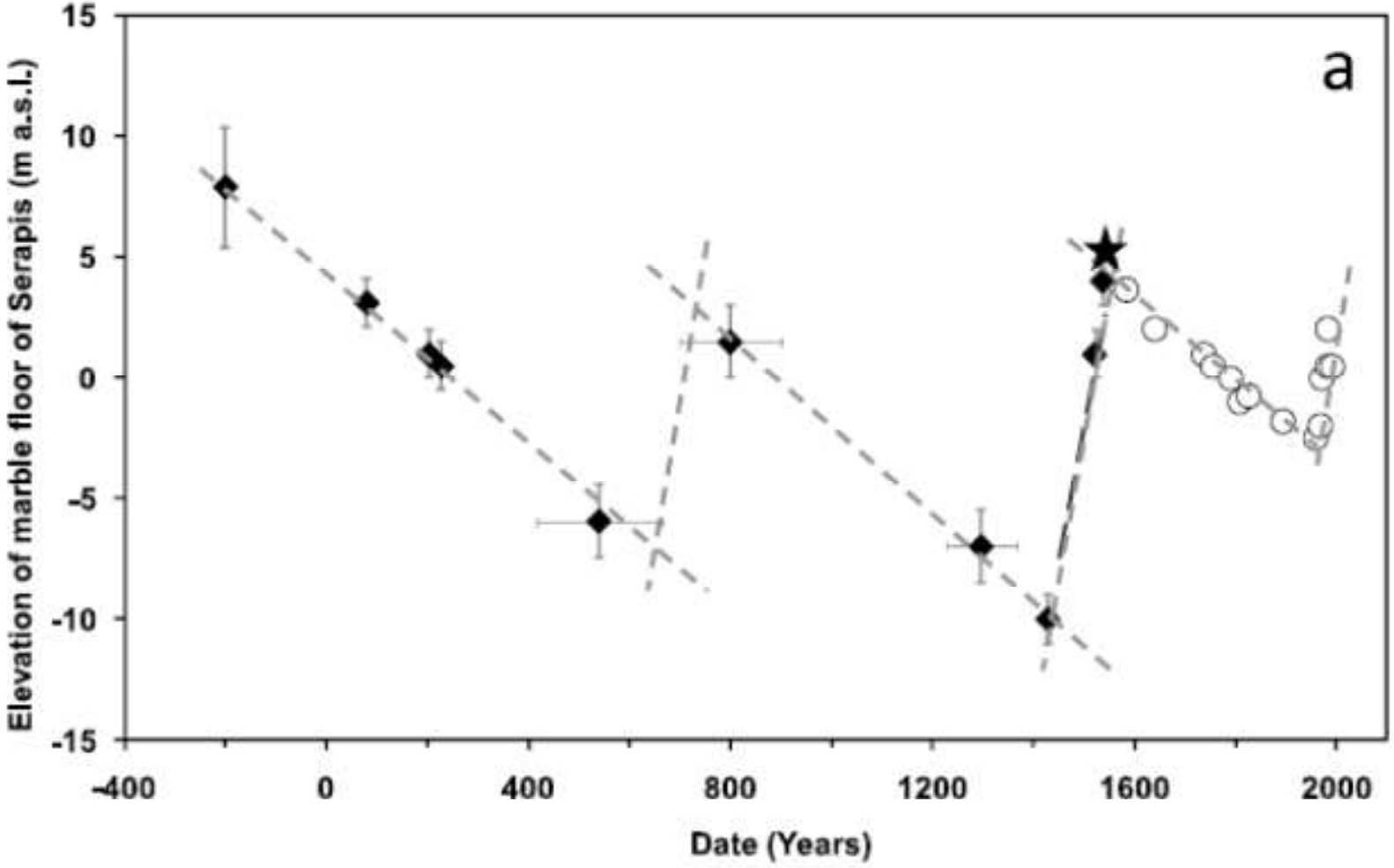


Campi Flegrei caldera

Ground movement at
Pozzuoli - Serapeo
over the past 2 ka






a
Elevation of marble floor of Serapis (m a.s.l.)
15
10
5
0
-5
-10
-15
-400
0
400
800
1200
1600
2000
Date (Years)

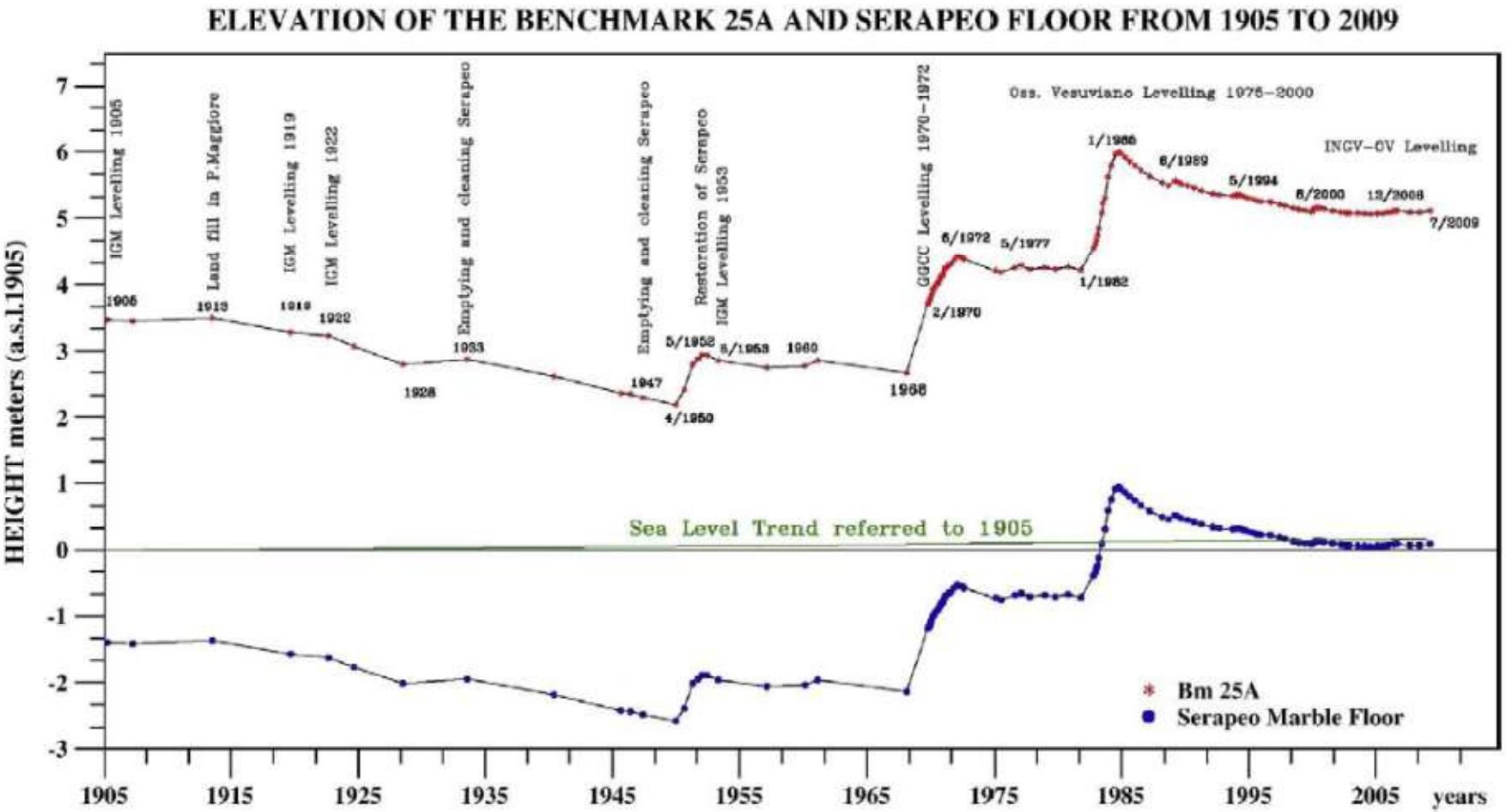
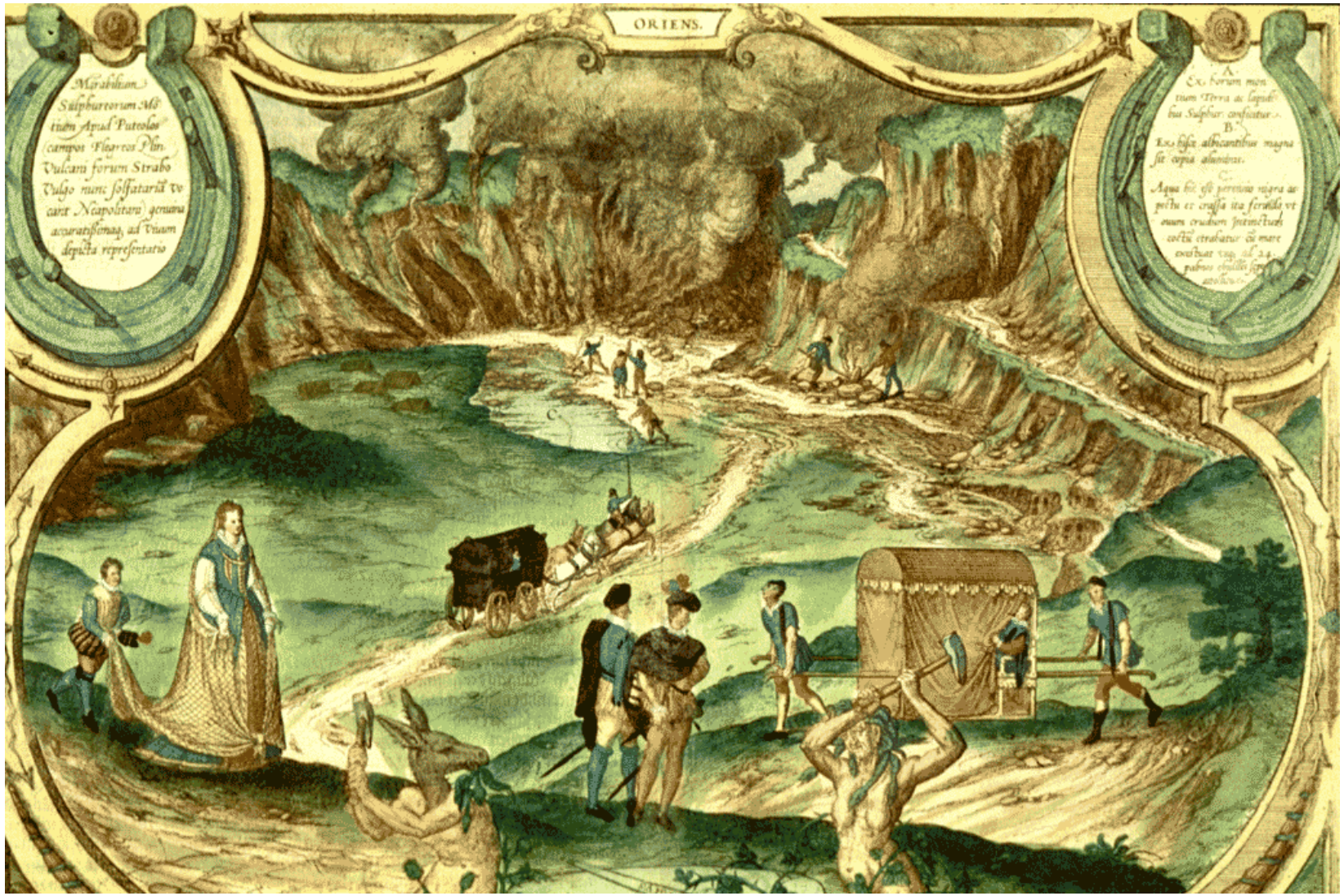


