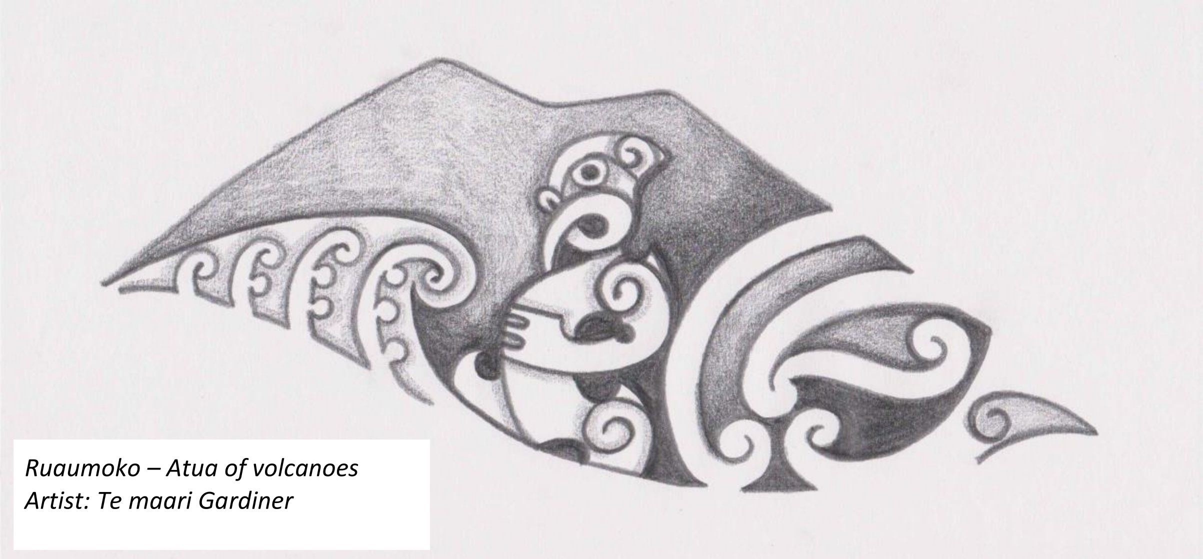
IAVCEI-Commission on Volcanic Lakes

Abstracts

CVL 10 Workshop, New Zealand
17-25 March 2019



Ruaumoko – Atua of volcanoes
Artist: Te maari Gardiner

1. Tracking lake water chemistry: the future of direct sampling of volcanic lakes

Conveners: *María Martínez-Cruz, Celine Mandon & Takeshi Ohba*

Active magmatic-hydrothermal system beneath Yugama crater lake at Kusatsu-Shirane volcano, Japan: Temporal variations in subaqueous fumarolic activities

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Kusatsu-Shirane volcano, Japan, contains a hot crater lake, locally called Yugama. The lake water has a pH of 1 and contains high chemical concentrations including Cl which show marked changes in response to volcanic activities. Stable isotope ratios of lake water have values that are larger than that of local meteoric water. Because lake water experiences somewhat complex processes including partitioning of evaporation, seepage through the lake bottom and meteoric input, we cannot directly evaluate chemical features of fluid emitting from subaqueous fumaroles. In this study we have developed a numerical model which take factors associated with variations of Cl and stable isotope ratios into account. Applying the model to observation data, we estimate mass flux, enthalpy, Cl concentration and stable isotope ratio of water emitting from the lake bottom. During a calm period in 2012 – 2013, a relation between Cl concentration and stable isotope ratio of water indicates that hydrothermal reservoir beneath Yugama is a mixture of magmatic high temperature volcanic gas and local meteoric water. Intense micro earthquake swarms and ground deformations occurred around Yugama in 2014, which were accompanied by changes in water temperature, Cl concentration and stable isotope ratios. Our model indicates an increase in supply of magmatic high temperature volcanic gas to the hydrothermal reservoir beneath Yugama crater lake.

The major chemical composition of lake water in Yugama crater at Kusatsu-Shirane volcano (Japan) and its changes in response to volcanic activity

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Mt. Kusatsu-Shirane, located approximately 150 km northwest of Tokyo, is an active volcano where there are several crater lakes in its summit area including lake Yugama. At this volcano, frequent phreatic eruptions have been observed since recorded history, and many of them occurred within or close to Yugama crater (Japan Meteorological Agency, 2013). The recent eruptions occurred at Yugama crater were in 1982 and 1983. The lake water that fills Yugama crater is characterized by strongly acidic pH (0.0~1.8), high concentrations of anionic species such as Cl and SO_4 with various concentrations of rock-forming elements such as Al, Fe, Ca and Mg (Ohba et al., 2008). These aqueous species have shown various changes in their concentrations in response to eruptive activities (e.g., significant increase in SO_4 and several cations while no increase in Cl was observed before and after the 1982-1983 eruptive period; Ossaka et al.,1997 and Ohba et al., 2008). Ever since 1983, no eruptions have been observed at Yugama crater, but unrest activities have been observed in recent years, such as earthquake swarms beneath Yugama crater in 2014 and 2018. In addition, a phreatic eruption occurred at Mt. Motoshirane which is located approximately 1.7 km south of Yugama crater on January 23th, 2018. In this presentation, we show the analytical result of the major chemical compositions of Yugama crater lake and its changes in response to recent volcanic activities will be discussed.

*This study was supported by the Earthquake Research Institute The University of Tokyo Joint Usage/Research Program.

Metal distribution and speciation in White Island hyperacidic crater lake

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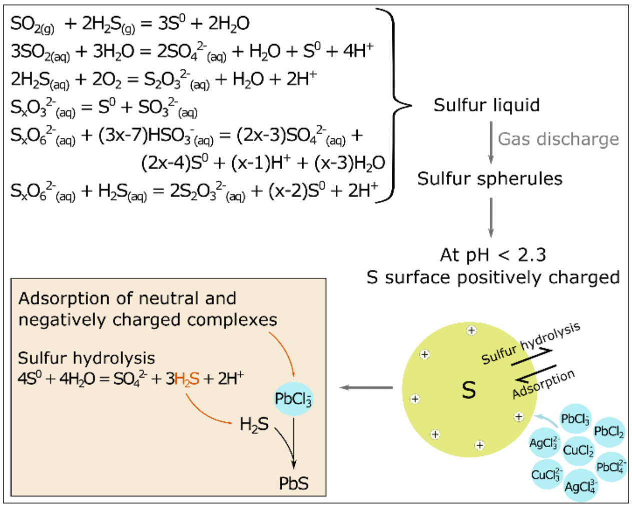
An hyperacidic crater lake has been occupying part of the crater floor of White Island volcano since the end of the 1976-2000 eruptive sequence. Monitoring of its level and composition showed seasonal variations as well as changes related with the volcanic activity. We present results from a study on metals in the lake environment conducted between October 2014 and December 2015. Most metals show a relatively steady content in the lake waters with time, while others such as Tl, Pb, Bi and Cd show variations between our three sampling campaigns. Black sulfur globules floating at the lake surface show an enrichment in chalcophile elements compared to their yellow counterparts, and pyrite crystals were observed on their surface by SEM. Metal enrichment is thus thought to be explained by incorporation of metals as minor elements in the pyrite. Another potential mechanism responsible for metal enrichment can be the formation of metal sulfides through adsorption of aqueous metal complexes at the surface of the sulfur globules and subsequent reaction with H_2S produced by hydrolysis of elemental sulfur. Study of sediment cores collected close to the lake shore in shallow environment reveal changes in lake water composition, switching from gypsum, alunite and silica as main components in June 2015, to sulfur- and anhydrite-rich in December 2015. Speciation of the lake waters estimated using thermodynamic modelling shows dominance of chloride aqueous complexes for most of the metals. Results of our modelling using different redox conditions shows that the speciation of Cu, Ag and Fe is affected by variations in redox conditions, whereas the dominant Pb and Zn complexes remain the same in the reduced bottom waters and in the superficial oxidized layer. The computed saturated phases using the analyzed SO_4^{2-}/H_2S as redox control comprise barite, silica phases and elemental sulfur, whereas anhydrite and gypsum are slightly undersaturated.



Enrichment of ferrous iron in the bottom water of Lake Nyos

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Lake Nyos is strongly stratified with 4 separated layers; shallow, intermediate, transitional, and bottom. In the bottom layer (205.5–209.5 m), Fe^{2+} and HCO_3^- are the major dissolved species and their concentrations increase sharply toward the bottom (Fig. 1, measured in Jan. 2001). Fe^{2+} ion dispersed by the degassing pipe was oxidized to $Fe(OH)_3$ at the lake surface and sank to the bottom where anaerobic microbial reduction took place to form Fe^{2+} and HCO_3^- at the water-sediment interface. Production of Fe^{2+} and HCO_3^- significantly increased the alkalinity and electric conductivity of the bottom-most water and was responsible for a small rise of pH between 205 and 209.5 m. The other dissolved ionic species resulted from the CO_2-water-basalt interaction at low temperatures (25°−30°C) in the sub-lacustrine fluid reservoir that exists in the diatreme beneath the lake bottom, and they seeped into the bottom layer. The variation of electric conductivity of the bottom water after initiation of the degassing operation (Fig. 2) may indicate the balance between the rates of Fe^{2+} supply and loss as siderite.

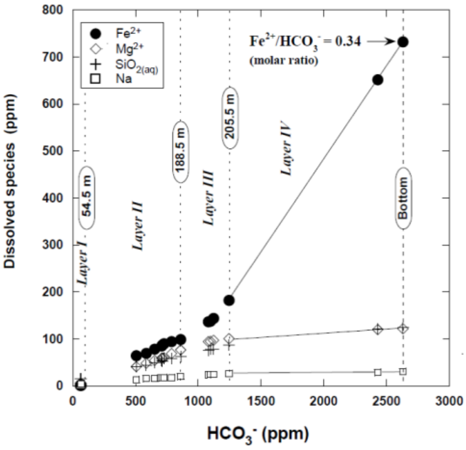

Fig. 1. Relationship between the concentrations of Fe^{2+}, Mg^{2+}, Na^+ and $SiO_{2(aq)}$ versus HCO_3^-.

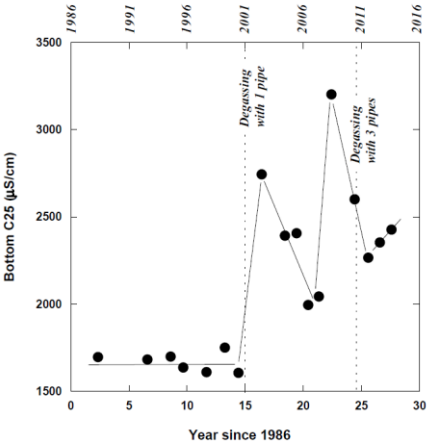

Fig. 2. Change in the conductivity of the bottom-most water at Lake Nyos during the period 1988 to 2014.

