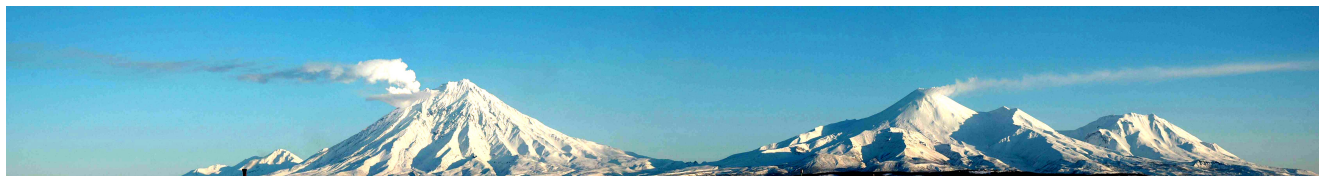


11th Gas Workshop, Kamchatka, Russia

CCVG-IAVCEI



**COMMISSION ON THE CHEMISTRY OF VOLCANIC GASES
(CCVG) – IAVCEI
11TH GAS WORKSHOP, KAMCHATKA, RUSSIA
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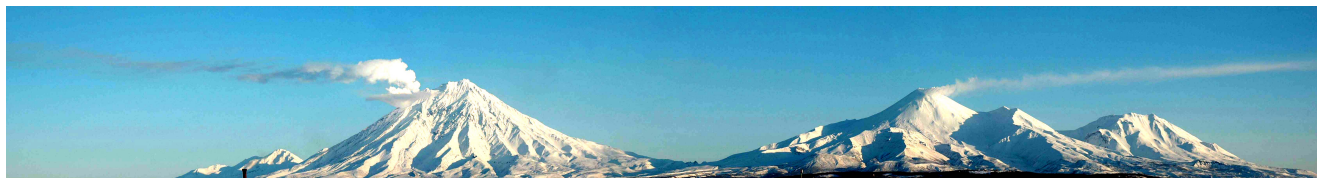


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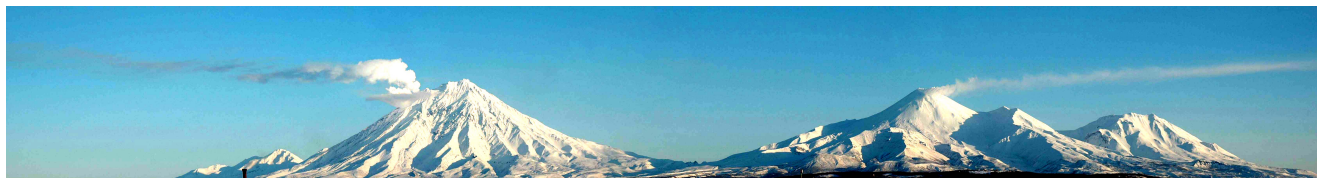
11th Gas Workshop Abstracts



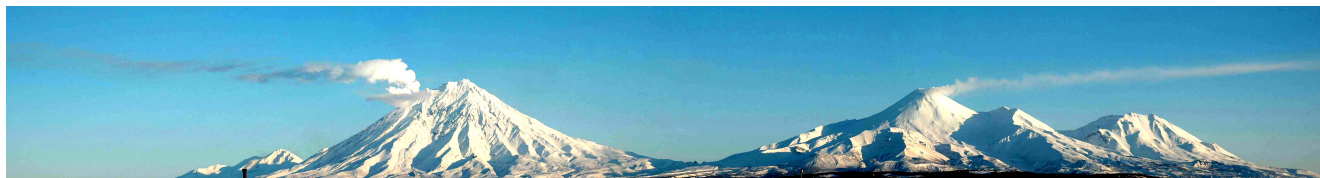


SUMMARY

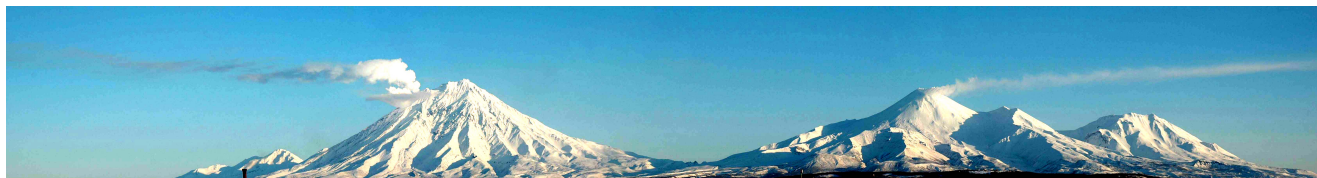
	Page
Summary	1
<i>F. Aguilera, F. Tassi, O. Vaselli, T. Darrah.</i> Geochemical and isotopic survey of fluid discharges from northern Chile volcanoes	4
<i>F. Aguilera, O. Benavente, F. Gutierrez, M. Agosto, A. Caselli.</i> Distribution of gas-water discharges and current geochemical survey along Planchon-Peteroa-Azufre Volcanic Complex, southern Chile	5
<i>A. Aiuppa, M. Burton, P. Allard, T. Caltabiano, G. Giudice, S. Gurrieri, M. Liuzzo, G. Salerno.</i> Linking plume CO ₂ flux emissions and eruptive activity at Stromboli volcano (Italy)	6
<i>P. Allard, A. La Spina, G. Tamburello, A. Aiuppa, A. Di Muro, M. Burton, T. Staudacher.</i> First measurements of magmatic gas composition and fluxes during an eruption (October 2010) of Piton de la Fournaise hot spot volcano, La Reunion island	7
<i>S. Arellano, B. Galle.</i> New developments on remote sensing studies of volcanic gas emissions by solar infrared spectroscopy	8
<i>Ausubel, J.</i> The New International Deep Carbon Observatory	9
<i>E. Bagnato, M. Pistolesi, A. Aiuppa, A. Bertagnini, C. Bonadonna, R. Cioni, M. Pedone.</i> Leachate analyses of volcanic ashes from the 2010 Eyjafjallajökull eruption	10
<i>N. Bobrowski, L. Vogel, G. Giuffrida, C. Hoermann, F. W. Klappenbach, J. Buxmann, P. Luebcke, M. Liuzzo, S. Calabrese, M. Liotta, D. Tedesco, H. Delgado, J. Alvarez, A. Munoz, E. Jaekel, R. von Glasow, U. Platt.</i> Can BrO/SO ₂ be used as a tracer of volcanic activity?	11
<i>S. Calabrese, W. D'Alessandro, F. Parello, S. Bellomo, L. Brusca.</i> Active biomonitoring (moss-bags) of volcanic emissions on Mt. Etna	12
<i>R. Champion, G. Pinardi, P.F. Coheur, G. Salerno, M. Burton, H. Delgado-Granados, M. Martinez-Cruz, S. Carn, A. Bernard.</i> Comparing and integrating SO ₂ measurements from ground and space	13
<i>R. Champion, A. Bernard.</i> Measuring SO ₂ emissions of Eyjafjallajökull with the infrared images of ASTER satellite	14
<i>C. Cardellini, G. Chiodini, S. Caliro, R. Avino, D. Granieri, C. Monopoli, F. Frondini, A. Baldini, M. Donnini.</i> 1998-2010 more than ten year of CO ₂ flux measurement at Solfatara of Pozzuoli (Italy)	15
<i>I. Chaplygin.</i> Magmatic degassing and ore-forming processes at Kudriavy volcano (Kuriles, Russia)	16
<i>G. Chiodini, S. Caliro, R. Avino, C. Minopoli.</i> The fumaroles of Solfatara crater (Campi Flegrei): thirty years of chemical and isotopic compositions	17
<i>B. Christenson, A. Mazot, K. Britten, J. Cole-Baker.</i> Magmatic gas transfer through Ruapheu Crater Lake: Insights into transfer processes and P-T-X conditions in the vent environment	18



<i>J. Fiebig, F. Tassi, W. D'Alessandro, O. Vaselli, A. Woodland.</i> Short chain hydrocarbons in Mediterranean hydrothermal systems: origins and geothermometry	19
<i>T. Fischer.</i> Gas discharges from Continental Rift Volcanoes: Case Study of Oldoinyo Lengai Carbonatite-Nephelinite System	20
<i>B. Galle, U. Platt, M. Van Roozendaal, C. Oppenheimer, T. Hansteen, G. Boudon, M. Burton, H. Delgado, A. Muñoz, E. Duarte, G. Garzón, D. Escobar, M. Kasareka, L. Molina, S. Carn, S. Hidalgo, E. Sánchez, S. Inguaggiato.</i> NOVAC – Network for Observation of Volcanic and Atmospheric Change, recent developments and present status	21
<i>G. Giudice, M. Liuzzo, G. Giuffrida, S. Gurrieri.</i> Example of volcanic gas composition measurements with multi-sensor integrated network	22
<i>T. Hansteen, S. Bredemeyer, K. Garofalo, P. Peña, Y. Dzierma, W. Rabbel, K. Bataille, F. Gil.</i> Gas monitoring and seismicity at Villarrica Volcano, Chile	23
<i>E. Hauri.</i> Grand Challenges in the Deep Earth Carbon Cycle	24
<i>S. Hidalgo, A. Steele, J. Bourquin, M. Ruiz, B. Galle.</i> Correlation between SO ₂ fluxes and acoustic energy related to explosive activity at Tungurahua volcano (Ecuador)	25
<i>S. Illing, P. Lübcke, N. Bobrowski, L. Vogel, U. Platt.</i> Volcanic plume observations with a SO ₂ camera at Popocatepetl and Colima, Mexico	26
<i>A.V. Kiryukhin, T.V. Rychkova, I.K. Dubrovskaya.</i> iTOUGH2-EOS3 modeling of the natural state of the Geysers Valley hydrothermal system (Kronotsky Nature Reserve, Kamchatka) preceding of the Giant Landslide	27
<i>HF. Lee, T.F. Yang, TF. Lan, HY. Wen, CC. Lin.</i> Temporal variations of gas compositions of fumaroles in the Tatun Volcano Group, northern Taiwan	28
<i>M. Liuzzo, G. Giudice, G. Giuffrida, S. Gurrieri.</i> CO ₂ flux time variations on Mt. Etna (Italy) measured by ETNAGAS soil gas network	29
<i>T. Lopez, S. Ushakov, P. Izbekov, C. Werner, C. Cahill, S. Carn.</i> Characterization and interpretation of volcanic activity at Bezymianny volcano from 2007 through 2010: A volcanic-gas perspective	30
<i>A.P. Maximov, P.P. Firstov, I.I. Chernev, V.N. Shapar</i> Gas composition in Mutnovsky geothermal field: Role of meteoric water	31
<i>D. Melnikov, S. Ushakov.</i> SO ₂ gas emission of Mutnovsky and Gorely volcanoes (Kamchatka): satellite data and ground-based observations	32
<i>R. Mora, C. Ramírez, G. González, D. Rouwet, A. Rojas.</i> Laguna Caliente, Poás Volcano, Costa Rica: The most active hyperacid crater lake of the world (2006-2011)	33
<i>O. Neussypina, H. Fischer, A. Krueger, P. Rusch, R. Harig, D. Melnikov.</i> Remote sensing of volcanic gas emissions using a scanning imaging uv-spectroscopy system and tomographic 3D cloud reconstruction	34
<i>A.Yu. Ozerov.</i> Gas regime defining the mechanism of periodic lava fountaining of basaltic volcanoes (experimental modeling)	35



<i>N.A. Ozerova, A.Yu. Ozerov.</i> Mercury in vapor-gas fumarole jets and products of their sedimentation at the Mutnovsky volcano	36
<i>L. Peiffer, Y. Taran, D. Rouwet.</i> Gas geochemistry of El Chichón volcano	37
<i>H. Pfanzen.</i> Volcanic CO ₂ emission and indicative vegetation	38
<i>U. Platt, N. Bobrowski, B. Galle.</i> Spectroscopic Observation of Volcanic Emissions – Status and Future Trends	39
<i>C. Ramírez, R. Mora, G. González.</i> Field Thermal Imaging monitoring of fumaroles, crater lakes and mud pools, at Costa Rican Volcanoes	40
<i>L. Rodríguez, C. Reyes, D. Gaetán, G. Chigna, C. Ramírez, R. Mora, G. Gonzalez.</i> OMI SO ₂ measurements of active volcanoes in Guatemala and Costa Rica	41
<i>C. Silva, F. Viveiros, T. Ferreira, JL. Gaspar, P. Allard.</i> ²²² Rn and CO ₂ soil diffuse degassing pattern anomalies and its relation with volcano-tectonic structures at Furnas Volcano (Azores, Portugal).	42
<i>G. Tamburello, A. Aiuppa, E.P. Kanzas, A.J.S. McGonigle, M. Ripepe</i> High temporal and spatial resolution UV camera measurements at Stromboli: insights on passive SO ₂ gas emission, Strombolian eruptions, and puffing	43
<i>Y. Taran.</i> Volcanic gas geochemistry. A Russian connection	44
<i>Y. Taran.</i> Review of the last 5 years volcanic gas papers: where we are and where we go?	45
<i>F. Tassi, J. Fiebig, M. Nocentini, O. Vaselli.</i> Origin of methane in fluid discharges from Italian volcanic and hydrothermal systems as inferred by the isotopic features and the chemical composition of light hydrocarbon	46
<i>D. Tedesco, F. Tassi, O. Vaselli, T. Darrah, R.J. Poreda, N. Bobrowki, E. Cuoco.</i> The Virunga volcanic active area: A complete (almost) geochemical approach to mitigate volcanic and other hazards	48
<i>SV. Ushakov, AA. Ovsyannikov, VN. Shapar, IF. Timofeeva.</i> Gas monitoring of Kamchatkan volcanoes (Russia)	49
<i>O. Vaselli, F. Tassi, D. Tardani, E. Fernandez, E. Duarte.</i> A discontinuous geochemical and isotopic monitoring at the Poás magmatic/hydrothermal system	50
<i>F. Viveiros, C. Cardellini, T. Ferreira, S. Caliro, C. Silva, G. Chiodini, JL. Gaspar.</i> CO ₂ hydrothermal emissions and thermal energy released at Furnas Volcano (São Miguel Island, Azores archipelago). Inferences on geomorphology and tectonics	51
<i>L. Vogel, N. Bobrowski, VR. Cáceres-Espinosa, C. Kern, C. Hörmann, R. Von Glasow, U. Platt.</i> Understanding BrO formation in volcanic plumes, measurements of plume chemistry at early plume ages	52
<i>HY. Wen, TF. Yang, Z. Guo, CC. Fu, M. Zhang.</i> Gas composition and soil CO ₂ flux at Changbaishan intra-plate volcano, NE China	53



GEOCHEMICAL AND ISOTOPIC SURVEY OF FLUID DISCHARGES FROM NORTHERN CHILE VOLCANOES

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The Central Andean Volcanic Zone (CAVZ) in northern Chile is a 1,500 km long volcanic arc related to the subduction of the oceanic Nazca plate beneath the South America plate. The CAVZ includes 44 active or potentially active volcanoes and several areas of geothermal interest. Lascar, whose largest historical eruption occurred on 19-20 April 1993, is currently characterized by extensive fumarolic activity and is considered the most active volcano in the CAVZ. There are recently documented phreatic to phreato-magmatic events at Isluga, Irruputuncu and San Pedro volcanoes, while intense fumarolic activity without historical eruptions occurs at Tacora, Guallatiri, Olca, Ollagüe, Putana, Alítar and Lastarria volcanoes. Topographic inflation ($\sim 9 \text{ mm yr}^{-1}$) has been detected since 2003 within a 6 km^2 area surrounding the Lastarria volcano. With the exception of Lascar volcano, little is known about the historical eruptions, activities, and/or volcanic structures from northern Chile volcanoes, because of their remote locations and limited accessibility.

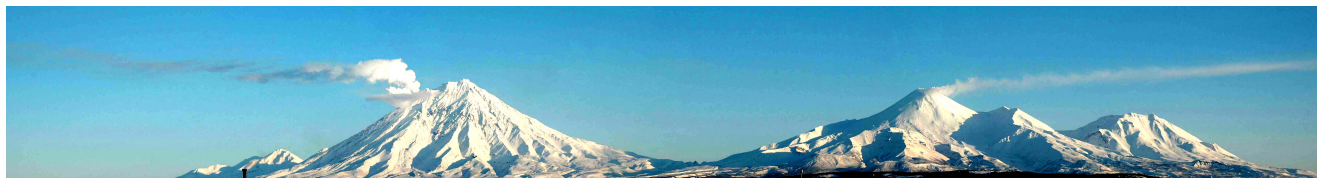
We present analytical results of the chemical and isotopic ($^3\text{He}/^4\text{He}$, $\delta^{13}\text{C}\text{-CO}_2$, $\delta^{18}\text{O}\text{-H}_2\text{O}$ and $\delta\text{D}\text{-H}_2\text{O}$) compositions of gas discharges (fumaroles and bubbling pools) from Tacora, Irruputuncu, Olca, Putana, Alítar, Lascar and Lastarria volcanoes collected during sampling campaigns carried out from November 2002 to June 2009. The main aims are to i) provide the first geochemical and isotopic data set for fluids discharged from these volcanoes and ii) investigate the physical-chemical processes affecting the uprising fluids that occur between the magmatic fluid source and the surface.

Fumarolic discharges from Irruputuncu, Putana, Lascar and Lastarria, whose outlet temperatures range from 30 to 385 °C, 83 to 240 °C, 82 to 88 °C and 80 to 408°C, respectively, are characterized by gases (i.e. SO_2 , HCl, HF, H_2 and CO) and isotopic ratios related to a magmatic gas source (e.g. R/Ra ratios up to 7.3). Inorganic and organic gas geothermometers indicate equilibrium temperatures exceeding 500 °C.

Tacora, Olca and Alítar fluid chemistry indicates lower amounts of magmatic-derived gas species. Accordingly, both helium and water isotopic compositions suggest the presence of a significant fraction of shallow, crustal/meteoric-originated fluids, indicating contributions from a hydrothermal environment with temperatures $< 400 \text{ °C}$.

A common feature in all northern Chile volcanoes is the high $\text{N}_{2\text{ex}}/{}^3\text{He}$ ratios (from 0.7×10^8 to 7.5×10^{10}), which are consistent with active subduction zone volcanoes where N_2 is related to sedimentary material incorporated in the subduction process. We found that $>90\%$ of CO_2 at northern Chile volcanoes is derived from sedimentary sources, mainly carbonates, involved in the subduction process.

Complementary works to the present program of investigation are: ii) a periodical geochemical survey (including DOAS and aerosols measurements) at three volcanoes of the CAVZ (Irruputuncu, Lascar and Lastarria); ii) production of new isotopic data ($\delta^{15}\text{N}$ and $\delta^{13}\text{C}\text{-CH}_4$); iii) a geochemical study of fluid discharges from 3 volcanic systems in southern Chile (Tupungatito, Planchón-Peteroa-Azufre and Quizapu).



DISTRIBUTION OF GAS-WATER DISCHARGES AND CURRENT GEOCHEMICAL SURVEY ALONG PLANCHON-PETEROA-AZUFRE VOLCANIC COMPLEX, SOUTHERN CHILE

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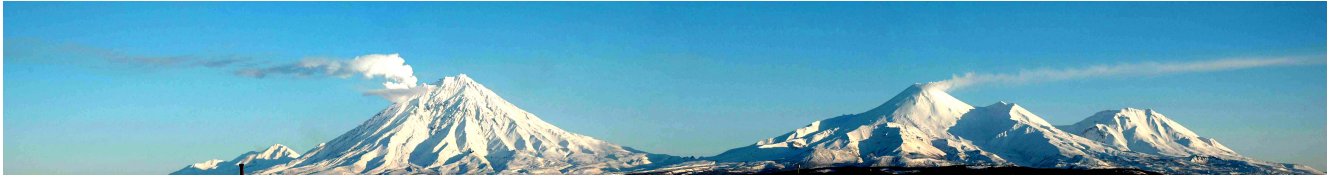
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The Southern Andean Volcanic Zone (SAVZ) located in SE Chile-SW Argentina (33-46°S) is consequence of the Nazca Plate subduction beneath South American Plate. The continental crust beneath the SAVZ ranges between 30 and 55 km of thick. As a consequence of high sedimentation rates since the Pliocene linked to high precipitation rates, glaciation/deglaciation and fast denudation of the Andes, the trench that runs parallel to SAVZ is filled by a high supply of sediments. Consequently, an accretionary prism and thick subducting channel (1.6-0.3 km thick) are developed, where 40-80% of sediments are transported by subduction to the melting zone. Actually, the central-southern Chile region is characterized by a Mediterranean climate regime, where the annual precipitation rate varies from 200 to 2000 mm.

