Impurity of Sulfur Layers and Magmatic Gas Scrubbing: Implication for gas monitoring

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ABSTRACT

The evidence of bodies of elemental sulfur (S_e) beneath acid crater lakes at the summit of composite active volcanoes has been recognized several decades ago [1,2] But S_e accumulation was already hypothesized a century ago at Kusatzu Shirane (Japan) based on the observation of sulfur spherules floating on its crater-lake [3] . Since these pioneering works, other studies have focused on understanding key aspects of molten sulfur bodies, considered a feature unique of volcanic lakes. Instead, it is reasonable to assume that S_e bodies occur in several volcanic settings because a) several reactions may lead to S_e deposition from S-bearing gases, and b) crater-lakes, surface expressions of hydrothermal systems, are transient features. The scrubbing of several magmatic gases, some of which critical for volcano monitoring, has been attributed to ground/surface waters [4]. Nevertheless, gas scrubbing could reflect viscosity variations of impure S_e within hydrothermal systems. Industrial experiments indicated that impurities (organics, H_2S, ammonia, HCl, HF, HBr, HI) hinder S_e polymerization at T ≥ 160ºC, allowing viscosity to remain low for long time depending on the maximum T achieved and heating rates [5]. However, a prolonged heating destroys the viscosity-modifying substances (e.g. H_2S_x formed by reactions with organics, H_2S) and dramatic S_e viscosity increases occur after a certain number of heating and cooling cycles. A prolonged boiling of S_e with organics was observed to release H_2S, following H_2S_x disruption. Some gases (e.g. SO_2) do not affect S_e viscosity. In volcanic environments non-reactive species (e.g. SO_2, CO_2) could therefore escape under S_e low viscosity regimes. Also, halogens absence in gas emissions could be caused by their participation in reactions within S-layers causing its viscosity to remain low
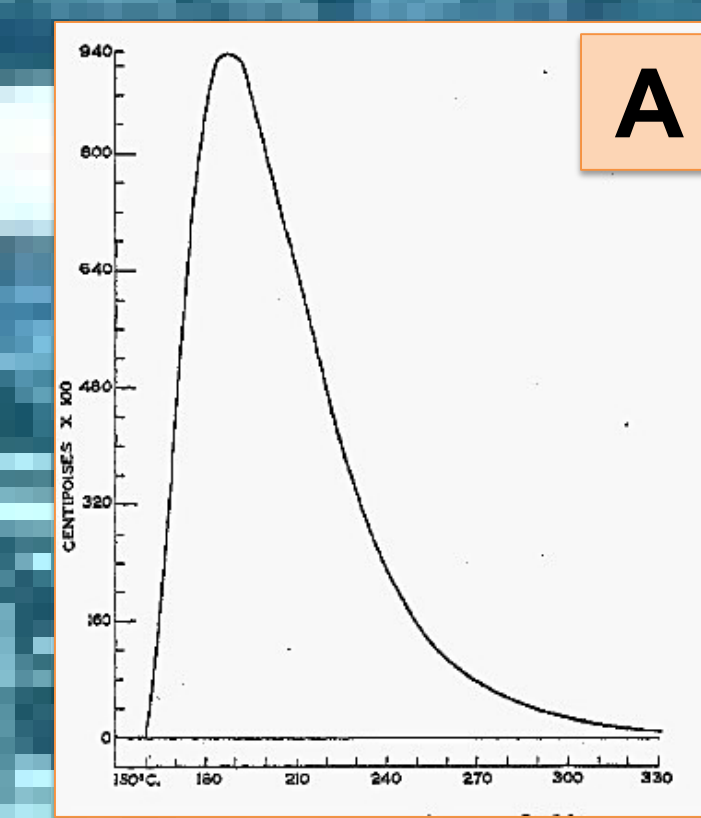
1. Sulfur properties