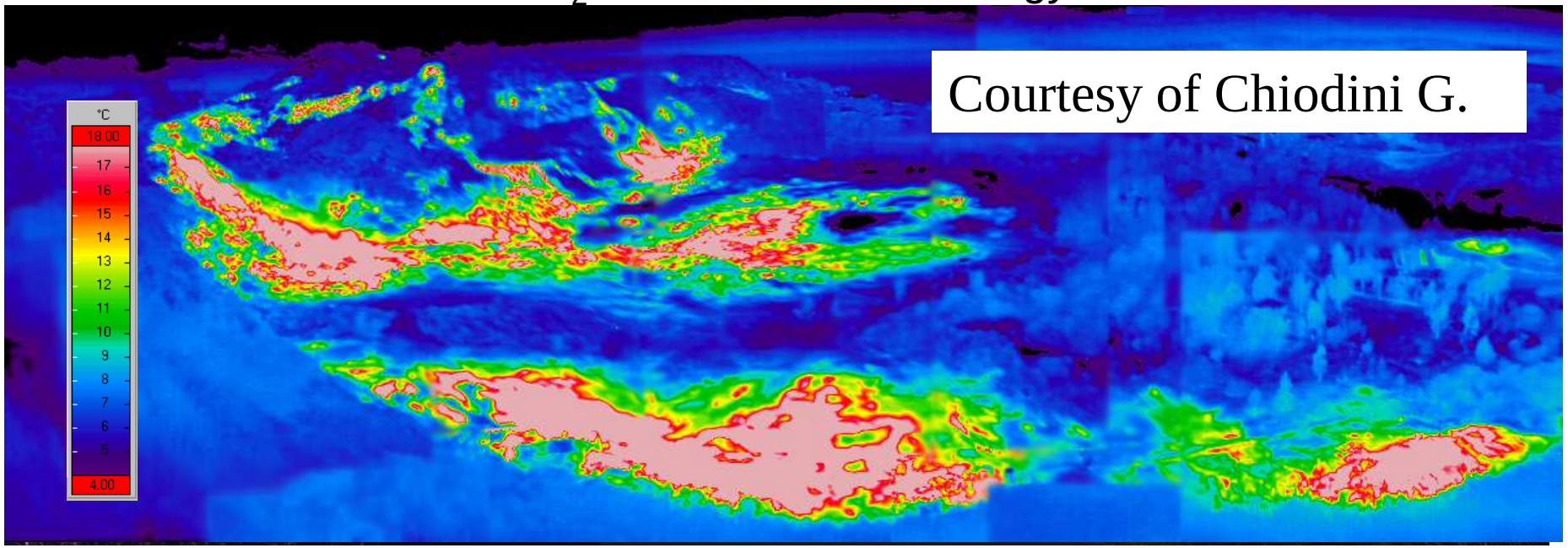
Fig. 7. Elevation changes of the floor of Serapeum and benchmark BM 25A (masl) from 1905 to 2009 referred to the sea level in 1905.


Solfatara
IPF

Sulfur Production in Solfatara Volcano (Naples)