Located in the north-central part of SAVZ, Planchón-Peteroa-Azufre volcanic complex (35°14'S-70°31'W) is a NE trend chain of 3 andesitic to rhyodacitic composite stratovolcanoes. The main edifice (Peteroa) is built in the centre of the chain and is constituted by a 4 km diameter crater, which hosted 4 craters and a scoria cone. The basement that underlay the complex consists in Cretaceous marine and evaporitic sediments, Tertiary basaltic to rhyolitic lava and piroclastic flows and Middle Tertiary granodiorite plutons. Diverse glaciers are present between the craters and valleys of the complex. Its historical activity is characterized by a permanent emission of gas plume (~100 m height), occasionally interrupted by phreatic to phreatomagmatic eruptions. At least 13 historical eruptions have occurred since 1660, being the biggest during February 1991, when eruptive columns reached up 2 km above the crater, being dispersed to ENE by 80 km, while several lahars were generated in the W side of volcano.

In the Peteroa crater, four active craters are nested, i) *Crater 1* (S side) is a NE-SW elongated crater (450 m length), hosting a green lake of 16,800 m² (7,4 °C and pH 2,91) with diffuse fumarolic emissions in its N and W walls; ii) *Crater 2* (east-central part) is a 200 m diameter crater with three fumarolic fields in the W, S and NE side, whose temperatures ranging from 87.7 and 88.4 °C. A green lake of ~1,000 m² was observed during February 2010, however, during March 2011, only a pool of 4 m² was present (43.2°C and pH 1.49); iii) *Crater 3* (north-central part), is a 170 m diameter crater with a reddish brown lake of 7,850 m² (19.1°C and pH 2.73) with diffuse fumarolic emissions in its N and S walls; iv) *Crater 4* (W side) is a NW-SE elongated crater (310 m length), hosting a green lake (38,600 m²) in its S side with strong fumarolic emissions. The last 4 phreatic eruptions (February 1991, September 2010 and February-April 2011) have occurred in this crater. Two fumarolic fields are present between Crater 2 and 3, and in the SE side of scoria cone, with areas of ~24,000 and ~5,000 m², respectively. The discharges present temperatures between 88.3 and 102.1 °C. Three new fumarolic fields have been discovered in the S side of the complex, i) *Azufres Fumarolic Field* (southern external flank of Azufre volcano) a 100 m² with fumaroles, mud pool and hot springs (70° - 88°C); ii) *Llulli*, located along the Colorado River valley, 200 m² area, dominated by fumaroles and mud pools (92°-94,5°C); iii) *Barros del Colorado* (Colorado River valley) ~5,000 m² area with fumaroles and mud pools (93.2 and 94.4 °C). Diverse thermal springs are surrounding the complex: i) *Vergara-Teno valley* (NE side), two thermal springs with Cl⁻-Na⁺ waters (15,2-23,7 °C and pH 6,55-7,92); ii) *El Yeso flat* (E side), three cold springs and one bubbling pool with SO₄²⁻ waters (5-24 °C and pH 6.02-6.88); iii) *Gendarmeria valley* (E side), two bubbling pools with HCO₃⁻ waters (26.3-28 °C and pH 6.14-6.18); iv) *Baños Los Azufres* (SE side), 11 bubbling pools and 2 cold springs dominated by HCO₃⁻ waters (2.3-46.2 °C and pH 6.13-6.69), v) *Baños Las Yeguas* (S side), one thermal spring with Cl⁻(HCO₃⁻)-Na⁺ waters (54°C and pH 6,7); vi) *Pellejo-Los Colores* (S side), 2 thermal springs and 1 bubbling pool with HCO₃⁻ waters (22.9-77.2 °C and pH 6.16-7.02).

Our current geochemical survey in the complex include gas and water sampling for inorganic and organic chemistry and isotopic (³He/⁴He, δ¹³C-CO₂, δ¹⁸O-H₂O, δD-H₂O and δ¹⁵N-N₂) compositions, and CO₂ diffuse measurements, in order to determine the influence of the climate in the degassing style, and the influence of the subducted sediments, continental crustal composition and crustal thickness in the fluid compositions emitted from this volcanic complex. *Work funded by FONDECYT 11100372.*



LINKING PLUME CO₂ FLUX EMISSIONS AND ERUPTIVE ACTIVITY AT STROMBOLI VOLCANO (ITALY)

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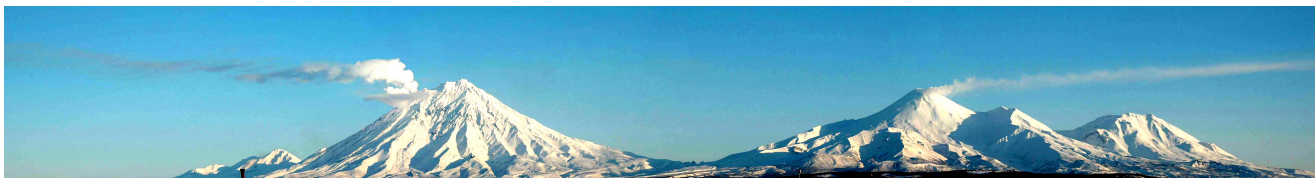
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The standard mildly explosive (Strombolian) activity of Stromboli volcano, in Southern Italy, is periodically interrupted by more energetic explosive events, which range in magnitude from (i) *major explosions* (~2-4 per year, jets >200 m high, ~100 m³ of erupted material) to (ii) more powerful but rarer '*paroxysmal explosions*' (~1 every 5 years, km-sized columns, and ~10⁴-10⁶ m³ of deposits). These explosions are very sudden, and thus represent a great hazard to inhabitants and visitors of the island. In spite of having been the target of extensive geological and geophysical research in the recent past, these highly hazardous explosions have been till now un-forecasted. According to prevailing theory, the most sizeable paroxysmal explosions are triggered by rapid ascent and decompression of CO₂-rich basaltic magma (Métrich et al., 2010) from a 7-10 km deep magma storage zone; while major explosions may result from the sudden ascent (and surface explosion) of CO₂-rich gas slug(s), formed by collapse of a previously accumulated foam at depth (Allard, 2010).

The significant role CO₂ may play in explosion generation has motivated recent efforts to systematically measure plume CO₂ fluxes by a permanent geochemical network (combining UV spectrometers for SO₂ flux and MultiGAS in-situ sensing of CO₂/SO₂ ratios) (Aiuppa et al., 2010). Here, we report on CO₂ flux daily variations measured on top of Stromboli in the period 2006-2010, a period during which 1 paroxysm and 12 major explosions have occurred. We show that the highest ever-measured (> 6,000 t/d) CO₂ emissions were observed for seven consecutive days prior to the 15th March 2007 paroxysmal explosion. We also demonstrate that major explosions were systematically preceded by brief (days) phases of increasing CO₂/SO₂ weight ratio (up to >40) and CO₂ flux (>1300 t/d) with respect to the time-averaged values of 3.7 and ~500 t/d (typical for standard Stromboli's activity). Our observations offer new constraints on the source mechanisms of the explosions, and demonstrate the possibility to forecast these events in advance from geochemical precursors.

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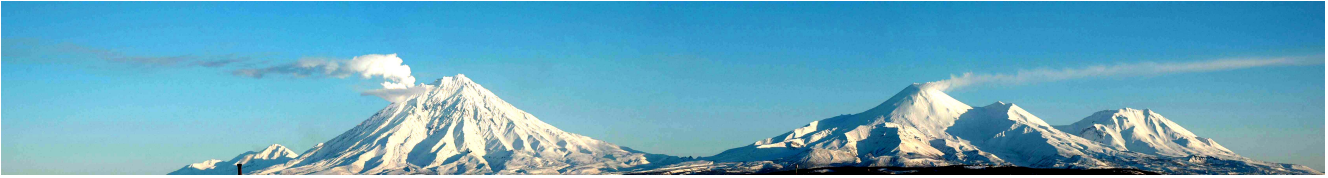


FIRST MEASUREMENTS OF MAGMATIC GAS COMPOSITION AND FLUXES DURING AN ERUPTION (OCTOBER 2010) OF PITON DE LA FOURNAISE HOT SPOT VOLCANO, LA REUNION ISLAND

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Piton de la Fournaise (PdF), in the western Indian Ocean, is a very active hot spot basaltic volcano, with 1-2 fissure eruptions per year on average. Its magmas have been widely studied and its eruptions are well anticipated by the local seismic-geodetic monitoring network. However, no datum was yet available for its magmatic gas emissions (restricted to only eruptive phases and hardly accessible). Here we report on the first measurements of the chemical composition and mass flux of magmatic gases emitted during a PdF eruption in October 2010. Hot gases arising from different eruptive vents were remotely measured with OP-FTIR spectroscopy, using molten lava fragments as IR radiation source, which allowed simultaneous detection of H₂O, CO₂, SO₂, HCl, HF and CO. In situ MultiGas direct analysis of H₂O, CO₂ and SO₂ was also performed in volcanic plumes downwind of the vents. The results reveal a surprisingly H₂O-rich (95-98 mol %) and CO₂-poor (3.2-1.2%) magmatic gas, with high S/Cl ratio (12-25, mean: ~18) and low C/S (1.2-3.2) and Cl/F (0.9-1.2) ratios. The gas composition slightly differed among the vents and evolved over time during the eruption. SO₂ fluxes, measured during helicopter-borne DOAS traverses under the volcanic plume, rapidly dropped from 5 to 1.8 ktons/day as the eruption intensity and lava effusion rate were lowering in the first days. This evolution is further confirmed from space-borne sensing of SO₂ burdens during the whole eruption. Combining OP-FTIR and DOAS data, we derive the emission rate of each gas species and, in reference to available melt inclusion data, the amount of degassing basalt. We find that: (i) Contemporaneous SO₂, HCl and HF fluxes and lava effusion rates were compatible with a pure syn-eruptive magma degassing process for S, Cl and F; (b) In contrast, the CO₂ emission rate suggest either a previously accumulated CO₂-rich gas phase or some separate transfer of CO₂ bubbles across the feeding dyke during the eruption; and (c) the H₂O flux was quite in excess, suggesting a likely entrainment of external steam from the hydrothermal system during dyke propagation. It remains that PdF hot spot mantle source is confirmed to be water-dominated, instead of CO₂-rich, as already inferred from olivine-hosted melt inclusions. Cross-correlation of our results with simultaneously recorded geophysical signals (seismic tremor, ground deformations) will provide increased insight into the conditions of magma ascent and degassing during dyke propagation through Piton de la Fournaise volcanic edifice.



NEW DEVELOPMENTS ON REMOTE SENSING STUDIES OF VOLCANIC GAS EMISSIONS BY SOLAR INFRARED SPECTROSCOPY

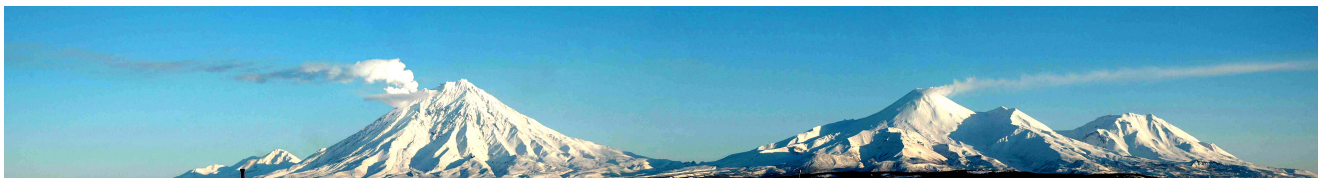
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In this contribution, we will present some recent developments made by our group on the application of solar occultation remote sensing to the measurement of volcanic gas emissions in the infrared spectral region. These include the automation of Fourier Transform Spectrometers (FTS) and novel methods for radiation collection and spectrometric analysis.

Solar FTS is a proven and versatile method for measuring volcanogenic gases. However, its relatively high cost and complexity on data collection and analysis have precluded its wider use by observatories as a permanent monitoring tool. We will present some results of a field experiment performed at Popocatepetl volcano (Mexico) within the FIEL-VOLCAN project in April 2010, to show the feasibility of automating a solar FTS on volcanic settings to measure SO₂/HCl molar ratios. The system includes a compact solar tracker for automatic radiation collection from a stationary point as well as an embedded computer for data acquisition. Data is evaluated off-line by using e.g., the Chalmers-QESOF program.

Further simplifications of the transfer optics and spectroscopic analysis have been investigated by our group and their operation principles and preliminary results will be presented.

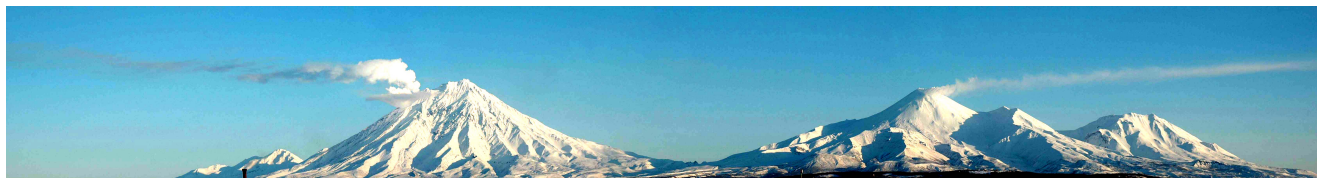


THE NEW INTERNATIONAL DEEP CARBON OBSERVATORY

J.H. Ausubel (1)

(1) Vice President, Alfred P. Sloan Foundation

A multidisciplinary, international decade-long effort initiated in 2009, the Deep Carbon Observatory aims to transform understanding of carbon's chemical and biological roles in the deeper parts of Earth's crust and in the mantle. Questions include how much carbon is stored within Earth and the nature of those deep repositories; how carbon moves from one deep repository to another, and the extent to which carbon moves to and from Earth's surface; the physical and thermochemical properties of deep carbon-bearing fluids, and how these fluids migrate within the deep interior and to the surface; the vast deep microbial biosphere, its diversity and extent, and the potentially unique biochemical characteristics of deep life; and implications for societal issues concerning energy, environment and climate. Mr. Ausubel will describe the motivations and plans for the DCO, including distributed but closely coordinated observational efforts, shared development of widely accessible analytical instruments, and integrative, open access databases.



LEACHATE ANALYSES OF VOLCANIC ASHES FROM THE 2010 EYJAFJALLAJÖKULL ERUPTION

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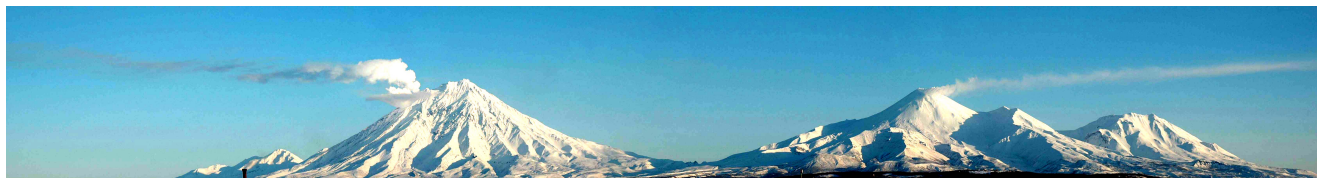
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Volcanic processes which lead to eruptions can be investigated by monitoring a variety of parameters, including the composition of ash leachates. Fine-grained tephra erupted from active vents, and transported through volcanic plumes, can adsorb, and therefore rapidly scavenge, volatile elements such as sulphur, halogens, and metal species in the form of soluble salts adhering to ash surfaces. Analysis of such water-soluble surface materials is a suitable complement for the remote sensing of volcanic gases at inaccessible volcanoes. The April 2010 Eyjafjallajökull eruption has been characterised by several distinct phases, with an initial effusion of alkali basalt on the volcano's northeast flank since March 20th, followed (since April 14th) by a complex summit, sustained, explosive to mixed activity, characterised by trachyandesitic magma. The first phase of the summit eruption (14 to 18 April) was initially characterised by interaction between glacial meltwater from the icecap and erupting magma, and by three main pulses during which dark ash plumes were dispersed to the SE and S. Following a decrease in the intensity in explosive activity associated to the emission of a lava flow (from 19 April to 4 May), activity renewed in intensity on 5 May, when an ash-laden plume, up to 10 km in height, was continuously dispersed until May 18. Activity progressively declined and eruption closed on 9 June^[1].

Here, we report on the chemical composition of leachates from volcanic ash samples deposited during the Eyjafjallajökull explosive phase (from 14 April to 8 May). Twenty-eight freshly fallen volcanic ash samples were collected at various distances from the eruptive vent, and their leached solutions were analyzed for major and trace elements. We show that ash leachate solutions from Eyjafjallajökull are dominated - among cations - by Na and Ca, while they display nearly equal S:Cl:F abundances (mean S/Cl and S/F molar ratios of 1.04 and 0.76 respectively), as characteristic of divergent-plate and within-plate volcanism. The good correlations between Ca and F ($r^2=0.8$), Ca and SO₄ ($r^2=0.7$), and Na and Cl ($r^2=0.9$) in ash leachates suggest that fluorite, anhydrite, and halite were the most likely soluble surface minerals formed in the plume (and therefore leached during our experiments). These correlations in the extracted solutions also indicate that either the sources of cations and anions in ash leachates were the same (e.g. direct condensation of NaCl_(g) and CaSO_{4(g)} from the plume) or, more probably, that the highest the condensation of plume acidic compounds (e.g., SO_{2(g)}, HCl_(g), HF_(g)) on ash, the largest the leaching of cations from silicate fragments. Indeed, our data bring evidence for that the extent of gas-ash reaction (likely, a proxy for ash residence time in the plume) was a key casual factor in determining ash leachate composition. Samples from the 4-8th May eruptive period, showing the most acid pH values (4.5-5.5), consistently have the highest abundances for all elements, and especially Mg, S and F. Large variations in S and halogens proportions are observed in our dataset, with samples from the 4-8th May eruptive period showing the highest S/Cl and lowest Cl/F ratios. To interpret these variations, and particularly to verify whether they reflect changes in plume gas composition, in gas-ash reaction dynamics and rates, will require in-depth comparison with direct (FTIR) measurement of the Eyjafjallajökull gas plume^[2].

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CAN BrO/SO₂ BE USED AS A TRACER OF VOLCANIC ACTIVITY?

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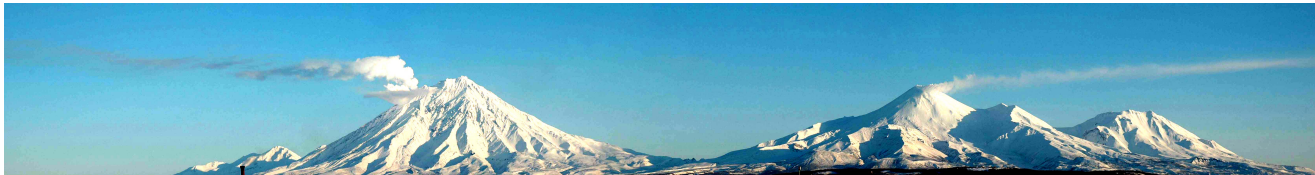
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Volcanic gas studies are an established tool for volcanic monitoring and enhance the understanding about volcanic manifestations. Nearly ten years ago, bromine monoxide was for the first time detected in volcanic plumes. The central question of this presentation is whether the ratio between bromine monoxide (BrO) to sulphur dioxide (SO₂) (two gases which are abundant in volcanic plumes) can potentially serve as indicator for volcanic processes. BrO and SO₂ have the advantage of being relatively easy measurable at a safe distances from the emission source by spectroscopy.

To answer the above question, it is of great importance to link the measurements of bromine oxides to the total emission flux of bromine species and to understand the influences of meteorological conditions on the formation and measurements of halogen oxides.

In order to gain a quantitative understanding of volcanic plume chemistry, gas emissions and volcanic plume composition of Mt. Etna, Italy, Popocateptl, Mexico, Masaya, Nicaragua and Nyiragongo, DR Kongo were analysed. In addition continuous monitoring measurements at Etna, Italy were performed. All measurements were made by Differential Optical Absorption Spectroscopy (DOAS) to characterize the concentrations of halogen oxides (BrO, OClO and IO), their ratios to SO₂ and to quantify emission fluxes. In-situ gas measurements, measurement of meteorological data and incident solar radiation complement the data-sets. In all investigated cases the BrO/SO₂ ratio was found to monotonously increase from very low values at the crater to a plateau level around 10⁻⁵ to 10⁻³ within the first few minutes of plume age.

From the data presented we will evaluate the feasibility of using halogen oxide measurements as an indicator of certain volcanic processes. Additionally, the impact of volcanic halogen chemistry on the atmosphere will be shortly reinvestigated in light of the novel insights.