Variations in impure S viscosity only occur above 160ºC, when S8 rings rupture (start of polymerization, maximum at 187ºC), the presence of impurities in S (organics, halogens, H_2S) cause reactions that shortens the polymer chains. Both H_2S_x (by product between organics and S, or H_2S and S) or halogens sticks to the terminal portions of S-polymers causing the decrease in viscosity [19].
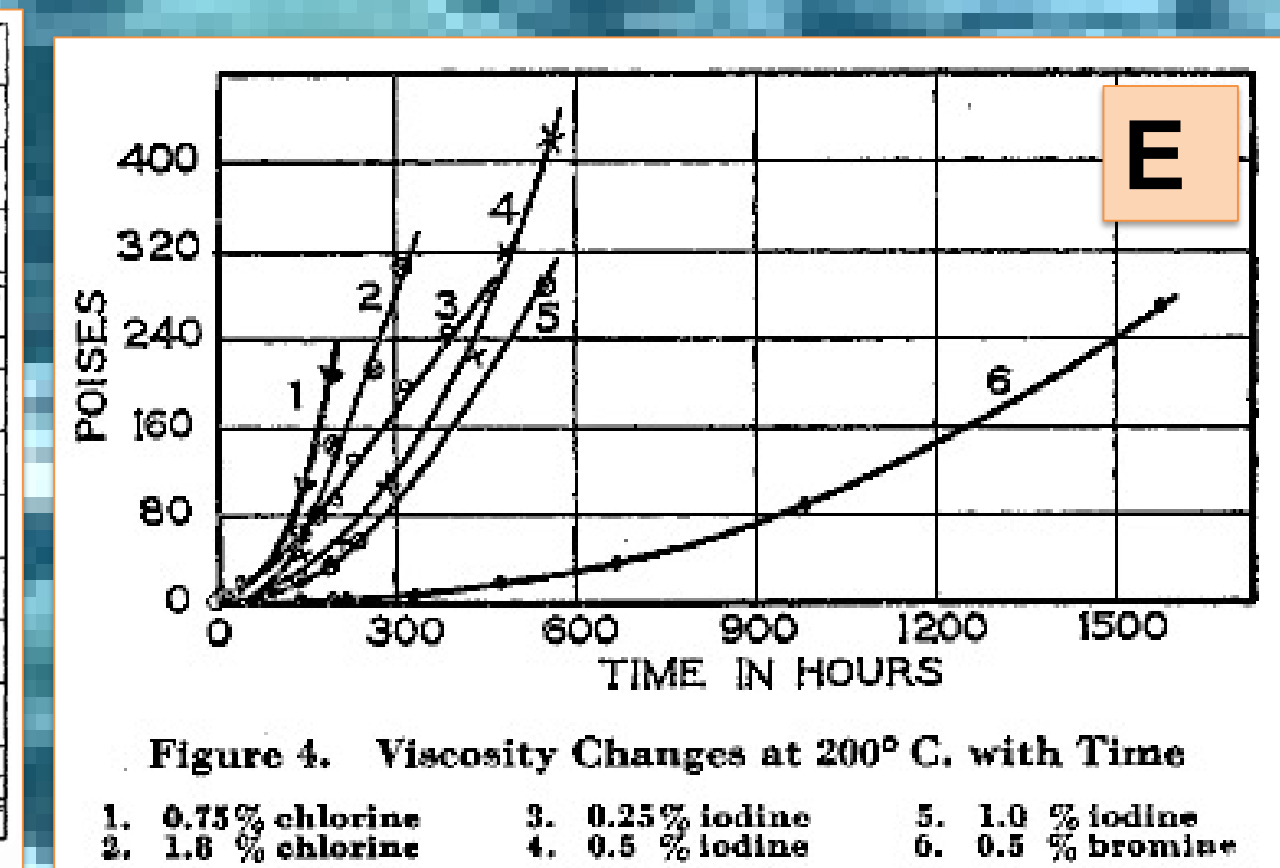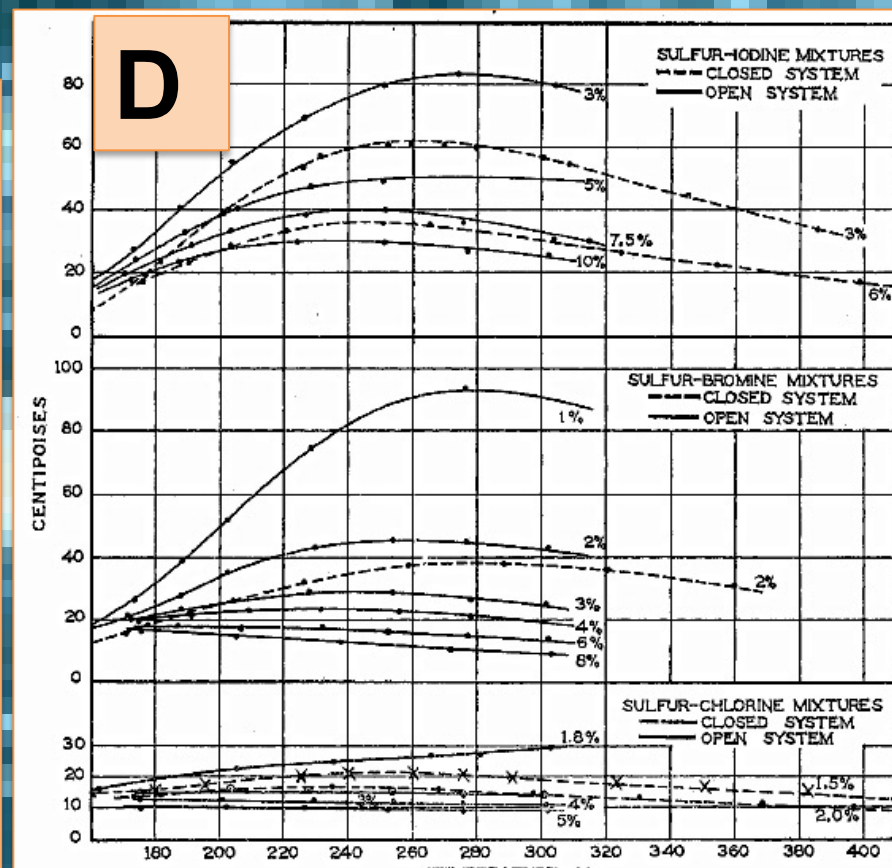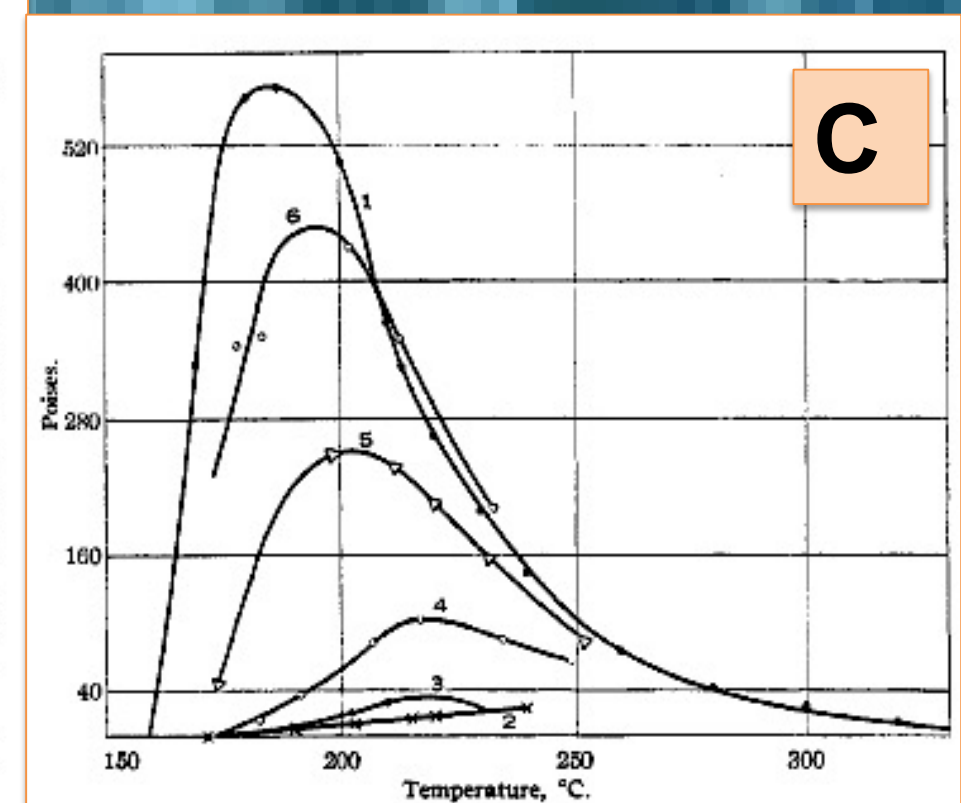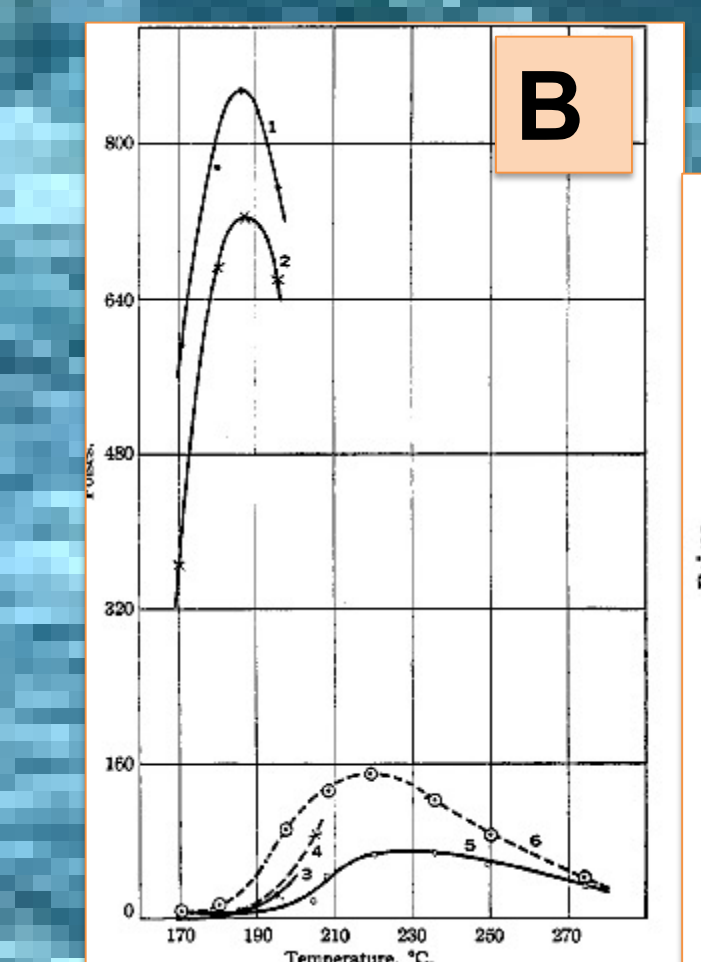
Halogens