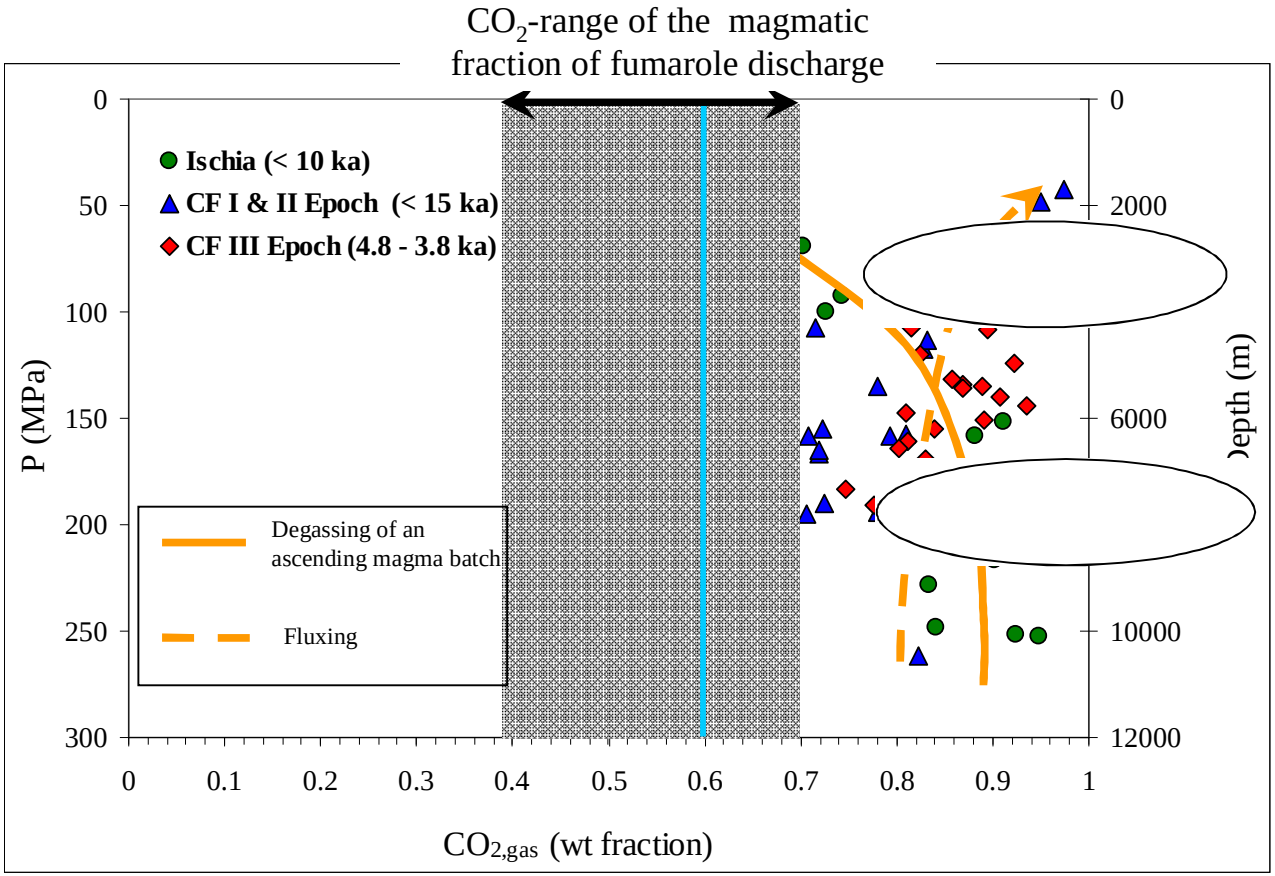
CO_2 flux and thermal energy release



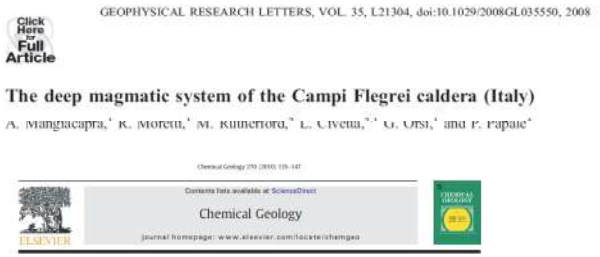
		Solfatara	Nisyros	Vesuvio	Vulcano
CO_2 t d^{-1}		1500	100	300	200
H_2O/CO_2 fumaroles		2.2	23.4	3.7	5.3
H_2O t d^{-1}		3300	2340	1100	1060
Condensation	J d^{-1}	7.3×10^{12}	5.2×10^{12}	2.4×10^{12}	2.3×10^{12}
Cooling of liquid	J d^{-1}	1.1×10^{12}	7.7×10^{11}	3.6×10^{11}	3.5×10^{11}
Thermal energy	J d^{-1}	8.4×10^{12}	5.9×10^{12}	2.8×10^{12}	2.7×10^{12}

The energy released by the DDS (mainly through steam condensation) are very large, and cannot be neglected in the thermal balance of a volcanic system.

Unrest: Petrologic & geochemical modelling



Mangiacapra et al., 2008 (GRL)


GEOPHYSICAL RESEARCH LETTERS, VOL. 35, L21304, doi:10.1029/2008GL035550, 2008

Click Here for Full Article

The deep magmatic system of the Campi Flegrei caldera (Italy)

A. Mangiacapra, R. Moretti, M. Rutherford, L. Civetta, G. Orsi, and P. Papale

Chemical Geology

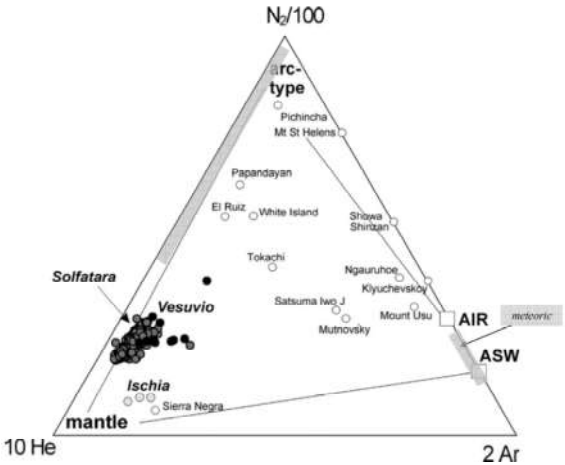
journal homepage: www.elsevier.com/locate/chemgeo

The feeding system of Agnano–Monte Spina eruption (Campi Flegrei, Italy): Dragging the past into present activity and future scenarios

I. Arienzo, R. Moretti, L. Civetta, G. Orsi, P. Papale

Arienzo et al., 2010 (CHEMGE)

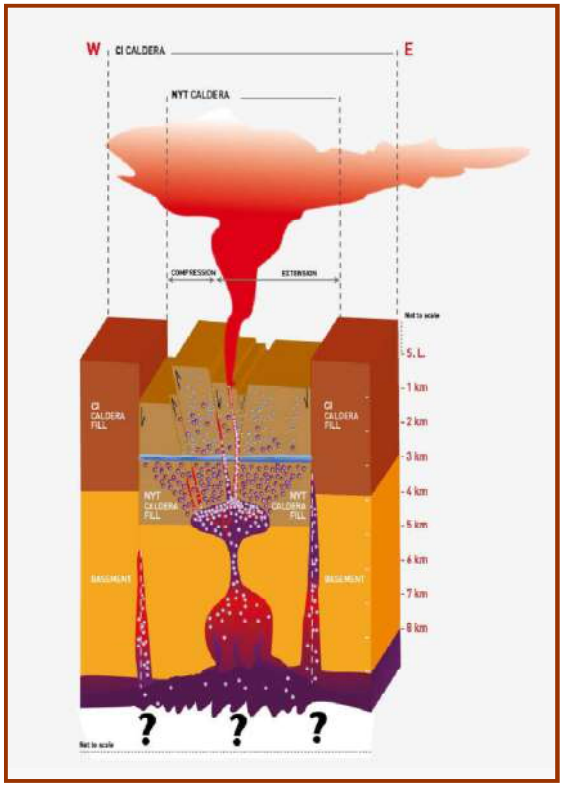
Moretti et al. under review in EPSL



Caliro et al., 2007 (GCA)

Ubrest: Petrologic & geochemical modelling

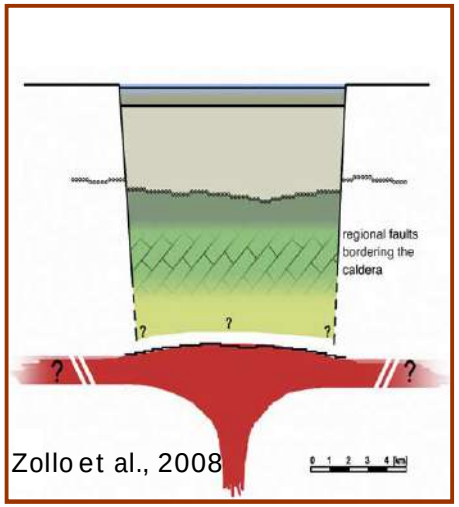
Magma System Architecture



Arienzo et al., 2010; Chem. Geol.