ACTIVE BIOMONITORING (MOSS-BAGS) OF VOLCANIC EMISSIONS ON MT. ETNA

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Biomonitoring may be defined as the use of organisms and biomaterials (*biomonitors*) to obtain informations on certain characteristics of a particular medium (atmosphere, hydrosphere etc.). In particular, mosses accumulate large amounts of trace metals, making them good bioaccumulators to estimate atmospheric pollution. The moss-bags technique, introduced in the early 1970', has become very popular. Such active biomonitoring technique is particularly useful in highly polluted areas and has been extensively used in industrial and/or urban areas to examine deposition patterns and to recognize point sources of pollution.

The main objective of this study, which represents the first application of the moss-bags technique in an active volcanic area, was to test its efficacy in such environment. Complementary objectives were: to determine the different behaviour and the areal dispersion of volcanogenic elements emitted from Mt. Etna; to characterize the morphology and mineralogy of particles transported in the plume-system, basing on microscopy investigation.

A mixture of Sphagnum species was picked in a clean area, treated in laboratory (rinsed, dried and packed) and exposed in field for 1 month. Sites were chosen considering the prevailing wind at Mt. Etna's summit. Milled samples were analysed for major and trace elements concentrations, after microwave digestion ($\text{HNO}_3 + \text{H}_2\text{O}_2$), by ICP-MS and ICP-OES techniques. Morphology and mineralogy of volcanic particulate were investigated by using a SEM with EDS.

Analyses clearly showed the efficacy of the moss-bags technique also in this peculiar environment. Several elements were strongly enriched in the mosses exposed to the volcanic emissions. The highest enrichment was measured close to the summit crater, but evidences of metals bioaccumulation were also found in down wind sites, at several km from the volcanic source. The accumulation factor (exposed/unexposed moss) allowed us to distinguish a group of elements (Tl, Bi, Se, Cu, As, Cd, S), which are highly mobile in the high temperature volcanic environment. Also alkali metals showed a significant increase in their concentrations, probably because of their affinity for the halide species carried by the volcanic plume.

Microscopic observations evidenced sulphate and halide crystals on particles trapped by the mosses. Mosses exposed at sites directly fumigated by the volcanic plume showed crystal growth also directly on the moss surface.



COMPARING AND INTEGRATING SO₂ MEASUREMENTS FROM GROUND AND SPACE

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Sulphur dioxide (SO₂) is a key parameter to measure when monitoring active volcanoes. Over the past 10 years our ability to measure SO₂ emissions from volcanoes has been improved significantly thanks to the appearance of 3 technological developments: (i) the generalization of small portable UV spectrometers (e.g. Galle et al, 2003) for measuring SO₂ with the DOAS technique. These spectrometers were adapted and automated to be deployed as networks around volcanic edifices, in order to ensure permanent monitoring of their SO₂ flux; (ii) the launch of ASTER (Pieri and Abrahms, 2002), a multispectral satellite sensor, whose bands in the thermal infrared are sensitive to SO₂ absorption with an unprecedented ground resolution of 90m; (iii) the launch of OMI (Levelt et al., 2006), an imaging spectrometer that measures the backscattered ultra violet (BUV) radiance. With its nearly global coverage and high sensitivity, OMI has become the paradigm of SO₂ observation from the space.

We present results of cross validation of these three methods over a number of volcanic plumes (Etna, Popocatepetl, Turrialba, Masaya, Eyjafjallajökull, Nyiragongo, Nyamuragira, Anatahan) located in different atmospheric settings. These comparisons show a generally good agreement between all three methods, with some well identified limitations intrinsic to each of them. This study also demonstrates that the three methods complement one another and can provide original information for volcano monitoring.



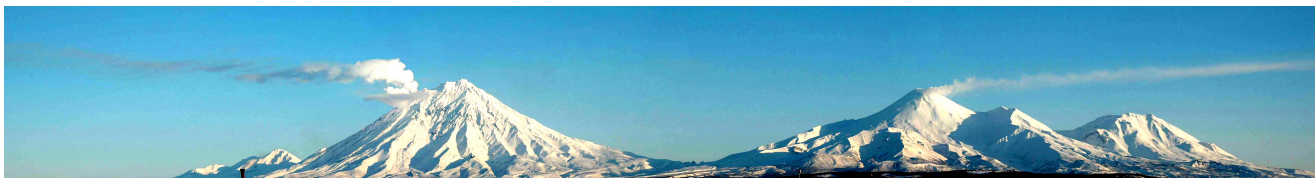
MEASURING SO₂ EMISSIONS OF EYJAFJALLAJÖKULL WITH THE INFRARED IMAGES OF ASTER SATELLITE

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(1) *Université Libre de Bruxelles, Belgique*

The eruption of the Eyjafjallajökull was a complex multistage event that had a profound effect on the life of hundreds of thousands of air travellers. ASTER is a multispectral visible and thermal infrared (TIR) imaging sensor flying on EOS-Terra satellite with a polar orbit. ASTER is a programmable sensor. Thanks to the high latitude of the volcano, and to the urgent acquisition protocol of ASTER, numerous images of the eruptions were acquired from March to June 2010. These images were processed with the band ratio algorithm to obtain distribution maps of the SO₂ in the eruption plume. This algorithm has minimal sensitivity to surface emissivity and altitude, sulfate aerosol in the plume and atmospheric humidity, four variables that often complicate SO₂ retrievals in the TIR. SO₂ fluxes computed from these maps provide insightful information about the eruptive dynamics.

Three regimes of SO₂ emissions could be distinguished, which reflected the three main phases of the eruption. In March 2010, SO₂ was emitted at a moderate rate of ~35kg/s in a small plume that was bearing high concentrations of SO₂ but no volcanic ash. On 17th April, while the eruption was at its highest ash production phase, very little SO₂ was detected by ASTER in the quite large eruption plume. We propose that magma-meltwater interaction promoted SO₂ dissolution and transformation into sulphate, so that only a small fraction of it was released into the atmosphere. Starting on 19th April copious amounts of SO₂ were again measured, indicating that the magma had found a dry pathway to the surface. Radiated energy was also significantly higher, a further evidence that only limited magma ice interaction was occurring. Flux in that last phase peaked at 200 kg/s. This value could still be slightly underestimated due to high ash content in the plume, which appeared nearly opaque in its proximal parts.



1998-2010 MORE THAN TEN YEAR OF CO₂ FLUX MEASUREMENT AT SOLFATARA OF POZZUOLI (ITALY)

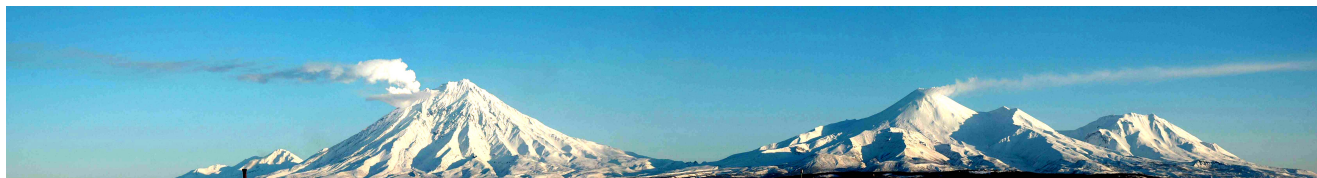
C. Cardellini (1), G. Chiodini (2), S. Caliro (2), R. Avino (2), D. Granieri (3), C. Monopoli (2), F. Frondini (1), A. Baldini (1), M. Donnini (1)

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With a flux of deeply derived fluids of about 5000 t/d and an energetic release of ~ 100 MW Solfatara of Pozzuoli (Campi Flegrei, Italy) appears to be one of the largest studied volcanic-hydrothermal manifestations of the world. Since 1998 surveys of CO₂ flux measurements were performed using the accumulation chamber method: i) over a large area, including the volcanic apparatus and its surroundings, ii) at fixed points in the floor of the crater and ii) by two automatic permanent stations located one inside and one outside the crater. Moreover a new method for the measurement of the carbon isotopic composition of soil CO₂ efflux was applied at Solfatara in order to better define the “real” source of the soil CO₂ flux.

The monitoring of CO₂ fluxes allowed to recognize both “long-period” and “short-period” variations in the degassing of the Solfatara system. The “long-period” CO₂ flux variation consisted in the expansion of the area interested by anomalous soil CO₂ degassing (DDS) which doubled since 2003. This variation mainly occurred external to the Solfatara cone in correspondence of a major fault system NE-SW oriented and was correlated with the occurrence in 2000 of relatively deep, long-period seismic events, which were interpreted as the indicator of the opening of an easy-ascent pathway for the transfer of a large amount of magmatic fluids towards the shallower domain hosting the hydrothermal system. The input of these magmatic fluids has been highlighted also by the changes in the chemical and isotopic compositions of fumarolic fluids. “Short-period” CO₂ flux variations were recorded by both automatic stations and at fixed measurement points. A marked peak of the mean CO₂ fluxes of fix points inside the crater occurred in 2000, probably connected with the 2000 seismic crises. The most evident CO₂ anomaly registered by the automatic stations, was measured outside the crater in 2006. This anomaly has been interpreted as a fast increase in CO₂ fluxes due to a shallow permeability changes along a NW–SE fault, induced by an earthquake swarm occurred in October 2006. The physical feasibility of these variations in the CO₂ diffuse degassing was assessed by simulations of the transfer of gas along a “faulted” hydrothermal system.

Even though the activity of Solfatara is most probably limited to the expulsion of large amounts of gases and thermal energy, as observed in other volcanoes and in the past activity of Campi Flegrei, the relevant changes observed at Campi Flegrei since 2000 have to be taken in to consideration for the interpretation of the future behaviour of this dangerous volcano.



MAGMATIC DEGASSING AND ORE-FORMING PROCESSES AT KUDRIAVY VOLCANO (KURILES, RUSSIA)

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Basaltic andesite Kudriavy volcano is well known for both rare-metal exhalative mineralization and long-lasting (>100 yrs) high-temperature (up to 940°C in 1992, 850°C presently) fumarolic activity (Korzhinsky et al, 1994; Taran et al, 1995; Korzhinsky et al, 2002).

Gases and acid condensates were sampled during the last 10 years at typical points within different fumarolic fields of the volcano. Analyses of these samples show that chemical composition and metal load of the gases vary insignificantly for certain fumaroles. Oxygen and hydrogen isotopic data confirm that most high-temperature gases (700–850°C) correspond to pure magmatic fluid. Intermediate- to low-temperature gases are mixtures of magmatic gas and meteoric water. Our data show that concentrations of metals in condensates can reach: Zn – 10 ppm, Cd – 1 ppm, Mo – 630 ppb, Re – 80 ppb. The comparison of metal concentrations in low density fluids (volcanic gases and vapor inclusions) to data on dense fluids (brines and liquid inclusions) shows that gases may be considered as an important transport medium for many metals including rare and noble metals.

The following ideas about possible causes of long-term high-temperature degassing of Kudriavy volcano have already been outlined in previous publications: a compositional convection in a stratified magma chamber (Simakin and Botcharnikov, 2001); a steady-state release of volatiles from the depth of arc magma generation (Fischer et al., 1998). In this paper convection of magma between shallow reservoir and larger magma chamber suggested by Taran et al. (1995) is accepted as the basis of the model of the ore-magmatic system of Kudriavy volcano. According to geophysical data there is a magma chamber at the depth of ~4–8 km which may be connected to bigger reservoirs at 11–19 km and 15–23 km via deep faults (Zlobin, 2004). Convection in the magmatic column can account for not only intensive long-term fumarolic degassing but also for the formation of ore deposits associated with small stocks of subvolcanic rocks (Shinohara et al., 1995). Gases released from melt at ~100 m below the crater area according to Bocharnikov et al. (2003) are further exposed to temperature gradient 100–150°C/m at the subsurface level. Gas transport reactions lead to the appearance of ore minerals in pores and cracks of lava blocks and between pyroclastic debris. Equilibrium constants of these reactions are very sensitive to temperature conditions and therefore certain minerals grow in specific narrow zones that are characterized by definite temperature intervals. The mechanism described above explains the separate deposition of geochemically close elements such as Mo and Re, Zn and Cd and is observed on Kudriavy volcano. Sampled ore bodies containing ReS₂, MoS₂, Pb-Bi sulfosalts, Zn-Cd-In sulfides and other ore minerals are located within the fumarolic fields at depths up to 2 m. The dynamic equilibrium between growth and dissolution of minerals in flowing gas controls the development of the ore bodies. Deposition of ore minerals is supposed to occur not only on the subsurface level, but also deeper along gas conduits. *The study is supported by RFBR, grant 10-05-00649.*

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THE FUMARoles OF SOLFATARA CRATER (CAMPI FLEGREI): THIRTY YEARS OF CHEMICAL AND ISOTOPIC COMPOSITIONS

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Based on several hundreds isotopic and chemical compositions in the period 1980-2011, Solfatara fumaroles are interpreted as mixture between fluids degassed from a magma body and the vapor generated at about 360 °C by the vaporization of hydrothermal liquids. A typical ‘andesitic’ water type and a CO₂-rich composition has been inferred for the magmatic fluids, while for the hydrothermal component a meteoric origin and a CO₂ fugacity fixed by fluid-rock reaction at high temperatures have been estimated. In the time the fraction of magmatic fluids in the fumaroles increased at each seismic and ground uplift crisis (bradyseism) which occurred at Campi Flegrei, suggesting that bradyseismic crises are triggered by periodic injections of CO₂-rich magmatic fluids at the bottom of the hydrothermal system.

Time series of the chemical composition of fumaroles and of soil CO₂ flux reveal that important variations in the activity of the Solfatara fumarolic field occurred in the 2000–2008 period. A continuous increase of the CO₂ concentrations and a general decrease of the CH₄ concentrations are interpreted to be the consequence of the increment of the relative amount of magmatic fluids, rich in CO₂ and poor in CH₄, hosted by the hydrothermal system. Contemporaneously, the H₂O - CO₂ - He - N₂ gas system shows remarkable compositional variations in the samples collected after July 2000 with respect to the previous ones, indicating the progressive arrival at the surface of a magmatic component different from that involved in the 1983–1984 episode of volcanic unrest (1983–1984 bradyseism). The change starts in 2000, concurrently with the occurrence of relatively deep, long - period seismic events which were the indicator of the opening of an easy ascent pathway for the transfer of magmatic fluids toward the shallower, brittle domain hosting the hydrothermal system. Since 2000, this magmatic gas source is active and causes ground deformations and seismicity as well as the expansion of the area affected by soil degassing of deeply derived CO₂.



MAGMATIC GAS TRANSFER THROUGH RUAPHEU CRATER LAKE: INSIGHTS INTO TRANSFER PROCESSES AND P-T-X CONDITIONS IN THE VENT ENVIRONMENT

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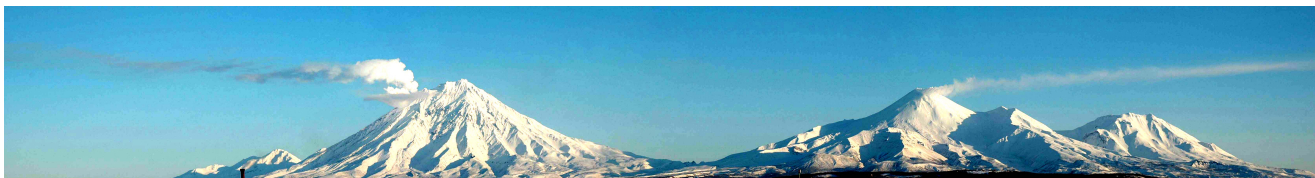
CO₂ emission through Ruapehu Crater Lake has been measured via airborne platform approximately monthly since 2003. At this sampling rate, CO₂ discharge appears to be cyclical, with rates variably ranging from <50 T/D to >2000 T/D. Emission cycles correlate with observed thermal cycling in the lake, pointing to an obvious relationship between magmatic heat and gas transport through the system. TOUGH2 modelling of this cycling points to temperatures varying between ca. 300 – 500 °C in the vent.

Following a gas-driven, phreato-magmatic eruption in 2007, we commenced routine surface sampling of the two major upwellings over the northern and central vents for analysis of their dissolved gases in addition to non-volatile solutes. The lake water is collected by helicopter into an under-slung 25 litres bucket which is then delivered to persons on shore, who immediately take water into evacuated flasks fitted with Teflon-stopcocks. The headspace gases are then analysed by GC and GC-MS for CO₂, H₂, He, Ar, N₂, O₂, CH₄, CO and C₁-C₆ hydrocarbons, with appropriate corrections made for distribution of gas between the vapour and water phases in the samples. The results show the expected influence of atmospheric and magmatic end member contributions to the dissolved gas species, but also a systematic variation in composition with thermal cycling of the lake. CO₂ is the predominant gas in solution, followed by N₂, H₂, Ar, O₂, CO and trace amounts of hydrocarbons (both alkanes and alkenes).

Relative variations in solute gas concentrations provide useful insights into potential equilibrium conditions beneath the lake. Both H₂/Ar and CO/CO₂ ratios, for example, show coherence with measured lake temperatures, indicating changing equilibrium conditions in the hydrothermal environment during the heating cycles. H₂/Ar ratios appear to adjust more rapidly to changing vent conditions than CO/CO₂ ratios. Although there is very little CH₄ in the solute gases, CH₄/CO₂ ratios appear to subtly increase during quiescent periods, pointing to the likely existence of a discreet hydrothermal component resident in the vent system.

Despite the coherent behaviour of temperature-sensitive ratios and lake temperatures, a concern over the general applicability of this approach for monitoring purposes stemmed from our incomplete understanding of the processes controlling gas transfer through the lake, and whether these had any bearing on the observed gas ratios. In 2010, water-borne sonar surveys, gas sampling and diffuse degassing measurements were conducted during a period of relatively low lake temperature and low gas emission (ca. 23 °C and ~180 T/D CO₂). During these surveys, several upwelling bubble/suspension columns were recognised as strong sonar reflectors rising through the water column from the vent regions. However, only very rare and intermittent bubbles were ever observed breaching the surface, indicating that the bulk of the gas was indeed dissolving in the water column during ascent, and that observed solute gas concentrations were likely representative of those discharged from the vent. Diffuse degassing measurements of CO₂, on the other hand, confirm that the dominant process of gas release from the lake is diffusion across the air-water interface.

Modelling of the dissolution process indicates that initial bubble size, path length and fluid viscosity are the dominant factors determining whether a discreet gas phase reaches the surface or the gas is completely dissolved into the lake water.



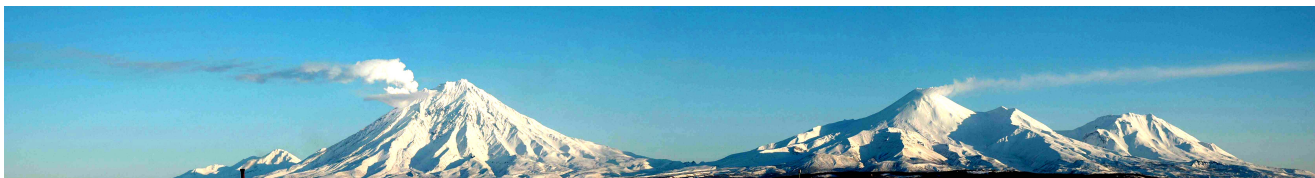
SHORT CHAIN HYDROCARBONS IN MEDITERRANEAN HYDROTHERMAL SYSTEMS: ORIGINS AND GEOTHERMOMETRY

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We have addressed the genetic relationship between CO₂, n-alkanes and n-alkenes in volcanic-hydrothermal gases emitted from Nisyros (Greece), Vesuvio, Campi Flegrei and Pantelleria (all Italy). Methane (C₁) attains chemical and isotopic equilibrium with CO₂ in the associated hydrothermal systems within the single liquid phase. Calculated aquifer temperatures at depth are ~360°C at Nisyros, 420-460°C at Vesuvio, ~450°C at Campi Flegrei and ~540°C at Pantelleria. CH₄ - CO₂ equilibrium temperatures are in agreement with propane (C₃) - propene concentration ratios. Temperatures >400°C are additionally confirmed by ethane (C₂) - ethene ratios. In contrast to CH₄ - CO₂, metastable equilibration of the alkane - alkene C₂ and C₃ pairs takes place in the saturated water vapor phase. Overall agreement of vapor and liquid equilibration temperatures suggests that boiling in the investigated high-enthalpy hydrothermal systems is essentially isothermal.

C₁/C₂ concentration ratios of the emitted gases vary between 20 (Campi Flegrei) and 4400 (Pantelleria). C₁/C₂ values higher than those reported for pure thermogenic sources (C₁/C₂ < 500) imply that CH₄ - CO₂ equilibration is linked to net production of methane through abiogenic reduction of mantle- and limestone-derived CO₂. In contrast, C₁/C₂ values as low as 20 may suggest that the equilibration reaction between CH₄ and CO₂ starts from excesses of thermogenic methane with respect to equilibrium abundances of CH₄ as dictated by hydrothermal temperatures, redox conditions and CO₂ concentrations.



