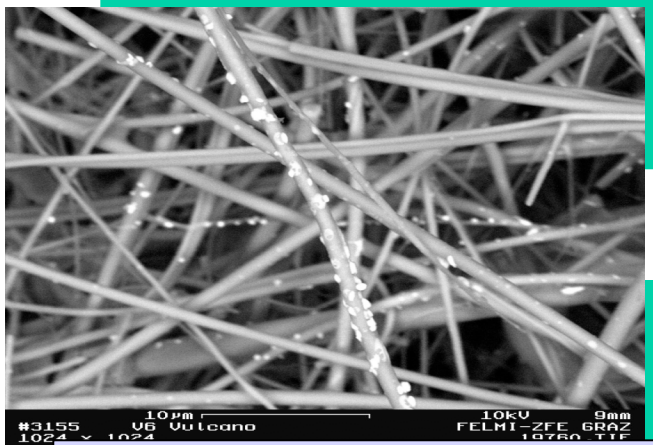
Chemical and physical properties of volcanic aerosols



$BaSO_4$ on glass fiber

More uncertainties in climate prediction?

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& M. Edwards (CEE/Virginia – USA)

Dear audience:

This ppp hopes to be an introduction to volcanology to the non-specialists. Please follow the provided links to learn more about state-of-the-art research and knowledge provided by hundreds of active researchers and scholars. All slides can be copied freely for non-commercial usage. Please drop a message to M. Edwards (edwardsm@vt.edu) and to J.H. Obenholzner (obenholzner@a1.net) if you use presented material for teaching.

Marc and I started to cooperate as my particle research and his gas and fluid chemical studies of the various environments produced many questions. This ppp tries to summarize open questions (physics- vs. chemistry-dominated approaches) concerning the volcanic aerosol, climate modelling, civil protection issues. An unpublished repository of ICP-MS, GC/MS, SEM and FESEM data exists. Please contact us, if you are interested.

As long as mankind has to cope with the dynamics of this planet, and maybe later with the dynamics of other planets, will we be able to filter air for breathing, and/or filter raw materials from i.e. volcanic exhalations?

- 1. Basics of volcanology
- 2. What is the typical volcanic aerosol? Gases (H_2O, CO_2, SO_2, H_2S, CO, COS, CH_4, H_2, HCl, HF, SiF_4, O_2, S_2, N_2, CS_2, SO_3, NH_3, B, Br, Hg, halogenides of metals and of rare earth elements), solid (glass, mineral/-oid and rock fragments) and liquid (H_2SO_4 droplets) particles (i.e. Wohletz & Heiken, 1985; Obenholzner et al., 2003; Delmelle et al., 2000; Francis et al., 1996).
- 3. Volcanic eruptions and climate (i.e. AGU book by Robock & Oppenheimer (eds.) 2005.
- 4. Approaches to quantify volcanism of Earth.
- 5. News: PH_3 as a trace gas of fumaroles and cooling lava flows. Unquantified fluxes of Ba,Tl etc.. Heterogeneous nucleation of particles on glass. Are such particles IN and/or CCN? Is Ba a nutrient for bacteria as CCN?

Ignimbrites of supervolcanoes are not included.

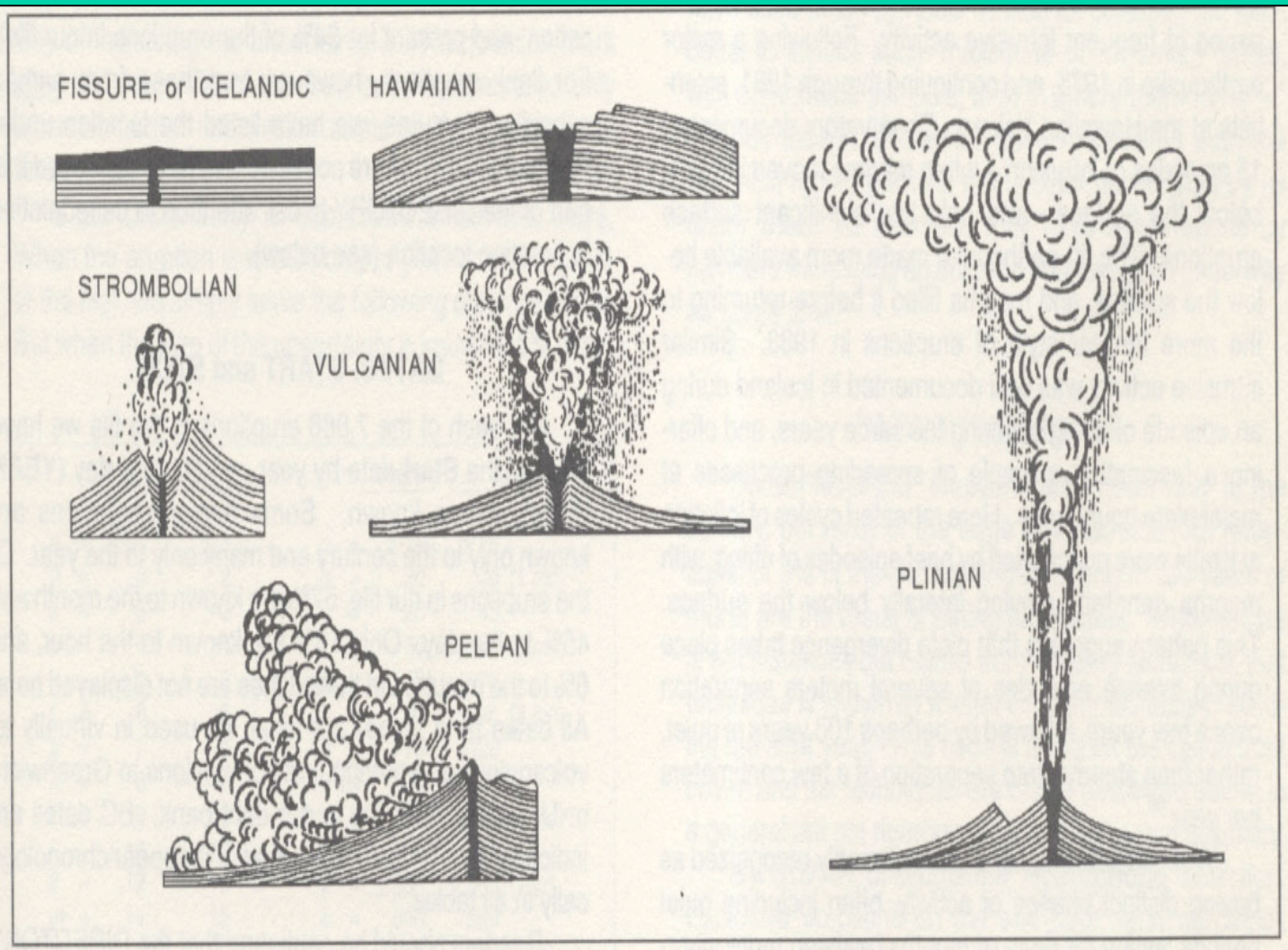


Figure 6. Types of eruptions: schematic cross-sections after Holmes.[51] The great range in explosivity depends upon many factors, particularly the magma's gas content and its viscosity (influencing the manner in which gas escapes the liquid).

Simkin & Siebert, 1994

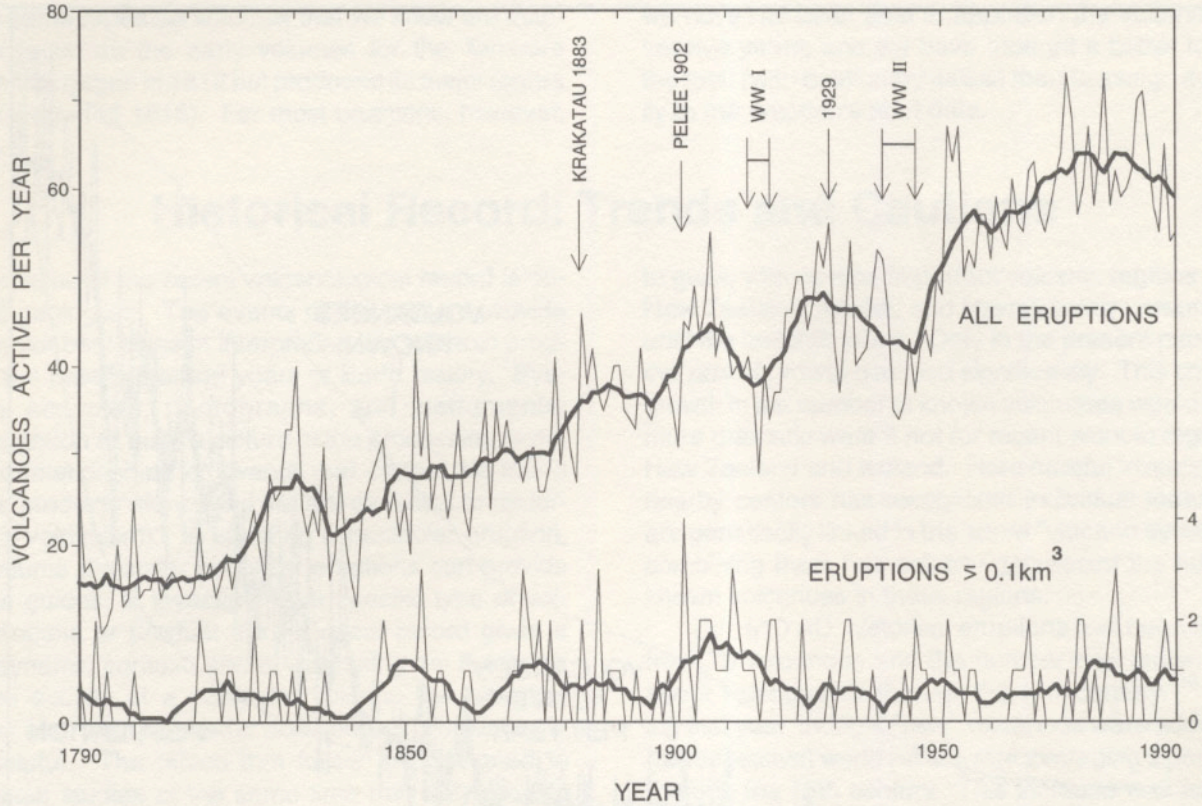


Figure 9. Last 200 years of volcano reporting. Total number of volcanoes erupting per year (thin upper line) and 10-year running mean of same data (thick upper line). These numbers are generally 5-10% higher than those for the same year in Figure 8 because these include uncertain eruptions[119] (preceded by ? in DIRECTORY and CHRONOLOGY). Lower lines show only the annual number of volcanoes producing large eruptions (≥0.1 km^3 of tephra or VEI ≥4) and scale is enlarged (on right axis). Thick lower line again shows 10-year running mean.

Simkin & Siebert, 1994

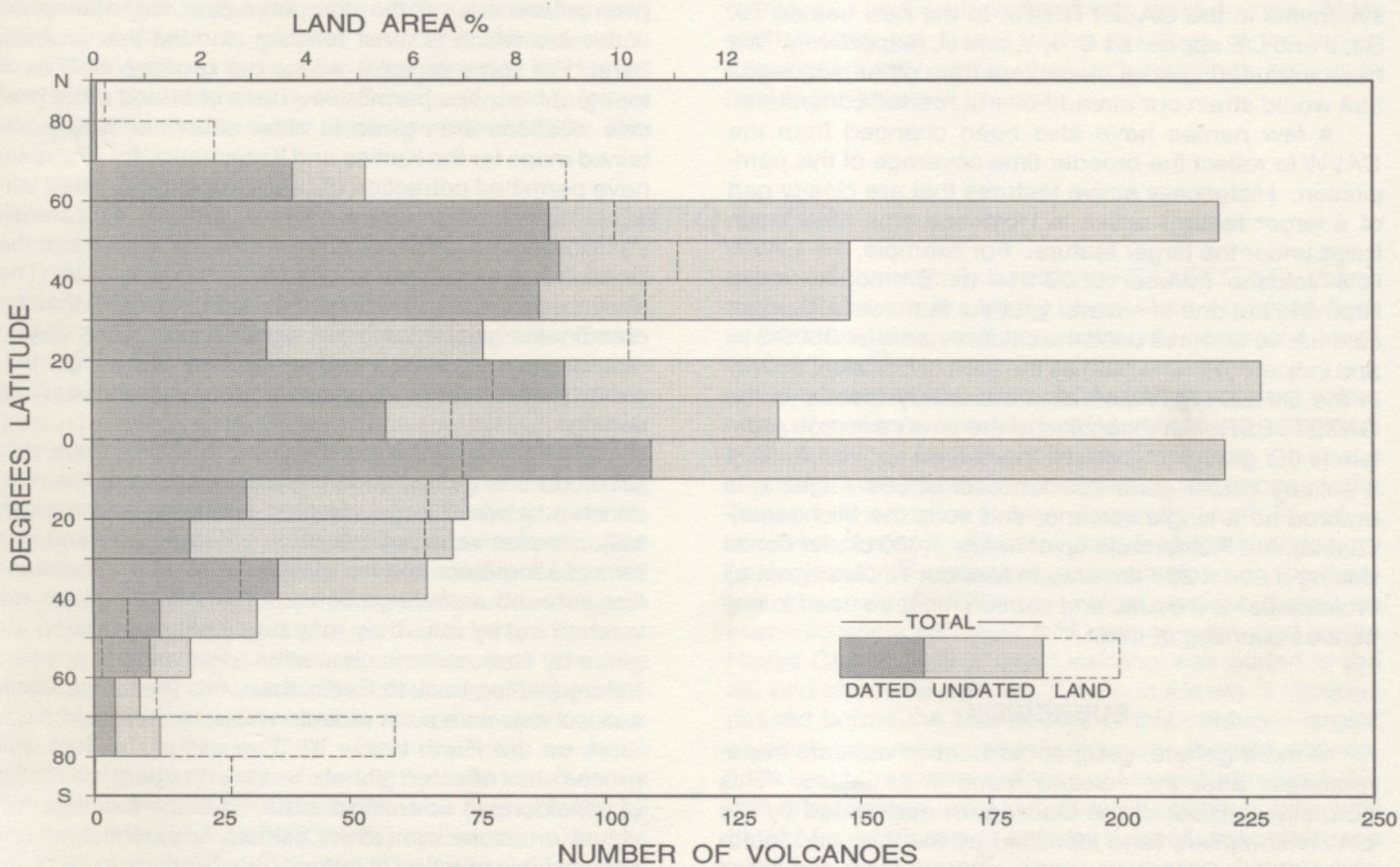
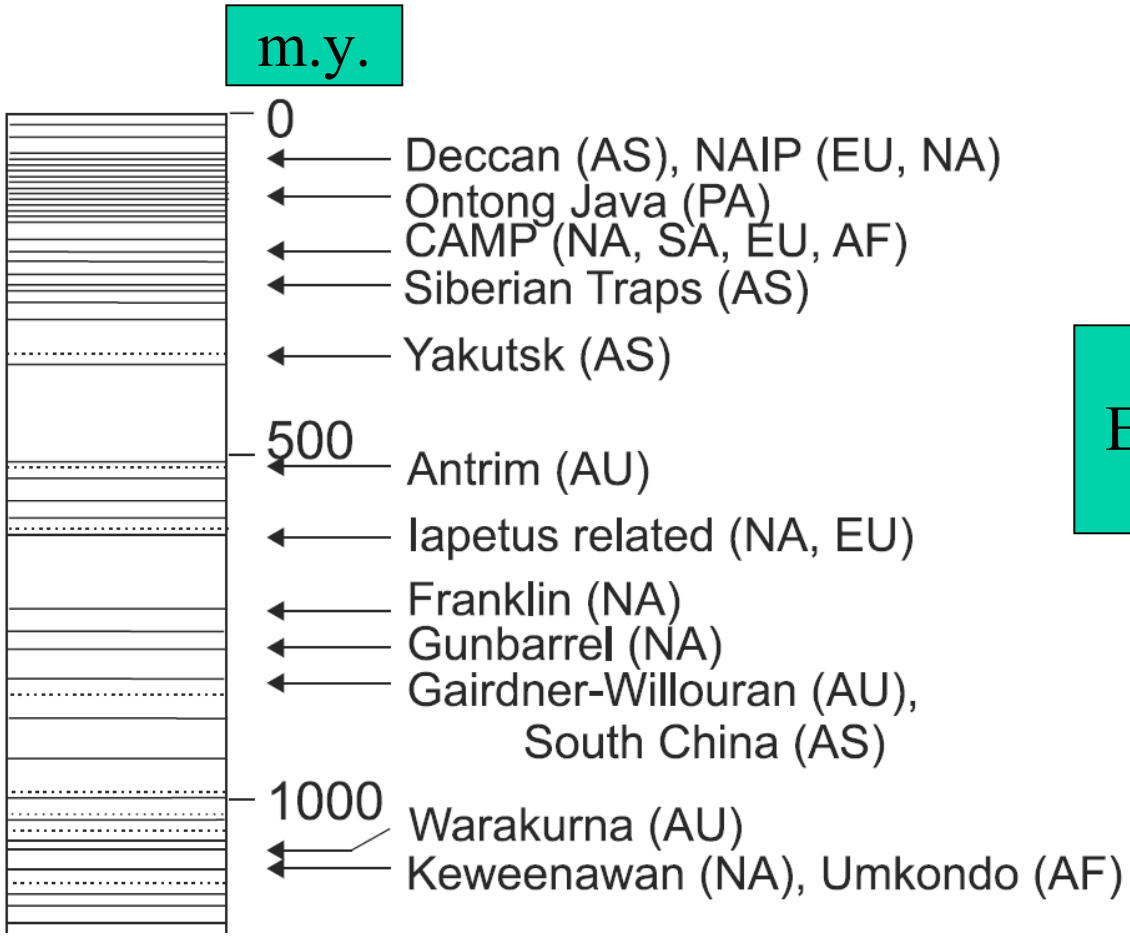


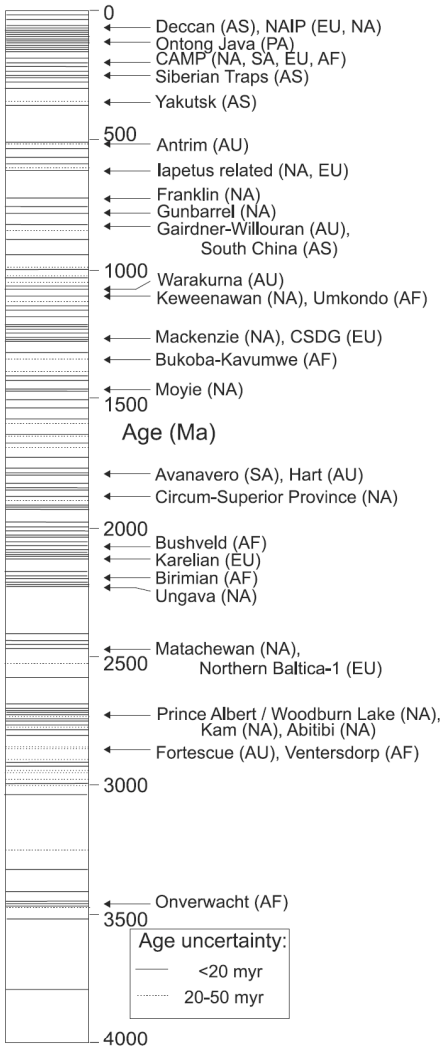
Figure 1. Distribution of known volcanoes per 10 degrees of latitude. Thin dashed line shows the percentage of land area per 10 degrees.[36]