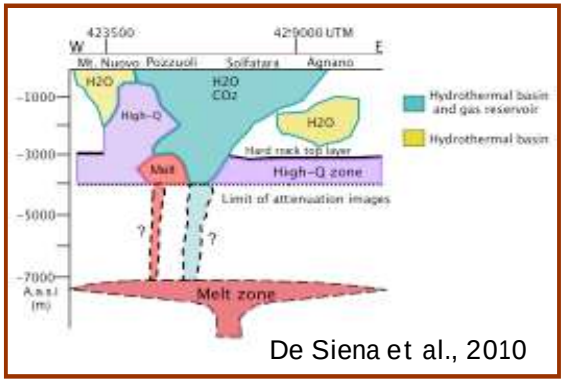
Melt Inclusions

=



Seismic Tomography

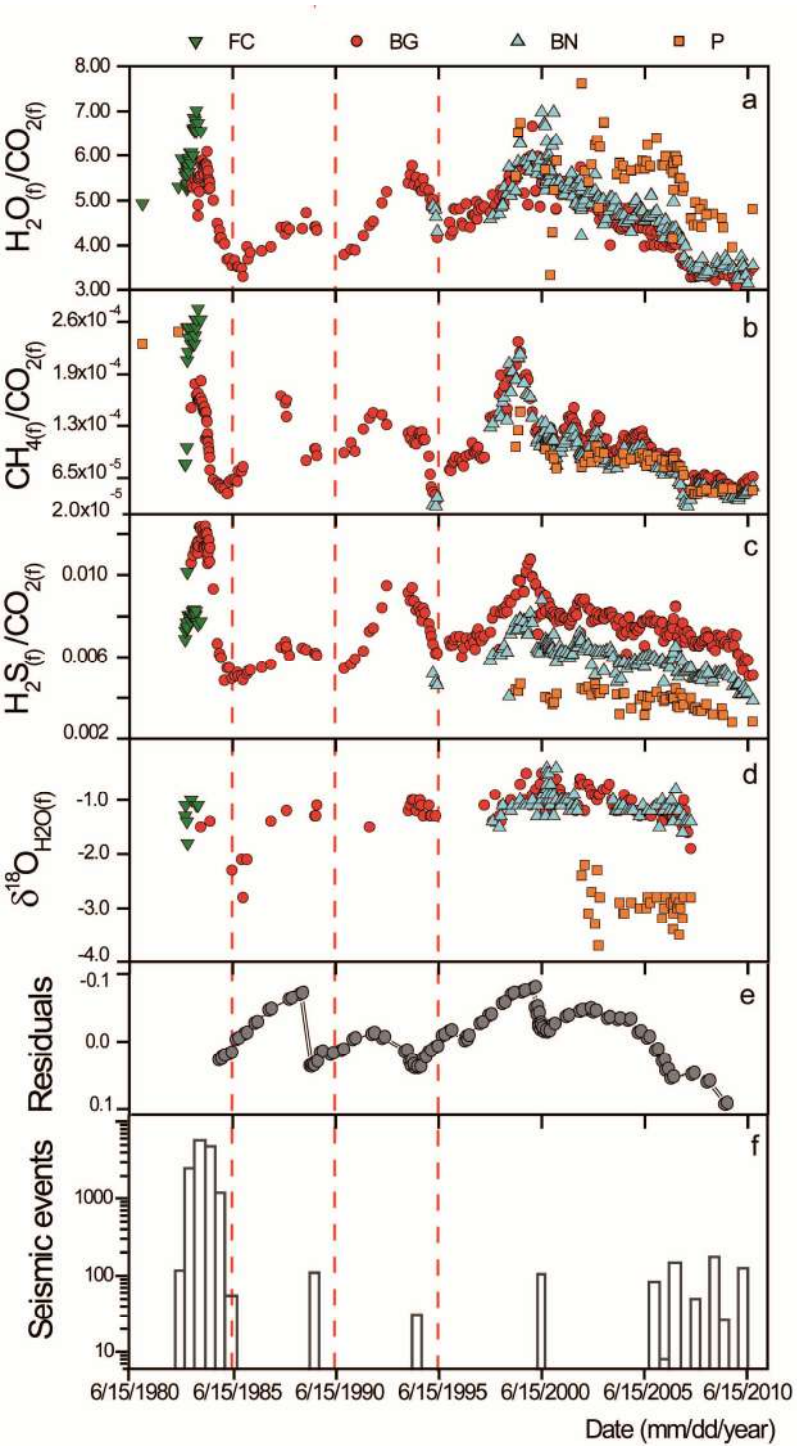
+

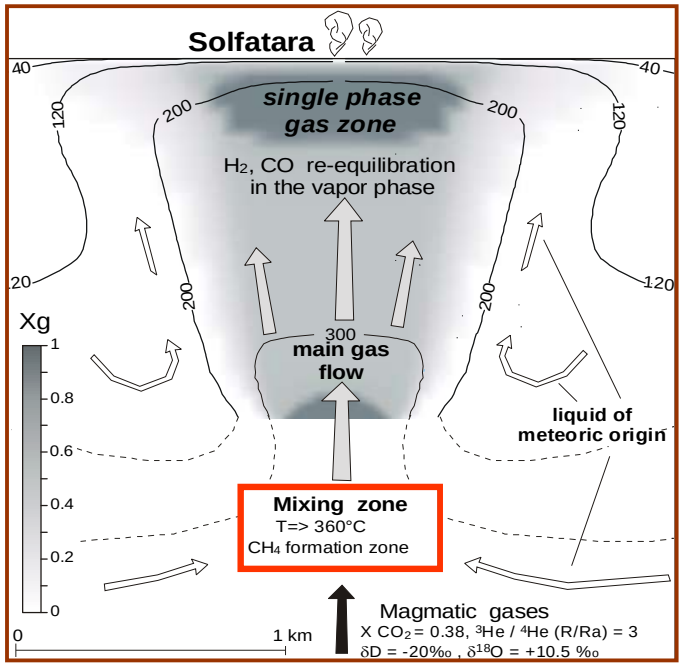


Seismic attenuation

Geo-volcanological picture of the A–MS magmatic feeding system and of the CFc sector involved in the eruption. The A–MS system can represent a useful proxy to sketch present and future scenarios in which magmas and their gases interact with the hydrothermal system.

Unrest: Fluid geochemical modelling





Caliro et al., 2007

Moretti et al., under review in EPSL

Melt composition (#) *(wt.%, volatile-free)*

SiO_2	TiO_2	Al_2O_3	FeO_{tot}	MgO	CaO	Na_2O	K_2O
59.04	0.46	17.14	3.83	0.68	2.42	4.22	7.64

Constrained features of the magma body after rise and emplacement at 4 km-depth

P = 100 MPa (&); **T** = 1173 K (§); **$logfO_2$** = NNO+1.2 (#)

H_2O^{TOT} = 3.5 wt% (£); **CO_2^{TOT}** = 2 wt% (£); **S^{TOT}** = 0.013 wt% (£)

