Ultra-acid volcanic waters: origin and response on volcanic activity. A review Yuri Taran and Elena Kalacheva Institute of Geophysics, UNAM, Mexico and Institute of Volcanology & Seismology, RAS, Russia

EGU

The moth of the Craterny Creek, Kuntomintar, Kuril Islands (pH = 2.1)

1. Here we discuss mainly ultra-acidic sulphate-chloride waters (pH <3) that discharge at volcanic edifices, that generally, do not host crater lakes.

2. The geographical distribution of this type of thermal water is considered.



- 3. It is shown what processes can be responsible for the formation of these waters
- 4. Criteria are proposed to assess the origin of waters using their chemical and isotopic composition.
- 5. An overview of available data on temporal variations in the composition of such waters over time is made with the discussion about a potential of these waters for monitoring of the volcanic activity.

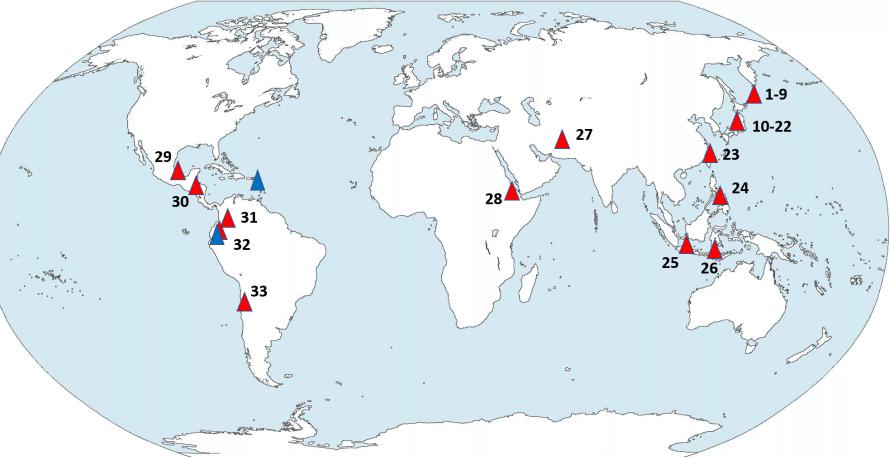
6. Hydrogeological conditions that contribute to the appearance of sources of such waters are also briefly discussed.



Geography

- 1-9 Kuril Islands
 10-22 Japan
 23 Taiwan, Tatun
 24 Philippines, Kaloan
 25 Kawa Ijen, Java, Indonesia
 26 Sirung, Pantar, Indonesia
- 27 Taftan, Iran
- 28 Dallol, Ethiopia
- 29 El Chichón, Mexico
- 30 Poás, Costa Rica
- 31 Nevado del Ruiz, Colombia
- **32** Puracé, Colombia
- 33 Copahue, Argentina





ULTRA-ACID VOLCANIC WATERS - UVW

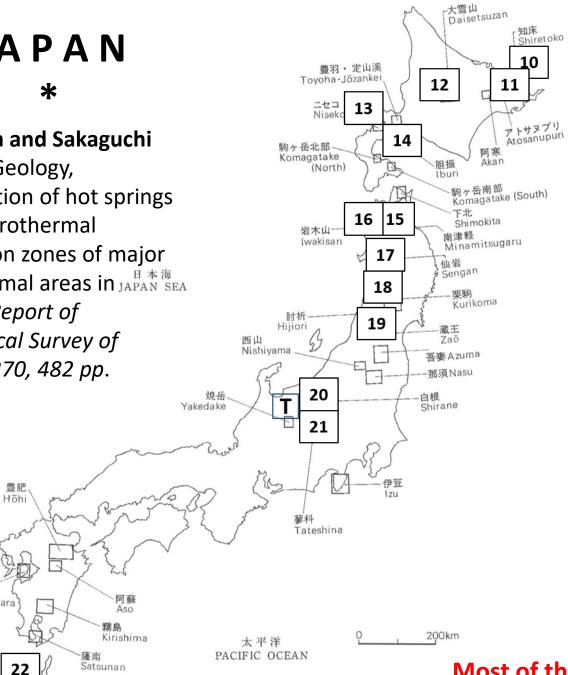
Blue triangles are acidic systems at Galeras volcano, Colombia, and Dominica island in the Lesser Antilles arc. But the published data are controversial