Simkin & Siebert, 1994

FLOOD BASALTS – LARGE IGNEOUS PROVINCES
AREA >0.1 Mkm²



Ernst et al. 2005



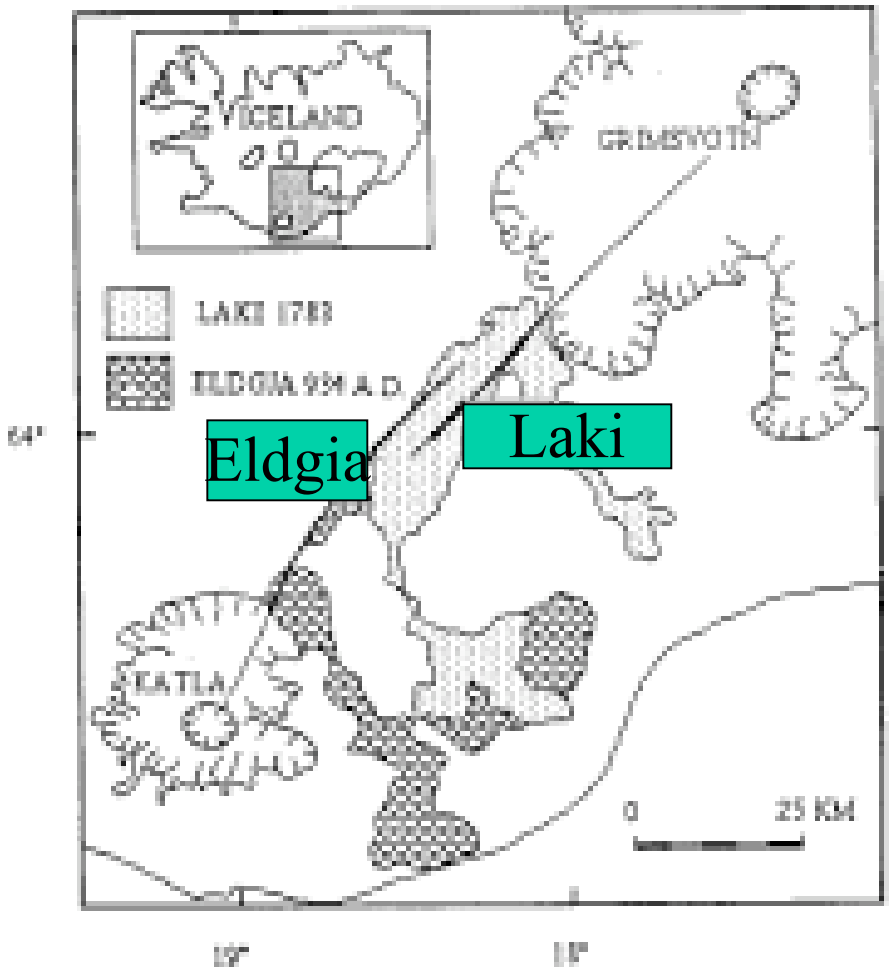
1. Age spectrum ('bar code') of large igneous provinces through . After Figs. 2b and 3b respectively in Ernst and Buchan (2001a, 2). Includes events rated as "well-established and probable plume l mafic magmatic events" according to criteria in Ernst and han (2001a). Selected events are labeled at the starting age of the pulse. Locations for events are indicated as follows: NA is North erica, SA is South America, EU is Europe, AF is Africa, AS is , AU is Australia, and PA is Pacific Ocean. Names are mostly Ernst and Buchan (2001a). Exceptions include Iapetus related fer, 2002), Warakurna (Wingate et al., 2004), and Circum-erior Province (www.largeigneousprovinces.org/LOM.html). uncertainty quoted at 2-sigma level.

LIPs OF THE RECORD OF EARTH

See also:

www.largeigneousprovinces.org

www.mantleplumes.org



Metrich et al., 1991

THE LAKAGIGAR (LAKI) FISSURE ERUPTION 1783-4: CA.15 km³ OF BASALT

-

A MINIATURE VERSION OF A LARGE IGNEOUS PROVINCE

SO_2 ca. 1.7Mt/day
Duration: 7-8 months.
Ca. 40 t of Zn, 1 t of Pb and Cd (reconstructed from ice-core chemistry)
Hong et al. 1996.

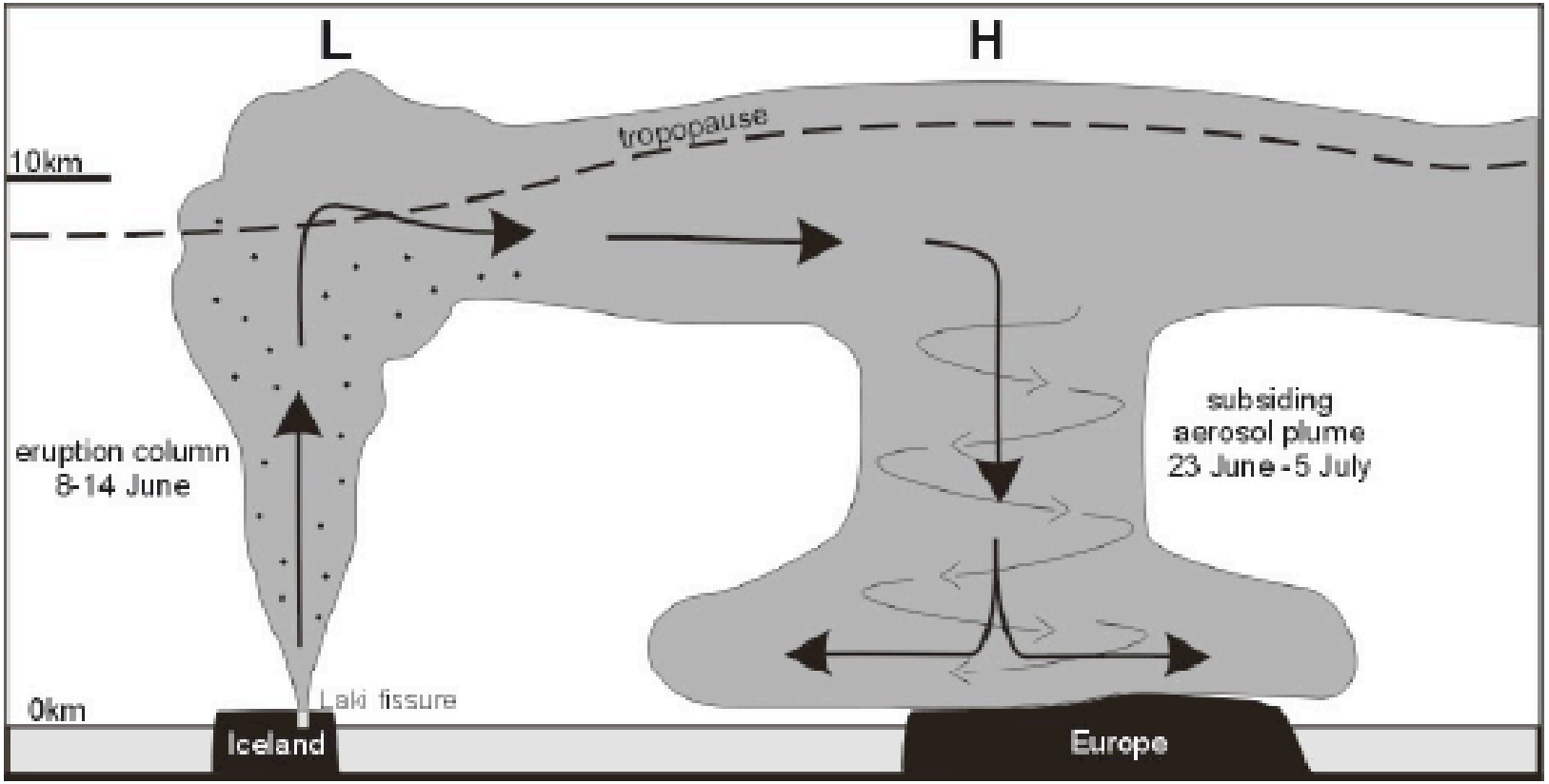


Figure 7. Simplified cross section (A-B on Figure 6c) from Iceland to mainland Europe showing the dispersal and development of the Laki plumes in the first 3-4 weeks of the eruption. Eruption columns produced by explosive activity at the Laki fissures carried ash, SO_2 and other gases to altitudes of 9-12 km. The sulfur-rich plumes (shaded) were dispersed eastward over Europe by the polar jet stream. Due to convergence of airflow at the tropopause level, the Laki aerosol cloud was sucked into a large quasi-stationary high-pressure cell (H) located over Europe at the time and re-introduced into the lower atmosphere by the subsiding air masses, spreading in a spiral-like fashion across the continent. The *arrows* indicate subsiding air within the core of the anticyclone from mid or upper tropospheric levels.

Thordarson & Self, 2003

Laki: SO_2 ca. 1.7 Mt/day 15 km³ 7-8 months

Columbia River basalts (USA): SO_2 ca. 12 000 Mt/10 years released by one flow of 200-300 flows during 1-2 m.y.; present volume: 1.8×10^5 km³; age 16 m.y.

Deccan (India - +/- KT boundary) and Parana (South America - early Cretaceous) flood basalts are at least one order of magnitude larger than Columbia River basalts.

Rampino & Self, 2000

The Miocene climatic maximum is earlier than CRBs!
$\delta^{13}C$ of deep sea sediments show high values for time-equivalent deposition (ca. +2.2‰) during the Cainozoic. Only late Paleocene values are higher (ca. + 2.4‰) – Zachos et al., 2001.

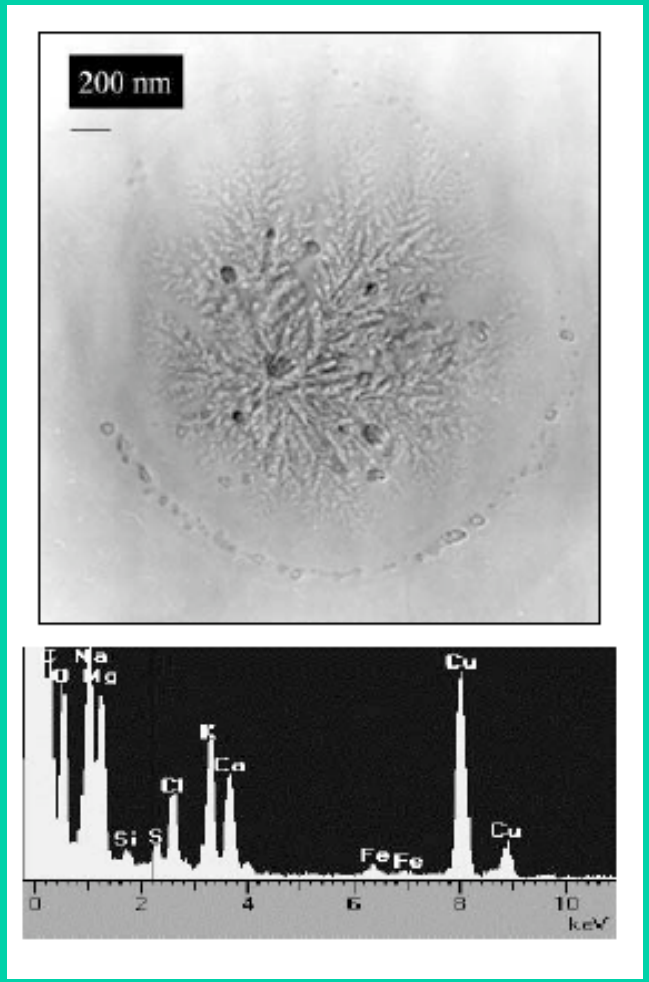
High volcanic activity would support greenhouse warming by volcanic CO_2 fluxes. Particles would support cooling.

Volcanoes and CO_2

Active volcanoes release
CO_2 through active and passive degassing. Many volcanoes release CO_2 diffuse through the edifice.
Many volcanoes are situated on massive carbonate platforms which can be contact metamorphosed at depth or assimilation of carbonates is happening (Obenholzner et al. 2003).

Popocatepetl volcano, Mexico released 16 Mt of CO_2 between December 1994 and November 1996 (Goff et al.,1998).

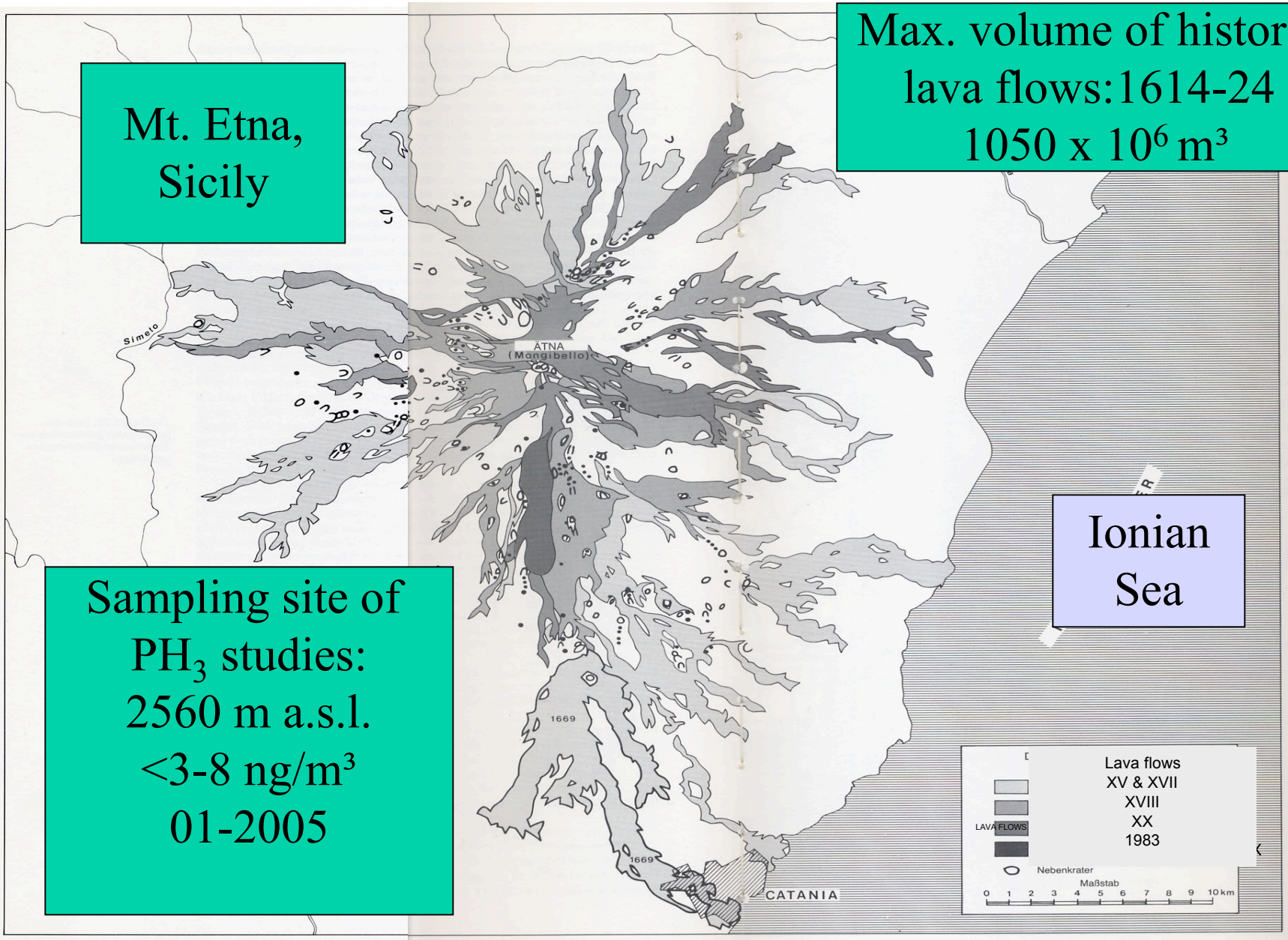
NANOPARTICLES OF PLUMES



Pfeffer et al. 2006 studied Particles of Poas volcano, Costa Rica by HRTEM and AFM.

Mt. Etna, Sicily

Max. volume of historic lava flows:1614-24
1050 x 10^6 m^3



Ionian Sea

Sampling site of PH_3 studies:
2560 m a.s.l.
<3-8 ng/m^3
01-2005

Tazieff 1988

Results of PH_3 studies

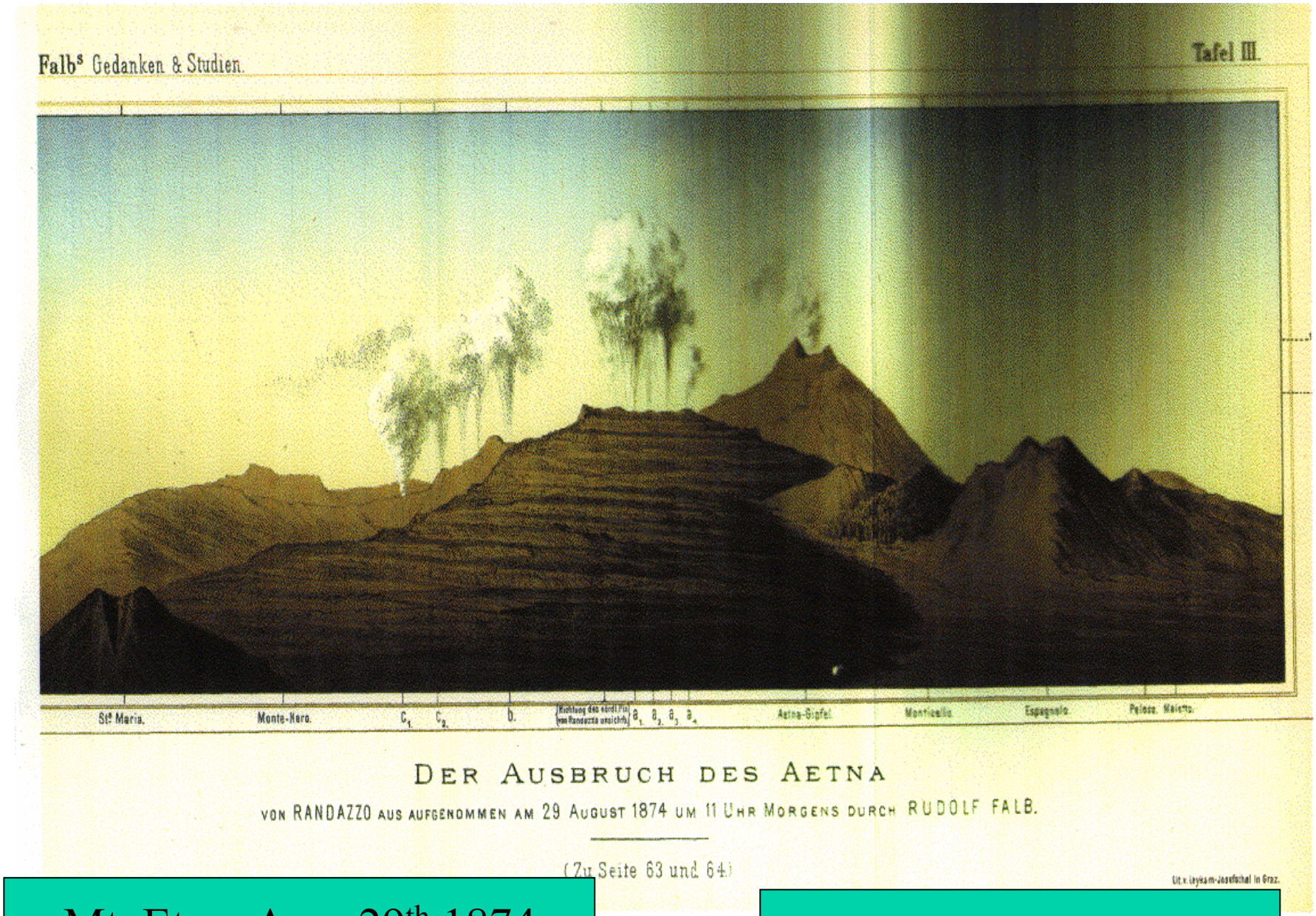
1. Mt. Etna: Sampling site had been close to the root zone of the lava flow (2001) at ca. 2560 m a.s.l.. Background levels are <3 ng/m³. Values of 3 samples range from <3 – 8.3 ng/m³ in the presence of SO_2 (7-12 ppm). Sampling time had been ca. 10 min/sample in Tedlar bags. P of downwind from the craters deposited snow range from 2-73 ppb (Jan. 2005). Distal lava flows emanated visible vapor during cold morning hours.
2. Vulcano Island: Sampling sites had been a beach fumarole, vents along the rim of La Fossa crater and water of bubbling, natural pools. The vents had been sampled twice in Jan 2005 and May 2005 utlilizing a Si-coated stainless steel probe in May 2005. The temperature of the vents ranged from 100-394°C. The PH_3 values (O-202 ng/m³) do not correlate with temperature but to a certain degree with H_2S values. Gas samples at the base of the crater and at the geothermal area reveal 3-10 ng/m³. Water samples: 1.2-1.3 ng/m³.
3. At Solfatara crater, Pozzuoli, Naples P had been detected in H_2O adsorber liquids by ICP-MS (bubbler 1: 25-198 ppb; bubbler 2: 4-16 ppb). The low solubility of PH_3 in H_2O (0.01 mol/L) might indicate the presence of PH_3 there as well.
4. It remains unknown if volcanic PH_3 is a precursor of bioavailable P species.
5. Reduced P in the environment (Morton et al.2005a+b).