The abundance of halogen gases varies according to tectonic settings and magma composition

HF, HCl, HBr, HI

MELT CONCENTRATIONS
F 10-100 ppm (sometimes >5%)
Cl 800-7500 ppm
Br 0.06-300 ppm
I 0.06-110 ppm
From [13]

MANTLE MINERALS CONCENTRATIONS
Ap 0.4-1,4 %F
    0.1-1% Cl
Cpx, Ol, Opx,Grt
    <50 ppm F <50 ppm Cl
PhI 0.43 % F
    0.08 % Cl
From [13]

Fig. 1. Variations in elemental S viscosity- Experimental results obtained in the 40's. (Scale: 1cP= 0.001 Pa·s; 1Poise= 0.1 Pa·s) [5,6] **A. Pure S viscosity**. 4-magnitude increase at ≈160° C. **B. Effect of H_2S**. *Curves*: *1*. untreated S. *2*. after 100hrs under H_2S at 140° C. *3-4*. S with dissolved H_2S after cooling and heating between 180-200° C (H_2S_xformation) *5-6*. S+ H_2S after cooling (170° C) and reheating (note :maximum shifts at low T) **C. Effect of organics**. *1*. S (+0.038 wt% organics) not previously heated at 180-200° C. *2*. on cooling after preheating (125-260° C for 1 hr.30'). Note the dramatic decrease in viscosity (!) (H_2S_xformation). *3*. with rising T after cooling (170° C). *4*. with rising T after cooling (160° C for 14 hrs). *5-6*. with rising T after twice cooling/heating cycles as in *4*. **D. Effect of halogens** at various concentrations with T in open or closed systems. Chlorine is the most effective. For 2wt% the viscosity is <0.015 Pa·s. Increasing concentrations (i.e. 3-4-5 wt%) produce lower viscosities, independent of T (compare to Fig. **A**). For equal concentrations values for closed systems are lower than open systems **E. Effects of halogens with time.** Mixtures maintained at 190-200° C for the time indicated. Measurements at 200° C Chlorine is the most effective, but high volatile (SCl_2) is the greatest. Iodine is more persistent than chlorine; bromine is better than either.

Table summarizing some of the studies of the last decade. (From [13])

Halogen Content (wt.%)	Ocean island basalts	MORB	Back-arc basin basalts	Subduction-related basalts	Subduction-related andesites	Subduction-related dacites	Subduction and high-SO_2 rhyolites	Evolved rhyolites	Non-mafic peralkaline volcanic rocks
F	0.004–0.22	0.01–0.07	0.01–0.09	0.01–0.24	0.01–0.09	0.01–0.3	0.01–0.5	0.07–7	0.01–1.7
Cl	0.009–0.1 (2.5 in Austral Islands[a])	0.0001–0.04	0.008–008 (0.84 in Lau Basin[b])	0.01–0.6	0.01–0.85	0.01–0.3	0.01–0.75	0.01–0.6	0.01–1.2
Br[c]					0.0005–0.03		0.00001–0.0002		0.00002–0.028
I[d]		0.0000007–0.0000014 0.0000006			0.00006–0.011		0.000002–0.000008		<0.00005
(Cl/F)[e]	0.3–5	0.01–0.45	ca. 0.4		0.5–3.5	ca. 0.5–1	ca. 1	ca. 0.05–1	ca. 5–6

Halogen abundances (in wt.%) of matrix glasses and silicate melt inclusions from different types of volcanic systems in varied tectonic environments.