GAS DISCHARGES FROM CONTINENTAL RIFT VOLCANOES: CASE STUDY OF OLDOINYO LENGAI CARBONATITE-NEPHELINITE SYSTEM

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(1) *University of New Mexico, Albuquerque, New Mexico, USA*

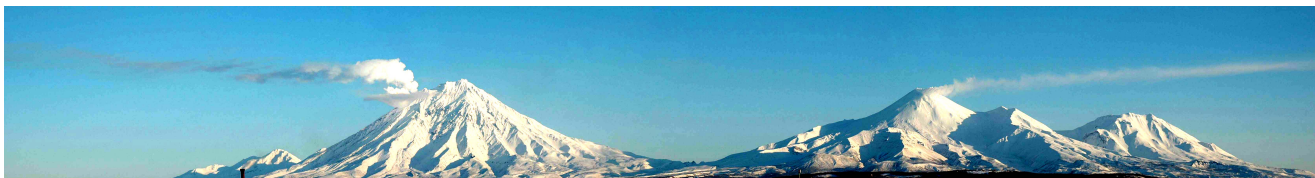
High temperature and accessible volcanic vents located in Continental and Oceanic Rifts settings are rare. Erta Ale Volcano in the Afar region of the Ethiopian rift discharges 1000°C gases and has a clear plume influence with $^3\text{He}/^4\text{He}$ ratios in lavas up to $15R_A$ (Pik et al., 2006). Although hydrothermal gas emissions from the Rift Zones of Iceland are common, nearly all surface expression of gas discharges are low temperature (<100°C) and the magmatic components often masked by atmospheric contributions. Therefore assessing the volatile composition of rift volcanoes and evaluating the magmatic processes occurring in these systems remains challenging.

One accessible location to study the upper mantle volatile composition using gas discharges is Oldoinyo Lengai (OL) Volcano in the East African Rift Valley. In addition, OL is a highly dynamic volcanic system that alternates between effusive and explosive volcanic eruptions. These transitions are likely driven by volatile processes. Oldoinyo Lengai (OL), the cone that rises to nearly 3000 m above Tanzania's Rift Valley, is the world's only active carbonatite volcano. Explosive eruptions have occurred at OL in 1966, 1983 and 1993 producing ash, cones and natrocarbonatite tephra. From Sept. 4 2007 to Nov. 2008, OL erupted explosively forming a ~60 m high ash cone. The magma composition of these eruptions is nephelinite mixed with carbonatite. In June 2009, a carbonatite lava lake occurred at the bottom of the ~100m deep crater. Volcanic products at OL have therefore transitioned from carbonatite erupted in 2005/06 to nephelinite back to carbonatite in three years; a tribute to the highly dynamic nature of the volcano.

Gas samples were collected from crater fumaroles in July 2005, May 2006 and June 2009, spanning the volcanoes recent cycle of activity. The gas composition of all samples is dominated by H_2O and CO_2 . The δD and $\delta^{18}\text{O}$ values of discharging steam lie to the left of the meteoric water line. Sulfur, HCl, and HF contents are < 1 mol%. Hydrogen and CO contents of 0.1 – 0.2 mol% and 0.0015 – 0.025 mol% respectively show the reduced nature of the gases consistent with H_2S being the dominant S species. The CO_2/S and CO_2/HCl ratios of gases are lower than those of carbonatite magmas which contain up to 8000 ppm S and Cl suggesting that S partitions preferentially into the carbonatite phase, rather than the gas phase. Isotopic compositions of He, N_2 , Ar, C show that the mantle below OL is characterized by volatiles indistinguishable from those of MORB sources (Fischer et al., 2009). H_2 - H_2O redox conditions indicate equilibrium with the 'rock-buffer' commonly controlling gases associated with silicic magmas. Gas equilibrium temperatures from ~ 400C to 600C are similar to carbonatite magmas (540C). The 2009 gases have CO_2/S ratios that are higher by factor of 10 than those collected in the 2005 and 2006, suggesting efficient condensation of S into the erupting carbonatite ~ 100 m below the sampling locality. Alternatively, the low S contents could be attributed to volatile depletion of the underlying silicate magma during explosive eruptions. Abundances of non-condensable gases (CO_2 , He, N_2 , Ar) are indistinguishable from those of 2005. This is consistent with the idea that carbonatite magma is a shallow reservoir extending at most several 100's m below the current crater bottom and contributing minimally to the overall volatile budget which is dominated by degassing of the deeper and presumably much larger nephelinite magma. Our data provides important constrains on the nature of carbonatite magmatism and the underlying nephelinite as well as the interaction between these two magmas that produces alternating effusive and explosive eruptive activity.

References

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NOVAC – NETWORK FOR OBSERVATION OF VOLCANIC AND ATMOSPHERIC CHANGE, RECENT DEVELOPMENTS AND PRESENT STATUS

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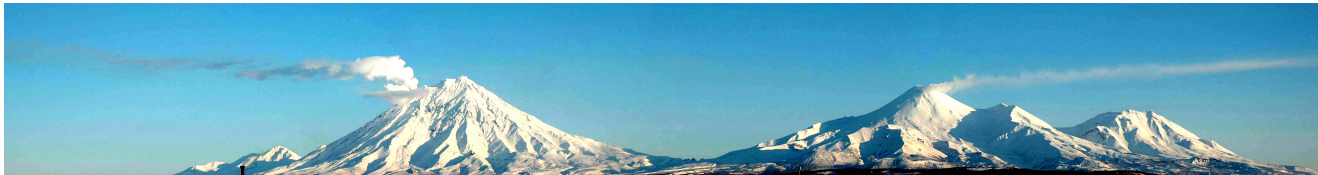
The NOVAC project, funded by European Union, was started in October 2005 with the aim to establish a global network of stations for the quantitative measurement of volcanic gas emissions. The network is based on a novel type of instrument, the Scanning Dual-beam mini-DOAS. Primarily the instruments will be used to provide new parameters in the toolbox of observatories for gas emission estimates, geophysical research and hazard assessment. In addition, data are exploited for other scientific purposes, e.g. global estimates of volcanic gas emissions, regional to global statistical analysis, and studies of atmospheric chemistry. In particular large scale validation of satellite measurements of volcanic gas emissions will be possible, bringing space-borne observation of volcanoes a significant step forward.

The Scanning Dual-beam Mini-DOAS instrument is capable of real-time automatic, unattended measurement of the total emission fluxes of SO₂ and BrO from a volcano with better than 5 minutes time resolution during daylight. The high time-resolution of the data enables correlations with other geophysical data, e.g. seismicity, thus significantly extending the information available for real-time hazard assessment and research. By comparing high time resolution gas emission data with emissions from neighboring volcanoes on different geographical scales, or with other geophysical events (earthquakes, tidal waves) mechanisms of volcanic forcing may be revealed.

The network today encompasses 58 instruments installed on 24 volcanoes, including some of the most active and strongest degassing volcanoes in the world.

In addition a mobile version of the instrument has been developed intended for rapid deployment at a volcano in relation to a volcanic crisis.

The project and its present status will be presented.



EXAMPLE OF VOLCANIC GAS COMPOSITION MEASUREMENTS WITH MULTI-SENSOR INTEGRATED NETWORK

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Recently, geochemical surveillance of active volcanoes has greatly improved, and many different kinds of devices have been installed with the purpose of monitoring the most active volcanoes in many parts of the world.

Different techniques for gas sampling and measuring have been developed and tested but, due to the very extreme environment conditions and technological limitations, only a few can be used for real time measurements and/or continuous monitoring. This has been a very severe limitation in the surveillance of volcanoes because the time delay between surveys is often inadequate to document the dynamic and fast-changing nature of volcanic processes.

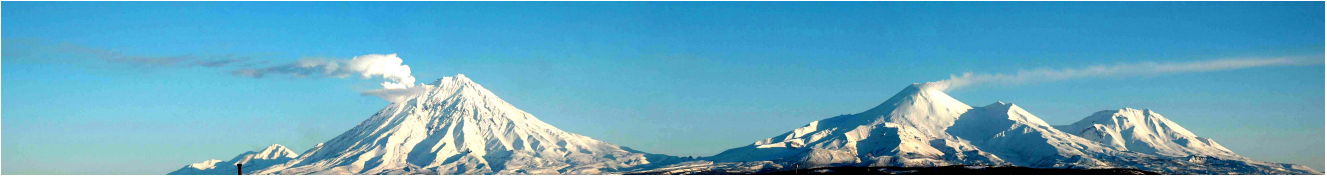
Recently in this field, a new series of gas analyzers has been independently developed by different institutions, such as INGV in Italy and GSJ in Japan, which allow a real-time, in-situ measurement of volcanic gas composition.

The first gas analyzers continuously measuring CO₂ and SO₂ concentrations in volcanic gases were installed at Stromboli and Etna volcanoes, Italy, in 2006.

Today, gas analyzers based on Italian technology are employed in different countries and volcanoes, and the technical knowledge subsequently acquired has improved significantly: in fact, problems due to different environmental conditions (from sub tropical to sub arctic), and the cooperation with other researchers (in Japan, USA, UK, France) have lead to a robust, light and easy to maintain measuring system.

In this work we intend to explain our experience regarding the problems and solutions encountered in different environments, and related scientific results.

Very good correlation between variation of recorded parameters and volcanic activity has been noted in many cases. On many occasions these data have been used in the forecasting of volcanic eruptions in Italian volcanoes with work in progress regarding the prediction of major paroxysms. The importance of this kind of measurement is becoming relevant for civil defence in calculating the level of risk in areas frequented by tourists who, throughout the world, choose to visit active volcanoes.



GAS MONITORING AND SEISMICITY AT VILLARRICA VOLCANO, CHILE

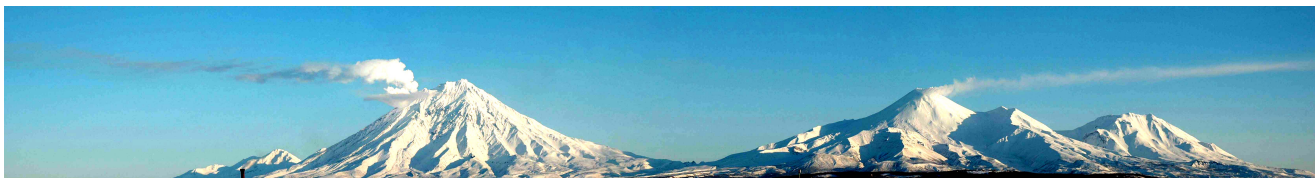
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Villarrica is one of the most active volcanoes in Chile and has a persistent lava lake within its crater. Since several years, Villarrica is characterized by continuous degassing and high-level seismicity. In order to investigate the mechanisms driving the persistent degassing and seismic activity at the volcano, we use a multiparameter approach based on high time-resolution gas flux measurements and seismic data. The instrumentation includes 3 stationary NOVAC-type scanning Mini-DOAS spectrometers for the quantification of SO₂ fluxes, installed at the volcano in March 2009, and for more than one year included 7 short period and broadband seismometers. This equipment complemented the existing OVDAS (Observatorio Volcanológico de los Andes del Sur) volcano monitoring network.

Since the gas monitoring network was installed we have registered several cases of correlation between SO₂ emissions and seismic activity (LP events). Increase in degassing activity following seismic events seem to occur on two different time scales.

Regional earthquake events in 2009 and 2010, and the 2011 Araucania event which occurred on January 2 and had a magnitude of 7.1 were followed by strongly increased degassing activity at Villarrica 2-4 days later, interpreted as due to increased bubble nucleation in the magmatic system at depth. The large Maule earthquake on February 27, 2010 with a magnitude of 8.8 had little immediate effect, but was followed several weeks later by an immense increase in degassing activity of about one order of magnitude compared to the baseline level. We speculate that this was a result of changing stress fields in the lower crust and at mantle depths caused by the Maule event, possibly changing melting conditions temporarily. Based on the combination of gas and seismological data we aim at gaining insight into magmatic and volcano-tectonic processes, especially factors playing a role for the onset of volcanic unrest.



GRAND CHALLENGES IN THE DEEP EARTH CARBON CYCLE

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There exist two carbon cycles on the Earth. The surface carbon cycle exhibits rapid movement of carbon through multiple biotic and abiotic reservoirs via the processes of biological respiration-photosynthesis, combustion of organic matter (by nature and man), weathering and burial of carbonaceous sediment, and exchange of CO₂ between the oceans and atmosphere. Yet the surface carbon cycle contains less than half of the Earth's budget of carbon. The deep-Earth carbon cycle contains most of the Earth's carbon, yet its characteristics are poorly understood when compared with the surface cycle. The deep Earth contains multiple carbon-bearing reservoirs; sizes, ages, distributions and forms of the carbon in these deep-Earth reservoirs are poorly understood, and the abundance of carbon in each reservoir is unknown. It is apparent that carbon can form a variety of stable compounds at the high-pressure conditions of the Earth's interior (diamonds, carbonates, graphite, C-O-H fluids and melts), but the presence of these carbon-bearing compounds is highly dependent on the abundance not only of carbon, but also hydrogen, oxygen, nitrogen and sulfur. Even more poorly-understood are the chemical exchange reactions between carbon and the silicate minerals of the Earth's interior, the solubility of carbon in common deep-Earth minerals, and the chemical environment of carbon within these minerals.

The interface and interconnection of the surficial and deep-Earth carbon cycles are volcanoes and subduction zones. The deep-Earth cycles of carbon and water are closely linked, and the volatile systematics of magmas erupted at mid-ocean ridges, hotspots, back-arc basins and convergent margins are key to observing the magmatic expression of the deep carbon cycle. We illustrate this by examining selected case studies from the Pacific Ocean. Mid-ocean ridge basalts from seamounts and intra-transform spreading centers provide small batches of melt that escape large-scale mixing at the ridge axis, and the data indicate the presence of depleted and enriched upper mantle components with different CO₂ and H₂O contents. Volatile-rich melt inclusions from Mariana arc-front volcanoes consistently range to higher CO₂/Nb than Pacific MORB, and these high CO₂/Nb ratios persist into the mantle behind the arc, as expressed in cross-chain volcanoes. Mariana Trough glasses and melt inclusions have CO₂/Nb ratios that do not exceed the values observed in Pacific MORB, suggesting minimal transport of subducted carbon into the back-arc.

Calcium carbonate is the most abundant alteration mineral in subducted MORB; altered MORB can approach 5% CO₂ in the oldest oceanic crust subducting beneath the Mariana arc. Volcanic degassing studies indicate that only 5-10% of subducted CO₂ is returned to the atmosphere in arc volcanoes. If average subducted MORB worldwide contains at little as 1% CO₂ and 90% of this carbon is carried into the mantle, the rate of carbon subduction would deplete the exosphere of carbon in only ~300 million years. It is clear that we have not yet identified all the pathways of carbon delivery between the Earth's mantle and its surface reservoirs, and the fluxes even along known pathways are very poorly estimated.

The net balance of the Earth's deep carbon cycle is so uncertain that we do not even know if there is net gain or loss of carbon at the Earth's surface. Key to this effort is science surrounding the chemistry and fluxes of CO₂ and other magmatic gases at volcanoes. This effort requires a combination of field work (gases, melt inclusions), ground-based remote sensing, and remote sensing measurements from aircraft and satellites, combined in a global network to monitor such volcanic activity on a coordinated global basis for the first time.



CORRELATION BETWEEN SO₂ FLUXES AND ACOUSTIC ENERGY RELATED TO EXPLOSIVE ACTIVITY AT TUNGURAHUA VOLCANO (ECUADOR)

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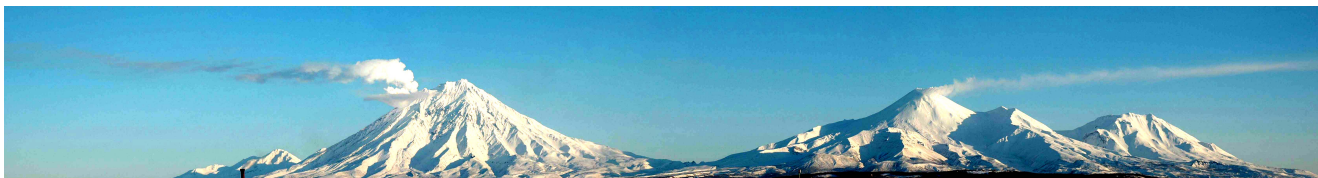
Tungurahua is a steep-sided (5023 m high) andesitic stratovolcano located in the southern part of the Ecuadorian volcanic arc, with its summit crater lying just 8 km to both the touristic town of Baños and to a hydroelectric power plant that supplies 13% of the country's total electric energy. Activity at Tungurahua resumed in September 1999 after 74 years of quiescence and since this time, the volcano has exhibited cyclic phases of activity. Typically, periods of high explosivity often characterized by strombolian to vulcanian behavior alternate with episodes of low to non explosive activity characterized by passive degassing.

The monitoring network deployed at Tungurahua is comprehensive, allowing an extensive record of seismic events, acoustic energy, SO₂ emissions and changes in deformation, to be recorded. In July 2006, five broad-band seismic stations with accompanying infrasound receptors were installed, allowing seismic and acoustic energy to be calculated for each discrete explosion event. As well, SO₂ fluxes have been recorded continuously since 2004 using two DOAS stations, before being enhanced to three sites in 2007. This complete record of both acoustic energy and SO₂ fluxes subsequently allows meaningful correlations between the two parameters to be detected. Two clearly different kinds of behavior were distinguished:

1.- From July 2007 to August 2008: degassing was most of the time above the normal background levels of passive degassing (1000 ton/day). During this corresponding period, explosive activity was also continuous. Total SO₂ released between July 2007 and October 2008 was in the region of 328 kton, giving a daily average emission of 960 ton/day, which was associated with a cumulate mean acoustic energy of 93 kPa, which daily average is 247 Pa.

2.- From August 2008 to the present: high SO₂ emissions are related to explosive activity. Passive SO₂ degassing which corresponds to approximately 65% of the time (during this period) reaches about 247 kton (456 ton/day) and is related to zero acoustic energy production. In contrast, explosive SO₂ degassing reaches a total release of 456 kton (1,534 ton/day) and is related to a cumulate mean acoustic energy of 137 kPa, with a daily average of 508 Pa.

These trends suggest that before August 2008 magma levels at Tungurahua may have been closer to the surface or that conduit geometry was more favorable for efficient degassing showing moderate explosive activity, displaying conditions reminiscent of an open-vent system. Since this time however, volcanic behavior appears to alter to a more closed or blocked conduit regime with degassing efficiency becoming appreciably reduced. During such activity, explosive behavior dominates within well defined eruptive episodes, characterized by more energetic explosions with associated pyroclastic flows and higher SO₂ fluxes, such as May and December 2010 eruptive events.



VOLCANIC PLUME OBSERVATIONS WITH A SO₂-CAMERA AT POPOCATÉPETL AND COLIMA, MEXICO

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Sulfur dioxide (SO₂) emission flux measurements are an important tool for monitoring volcanoes and eruption risk assessment. For instance, changes in the SO₂ flux have been recorded already in the late seventies prior the eruption of Mt Etna (Italy) 1977 or together with an increased seismic tremor prior to volcanic eruptions at Santa Ana volcano in 2005 (El Salvador).

The SO₂-Camera is a technique for remote sensing of volcanic emissions. It images the ultraviolet absorption of SO₂ in a narrow wavelength range around 310 nm on a 2-D UV-sensitive CCD detector employing scattered sunlight as a light source. The effect of aerosol scattering can be eliminated to a certain degree by additionally measuring the incident radiation around 330 nm where the absorption of SO₂ is no longer significant, thus rendering the method applicable to plumes containing aerosols. The ability to deliver spatially resolved images of volcanic SO₂ distributions at a frame rate of the order of 1 Hz makes the SO₂-Camera a very promising technique for volcanic research. The high time resolution allows the calculation of the wind-speed directly from the measurements, thus largely eliminating one main error source of flux measurements. Another advantage of the high time resolution is the possibility to correlate the gas flux with other data sets of equal timescales.

Here we present results of measurement campaigns conducted at Popocatépetl and Colima, Mexico in February and March 2011. Our camera incorporates an additional Differential Optical Absorption Spectroscopy (DOAS) system, thus combining the high sensitivity of spectroscopy with the capability of 2-D the possibility of continuous calibration of the SO₂-Camera. The built in DOAS system executes point measurements of the volcanic plume in a known region of the SO₂-Camera images. This yields column density / apparent absorption pairs that can be used to determine a better calibration curve for the SO₂-Camera images.