High Temporal Resolution pCO_2 Monitoring in Taal Volcanic Lake

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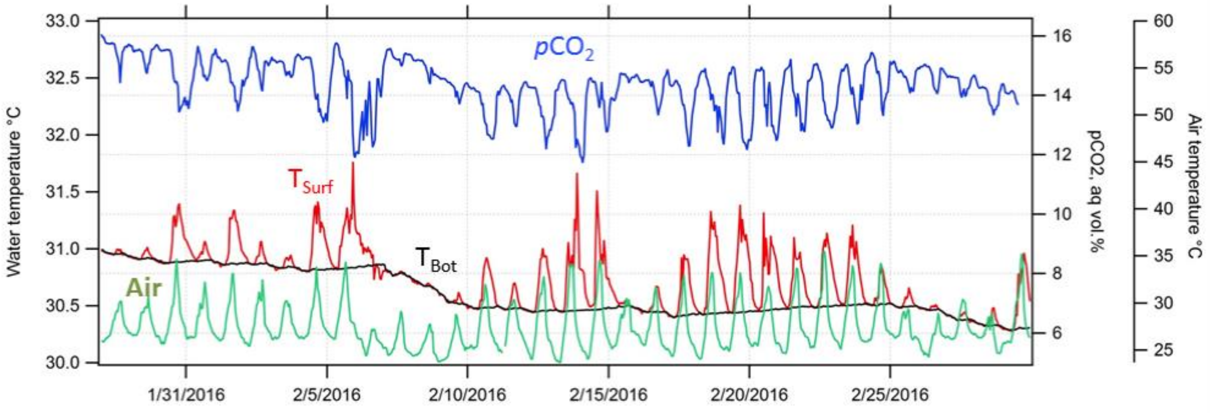
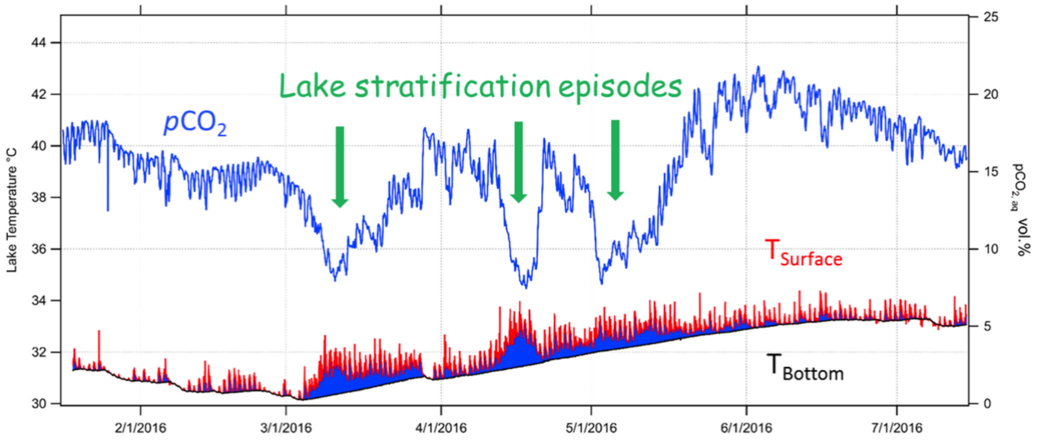
Since January 2013, a miniaturized NDIR CO_2 gas analyser is used for continuous monitoring of the pCO_{2aq} in the lake and show that the surface waters are highly supersaturated in CO_2 with respect to the atmosphere (with dissolved concentrations up to 430mg/l).
Large temporal variations observed suggest that pCO_{2aq} is a very sensitive indicator of activity at Taal volcano compared to other lake's parameters that remained almost constant during the same period (i.e. temperature, pH, chemistry). Contrary to sulfates, chlorides and other solutes which are largely conservative species in lake waters, dissolved free CO_{2aq} has a more dynamic behaviour in the lake (much like temperature). Taal lake acts as a simple gasometer where pCO_{2aq} reflects a steady-state equilibrium between CO_2 supplied to the lake by hot springs and by direct degassing and CO_2 lost by diffusion at the air-water interface.



Moreover, the evolution of pCO_2 shows a diurnal pattern clearly correlated with the heating and cooling cycles of the lake waters. During day time, surface waters are depleted in CO_2 lost by diffusion to the atmosphere. At night, cooling at the surface forces vertical convective mixing in the lake, bringing up to the surface deep waters not degassed in CO_2.



During the hot summer seasons (March to June), periods of permanent stratification lasting up to several weeks are typically observed when the temperatures of the surface waters remain at night warmer than the deep waters.

Mass balance and heat input into the Kipyaschee Lake, Golovnin caldera, Kunashir, Kuril Islands

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The Golovnin caldera at the Kunashir Island (southern Kuril Islands) hosts an acidic hydrothermal system with hot springs and steam vents and two caldera lakes: Goryachee (Hot) and Kipyaschee (Boiling). The Kipyaschee Lake (pH 2.2, S ~ 4.5 ha, 17 m max. depth) is connected with the Goryachee Lake (pH 2.8-3.2, ~ 290 ha, 63 m max. depth) by a 400 m -long Sernyi (Sulfur) Creek, and Goryachee is drained by the Ozernaya River to the Sea of Okhotsk. Volumes of the lakes calculated from the bathymetry data are 2.6×10^5 m^3 and 6.1×10^7 m^3, respectively. The integrated anion composition of the Kipyaschee Lake at the source of Sernyi Creek in 2015 was 687 mg/L of Cl and 254 mg/L of SO_4, pH 2.22, with temperature of 30°C. The outflow rate of the creek was measured in 2015 as 0.093 m^3s^{-1}. Because of the drainage, the lake has a stable water level; its chemical composition has not been changed during the last several decades.

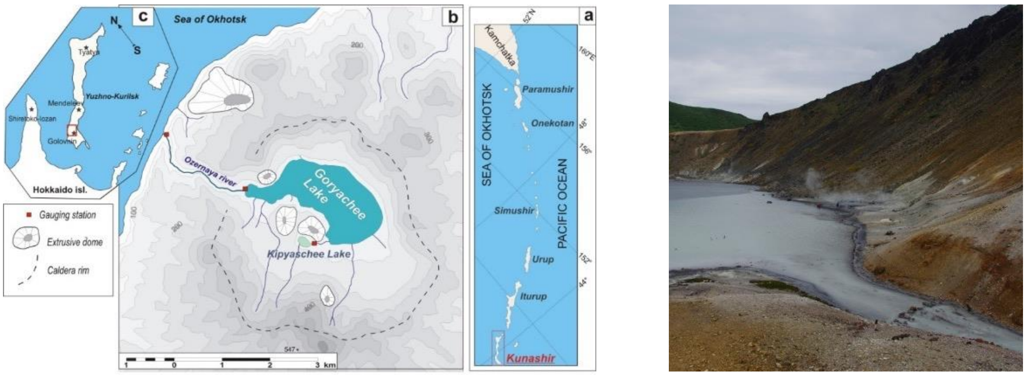

Figure 1*. Location of the Golovnin caldera (a,b,c) and a fragment of the Kipyaschee Lake with the draining Sernyi (Sulfur) Creek. Photo by Tatiana Kotenko.*

The water balance of the Kipyaschee Lake is controlled by precipitation, cold water flows into the lake, runoff during rainfall and snow melt from the catchment area, evaporation from the lake surface, infiltration through the lake bottom and the drainage by the Sernyi Creek. For the Kipyaschee Lake the evaporation rate can be estimated as 6 to 12 kg/sec, depending on the used equation, which is close to the feeding of the lake by meteoric water. It does mean that the total discharge from the lake is mainly provided by the up-flowing hot springs from the lake bottom, and the composition of these springs does not differ significantly from the composition of the lake water. With assumption that these hot springs are near boiling temperature, the heat input into the Kipyaschee Lake by hot water can be estimated as ~39 MW.

Redox processes and metal deposition beneath volcanic lakes

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High temperature fumaroles provide us a glimpse into the otherwise inaccessible interiors of active volcanoes. Their dominant components are H_2O, CO_2, SO_2 and H_2S and H_2 together with smaller amounts of HCl and HF and nitrogen compounds. Above about 500 °C, homogenous gas reactions, such as $SO_{2(g)} + 3H_{2(g)} = H_2S_{(g)} + 2H_2O_{(g)}$, determine the equilibrium speciation of these components as gas mixtures expand from fumarolic vents but little is known about what processes determine the relative abundances of $H2_{(g)}$ and sulfur. For example, control of their redox state ($r_H = X_{H_2}/X_{H_2O}$) has generally been attributed to subsurface reactions involving accessory minerals, such as magnetite, or estimated through proxy buffer reactions (e.g.Ni/NiO + n), but these reactions have little buffer capacity at the $100km^3$ scale of active volcanic systems.

By contrast, it is now evident, through combining analytical data from high temperature fumarole with observations on now deeply eroded arc volcanoes (‘porphyry Cu-Mo-Au deposits’) that the abundant and widely distributed phase, anhydrite ($CaSO_4$) controls both the redox state and the total concentration of sulfur of volcanic gas mixtures within volcanic systems. Anhydrite-forming gas-solid reactions have been shown by experiment to be both fast and reversible[1]. This talk will explore the systematics of these chemisorption reactions, and show their overall importance in controlling the flux of sulfur through eruptive cycles, reactive mass transport of trace elements, including metals, inside volcanoes, the flux of acidic gases into volcanic lakes[2] *and* the formation of the world’s largest mineral deposits of Cu-Mo and Au[3].

This talk will use, as its case study, the coupled rock alteration and mineralization in the 3Ma Grasberg (Papua Province, Indonesia) porphyry copper deposit, one of the world’s largest[4]. The deposit occupies a breccia-filled volcanic vent that preserves evidence of lake sediments and the present surface is estimated to be only 1 to 1.5 km below the paleo-surface of a, then active, maar volcano.

1 Henley, R. W. *et al.* Porphyry copper deposit formation by sub-volcanic sulphur dioxide flux and chemisorption. *Nature Geoscience* **8**, 210-215 (2015).
2 Henley, R. in *Volcanic Lakes* 155-178 (Springer, 2015).
3 Henley, R. W. & Seward, T. M. Gas-Solid Reactions in Arc Volcanoes; Ancient and Modern. *Reviews in Mineralogy and Geochemistry* **84**, 309-350 (2018).
4 Leys, C. A., Cloos, M., New, B. T. & MacDonald, G. D. Copper-gold±molybdenum deposits of the Ertsberg-Grasberg District. *Papua, Indonesia: Society of Economic Geologists, Special Publication* **16**, 215-235 (2012).

Poás volcano (Costa Rica): the pulsing heart of the Central America Volcanic Zone

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The book on the Poás volcano (Costa Rica) consists of 13 contributions about different aspects and approaches related to geodynamics, volcanology, seismology, fluid geochemistry, botanic and zoology and legends related to one of the most active volcanoes in the World. In April 2017, when a new eruptive phase commenced, we started receiving the contributions by the Authors and some of the chapters had to be modified to have as much as possible an up-date related to the renewal activity at Poás. This was one of the reasons why this book was a little bit delayed with respect to what was planned. Poás is a complex strato-volcano, located in the Province of Alajuela, with an altitude of 2,708 m a.s.l. The Poás summit is characterized by three volcanic cones: Von Frantzius, Botos and the Active Crater, the latter being the site where the latest eruptions occurred. The surrounding area hosted vigorous fumaroles, particularly close to a pyroclastic cone (or dome) formed in the early fifties. The outlet temperatures of the fumaroles close to the pyroclastic cone (or dome), which was almost completely destroyed during an intense phreatomagmatic activity on the 22nd of April, 2018, have shown dramatic changes from water boiling to magmatic (900 °C) temperatures. Laguna Caliente is a hyper-acidic lake regarded as the most active crater lake in the world. The lake disappeared several times in the past: 1953, 1989 and 1994, 2017 and March 2018. Between March and August 2018, the lake was newly restored. The final versions of the chapters were submitted to Springer in early September 2018 that marked the second anniversary of the premature death of Bruno Capaccioni, an eminent scientist and volcanologist but, first of all, a friend. Bruno has worked with the Editors and most of the Authors of this book at Poás that was one of his favorite volcanoes. His sympathy and his love for volcanoes will always remain with all those who were lucky to know him. We do wish to dedicate this book to his memory.

Four decades of geochemical monitoring at Poás (Costa Rica): recurrent patterns in phreatic activity

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[1]Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Bologna, Italy; [2]Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, Italy; [3]Escuela Centroamericana de Geología, Universidad de Costa Rica, San José, Costa Rica, PREVENTEC, Universidad de Costa Rica; [4]Escuela Centroamericana de Geología, Universidad de Costa Rica, San José, Costa Rica, Red Sismológica Nacional, Universidad de Costa Rica; [5]Volcanes Sin Fronteras-VSF, Costa Rica; [6]BIGEA, Università degli Studi di Bologna, Bologna, Italy (*deceased)

Since 1978 water chemistry of Poás' Laguna Caliente crater lake has been used to monitor volcanic activity, making it arguably the best studied hyper-acidic crater lake on Earth. During these four decades, three phases of unrest occurred, manifested through frequent phreatic eruptions, with each a duration of several years to over a decade (1978-1980, 1986-1996, 2006-2016). We here present a novel technique to deal with the long time series of available water chemistry. Common patterns of chemical parameters in relation with phreatic eruptive activity for the period 1978-September 2014 are sought, applying the objective statistical method of Pattern Recognition (PR). This resulted in the definition of the strongest precursory signals and their respective thresholds. Numerical outcomes often confirm findings based on geochemical models (e.g. SO_4, SO_4/Cl and pH are strong monitoring parameters), however, some surprising parameters still need an explanation and should be a focus for future research strategies. Posteriorly, the obtained parameters and thresholds were retrospectively applied for the "test period" of the PR (November 2014-February 2016). This test provided hints that suggested that eruptive activity at Poás was not yet over, despite apparent quiescence in early 2016. Indeed, after renew phreatic activity since May 2016, the 2006-2016 phreatic eruptive cycle culminated in phreatomagmatic activity in April 2017 (ongoing to date). We conclude that evaluating time series of crater lake water chemistry framed in the PR method can be a useful monitoring approach. Moreover, increased sampling frequency can provide extra details and adequate prediction of phreatic activity at Poás. Comparing Laguna Caliente with other two well monitored acidic crater lakes (Ruapehu Crater Lake, New Zealand and Yugama, Kusatsu-Shirane, Japan) Poás results unique in many ways and undoubtedly the most active crater lake of the three during the past four decades.