2. Examples

Soufrière Hills, Montserrat

Between 1995-2013, SO_2 emissions at SHV were decoupled from lava extrusion in a time scale of months to years, leading to the paradox that more SO_2 was emitted during periods of no lava extrusion [7]. These periodical emissions have been attributed to A) change in the system permeability; B) advection of the gas phase to shallower levels. Long-period (2 years) and short-period (4-5 months) cycles were also linked to a) the entrainment of moist air into the plume, or B) gas scrubbing in the hydrothermal system. *Both processes involving a reaction between SO_2 and H_2O failed in explaining the periodical SO_2 release* [7]. Similarly localized induced pressure changes within a deeper second magma chamber [8] (was considered not in agreement with observation of magma fluxes [7] .
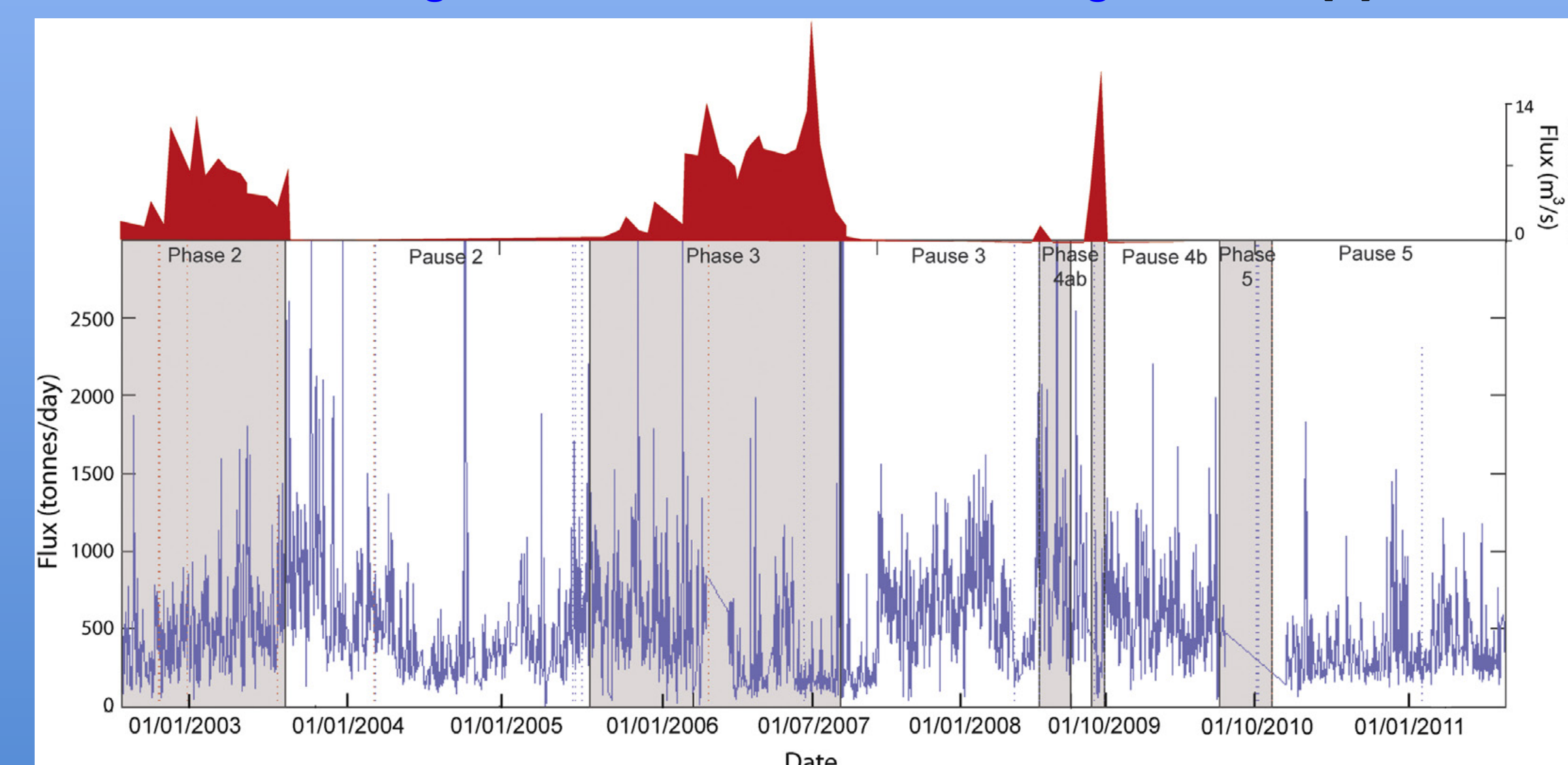
Fig. 2. Daily mean SO_2 flux at SHV since the onset of continuous sampling (2002-2011) after the beginning of the 1995 eruption. Shaded areas are periods of dome growth. In red magma efflux rate (DRE) (from [8]).The *cyclic* degassing (variable periodicity: 509-1014 days; 41-63 days; 17-26 days; 11-14 days), could not be conciliated with closed-system degassing of a single batch of magma [10] and long-term degassing trends appears to be independent of magma extrusion phases [11].
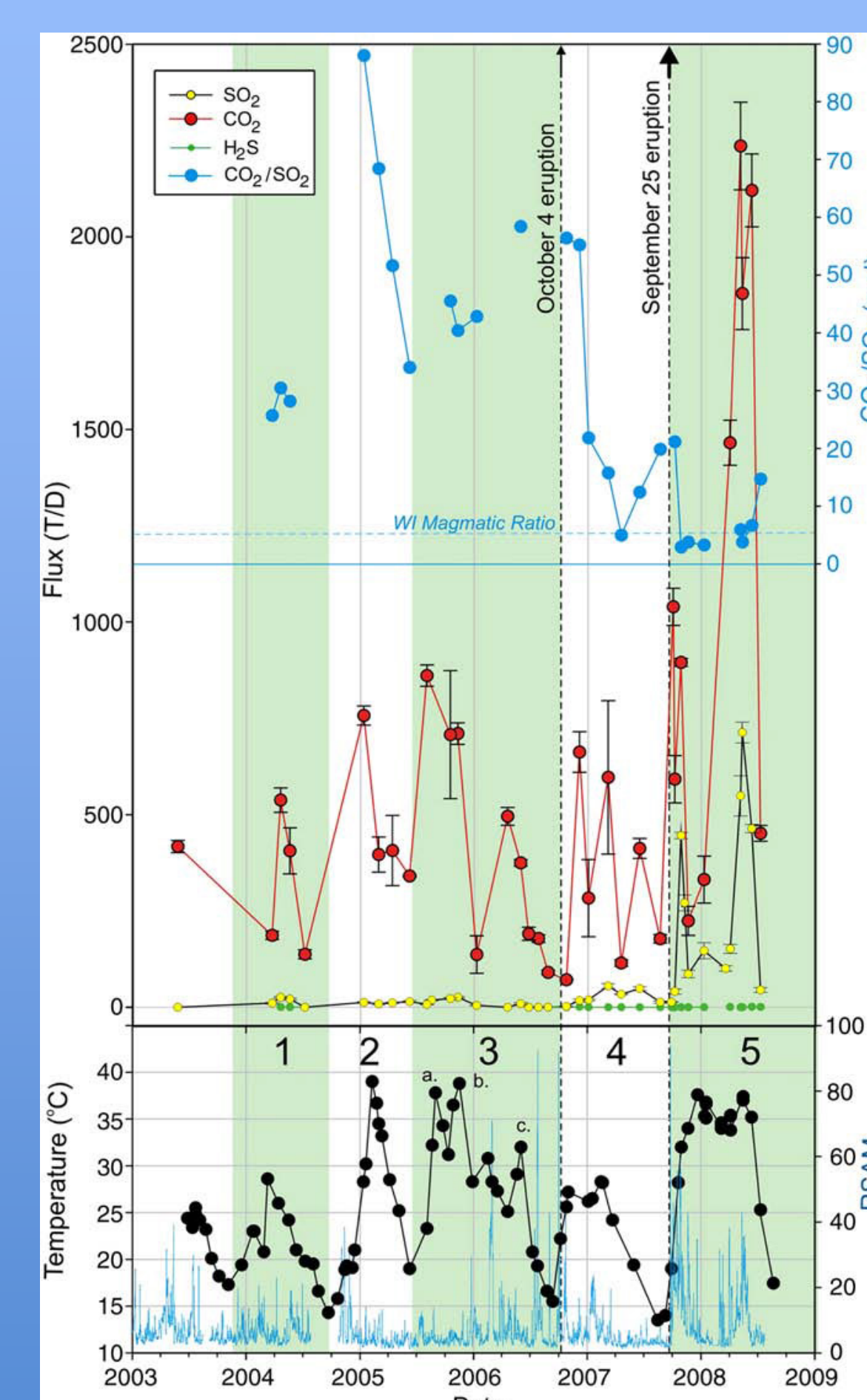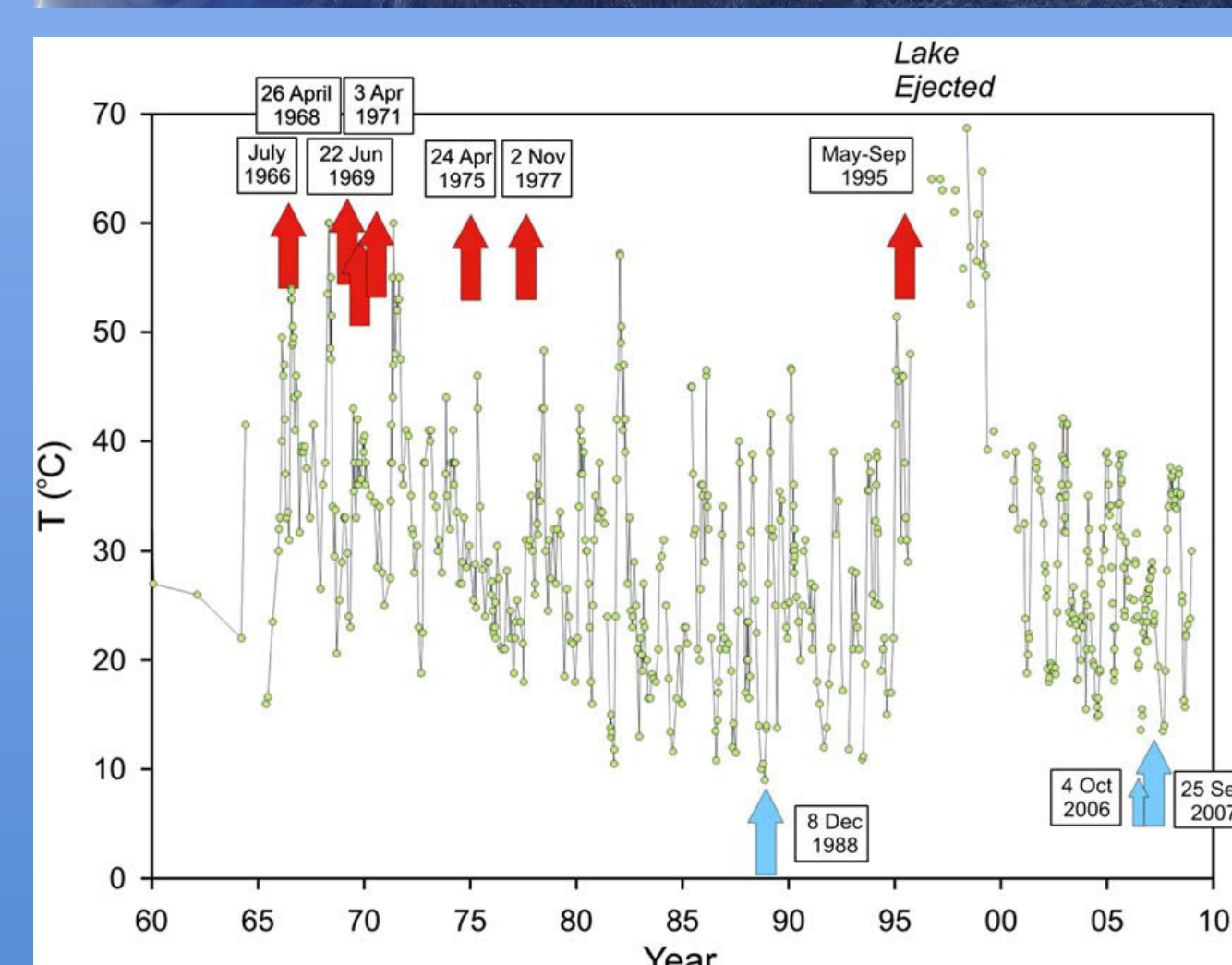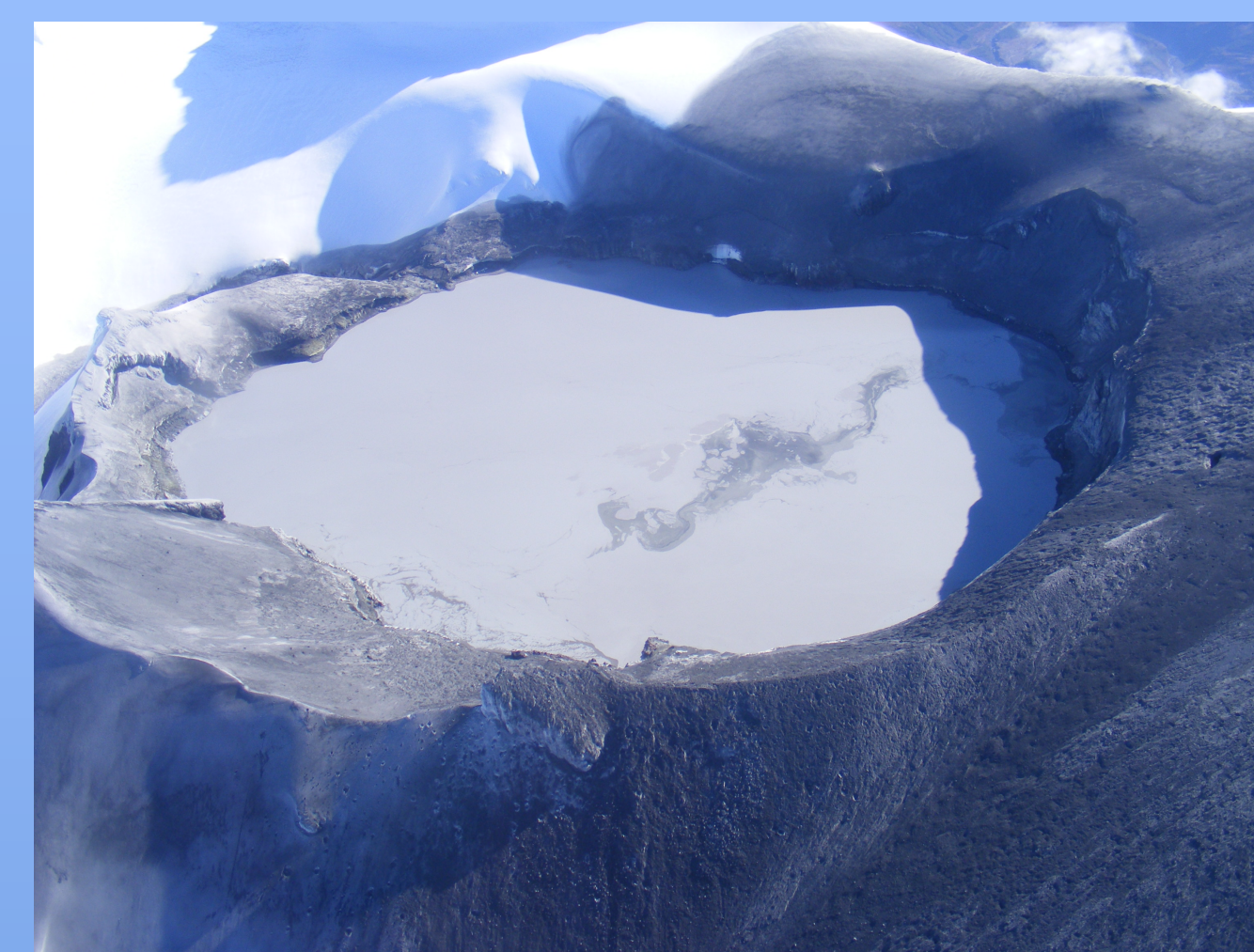
Ruapehu, New Zealand