Mobile phosphorus in the volcanic environment:

Micro-mineralogical studies revealed rare phosphates on ejecta of Mt. Vesuvius: Ce-britholite and monacite (Russo et al. 2004). Florencite (REE phosphate) is known from the rock coatings of La Fossa crater (Fulignati et al. 2002).

Stanton (1994) summarized volcanic aerosol and ore deposit data of P and speculated about the existence of P-S compounds in plumes (see also Obenholzner et al. 2003). Recent petrological studies also indicate volatility of P at magmatic temperatures and pressures (Dreher 2002).

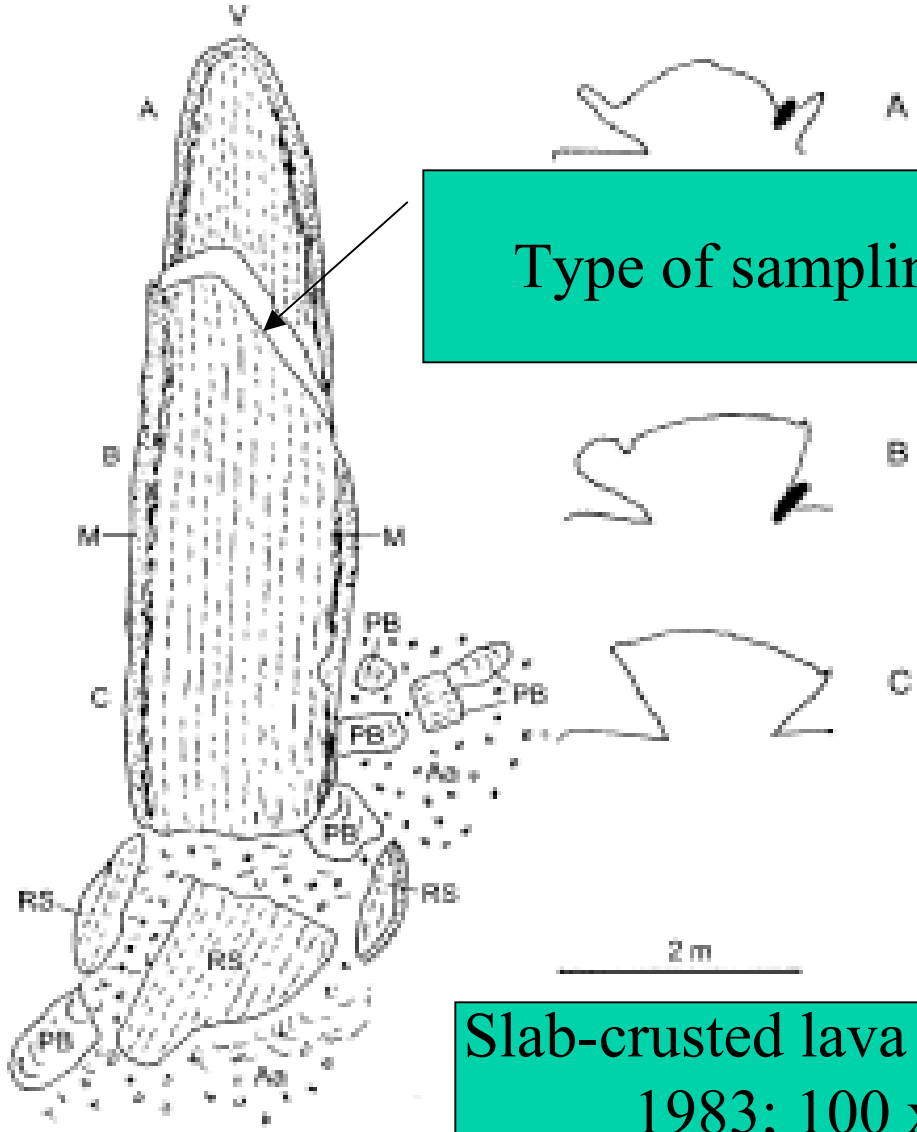
At the moment no model exists if low-temperature (<450°C) PH_3 could be a precursor of phosphate minerals.



Mt. Etna, Aug. 29th 1874

Falb 1875

Guest & Stofan, 2005



Type of sampling site

Slab-crusted lava flow, Mt. Etna 1983; 100 x 10^6 m^3

Fig. 2. Measured sketch map and true scale cross-sections of a slab-crusted flow showing typical features. V=vent, A,B,C=cross-sections and their location, M=marginal zone, PB=pahoehoe breakout and RS=rafted slab. Areas of aa textured flows that have broken out from the core of the main flow are indicated.

Approaches to quantify volcanic activity of Earth

Tardy 1989

Table 1. Global characteristics of geological periods : (1) age (my) ; (2) duration (my) ; (3) temperature (°C) estimated from the sea level ; (4) global runoff ($10^9 km^3/my$) modulated by the ocean water budget, from Probst and Tardy (1989) ; (5) global runoff (10^9 km^3/my) over continents only ; (6) carbonate sedimentation rate ($10^{15}t/ma$) ; (7) volcanism rate ; (8) HCO_3^- mmol/kg H_2O corrected by temperature ; (9) WRIGR ($10^{15}t/ma$) equivalent calcite ; (10) ratio (9)/(6) ; (11) WRIGR ($10^{15}t/ma$) calculated for a constant bicarbonate concentration (0,571 mmol/kg H_2O) ; (12) ratio (11)/(6) ; (13) sedimentation rates ($10^{15}t/ma$) ; (14) specific erosion rates or river loads (mg/l).

Geological periods	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)
Present	0	0	15.0	39.7	39.7	1.25	-	0.571	2.28	1.82	2.27	1.82	16.00	403
Cenozoïc	32	66	20.5	44.7	45.6	1.44	1.43	0.739	3.32	2.31	2.55	1.77	9.76	218
Cretaceous	99	66	22.3	47.5	49.7	1.75	1.82	0.851	4.93	2.82	2.71	1.55	8.24	173
Jurassic	159	53	16.5	37.6	40.5	1.41	0.82	0.627	2.38	1.69	2.15	1.52	6.61	176
Triassic	210	50	16.0	37.1	43.8	0.76	1.70	0.599	2.22	2.92	2.12	2.79	4.70	127
Permian	258	45	16.2	42.0	43.2	1.13	1.59	0.599	2.58	2.28	2.40	2.12	4.77	114
Carboniferous	313	65	18.9	48.1	45.0	1.63	1.58	0.627	3.13	1.92	2.75	1.69	5.11	106
Devonian	373	55	21.1	53.0	49.2	1.84	3.99	0.739	4.36	2.37	3.03	1.65	9.20	174
Silurian	418	35	23.0	65.4	54.7	0.83	0.75	0.823	6.42	7.73	3.73	4.49	6.65	102
Ordovician	463	55	22.2	56.4	57.8	1.03	1.55	0.796	5.17	5.08	3.22	3.13	6.82	121
Cambrian	530	80	17.0	51.9	63.1	2.11	1.27	0.599	3.11	1.41	2.96	1.40	9.36	180
Average				47.6	48.4	1.38	1.64	0.719	3.66	2.65	2.72	1.97	7.12	172

(7) Volcanism rate

Table 3

Time Distribution of Phanerozoic Sediments and Volcanities in Continents and of Masses of CO_2 and Carbon Stored in Sediments

Stratigraphic range	Total volume, 10^6 km^3	Rock mass*, 10^{15}t			CO_2, 10^{15}t		Carbon mass 10^{15} t		Mean % C in sediments		Mass per unit time ($10^{14}/10^6$ hr)	
		Sediments	Volcanic rocks	Total rock mass	In carbonate rocks	Carbonates mixed with terrigenous rocks	C_{org}	C_{carb}	C_{org}	C_{carb}	C_{org}	C_{carb}
Pliocene (N_2)	9.52	21.16	2.24	23.40	0.20	0.32	0.10	0.14	0.47	0.66	0.14	0.20
Miocene (N_1)	18.51	40.13	5.57	45.70	2.07	0.75	0.31	0.77	0.77	1.89	0.19	0.48
Oligocene (PG_3)	9.58	21.56	2.04	23.60	0.68	0.22	0.20	0.25	0.93	1.11	0.17	0.21
Eocene (Pg_2)	20.55	43.62	7.78	51.40	5.09	1.46	0.42	1.79	0.96	4.06	0.20	0.85
Paleocene (Pg_1)	6.43	13.54	2.46	16.00	1.41	0.21	0.10	0.44	0.74	3.25	0.12	0.55
Late Cretaceous (Cr_2)	47.94	98.56	22.04	120.60	11.89	3.02	0.62	4.07	0.63	4.09	0.18	1.19
Early Cretaceous (Cr_1)	51.16	106.81	21.39	128.20	9.42	1.70	0.75	3.04	0.70	2.82	0.23	0.95
Late Jurassic (J_3)	25.22	55.95	6.55	62.50	7.11	1.35	0.59	2.31	1.05	4.09	0.28	1.10
Middle Jurassic (J_2)	22.23	49.59	5.71	55.30	4.91	0.88	0.49	1.58	0.99	3.15	0.33	1.05
Early Jurassic (J_1)	21.03	46.53	5.57	52.10	4.79	0.54	0.28	1.45	0.60	3.09	0.16	0.85
Late Triassic (T_3)	33.76	59.44	21.17	80.60	5.22	1.74	0.22	1.90	0.37	3.16	0.09	0.76
Middle Triassic (T_2)	13.01	22.26	11.04	33.30	2.70	0.68	0.04	0.92	0.18	4.09	0.04	0.92
Early Triassic (T_1)	11.31	23.37	4.73	28.10	1.76	1.02	0.06	0.76	0.26	3.21	0.04	0.51
Late Permian (P_2)	18.08	37.83	6.97	44.80	2.19	2.33	0.10	1.23	0.26	3.17	0.05	0.61
Early Permian (P_1)	33.58	61.76	23.74	85.50	13.38	1.75	0.22	4.13	0.36	6.54	0.09	1.65
Late and Middle Carboniferous (C_{2+3})	32.14	69.25	10.95	80.20	10.71	1.18	0.38	3.25	0.55	4.58	0.10	0.81
Early Carboniferous (C_1)	33.58	60.48	25.62	86.10	16.78	0.72	0.55	4.78	0.91	7.72	0.22	1.91
Late Devonian (D_3)	31.80	54.84	26.46	81.30	9.22	1.04	0.36	2.80	0.66	4.98	0.24	1.86
Middle Devonian (D_2)	32.06	58.65	22.85	81.50	9.30	1.25	0.29	2.88	0.49	4.79	0.18	1.80
Early Devonian (D_1)	27.14	53.22	14.78	68.00	4.43	1.30	0.08	1.56	0.15	2.87	0.03	0.65
Silurian (S)	29.00	65.06	6.64	71.70	6.10	1.71	0.18	2.13	0.28	3.24	0.05	0.60
Ordovician (O)	44.19	92.55	17.95	110.50	10.94	3.67	0.48	3.99	0.52	4.27	0.09	0.72
Late Cambrian (Cm_3)	19.38	44.53	3.47	48.00	7.96	0.13	0.08	2.21	0.18	4.92	0.03	0.88
Middle Cambrian (Cm_2)	21.95	49.20	5.40	54.60	9.30	0.33	0.14	2.63	0.28	5.28	0.05	0.87
Early Cambrian (Cm_1)	26.04	56.25	8.85	65.10	10.68	0.62	0.23	3.08	0.41	5.42	0.09	1.23
Sum or mean for Phanerozoic (N_2–Cm_1)	639.35	1305.95	292.15	1598.10	168.24	29.92	7.27	54.09	0.56	4.14	0.12	0.95

*In the mass calculations, the density was taken as 2.52 for carbonate rocks, 2.49 for argillites and shales, 2.28 for sandstones, 2.30 for halides, etc., and 2.80 for volcanic rocks [24].

Ronov 1976

Table 1

Areas of Erosion, Deposition, and Marine Sedimentation and Volumes of Major Rock Formations in Platforms, Geosynclines, and Continents as a Whole for Various Phanerozoic Epochs [12-19]

Epoch or period	Duration in 10^6 yr**	Platforms, geosynclines, and continents	Area 10^6 km^2		% of total area of platforms, geosynclines, or continents		Volumes of formations in 10^6 km^3											Total rock mass, 10^{15} tons****	m per 10^6 yr		
			Erosion regions	Deposition regions	Deposition regions	Areas covered by sea	Continental clastics (including molasse)	Coal-bearing sands and clays	Glacial clastics	Marine sands and clays (including terrigenous (flysch, marine molasse)	Carbonates	Salt-bearing (salts, gypsum, anhydrite) deposits	Siliceous deposits***	Land volcanics	Underwater volcanics	Total volume	CO_2 in carbonate rocks		Mean uplift rate in eroston areas	Mean subsidence rate in depositon areas	Extent of volcanism
Pliocene (N_2)	2—9=7	Platforms	83.80	25.63	23	4	1.65	0.06	—	0.47	0.12	—	—	0.26	—	2.56	0.05	6.3	3.7	14	1.4
		Geosynclines	12.15	11.53	49	12	3.84	0.26	—	2.25	0.06	0.01	—	0.32	0.22	6.96	0.03	17.1	75	86	6.7
		Continents	95.95	37.16	28	5	5.49	0.32	—	2.72	0.18	0.01	—	0.58	0.22	9.52	0.08	23.4	13	37	3.0
Niocene (N_1)	9—25=16	Platforms	84.72	23.93	22	8	2.16	0.26	—	0.98	0.70	0.07	0.01	0.89	—	5.07	0.31	12.7	2.5	13	2.3
		Geosynclines	11.02	13.07	54	27	4.29	0.44	—	6.07	1.17	0.33	0.04	0.82	0.28	13.44	0.51	33.0	61	64	5.3
		Continents	95.74	37.00	28	10	6.45	0.70	—	7.05	1.87	0.40	0.05	1.71	0.28	18.51	0.82	45.7	9.2	31	3.6
Oligocene (Pg_3)	25—37=12	Platforms	87.52	20.12	19	5	1.04	0.27	—	1.41	0.10	—	—	0.26	—	3.08	0.04	7.6	2.6	13	1.1
		Geosynclines	13.29	10.72	45	26	1.60	0.30	—	3.59	0.52	0.02	—	0.17	0.30	6.50	0.23	16.0	34	51	3.7
		Continents	100.81	30.84	23	9	2.64	0.57	—	5.00	0.62	0.02	—	0.43	0.30	9.58	0.27	23.6	6.7	26	1.9
Eocene (Pg_2)	37—58=21	Platforms	81.80	27.12	25	14	1.62	0.57	—	2.93	2.05	0.16	0.36	0.59	—	8.28	0.90	20.6	3.0	14	1.0
		Geosynclines	10.56	13.11	55	37	0.87	1.10	—	5.49	2.54	0.04	0.04	0.49	1.70	12.27	1.12	30.8	34	45	8.0
		Continents	92.36	40.23	30	18	2.49	1.67	—	8.42	4.59	0.20	0.40	1.08	1.70	20.55	2.02	51.4	6.5	24	3.3
Paleocene (Pg_1)	58—66=8	Platforms	87.04	22.25	20	12	1.10	0.20	—	0.99	0.85	0.02	0.01	0.15	—	3.32	0.37	8.2	3.2	17	0.9
		Geosynclines	13.17	10.07	43	31	0.59	0.07	—	1.28	0.42	0.01	0.01	0.40	0.33	3.11	0.19	7.8	18	39	9.0
		Continents	100.21	32.32	24	15	1.69	0.27	—	2.27	1.27	0.03	0.02	0.55	0.33	6.43	0.56	16.0	5.2	25	3.4

Ronov 1976

Early Würm glaciation
In the Alps.