Computed conditions

H_2O^{gas} = 31.61 wt% **H_2O/CO_2** (mol) = 1.14

CO_2^{gas} = 68.01 wt% **H_2S/CO_2** (mol) = 0.004

SO_2^{gas} = 0.16 wt% **SO_2/H_2S** (mol) = 0.4

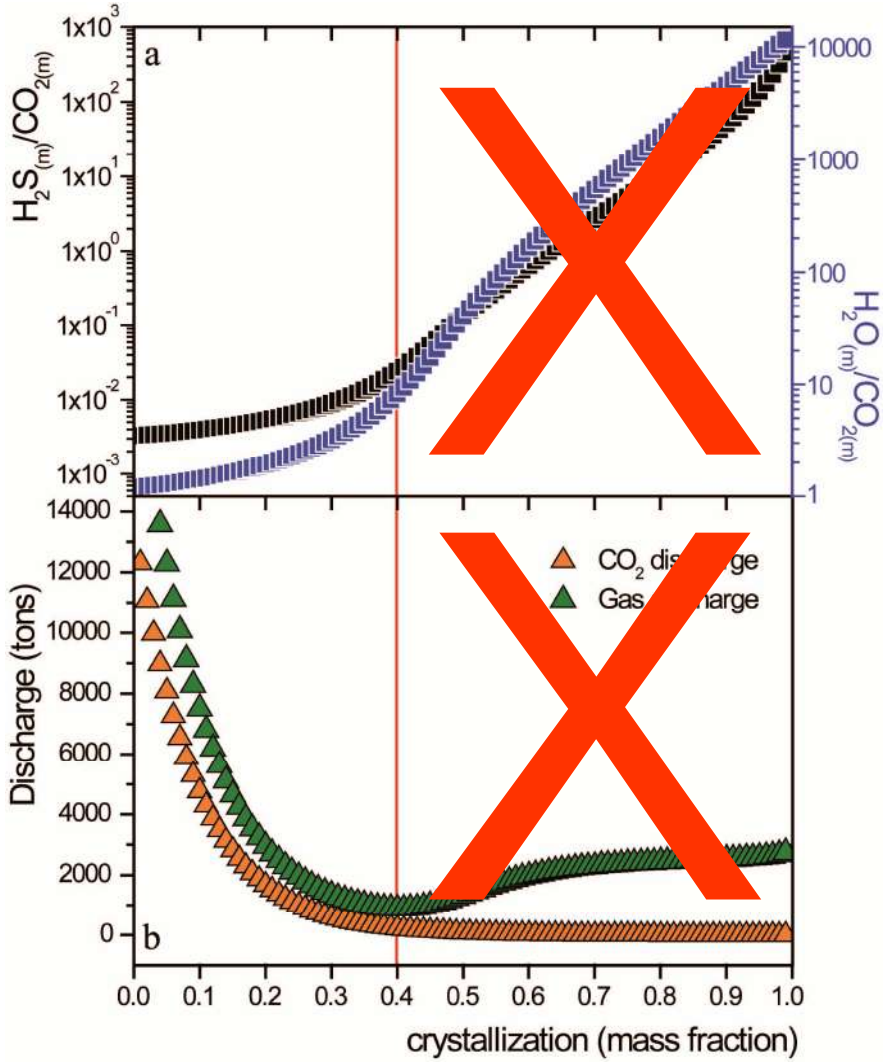
H_2S^{gas} = 0.22 wt%

$\rho_{melt+gas}$ = 2008 kg/m^3

ρ_{melt} = 2511 kg/m^3

m^{gas} = 3 wt%

V^{gas}/V^{tot} = 0.21

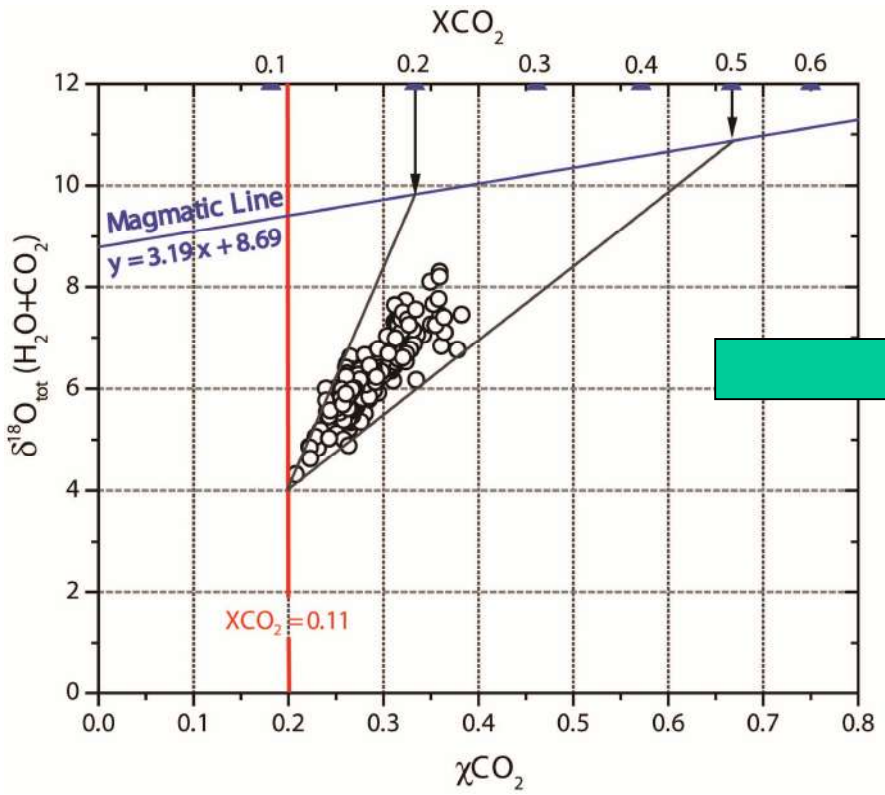


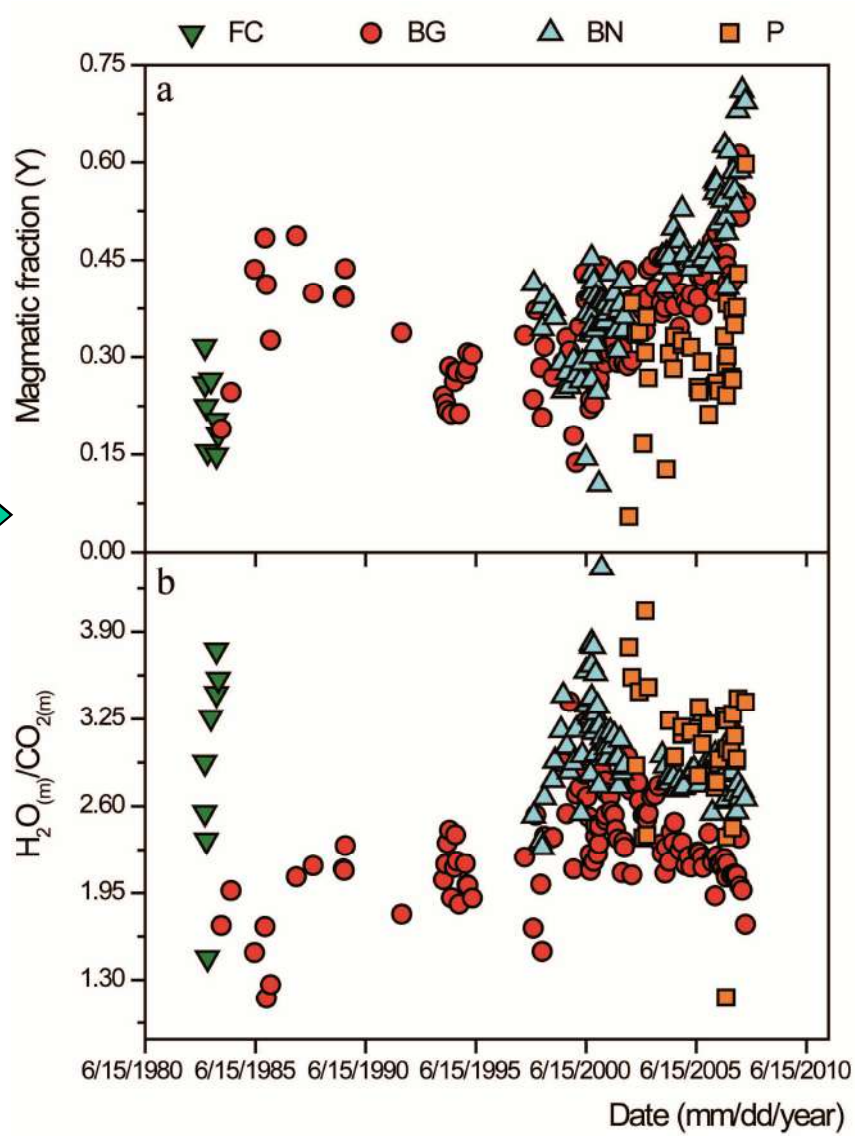
Simulation performed for a magma crystallizing and degassing (open-system) continuosly → no volatile rejuvenation

Calculation scaled to $2x10^{11}$ kg of magma.

The shallow body crystallizes and cools in 20-30 years !

Unrest: Fluid geochemical modelling





Moretti et al., Under Review in EPSL

Melt composition (#) *(wt.%, volatile-free)*

SiO_2	TiO_2	Al_2O_3	FeO_{tot}	MgO	CaO	Na_2O	K_2O
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Constrained features of the magma body after rise and emplacement at 4 km-depth

P = 100 MPa (&); **T** = 1173 K (§); **$logfO_2$** = NNO+1.2 (#)

H_2O^{TOT} = 3.5 wt% (£); **CO_2^{TOT}** = 2 wt% (£); **S^{TOT}** = 0.013 wt% (£)

Computed conditions

H_2O^{gas} = 31.61 wt% **H_2O/CO_2** (mol) = 1.14

CO_2^{gas} = 68.01 wt% **H_2S/CO_2** (mol) = 0.004

SO_2^{gas} = 0.16 wt% **SO_2/H_2S** (mol) = 0.4

H_2S^{gas} = 0.22 wt%

$\rho_{melt+gas}$ = 2008 kg/m^3

ρ_{melt} = 2511 kg/m^3

m^{gas} = 3 wt%

V^{gas}/V^{tot} = 0.21

Composition of the deep gas separating from the trachytic body 8 km deep

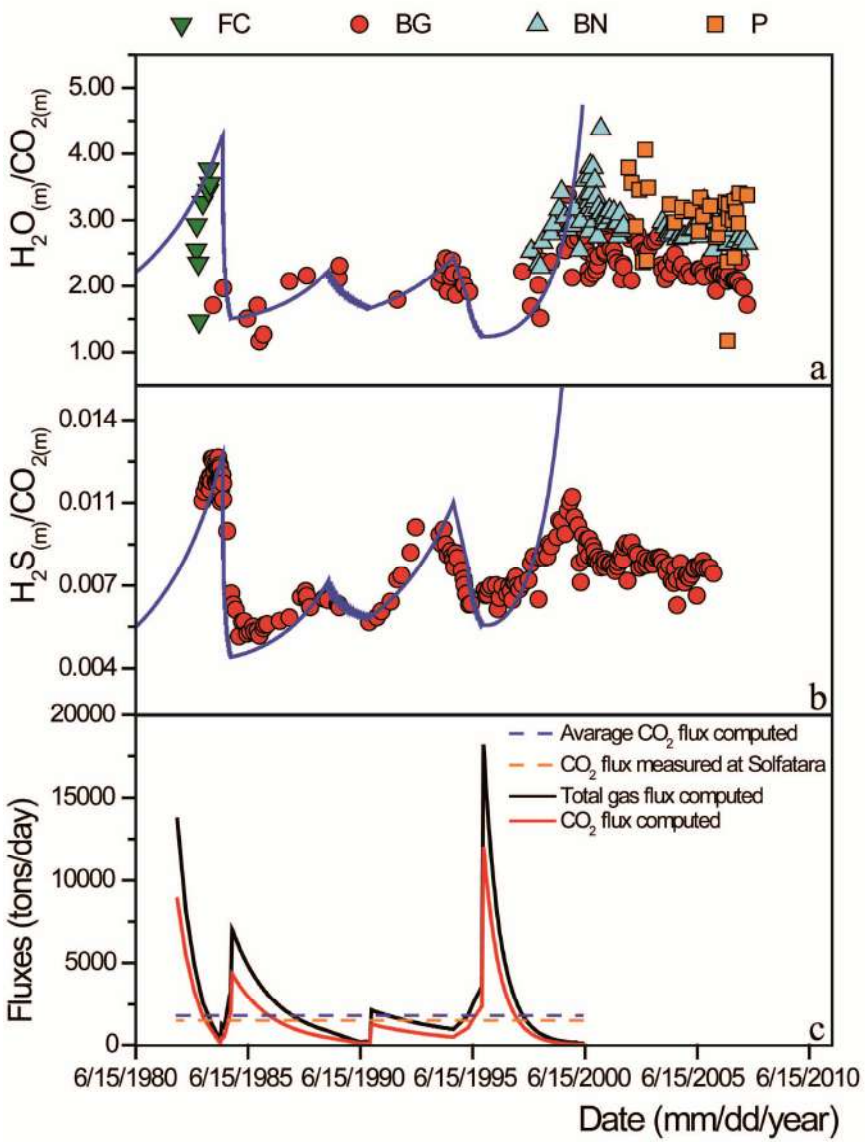
P = 200 Mpa (@); **T** = 1223 K (§); **$logfO_2$** = NNO+1.2 (#)