Fig. 3. *Left*. Volatile emissions, lake T and seismic amplitude time series 2003-2008 at Ruapehu volcano. Flux values are plotted for CO_2, SO_2 and H_2S. *Upper right*: Crater Lake temperature and eruptions through time (red arrows during unrest and lake T>20° C. Blue arrows during unheralded eruptions occurred with lake T<20° C (From [12]) .
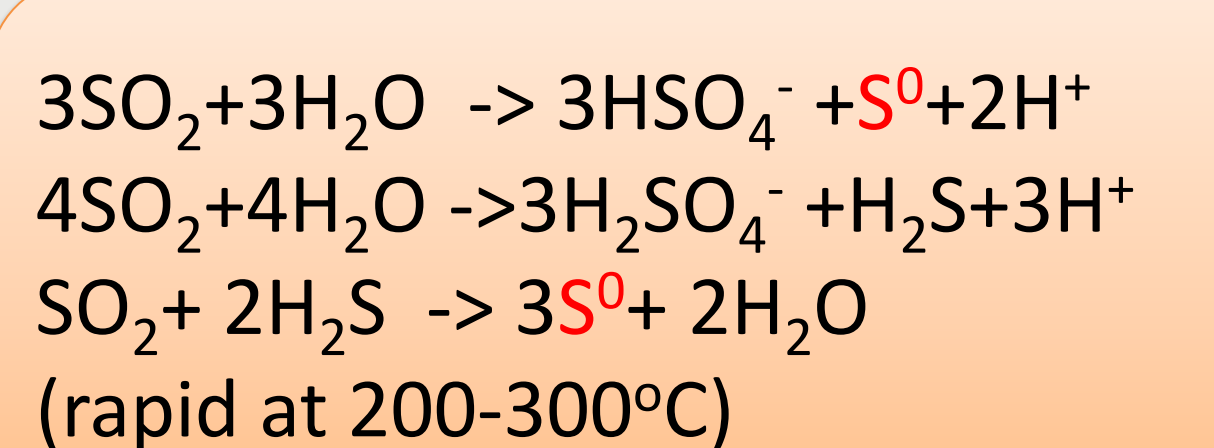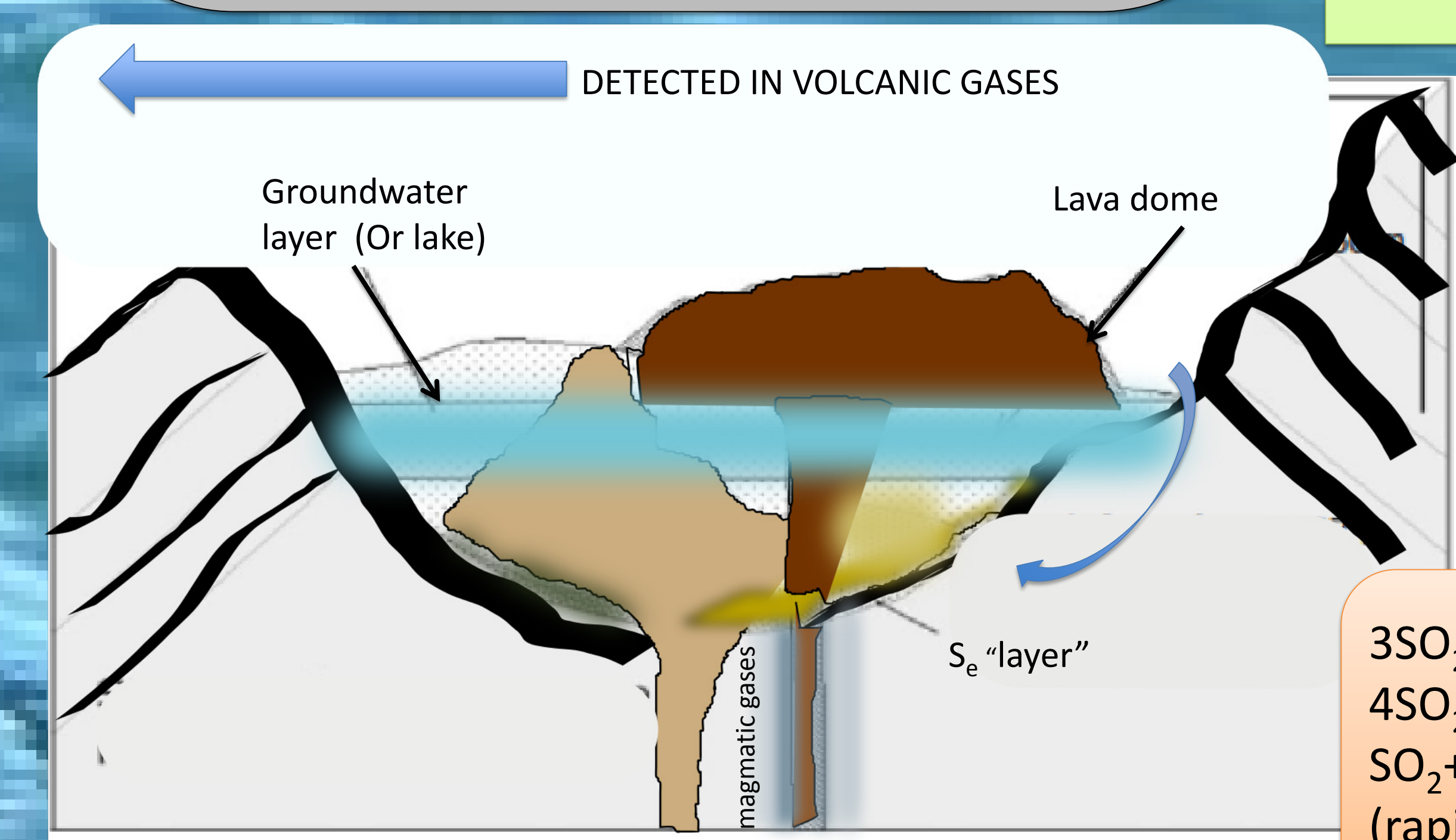
Organics