Perrota & Scarpati
2003

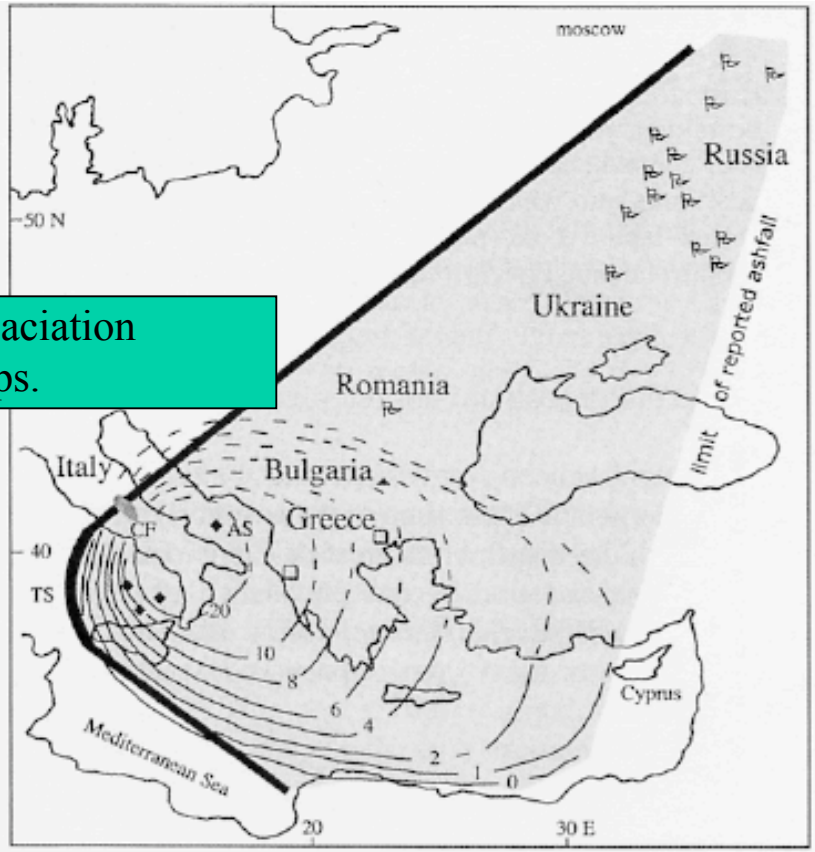
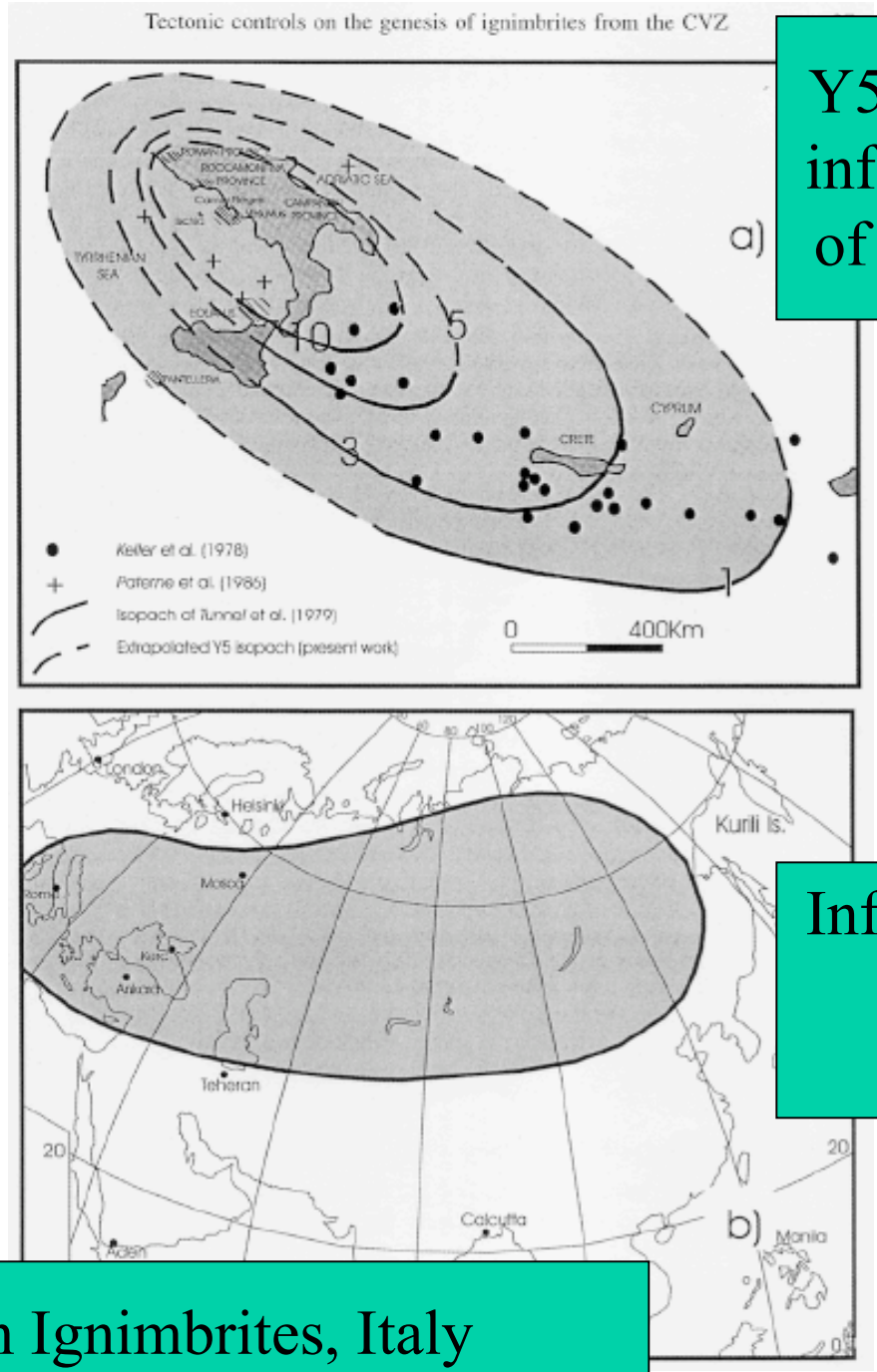


Fig. 3. Distribution of distal ash fall tephra associated with the Campanian Ignimbrite eruption. Note that the eastern trend of the dispersion is compatible with the trend of the proximal plinian fall products shown in Fig. 1. Isopachs on the Mediterranean Sea are redrawn from *Cornell* et al. (1983). Locations of this tephra layer are indicated by: flags in eastern Europe (*Melekestsev* et al., 1988), a triangle in Bulgaria (*Harkovska* et al., 1990), squares in Greece (*Seymour* and *Christanis*, 1995). Grey area in central Italy (redrawn from *Narcisi* and *Vezzoli*, 1999) is the distribution of a paleosol related with the CI fall deposit (*Frezzotti* and *Narcisi*, 1996). Diamonds indicate Tyrrhenian and Adriatic coring locations (*Paterne* et al., 1988). *CF* Campi Flegrei; *AS* Adriatic Sea; *TS* Tyrrhenian Sea

Campanian Ignimbrites, Italy

Rolandi et al. 2003

Y5 ash layer and inferred isopachs of air-borne ash.



Inferred distribution of <1 cm Y5 ash layer

Campanian Ignimbrites, Italy

The CI (39 ka) is at a distance of ca. 1500 km from vent still detectable by co-ignimbrite ash (particle diameter ca. 1.5 µm).
Rietmeijer (1988) modeled settling velocities for Si-rich grains in the atmosphere. Single Si-rich grains (density 2.35 g/cm³, particle diameter ca. 1.5 µm)
would need ca. 1000 days for a height of ca. 6 km, ca. 200 days for ca. 2 km, and ca. 150 days for ca. 0.5 km assuming dry deposition.
Particles below 1 µm in diameter will settle below Stoke´s law values (Bonadonna et al., 1998).
The density of bubble wall shards and pumice fragments is 2.34 g/cm³ and 2. 46 g/cm³, respectively.
The minimum volume of the CI is ca. 200 km³ (DRE).

Volcanic ash deposits are a skeleton of an eruption. Volatiles (one of the driving forces of an eruption), condensed volatiles, soluble nucleated particles and +/- sub-µm particles cannot be studied anymore. Exceptions are trace elements of tree rings, ice cores, ombrotrophic peat bogs and to a certain degree the paleontological record and ore deposits.

The Campanian ignimbrites (7: >300 ka -23 ka) and the Neapolitan Yellow Tuff (12 ka) are relative small products of supervolcanoes. Scientific discussion continues if most of them are related to graben-forming, extensional tectonics or to a nested caldera (De Vivo et al., 2003; Orsi et al., 1992).

The Toba caldera (Sumatra, 100 km x 30 km) erupted ca. 75.000 years ago and caused stratospheric aerosol burden for ca. 7 years. Chlorine injected into the stratosphere destroys ozone (Pinatubo 1991: 4.5 Mt of HCl - Tabazadeh & Turku, 1993). Human genetic research indicates that the „bottle-neck“ phenomenon orignated at this time.

The Ordovician of the Eastern Alps hosts a metamorphosed ignimbrite (?) sequence (ca. 600 m thick) exposed along ca. 300 km (Heinisch, 1980). The circular-shaped plutonic complex of the Jurassic White Mts., New Hampshire, USA might represent the exposed root zone of a supervolcano (diameter ca. 300 km).

Geology of Yellowstone National Park

SUPERERUPTIONS:
:www.geo.mtu.edu/~raman/EhazSuperEruption.html

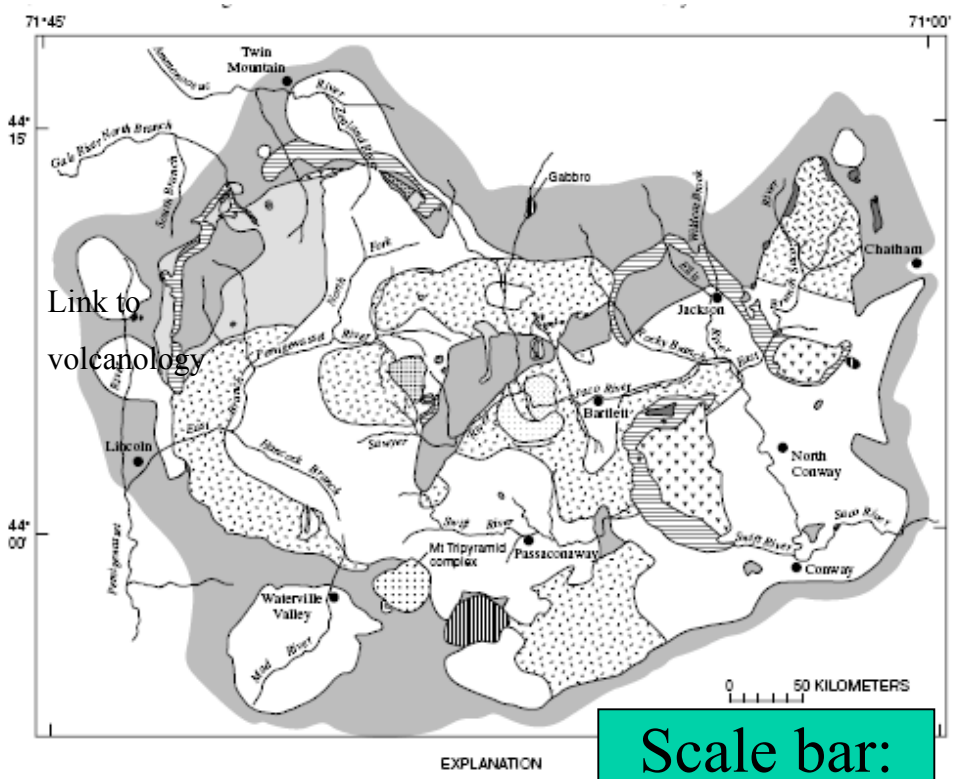
The Quaternary and Pliocene Yellowstone Plateau Volcanic Field of Wyoming, Idaho, and Montana

By Robert L. Christiansen

2001

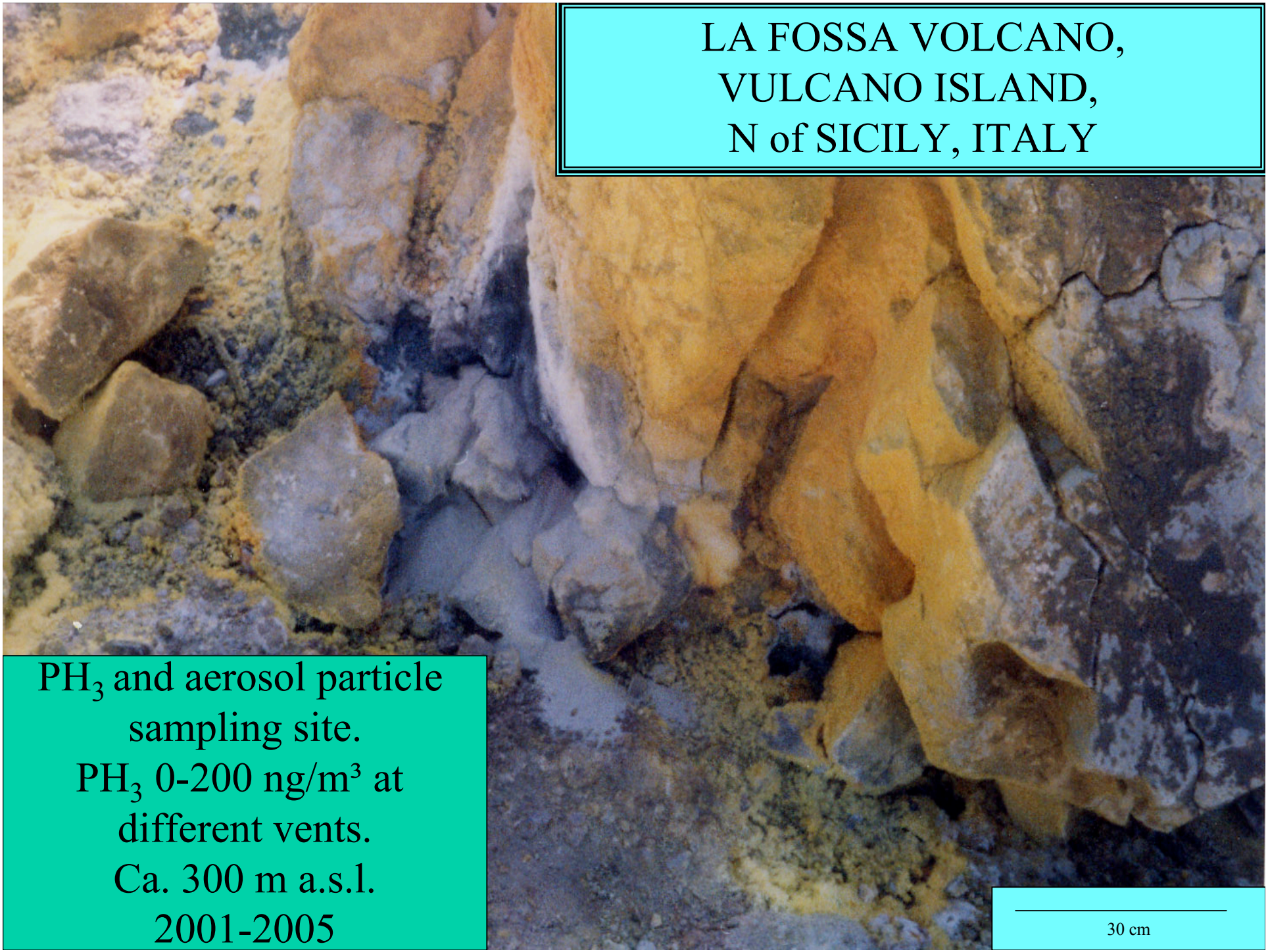
Professional Paper 729–G

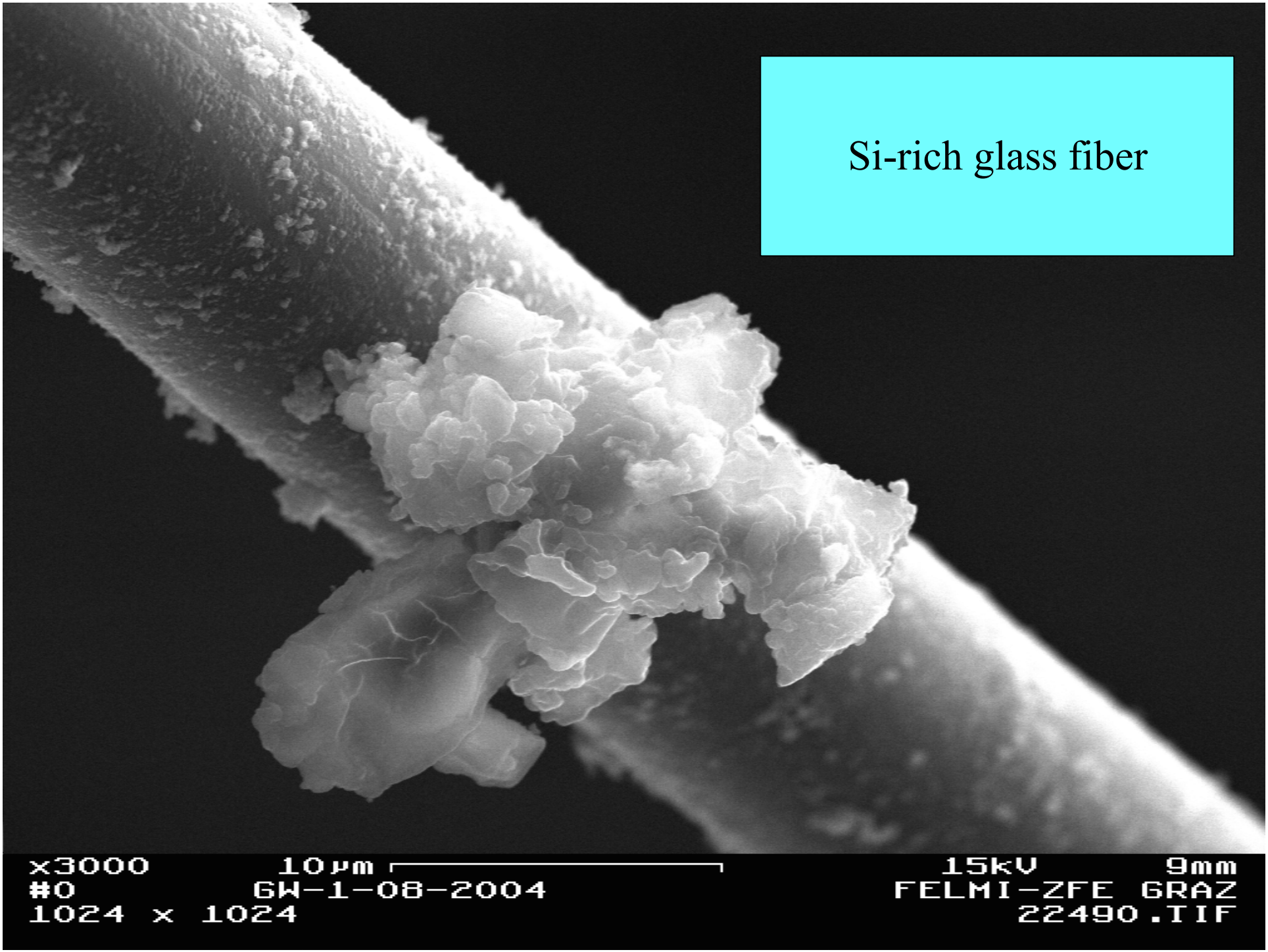
Link to volcanology

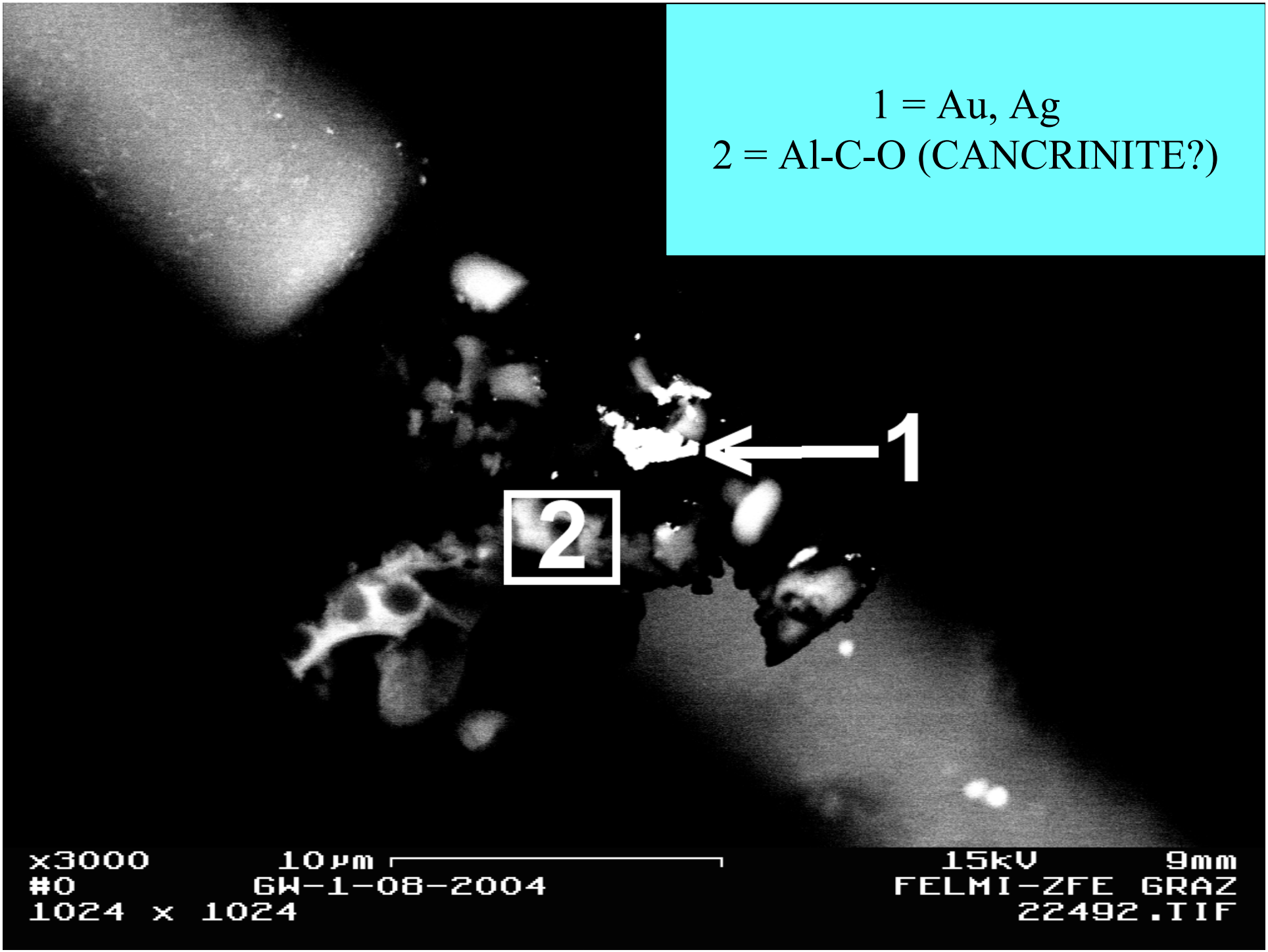


Scale bar: 5o km

Figure 45.—Generalized geologic map of the Jurassic White Mountains batholith, New Hampshire (modified from Creasey, 1974). The White Mountains batholith is a possible analogue for the plutonic underpinnings of the Yellowstone Plateau volcanic field.