Poás volcano: Significance of mobile trace elements in the hyperacid crater lake

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The hyper acid brines of Poás volcano crater lake in Costa Rica have been monitored in a nearly monthly basis for ca. 40 years for major aqueous anions (F^-, Cl^-, Br^-, SO_4^{2-}, SxO_6^{2-}, etc.) derived from the input and hydrolysis of magmatic volatiles (i.e. SO_2, H_2S, HCl, HF, HBr) in the hydrothermal fluids, due to their high abundance and the availability of laboratory facilities at OVSICORI-UNA.

Trace elements TE that are known to be highly mobile in volcanic environments but have rarely been investigated as yet, have been recently incorporated in the analytical routines to gain insights into the transport of chemical elements from deep to surface, and changes in the Poás´s lake water composition with time that can reflect dynamic volatile-water-rock processes in the subsurface magmatic-hydrothermal system. Ultimately, we are interested in assessing the potential of the TE as a monitoring tool to envisage transient subsurface processes and the occurrence of eruptive events. Based on previous and new TE analytical data obtained by ICP-MS and covering ca. 4 decades of geochemical monitoring of the hyper acid crater lake of Poás volcano, which has shown sharp fluctuations in the activity with frequent periods of phreatic eruptions, and rare phreatomagmatic eruptions, separated by time intervals of relative quiescence (between 1980 and 2018), we focus on the element transfer ratio behavior of B, Zn, As, Mo, Sn, Sb, Tl and Pb to identify possible sources in this volcanic lake system as well as to envisage the potential of the TE as a monitoring tool.

Time- series profiles of the TE in question indicate increased concentrations when the lake system was most active and vice-versa. There is a general correlation between concentration levels and lake temperature, and an inverse correlation with pH. These patterns point to an enhanced input of the elements during intervals of increased activity and phreatic to phreatomagmatic eruptions, in agreement with evidence for a stronger influx of magmatic gas. For most of these elements, the lake water show enrichment relative to magnesium and other rock-forming elements, which argues against congruent rock dissolution as main source but is consistent with preferential input of supercritical fluids via subaqueous fumarolic gas.

Preliminary results of this study demonstrate the potential of monitoring this group of mobile elements in crater lakes and associated surface manifestations since they provide insights into the nature and conditions of processes in magmatic-hydrothermal systems that can be different and complementary to those provided by more traditional monitored elements such as the anions.

Changes in hydrothermal vent fluid chemistry at Brothers submarine volcano, Kermadec arc

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Brothers submarine volcano, located along the Kermadec arc north of New Zealand, provides us with unique opportunity to study two distinct end-member hydrothermal systems in close proximity. Hydrothermal fields at the NW Caldera and Upper Caldera sites are most similar to mid-ocean ridge counterparts featuring “black smokers” massive sulfide chimneys and chemistry dominated by water-rock interactions. Two cones (Upper and Lower cones) emerge from the southern part of the caldera. These volcanic edifices are host to separate vent fields that feature “white smokers” and evidence for strong magmatic degassing and elemental sulfur deposits. Multiple voyages to Brothers volcano from 2004 to 2018 have allowed us to evaluate both the spatial and temporal changes in the hydrothermal vent fluid chemistry at these sites.

Fluids from the cone sites are strongly influenced from magmatic degassing dominated by SO_2, H_2S and CO_2. Unlike “black smoker” water-rock systems, the end-member fluids are not characterized by zero magnesium. In fact, in 2004/2005, fluids from the Upper Cone site had Mg values slightly elevated (53.5 mmol/kg) over background seawater concentrations, as did the Lower Cone in 2018 (59 mmol/kg). Sulfate concentrations are also elevated above seawater values in these samples, partly due to the disproportionation of SO_2. The pH of vent fluids from the two cones vary dramatically, from ~2 at the Upper Cone to 4-5 at the Lower Cone. Greater concentrations of CO_2 occur at the Lower cone site. Changes in gas fractionation, system permeability and gas/water/rock interactions are likely responsible for the temporal variations in the fluid chemistry at the different Cone sites.

2. Gas emissions from acidic crater lakes

Conveners: *Cindy Werner & Orlando Vaselli*

Gas emissions from crater-lake volcanoes compared to hydrothermal systems in the Taupo Volcanic Zone, New Zealand

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The volcanoes of New Zealand rank among the best studied in the world in terms of their gas emission. Routine monitoring flights of gas emissions from two crater-lake hosting volcanoes began in the early 2000’s, resulting now in nearly two decades of measurements. Over this time frame, Ruapehu volcano hosted a persistent crater lake, whereas White Island hosted an ephemeral crater lake. The long-term cumulative CO_2 emissions from both lakes has been steady over this time period, regardless of whether a crater lake was present or whether the volcano was experiencing heightened eruptive activity (Figure 1). Cumulative SO_2 emissions, however, show much more dynamic behavior. The long-term average emissions were 1480 t/d and 590 t/d CO_2, and 290 and 60 t/d SO_2, from White Island and Ruapehu respectively, between 2005 to 2015. The molar C/S ratio based on the long term averages are 7.5 and 14, thus showing a greater influence of crater lake reactive processes at Ruapehu.

New Zealand also hosts over 20 active hydrothermal areas, seven of which have been measured for their diffuse CO_2 emission. Here we show that the CO_2 emitted from hydrothermal areas (either diffuse degassing or through lakes) for several well-studied systems (e.g. Rotorua, Rotomohana, Rotokawa, New Zealand) can rival that of the active volcanoes. In fact, if hydrothermal emissions are constant over time, which recent research suggests, the cumulative CO_2 emissions from dormant volcanoes far exceeds that of the active volcanoes in New Zealand. Together the measured systems equal a total of ~ 2000 t/d, which is greater than previous estimates of the Taupo Volcanic Zone (TVZ) as a whole.

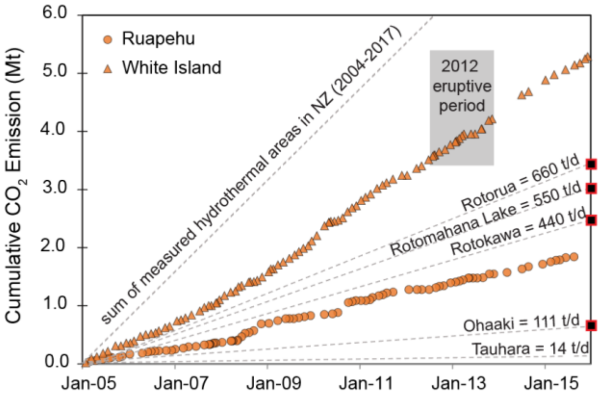

Figure 1. Cumulative CO_2 emissions for White Island data, Ruapehu, and a number of TVZ diffuse degassing regions between 2005-2015.

First characterisation of Santa Ana crater lake gas composition (El Salvador) during the period 2017-2018.

Nathalie Hasselle[1], Dmitri Rouwet[2], Alessandro Aiuppa[1], Angelo Battaglia[1], Eduardo Gutierrez[3], Francisco Montalvo[3], Ana Mirian Villalobos[3], Maarten de Moor[4], Demetrio Escobar[3], Jacqueline Rivera[3], Marcello Bitetto[1]

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Characterisation of volcanic gas composition and its variation in time is a useful chemical tool to detect changes in the underlying hydrothermal-magmatic system. The presence of a crater lake can strongly modify the original composition, however, in case of hyper-acidic lakes, volcanic gases, such as CO_2 and SO_2, are poorly scrubbed and the gas signature is commonly magmatic. Here, we present the first chemical composition of gases emitted by the hyper-acidic crater lake (pH -0.2 to 2.5) of Santa Ana volcano (NW El Salvador). Measurements were done in 2017 and 2018 by means of the Multi-GAS instrument. In March and June 2017, prospective surveys at various distances from the lake (rim, plateau and lake shore, in decreasing distance from the lake) were executed to identify the most adequate site (i.e. plateau) for punctual gas monitoring and installation a semi-continuous instrument (such as during the period April-June 2018). The results of these first lake plume gas composition measurements were contextualized within the long-term degassing dynamics for the period 1992-2017 (affected by several eruptions, magmatic in 2005 and phreatic in March-April 2007), modelled from the 25-year variations in lake water chemistry. Between 2017 and 2018, Santa Ana lake gas became apparently more SO_2-rich, the CO_2/SO_2 ratios decreasing by one order of magnitude, from 37.2 ± 9.7 to 2.4 ± 0.5, respectively. We suggest that this apparent more magmatic gas signature in 2018, without an increase of SO_2 flux, could be overprinted by a smaller lake volume (it significantly decreased from 2017 to 2018), and hence reducing it is S-scrubbing capacity. In addition, the small size of Santa Ana lake makes it arguably highly sensitive to external (e.g., meteoric input and evaporation) and internal (e.g., underlying magmatic-hydrothermal system and volcanic activity) variations. Those changes, affecting lake characteristics, will be reflected into lake gas chemistry and enable to be monitored by the semi-continuous Multi-GAS instrument installed at a safe distance.

Varying CO_2/H_2S ratios above the shallow Fangaia mud pool, Solfatara (Campi Flegrei, Italy)

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Recent studies have investigated degassing of acid species (HCl, SO_2, H_2S) from the surfaces of the most active crater lakes (Poás, Aso, Kawah Ijen, Copahue). We here consider Fangaia, a small (20 m x 25 m max) mud pool in the Solfatara crater (Campi Flegrei, Naples, Italy) as a "mini-crater lake", being a steam-heated mud pool (sulfate content near 2000 mg/L, pH 1.5). Hence, understanding degassing from Fangaia can provide insights into the diffuse degassing regime for the Solfatara crater area. In June 2017, we conducted the first MultiGAS measurements by moving a syringe attached to a fishing cane approx. 10 cm above the surface of the mud pool, pumping the gas to a MultiGAS instrument. The measurement procedure (approx. 50 minutes) is filmed with a GOPro camera, covering the view of the entire area with a fish-eye lens. The exact location of the measuring points (syringe) is consequently elaborated using the open-source graphical software ImageJ and MTRackJ, within a reference frame fixed in the field by clearly visible cones. Images are extracted from the GOPro time lapse with a frequency of 5 seconds, and synchronized with the 2 Hz frequency of the MultiGAS data acquisition. A bathymetric map of the Fangaia basin is obtained by direct measurements of the lake depth (61 points, max depth 1.25 +/- 0.05 m), and elaborated graphically following the procedure above.

Maps for CO_2 (321 to 75,824 ppm) and H_2S (9 to 224 ppm) concentrations for the Fangaia mud pool show highest concentrations above strongly bubbling areas, and lowest concentrations above diffuse degassing areas. Despite this observation, CO_2/H_2S ratios are lowest above bubbling degassing areas, and highest above the deepest areas of the Fangaia. These observations strongly suggest more efficient H_2S scrubbing when gas diffusely flushes through a thicker water layer, whereas CO_2 will pass without being affected due to the high acidity of the water. H_2S is less scrubbed when exiting at bubbling degassing vents. Time-framing this degassing process is a challenge for ongoing research. These first findings are insightful as they reflect the fast dynamics of the Fangaia mud pool, a "window" into the hydrothermal system underlying the emblematic Solfatara crater.