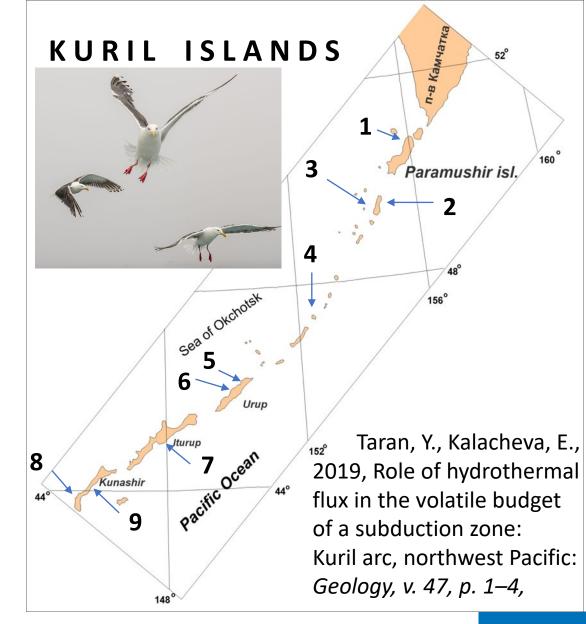
To authors' knowledge, there are no such systems in Kamchatka and New Zealand

JAPAN

Kimbara and Sakaguchi (1989) Geology, distribution of hot springs and hydrothermal alteration zones of major geothermal areas in $_{\rm JAPAN}^{\rm H~{} a \#}$ sea Japan. Report of Geological Survey of Japan, 270, 482 pp.

島原 { Shimabara







Most of the UVW are known in Japan and Kuril Islands





Typical low-pH springs with temperature < 50°C

Possible mechanisms of formation of UVW

Condensation of volcanic gases in groundwaters, recombination of SO2 to H2S, S, and HSO4-

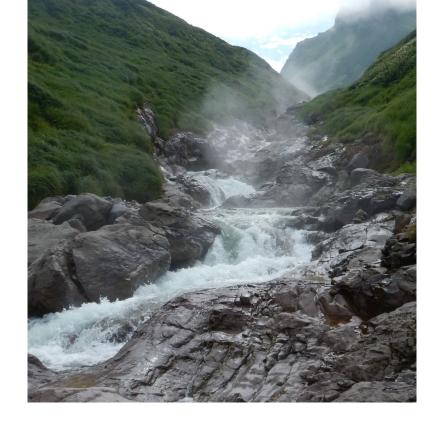
Shallow or superficial mixing of Cl-Na deep and steam-heated shallow SO4 waters. SO4 is the result of oxidation of H2S by O2

Hydrolysis of elemental S at high temperature by Cl-Na water

Water-rock interaction with highly altered rock (advanced arigillic alteration) with additional hydrolysis of S

Superficial oxidation of the dissolved and free H2S of hot hydrothermal Cl-Na fluid.

A combination of two or more mechanisms



Hot Yurieva River. Q ~ 1.5 m3/s, pH < 2, Cl ~ 1 g/l . Paramushir, Kuril Islands



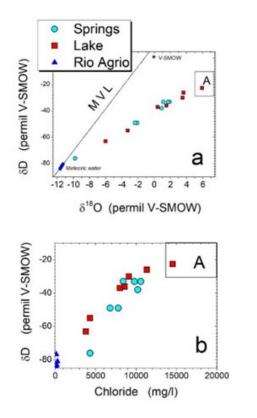
How to choose between the proposed mechanisms?