LA FOSSA VOLCANO,
VULCANO ISLAND,
N of SICILY, ITALY
PH_3 and aerosol particle sampling site.
PH_3 0-200 ng/m³ at different vents.
Ca. 300 m a.s.l.
2001-2005
30 cm


Si-rich glass fiber
x3000
10µm
15kV
9mm
#0
GW-1-08-2004
FELMI-ZFE GRAZ
1024 x 1024
22490.TIF


1 = Au, Ag
2 = Al-C-O (CANCRINITE?)
1
2
x3000
10µm
15kV
9mm
#0
GW-1-08-2004
FELMI-ZFE GRAZ
1024 x 1024
22492.TIF

FROM 2001 –2005 SEVERAL AEROSOL COLLECTION (AC) AT 25-70°C AND CLOGGING EXPERIMENTS (CE) HAD BEEN PERFORMED AT A FUMAROLE (ca. 317°C, MAY 2005). A VARIETY OF FILTER MATERIALS AND MINERAL SURFACES HAD BEEN TESTED. PARTICLES HAD BEEN STUDIED BY FESEM/EDS AT ZFE/TU-GRAZ, AUSTRIA.

ONE OF THE MOST INTERESTING FEATURES IS: AFTER 4 HOURS OF CE SINGLE GLASS FIBERS ARE OCCUPIED BY A SINGLE METAL CHLORIDE, NEIGHBOURING FIBERS ARE FREE OF NUCLEANTING PARTICLES. TO A MINOR AMOUNT ALSO METAL SULFIDES ARE NUCLEATING ON SINGLE FIBERS

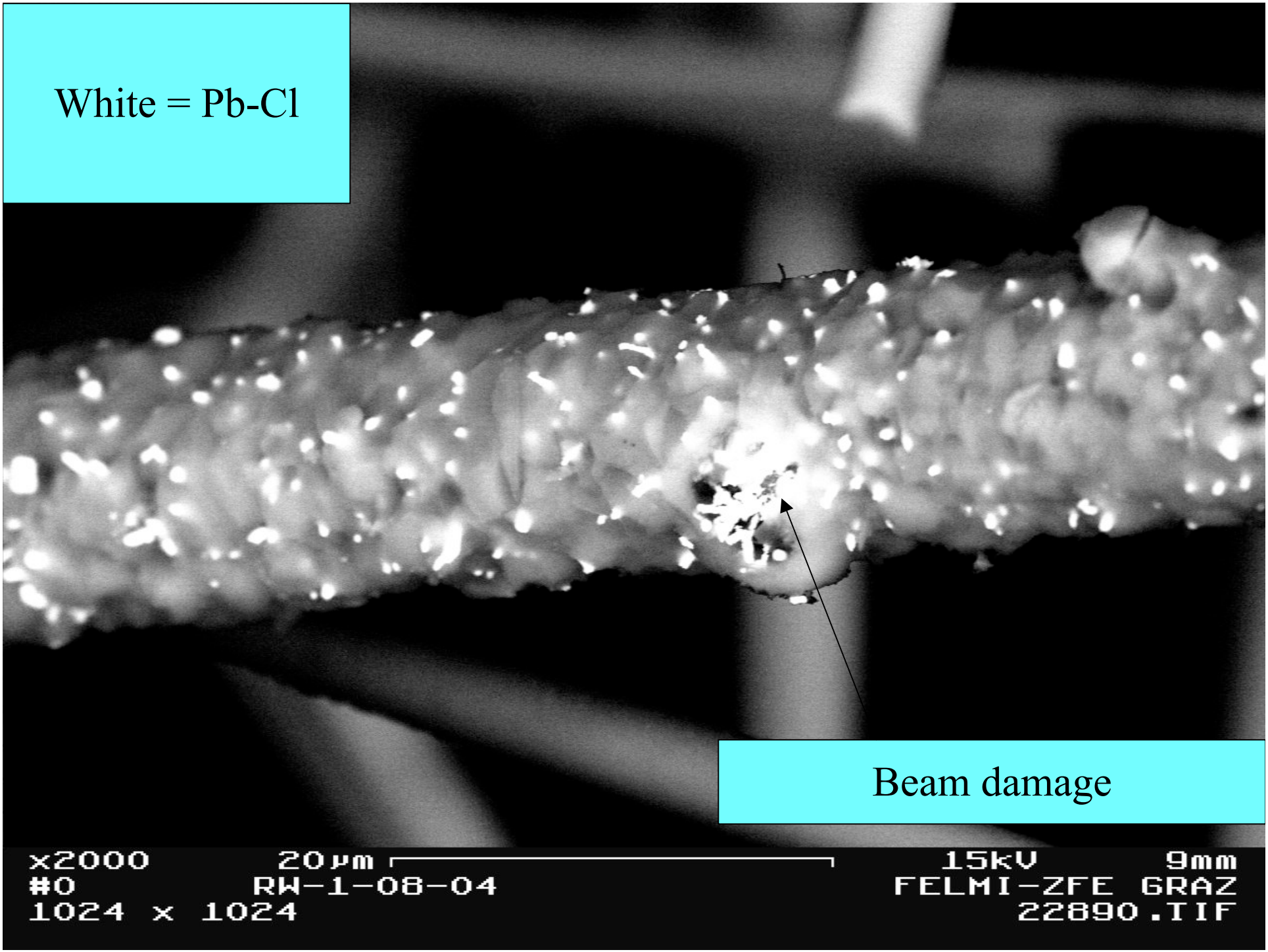
Filter material	**Nucleating particles**
Borosilicate fiber AC	Pb-Tl-S-Cl, Ba-S-O, NaCl
Rock wool (RW)	Bi-S, Bi-Cl, Bi-S-Cl, Pb-Cl, Pb-S,
& Glass wool (GW)	Pb-S-Cl, Tl-Cl, Tl-S, Tl-S-Cl,
- (CE) -	Pb-Bi-S-Cl, Pb-Tl-S-Cl, Au, Ag,
	Ba-S-O
Millipore 0.2 µm AC	S (*)
Keddeg coalescer AC	NaCl, KCl, Ti
Quartz CE	Pb-Cl, Pb-S, Pb-S-Cl, Tl-S-Cl-Br, Tl-Pb-S-Cl

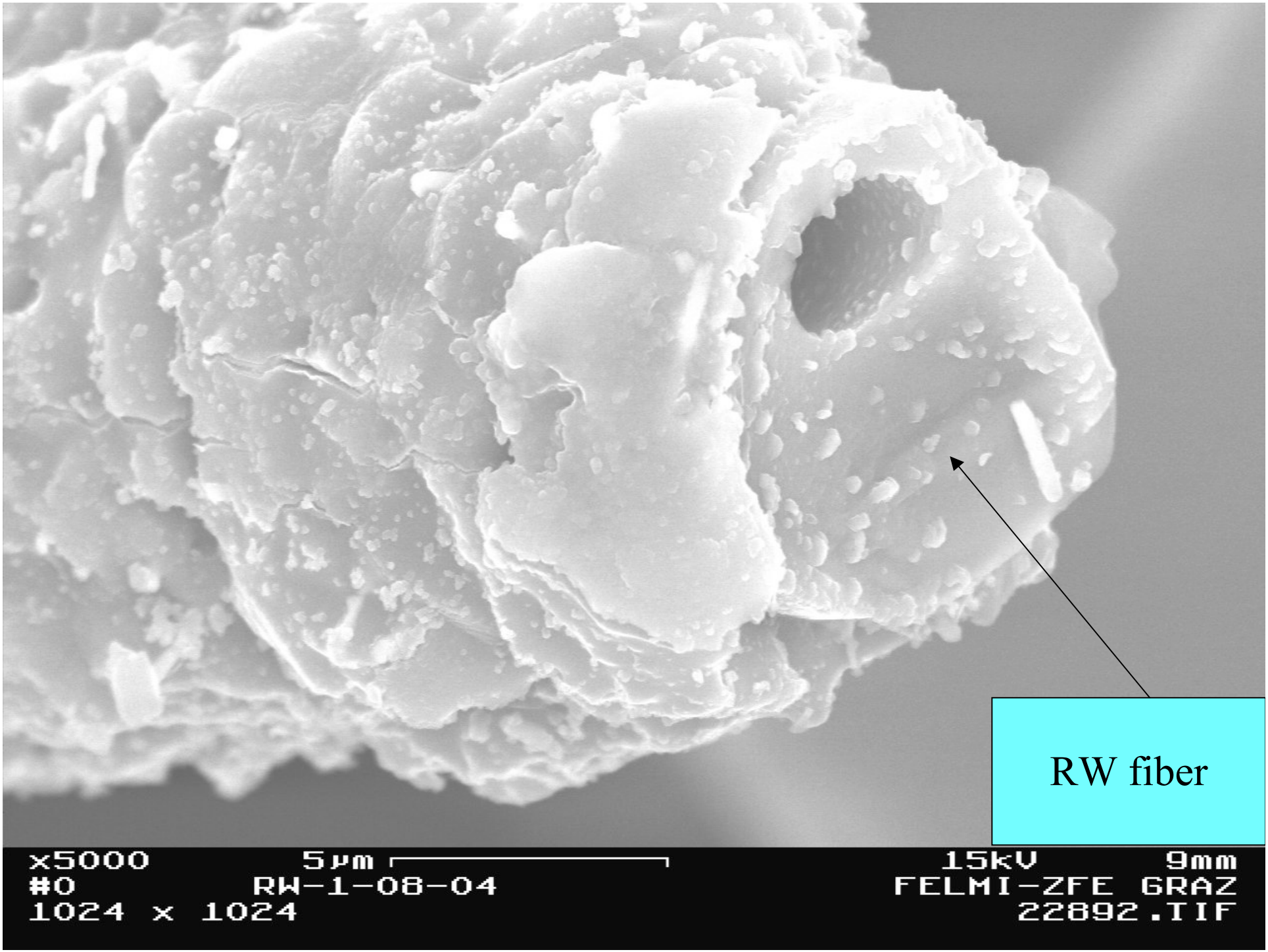
(*) S is nucleating on all filter materials at the coolest parts. These S particles are unstudied yet.

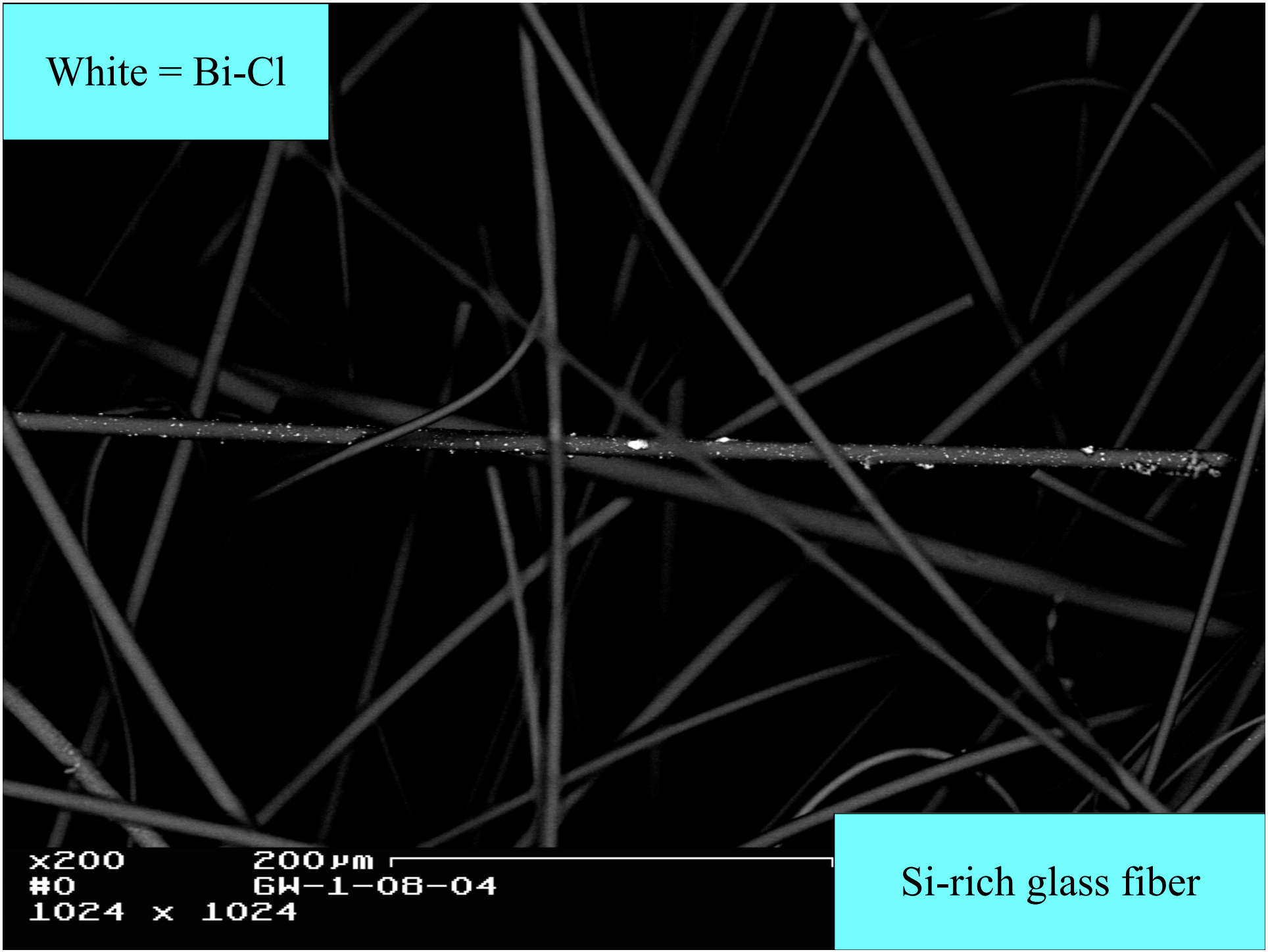
Gold particles from the fumaroles (170-540°C) of La Fossa volcano had been described by Fulignati et al. (1998). They observed them in siliceous, hydrothermally altered pyroclastic rocks.

Our study documents Au and Ag on GW fibers of the CE at ca. 300°C, and on RW fibers of the AC at 25-70°C (Au-Cl).

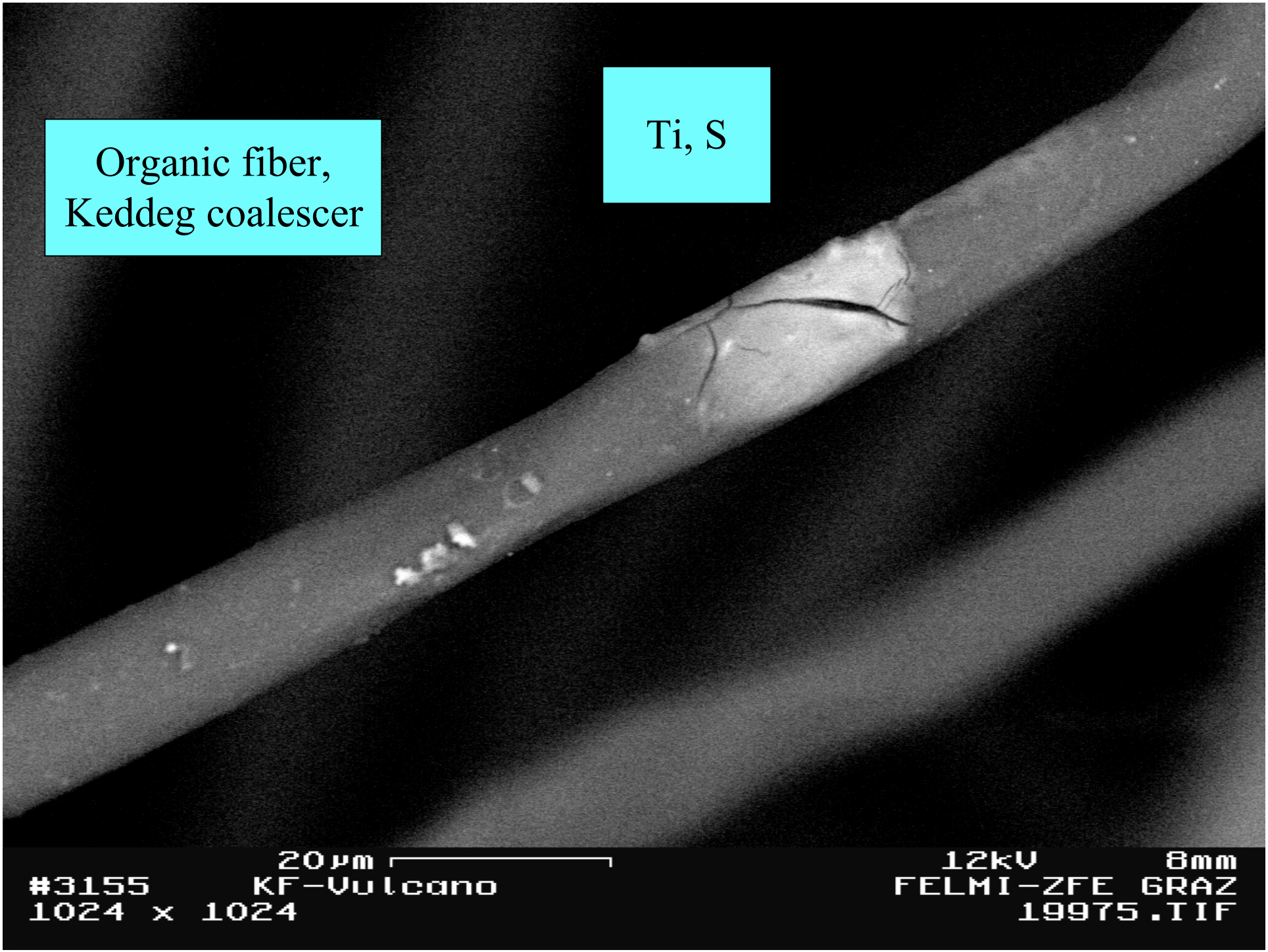
According to Taran et al. (2000) the precipitation of Au from the volcanic gas indicates oxidizing conditions and starts at ca. 400°C.
However, no free air should be able to enter the clogged vent during CE. Nota bene: Only the samples from Aug. 2004 showed Au and Ag particles.