H_2O^{gas} = 21.21 wt% **H_2O/CO_2** (mol) = 0.66

CO_2^{gas} = 78.59 wt% **H_2S/CO_2** (mol) = 0.00058

SO_2^{gas} = 0.17 wt% **SO_2/H_2S** (mol) = 2.26

H_2S^{gas} = 0.04 wt%



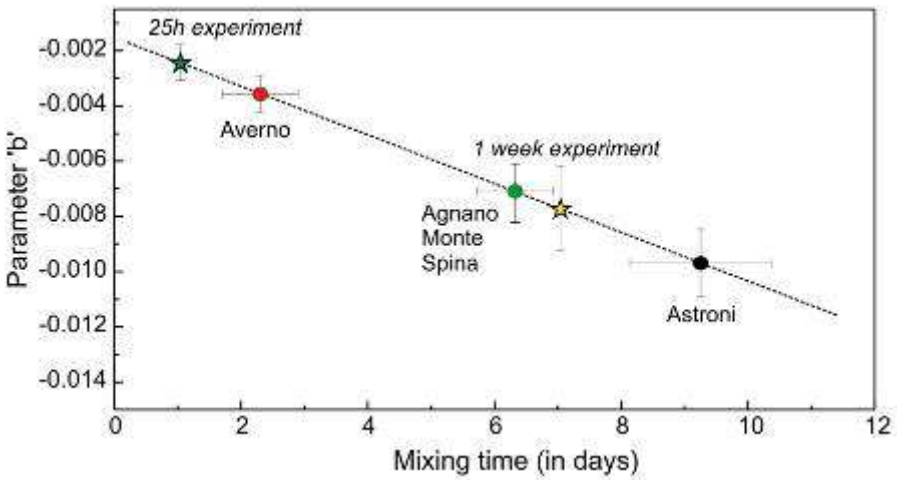
#: from MI studies (Arienzo et al., 2010) and experimental petrology (Roach, 2005);
&: from MI studies (Arienzo et al., 2010; Mangiacapra et al., 2008) and geophysical observations (Berrino, 1994; De Siena et al., 2010; Woo and Kilburn, 2010);
§: from experimental petrology (Roach, 2005);
£: from MI studies (Arienzo et al., 2010);
@: from MI studies (Arienzo et al., 2010; Mangiacapra et al., 2008) and seismic tomography (Zollo et al., 2008).

Possible scenarios and future (?) evolutions

3 scenarios can be reasonably hypothesized:

-Only deep gas reaches the surface, fluxing the shallow system
-The 4 km-deep (solidified) magma is experiencing re-melting
-The 8 km deep magma is rising from the large regional reservoir

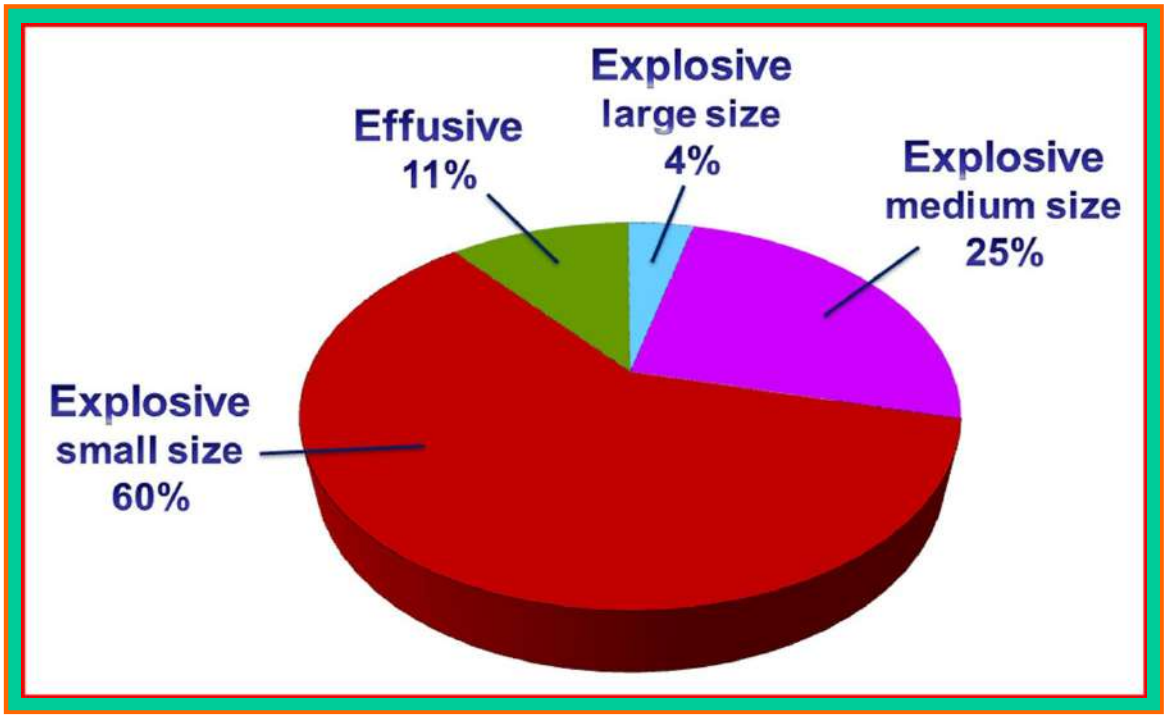
➔ Petrologic data show that Phlegrean eruptions regularly follow episodes of new magma arrival and subsequent mixing in the shallow system → Timing is very Fast



Orsi et al. 2004

Possible Eruptive Scenarios

Size and style of a future eruption



Size	A_{1cm} (km^2)	V_{Tephra} (km^3)	V_{DRE} (km^3)	TEM ($kg*10^{11}$)	Magnitude	Type eruption(s)
Large	> 500	> 0.40	> 0.3	> 5	> 5	Agnano-Monte Spina
Medium	500 - 1000	0.15 – 0.40	0.1 – 0.3	2 - 5	4.3 - 5	Astroni 6
Small	0 - 500	0 – 0.15	0 – 0.1	0 - 2	< 4.3	Monte Nuovo; Averno2

Orsi et al., 2009; E. Planet. Sci. Lett.