In order to test and validate this approach, simultaneous measurements with an imaging-DOAS (IDOAS) and two cameras were conducted. The IDOAS measures spatially resolved 1-D trace gas distributions along a vertical viewing direction. The second image dimension is obtained by using a scanning mirror. Despite the lower measurement time resolution (about 30 minutes), the inherent calibration of the IDOAS allows comparison with the camera retrieved values over the whole field of view of the camera.

At Colima, the high time resolution of the SO₂ camera enabled us to determine the amount of SO₂ released during an explosive event, which might in turn be linked to the mass of magma necessary to release the measured SO₂ mass.

Focus of measurements at Popocatépetl are next to assess SO₂ fluxes in a thorough analysis of camera capabilities and limits of the current technique as well as additional gas species with the IDOAS instrument.

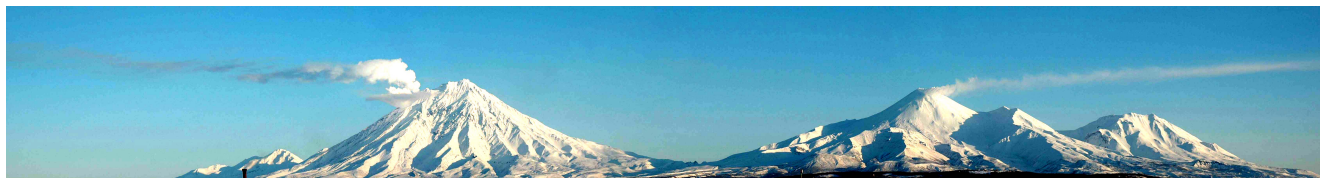


**ITOUGH2-EOS3 MODELING OF THE NATURAL STATE OF THE GEYSERS VALLEY
HYDROTHERMAL SYSTEM (KRONOTSKY NATURE RESERVE, KAMCHATKA)
PROCEEDING OF THE GIANT LANDSLIDE**

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(1) Institute of Volcanology and Seismology FEB RAS

On June 3, 2007, a catastrophic Giant landslide took place in the Geysers Valley, Kamchatka. It occurred synchronously with a steam explosion and was then transformed into a debris mudflow. Within a few minutes, 20 x 106 m³ of rocks were shifted 2 km downstream the Geysernaya river, which created a dam with Podprudnoe lake behind, and buried more than 23 geysers. The 20-30 m deep Podprudnoe lake started to inject cold water into the remaining part of the Geysers Valley hydrothermal system. The objectives of the present study are to integrate available hydrogeological data to develop 3D thermal hydrodynamic (chemical) models to deduce a mechanism for the formation hydrothermal system and its response to changing recharge/discharge conditions after the Giant landslide of June 3, 2007, and to understand triggers of such catastrophic events to be able to forecast future ones. TOUGH2-EOS3 software and PetraSim pre- postprocessor were used. EOS3 (equation of state 3) module is capable of describing two-phase (liquid+gas) two-component (water+air) unsaturated zone conditions prevalent in the elevated parts of the Geysers Valley. The model boundary was defined so as include the main thermal features: Lower Geysers Field and Upper Geysers Field, where most of the deep component thermal discharge of 260-300 kg/s occur. The top of the model coincides with the topographic elevations and the bottom is at -2000 m.a.s.l. The polygonal mesh generated model includes 10,500 of grid elements. Model zonation includes the domains with different material properties: caprock units, composed of caldera lake tuffs; host reservoir; fractured reservoir (two permeable fault zones); more permeable lateral contact zone in reservoir (contact between caldera lake tuffs and pre-caldera volcanic units); host basement; fractured basement (two permeable fault zones); reservoir earth surface - top mesh sub layer used to assign atmospheric conditions. Thermal discharge features were assigned as “wells on deliverability”. Initial conditions were deduced corresponding to conductive heat flow of 60 mW/m² at the bottom of the model and hydrostatic pressure distribution. Heat and mass sources (high temperature upflow recharge) were distributed in the elements at the bottom of the model basement layer along permeable faults (with an enthalpy of 900 kJ/kg). Modeling runs were completed in order to explore the possible timing of the Geysers Valley formation. Modeling different scenarios shows, that the formation of Geysers Valley hydrothermal system took from 20,000 to 30,000 years in terms of temperature distributions and discharge flowrates, and meteoric recharge took place on the outcrops of Mt. Geysernaya rhyolite extrusion on the right bank of Geysernaya river. Model analysis shows wide high pressure two-phase zone at a depth of 150-250 m between steam vent, backing Giant landslide of June 3, 2007 and geyser Velikan, which are conditions of potential steam explosion, if steam pressure transmits to shallower levels. Inverse modeling capabilities of iTOUGH2-EOS3 were used to estimate upflow rate, reservoir permeability and productivity indexes of 39 most significant hot springs based on their flowrates data. Model parameters are also verified by the isotopic composition of thermal fluids (δD , $\delta^{18}O$) and geothermometry.



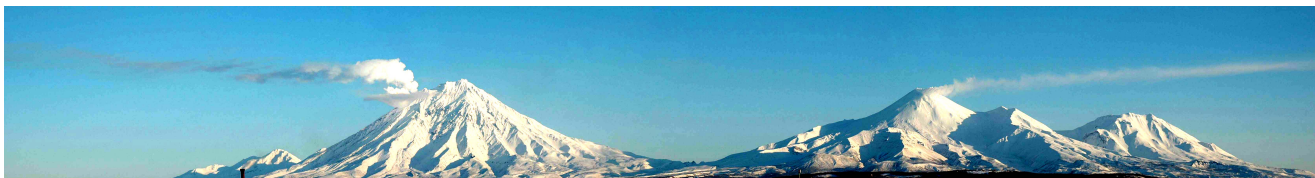
TEMPORAL VARIATIONS OF GAS COMPOSITIONS OF FUMARoles IN THE TATUN VOLCANO GROUP, NORTHERN TAIWAN

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The Tatun Volcano Group is located in the northern part of Taiwan. It was considered dormant because of no previous historical eruptions. However, helium isotopic results and seismic results both inferred that a magma reservoir might exist beneath this area. The recent study of volcanic ash revealed the existence of eruptive activity younger than 6000 years. Considering these evidences, the Tatun Volcano Group should be treated as an active volcano. The Tatun Volcano Group is about 15 km north of metropolitan Taipei city. Also there are two nuclear power plants located only a few kilometers away. Thus, monitoring potential volcanic activity in this area is an urgent task.

We present the variations in chemical and isotopic composition of volcanic gases in the Tatun Volcano Group from 2003 to 2010 and explain possible reasons for the observed phenomena. Progressive increases of HCl concentrations and SO₂/H₂S ratio in fumaroles from Da-you-keng have been observed since August 2004. The HCl concentration changed from almost the detection limit to thousands of ppm, even up to thirty thousand ppm. SO₂/H₂S ratios varied from almost 0 to 3; hence SO₂ became the dominated S species in this area. These variations were accompanied by rising temperature of fumaroles in the Tatun Volcano Group, especially in the area of Da-you-keng (from boiling point to 131°C). Meanwhile, ³He/⁴He ratios showed a decreasing trend but returned to normal values shortly thereafter. Until January 2009, HCl concentrations, SO₂/H₂S ratio and temperature decreased unexpectedly. We propose two possible processes, 1) new magma supply and 2) recent opening of fractures in local area, to explain these observations. Based on the change of ³He/⁴He ratio, lack of ground deformation and no eruption after this period, we consider the latter might be more plausible.



CO₂ FLUX TIME VARIATIONS ON MT. ETNA (ITALY) MEASURED BY ETNAGAS SOIL GAS NETWORK

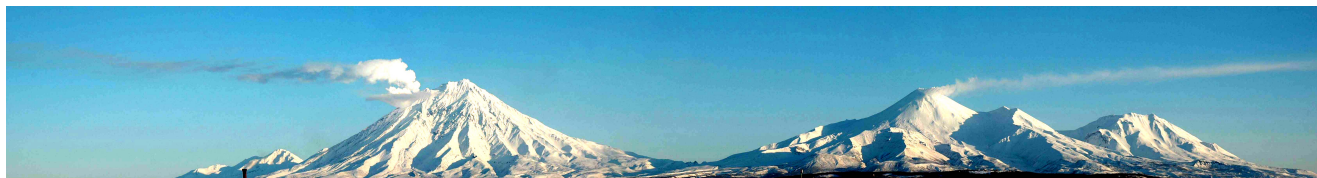
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The phenomenon of CO₂ flux soil variations correlating to volcanic activity is well known. For this reason many measurements of CO₂ fluxes have been carried out on many active volcanoes, bringing profound insights into our understanding of volcanic processes. In the past, almost all of the measurements of CO₂ flux from the soil has been conducted by methods of direct sampling. However, in the last ten years devices have been developed that are able to record data in real time and that are also adaptable for continuous monitoring. In order to further our understanding of volcano dynamics concerning soil degassing, a network of stations for measuring geochemical parameters (ETNAGAS) has been installed on the flanks of Mt. Etna. This network has contributed to volcano monitoring since December 2002. Today, ETNAGAS consists of 18 automatic stations located close to the main volcanic structures of Mt. Etna in areas of the volcano characterized by strong soil CO₂ emissions. The monitoring stations of the network have been entirely developed by the INGV at Palermo and are able to monitor different parameters, such as CO₂ (eventually CH₄) soil flux, T, P, rain, Rh, wind speed and wind direction. Data are acquired at hourly intervals, although it is possible to set the time frequency of acquisition at different intervals of time: one data per hour is considered a good compromise. The soil CO₂ flux measuring system follows the principles proposed by Gurrieri and Valenza (Gurrieri & Valenza 1988), which is based on CO₂ content in a mixture of air and soil gas (dynamic concentration, Cd).

We report here on the very large CO₂ flux variations recorded by the above network during the last 8 years. During this interval of time on Mt. Etna, many eruptive phenomena have taken place and, over the course of this time, it has been possible to identify different episodes of flux increase that correlate well with volcanic activities. A simple statistical analysis showed that anomalous flux of CO₂ from the soil is clearly attributable to a new input of volcanic source, and it is interesting to note that generally the anomalous flux anticipates volcanic activities.

These results suggest the importance of continuously monitoring the CO₂ emitted from soil to the surveillance of volcanic activity in this area (Mt. Etna), and moreover, open up an interesting scenario for the surveillance of active volcanoes.



CHARACTERIZATION AND INTERPRETATION OF VOLCANIC ACTIVITY AT BEZYMIANNY VOLCANO FROM 2007 THROUGH 2010: A VOLCANIC-GAS PERSPECTIVE

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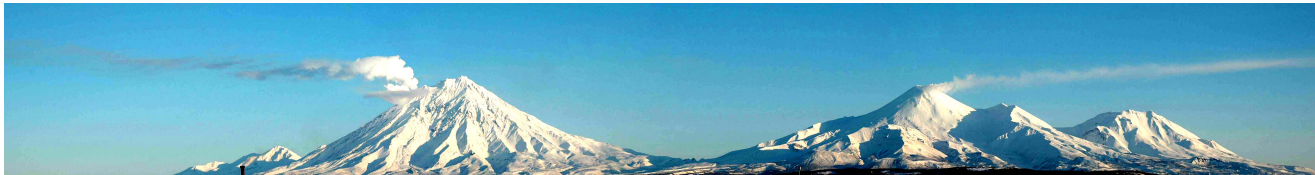
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Volcanic gas measurements at Bezymianny volcano, Kamchatka, Russia, from 2007–2010 are used herein to (1) infer the relative depth or degassing state of a source magma according to solubility differences among gas species, (2) distinguish between open and plugged conduit systems through changes in sulfur dioxide (SO₂) emission rates, and (3) estimate the first-order total eruptive mass of magma through estimates of total eruptive SO₂. To characterize and interpret recent activity at Bezymianny, we measured volcanic gas composition from fumarole samples, calculated SO₂ emission rates from scanning FLYSPEC ultraviolet (UV) spectrometer measurements, and derived eruptive SO₂ masses from Ozone Monitoring System (OMI) satellite data. During the study period, five explosive eruptions occurred at Bezymianny: May 2007, October/November 2007, August 2008, December 2009, and May/June 2010. Preliminary results are shown in the table below.

Year	CO ₂ /H ₂ O	SO ₂ /HCl	SO ₂ Emission Rate (t/d)	Total Emission Rate (t/d)	OMI Eruptive SO ₂ Mass (t)	Magma Eruptive Mass (t)
2007	0.02	0.42	278 +/- 130	~33,900	~4,900	~1.5*10 ⁶
2008	NA	NA	140 +/- 95	NA	NA	NA
2009	0.34	23.61	97 +/- 50	~800	NA	NA
2010	0.02*	6.03*	NA	NA	~4,900	~1.5*10 ⁶

*These samples were collected six weeks after the May 31, 2010 eruption.

We interpret the low ratios of CO₂/H₂O and SO₂/HCl observed in the August 2007 fumarole samples to indicate degassing of a shallow, largely degassed magma source, and the high total emission rates to suggest an open conduit system. If the system remained open, the October 2007 eruption may have been triggered by a partial lava dome collapse, which decreased pressure on the magmatic system at depth, prompted magma ascent, and culminated in an explosive eruption. Using the OMI SO₂ eruptive mass and the method by Blake (2003), the mass of eruptive magma was ~1.5 x10⁶ tonnes for this eruption. In contrast, the high ratios of CO₂/H₂O and SO₂/HCl observed in the July 2009 fumarole samples may indicate degassing of a fresh and/or deep magma source and low total emission rates suggest a partially sealed conduit. Thus, we propose that the December 2009 eruption may have been the result of overpressure in the conduit due to confined degassing of a fresh, ascending magma. An alternate hypothesis is that hydrothermal or meteoric water preferentially scrubbed the highly water-soluble gases and decreased the overall emission rates. No SO₂ was detected by OMI for this event due to poor signal-to-noise for high latitude, winter conditions. Incomplete datasets in 2008 and 2010 prevent us from proposing eruption mechanisms for those events. In 2008, no gas composition data were acquired and the observed SO₂ emission rates were not significantly different from 2007 and 2009 emissions. Additionally, SO₂ from Bezymianny eruptions in 2008 was not conclusively detected by OMI due to a contemporaneous eruption of Kasatochi volcano, Alaska. Derived eruptive SO₂ masses from OMI for the 2007 and 2010 eruptions were strikingly similar, suggesting that these eruptions had similar eruption masses. This study suggests that combined measurements of volcanic gas composition, SO₂ emission rates, and eruptive SO₂ masses can be used to elucidate volcanic behavior and help characterize eruptive activity. Notably, the October 2007 and December 2009 eruptions of Bezymianny may have been triggered by partial dome collapse and intrusion of new magma combined with conduit sealing, respectively; multidisciplinary datasets could be used to test these hypotheses.



GAS COMPOSITION IN MUTNOVSKY GEOTHERMAL FIELD: ROLE OF METEORIC WATER

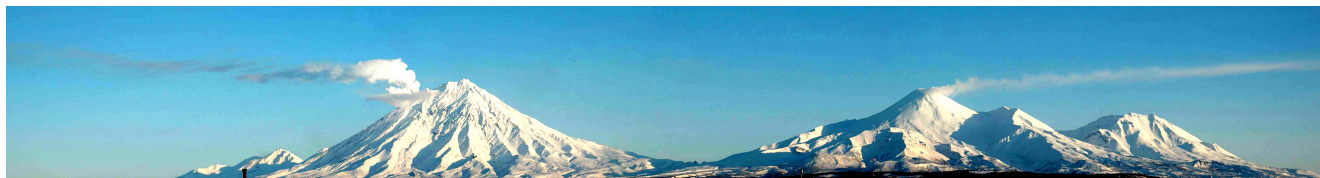
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The gas regime in the boreholes within geothermal field has been under the monitoring since June 2004. Water is a dominating component in the gaseous mixture comprising 99 mass %. H₂S and CO₂ usually comprise more than 90% among other gases. Nitrogen and oxygen rank second.

Analysis of oxygen, nitrogen, and argon relations in gases of Mutnovsky geothermal field revealed that their composition is influenced by 3 components: a deep fluid, meteoric water with dissolved air gas, and atmospheric air. Many samples show the O₂/N₂ relation in gases from various boreholes to be higher than in the air. This obviously is caused by air gases delivered by meteoric water into the geothermal field, due to higher O₂/N₂ relation in dissolved gas than in the air. Estimation of fractions of deep and meteoric components may provide a new data on hydrogeologic regime of the geothermal field.

Estimation of these fractions requires data on composition of geothermal gas, its part in the geothermal field, gas concentrations in meteoric water under a certain temperature, composition of common air, and composition of deep fluid. The later was derived with help of analysis of O₂-N₂-Ar*10 diagram. The majority of points of gas composition for various boreholes on the diagram are located within a triangle two vertexes of which indicate air composition and composition of gas dissolved in water. The third vertex lies on the N₂-Ar*10 side and corresponds to Ar*10/ N₂ ~ 0.19 – 0.20. This data allowed us to estimate the fractions for hydrothermal, meteoric, and air components in the geothermal field in various boreholes. The part of the later is incredibly low but influences the calculations significantly. The calculated parts of meteoric component varies greatly from a few percent to more than 90%. The estimations are apparently doubtful due to inaccurate sampling and analysis, simple model for interaction between flows of deep fluid and meteoric waters, and certain assumptions. However, we suppose this method to be useful for calculation of composition of hydrothermal solution and analysis of processes in geothermal reservoir.



SO₂ GAS EMISSION OF MUTNOVSKY AND GORELY VOLCANOES (KAMCHATKA): SATELLITE DATA AND GROUND-BASED OBSERVATIONS

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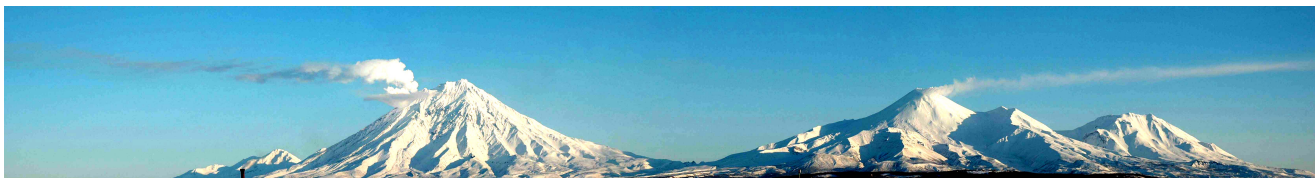
SO₂ is one of the main magmatic gases. Its emission into the atmosphere always accompanies volcanic activity. Measurements of SO₂ content in the atmosphere allow estimating of the energy of the volcanic eruption – in total and at particular stages. Monitoring of the volcanoes degassing (including SO₂) is the important part of the volcanoes activity forecast.

Mutnovsky and Gorely volcanoes (Kamchatka) are active and are located near each other, in 10 km distance. The last eruptions of Mutnovsky volcano were phreatic and took place in 2000 and 2007. At Gorely volcano, a strong gas emission is observed from 2010 until now.

Mutnovsky volcano. Using ground-based instrumental methods (COSPEC) [Fisher, 1999] determined that the average SO₂ degassing volume was about 50 tons/day in 1999. During the whole April 2007 OMI/AURA satellite data fixed elevated concentrations of sulfur dioxide, which gradually increased and reached maximum value at April 17th (at the moment of satellite vault above the crater at 2:50 UTC SO₂ weight was ~330 tons/day), and declined after that. It is supposed that a small phreatic eruption took place at April 17th, 2007. Visual data, obtained during the fieldwork at May 25-28th, 2007, confirm this hypothesis [Gavrilenko, 2007]: the thin layer of the resurgent ash covered western slopes of the volcano, and a new explosive crater (about 200 meters diameter) was observed at the bottom of the Active crater. AVHRR and MODIS satellite data fixed a small ash cloud near the volcano at April 17th.

Gorely volcano. In June 2010 an intensive gas emission started from the Gorely volcano crater. A bocca formed at the basement of the wall of the active crater. High-temperature gas emitted from this bocca under the high pressure and inflamed in the atmosphere [Ovsyannikov, 2010]. OMI/AURA and TERRA ASTER (infrared channel) satellite data have frequently shown large vapor-gas plumes with high SO₂ concentrations, which may be a proof of the fresh magma degassing during the volcano activation.

Constant monitoring of these volcanoes using satellite and ground-based methods of study of SO₂ degassing allows discovering of the indicators of the increasing volcanic activity in time.