Insights into sulphur degassing dynamics through H_2S-dominated acidic volcanic lakes

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Sulphur gas species (SO_2 and H_2S) are partially or totally scrubbed by volcanic lakes depending on water physico-chemical characteristics. Hyper-acidic volcanic lakes, directly fed by magmatic gas, discharge large quantity of SO_2 (SO_2-dominated lakes), while less acidic lakes, mainly fed by hydrothermal gases (more S-poor), absorbed most of the S-gas species (mostly H_2S) and emit low amounts of H_2S (H_2S-dominated lakes). Here, we studied with the Multi-GAS instrument the lake gas composition of El Chichón (Mexico) and Víti (Iceland), both being pH 2-3 steam-heated volcanic lakes with SO_4^{2-} contents of ~700 mg/L. Víti lake is deeper (maximum depth ~60 m) and cooler (T 21.8 ± 1 °C in 2016) than El Chichón (~11 m and T 30.1 ±1 °C (in 2016), respectively). Firstly, the results evidenced the presence of H_2S (1-100 ppmv) and, more surprisingly, trace amounts of SO_2 (0.003-0.3 ppmv) in both lake gas plumes. Secondly, by using offshore fumaroles gas composition as a proxy of the subaquatic fumaroles, we highlighted the scrubbing effect of both lakes on the feeding volcanic gas. Indeed, higher CO_2/H_2S and H_2/H_2S ratios (31.5-5685 and 0.77-35.1, respectively) were measured in lake plumes compared to the offshore fumaroles (12.7-28.6 and 0.08-0.49, respectively). Hence, a small part of the H_2S entering at the lake bottom is able to flush through the water body (at El Chichón, we estimated a lake H_2S flux at 0.02-0.06 t/d). Then, we proposed that a small fraction of the dissolved H_2S generates SO_2 via oxidation reactions into waters, with SO_3^{2-} as transient S species. We concluded that sulphur degassing through pH 2-3 volcanic lakes is a non-equilibrium process and that kinetics appears to be very fast. It also highlights the need to constrain parameters (e.g., lake depth) controlling the degassing process.

Hazardous CO_2-rich gas expulsions from the hyper-acid crater lake at Kawah Ijen, Indonesia

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Kawah Ijen, East Java, Indonesia, hosts the largest natural acid crater lake in the world (28×10^6 m^3, T > 30°C, 170 m deep, pH < 0.5). It is well known for its active sulfur mining operation and for the photogenic blue flames that issue from its vigorous (T > 400°C) fumaroles. Ijen last had a major eruption in 1817 (VEI 2) but ongoing earthquake swarms, occasional geyser-like activity from the lake and discrete degassing events testify to the dynamic character of its limnic and hydrothermal systems.

Reports of hazardous gas expulsion events from the lake have long been reported by local observers and miners, but the compositions of gases emitted during these events have not been previously measured. We report observations from multi-GAS instruments installed in 2015 and 2016 that have recorded at least 6 limnic gas expulsion events. Our data show that the gases emitted during limnic expulsions are extremely CO_2 rich (CO_2 > 95% with subordinate H_2O and SO_2) and tend to occur during the second half of the rainy season, between January and April. Most of the events are relatively small, but a large event in March 2018 resulted in a dense flow of gas that left the crater and travelled ~10 km down a river valley to the west. A gas expulsion of this size has not been observed or reported at Ijen previously. The flow destroyed ~6 km^2 of crops and eventually impacted a village, resulting in over two dozen people seeking medical attention at a local hospital. The proximal multi-GAS measurements indicate that gas concentrations 10's of meters above the lake surface likely exceeded 25% CO_2 and 1000 ppmv SO_2 during the event and would have posed a lethal hazard to anyone nearby. These data show that highly-acidic volcanic lakes can produce large-scale CO_2-rich gas expulsions. We will explore these data and their implications for assessing and monitoring hazards and suggest possible future work that could lead to an improved understanding of the limnic and hydrothermal systems at Kawah Ijen.

3. Hydrothermal systems surrounding volcanic lakes: surveys and models

Conveners: *Joop Varekamp & Jennifer Lewicki*

Reconstruction of the geology and structure of Lake Rotomahana and its hydrothermal systems from high-resolution multibeam mapping and seismic surveys: Effects of the 1886 Tarawera Rift eruption

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Present-day Lake Rotomahana is one of the two focal points of the most destructive eruption in New Zealand's historical record, i.e., that of Mt. Tarawera on 10 June 1886, with devastating loss of life and presumed destruction of the iconic Pink and White Terraces that adorned the margins of the lake. Basaltic dikes are considered to have ascended near surface in the area, intruding into hydrothermally altered and water-saturated ground beneath the existing lake. The eruption buried the natural outlet of the lake, with the bottom of the craters becoming filled by water within months and completely concealed from view within years; today Lake Rotomahana has depths up to 118 m.

High-resolution (0.5 m) bathymetric mapping, when combined with a 2-D seismic reflection survey, enables us to 'see' details of the maar craters on the lakefloor, including those parts subsequently buried by sediment. The large Rotomahana Crater described by workers immediately after the eruption measures ~2.5 km in diameter near its southwestern end, and excavated ground to 155 m below present-day lake level. The vent system, as revealed by the present study, forms an array of right-stepping (dextral) craters, with the main crater being host to two sub-craters Rotomahana West Crater and Rotomahana East Crater today buried beneath the lakefloor, and which are in-filled by 36 and 37 m of sediment, respectively. Other features highlighted by the bathymetric data include; craters not filled by sediment, sediment fan deltas, volcanic ridges and dikes, submerged wave-cut terraces formed during times of lower lake levels and gas pockmarks, all either related to the 1886 eruptive episode or post-eruption hydrothermal and erosional processes.

Application of results from bubble plume, CO_2 flux, magnetic and heat flux surveys of Lake Rotomahana to this study, when combined with regional earthquake relocation analysis and broadband magnetotelluric data, suggest an explanation in terms of a magmatic heat source located south of Waimangu and a corresponding convective water/heat transport system extending thence to beneath the western end of the lake. The newly named Pink Terraces hydrothermal system (~1.5 km^2) is a continuation of the historical hydrothermal activity that was concentrated on the western shores of the old lake, and together with the formation of the new, post-1886 Patiti hydrothermal system (~1 km^2) located SW of Patiti Island, mark the two distinct areas of hydrothermal activity in the lake today.

Long-term monitoring of hydrothermal features around the caldera lakes of Newberry Volcano, Oregon, USA

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Newberry Volcano is a large, basaltic to rhyolitic shield volcano (~400-1.3 ka) located in Oregon's Cascade Range with a summit caldera that hosts two lakes: Paulina Lake and East Lake. Geophysical studies and a measured temperature of 265°C at 932 m depth in a drill hole suggest that the caldera is underlain by a magma chamber at shallow (3-5 km) depth. Caldera hot springs and magmatic gas emissions are surface manifestations of an active magmatic-hydrothermal system. Based on the distinct water chemistries and sediment compositions of Paulina and East Lakes, a conceptual model has been proposed whereby phase separation from rising hydrothermal fluids occurs at shallow depth beneath East Lake, CO_2 and H_2S-rich gases enter East Lake, and the residual hydrothermal fluids discharge into Paulina Lake (Lefkowitz et al., 2017). We present the results of the USGS's long-term hydrothermal monitoring program at Newberry Volcano, which focused on three surface features: (1) Paulina Hot Springs (PHS) on the shore of Paulina Lake, (2) East Lake Hot Springs (ELHS) on the shore of East Lake, and (3) Obsidian Flow Gas Seep (OF), an area of diffuse gas emissions in an area of intermittent water ponding at the edge of the Big Obsidian Flow. In 1991-1993, the USGS installed a set of three shallow (1.5 to 2.6-m-deep) piezometers at PHS to establish stable observation points in the underlying shallow groundwater system. Subsequent intermittent measurements (n = 17 from 1993 to 2018) have documented remarkably consistent temperatures (56.3±2.2°C) and specific conductance (1166±166 mS cm^{-1}) below the hot-spring vents. From 1978 to 2018, gas samples were intermittently collected for geochemical analysis from PHS (n = 18), ELHS (n = 8) and OF (n = 8). Gases from all three sites are CO_2-rich (≥79 mol.% in dry gas), with varying amounts of gas stripped from air-saturated meteoric water (ASMW). ELHS and OF gases contain detectable H_2S (H_2S was below detection in PHS) and higher CH_4 contents than PHS. The ™^{13}C-CH_4 values at ELHS (-72.2 and 63.6 ‰) reflect a shallow microbial origin of CH_4. Helium concentrations in gases from all three sites are poorly correlated with $^3He/^4He$ ratios (5.10 to 8.12 R_A) but show an inverse relationship with CO_2 concentrations due to preferential loss of CO_2 to ASMW. $CO_2/^3He$ and ™^{13}C-CO_2 values range from 4.9 x 10^8 to 2.3 x 10^{10} and -8.90 to -5.35 ‰, respectively, but after accounting for CO_2 loss to ASMW, they fall within the range of Cascade Arc volcanoes. Despite the large internal variation owing to interaction with ASMW, the PHS, ELHS and OF samples exhibit distinct groupings on the basis of ™^{13}C-CO_2 versus $^3He/^4He$ ratios. ELHS and OF have higher ™^{13}C-CO_2 values than PHS, likely resulting from microbial reduction of CO_2 to CH_4, and EL has generally lower $^3He/^4He$ ratios than OF and PHS. We will discuss implications of our results for the conceptual model of the caldera lakes and future monitoring at Newberry Volcano.

Hydrothermal sediment from Paulina Lake, Newberry Volcano (OR): modern BIFs?

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Paulina Lake (PL) at Newberry Volcano (OR, USA) is an 80m deep, bowl-shaped lake with an outlet and subaqueous hot spring water inputs. Its flat bottom features a steep, 60m tall subaqueous mound, possibly of hydrothermal origin. PL water is slightly basic, rich in HCO_3^- (~400 ppm) and dissolved silica (~20 ppm), all suggestive for a carbonate-rich hot spring input. Most unusual is the PL sediment, made of precipitates rich in Fe and Si, similar to ancient Banded Iron deposits. Water profiles analysed from 2010 through 2018 indicate that most chemicals are in steady state. The carbon cycle has a dissolved carbonate input, CO_2 degassing, photosynthesis, and minor carbonate precipitation. CO_2 monitoring in 2018 yielded a flux estimate of ~50 tonnes CO_2/day in summer. Sediments consist of hydrothermal silica (geyserite), opal diatom frustules, and Fe-oxides, with relatively high concentrations of P, As, Mn and V. The lake has an active ecosystem, with 5-10% organic carbon in the sediments. Ostracods, small, nektobenthic shrimp-related creatures with calcite valves, live on and above the lake bottom.

Cores PL1 (2.6m) and PL2 (5m), provide a ~ 5000-year record of sediment chemistry, reflecting rates of hydrothermal input over time. The Paulina Lake Ash Flow (~1300 BP) occurs at ~140cm depth, and ^{210}Pb data provide sediment mass accumulation rates over the last 100 years. The sediment contains up to 14% Fe, 65-70% SiO_2, a few % of volcanic ash, and organic matter and minor carbonates. Sediments deposited at 2000-2600BP have higher concentrations of Fe-P-Mn-As, and we surmise that this was a period of enhanced hydrothermal inputs. Ostracod valves occur directly below the interval with enhanced hydrothermal input, are absent within this interval, and then return above the ash layer to persist over the last 1300 years. Stable isotope data on their calcite valves provide insights in the paleoclimate (™^{18}O) and the paleo-carbon cycle, notably the past degree of CO_2 degassing.

Chemical elements of hydrothermal origin in PL are separated into three groups: 1. Conservative elements that enter the lake and are flushed out through the outgoing river, 2. Elements such as Fe, As, P, Mn, and Si that are poorly soluble in the cold oxygenated lake water, and form chemical precipitates in the sediment, and 3. Elements that enter the lake, are taken up by biota, but then are incorporated as biogenic components in the sediment (C, Si, P). Iron is brought in as Fe^{2+} in the hot spring fluids, and precipitates upon mixing with lake water as hydrous ferric oxides, scavenging P, As and V from the surrounding fluids. After burial, these oxides are reduced with organic matter, and Fe re-precipitates in siderite, vivianite and poorly characterized mixed Fe-oxides. A preliminary silica balance suggests an input of 550 tonnes Si/yr, of which 330 tonnes are flushed out. The remainder is precipitated either directly as geyserite or, after cycling through the lake's ecosystem, as diatom frustules. The silica balance also provides a rough first estimate of the volcanic heat flux (~100MW), a magnitude in agreement with the presence of magma at a few km depth below PL. The PL sediment strongly resembles Precambrian Banded Iron Formations (BIF), and the PL depositional environment may have similarities with the much larger oceanic BIF basins with their massive hydrothermal inputs.