Hazard and Risk

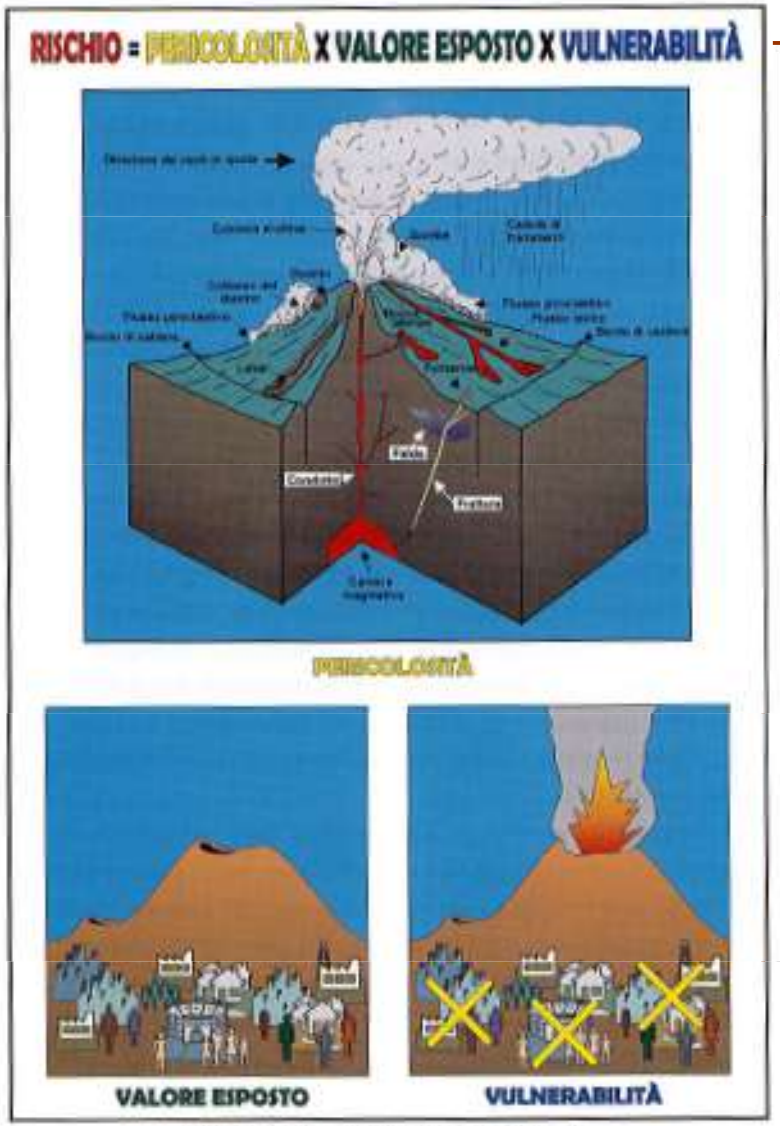
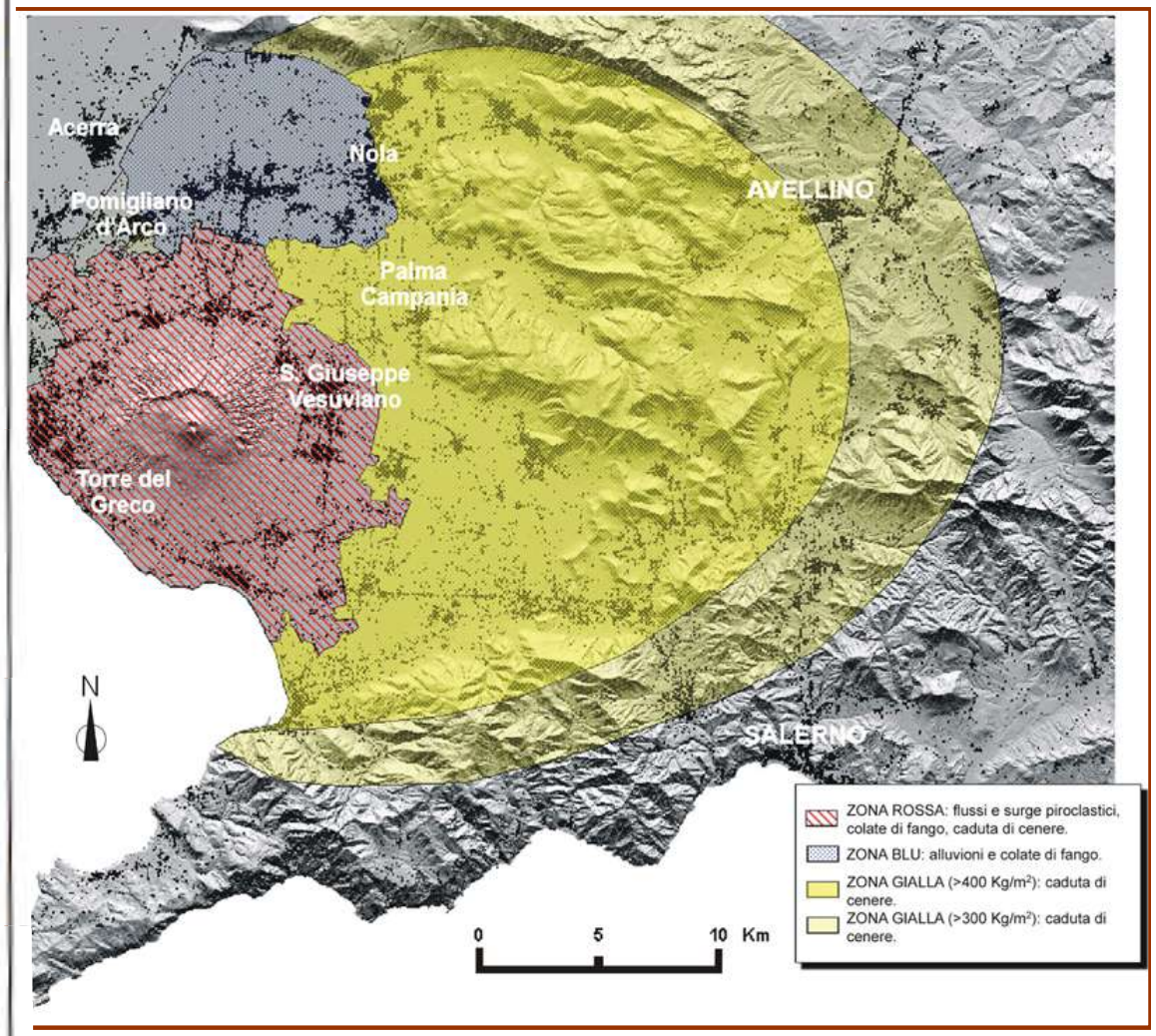
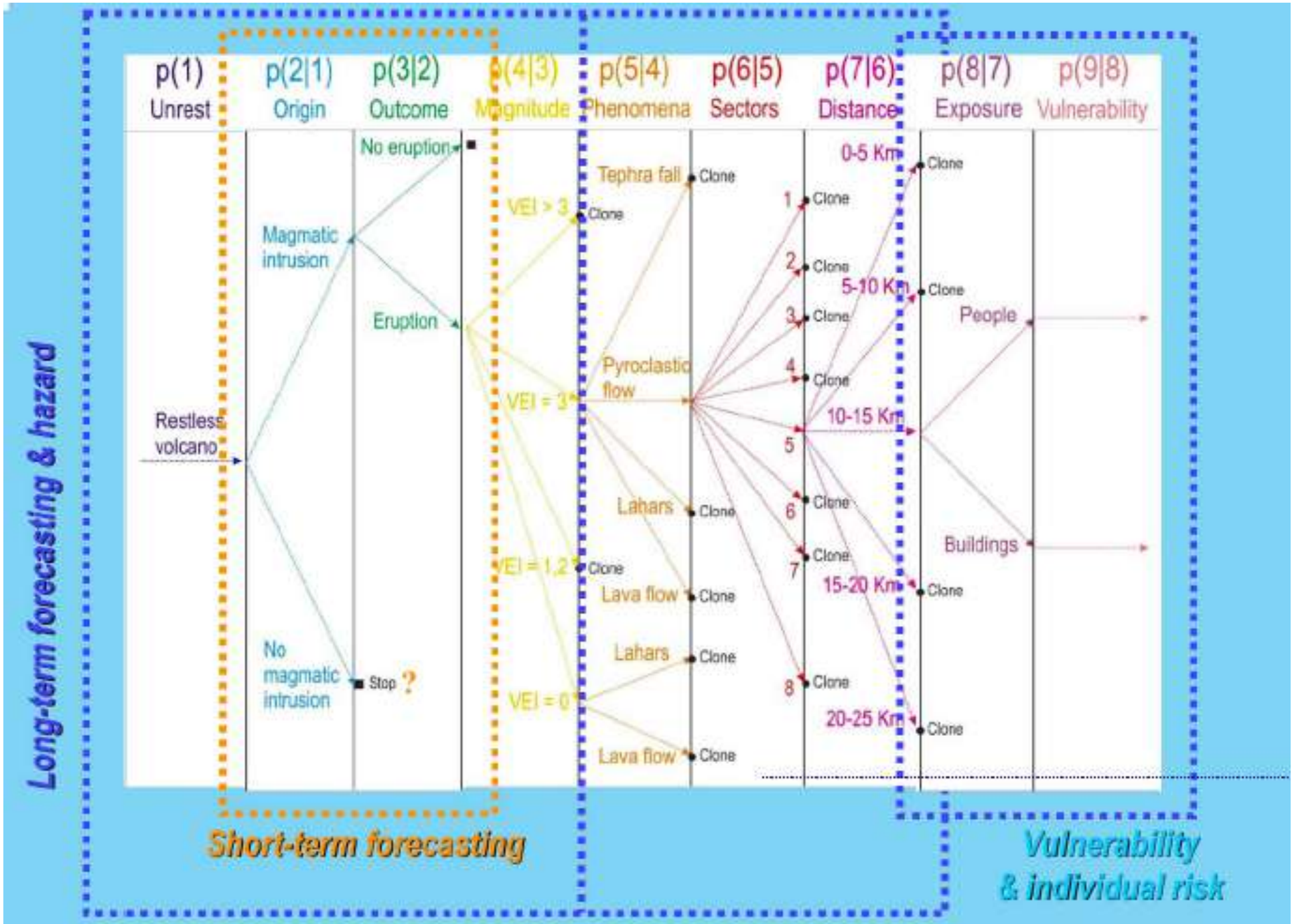


Fig. 1 – Illustrazione delle definizioni di rischio vulcanico.