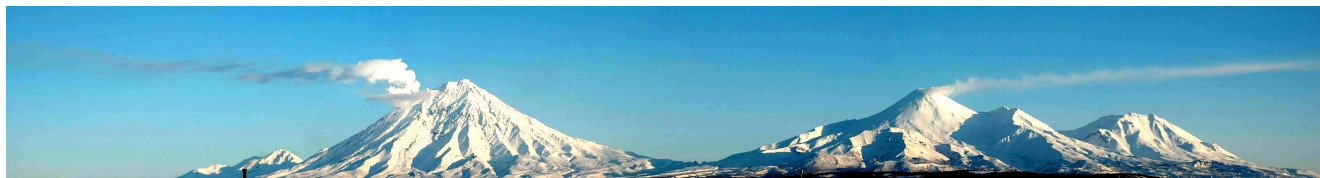


LAGUNA CALIENTE, POÁS VOLCANO, COSTA RICA: THE MOST ACTIVE HYPERACID CRATER LAKE OF THE WORLD (2006-2011)

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Poás volcano is a complex stratovolcano with an altitude of 2708 m a.s.l., with a subconic irregular shape (300 km²), it has three recent main structures: the active crater, Botos lagoon and the old crater von Frantzius. In the southern sector of the active crater, a dome (ascended in 1953) and the hyperacidic Laguna Caliente are located, with a diameter that varies from 320m to 280m and a depth that varied from 46 to 8-10 m between 2006 and 2011. After 12 years without an eruption from Laguna Caliente, in March 2006, a new period of phreatic eruptions resumed and continues till present. Until this moment (June 01, 2011) 554 phreatic eruptions have been reported: 17 in 2006, 2 in 2007 and in 2008 together, 5 in 2009, 340 in 2010 and 180 in 2011. We divide these phreatic eruptions in three types: A, B and C. The A-type, reaches heights from 2 m to 50 m, the B-type from 51 m to 250 m, and the C-type with eruptions higher than 250 m. The data base indicates that approximately 84% is of the A-type, 14% of the B-type and 2% of the C-type. The A- and B-type eruptions are generally jets of mud that rise from the center of the lake falling down at the same spot. The C-type and some of the B-type eruptions, are able to exit the intracrater, generating a kind of a whitish spray that has ended up wetting the lookout point and the visitors center, located at 2 km distance, and in an occasion it even reached to the town of Trojas, located at 8 km. Recently, a migration of the eruptive center has been observed: from the center toward the south of the lake, very close to the dome. The dome fumaroles have reached temperatures above 600 °C, and blue flames of more than 10 meters due to sulfur combustion have been observed. Due to the bad climate (common rain and fog) or absence of observers at the lookout point, in many occasions it is impossible to observe the Laguna Caliente during the eruptions. Approximately, the volcano is observed a fifth part of the day time. This is why the real quantity of eruptions can easily pass a 2500 in number. During the entire period 2006-2011, the Laguna Caliente has descended its level by approximately 29 m, and it has lost 1.8x10⁶ m³ of water. The pH of the water has varied from 0.55 to -0.74, with a surface water temperature between the 36.1°C to 61°C. Its water presents a light turquoise to light milky yellowish gray color, which is accentuated after every phreatic event. Spherules of sulfur floating on the surface of the lake are observed throughout the entire period, indicating the presence of subaqueous sulfur pools at the bottom of the lake with temperatures between 116°C and 155°C. The Laguna Caliente has dried out completely in 1953, 1989 and in 1994. It is not improbable this will happen again in the near future.



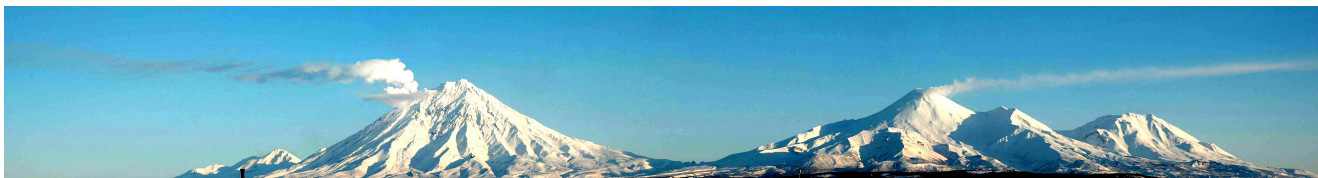
REMOTE SENSING OF VOLCANIC GAS EMISSIONS USING A SCANNING IMAGING UV-SPECTROSCOPY SYSTEM AND TOMOGRAPHIC 3D CLOUD-RECONSTRUCTION

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This work involves the design and construction of a UV-spectroscopy system for remote sensing of volcano gas concentrations and its exploitation on different volcanoes in Kamchatka. The system scans the field of view with an integrated scanner system and for each pixel a spectrum is being recorded with a USB 2000+ UV-spectrometer (Ocean Optics). The radiation is lead into the spectrometer through a small telescope to narrow the input angle. The recording, analysis and the calculation of the column densities is performed with institute-own software. The system then contains a PCB for system control, a GPS module and a notebook. With the help of a GSM modem a remote control via GSM/GPRS is possible. Using two or more identical exemplars of the system, a tomographic 3D cloud reconstruction of the measured cloud is possible, when the systems are placed at different places around the measured cloud. The 3D model of the cloud can then be used to examine the distribution of gases inside the cloud, to monitor its position and the direction of its propagation.

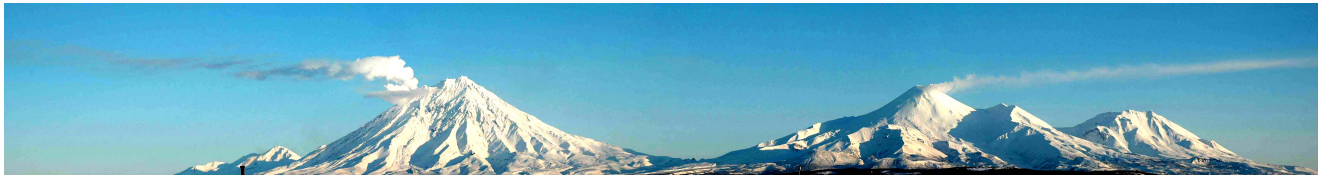


GAS REGIME DEFINING THE MECHANISM OF PERIODIC LAVA FOUNTAINING OF BASALTIC VOLCANOES (EXPERIMENTAL MODELING)

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Processes determining periodic fountaining of basaltic volcanoes were studied using our Complex apparatus for modeling basaltic eruptions - CAMBE [Ozerov, 2007]. It is 18 m high and consists of modeling and recording systems. When creating the Complex, geometric parameters ratio in the actual feeding system of basaltic Klyuchevskoy volcano was considered (taken as etalon); so the ration of CAMBE's channel diameter to its height is $\sim 1:1000$. Formation and transformation of gas structures occurring when gas bubbles pass through up liquids of various densities have been studied. Experiments revealed a new mode of two-phase mixtures (gas-liquid) flow in vertical column – mode of free bubble clusters characterized by regular alteration of gas bubbles assemblages (clusters) isolated by liquid not containing free gas phase. Comparison of CAMBE acoustic records with diagrams of Klyuchevskoy volcanic tremor showed good correlation between modeled and natural data. Results obtained allowed suggesting a new pattern for gas-hydrodynamic migration of magmatic melt in the supply channel, where the regime of open gas clusters accounts for periodic fountaining of incandescent bombs during basaltic volcanoes eruptions.



MERCURY IN FUMAROLIC GASES AND MUD POOLS OF THE MUTNOVSKY CRATER

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High Hg content was measured in acid condensates of fumarolic gases and in dry volcanic gas (without H₂O vapor), up to 2 mg/kg and $\sim 10^{-6}$ mol%, respectively. Mercury concentration in sediments from boiling mud pools reaches values of 3.5×10^{-2} wt% which is close to values found in some Hg ore deposits. The Hg speciation in mud pools is represented by small cinnabar aggregates ($< 20 \mu$) or grains of 3-5 μ . The Vulcannaya stream that drains all crater springs, pools and fumarolic fields transports mercury (cinnabar) outside the crater to distances up to 12 km. The cinnabar structures were investigated using the MS-46 "Cameca" instrument.

We have studied the temperature dependence of the Hg releasing from the mud pool sediments using heating of dry mud samples to $>600^\circ\text{C}$ with the continuous measuring of Hg using the atomic absorption techniques (with assistance by I.I.Stepanov). Three temperature maximums of the Hg releasing were established: 190-220 $^\circ\text{C}$, 380-410 $^\circ\text{C}$ and $>600^\circ\text{C}$. The medium and high temperature peaks are attributed to the breakdown of cinnabar and meta-cinnabar (380-410 $^\circ\text{C}$) and Hg-bearing pyrite ($>600^\circ\text{C}$). The low-temperature peak is most probably related to the thermo-dissociation of Hg chlorides. Their formation in the Mutnovsky pools is quite probable taking into account that the pool solutions are very acid and chloride enriched.

The Hg speciation in acid solutions with compositions similar to those of acid pools of Mutnovsky was also studied using thermochemical computer codes. It was found that at pH \sim 0 in a chloride-bearing solution with a low sulfide the stable species of Hg are HgCl₄⁻, HgCl₃⁰ and HgCl₂⁺. With increasing pH to 1.3, elemental Hg becomes also relatively stable.

A strong correlation was observed between Hg concentrations in Mutnovsky fluids and the volcanic tremor activity of Gorely volcano (15 km to NW). These studies were conducted in collaboration with V.A.Shirokov and they showed a regional character of the mercury degassing that most probably originates from the underlying mantle wedge.

High concentrations of mercury observed in fumaroles and thermal mud pools of the Mutnovsky crater make the local air pollution by Hg essentially higher than the health hazard limits. This may affect volcanologists and tourists visiting the crater of Mutnovsky volcano.



GAS GEOCHEMISTRY OF EL CHICHÓN VOLCANO

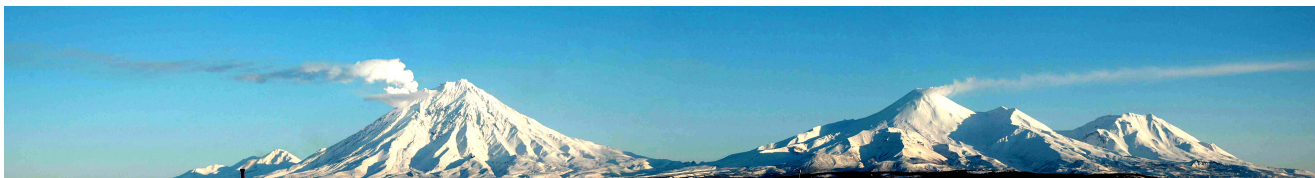
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El Chichón 200-m deep crater is partially filled by a warm acid lake surrounded by numerous hot springs, bubbling pools and numerous low-temperature fumaroles (99°C). Several hot springs are also present on the volcano flank. Recently, bubbling gases were first time sampled in ‘Agua Salada’ springs (AS), located two kilometers NNW from the crater. Together with ‘Agua Caliente’ springs (AC, 1km SE from crater), they constitute the only flank springs presenting bubbling gases. In this study, we compare the composition of AS gases with AC and crater gases; and discuss carbon isotopic composition of CO₂ and alkanes C₁ to C₆ in AS gases.

The most abundant species in AS bubbling gases is, after water vapour, CO₂ (96.8 mol %). The same content is observed in most crater gases (~96 mol%), while AC has lower CO₂ content of ~ 84 mol%. N₂ and Ar concentrations for AS gases are of 1.26 and 0.011 mol%, respectively, leading to a N₂/Ar ratio of 115, superior to average N₂/Ar ratio of AC gases (78) but similar to lake bubbles (122). He content of AS gas is 23 ppmv, close to He mean content in AC gas (19 ppmv) when a maximum is observed for fumaroles and lake bubbles (84 ppmv). Magmatic gases such as HCl, SO₂, HF, and HCl are nearly absent in all Chichón gases. The corrected ³He/⁴He ratios of AS gas (2.16 Ra, with He/Ne = 40) is quite unusual at El Chichón. In fact, ³He/⁴He for AC gases (5-5.5 Ra) and crater gases (~7.5 Ra) are higher and probably correspond to a mixed arc-mantle contribution. The lower ratio of AS gas may be related to the higher distance of the AS springs from the central vent and to mixing with crustal He. The δ¹³C in CO₂ gas (-3.25‰) from AS springs corresponds to the lowest values observed for crater (-1.9 to -8.1‰) and AC gases (-3.6 to -5.5‰) and is probably related to a mixed sedimentary and magmatic CO₂.

An interesting feature of AS gas is a high CH₄ content (1 mol%) compared to AC (0.23%) and most crater gases (<0.02%). This high methane content is combined with a low C₁/(C₂+C₃) of 23 which is typical for a thermogenic origin of hydrocarbons. Furthermore, δ¹³C of methane (-38‰) corresponds to typical values for oil-type methane of the region. The heavier alkanes present a monotonic enrichment in ¹³C (C₂: -23‰, C₅: -18‰), which is also characteristic of a thermogenic origin. Despite their lower concentration in C₁-C₅ alkane, AC and crater gases (ΣC₁-C₅: AC= 575 ppmv vs. AS = 3854 ppmv) present similar concentration patterns than AS gases which could attest of a common origin.



VOLCANIC CO₂ EMISSION AND INDICATIVE VEGETATION

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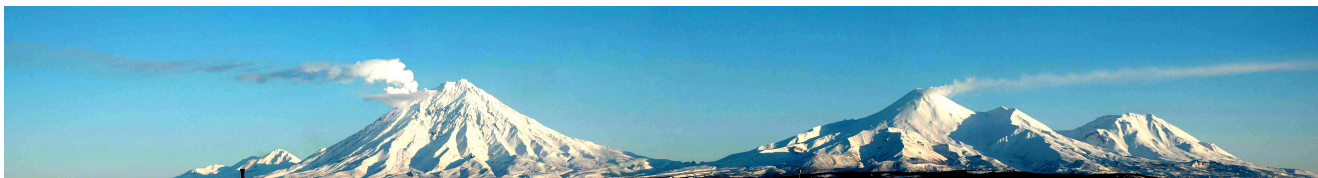
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Volcanic and non-volcanic CO₂ emissions are a geo-biological phenomenon, which is rarely described and frequently overlooked (but see Raschi et al. 1997, 1999, Paoletti et al. 2005, Pfanz 2008). Geogenic carbon dioxide springs (mofettes) are a special form of volcanic gas exhalations liberating nearly pure carbon dioxide. The gas is produced in magmatic chambers and reaches the earth's surface via cracks and fissures (Geissler et al. 2005). In the heart of Europe, in Africa, Asia and America this phenomenon kills animals and men, and many plants are on the verge of death (Raschi et al. 1997, 1999, Pfanz et al. 2004, Pfanz 2008). Above concentrations of 8-10% CO₂ irritates animals leading to a loss in consciousness and to death because of anoxia or acidosis if concentrations exceed 15-20%. In the neighbourhood of mofettes, soil fauna and soil microbes have adapted to hypoxia stress. Several plant species are able to cope with anoxic mofette soils and the cellular acidification stress caused by the penetration of the magmatic CO₂ gas (Pfanz et al. 2004, 2005, 2007, Vodnik et al. 2002, 2006, Macek et al. 2005). Sometimes mofettes can be distinguished from their surroundings due to their specific "azonal" vegetation regime. In some special mofettes, plants form concentric rings around the CO₂ vents which correlate with the CO₂ concentration within the rooting zone. Aside from changes in species composition, plants occurring within mofettes reveal morphological and physiological differences. Therefore some indicative species hint to the presence of CO₂-gas emissions in volcanic areas.

According to absorption of infrared, mofettes may be detected even from space (Tank et al. 2008). A change in vegetation may also hint to changes in the movement of the earth's crust (faults) or to forthcoming volcanic eruptions.

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SPECTROSCOPIC OBSERVATION OF VOLCANIC EMISSIONS – STATUS AND FUTURE TRENDS

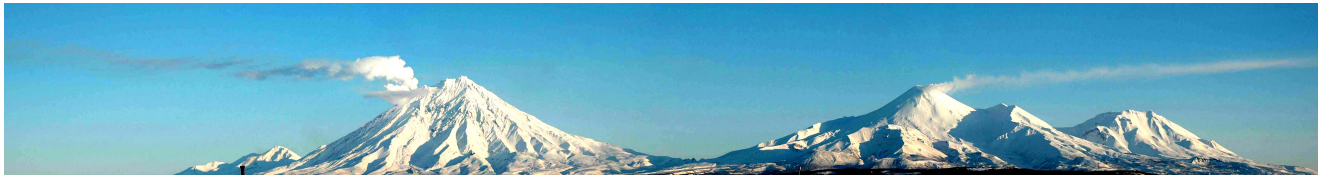
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In recent years spectroscopic quantification of gas emissions from volcanoes made considerable progress. In particular spectroscopic approaches observing volcanic gases in the ultra-violet spectral range evolved from an art to mature techniques, which are routinely applicable in automated installations. Using spatio-temporal correlation techniques also absolute amounts of trace gas fluxes can be determined. This is e.g. demonstrated by the NOVAC network.

In addition systems operating in the infra-red (IR) spectral range have also made enormous progress. Here two varieties are in use: Absorption spectroscopy using direct sunlight and Emission spectroscopy using thermal emission from the trace constituents to be studied. Although neither of the two IR varieties is yet applicable in automated routine observation these techniques have considerable potential as well. For instance thermal emission spectroscopy would also allow observations at night. Moreover, novel techniques for remote sensing of volcanic emissions, the SO₂-Camera and imaging-DOAS (I-DOAS), where the I-DOAS technique trace gas distributions using the DOAS principle, came into widespread use recently. In particular the SO₂ camera allows real time observation of the 2-dimensional evolution of volcanic plumes.

Here we present a brief technical description and a critical assessment of the techniques listed above and discuss the relative merits of the different approaches for quantifying volcanic emissions by giving examples of successful applications in the field. Also expected future developments and requirements for volcanic surveillance are discussed.



FIELD THERMAL IMAGING MONITORING OF FUMARoles, CRATER LAKES AND MUD POOLS, AT COSTA RICAN VOLCANOES

C.J. Ramírez (1, 2, 3), R. Mora-Amador (2, 1, 3), G. González (1, 2, 3)

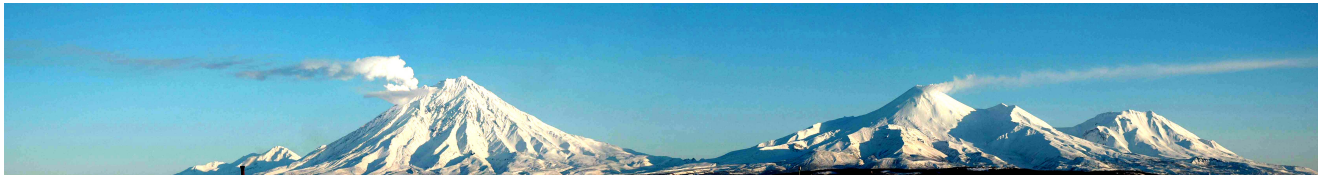
(1) Centro de Investigaciones en Ciencias Geológicas (CICG), (2) Escuela Centroamericana de Geología, Universidad de Costa Rica (UCR), (3) Red Sismológica Nacional (UCR-ICE)

Since November 2010, the Costa Rican volcanoes and hot springs began monitored by 5 thermal cameras, 4 FLIR A320 located permanently at Turrialba, Poás and Arenal volcanoes, plus one portable FLIR P660 that is used for more detailed images of fumaroles, crater lakes, mud pools and gas plumes among other volcanic purposes.

The A320's are located on different settings depending on the volcano. At Turrialba volcano the camera is set at the crater rim focused the new vent formed on January 2010, from there at $\approx 500\text{m}$ it is possible to monitor the temperature of the gases from the new vent plus the direction and speed of the plume, that helps the Mini-DOAS measurements; at Poás volcano the camera is fixed on a bunker structure located at $\approx 700\text{m}$ from the active lagoon, from there it is possible to cover the complete crater with a wide angle lens, and safely track eruptions, observe convective cells from the lake, fumaroles activity, as well as temperature, direction and speed of the gas plume. Finally at Arenal volcano because of the changing of the pattern of the lava flows and gas plume, two cameras will be installed within a distance of one km, for monitoring eruptions, pyroclastic flows and gas plume.

The thermal camera FLIR P660, it has been used to carry out periodic measurements in the active volcanoes and hot springs of Costa Rica. At Turrialba and Poas volcanoes, it is possible to get closer views, measuring more precise high inaccessible fumaroles of the new vent of Turrialba, or at the Dome at Poás, places that can reach temperatures of more than 600°C . With the help of this thermal camera, convection cells (61°C), fumaroles migration and phreatic eruptions (130°C) can be appreciated at the Laguna Caliente. Also on the Pailas sector at Rincón de la Vieja volcano, is possible to determine the thermal images of small hot lagoons, hot springs and mud pools, with temperatures of $\approx 90\text{C}$ that allow the life of extreme organisms to survive.

The use of the thermal cameras at active volcanoes is a valuable tool to detect changes from a secure distance, which can complement the physical and chemical analyses of lakes, fumaroles, etc., making it an ideal counterpart to equipment's like Mini-DOAS and Flyspec.

