

## Thermal and chemical changes in the crater lake of Copahue volcano (Argentina) prior to the December 2012 phreatomagmatic eruption.

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Copahue volcano is part of the Caviahue caldera (Argentina-Chile), located in the Southern Andean Volcanic Zone. During the last 250 years, at least 12 low-magnitude phreatic and phreato-magmatic eruptions occurred and affected the nearby villages. The onset of the last eruptive cycle started on December 22<sup>nd</sup> 2012. During the hydrothermal activity phase, Copahue volcano hosts a hot acid (30-40 °C, pH~1) crater lake with a diameter ~200 m. Two acidic hot springs (V1 and V2, pH=1-2) on the eastern flank, located at about 200 m below the crater rim, enter the Upper Rio Agrio (pH~2) that discharges into the acidified (pH~3) glacial Lake Caviahue. This study presents the temporal variations of the physical-chemical parameters of the Copahue crater lake along with those of the V1 and V2 thermal springs and the Upper Rio Agrio since 2004, i.e. prior to the phreatomagmatic eruption that occurred at the end of 2012.

In July 2004, ~80% of the lake surface was frozen probably for the first time, while hot springs displayed the highest temperatures: 81 °C V1 and 69 °C V2. From the lake water the deposition of gypsum, quartz, cristobalite and amorphous silica increased. This process likely produced a mineral cap able to partly isolate the lake from the uprising magmatic fluids, explaining the frozen lake in that period. By the end of 2004 the crater lake surface melted again, and during the following years (2005-2010) it had temperatures between 30 and 40 °C, while the outlet temperature of the two hot springs had dropped and remained relatively constant ( $T_{V1}=60-70$  °C, and  $T_{V2}=40-50$  °C). Between 2005 and 2011, the crater lake had no significant changes in temperature, and water level. On the other hand, anions related to the dissolution of magmatic gases progressively increased. Similarly, the discharge rate of fluids from the Copahue summit increased since November-December 2011. In March-July 2012, the crater lake and hot springs were characterized by pH<0, relatively high temperature (65 °C) and high concentrations of magmatic-related species ( $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{F}^-$  up to 42000, 18500 and 2000 mg/L, respectively). The level of crater lake water significantly dropped, and before the December 2012 eruption the lake had become very small (~20 m in diameter). Liquid native sulfur was recognized in the erupted pyroclastic material, suggesting filling of voids beneath the lake or a molten sulfur pool at the lake bottom. As the eruption continued, the crater lake disappeared, the hot springs were covered by a pyroclastic surge and the course of Upper Rio Agrio was modified. Presently, a geochemical monitoring of the acidic springs and Rio Agrio is carried out to forecast the evolution of the volcanic activity at Copahue.