Isotopic composition
 1.1 Water
 1.2 Sulfur

2. Chemical composition2.1 Anions2.2 Cations

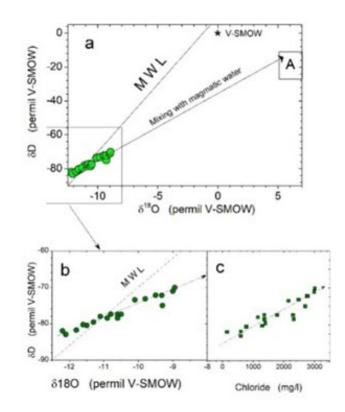


Copahue (Agusto and Varekamp, 2016)



Water isotopes

Does not work with low Cl concentration and in tropical zones (high δD in meteoric water) Yurieva, Paramushir – Kurils (Kalacheva et al., 2016)

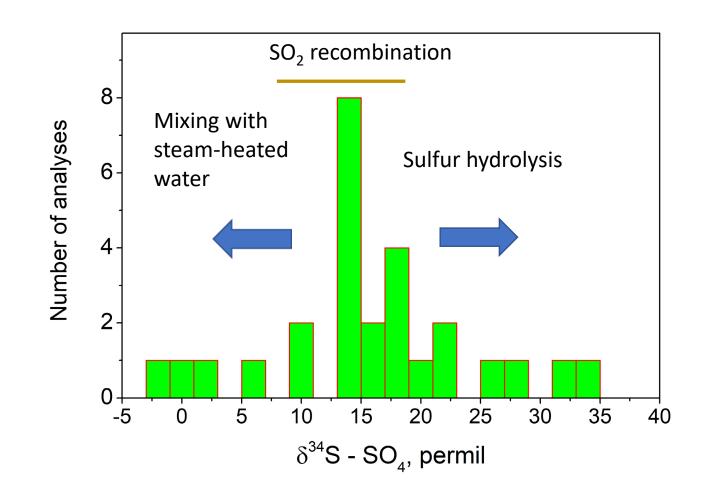


High Cl concentration, mixing between magmatic and meteoric endmembers. High probability for the mechanism of the condensation of mgmatuc gases in groundwater

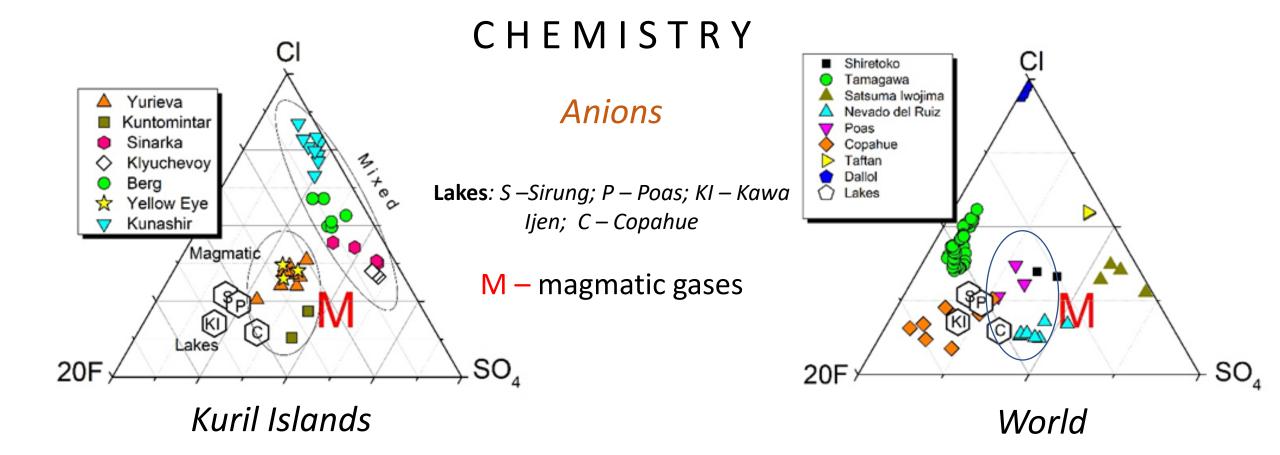
Same, but with much lower Cl concentrations.