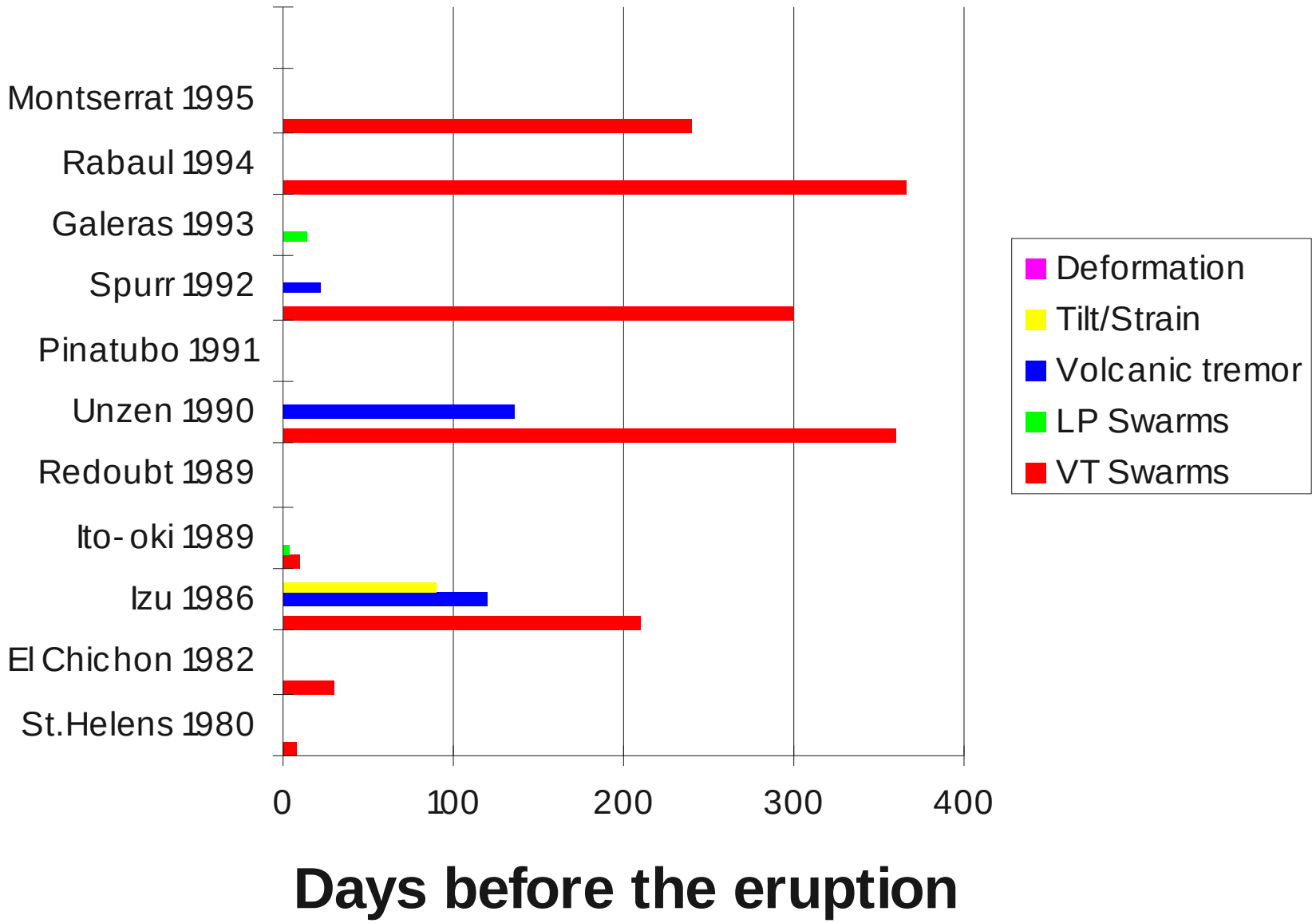


Alert Tresholds and Actions for Risk Mitigation - Vesuvius

LIVELLI DI ALLERTA	STATO DEL VULCANO	PROBABILITÀ DI ERUZIONE	TEMPO DI ATTESA ERUZIONE	SISTEMA DI PROTEZIONE CIVILE			FASI
				Comunità Scientifica	Risposte Operative		
Base	Nessuna variazione significativa di parametri controllati	Molto bassa	Indefinito, comunque non meno di diversi mesi	Attività di sorveglianza secondo quanto programmato	Commissione Nazionale	Attività ordinaria	
Attenzione	Variazione significativa di parametri controllati	Bassa	Indefinito, comunque non meno di alcuni mesi	Stato di allerta tecnico scientifico ed incremento dei sistemi di sorveglianza	Dipartimento della Protezione Civile	- Attivazione della fase di attenzione - Comunicazione al Prefetto di Napoli	I FASE Attenzione
					Prefettura di Napoli	- Convocazione del C.C.S. - Organizzazione supporto logistico alla Comunità Scientifica - Organizzazione delle prime informazioni alla popolazione unitamente ai Sindaci dei comuni interessati - Comunicazione a: a) Dipartimento della Protezione Civile b) Ministero dell'Interno c) Presidente Giunta Regionale Campana d) Presidente Amministrazione Provinciale di Napoli e) Sindaci	
Preallarme	Ulteriore variazione di parametri controllati	Media	Indefinito, comunque non meno di alcune settimane	Continua l'attività di sorveglianza; simulazione dei possibili fenomeni eruttivi	Dipartimento della Protezione Civile	- Attivazione della fase di preallarme - Richiesta dichiarazione Stato d'Emergenza - Convocazione Comitato Operativo di Protezione Civile - Nomina del Commissario Delegato da parte del P.C.M. - Attivazione della Direzione di Comando e Controllo	II FASE Preallarme
					Dipartimento della Protezione Civile (DI.COMA.C.)	- Attivazione del C.C.S. nelle Prefetture della Campania e delle regioni ospitanti - Attivazione degli organismi Regionali e Provinciali di P.C. della Campania e di tutte le regioni ospitanti - Posizionamento soccorritori - Allontanamento spontaneo della popolazione	
Allarme	Comparsa di fenomeni e/o andamento di parametri controllati che indicano una dinamica pre-eruttiva	Alta	Da settimane a mesi	Sorveglianza con sistemi remoti	Dipartimento della Protezione Civile (DI.COMA.C.)	- Attivazione della fase di allarme - Evacuazione dei 18 comuni vesuviani - Allontanamento capi famiglia con mezzi propri - Attivazione Sala Operativa alternativa - Ripiegamento dei soccorritori - Spostamento Centri Operativi in Zona Gialla - Controllo del territorio evacuato al limite esterno della zona rossa - Allertamento strutture ricettive della Campania	III FASE Allarme
	Evento in corso (Eruzione)			Sorveglianza con sistemi remoti; definizione cono di interferenza dell'eruzione con la zona gialla	Dipartimento della Protezione Civile (DI.COMA.C.)	- Controllo fenomeno per la definizione delle aree della zona gialla da evacuare - Raccolta, elaborazione e catalogazione dati sull'andamento del fenomeno e della operazione - Predisposizione strutture ricettive della Campania ed evacuazione Zona Gialla	IV FASE Evento in corso
				Continua la sorveglianza con sistemi remoti; inizia la ricostruzione dei sistemi di sorveglianza in loco	Dipartimento della Protezione Civile (DI.COMA.C.)	- Ricollocazione delle strutture operative sul territorio - Operazioni tecnico-scientifiche di verifica del territorio finalizzate al rientro della popolazione (Regione, Provincia, Comuni, Provv. OO.PP., Gruppi Nazionali, VV.F.)	V FASE Dopo l'evento
					Dipartimento della Protezione Civile	- Rientro controllato - Richiesta revoca stato di emergenza	



Newhall & Hoblitt (Bull. Volcanol., **64**, 3-20, 2002)


Montserrat 1995
Rabaul 1994
Galeras 1993
Spurr 1992
Pinatubo 1991
Unzen 1990
Redoubt 1989
Ito-oki 1989
Izu 1986
El Chichon 1982
St.Helens 1980
0
100
200
300
400
Days before the eruption
Deformation
Tilt/Strain
Volcanic tremor
LP Swarms
VT Swarms

Thanks for your attention!

Andy Warhol, 1985