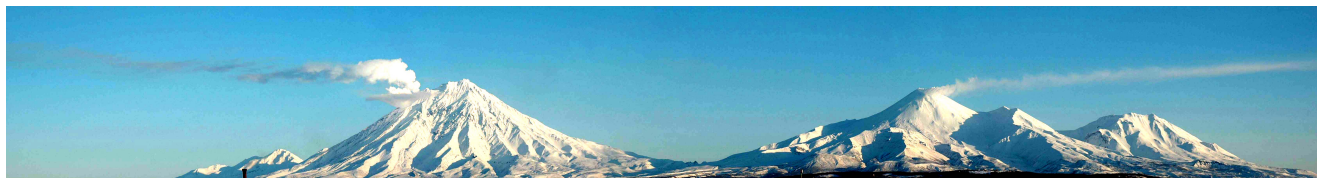


OMI SO₂ MEASUREMENTS OF ACTIVE VOLCANOES IN GUATEMALA AND COSTA RICA

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Ground-based and satellite remote sensing techniques have been applied to study a number of parameters at volcanoes, including their emissions (mainly gas and ash), temperatures, and morphology. Remote sensing of volcanic emissions takes advantage of the absorption of electromagnetic radiation that characterizes different species. Sulfur dioxide (SO₂) is the third most abundant volcanic gas and it is the focus of this research. SO₂ can damage the environment and it is an atmospheric pollutant, especially through the action of sulfate aerosol, to which it can change chemically in the volcanic plume. SO₂ column amounts and emission rates are used at volcanoes worldwide to study and better understand magmatic processes and volcanic activity. The Ozone Monitoring Instrument (OMI) is one of three instruments aboard the Aura satellite, which was launched in July 2004. OMI measures total column amounts of a number of species, including SO₂. This research is part of an ongoing project, which started January 2011, on the use of OMI data products to determine SO₂ masses from plumes produced by active volcanoes in Guatemala and Costa Rica. Pacaya and Turrialba are the highest SO₂ emitters in Guatemala and Costa Rica, respectively, and we expect their plumes to be detected. The images will also be used to determine SO₂ fluxes at different dates, which will be compared, when possible, with ground-based data measured with correlation spectrometers (COSPEC) and mini-UV spectrometers. The fluxes will also be used to estimate SO₂ loss rates for the plumes studied. A number of dates have been identified (since 2004) and the data is currently being processed and analyzed. The dates were chosen based on changes in activity of the different volcanoes and on periods of heightened activity and vigorous degassing, which could be detected by satellite remote sensing measurements.



²²²Rn AND CO₂ SOIL DIFFUSE DEGASSING PATTERN ANOMALIES AND ITS RELATION WITH VOLCANO-TECTONIC STRUCTURES AT FURNAS VOLCANO (AZORES, PORTUGAL)

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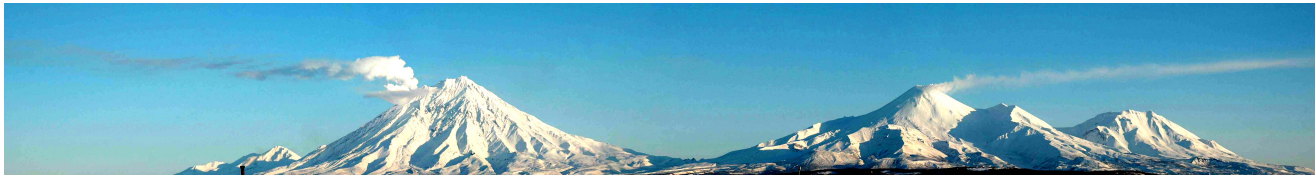
The Azores archipelago (Portugal) is located on the triple junction of the American, Eurasian and Nubian plates and is formed by nine volcanic islands. Furnas Volcano is a quiescent central volcano located on the eastern part of S. Miguel Island. This volcano erupted at least 10 times in the last 5000 years, with plinian and sub-plinian eruptions characterized by alternating episodes of magmatic and phreatomagmatic activity. Geomorphologically, in the summit of Furnas Volcano two main nested calderas, several craters and various domes are identified. The most recent eruptions (1439-43 AD and 1630 AD) were characterized by initial explosive episodes responsible by the formation of pumice rings and ended with more effusive episodes marked by the emplacement of inner crater trachytic domes.

In nowadays, Furnas Volcano presents a moderate seismic activity and shows several secondary volcanic phenomena such as fumarole grounds, thermal springs, cold CO₂ rich mineral waters and soil diffuse degassing areas.

²²²Rn and CO₂ gases may give important information about deep processes. Soil diffuse degassing studies may be applied on the identification of active faults, seismovolcanic monitoring and geothermal prospection. The quiescent period of Furnas Volcano is ideal to define the background level of ²²²Rn and CO₂ degassing and may contribute to the recognition of future signals of volcanic unrest. In what concerns ²²²Rn mapping, a soil radon survey was performed during summer months from 2005 to 2010. A total of 489 station points were measured with a solid state alpha detector (RAD7). ²²²Rn measurements oscillated between 0 and 387527 Bq/m³ being the average value 11733 Bq/m³. During this survey soil temperature measurements were also performed in the same station points at about 20 cm depth. The temperature ranged between 16,5 and 100 °C with an average of 23,7 °C.

Soil CO₂ concentration measurements were performed with a GA 2000 gas analyzer, which operates by a dual wave-length infra-red cell. Data sampled during 2001 and 2002 (Sousa, 2003), as well as the measurements performed between 2005 and 2010 were integrated to produce a final CO₂ map, based on 1535 sampled points. Soil CO₂ concentration values oscillated between 0 and 99,9 %vol. with an average value of 6,3 %vol.

The spatial distribution analysis of the data allowed to identify ²²²Rn and CO₂ anomalous zones that were compared with structural and geological structures. Anomalous zones, for both gases, seem to be associated mainly with NW-SE fault/fracture zones, the presence of craters and the caldera rims. On the top of the domes of the last eruptions these gases are practically absent. The temperature anomalous zones, as well as the CO₂ degassing anomalies, are mainly associated with the presence of the main fumarolic fields of Furnas Volcano.



HIGH TEMPORAL AND SPATIAL RESOLUTION UV CAMERA MEASUREMENTS AT STROMBOLI: INSIGHTS ON PASSIVE SO₂ GAS EMISSION, STROMBOLIAN ERUPTIONS, AND PUFFING

G. Tamburello (1), A. Aiuppa (1,2), E.P. Kantzas (3), A.J.S. McGonigle (3), M. Ripepe (4)

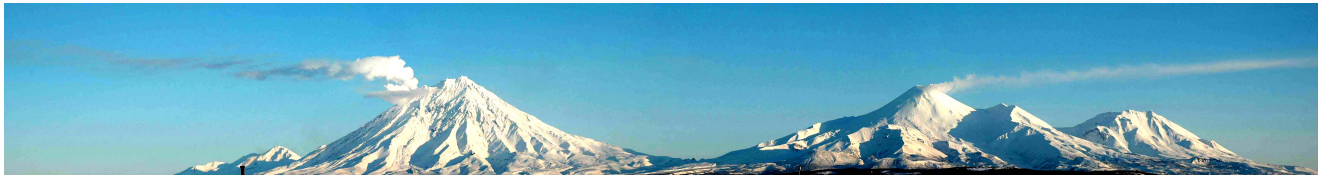
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Stromboli is one of the most active volcanoes on Earth, and one of the few where passive degassing persistently coexists with the (non-passive) release of over-pressurized gas pockets during both explosions and gas puffing activity. These transient gas bursting-puffing phenomena are difficult to study by conventional spectroscopic scanning techniques (e.g., DOAS), since these have far too low temporal resolution. Here, we take advantage of the high spatial and time resolution (0.6-1 Hz) of the recently developed UV camera technique to obtain a simultaneous characterisation of all the different forms of SO₂ release at Stromboli (including passive degassing, Strombolian eruptions and puffing).

During a field campaign from 10th to 16th July, 2010, we observed at Stromboli a total SO₂ flux averaging at $\sim 70 \text{ t}\cdot\text{d}^{-1}$, but also showing large (10-30 $\text{t}\cdot\text{d}^{-1}$) cyclic fluctuations with periodicity of 400-1000 seconds. This periodic degassing behaviour, which was recently also detected at Mt. Etna, Erebus and Fuego, may be a systematic feature of basaltic volcanoes; a fact which - if confirmed - would bring profound implications for models of magma-gas flow in conduits, and for generation of basaltic explosions.

These periodic SO₂ flux variations were punctuated by brief SO₂ flux peaks in coincidence with explosions. We obtained UV camera observations for 130 discrete explosions overall, and we found that the erupted SO₂ mass per explosion ranged 2-55 kg, and averaged at ~ 20 kg. This corresponds to a daily explosive SO₂ output rate of $4.2 \pm 1.2 \text{ t}\cdot\text{d}^{-1}$, or 5-8% of the total SO₂ flux ($\sim 70 \text{ t}\cdot\text{d}^{-1}$). Our SO₂ explosive dataset data was integrated and inter-compared with infrared radiometer data and very long period (VLP) seismic traces, yielding a complete geophysical-geochemical data corroboration.

Finally, we also obtained a very first direct estimate of the puffing contribution to the total SO₂ budget. It is known that Stromboli's active vents continuously release gas in a stream of gas puffs (emission of gas in discrete packages). After a few tens of meters, puffs cool, decelerate, expand, and finally mingle within the surrounding plume contributed by other vents; therefore, only a few puffs retained their shape long enough to be imaged with UV camera (at least during our observations). According to our preliminary data, the SO₂ mass contributed by each single puff varies between 0.14 and 0.45 kg. We thus conclude that puffing may account for 10-20% of the total SO₂ daily output from Stromboli. Finally, we confirm that passive degassing is likely to be the most significant form of SO₂ release at Stromboli (and possibly other open-vent basaltic volcanoes).



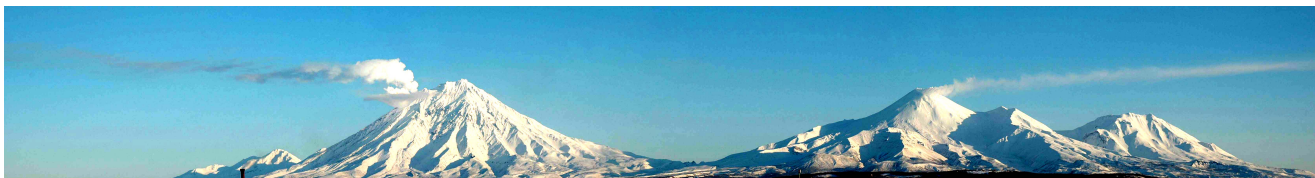
VOLCANIC GAS GEOCHEMISTRY. A RUSSIAN CONNECTION

Y. Taran (1)

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This presentation is kind of an introduction into the history of the volcanic gas geochemistry in Russia. The history is strong tied to geography, namely to Kamchatka, where in 1935 the first volcanological laboratory was organized by enthusiastic geologists from Academy of Sciences of USSR. It was named “Kamchatka Volcanological Station” and hosted in Klyuchi village, at the base of Klyuchevskoy volcano. First scientific staff were V.I.Vlodavets, A.A.Menyailov (Igor Menyailov’s father), S.I.Naboko (Igor’s mother) and the first in Russia an official volcanic gas chemist I.Z.Ivanov.

Since that time volcanic and geothermal gas chemistry was an object of almost every issue of the Bulletin of the Kamchatka Volcanological Stations, the precursor of the currently issuing “Volcanology and Seismology” journal. There was also an annual issue of “Trudy” – “Transactions of the Volcanological laboratory and Kamchatka volcanological station”. Trudy was as a monograph with a single text or review papers. Before 1980 when V & S journal became copied as a cover-to-cover translation in English, most of the gas chemistry studies in Kamchatka were not accessible for the world scientific community. Here I present a brief review of the most important studies carried out by a team of Soviet-Russian geochemists before 1975 when Igor Menyailov published his famous paper in Bulletin of Volcanology. There have been published a number of studies on methodology (sampling and analysis), volcano monitoring, thermodynamics, trace elements, incrustation mineralogy and chemistry, discoveries of new minerals in incrustations, fluxes, occluded gases and organic components. Many ideas and papers even now look as modern though the time was well before the plate tectonics era that came to USSR about ten years later than became accepted in the world.



REVIEW OF THE LAST 5 YEARS VOLCANIC GAS PAPERS: WHERE WE ARE AND WHERE WE GO?

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This presentation is open for discussion and if I have missed something, any comment about missed important contribution is very welcome.

1. Direct sampling.

1.1 The appearance of a new large database on Latin America volcanoes. The Chilean-Florence group did a huge and hard work sampling fumaroles at >5000 m asl on Chilean volcanoes with a complete set of isotopic data (in collaboration with the Rochester University) and hydrocarbons - A detailed study of Mutnovsky fumaroles with a good set of isotopic data and hydrocarbons - A long-term data set on fumarolic gases from Solfatara, Campi Flegrei and its correlations with seismicity and deformations and new ideas about the deep structure of the volcano-hydrothermal system - Chemical and isotopic data on poorly known Japanese volcanoes with elements of a monitoring - Mt.Etna fumarolic gases - Sierra Negra (Galapagos) gases with a full set of isotopes including noble gases.

1.2 The Italian-German group is trying to convince the readers in a partially abiogenic origin of CH₄ (hydrocarbons) in Mediterranean volcanic gases. -Same about H₂-CH₄ enriched Socorro island gases from Mexico.

1.3 Oldoinyo Lengai carbonatite volcano. Both poor (2008) and good (2011) samples in terms of air contamination, new data showing high R/Ra (~7), negative δ¹⁵N but still no data on volcanic gas condensates (D, ¹⁸O, metals).

1.4 Waiting for data on Erta Ale (international expedition in January 2011)

2. Remote spectroscopic measurements.

2.1 Excellent data coming from three strong groups: British (Montserrat, Latin America, Erta Ale, Yasur), European (Mt.Etna, Stromboli, Latin America) and Japanese (Aso, waiting for Kirishima..)

2.2 A swarm of papers about halogen oxides in volcanic plumes: a contribution from the atmosphere chemistry.

3. MultiGas

3.1 A new “Japanese Box” but now filled instead of alkali with electronics. Very good data starting from the 2005 CCVG workshop at Vulcano (Villarica, Mt.Etna....)

4. Diffuse degassing

4.1 “Floating chamber” for crater lakes; looks like a new fashion.

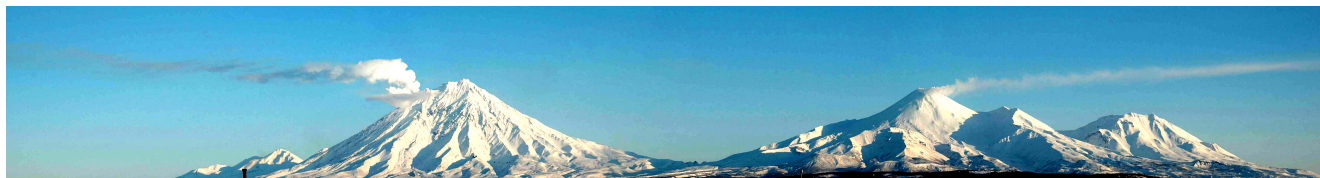
5. Review papers

5.1 In a Special volume of ChemGeo on halogens - Cl in basaltic gases and “a missing link”

5.2 In Reviews in Mineralogy 65

5.3 A set of review papers related to ore deposits with using data on trace elements in high-temperature condensates and sublimate mineralogy.

I also discuss what in my opinion were the most important achievements and discoveries in our science during the last decade; what we still do not know but able to recognize using our techniques. I touch also some still persistent myths and legends about unusual chemistry of gases from usual volcanoes (like extremely high Cl in Mt.Augustine fumaroles). And at last, a bit of criticism related to some inconsistencies in data presentation that I found in some papers.



ORIGIN OF METHANE IN FLUID DISCHARGES FROM ITALIAN VOLCANIC AND HYDROTHERMAL SYSTEMS AS INFERRED BY THE ISOTOPIC FEATURES AND THE CHEMICAL COMPOSITION OF LIGHT HYDROCARBONS

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The origin methane in fluids from volcanic-hydrothermal systems has been extensively investigated on the basis of the $^{13}\text{C}/^{12}\text{C}$ and $^2\text{H}/^1\text{H}$ isotope ratios, suggesting that CH_4 production in continental hydrothermal fluids is related to kinetically controlled thermal decomposition of organic matter (e.g. Schoell, 1980, 1988; Welhan, 1988; Whiticar, 1999; Bréas et al., 2001). There is no a clear indicator for the abiogenic CH_4 production in natural systems, likely due to the ubiquitous presence of biological and thermogenic products in surface and near-surface environments tending to mask signals indicating the presence of abiogenic organic compounds. However, recent studies (Fiebig et al. 2004, 2007, 2009) have shown that CO_2 and CH_4 in hydrothermal fluids from Mediterranean volcanoes seems to be in chemical and isotopic equilibrium, providing evidences for the occurrence of an abiogenic step in the CH_4 genesis and/or consumption.

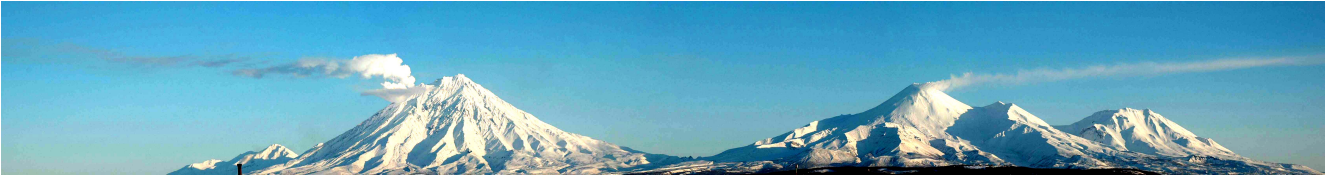
In this study we present a large dataset of $\delta^{13}\text{C}\text{-CH}_4$ and $\delta\text{D}\text{-CH}_4$ ratios measured in fluids from thermal and cold discharges of the Italian Peninsula, and Ischia, Panarea and Pantelleria islands. The main aim is to use these isotopic data, coupled with the $\delta^{13}\text{C}\text{-CO}_2$ ratios and the chemical composition of light hydrocarbons (C_2H_6 , C_3H_8 and C_6H_6), to investigate the CH_4 genetic processes and their relation with the complex geodynamic and hydrogeological settings of Italy.

Our results show that fluid discharges from the main geothermal systems of the peri-Tyrrhenian area (Mt. Amiata, Larderello, Latera, Manziana) show $\delta^{13}\text{C}\text{-CH}_4$ and $\delta\text{D}\text{-CH}_4$ values > -28 ‰ V-PDB and > -160 ‰ V-SMOW, respectively. These fluids are characterized by C_1/C_{2+} ratios >1000 . Fluids discharging from Phlegrean Fields, Vesuvio, Panarea and Pantelleria have a CH_4 isotopic signatures even less negative than those of the geothermal fluids ($\delta^{13}\text{C}\text{-CH}_4$ and $\delta\text{D}\text{-CH}_4$ values > -21 ‰ V-PDB and > -120 ‰ V-SMOW, respectively), and C_1/C_{2+} ratios <900 . The $\delta^{13}\text{C}\text{-CH}_4$ and $\delta\text{D}\text{-CH}_4$ values in fluid discharges located between the geothermal-volcanic systems and the Apennine sedimentary chain almost regularly diminish toward east, corresponding to a decrease of the C_1/C_{2+} ratios, from 2000 to 20. The CH_4 -dominated fluid discharges of the Adriatic side of the Italian peninsula are characterized by the lowest $\delta^{13}\text{C}\text{-CH}_4$ and $\delta\text{D}\text{-CH}_4$ values, i.e. as low as -69 ‰ V-PDB and > -190 ‰ V-SMOW, respectively, with C_1/C_{2+} ratios up to >6000 .