Sulfur isotopes

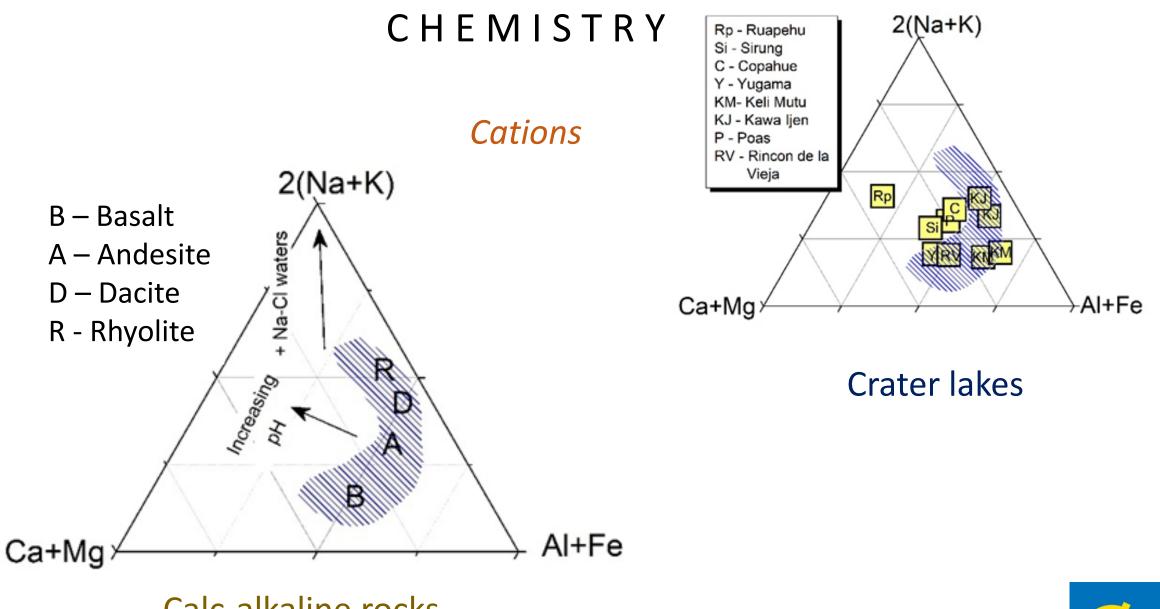






Higher CI, lower F – more hydrothermal component



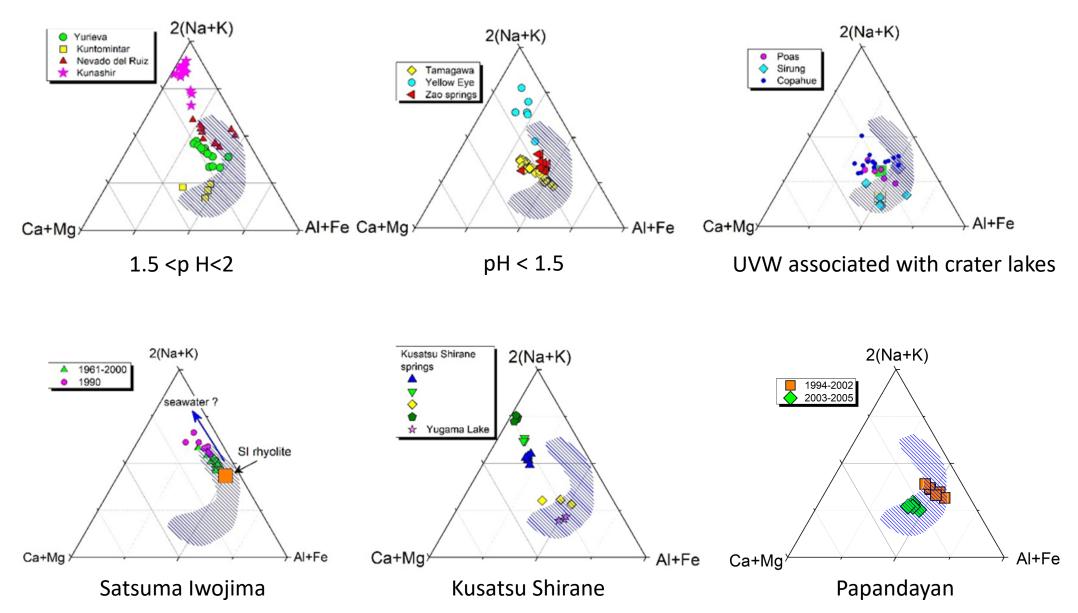


Calc-alkaline rocks



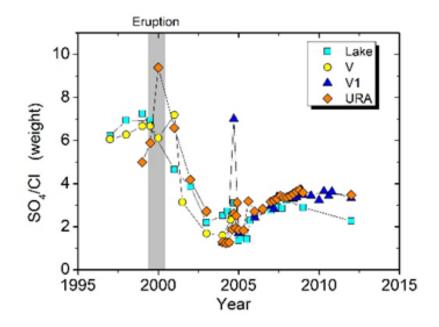
CHEMISTRY

Cations





TEMPORAL VARIATIONS OF ULTRA-ACID VOLCANIC WATERS 1. UVW associated with crater lakes: Copahue and Poás



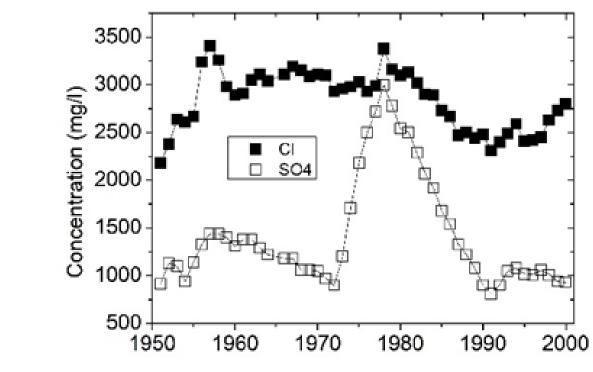
 Rio Agrio 10 Crater lake (weight) 8 SO4/CI 84 85 92 86 88 89 90 91 87 Year

Copahue: spring V1 and Rio Agrio repeat variations in SO4/Cl recorded for the crater lake. Short recharge time **Poás**: Rio Agrio springs repeat SO4/Cl Ratio recorded in the crater lake before 1986 Long recharge time, > 3 years.