White = Pb-Cl
Beam damage
x2000
20µm
15kV
9mm
#0
RW-1-08-04
FELMI-ZFE GRAZ
1024 x 1024
22890.TIF


RW fiber
x5000
5µm
15kV
9mm
#0
RW-1-08-04
FELMI-ZFE GRAZ
1024 x 1024
22892.TIF


White = Bi-Cl
x200
200µm
#0
GW-1-08-04
1024 x 1024
Si-rich glass fiber

- Nucleating crystals (mineraloids) and the melting point problem of the clogging experiment (CE):
-
- All analyzed chlorides and sulfides on filters (fibers) have higher melting points and boiling points than the measured T of the vent in consideration (min. 317°C) - the exception is Bi-Cl. $BiCl_4$ (known only as a chemical compound) melts at 226°C. $BiCl_3$ (only known as a chemical compound) melts at 230-232°C; boiling point is 447°C. According to the mineralogical data base (ATHENA) no Bi chloride is known in nature. An interpretation of our Bi-Cl data favoring bismoclite (BiOCl) can be excluded as the O peaks are within the range of background from the glass fibers. Other metal chlorides and sulfides (Bi-S, Pb-Cl, Mn-Cl, Pb-S, Tl-Cl = TlCl(?)) have melting points higher than 430°C.


Organic fiber,
Keddeg coalescer
Ti, S
20µm
#3155 KF-Vulcano
1024 x 1024
12kV 8mm
FELMI-ZFE GRAZ
19975.TIF

„Filter material“ produced by volcanic eruptions,
best studied at Kilauea, Hawaii (Heiken & Wohletz, 1985;
Meeker & Hinkley, 1993):

Pele´s hair – glass fibers
Pele´s tears – glass spheroids/droplets
Microspheres –partially crystalline
Reticulite – open-framework structure, glass

Artificial basaltic spheres exposed to fumarole of
Mt. Etna (Spadaro et al., 2002).

FESEM or HR-EM studies of nucleated crystals are missing.
Are volcanoes teaching us how to protect ourselves from them?

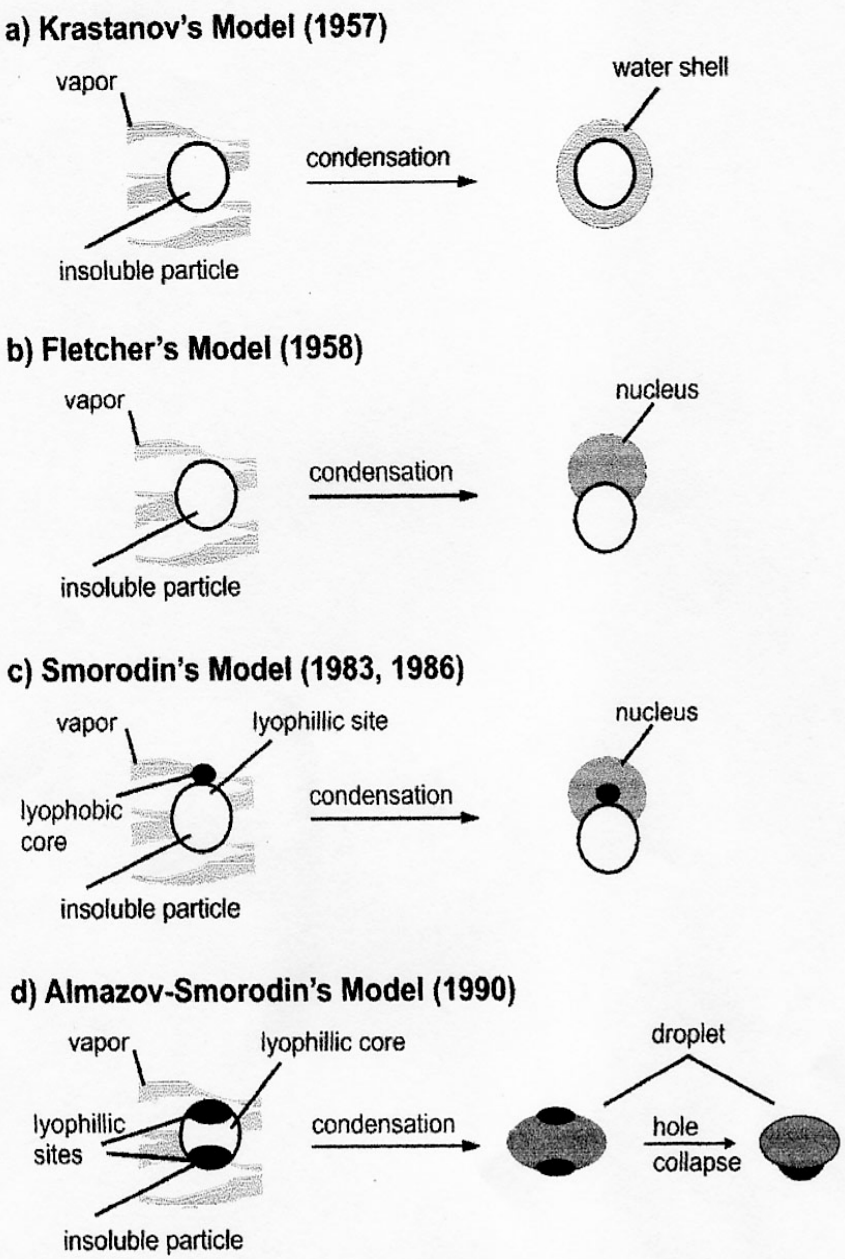


Figure 2. Schematic diagrams of models for heterogeneous nucleation on insoluble particles.

Smorodin & Hopke, 2004

CLASSICAL THEORIES OF HETEROGENEOUS NUCLEATION CANNOT EXPLAIN OBSERVED PARTICLE DISTRIBUTION:

+ NO FLUID PHASE
+ SINGLE FIBER ANOMALY

AVAILABLE DATA SETS ARE IN AGREEMENT WITH THE SINGLE FIBER ANOMALY FOR THE ca. 317°C VENT.
RW AND GW SAMPLES DOCUMENT THIS ANOMALY (08-2004 and 01-2005).
RW-MD AND RW-HD SAMPLES FROM A ca. 400°C VENT DO NOT DOCUMENT THE SINGLE FIBER ANOMALY (01-2005). METAL SULFIDES NUCLEATE IN A „FLOWERY“ VERSION ON FIBERS.

The single fiber anomaly had been also detetcted on tremolite asbestos (O, Ca, Mg, Si) fibers (Al, S, Cl, Ti, Ni).

Is the single fiber anomaly expressed by metal chlorides and to a minor degree by metal sulfides linked to a T-dependent window? (Nuccio et al. 1999 considered T of fumaroles as a subordinate parameter regarding its potential monitoring value.)

Preliminary data confrontation suggests that at ca. 400° C the single fiber anomaly cannot be detected anymore. It is also important to mention that at ca. 400°C RW-MD and RW-HD had been employed as filter material relative to RW-LD and GW at ca. 300°C.

According to classical physics and chemistry no obvious reason exists for such a bias. Is the natural situation the only possible set-up for experiments and the reason for the bias, or is it necessary to design new experiments at old fumaroles?

Preliminary data could be also interpreted as evidence for phenomena related to non-classical physics.

PARTICLE CHEMISTRY IS IN CONCORDANCE WITH ACCEPTED GEOCHEMICAL MOBILITY OF ELEMENTS, EXCEPT REEs, Ti AND Al.

QUESTIONS REGARDING VOLATILITY REMAIN UNANSWERED ACCORDING TO SAMPLING SITES AND DIFFERENT ANALYTICAL TECHNIQUES.

F0 FUMAROLE, LA FOSSA VOLCANO, ITALY (MTE = METALLIC TRACE ELEMENTS by ICP-MS)

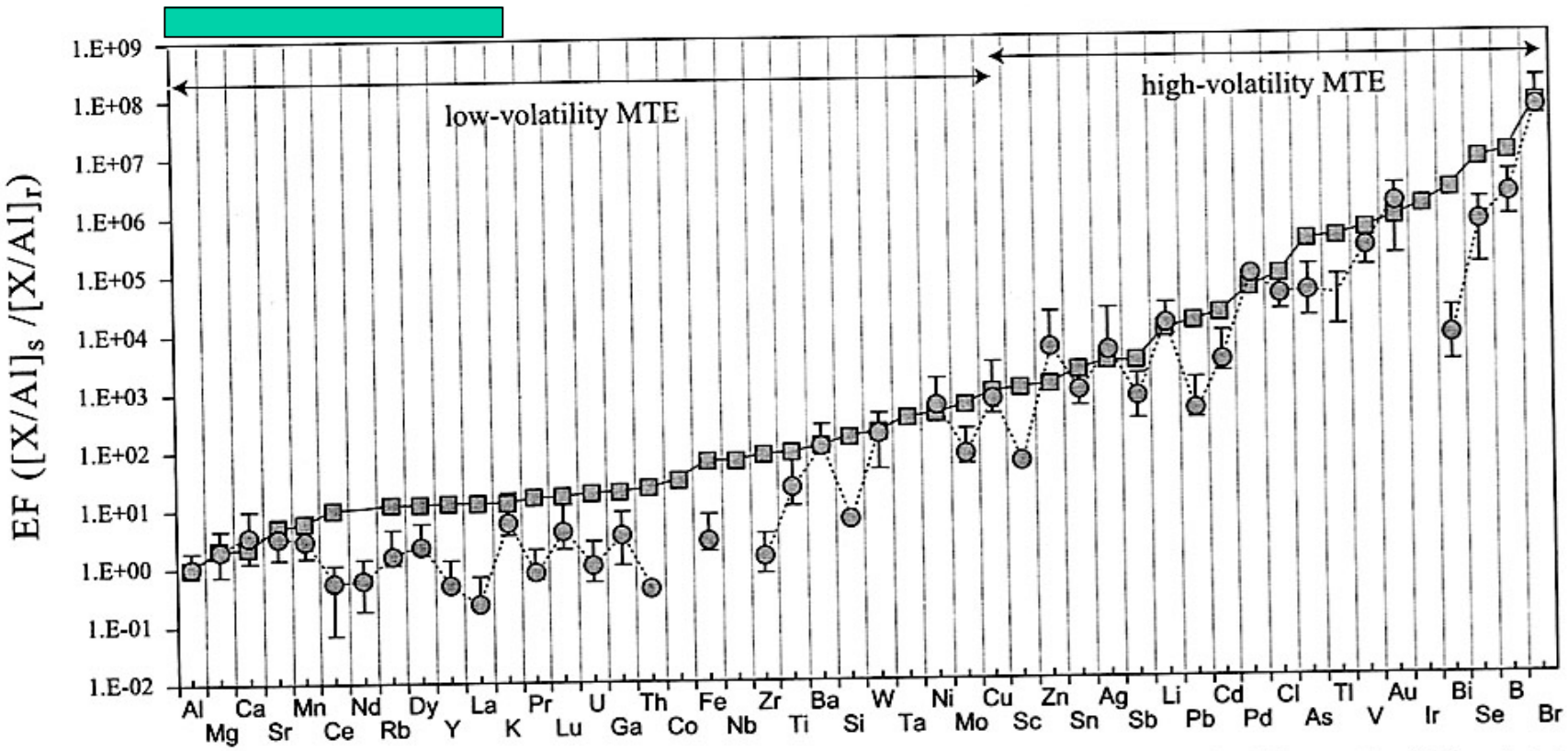


Fig. 4. Comparison of EF calculated in the fumarolic fluid (1 NH_4OH sample, plain squares) and VES samples (plain circles). Mean, maximum and minimum values are displayed for VES samples ($n = 5$).

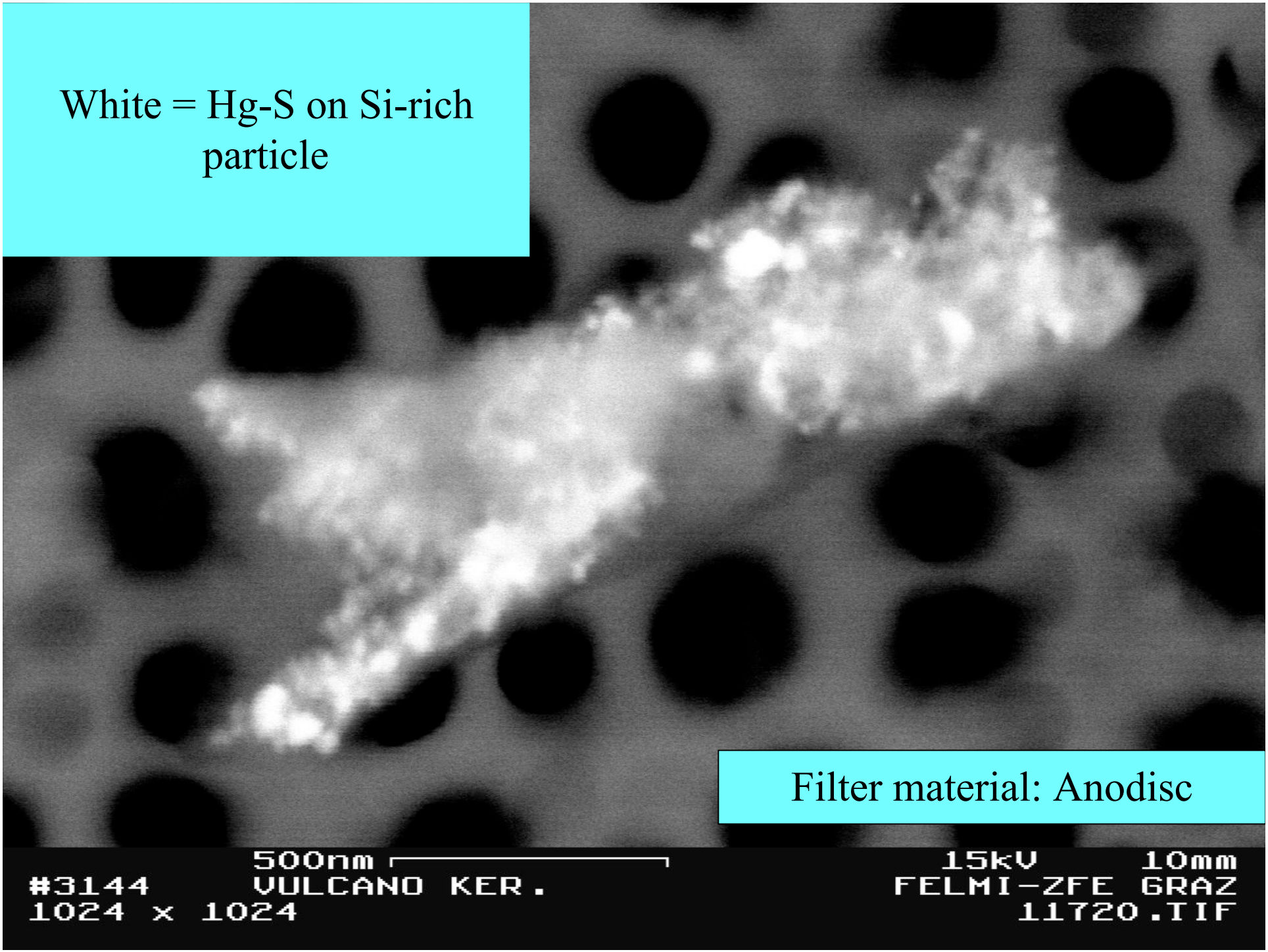
VES:Venturi effect system

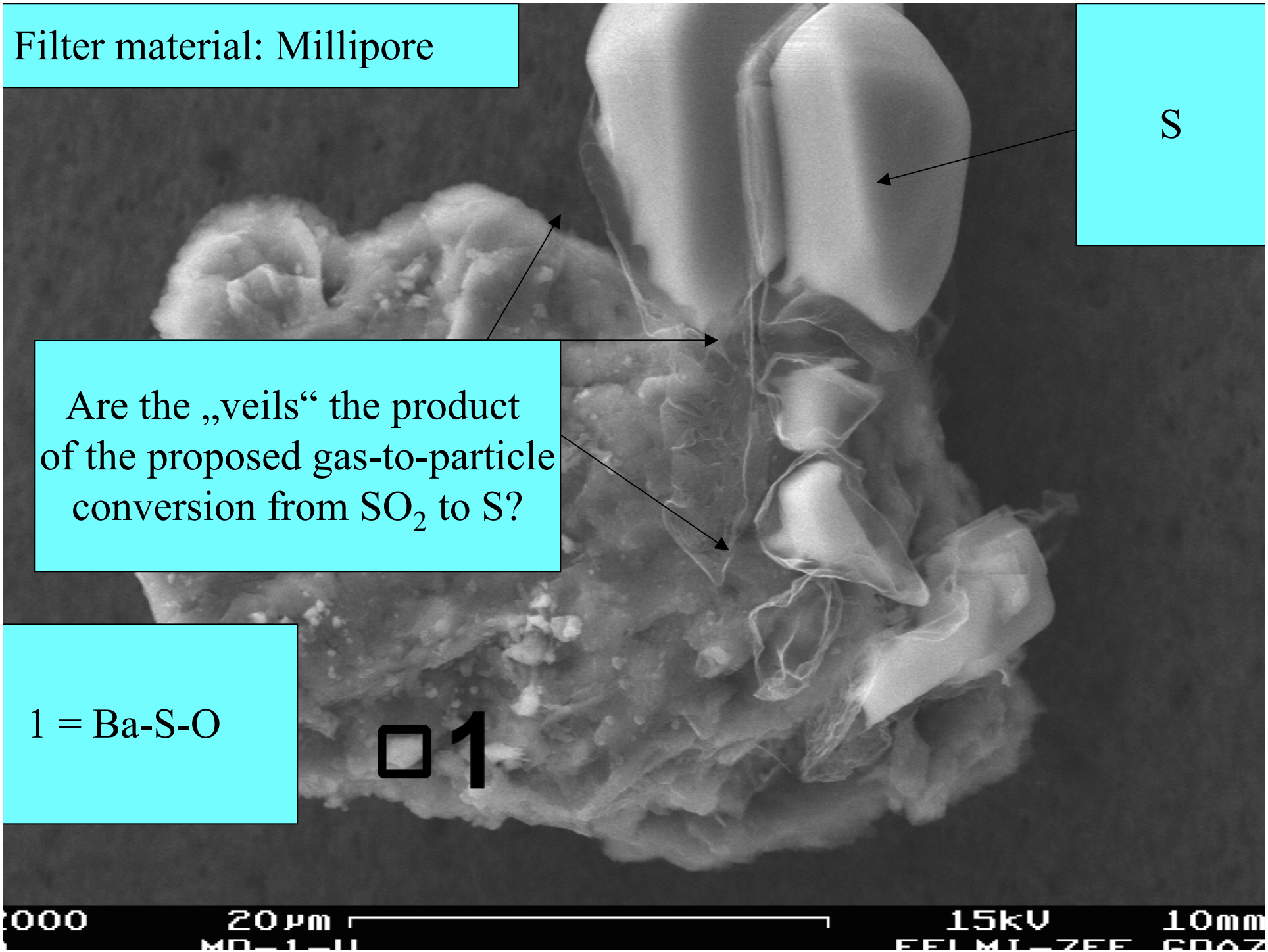
OUR SAMPLING SITE IS NOT EQUAL TO F0, BUT ONLY SEVERAL METERS AWAY. THE SMALL DIAMETER OF THE VENT PERMITTED THE CE. FESEM/EDS COULD ANALYZE ELEMENTS OF PARTICLES (MTE = METALLIC TRACE ELEMENTS):

Low-volatility MTE: Al, Mg, Ca, Mn, Ce, La, K, Co (<>Fe?), Fe, Ti, Ba, Si, W, Ni, Mo (<>S?), Cu.
High-volatility MTE: Zn, Sn, Ag, Pb, Cd, Cl, As, Tl, Au, Bi, B (indirect in barberiite [NH_4BF_4] on GW at AC), Br.
Toutain et al. (2003) analyzed SO4=, F-, Cl- and MTEs. This study comprises MTEs and F, I, S, N, P, Cr, Hg, Ag, O of particles.