The Hydrothermal Heartbeat of Copahue volcano, Argentina

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Copahue (37.8 ^{o}S) in the Argentine Andes has an acid crater lake, and near-summit hot springs that feed the Upper Río Agrio. This acid river enters Lake Caviahue, a 0.5 km^3 glacial lake at pH~2.5, with the Lower Río Agrio as its outlet. Copahue had eruptions in 2000 and late 2012, and a failed eruption/intrusion in 2004. We measured element fluxes from the hydrothermal system between 1997 and 2013, showing pre-eruptive enrichment in S, followed by enhanced fluxes of rock-forming elements, and then rapid and significant post-eruptive attenuation of all element fluxes. The Cl export rate from the system varied from 1700 Mg Cl/month prior to the late 2012 eruption to 280 Mg Cl/month a few months later. The Al fluxes varied from 650 Mg Al/month during the 2000 eruption to 70 Mg Al/month in late 2001. Similarly, the K flux varied from 100 Mg K/month prior to the 2012 eruption to 20 Mg K/month in early 2013. Prior to eruptions, the hydrothermal system acidifies and heats up, followed by magma intrusion, possibly culminating in an eruption. Reactions of the newly emplaced magmatic rock with the hot acid fluids lead to an increase in concentrations of the rock forming elements and element export rates. This increase is quickly followed by oversaturation and precipitation of secondary minerals such as alunite in the hydrothermal reservoir, reducing overall permeability. This reduction in permeability leads to strongly reduced element fluxes, especially K and Al, and a higher contribution of meteoric waters to the hot springs. When the hydrothermal system matures and the acidity increases again with further magmatic gas inputs, alunite may start to re-dissolve. The annual flux measurements in the Upper Rio Agrio are tuned for intra-annual variations with calculations for non-steady state dynamics for Lake Caviahue water compositions. Saturation modeling of the hot spring fluid compositions shows that alunite is saturated during and past the eruptive episodes, and it ultimately ‘clogs up’ the system. This alternation of acidification – rock dissolution - mineral precipitation – re-dissolution is the ‘heartbeat’ of the Copahue magmato-hydrothermal system.

Electrical Resistivity Tomography Images of a Hydrothermal System Modulated by an Active Crater Lake

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To investigate the relationship of fumarolic areas to the main lake filled crater at Whaakari/White Island we undertook the first Electrical Resistivity Tomography (ERT) on the island. A recent field campaign made more than 25000 transfer resistance measurements along a series of 2D and 3D profiles, sampling depths up to 150 m below surface. We made measurements in the main fumarolic area around the south crater wall with the aim of imaging conduits that feed the fumaroles from the main crater. We measured one long profile spanning the length of the crater from the lake to ocean to investigate the broader electrical structure of the crater.

Preliminary 2D inversion results show a nearly 3 order of magnitude range of apparent resistivity values from 0.1 to ~100 Ωm. A shallow (~5m), very low resistivity (<1 Ωm) layer limited to the main fumarolic areas around Fumaroles 0 and 1 likely represents low pH, chloride rich condensate brines, visible as springs adjacent to the fumaroles. Away from the fumarole regions surface apparent resistivity of 50-60 Ωm are recovered by the inverse model. Coincident to Fumarole 0 is a narrow (<5 m) sub-vertical zone of higher resistivity bisecting the shallow low resistivity layer. This sub vertical resistive feature connects to a deeper (20-30 m below surface) region of higher resistivity (20 Ωm) that is surrounded on both sides by a widespread 1 Ωm layer at 30 m depth, interpreted as saturated sediments. The relatively resistive subvertical feature may represent the shallow part of the conduit feeding Fumarole 0.

Despite very low apparent resistivity ground, ERT measurements have successfully delineated several features of interest in the shallow hydrothermal system. Future 3D inversion of the entire dataset will provide a high resolution electrical model to understand the distribution of multiphase fluids in the shallow subsurface at White Island and the influence a rising crater lake has on their distribution.

Time variation in the chemical and isotopic composition of fumarolic gases at Taal volcano, Philippine

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Taal volcano island is located in the southern part of Luzon Island, Philippine, about 50 km south of Manila. Taal volcano island has a mountainous body of about 5 km across surrounded by lake water from Taal Lake. Located at the center of Taal volcano island is the Taal Main Crater Lake (MCL) with a diameter of 1 km. Thirty-three (33) eruptions have been recorded between 1572 and 1977 at Taal volcano island. From the last eruption in 1977 to the present, the relatively long dormant period has continued. However, due to the high possibility of eruption at Taal volcano island in the near future, it was chosen as one of the Decade Volcanoes. Also, many residents live within Taal volcano island, and it is often crowded with tourists. In order to prevent disasters and minimize risks caused by eruption, PHIVOLCS (Philippine Institute of Volcanology and Seismology) conducts multidiscipline volcano monitoring and research at Taal volcano island. Gas monitoring includes continuous monitoring using the multiGAS station on the shore of Taal MCL, along with campaign monitoring of volcanic gas in ambient air using multi gas sensors. In addition to their current gas monitoring, direct gas sampling of fumarolic gas via gas condensates is important. Fumarolic gas contains components degassed from magma, so it responds to the rise and fall of volcanic activity, and chemical composition and stable isotopic ratio fluctuate sensitively. In this research, we aim mainly to pursue the time change of the fumarolic gas and to contribute to the activity evaluation of Taal volcano.

4. Phreatic eruptions from Wet Volcanoes

Conveners: *Bruce Christenson & Akihiko Terada*

Permeability reduction and other processes leading to phreatic eruptions from wet volcanic systems: Insights from the 28 April 2016 eruption from White Island, New Zealand

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A small but dangerous ballistic-laden phreatic surge eruption occurred through a rapidly evaporating crater lake in the eruption crater complex of White Island on 28 April 2016. The eruptive activity lasted for 35 minutes, with 6 distinct seismo-acoustic pulses sourced from at least 3 vents on the lake floor. No juvenile material was recognized. A large proportion of the ballistics showed extensive hydrothermal alteration, exhibiting both dissolution of primary mineral phases and varying amounts of sulphate mineral precipitation as both groundmass replacement and fracture-bound infillings. Permeabilities vary inversely with dry rock density in a suite of some 15 ballistic samples (ranging $5x10^{-14}$ to $5x10^{-18}$), largely reflecting the effects of protolith dissolution. However, some highly altered samples are also of low permeability, containing vug and vein fillings of silica (cristobalite/chalcedony), natroalunite and anhydrite, whereas hydraulically fractured samples typically show fracture fillings of natroalunite and anhydrite. Fluid inclusions in anhydrite homogenising in the liquid phase have entrapment temperatures of between ca. 160 °C to 230 °C. A number of these inclusions are clathrate bearing, with indicative entrapment pressures ranging up to 40 bar.

Tough2 modelling of the vent environment provides valuable insights into physical processes operating beneath the lake. Magmatic vapours, simulated as mixtures of H_2O and CO_2, flow into the liquid saturated sub-lake environment along vertical zones of elevated permeability (fumarolic conduits). With free degassing of the conduit at the surface, this has the combined effect of both heating the conduit and adjacent aquifer environments, but it also convectively draws adjacent aquifer fluids (of lake composition) towards the conduit along a positive thermal gradient. Uncoupled reactive transport modelling (X1t) of crater lake waters flowing along such gradients shows that they become supersaturated with respect to natroalunite at temperatures of ca. 200 °C, leading to precipitation of this phase and the drastic reduction of permeability along fairly narrow lateral intervals. Higher in the system, uncoupled reactive transport modelling of magmatic vapour flowing into the lower temperature, shallower lake (i.e., liquid-saturated) environment shows rapid precipitation of elemental sulfur and associated sulfate mineral phases, which also abruptly decreases permeability. In time, both processes serve to encapsulate the upper conduit passage, effectively sealing it from the adjacent hydrothermal environment.

Once established, such sealed environments take the form of vertically-oriented volumes, open at the base and resembling “silos” enclosing the conduits. These have the potential to become loci for the collection of non-condensable and compressible gas columns (principally CO_2). The maximum pressure derived from clathrate stability of ca. 40 bars equates to a hydrostatic pressure at the base of the sealed column at a depth of 400 m. The tensile strength of the natroalunite seal material is measured at 31.7 bar, and suggests a confining pressure of 8.3 bar, thus constraining a seal failure depth of between 50 m and 85 m (hydrostatic and lithostatic depths, respectively). The occurrence of multiple vents in close proximity to one another points to the formation of multiple near-surface silos, all connected to a common pressure source at depth.

Seismic precursors to phreatic and phreato-magmatic eruptions in New Zealand

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In the past 12 years, several small scale phreatic, phreato-magmatic and magmatic eruptions have occurred in New Zealand. Precursors to the eruptions have been widely variable and reflect the interplay of magmatic fluids from depth, with the rock-mass overburden and hydrothermal system from above. This work will examine precursors to the 2006, 2007 Ruapehu, the 2012 Te Maari, and the 2012-2016 White Island eruptive activity as expressed in tremor and discrete volcanic seismicity. These examples illustrate the challenges presented for eruptions with weak or no useful precursory activity, and the opportunities to reveal underlying precursors occurring hours, weeks and months before an eruption.

The review will then focus on the range of possible underlying processes ahead of eruptive events which may provide a framework for interpretation and assessment. We will focus specifically on the role of pinch points, discontinuities and phase transitions as possible seismic sources and how these sources might be preferentially excited prior to eruptive activity. We will also examine the role of magmatic fluid migration as a driver of eruptions.

Finally, the review will examine the range of tools that may be applied to the observed precursors and potential improvements to automation and early warning. These, in turn may improve useful forecasts for unrest at hazardous volcanic systems.

The chemical and isotopic changes of the hot springs and fumaroles in the Jigokudani Valley, Tateyama Volcano, Japan

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Tateyama Volcano, located in central Japan, has an active geothermal field called the Jigokudani Valley where numbers of fumaroles and hot springs varying in size from small to large are present. Phreatic eruption repeatedly occurred around the Jigokudani Valley during the last 40,000 years (Harayama et al., 2000), which formed some crater lakes that were present until 1300 years ago (Mizutani et al., 2001). Seki et al. (2016) revealed the resistivity structure of the shallow hydrothermal system beneath the Jigokudani Valley, and found the surface cap layer and the gas-rich reservoir underneath. In addition, some hot springs were considered to be derived from the vapor phase separated from the magmatic fluids at a shallow depth, and Cl^- concentration of those spring waters showed drastic changes probably reflecting the temperature changes of the two-phase zone. In this paper, we show the time change of chemical composition of hot-spring waters in the Jigokudani Valley for five years from 2014. We also report the analysis results of the fumarolic gases, which were sampled in 2016 and 2018 in order to have better understandings of the hydrothermal system. Based on these results, we propose that the monitoring of Cl concentration in certain hot springs could be useful as a proxy for the temperature of the reservoir located in the shallow hydrothermal system. The partitioning of HCl between the vapor phase and the liquid phase strongly depends on the temperature. By adding information on the subsurface structure to this, we can know the state of the reservoir beneath the surface cap layer, which will lead to the risk assessment of unheralded phreatic eruption.

Extraordinary sulfur volcanism at Poás (Costa Rica) during the past two centuries

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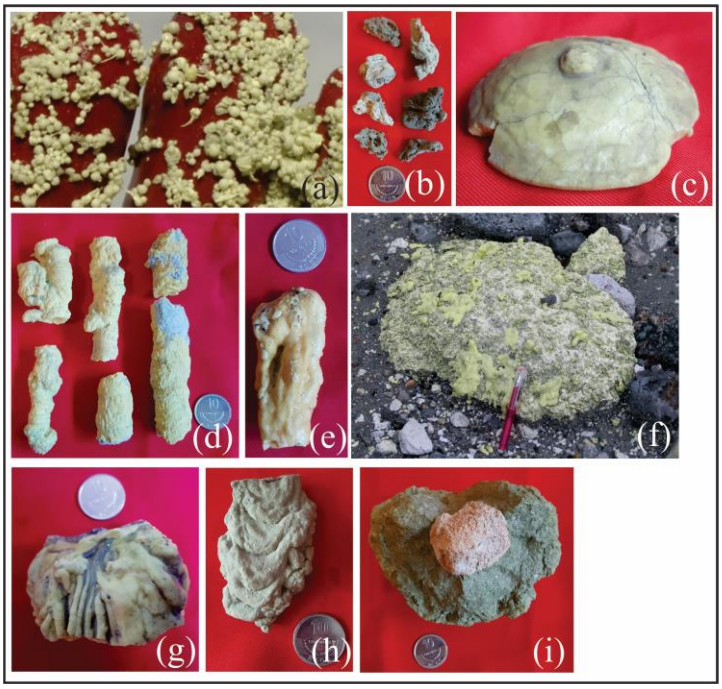
This study is arguably the most complete compilation of sulfur volcanism of any given volcano on Earth: Poás. Sulfur volcanism at Poás is described in historical literature since 1828, and in scientific literature since the 1960's. We first classify the various manifestations of sulfur volcanism at crater lake bearing volcanoes (subaerial and sublacustrine sulfur pools, sulfur spherules, flows, cones/hornitos, and sweat, and pyroclastic and burning sulfur), based on observations at Poás (see Figure) and work by Japanese pioneers of the early 1900's. Their first observations and models have passed the test of time and still stand as theories today. We discuss the role of sulfur as sealing agent during phreatic eruptive activity. Comparing the sulfur volcanism at Poás with the one at other (56) volcanoes, it is honest to say that only White Island (New Zealand) and Kawah Ijen (Indonesia) are the only valid "competitors" to the Poás, being the most dynamic of them all.



