Ultra-acid volcanic waters: origin and response on volcanic activity. A review

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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.

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

Most of the UVW are known in Japan and Kuril Islands.
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 argillic 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
How to choose between the proposed mechanisms?

1. Isotopic composition
   1.1 Water
   1.2 Sulfur

2. Chemical composition
   2.1 Anions
   2.2 Cations
**Water isotopes**

Does not work with low Cl concentration and in tropical zones (high δD in meteoric water)

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

Same, but with much lower Cl concentrations.
Sulfur isotopes

SO$_2$ recombination

Mixing with steam-heated water

Sulfur hydrolysis

$\delta^{34}$S - SO$_4^-$, permil

Number of analyses
CHEMISTRY

Anions

Lakes: S – Sirung; P – Poas; KI – Kawa Ijen; C – Copahue

M – magmatic gases

Higher Cl, lower F – more hydrothermal component
CATIONS

Cations

Calc-alkaline rocks

Crater lakes

B – Basalt
A – Andesite
D – Dacite
R - Rhyolite
C H E M I S T R Y

Cations

1.5 < pH < 2

pH < 1.5

UVW associated with crater lakes

Satsuma Iwojima

Kusatsu Shirane

Papandayan
TEMPORAL VARIATIONS OF ULTRA-ACID VOLCANIC WATERS

1. UVW associated with crater lakes: Copahue and Poás

**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
TEMPORAL VARIATIONS OF ULTRA-ACID VOLCANIC WATERS

2. UVW associated with volcanoes without historical eruptions

Obuki springs, Tamagawa Group, Japan

Yoshiike, 2003

SO$_4$/Cl (weight) from 0.3 to 0.9

Isotopic data suggest a temporal increase in the magmatic contribution
TEMPORAL VARIATIONS OF ULTRA-ACID VOLCANIC WATERS

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

3.1


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

3.2

**Higashi Springs, Satsuma Iwojima** Island – volcano 70°C, at the base of the volcano on the seashore. Explosions in the crater 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
TEMPORAL VARIATIONS OF ULTRA-ACID VOLCANIC WATERS

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
TEMPORAL VARIATIONS OF ULTRA-ACID VOLCANIC WATERS

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 SO$_4$/Cl ratio with additional contribution of sulfate from hydrothermal source (see differences in the sulfur isotopic composition of dissolved sulfate)

Mazot et al., 2008
CONCLUSIONS

- The data are presented on the chemical composition of more than 30 systems of ultra-acid 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.