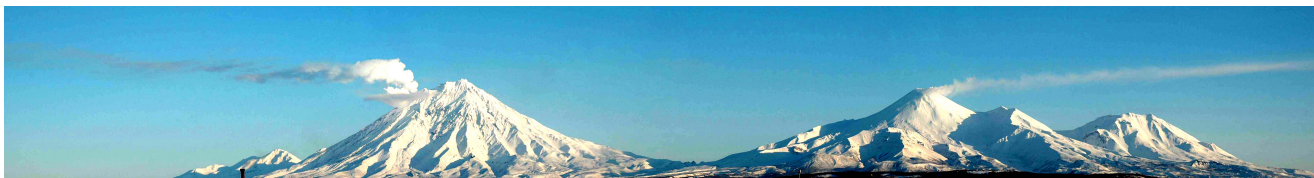
The CH_4 isotopic features and the composition of light hydrocarbons suggest that CH_4 in geothermal and volcanic fluids is mainly produced by CO_2 reduction and is non-genetic with the higher hydrocarbons that entirely derive from the thermal decomposition of organic matter. At hydrothermal conditions, the $\text{CO}_2\text{-CH}_4$ reaction produces CH_4 in excess with respect to the thermogenic one. Under oxidizing conditions and relatively high temperatures characterizing volcanic gases, CH_4 is mostly oxidized to CO_2 , explaining the relatively low C_1/C_{2+} ratios measured in Phlegrean Field, Vesuvio, Panarea and Pantelleria fluids. Thermogenic CH_4 enhances from west to east, as the fluid reservoir temperatures decrease, whereas the easternmost discharges of the Po Valley and the Adriatic coast, where organic matter evolves at relatively shallow depth in presence of a low geothermal gradient, are dominated by CH_4 from bacteria-driven processes.

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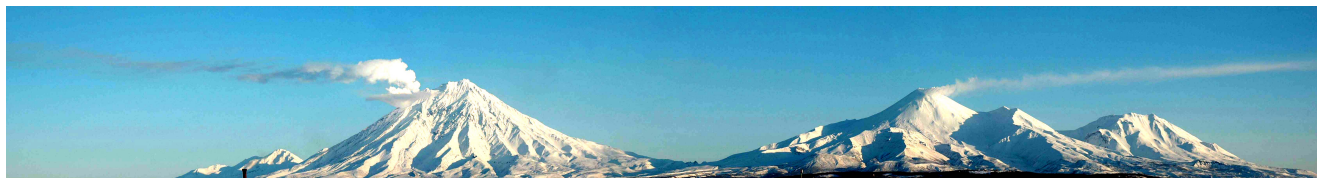
THE VIRUNGA VOLCANIC ACTIVE AREA: A COMPLETE (*ALMOST*) GEOCHEMICAL APPROACH TO MITIGATE VOLCANIC AND OTHER HAZARDS

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On January 17, 2002 the city of Goma was partly destroyed by two of several lava flows erupted from a roughly N-S oriented fracture system opened along the southern flank of Mt. Nyiragongo (Democratic Republic of Congo, DRC), in the Western Branch (WB) of the Eastern African Rift System (EARS). A humanitarian and scientific response still continuing today was promptly organized by international, governmental and non-governmental agencies coordinated by the United Nations and the European Union. Among the different scientific projects undertaken to study the mechanisms triggering this and possible future eruptions, we focused on the chemical and isotopic (He, C and Ar) composition of the magmatic fluids within the Nyiragongo crater, cold and dry CO₂-rich gas discharges (locally called *mazukus*) related to both Nyiragongo and Nyamulagira volcanic systems, the lake Kivu and the broader Virunga region, including peripheral areas inside and outside the rift. We also measured plume fluxes and routinely collected rain samples from all areas on top (and around) the two volcanoes in order to : (i) monitoring the volcanic activity through the plume gas emissions studying the main gas ratios, namely F/SO₄, Cl/SO₄ and F/Cl and (ii) to understand the possible health hazards drinking waters sometimes highly contaminated by acid species. Gas emissions (and lake chemistry) from different basins of Lake Kivu were also collected to better constrain sources regions and end members existing in the whole area, within and outside the rift.

Seven (7) areas have been characterized having distinct ³He/⁴He (expressed as R/R_{air}) ratios and/or δ¹³C-CO₂ values. The Nyiragongo summit crater fumaroles, whose R/R_{air} and δC-CO₂ values are up to 8.73 and from -3.5 to -4.0 ‰ V-PBD, respectively, show a clear mantle, MORB-like contribution. Similar mantle-like He isotopic values (6.5-8.3 R/R_{air}) are also found in CO₂-rich gas emanations (*mazukus*) along the northern shoreline of Lake Kivu main basin, whereas the ¹³δC-CO₂ values range from -5.3 to -6.8 ‰ V-PBD. The mantle influence progressively decreases in i) dissolved gases of Lake Kivu (2.6-5.5 R/R_{air}), and ii) the distal gas discharges within and outside the two sides of the rift (from 0.1 to 1.7 R/R_{air}). Similarly, δC-CO₂ ratios of the peripheral gas emissions are lighter (from -5.9 to -11.6 ‰ V-PBD) than those of the crater fumaroles. Therefore, the spatial distribution of He and C signatures in the Lake Kivu region is mainly produced by mixing of mantle-related (e.g. Nyiragongo crater fumaroles and/or *mazukus* gases) and crustal-related (e.g. gas discharges in the Archean craton) fluids. The CO₂/³He ratios (up to 10x10¹⁰), is one order of magnitude higher than those found in MORB and it is due to the increasing solubility of CO₂ in the foiditic magma feeding the Nyiragongo volcano. On the other hand, the exceptionally high ⁴⁰Ar*/⁴He ratio (up to 8.7) of the Nyiragongo crater fumaroles may be related to the difference between He and Ar solubility in the magmatic source. The results of the present investigation suggest that in this area the uprising of mantle-originated fluids seems strongly controlled by regional tectonics in relation to the geodynamic assessment of the rift. These fluids are mainly localized in a relatively small zone between Lake Kivu and Nyiragongo volcano, with important implications in terms of volcanic activity.



GAS MONITORING OF KAMCHATKAN VOLCANOES (RUSSIA)

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In Kamchatka (Russia), there are 30 active volcanoes. Each year, about 5-6 eruptions are occurring on average. Some volcanoes are closed to populated areas and dangerous for the population of Kamchatka. The study of volcanic gases is one of the methods in the search for possible precursors of volcanic eruptions, as well as the key to understanding this mechanism. The team of authors presents the preliminary results of a study of volcanic gases of Avachinsky, Mutnovsky, Bezymianny and Kizimen volcanoes.

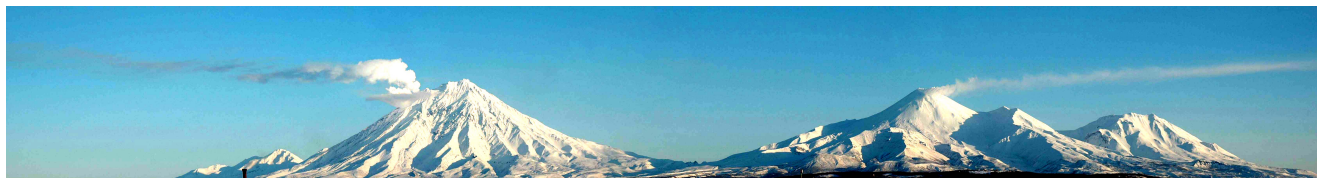
Avachinsky is the nearest active volcano to the main town of Kamchatka peninsula - Petropavlovsk-Kamchatsky, constructed on explosive sediments from its ancient eruptions. It is one of the most active volcanoes of the Kurile-Kamchatka region, with height 2741 m above sea level. On January 13th, 1991, after a 46-year-quiet, an explosive-effusive eruption has occurred. Since August 1994 gas sampling has become available from high-temperature fumarole (473 degrees centigrade), located in southwest sector of a new cone. From 1994 to 2001 the temperature of the fumarole has slightly decreased from 470 up to 400 °C. Then the temperature gradually went up and reached 470 °C in 2001 prior to a new period of activity. Following years, there was a gradual downturn of temperature up to 130 °C

Mutnovskiy volcano - one of the largest volcanoes in the South Kamchatka with a complex structure and a long history of development. In the crater and on its northern slope are discharged powerful high-temperature fumaroles and thermal springs. In 2000 and 2007 on Mutnovskii volcano occurred phreatic eruption. Institute of Volcanology and Seismology continues periodic sampling and analysis of gases from fumaroles on the active crater.

Bezymianny Volcano. Catastrophic eruption of 1955-1956, after a long interval of rest, lasted about 900-1000 years, opened a new period of activity of the volcano, which continues to this day. Eruptions at the volcano in the last decade are occurring an average of two per year. In the period 2007-2010 on the volcano were sampled volcanic gases.

Volcano Kizimen. Volcanic eruption began in late 2009. After nearly 83 years of quiet. Prior to that, the volcano is under active fumarole-solfatar activities. Active fumaroles and solfatar exits at the top of the north-eastern slope, 300 m from the top. Temperature fumaroles at the output of - 230-240 °C.

Comparing the data on changes in the composition of volcanic gases and in particular SO₂ emissions from other remote gas measurement, seismic, geodetic, and petrological data, we may be able to identify gas components, control systems, the main magmatic eruptions.



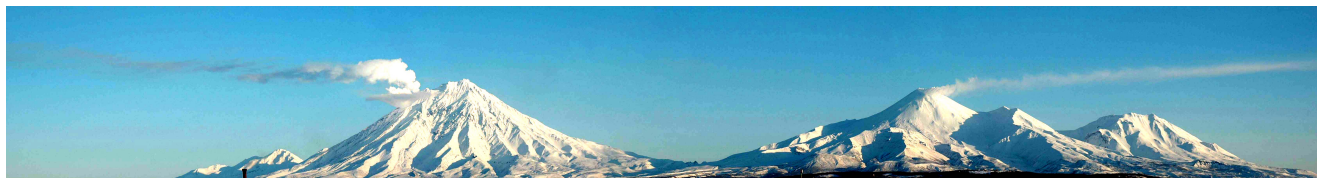
A DISCONTINUOUS GEOCHEMICAL AND ISOTOPIC MONITORING AT THE POÁS MAGMATIC/HYDROTHERMAL SYSTEM

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Prediction of volcanic events and evaluation of volcanic hazard are the main concerns for the volcanological community. Despite the many efforts to clarify the processes leading to volcanic eruptions, constraints on timing, magnitude and intensity on impending volcanic activity are still poorly understood. Physical and chemical changes of volcanic fluids are commonly generated by interactions between juvenile (magmatic) and shallow (hydrothermal) components, depending on seismic activity, permeability variations and input of new magmas. Thus, geochemical and isotopic monitoring of volcanic fluid emissions has to be regarded as a reliable tool to verify the status and the evolution of a given volcanic system. In this work the results of a discontinuous geochemical monitoring carried out at Poás volcano (Costa Rica) in the last 12 years are presented and discussed. In this span of time severe changes of fumarolic fluid chemistry, accompanied by migration of emitting vents and phreatic eruptions, have occurred. The main aim is to investigate the mechanisms at the source of the modifications affecting this volcanic system.

The basaltic-to-dacitic Poás volcano (2,708 m a.s.l.) is one of the most active in Costa Rica and is characterized by three N-S oriented craters: Von Frantzius, Botos and the active Laguna Caliente. The latter two host a volcanic lakes: Botos is cold with the latest eruption dating back to ca. 7,500 years ago; Laguna Caliente is one of the most acidic lakes of the world (pH \approx 0) and is the site where phreatic, phreato-magmatic and strombolian events have frequently occurred since 1828. In 1952, two volcanic vents opened within the Laguna Caliente crater. The first one developed a pyroclastic cone (named as the Dome) that still stands today, while the other one collapsed and formed the Laguna Caliente lake basin. In 1988-1991 the acidic lake dried out revealing sulfur vents and fumaroles with temperatures up to 900 °C. In 1998, when our geochemical survey started, the sampling of fumarolic gases was only concerning a low-flux fumarole (no longer existing) discharging in the southern part of the inner crater. After 1999, the main fumarolic activity shifted to E-NE. Since 2006, the fumarolic activity centered at the interface between the Dome and the acidic lake has progressively increased. Several phreatic events have also been occurred. No significant outlet temperature variations of the fumaroles located near the Dome (always ranging between 90 and 120 °C) occurred until July 2008, when a jet-fumarolic discharge reached a temperature of 700 °C. In June 2010, despite of the increasing difficulties to reach the sampling site, the highest temperature (\approx 800 °C) was measured since the 1988-1991 crisis. As far as the chemical variations are concerned, in the last 5 years the Dome fumaroles evidence an overall increment of the concentrations of magmatic-derived gases (e.g. SO₂, HCl, HF) as well as of the N₂/Ar, CO/CO₂, H₂S/CO₂ and CO₂/CH₄ ratios. The complex interplay between the magmatic and hydrothermal components is likely regulated by permeability variations triggered by enhanced convective heat transfer toward the surface. Overpressuring and hydrofracturation may be responsible for the observed phreatic events that so far have only produced relatively large vapor blasts and ballistic products affecting the lake sediments. The presence of a spine of magma close to the surface (about 500 m), the increasing values of the outlet temperatures and of the magmatic species in the fumarolic discharges cannot rule out the possibility of more explosive events.



CO₂ HYDROTHERMAL EMISSIONS AND THERMAL ENERGY RELEASED AT FURNAS VOLCANO (SÃO MIGUEL ISLAND, AZORES ARCHIPELAGO). INFERENCES ON GEOMORPHOLOGY AND TECTONICS

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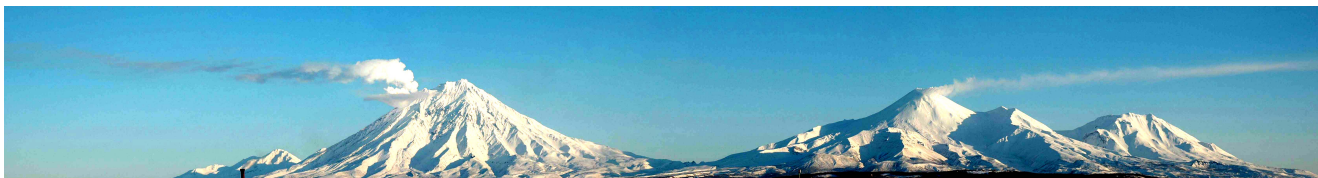
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Furnas Volcano is a polygenetic quiescent volcano located in the eastern part of São Miguel Island (Azores archipelago, Portugal) and started to be formed at about 100 000 years BP. Geomorphologically Furnas Volcano comprises a summit depression 5 x 8 km wide formed by two nested calderas controlled by NW-SE and NE-SW faults. Since the settlement of the island, in the 15th Century, two intracaldera subplinian volcanic eruptions occurred in this volcano, in 1439-43 and in 1630. Both events started with the formation of a pumice ring and ended with the emplacement of a central crater trachytic dome. At present, Furnas Volcano has a moderate seismic activity and exhibits hydrothermal manifestations characterized by low temperature fumaroles (around 97 – 99 °C), steaming grounds, thermal and CO₂ cold springs and soil diffuse degassing areas.

During the summer months from 2005 to 2008 several soil CO₂ flux surveys were carried out at Furnas Volcano applying the accumulation chamber method. A total of 2886 measurements were done and the measured values showed high variability ranging from absence of soil CO₂ flux to values higher than 25 000 g m⁻² d⁻¹. The data set obtained is positively skewed and soil gas flux was modelled as combination of three overlapping populations, which suggest the existence of multiple sources (biogenic and volcanic-hydrothermal) feeding the soil CO₂ diffuse degassing in Furnas Volcano. The δ¹³C compositions of soil CO₂ efflux collected in the volcano caldera varied from -12.28 ‰ to -3.11‰, confirming different sources for the CO₂ degassing. The statistical approach combined with the isotopic composition of the CO₂ efflux suggested a value of ~ 25 g m⁻² d⁻¹ as a reliable limit for the biogenic flux.

Diffuse degassing maps were produced based on one hundred sequential Gaussian simulations. Main diffuse degassing structures observed at Furnas Volcano are associated to the fumarolic fields showing that in these areas CO₂ is carried by the steam upflow. Important DDS (diffuse degassing structures) are found out in depressed areas in the inner slopes of some crater rims showing the strong morphostructural control on the gas release. In addition to hydrothermal CO₂ degassing measured along previously mapped NW-SE and WNW-ESE tectonic structures, soil CO₂ flux patterns allowed to infer new general WNW-ESE trends that probably represent hidden tectonic structures. Luxuriant vegetation and thick pumice deposits observed in this volcanic system difficult the identification of tectonic structures and these degassing maps are therefore useful tools to reveal weak structural zones. Gas geochemical transects performed across historical eruptive centres show low soil CO₂ degassing, which is probably explained by the presence of the trachytic domes. Only some residual endogenous degassing was found contouring the domes.

Hydrothermal CO₂ output from the whole Furnas Volcano was estimated to be ~ 954 t d⁻¹ (from an area with ~ 5.2 km²). The thermal energy release associated with diffuse degassing at Furnas caldera was estimated to be about 116 MW based on the H₂O/CO₂ ratio in fumarolic gas.



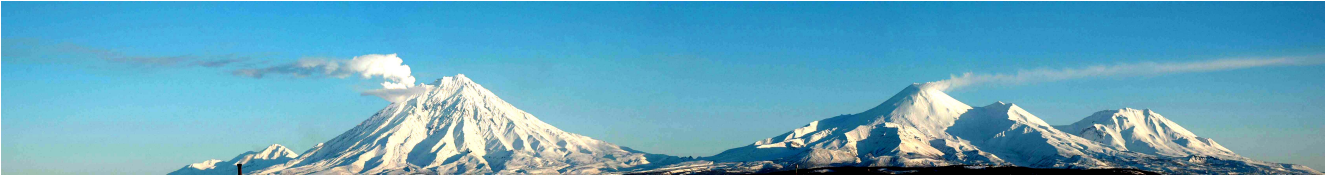
UNDERSTANDING BrO FORMATION IN VOLCANIC PLUMES, MEASUREMENTS OF PLUME CHEMISTRY AT EARLY PLUME AGES

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Ground based remote sensing measurements in the near UV and VIS using Differential Optical Absorption Spectroscopy (DOAS) are now a standard tool to quantify volcanic emissions. Next to the detection of sulphuric dioxide (SO₂), the technique also allows detection of halogen oxides (e.g. BrO, ClO and OCIO), which are secondary, chemical products of primarily hydrogenated halides. These products have a great impact on atmospheric chemistry due their high reactivity and their contribution to ozone destruction cycles. The fastest reaction cycle involves Bromine and is analogous to the polar “Bromine Explosion” and observed Ozone Depletion Events. By using chemical models, one can relate these measurements to the primary constituents and gain insight into volcanic processes as well as determine the impact of volcanic emissions on the atmosphere.

In recent years, many studies were conducted to improve our knowledge of the chemical pathways and kinetics in volcanic plumes and better constrain chemical models. Simultaneous measurements at different plume ages are one approach to resolve halogen chemistry and compare measured gradients to model simulations. To be successful, information on additional species participating in the complex reactions are necessary. Although the DOAS technique is a powerful tool in remote sensing volcanic gases, it might yield erroneous misleading results under unfavourable conditions. In the light of these necessities, both modelling and instrumental, we re-assess previously presented measurements at Mt Etna, Italy, taken in July 2008 and 2009, were simultaneous measurements at several different distances from the crater and thus different plume ages (2 to 60 minutes after emission) have been performed. We will also present data on volcanic emissions at early plume ages (<5 min) of Pacaya volcano, Guatemala. Here, the plume was scanned in vertical as well as horizontal direction, mapping ongoing bromine chemistry at high temporal resolution. It allowed to report the first detection of BrO at Pacaya volcano and the hitherto first detection of volcanic BrO chemistry at high resolution at very early (<5 min) plume ages. Alerted by some inconsistencies in a first order evaluation of the BrO concentrations, we discovered a noticeable formaldehyde (HCHO) abundance in the lower atmosphere around Pacaya.



GAS COMPOSITION AND SOIL CO₂ FLUX AT CHANGBAISHAN INTRA-PLATE VOLCANO, NE CHINA

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Changbaishan, located on the border of China and North Korea, is one of the most active volcanoes in China. This volcano violently erupted 1000 years ago and produced massive magma and widespread volcanic ash, resulting in one of the largest explosive eruptions during the last 2000 years. If it eruptive, then 1 million residents living near this area shall be endangered by enormous volcanic hazards.

In order to better understand current status of Changbaishan, we investigated gas geochemistry of samples from the Tianchi crater lake and surrounding areas. Bubbling gas from hot springs were collected and analyzed. The results show that CO₂ is the major component gas for most samples. The maximum value of helium isotopic ratio 5.8 RA (where RA = ³He/⁴He in air) implies more than 60% of helium is contributed by mantle component, while carbon isotope values fall in the range of -5.8 to -2.0‰ (vs. PDB), indicating magmatic source signatures as well. Nitrogen dominated samples, 18Dawgo, have helium isotopic ratio 0.7 RA and carbon isotope value -11.4‰ implying the gas source might be associated with regional crustal components in 18Dawgo. The first-time systematic soil CO₂ flux measurements indicate the flux is 22.8 g m⁻² day⁻¹ at the western flank of Changbaishan, which is at the same level as the background value in the Tatun Volcano Group (24.6 g m⁻² day⁻¹), implying that Changbaishan may not be as active as TVG.