Shifting of eruptions behavior activity (phreatic/magmatic) at two hyperacidic lakes during 2017, Costa Rica

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Costa Rica have two hyperacid lakes, one is located in the northern part, at the active crater of Rincón de la Vieja volcano, the other is close of the Capital San José, also at the active crater of Poás volcano, called Laguna Caliente. These lakes have had a large eruptive activity in historical times, however during 2017 both lakes change the activity drastically during the first six months of the year.

In the case of the one located at Rincón de la Vieja, since 2011 began with sporadic phreatic eruptions, some periods with more intensive eruptions, like 2012, 2014 y 2016. On May 23th of 2017, an eruption occurred with some small pyroclastic flows at the North flank, follow by small hot lahar in the Pénjamo and Blue Rivers (located at the North flank). Another and more energetic eruption happened June 11th, with a diluited Pyroclastic density current close to the vent, also follow by another hot lahar that reach on some places of the river 4 meter height, also got as far as 8 kms of the vent. The ashes of the eruption were collected and analyzed by scanning electron microscope (SEM), the results show evidence of water/magma interaction in these events.

The Laguna Caliente at Poás volcano, show phreatic eruptions since 2006 with periods of calm, but suddenly on April 1st of 2017, the activity change drastically, increasing lake leve and the lake temperatures from 35 ºC to 45 ºC, show black sulfur slicks floating in the lake, new fumaroles and hot springs in the South part crater; later on the night of Abril 12th, an moderate eruption occurred and produce a lahar of 5 meter height in the Northwest flank. This eruption break partially the "Dome". Another strong eruption occurred on April 14th and destroy partially the Dome. Collected ash samples show the evidence of phreatomagmatic activity from the April 12 eruption. The biggest eruption was on April 22, when the Dome was almost destroyed, also ballistic activity affect the tourist lookout point with rocks of more than 30 cm, which reach as far as 1.5 km. The calculated velocity and energy of the ballistic rocks on 60 m/s and 30 KJ respectively, this eruption was classified as Vulcanian. Later on a tuff ring was formed almost the same site of the past Dome that was formed during early 1950´s.

Nowadays (January 2019) both hyperacidic lakes are still erupting, with strong phreatic activity, the question if this activity is the remnant of the last magmatic phase or if this is the precursor of another magmatic eruptions?

5. The impact of volcanic lakes on society: from mythology to risk mitigation

Conveners: *Hollei Gabrielsen & Dmitri Rouwet*

Finding a balance; the holistic importance of water

Hollei Whiungarangi Gabrielsen

Tongariro District Department of Conservation

Water, essential to life, is highly valued and respected by the indigenous tribes of Aotearoa, New Zealand. This reverence for water originates from a profound relationship, a longstanding association with the natural world, bound together and reinforced through genealogy. Water, often referred to as the lifeblood of Papatūānuku, the earth mother, emphasizes its ability to feed and nourish the landscape whilst also sustaining and enabling the creation of life. Therein lies the absolute importance of water, in its purest state. We will explore traditional and contemporary relationships between indigenous tribes and water to understand how and if volcanic lakes hold the same significance, and if so, the potential implications for science going forward.

Phreatic activity of the past and…the future: the study case of Greece

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The geological background as well as the major geodynamic activity of Greece gave rise to a geological evolution expressed in volcanism, orogenetic processes and active tectonics. The widespread volcanic activity in the Aegean Sea started in the Oligocene and continues till now. Two major phases of volcanism took place in Greece, with the first one being developed in the North Aegean area at Late Messinian and the 2nd one in the Pliocene resulting in the South Aegean Active Volcanic Arc (SAAVA). SAAVA was developed in the back arc region of the Hellenic subduction zone, about 150 km north of the Hellenic Arc, with the arc being delineated by the volcanic centers of Sousaki, Methana-Egina, Milos, Santorini, Kos, Nisyros and Gyali. Some of these centers have produced in the past explosive events of phreatic character and are still of potential risk.

Milos Island was formed in Mesozoic, whereas the youngest volcanic activity was of Upper Pleistocene age and concentrated in correspondence with the volcanic centers of Fyriplaka in the south and Trachilas in the north, which are also present-day exhaling areas. This activity resulted in lava domes and phreatic explosion craters, with the latter commonly producing overlapping craters rarely more than 1 km in diameter, continued from late-Pleistocene to recent times. Additionally, Nisyros was formed during the late Pleistocene-Holocene, through five distinguished stages that led to the formation of a caldera about 4 km in diameter. The most recent activity (1873-1887) is represented by hydrothermal explosions forming several phreatic craters. The volcanic activity in the island was always accompanied by intense seismic activity that played an important role in triggering the hydrothermal eruptions and therefore contributed in the ascent of deep fluids. It is worth noting that significant changes were noticed in the chemical composition of the gases after the seismic crisis of 1996-1998. Both volcanic systems are considered potentially active volcanoes and explosive hydromagmatic eruption is considered the most probable event. Kolumbo volcano last erupted in 1650 and its emissions caused the death of more than 70 people on the nearby island of Thera; this fatal event was attributed the volcanic gases released by the eruption. The morphology of its submarine crater is so that the water exchange with the open sea is limited and the CO_2-rich gases completely dissolve in water and accumulate at the bottom of the crater creating a CO_2-rich lake; a process similar with that preceding the lethal outburst of CO_2 from the Nyos Lake.

Lago Albano, Rome, Italy: an updated hazard assessment by revising 2,800 years of literature

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The 1986 Lake Nyos roll-over triggered scientific research on volcanic lakes, creating "Nyos biased" interpretations: the search for dissolved CO_2 in other lakes might have led to over-interpretations regarding hazard assessment.

In this study, we review the historical literature on Lago Albano over the past approx. 2,800 years and demonstrate that there is no clear evidence of Nyos-type bursts at Lago Albano in the past, contrary to previous ideas. In 1989 Lago Albano was subjected to a large CO_2 input, related to a seismic swarm below Colli Albani volcano. Earthquake reports of the more recent history mention at least two similar anomalous degassing events that occurred out of five seismic crises between 1829 and 1927. Partial temperature- and density-driven roll-over of the top-9 m of Lago Albano commonly releases accumulated CO_2 during winter (Chiodini et al., 2012, and CVL9-Cameroon Talk), hence avoiding long-term CO_2 accumulation in bottom waters, as is the case at meromictic lakes in the tropics, such as Lake Nyos.

Here we introduce the term "anti-Nyos-type" lake, with Lago Albano arguably as its best example: sudden recharge and regularly periodic release of CO_2 (Lago Albano) vs. steady recharge and sudden release of CO_2 (Lake Nyos). Although the CO_2 concentration in bottom waters was far from saturation during the last survey in May 2010 (Chiodini et al., 2012), leading to low probabilities of hazardous limnic roll over, it is paramount to know the saturation state of CO_2 in bottom waters and physical lake stability at any time. Considering the tight relationship between CO_2 degassing and seismicity, a combined seismic and geochemical monitoring setup is required to timely detect potentially anomalous CO_2 recharge at the bottom of Lago Albano. A continuous system of temperature loggers at thermoclines (at 9 and 95 m depth) and a CO_2 sensor at the lake surface has recently been installed, with the scope to better understand the dynamics of CO_2 degassing during winter.

6. Limnology of Lake Nyos and its nephews: searching for strata

<u>Conveners:</u> Minoru Kusakabe, Bill Evans & Greg Tanyileke

Crater lakes of monogenetic (*sensu lato*) volcanoes and their complex geological origin

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Monogenetic volcanoes are those erupt only once and they active up to several days or weeks. In contrary, small volume of eruptive products of such volcanoes could formed through multiple magma injections hence the "*monogenetic*" nature of this type of volcanism is under reconsideration. The total number of magma batches and eruptive events associated with these volcanoes still remain far below the number of events recorded in a polygenetic volcano. Therefore, such volcanoes are commonly defined as compound, nested or polymagmatic/polycyclic monogenetic volcanoes (*sensu lato*). These scenarios determine the type of craters appear on such volcanoes. Mafic magmas may produce scoria cones. In humid climates, weathering and rainfall together can facilitate the infill of their craters with lakes (Samoa, SW Pacific). In temperate climate, if abundant organic material input can develop quickly impermeable bottom layers on the crater floors, crater lakes may form (Moon Lake, China). Scoria cones are formed by repeated low energy explosions due to magmatic volatiles but commonly have phreatomagmatic explosive events. Such eruptions can take place in the beginning (abundant ground water, low magma discharge), intermittently (magma supply varies, external water can access feeder dykes), or in late stage (full cone destruction). The most common crater lakes of monogenetic volcanoes are the maars. Maar volcanoes have a flat crater floor that is subsided below the syn-eruptive landscape. While this definition seems simple, to establish the maar origin of a crater lake is difficult. Commonly, the crater wall - where such contact could be visible - is covered by debris flanks or the lake itself. Maars can cut into a rugged syn-eruptive topography creating complex facies distribution of their deposits and complexity in the position of the crater floor. Maar origin is argued often by the presence of tephra ring being formed due to phreatomagmatic explosions dominated by pyroclastic density current and debris jet deposits. While the phreatomagmatic origin of maars is widely accepted, there are maar-like volcanoes that either have no preserved tephra rings (Cerro Overo, Cerro Tujle and Tilocalar, Chile), or their tephra rings composed of deposits lack of positive evidence to support magma-water interaction (Tanzania), or the craters are (even they flat floored) are elevated and seemingly sitting on a "*positive*" landforms and associated with felsic magmas (Saudi Arabia). In this presentation a critical review will be given over these peculiar features of craters of monogenetic volcanoes.

Biogeochemical Characterisation of a Geothermal Spring Input to Lake Rotoehu: Implications for Phosphorus Cycling

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Lake Rotoehu is a shallow, polymictic lake on New Zealand's North Island within the active Taupo Volcanic Zone. The geothermal Waitangi Springs, which discharge into Lake Rotoehu, contribute ~69 % of the lake's total ionic content, and are responsible for major contributions to biologically limiting nutrients including phosphate, silicon, nitrate, ammonium, and iron. This geothermal input contributes to several lake management issues including elevated nutrient concentrations. In an effort to curb in-lake phosphorus levels, in-stream alum-dosing has been employed to floc dissolved reactive phosphorus (DRP) and remove it from the water column via sedimentation. We report results of an investigation of the physicochemical and geochemical dynamics across the mixing zone to the main lake body. A combination of approaches was used to understand these dynamics: two field experiments with fixed location and transect measurements, laboratory analysis and geochemical speciation modelling with PHREEQC. There were sharp changes in physicochemical water properties across the mixing zone within the bay and within beds of invasive submerged macrophytes (*Ceratophyllum demersum*): pH, O_2 and DRP values increased with distance from the stream outlet, whereas major ion concentrations, temperature and conductivity values decreased. Initial in-stream phosphorus stripping through alum dosing was effective in reducing the DRP load by ~50 % of background concentration. As alum was introduced to the stream water (~pH 6) it precipitated to form amorphous aluminium hydroxide ($Al(OH)_{3(am)}$) and adsorbs phosphorus via hydroxyl ligand exchange. However, elevated levels of iron in amorphous hydrous ferric hydroxides $Fe(OH)_{3(am)}$ are also likely to contribute to natural phosphorus binding capacity. Sediment core data also indicated that settled $Al(OH)_{3(am)}$ floc and $Fe(OH)_{3(am)}$ particulates were primarily concentrated within the inner portion of the bay. Geochemical speciation modelling also indicated that the primary dissolved Al species was $Al(OH)_4^-$ under the observed daytime conditions, and that Fe was primarily in colloidal form $Fe(OH)_{3(am)}$, which was confirmed through diffusive gradients in thin films (DGT) measurements. These results emphasise the that geothermal inputs can induce major geochemical changes in natural lakes and may hinder lake restoration efforts in such systems.

