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Tracing changes in SO_2/H_2S ratios in subaqueous fumarole gases by monitoring polythionates in the ultra-acidic crater lake of Rincón de la Vieja Volcano (Costa Rica)

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Rincón de la Vieja is an active stratovolcano located in NW Costa Rica (10°49'40''N, 85°19'42''W, 1805 m.a.s.l.). It hosts a hot ultra-acidic crater lake, which has been the focus of fumarolic degassing and various phreatic eruptions. After Rincón's last phreatomagmatic activity in 1983, a number of phreatic eruptions have been registered in 1983-87, 1991, 1995 and 1998. Some of these events triggered lahars, forcing the evacuation of some villages, and destroyed bridges and aquatic life in some rivers draining the northern flank. Thus, monitoring the degassing activity at Rincón through measurements of physico-chemical properties of the lake is one of Ovsicori's high-priority efforts aimed at minimizing potential hazards from phreatic eruptions. In this work we present time-series trends for polythionates and other relevant physico-chemical and geophysical data for the period 1992-2006. Total polythionate concentrations ranged between 2050 ppm and below detection levels within this period. Overall, the most predominant thionate is tetrathionate, whereas hexathionate is always the least abundant of the species measured. Polythionates have generally been present in the lake, except for some periods. From 1992 to 1998 polythionates were absent or close to detection limits. The average temperature of the lake was 39°C, while the pH ranged between <0 and 1. These physico-chemical conditions together with the occurrence of a series of strong phreatic eruptions in 1995 and 1998 indicate that the

1992-1998 interval was characterized by a high input of heat and volatiles. This could explain the virtual absence of polythionates, since they will decompose at relatively high temperatures and/or via sulphitolytic breakdown (i.e. fumarolic molar SO_2/H_2S ratios could have been much greater than one). In contrast, polythionate concentrations were at their highest levels between 1999 and 2006, reaching 2050 ppm in June 2005 (suggesting a fumarolic molar SO_2/H_2S ratio of around 0.13), despite some occasional sharp drops down to below detection limits, revealing short-lived drastic changes in gas and heat input. Between June 2000 and April 2002, the crater lake showed steadily increasing trends in polythionate concentrations and temperatures. Polythionates reached maximum concentrations in February 2001, but by July 2001, when the lake reached 58°C and the pH was lowest, they were hardly detectible. This condition persisted until December 2002 when polythionates re-appeared in quantities on the order of several hundreds of ppm. Thus, it can be inferred from the observations that the thermal and volatile input between 2000 and 2002 became so strong that polythionates were decomposed.