Agusto and Varekamp, 2016; Rowe et al., 1995



 UVW associated with volcanoes without historical eruptions Obuki springs, Tamagawa Group, Japan Yoshiike, 2003



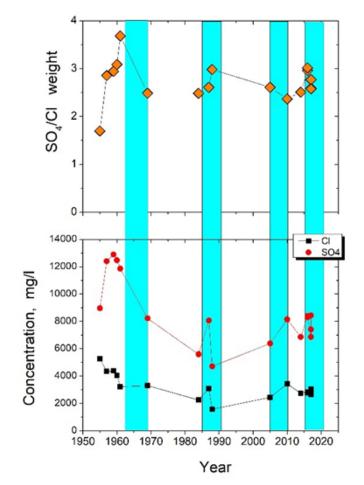
SO4/Cl (weight) from 0.3 to 0.9

Isotopic data suggest a temporal increase in the magmatic contribution



year

3. UVW associated with volcanoes with phreatic and phreatic-magmatic eruptions



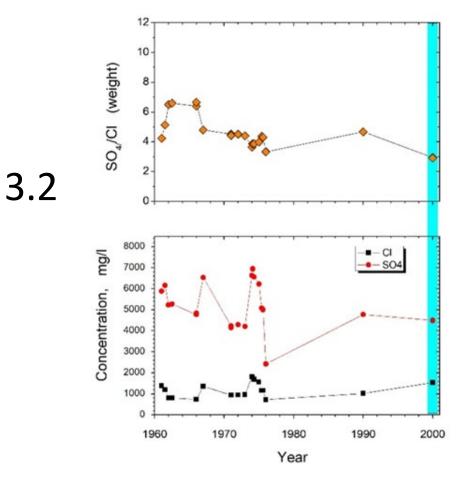
3.1

Yurieva Springs, Paramushir, Kuril Islands. 500 m lower the fumarolic fields of Ebeko volcano. 90°C, Flow rate > 200 l/s. Blue bands – periods of phreatic activity of Ebeko