Up to now elements analyzed by Toutain et al. (2003) have not been detected yet by FESEM/EDS: LV-MTE: Sr, Nd, Rb, Dy, Y, Pr, Lu, U, Ga,Th, Nb, Zr, Ta, Sc(**); HV-MTE: Sb, Li, Pd, V, Ir, Se(*).
(*)Te grains with minor amounts of Se had been detected by Fulignati & Sbrana (1998) utilizing SEM/EDS.
(**) 1 Sc-bearing particle had been detected by P. Hopke on May 2005 glass wool (CE).
Sulfosalts from the fumaroles of La Fossa v. contain: Pb, As, Bi, Cd, Se, S (Borodaev et al. 1998, 2000, 2001; Vurro et al. 1999).

AEROSOL PARTICLE COLLECTION ON VARIOUS FILTERS SHOWS A WIDE VARIATION OF PARTICLES. ANODISC (Al-P-O) CERAMIC FILTER COLLECTED ONCE Hg-S PARTICLES, AT ANOTHER TIME REE-CARBONATE PARTICLES. THESE PARTICLES HAD NEVER BEEN DETECTED ON OTHER FILTERS.


White = Hg-S on Si-rich particle
Filter material: Anodisc
500nm
#3144
VULCANO KER.
1024 x 1024
15kV
10mm
FELMI-ZFE GRAZ
11720.TIF


Filter material: Millipore
S
Are the „veils“ the product of the proposed gas-to-particle conversion from SO_2 to S?
1 = Ba-S-O
1
20µm
15kV
10mm

IS THERE A MONITORING VALUE OF DEPOSITED AND NUCLEATING PARTICLES?

+ DESIGN OF EXPERIMENTS TO CONTROL/MONITOR CHEMICAL AND PHYSICAL PARAMETERS

+ COMBINATION OF TECHNIQUES (FESEM/EDS, GC, ICP-MS)

+ SAMPLE CHANGER, I.E. MODIFIED TIME-RESOLVED AEROSOL COLLECTOR (TRAC)
(LASKIN ET AL., 2003)

ADVANTAGES OF FESEM/EDS:

+ HIGH RESOLUTION
+ PARTICLES >70 nm CAN BE ANALYZED
+ DETECTORS: SE, BSE, EBSD, TE (LASKIN ET AL.,2005)
+ COATING NOT NECESSARY

PARTICLES NUCLEATING ON FIBERS CONTAIN ELEMENTS WHICH ARE IMPORTANT FOR CATALYTICAL PROCESSES AND STORAGE COMPOUNDS OF THE HYDROGEN ECONOMY.

CAN VOLCANOES SUPPORT NEW CONCEPTS OF ENERGY?

Crabtree et al.,
Physics Today,
Dec. 2004

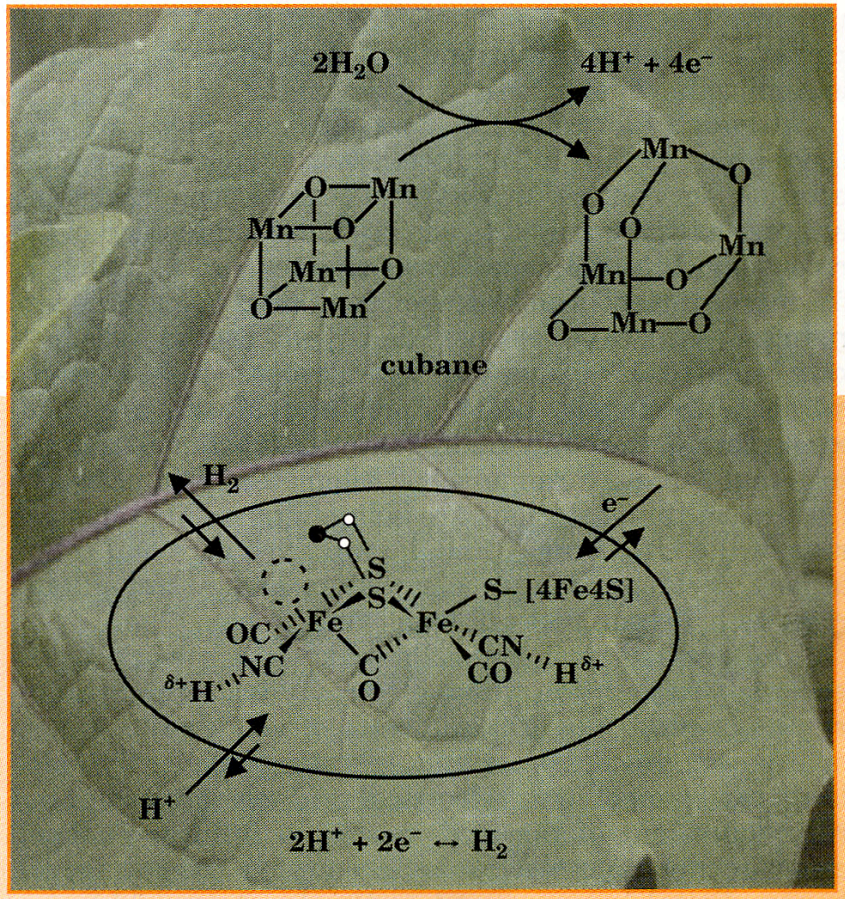


Figure 2. Nature has developed remarkably simple and efficient methods to split water and transform H_2 into its component protons and electrons. The basic constituent of the catalyst that splits water during photosynthesis is cubane (top)—clusters of manganese and oxygen. Researchers are only beginning to understand cubane's oxidation states using crystallography and spectroscopy (see J.-Z. Wu et al., ref. 6). Bacteria use the iron-based cluster (bottom, circled) to catalyze the transformation of two protons and two electrons into H_2. The roles of this enzyme's complicated structural and electronic forms in the catalytic process can be imitated in the laboratory. The hope is to create synthetic versions of these natural catalysts (see F. Gloaguen et al. and J. Alper, ref. 6).

Crabtree et al., Physics Today, Dec. 2004

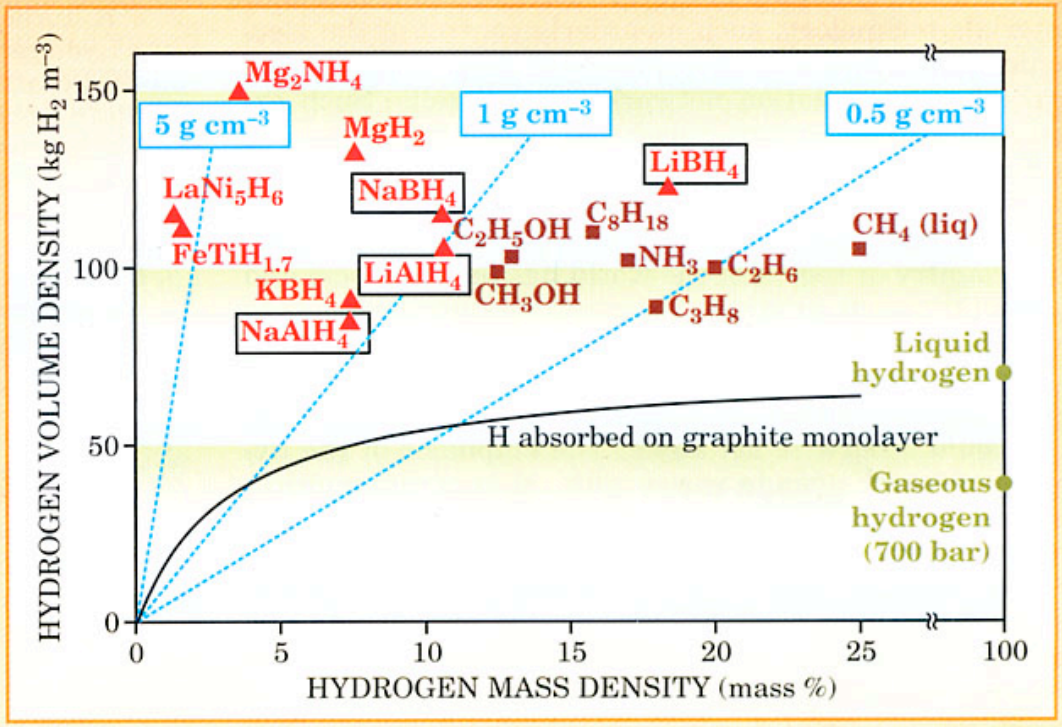


Figure 4. The storage density of hydrogen in compressed gas, liquid, adsorbed monolayer, and selected chemical compounds is plotted as a function of the hydrogen mass fraction. All compounds here except the graphite monolayer store hydrogen at greater than its liquid density at atmospheric pressure; green data points on the right-hand side indicate liquid and gaseous H_2 densities. The straight lines indicate the total density of the storage medium, including hydrogen and host atoms. Of the inorganic materials (plotted as triangles), the compounds shown in boxes all form the alanate structure, composed of a tetrahedral, methanelike AlH_4^- or BH_4^- anion and a metal cation. Those compounds are among the most promising hydrogen-storage fuel-cell materials. (Adapted from L. Schlapbach and A. Zuttel, ref. 7.)

WHICH DATA INITATED THESE EXPERIMENTS?
SEM/EDS STUDIES OF TRIASSIC AND MIOCENE
ALTERED/METAMORPHOSED
PYROCLASTIC ROCKS AT EES/LANL
HAD BEEN THE FUNDAMENTAL DATA SET
FOR EXPERIMENTS AT FUMAROLES
(see next 2 slides).

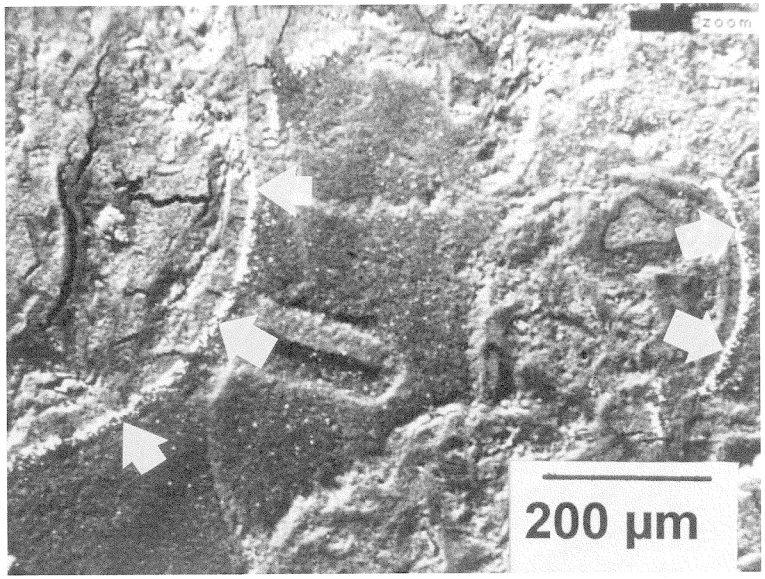


Fig. 15: Partially preserved relict texture of a bubble wall shard replaced by smectite. White arrows indicate distribution of unidentified La<Ce-mineral. Locality Santa Maria Ayu. Tertiary. BSE image.

REE-phosphates: Ce:La:Nd:P = 9:4:3:4. The electron beam also accelerates elements of the matrix minerals of the surrounding of the REE-bearing minerals. To our knowledge these occurrences are not mentioned in the scientific literature. Maybe related observations are published by BRUNO et al. (1989), MILODOWSKI et al. (1989), Rubin et al. (1989), HOLE et al. (1992), JANECKY et al. (1989) and DRISTAS et al. (1996). A preliminary presentation of two examples is given below to make other students of similar rocks aware of this phenomenon.

4.1. REE minerals outlining pyroclastic particles

Samples from the Miocene Mixteca Alta bentonites showed infrequently outlinings of partially preserved relict shards by a La<Ce-mineral (figure 15). The EDS diagram also shows small Y- and Th-peaks. The co-occurring Ca-, Al- and Si-peaks are probably generated by the smectite. The shard relict and the surrounding cement consist of smectite.

Obenholzner & Heiken, 1999

SEM/EDS study of a Triassic ignimbrite

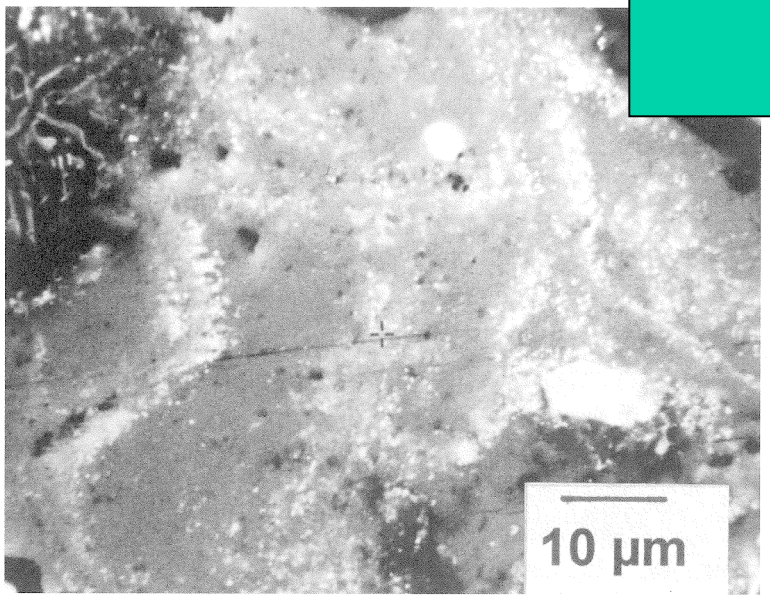


Fig. 16: Calcite filled vug in hydrothermally altered, welded tuff. Band-like oriented white dots are unidentified Zr>Y-Si-minerals. Triassic. BSE image.

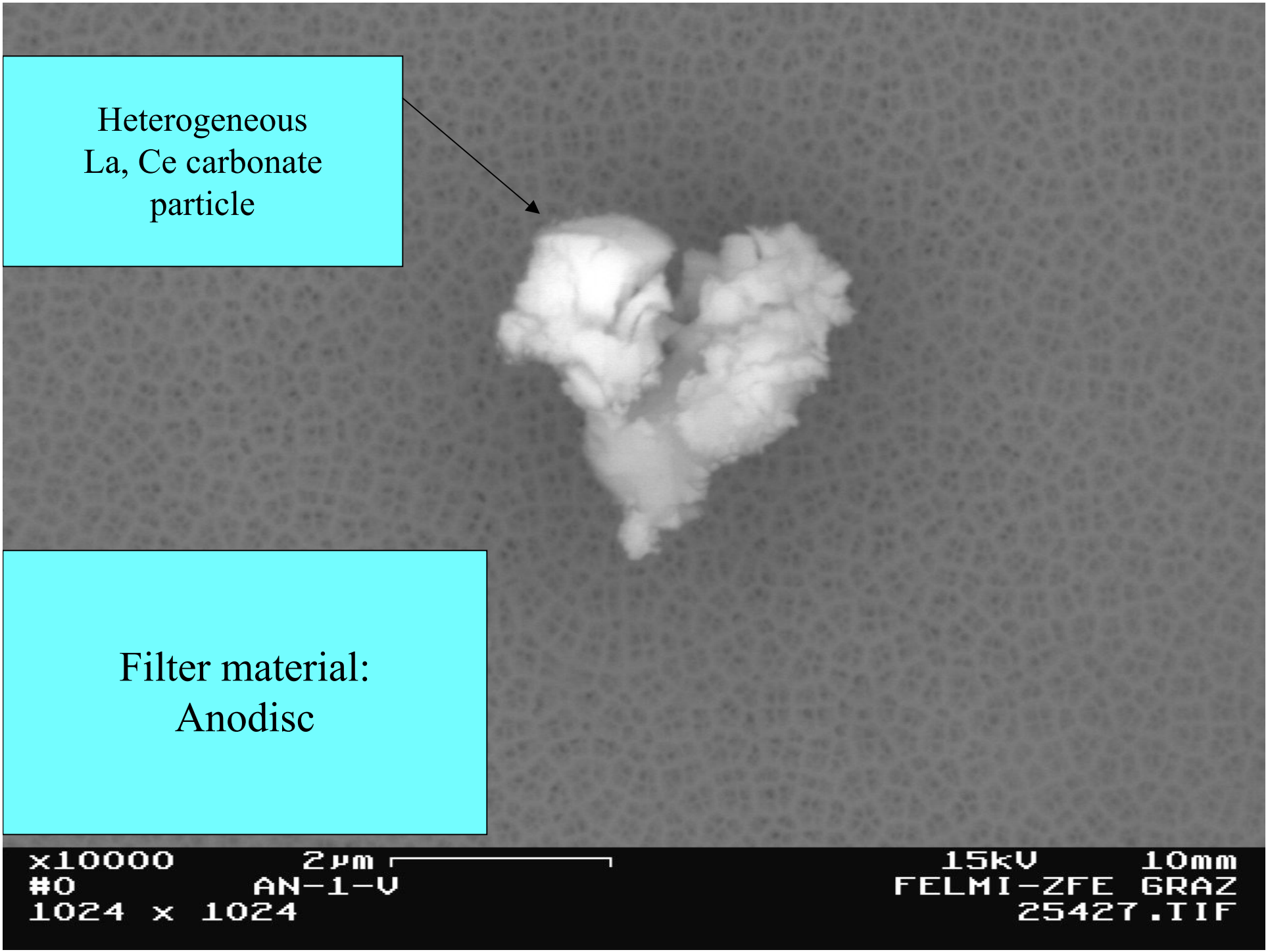
4.2. REE minerals associated with hydrothermal textures

A hydrothermally altered part of the Rio Freddo ignimbrite contains vugs that are filled with calcite (medium grey), and a band-like oriented Zr>Y-Si-mineral (figure 16), which appears white on the BSE image. The white dots are smaller than 1 µm in diameter, so that only selected area EDS analyses could be performed. The larger white dot in the upper central part of the image shows an identical EDS pattern. Co-occurring Ca- and minor Mn- and Fe-peaks are generated by the surrounding calcite. The white mineral above the scale bar is apatite.

5. Acknowledgements

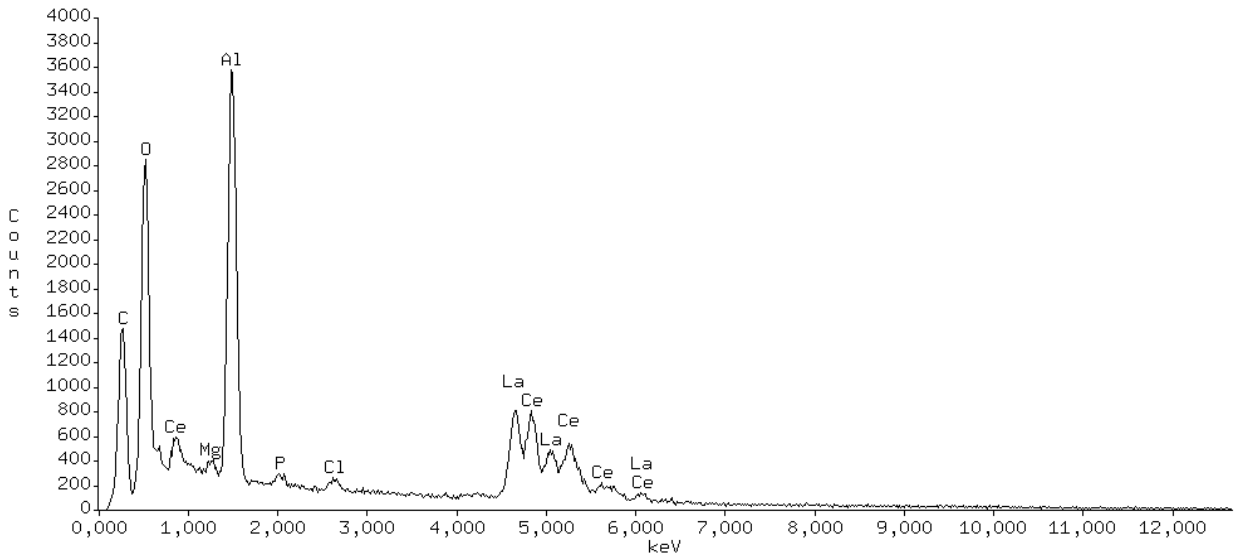
This project was sponsored by the Austrian Science Foundation (FWF) through an E. Schrödinger Grant to J.H. Obenholzner and by the Institute of Geophysics and Planetary Physics (IGPP) at the Los Alamos National Laboratory (LANL), under the auspices of the U.S. Department of Energy.