A great variety of organic compounds hydrocarbons, and non-aromatic S-bearing species (i.e. CS_2) have been detected in fumarolic emissions since 1971 at different volcanoes [14,15,16,17,18, 19]. A thermal decomposition of organic matter in sedimentary basements is commonly invoked to explain their occurrence in hydrothermal systems, but other reactions are also possible [18] . Halogenation reactions following thermolytic cracking of CH_4 lead to organohalogens compounds (CH_3Cl, CH_3Br,CH_3I, CH_2Cl_2, CCl_3Br, CCl_4) [19].

Transitions between periods of dome extrusion and presence of crater lakes have been observed at several volcanoes. Crater lakes are transient in time. Aquifers can act as lakes Elemental S deposition can occur in several volcanic settings. When a threshold of 180-200ºC is overcome, S viscosity remains low under 1) H_2S gas fluxes, 2) organics or 3) halogens inputs, all of which are "scrubbed" by elemental S. A prolonged heating destroys the viscosity –modifying substances causing a system sealing
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In contrast, SO_2 does not react with elemental S. The "periodic" emissions observed at the surface may likely reflect its release during periods of low S viscosity.

Fluorinated compounds
Chlorofluoromethane — CHF_2Cl
Dichlorofluoromethane — $CHFCl_2$
Trichlorofluoromethane — $CFCl_3$
Dichlorodifluoromethane — CF_2Cl_2
Tetrafluoroethene — $C_2H_2F_2$
Chlorodifluoroethane — $C_2H_3F_2Cl$
Trichlorofluoroethane — $C_2F_3Cl_3$
Tetrachlorodifluoroethane (2) — $C_2F_2Cl_4$
Trifluoropropene — $C_3H_3F_3$
Hexafluoropropene — C_3F_6
Fluorobenzene — C_6H_5F
Tetrafluorobenzene — $C_6H_2F_4$
Fluorochlorobenzene — C_6H_4FCl

Iodinated compounds
Methyl iodide — CH_3I
Chloroiodomethane — CH_2ICl
Iodoethane — C_2H_5I
Iodoethene — C_2H_3I

Brominated compounds
Bromomethane — CH_3Br
Dibromomethane — CH_2Br_2
Tribromomethane — $CHBr_3$
Chlorobromomethane — CH_2ClBr
Dichlorobromomethane — $CHCl_2Br$
Trichlorobromomethane — CCl_3Br
Chlorodibromomethane — $CHClBr_2$
Bromoethene — C_2H_3Br
Bromoethane — C_2H_5Br
Bromochloroethane — C_2H_4ClBr
Bromodichloroethane (2) — $C_2H_3Cl_2Br$
Bromotrichloroethane — $C_2H_2Cl_3Br$
Bromopropene (3) — C_3H_5Br
Bromochloropropene (3) — C_3H_4ClBr
Bromochloropropane — C_3H_6ClBr
Bromochloropropyne — C_3H_2ClBr
Bromochloropropyne — C_3H_2ClBr
Bromobutane — C_4H_9Br
Bromobutene — C_4H_7Br
Chlorobromobutene — C_4H_6ClBr
Bromobutyne — C_4H_5Br
Bromobutyne (2) — C_4H_5Br
Bromofuran (2) — C_4H_3OBr

DETECTED IN VOLCANIC GASES

Groundwater layer (Or lake)

Lava dome

magmatic gases

S_e "layer"

$$3SO_2+3H_2O \rightarrow 3HSO_4^- +S^0 +2H^+$$
$$4SO_2+4H_2O \rightarrow 3H_2SO_4^- +H_2S+3H^+$$
$$SO_2+ 2H_2S \rightarrow 3S^0 + 2H_2O$$
(rapid at 200-300ºC)

The variations in viscosity of impure S_e accumulated at depth (under the influx of different gases/ at different heating rates/ T) could offer an alternative explanation to the data observed at both volcanoes.

REFERENCES :
[1] Oppenheimer C., Stevenson D. (1989) Nature 342:790-793; [2] Christenson BW, Wood CP (1993) Bull Volcanol 55:547-565; [3] Ohashi, R. (1919) J. Akita Min. Coll 1:1-10; [4] Symonds, R.B., Gerlach, T.M., Reed, M.H. (2001) JVGR 108:303-341
[5] Bacon R.F., Fanelli, R. (1943) J Am Chem Soc 65:639-648; [6] Fanelli R. (1946) Industr. Engin Chem 38(1):39-43; [7] Christopher, T., Edmonds, M., Taisne, B., Odbert, H., Costa, A., Hards, V., Wadge,G., (2014).Geol.Soc.Lon. Spec.Pub. DOI:10.1144/SP410.11; [8] Melnik, O., Costa, A. (2014) Geol.Soc. Lon. Spec.Pub 39:61-69; [9] Nicholson EJ, Mather, T.A., Pyle, D.M., Odbert, H.M., Christopher, T. (2013) EPSs 375: 209-221; [10] Edmonds M., Oppenheimer, C., Pyle, D.M., Herd, R., Thompson, G. (2003) J Volcanol Geoth Res 124:23-43; [11] Edmonds M, Aiuppa, A., Humpreys, M., Moretti, R., Giudice, G., Martin, R.S., Herd, R.A., Christopher, T. (2010) Geoch Geoph Geosys 11(Q04005); [12] Christenson, B.W., Reyes, A.G., Young, R., Moebis, A., Sherburn, S., Cole-Baker, J., Britten, K. (2010) J Volc Geotherm Res 191:15-32; [13] Aiuppa, A., Baker, D.R., Webster, J.D. (2009) Chem.Geo. 263:1-18; [14] Stoiber, R.E.,Leggett, D.C., Jenkins, T.F., Murmann R.P., Rose, W.I. (1971) Geol.Soc. Am. Bull. 82: 2299; [15] Capaccioni, B., Martini, M., Mangani, F. (1995) Bull Volc 56:593; [16] Giggenbach, WF (1996). in Scarpa, R., Tilling, R.I. Monitoring and mitigation of volcanic hazards Springer Verlag; [17] Taisi F., Venturi S., Cabassi J., Capecchiacci F., Nisi, B., Vaselli, O.(2015) Appl. Geochem. 56: 37-49; [18] Taran, Y., Giggenbach, W.A. (2003) in: Volcanic, Geothermal, and Ore-Forming Fluids: Rulers and Witnesses of Processes Within the Earth -Society of Economic Geologists- Spec. Publication; [19] Jordan (2003) in The Handbook of Env. Chem. 3: part P 121-139.