Characteristics of underwater topography in Lake Monoun, Cameroon

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The underwater topography of Lake Monoun, Cameroon was scanned on 2nd and 3rd November 2014, using a multibeam sonar (Sonic2022, R2SONIC co Ltd) with the precision of ±30 cm in depth. The survey revealed the following topographic characteristics.

1) <u>Two significant depressions and small six depressions located on the rim of bottom floor</u>

Based on a CTD measurement after the multibeam survey, it was confirmed that the depression located in the northeast rim (D1) kept lake water the CO_2 concentration of which was higher than the concentration of lake water outside of D1. In the depression of south rim (D2) did not keep a lake water containing excess CO_2.

2) <u>Many grooves and steps scraped on the inner slope of lake</u>

Most of the grooves were distributed on the northeast side of inner slope. A region free from the grooves was found in the northeast side of inner slope.

3) <u>Protrusions located along the edge of bottom floor</u>

4) <u>Gently sloped bottom floor</u>

The bottom floor of lake was gently sloped in the direction from north to south. The north floor was about 4 m higher than the south floor.

The origin of above characteristics will be interpreted along the scenario of limnic eruption in 1984 at Lake Monoun.

Fig.1. Underwater topographic features of Lake Monoun revealed by multibeam survery. Solid curves indicate grooves and steps on inner slope. D:depression, P:protrusion, F:grooves free area, R:ridge, L:shore of lake.

Structural reinforcement and geochemical monitoring of Lake Nyos dam: Implications for environmental sustainability and social wellbeing

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In addition to the continuous recharge of the bottom layers of Lake Nyos with magmatic carbon dioxide, the natural dam at its outlet, estimated to be ≈ 5000 – 8000 years old, constitutes a further potential hazard to the environment and surrounding population. The upper 40 m, composed of poorly consolidated pyroclastic rocks, is apparently structurally weak, and subjected to both mechanical and chemical erosion. Its collapse could result in the release of a hazardous volume of water estimated at 50 million m^3 into River Katsina Ala, resulting in a major flood with severe damage to communities downstream as far away as neighboring Nigeria. Evidence-based results from geological, geotechnical, geophysical and hydrological studies led to a successful reinforcement using the jet grouting technique. The structural reinforcement constituted of two lines, one 90 m long and the other 80 m of concrete pillars that were injected into the dam at varying depths, and on those lines is a concrete slap. This high-tech engineering technique stabilized the Lake Nyos natural dam, thus reducing erosion. An overhead bridge on this facilitates transportation of the population and goods between neighboring villages in the vicinity of Lake Nyos. Hydro-geochemical monitoring of 13 monitoring boreholes and a spring on the dam commenced in 2012. The results of the complementary studies, the dam reinforcement works, and monitoring are presented in this paper.

Mining lakes with extreme gas pressures in the deep waters: responsible gases, their origin and how to deal with the issue

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Besides the famous volcanic lakes with high gas pressures in the deep water, also mine pit lakes are known to show this feature. We report the situation in two mine pit lakes: Guadiana mine pit lake in southern Spain (Sanchez-España et al 2014, Boehrer et al 2016) and Lake Vollert-Sued in Germany (Horn et al 2017): Both lakes show gas pressures close to the absolute pressure. While in Vollert-Sued methane bubbles continuously ascend through the water column, in Guadiana pit lake gas ebullition has not been documented so far. In Vollert-Sued the gas load stems from organic pollution and hence the gas pressure is mainly build by methane, as carbon dioxide is well soluble and hence does not contribute similarly to gas pressure. On the contrary in Guadiana pit lake, most of the gas pressure come from dissolved carbon dioxide. After mining had ceased, acidic mine drainage had come into contact with carbonates like calcite and dolomite disseminated in the ore and the volcanic host rocks. The chemical reaction produced carbonic acid, which dissolved in the monimolimnion of the lake. For both lakes, we did a risk assessment, and in the case of Vollert-Sued it was decided that the risk for people dwelling in the surroundings is not as high as in the Guadiana pit lake. The reason in the end was that despite of high gas pressure, the volume of potentially escaping gas was not enough when exclusively methane (plus nitrogen) was responsible for gas pressure. Hence remediation action was only taken for Guadiana pit lake.

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Unusual water geochemistry at Coatepeque, Ilopango and Chanmico volcanic lakes (El Salvador, Central America)

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In November 2016, a geochemical survey based on water and dissolved gas chemistry was carried out at Coatepeque (on the E slope of Santa Ana Volcano), Ilopango (inside Ilopango Caldera) and Chanmico (associated with San Salvador Volcano) volcanic lakes in El Salvador, a land characterized by complex fault systems and associated volcanism. The three lakes showed a thermocline at a relatively shallow depth (from 30 to 40 m, from 20 to 40 m and from 5 to 15 m depth, respectively) and anoxic conditions below 33, 24 and 4 m depth, respectively. Along the vertical water columns, increasing salinity and decreasing pH were measured. The Na^+–Cl^- composition of the Coatepeque and Ilopango lakes, displaying TDS values up to 1,226 and 1,216 mg/L, respectively, is likely due to the presence of hydrothermal fluids feeding these two lakes, as also confirmed by Cl^-/Br^- molar ratios ≤ 650, high As, B, Li and Si contents and Cl^-/SO_4^{2-} ratio > 1. The Mg^{2+}–HCO_3^- water composition of Lake Chanmico, whose TDS values were between 566 and 856 mg/L, suggests water-rock interaction with mafic/ultramafic rocks variably affected by serpentinization processes, resulting in high Mg^{2+}, Si and B concentrations. Waters at depth were characterized by the presence of CO_2 with a likely hydrothermal signature based on the $\delta^{13}C$-CO_2 values, albeit this gas was found in smaller quantities than other meromictic lakes hosted in quiescent volcanic systems (e.g. Lake Kivu in DRC, Monticchio, Albano and Averno lakes in Italy, Hule and Rio Cuarto lakes in Costa Rica, Lake Pavin in France). The occurrence of CH_4, whose concentrations in Lake Chanmico were up to two orders of magnitude higher than those recorded in Coatepeque and Ilopango lakes, suggests bacterial methanogenesis. Further surveys to provide isotopic (™^{13}C-CH_4) and microbiological data are needed to support such hypothesis and to investigate the complex biogeochemical processes acting in these lakes.

Dissolved major and trace elements along a vertical profile in Barombi Mbo lake (Cameroon)

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Lake Barombi Mbo (BM) is a maar crater lake (4.1 km^2) located in the Kumba Plain, a volcanic basin in the proximity of Mt Cameroon, Mt Manengouba and the Rumpi Hills, on the Cameroon Volcanic Line. The area is characterised by high rainfall (up to >3500 mm/y) and warm to hot air temperatures (T>26°C). The lake has a round-shaped morphology with an almost flat bottom, a surface area of about 4.1 km^2 and a maximum depth of 112m. Two events of water overturn, resulting in water color changes into brown, and fish kill, were recorded in 1940 and 2012. In the occasion of the IAVCEI-CVL9 Workshop (13-23 March 2016), organised for the 30 years anniversary of the dramatic Lake Nyos disaster, a pioneering geochemical prospection at BM was organized. Thirteen water samples were collected from BM along the vertical profile at approximatively every 10 meters. The main chemico-physical parameters (T, EC and pH) of the water column were recorded by a multiprobe portable instrument. Water sampling was carried out by using a 6 mm diameter Rilsan© tube, lowered at the sampling depth and connected to a 100 mL syringe equipped with a three-way Teflon valve to pump up the water. Samples were analysed for major and a large suite of trace elements. Lake water temperature did not show significant variations along the profile, ranging from 30°C, at the surface, to 26°C, at the bottom. Collected waters are characterised by low electrical conductivity (from 0.06 to 0.13 mS/cm) and increase in the deepest layers of the lake; while the pH values range from 8.4 at the surface to 6.8 in the deeper layers (> -20 m). HCO_3 is the dominant dissolved component, followed by Ca, Mg and Na. The increase of HCO_3 in the vicinity of the lake bottom is a frequently observed phenomenon in active volcanic lakes, due to interaction with CO_2 of magmatic origin. Major cations, together with B and Fe, show a positive correlation with HCO_3 content and an inverse correlation with pH, indicating an intense rock leaching. Sr and Ba are the most concentrated among the trace elements. The redox sensitive elements show a different behaviour: Mn and Fe are absent in the upper 20 m of oxidised water, whereas V is generally more concentrated. These preliminary results highlight that the lake is stratified, with a thermocline at 20 m depth and a chemocline at about 30-40 m depth, corresponding to the increasing electrical conductivity. Moreover, evidences of CO_2 magmatic input were recognised, although far from supersaturation conditions, underlining the importance follow up studies of this potentially hazardous active system.

Biogeochemical processes in a small Kenyan Rift Valley soda lake (Lake Sonachi): implications for methane emissions

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Biogeochemical sampling was carried out at Sonachi Crater Lake, a small (0.18 km^2) soda lake of volcanic origin located within the Eastern Rift Valley, 90 km NW of Nairobi (central Kenya), immediately south-west of lake Naivasha. The lake is protected from winds by steep crater walls and the water level is regulated by rainfall, very limited runoff, evaporation and groundwater inflow. Despite its shallowness (max depth approx. 5 to 7 m), Lake Sonachi shows a permanent strong chemical stratification with a meromictic structure consisting of (i) an upper water layer (mixolimnion; EC around 9.8 mS cm^{-1}), affected by diel stratification and mixing, and (ii) a deeper and persistent layer (monimolimnion; EC up to 20 mS cm^{-1}). Meromixis is reinforced by high amount of organic solutes accumulated at the bottom (up to 500 ppm of dissolved organic carbon) related to leaching and degradation of abundant organic matter stored in sediments. Dissolved gas concentrations along the water column are largely regulated by biological processes, i.e. by a balance between photosynthetic production and microbial consumption. Aerobic metabolism consumes oxygen in the mixolimnion, whilst microbial respiration in the anoxic deep layer leads to a significant accumulation of ΣS^{2-} and CH_4, as well as CO_2. The high pH (~9.5) limits CO_2 concentration in bottom waters, where CH_4 is abundant (up to 615 µmol L^{-1}). $\delta^{13}C\text{-}CH_4$ values $\leq$-60 ‰ vs. V-PDB point to the occurrence of methanogenic activity even in the presence of relatively high SO_4^{2-} concentrations. The coexistence of methanogens with sulphate reduction processes is probably favoured by the large availability of accumulating organic matter. Moreover, in the aerobic epilimnion, high CH_4 concentrations (~150 µmol L^{-1}) suggest that oxidation is counteracted by biogenic CH_4 production even in oxic conditions, as confirmed by a sharp decrease in $\delta^{13}C\text{-}CH_4$ values. Concentrations of dissolved CH_4 measured in lake's epilimnetic waters are several orders of magnitude higher than those expected for equilibrium with atmosphere. The estimated water-air CH_4 exchange flux, up to ~3.65 g C m^{-2} d^{-1}, is possibly the largest diffusive flux ever measured from a lake, according to available literature. Moreover, our simulations indicate that ebullition along the water column might further contribute to CH_4 emissions from the lake, a factor that might become increasingly relevant because of current and future potential temperature increase.