OBENHOLZNER & HEIKEN, 1999


Heterogeneous
La, Ce carbonate
particle
Filter material:
Anodisc
x10000 2µm
#0 AN-1-V
1024 x 1024
15kV 10mm
FELMI-ZFE GRAZ
25427.TIF

Spectrum of La, Ce carbonate particle

gx15487: AN-1-V, 25427-1, 15kV



REEs:

Mineralogical and geochemical data exist on the mobility of REEs in mostly hydrothermally influenced geo-environments (i.e. Jones et al., 1996).

REEs are important to characterize the descendence of magmatic rocks.

Data of recent to sub-recent fluids containing REEs are rare (Nozaki: La-bearing fluids, REE contents of sea water; Metzger et al.: La-bearing daughter minerals of fluid inclusions of carbonatites (Magnetite Cove; USA)). Banks et al., 1994: Fluids of El Capitan pluton, NM.

We report for the first time of Ce-La carbonate aerosol particles collected in a high-sulfidation, fumarolic environment – La Fossa crater, Vulcano island (CO_2 is present!).

CANCRINITE – ideal formula: $Na_6Ca_2[Al_6Si_6O_{24}](CO_3)_2.2H_2O$ (Hassan 1996)

Maximum losses of H_2O at 304°C and at 683°C.

Maximum loss of CO_2 at 949°C

CANCRINITE (Litvin et al., 1981)

General formula: $(Na, K, Ca)_6(AlSiO_4)_6.R.H_2O$

R=Cl',(OH)', CO_3'' or SO_4''

Spontaneous crystallization at 300-550°C at ? atm.; channels.

CANCRINITE (Jatchow et al., 1966)

Synthetic, hydrothermal Na_2CO_3-cancrinite: needles with channels at ca. 400°C and 800 atm.

Synthetic, hydrothermal $CaCO_3$-cancrinite: needles at 410-470°C and 300-1000 atm.

VISHNEVITE (Hassan et al. 1984) – solid solution with cancrinite

$Na_8Al_6Si_6O_{24}.2H_2O.SO_4$

DAVYNE (Bonaccorsi et al., 1990)

$(Na_{4.4}K_{1.5}Ca_{0.1})Ca_2(Si_{5.9}Al_{6.1}O_{24})(SO_4)_{0.6}Cl_{2.8}$

UTOPIC AT THE MOMENT:

Is it possible to introduce channel-bearing, capillaric particles/crystals (i.e. cancrinite, C-nanotubes) into a hydrothermal/fumarole system to recover fluids from depth at the surface?

What would the fluid chemistry tell us?

Elements in nucleating crystals (mineraloids?) on fibers – unknown resources for a future hydrogen economy?

Elements necessary for H_2 production:

MnO – cubane and photosynthesis – a powerful catalyst to split water

Mn: Mn-Cl on GW at CE – Vulcano (contamination?)
Mn-Cl with traces of $BaSO_4$ on GW at CE – Vulcano

Mn known from i.e.:
+ M. St. Augustin - fumaroles (Getahun et al., 1996)
+ Kudriavy volcano – fumaroles (Wahrenberger et al., 2002)
+ Valley of Ten Thousand Smokes – leachate of ash-flow tuff (Keith et al., 1989)
+ Cerro Negro volcano – fumaroles (Stoiber & Rose, 1973)
+ Soufriére de Guadeloupe etc. (Petites Antilles) – H_2O-soluble on ash (Jérémie & Pascaline, 1982)
+ Irazu etc. (Central America) – H_2O-soluble on ash (Taylor & Stoiber, 1973)

Fe: Fe clusters used by bacteria
$FeCl_3$ is common at many fumaroles

Elements necessary for H storage:

Ti: Ti enrichment on Keddeg (organic) filter at AC – Vulcano 19975
Traces of Ti on GW at CE – Vulcano
Traces of Ti, Cr<>Mn(?), Ni, Pb!, Fe! – Cl, - S<>Mo(?) on GW at CE
- fibers attached to stainless steel (grade 316; no Ti, no Pb)
N + B: Barberiite (?), NH_4BF_4 on GW at AC – Vulcano 21178, 79, 81, 82, 84
Al: i.e. in cancrinite on GW at CE - Vulcano
Ni + Fe : Fe-Ni-(Cr)-Cl on RW & GW at CE - Vulcano
Mg: Mg-Fe & Bi-Cl on GW at CE – Vulcano (common)
La: REE-phosphate in rock coatings – Vulcano (Fulignati et al., 2002); Ce, La carbonate particles on An - Vulcano
Na: NaCl on various fibers at AC - Vulcano
K: KCl on various fibers at AC - Vulcano

Clocchiatti et al., 2003

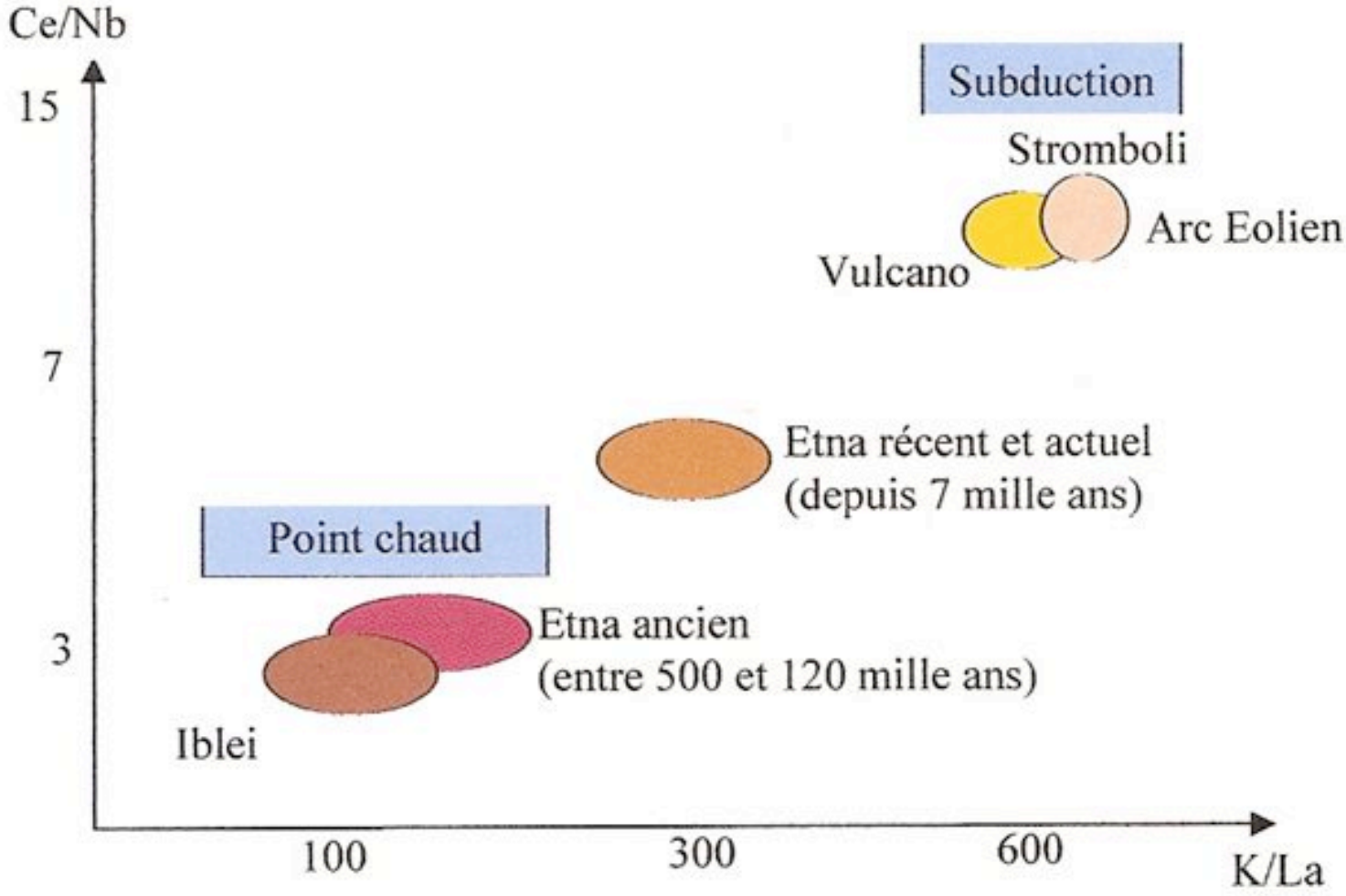


Figure 1 : Diagramme Ce/Nb,vs,K/La comparant les inclusions vitreuses des olivines précoces des laves de l'Etna, des Monts Iblei et des Iles éoliennes (Vulcano et Stromboli).

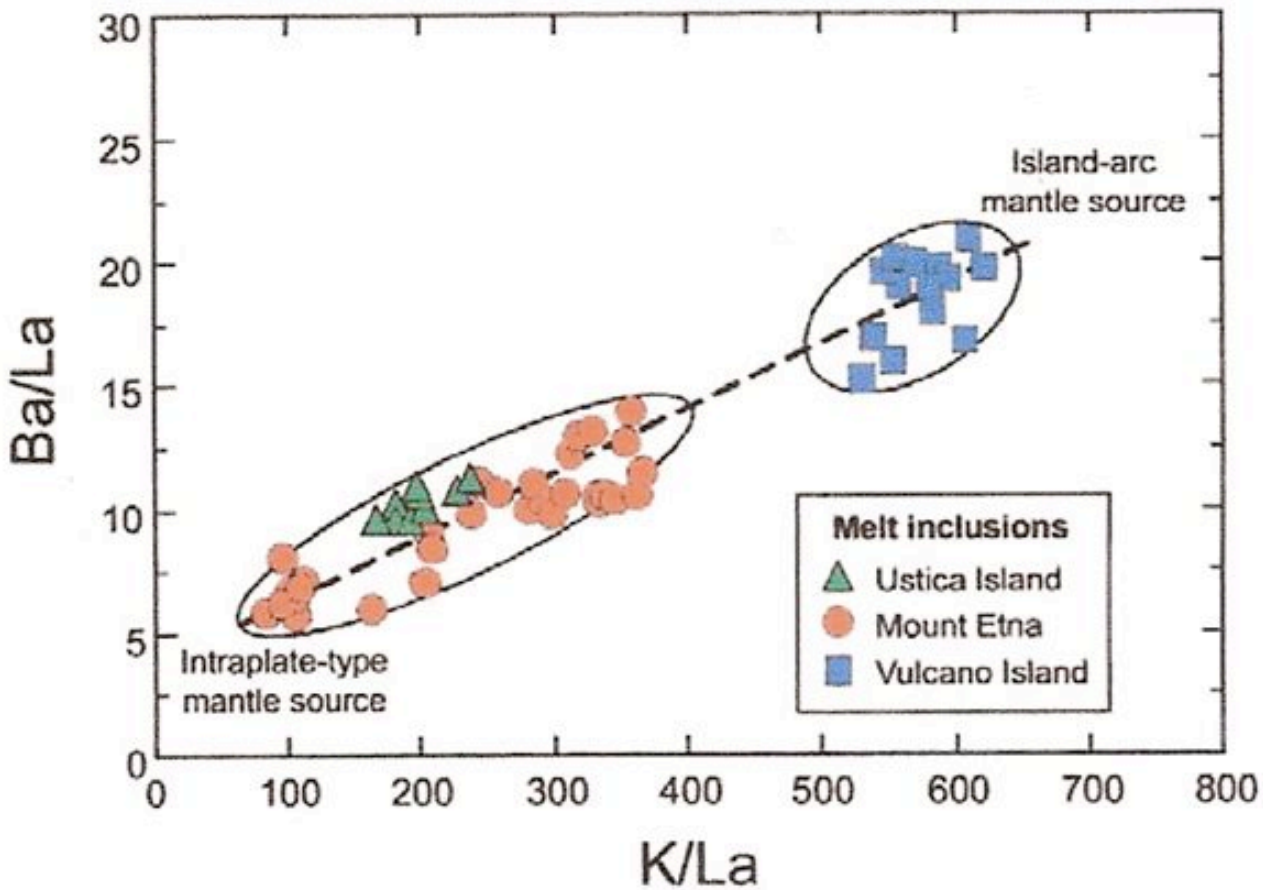


Figure 2 : Diagramme Ba/La contre K/La comparant les inclusions vitreuses des olivines magnésiennes des vulcanites d'Ustica à celles de l'Etna et de Vulcano (Iles éoliennes).

CLOCCHIATTI et al., 2003

Ba:

1. classical petrology considers it as +/- immobile. Therefore several discrimination diagrams and magma path reconstruction plots use it.
2. All soluble Ba salts are toxic. Barite ($BaSO_4$) is very unsoluble and therefore not toxic (+/-?). It is used in X-ray studies of the human digestive apparatus. Ba SO_4 gets deposited in the bones. Does it help the bones to become harder (a cure against osteoporosis?)?
3. Ba is toxic for several marine organisms (see paleontology/reconstructions of volcanic effects) and for viruses (AIDS?).
4. Several bacteria need Ba. Bacteria also act as cloud condensation nuclei. It is unknown if these bacteria actually need Ba. However, volcanic Ba could influence the weather via these bacteria (see volcano climate interaction) .
5. Marine organisms exist which can synthesize barite.

More information on Ba: www.inchem.org

Tl: a review of Tl in the environment has been compiled by Rehkämper et al. 2004

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The mass balance of dissolved thallium in the oceans

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Abstract

This study provides a comprehensive and quantitative discussion of the inventory and mass balance of dissolved thallium (Tl) in the oceans. The calculations are based on a critical evaluation of recently published analytical data. Thallium is estimated to have a mean seawater concentration of 65 pmol/kg and this implies a total oceanic inventory of about 8.76×10^4 Mmol Tl. The five primary sources of dissolved Tl in the oceans are rivers, hydrothermal fluids, eolian contributions from volcanic emanations and mineral aerosols, and benthic fluxes from continental margin sediments. Combined, these sources generate a Tl flux of between 1.4 and 12 Mmol/year, with a best estimate of 5.2 Mmol/year. Based on this, an oceanic residence time of 7–63 ky is calculated for Tl, with a best estimate of 17 ky. The two main oceanic sinks of Tl are scavenging from seawater by the authigenic phases of pelagic clays and uptake of Tl during low-temperature alteration of oceanic crust. These sinks remove about 1.6–7.7 Mmol/year of Tl, with a best estimate of 4.2 Mmol/year. This indicates an oceanic residence time of 11–56 ky, with a best estimate of 21 ky. The mass balance yields input and output fluxes which are identical, within the uncertainties, and this is in accord with a budget that is in steady state.

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3. It remains unknown if sulfide deposits formed earlier in the history of these 2 edifices are mobilized by gases or interaction with magma. The massive sulfide samples dredged from Palinuro seamount (N of the Eolian Islands) might be such an example (Tufar 1992). Tufar mentions that these ores are rich in pyrite, barite and Tl. Sphalerite is common.

Obenholzner et al. 2006

Mather et al. 2005

A quantification of volcanic particles operating as CCN or IN is missing.

Table 1a. Estimates of some tropospheric aerosol and gas emission rates from volcanoes and other sources.

Material	Mean annual emission rate (Tg/yr)	Range	Reference
Primary Particle Emissions			
Sea salt	3340	1000–6000	a, b
Soil dust	2150	1000–5000	a, b
Carbonaceous aerosols	150	66–220	b
Fine ash production from small volcanic eruptions	20		c
Time-averaged volcanic sulfate return flux to the upper troposphere from the stratosphere	0.5–2	0–25	d, e
Emissions available for gas-particle conversion (Tg S/yr)			
Biogenic sulfides	25	12–42	b
Anthropogenic SO_2	79	60–110	b
Volcanoes (SO_2), troposphere only.	5–10	3–25	e, f

a – *Raes et al.* [2000]; b – *Penner et al.* [2001]; c – this work; d – *Pyle et al.* [1996]; e - *Halmer et al.* [2002]; f – see also Table 1b.

Table 1b. Recent estimates of volcanic SO_2 release to the atmosphere.

Source of estimate	Total volcanic emission (Tg S/yr)	Sporadic# volcanic emissions (Tg S/yr)	All continuous volcanic emissions (Tg S/yr)		
			Total	*Continuously erupting*	*Non-erupting*
Stoiber et al. [1987]	9.4	4.8	4.6	1.2	3.4
Andres and Kasgnoc [1998]	6.7	2.0	4.7		
Halmer et al. [2002]	7.5–10.5	4.5–6.3	3.0–4.2		

#– includes both 'small' eruptions that release SO_2 only to the troposphere, and 'large' eruptions that release SO_2 to the stratosphere. The time-averaged sulfur flux to the stratosphere from large eruptions is ~ 0.5–2 Tg S/yr [*Pyle et al.*, 1996; *Halmer et al.*, 2002].

CONCLUSIONS:

+ PARTICLE RESEARCH PROVIDES ADDITIONAL INFORMATION ON VOLATILITY OF ELEMENTS IN VOLCANIC ENVIRONMENTS!

+ DOES THE GAS-TO-PARTICLE CONVERSION REALLY EXIST?

+ NEW INSIGHTS INTO HEALTH-RELATED PROBLEMS: PARTICLE SIZE, MORPHOLOGY AND COMPOSITION

+ WHAT ARE THE REASONS FOR OBSERVED PARTICLE-FILTER INTERACTIONS (NUCLEATION, COLLECTION, NON-COLLECTION)AND PARTICLE SPECTRA ON DIFFERENT FILTERS?

+ CAN PARTICLE RESEARCH IN COMBINATION WITH TIME-RESOLVED SAMPLING BECOME A NEW MONITORING TOOL FOR ACTIVE VOLCANOES AND THE ENVIRONMENT IN GENERAL?

Missing:

Better aerosol particle sizing during various types of volcanic degassing. Watson et al. 2000 had been very successful applying sun photometry at Mt. Etna. They could document particles <0.1 μm - >1.0 μm.

Better particle morphology and chemistry applying FESEM/EDS, HRTEM and/or AFM.

We could demonstrate that even after ca. 0.5 years past the clogging experiment, prefiltered ambient air at room temperature could mobilize As from the exposed glass wool. As (nanoparticles or AsH_3?) passed a 0.02 µm filter at 1L/min and got adsorbed in H_2O. Detected amounts of As after 3 days are very low (ca. 1 ppb). FESEM/EDS could not detect As-bearing particles on the glass wool, only on quartz surfaces exposed to the fumarole. Leaching experiments document 6- 4000 ppb of As. These preliminary experiments had been performed to recover unsoluble particles deposited/nucleated in the interior of the filter body, not to produce a quantifyable leachate!

<u>Volcanic clouds or aerosols can reach all places on Earth.</u>

Air filters operating in volcanically polluted environments (volcanic aerosol or recent ash deposits) might permit the penetration of a variety of toxic substances.

Emergency concepts are needed to recommend better systems for
household and critical infrastructure. A combination of filters and
gas scrubbers could be assembled for critical infrastructure.
Is it possible to assemble a reliable air purifier made from cheap parts
available in local hardware stores as an emergency kit for the household?

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We are sorry that we cannot present a theory or hypothesis related to many of the observed facts at the moment.

Dangerous field and sophisticated lab work permitted this contribution to science.

We hope that our work can stimulate young researchers to fill the theoretical gap(s).

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