The response is seen in the increase of concentrations of SO4 and Cl and in the SO4/Cl ratio. Difficult to say about precursors



3. UVW associated with volcanoes with phreatic and phreatic-magmatic eruptions



Higashi Springs, Satsuma Iwojima Island – volcano 70°C, at the base of the volcano on the seashore. Explosions in the cráter with formation of a small pit crater in 1998

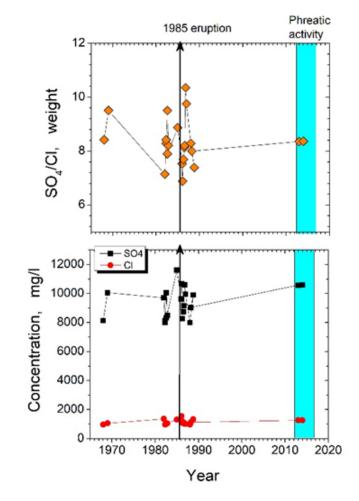
Strong variations in concentrations but not in ratios, and without visible response on the phreatic event.

Need more data...

Shinohara et al., 1993; Sakamoto, 2015



3. UVW associated with volcanoes with phreatic and phreatic-magmatic eruptions



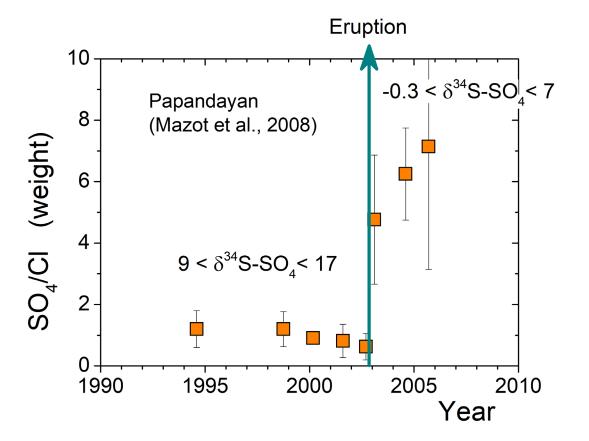
3.3

Nevado del Ruiz, Colombia. Agua Caliente springs. Strong fluctuations around the date of the 1985 eruptions in both concentrations and ratios. No more data

Sturchio et al., 1990, Federico et al., 2017



3. UVW associated with volcanoes with phreatic and phreatic-magmatic eruptions



3.4

Papandayan volcano, Java, Indonesia

Acidic springs. Response on the phreatic eruption in November 2002. Increase in the SO4/Cl ratio with additional contribution of sulfate from hydrothermal source (see differences in the sulfur isotopic composition of disolved sulfate)

Mazot et al., 2008



CONCLUSIONS

- The data are presented on the chemical composition of more than 30 systems of ultraacid thermal waters discharging on the slopes of volcanoes in various volcanic regions of the world (UVW - ultra-acidic volcanic waters).
- The systematics of these waters is presented based on their chemical composition, the isotopic composition of sulfur sulfate and partially based on the isotopic composition of water.
- The mechanisms of formation of UVW are discussed and it is shown how, using their anionic and cationic composition, as well as the isotopic composition of sulfur sulfate, it is possible to interpret the features of formation of a specific UVW system.
- Temporal variations in the composition of some UVW systems are shown, with relation to the discussion of the problem of UVW monitoring in order to track the activity of the host volcano. It is assumed that an important parameter in this case is the recharge time of the system. Only with short recharge times the UVW chemical response may precede the observed volcano activity, and monitoring can make sense.