Petrogenesis of rocks from Nyos maar (Cameroon): Implication for plumbing below the volcano

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Lake Nyos is one of over 35 maar volcanoes on the Cenozoic – Present mainly alkaline Cameroon volcanic line in west central Africa. The lake released a large amount of carbon dioxide 30 years ago, that killed many people and animals, but its underlying plumbing and formation history are not known. Knowledge on its plumbing and formation history is important for hazard evaluation. We present new whole-rock major and trace element data for 45 samples from and around the Nyos maar. SiO_2 contents are within 52 - 45wt%, total alkalis vary from 5.3 - 3.9 wt%, and MgO varies from 10.5 - 6.1wt%. Most samples classify as hawaiites. Major and trace element variations distinguish rocks of the volcano into 2 groups. Group 1 rocks have lower MgO, CaO/Al_2O_3, but higher Al_2O_3, FeO*, K_2O and P_2O_5. Compatible trace elements (Ni, Cr, V, Co) are lower in group I than in group II rocks. However, primitive mantle (pm) and chondrite-normalized trace elements patterns show similar trends for the 2 groups: marked K and Ti troughs, a prominent Pb peak that corresponds to the composition of the local Nyos continental crust, and similar enrichment in LREEs (average La/Yb ~17pm). High field strength elements (HFSEs) are highly fractionated, with average Ti/Eu ratio ~25% lower, and Zr/Hf ratio ~30% higher, than in chondrites. Thin sections of the 2 rock groups do not show mineral zoning. When screened for meteoric alteration and crustal contamination, the data suggest that magmas that formed the 2 groups were produced by small degree partial melting of the same garnet-bearing ocean island basalt (OIB)-like asthenospheric mantle source. After separation from the source, the magmas then evolved mainly by fractional crystallization in independent magma batches, and subsequently erupted without mixing. The HFSE composition of Nyos rocks suggests that the source was previously 'spiked' by carbonatitic fluids. Such a geochemical mantle process (carbonate metasomatism) might be responsible for the CO_2 that is venting into Lake Nyos and nearby soda springs today. Our work should constitute an important basis for hazard and vulnerability analyses in the rehabilitation of the Lake Nyos area for potential return of the 1986 gas disaster victims.

7. Carbon dioxide degassing at volcanic lakes: theory and practice

<u>Conveners:</u> Artur Ionescu & Agnes Mazot

The carbon cycle of East Lake, Newberry Volcano, OR

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We determined carbon fluxes and their ™^{13}C values at East Lake (EL) in the Newberry volcano caldera (OR, USA) at ~2km elevation. The lake is a 60m deep drowned crater with a large shelf area of ~20m water depth, which formed ~ 6500 years ago. EL freezes from November until April, and becomes thermally stratified in the spring-summer with a thermocline at 15-20m depth. Bottom waters remain at 4 ^{o}C year-round. Volcanic CO_2, with minor H_2S and Hg, is vented through the lake bottom, especially near hot springs on the beach that extend into the lake. In winter, volcanic CO_2 dissolves and accumulates below the ice, only starting to escape again upon ice melting.

We measured diffusive surface CO_2 fluxes with a *West* float chamber in June-August from 2015 through 2018, with a 5th field trip in mid-May 2018, just after ice melt. We collected chemical and physical data including ™^{13}C(DIC) along depth profiles, and determined ™^{13}C(CO_2) - ™^{18}O in air samples and accumulation chamber gas. In summer, 40-50 tonnes CO_2/day escaped from EL, whereas 95 tonnes CO_2/day were measured in May. We fitted an exponential decay function to the data to model the release of accumulated winter CO_2. Steady state is established only in the fall; estimated year-round volcanic CO_2 input is ~30 tonnes/day. During 2017-2018, the underwater degassing hot spot near the beach hot springs nearly doubled in extent, without a change in total lake-wide CO_2 flux.

The lake ecosystem is largely fed by geothermal influxes: volcanic/geothermal CO_2, P, and Si are used for photosynthesis and diatom frustule construction. Bioavailable nitrogen is supplied by colonies of cyanobacteria, making this a *geophytic* lake – an ecosystem driven by geologic nutrients from below. Sunshine is the only required external input for this highly productive ecosystem, and the rest is provided by '*the juices of the earth*.' The ™^{13}C(DIC) in the epilimnion increases from ~+2‰ after ice melting to a record-breaking +6‰ in late summer (as compared to non-volcanic lakes, commonly ranging from -20 to 0‰). The hypolimnic waters become depleted in ^{13}C over the summer. Both the escape of isotopically light CO_2 (~ -5‰) and photosynthetic CO_2 sequestration (™^{13}C(algae) ~ -24‰) lead to the high ™^{13}C(DIC) in the surface water, whereas respiration and volcanic CO_2 input (~ -4‰) create a decreasing ™^{13}C(DIC) seasonal trend at depth. Keeling diagrams show mixtures of ambient CO_2 and lake CO_2 gas, the latter with an observed ™^{13}C close to the theoretical value. With these data, we developed a numerical two-box model to simulate the EL carbon cycle, applying the measured C fluxes and long-term average steady state, and using the induced seasonal isotopic gradients as our checkpoints.

This EL study shows 1. the existence of *geophytic* volcanic lakes, 2. that CO_2 flux data for monitoring volcanic activity vary in seasonally frozen lakes, and 3. that the escape of isotopically light CO_2 gas can induce immense carbon isotope fractionations with steep depth gradients (⊗™^{13}C(DIC) = 3-4 ‰). Almost no ambient CO_2 enters the lake, so the waters are devoid of ^{14}C. The volcanic CO_2 carries Hg into EL, leading to extreme Hg-rich fish (2.8 ppm Hg) and sediment (14 ppm Hg) in this natural volcanic lake. The worldwide storage and subsequent escape of winter CO_2 in lakes may dampen the seasonal oscillation and isotopic signals in global atmospheric CO_2.

The Carbon Dioxide Budget of Taal Volcanic Lake

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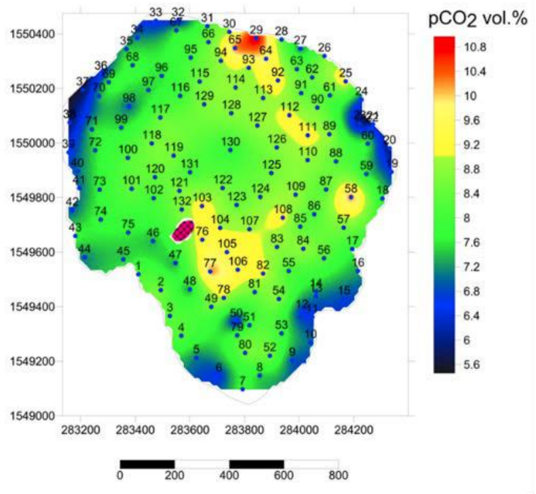
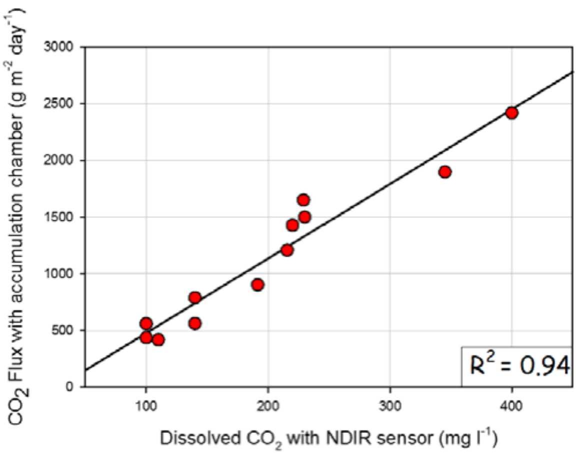
Taal Volcano hosts a lake of warm (~32°C) and acidic waters (pH: 3.0) with a volume of 42 million m^3. The volcanic lake is fed by hydrothermal waters from a subsurface magma-hydrothermal system. The surface waters are highly supersaturated in CO_2 ($\delta^{13}C$ = - 5.83 ‰). Several methods were developed during the past years to obtain a comprehensive view of the different sources of CO_2 entering the lake: to evaluate their respective contributions to the CO_2 stored into the lake waters and to understand how CO_2 is transferred into the atmosphere. During 2011-2018, large variations in the total CO_2 content stored in the lake were observed and ranged between 4,300 and 17,700 T. The residence time of carbon dioxide in the lake is surprisingly short (between 4 and 9 days) and reflects high gas transfer velocities of CO_{2aq} into the atmosphere by diffusion. The calculated k_{600} range from 13 to 33 $cm.h^{-1}$, averaging 22 cm.h-1, for low wind speed conditions (< 2.5m s^{-1}). These values are surprisingly high compared to all previously published models and can be explained by a thermal enhancement effect (evaporation and sensible heat fluxes) at the surface of a warm volcanic lake.

Distribution of pCO_2 measured in situ with a new headspace method show that a large part of the lake is homogeneous except close to the shoreline where shallow waters are not well mixed with the rest of the lake and two anomalies with higher concentrations related to zones where upwelling waters are identified.





Average flux data obtained with the accumulation chamber method during 12 individual field surveys (between 2011 and 2017) show an excellent correlation (R^2 = 0.94) with dissolved CO_2 measured with NDIR sensor and strongly suggest that diffusion is the main process of CO_2 transfer to the atmosphere.

Echosounder surveys reveal that spectacular degassing is present on the western side of the lake with hundreds of individual gas vents discharging CO_2 gas into the lake. However, evaluation of gas fluxes measured above these bubbling zones clearly shows that direct degassing is a minor contribution (< 20%) to the total amount of carbon dioxide entering the lake. Most of the CO_2 is discharged in the lake in a dissolved form via hot springs.

CO_2 degassing from White Island (Whakaari), New Zealand

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The Tunable Laser Diode (TDL) absorption spectroscopy method has been recently used for estimating CO_2 emissions in different geological settings such as in geothermal and volcanic systems. At White Island, CO_2 concentration measurements were made over 3 transects above the active fumarole fields present in 2014 and 1 above the lake. The mean CO_2 concentration for the first transect was about 466 ppm (± 35 ppm), with the maximum value of 657 ppm. The high CO_2 concentrations measured in the crater floor is explained by the enclosed environment of the crater making difficult for the volcanic gases to escape to the atmosphere and the presence of eddies. For the second transect, the mean background CO_2 concentration was 465 (± 20 ppm) and the highest value was 555 ppm. The values are not as extreme as for the first transect as it is further from the most active fumarole. The third transect measurement was made over an area with two small fumaroles present on the path of the laser. The mean CO_2 value is much lower than the values in the previous 2 other transects (402 ± 10 ppm). The fourth transect measurement was performed across the carter lake above the most active area. The highest CO_2 concentration was 549 ppm with an average of 477 ppm.

CO_2 emission measurements were also made from an airborne platform (plume measurements) and by using the accumulation chamber method (soil gas measurements). From airborne platform measurements, the mean CO_2 emission rate estimated for the period January-November 2011 was 1349 (± 90) t day^{-1} with values ranging from 928 (± 57) to 1930 (± 78) t day^{-1}. The CO_2 flux values, measured by the accumulation chamber, range from 0 to 29,900 g m^{-2} day^{-1} with a mean of 368 (± 45) g m^{-2} day^{-1} (Bloomberg et al, 2014). The total CO_2 emission from the crater floor (629,000 m^2) was estimated to be 130 ± 9.8 t day^{-1}.

Although accumulation chamber and airborne platform measurements are made to accurately estimate CO_2 emission, TDL offers the opportunity to monitor in continuous CO_2 emission above the most active volcanic fumaroles.

Geochemistry and carbon-dioxide flux of the St.Ana crater lake (Ciomadul volcano, Romania)

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The Ciomadul volcano, located in the South Harghita Mountains (Eastern Carpathians, Romania) is the youngest volcano (200-32 ka) built by the Neogene volcanism in the Carpathian-Pannonian Region. This volcanic area is characterized by intense cold gas emissions (CO_2, CH_4, H_2S), in the form of bubbling pools, mofettes and mineralized sparkling waters. The lake has a surface area of 22 ha, a maximum depth of ~6 m and 12 m thick sediments.

Since 2017, we started a survey to constrain the amount of gas released from the crater through measurements of diffuse degassing from the soil, and to constrain the hydrochemistry of the lake to quantify the amount of carbon dioxide dissolved in the water. For the chemistry of the lake, we performed 39 drillings on the ice of the lake in wintertime and sampled the water meter by meter from the bottom, collecting a total of 93 water and 39 ice samples. The pH of the water ranged between 3.35 and 7.12. Based on the chemical composition of the major ions and isotopic parameters the water of the lake is of Ca-Cl-HCO_3 type. The isotopic composition, $\delta^{18}O$ ranging between -10.63 and -1.08‰ VSMOW, δD ranging between -89.4 and -27.2 ‰ VSMOW suggests the meteoric origin of the water with intense evaporation signature. The amount of TDIC varies between 30.41 and 638.56 mg, while the $^{13}C_{TDIC}$ values range between -6.17 and -19.77 ‰ VPDB suggesting the concomitant presence of different sources for CO_2.

For the estimation of CO_2 output around the lake shore a total of 1946 measurement points were selected around the lakeshore. The fluxes of the diffuse CO_2, varied between 0.85 and 12.36 x 10^2 g/m^2/day, much lower in comparison with the older structures of Ciomadul.