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Carbon sources and biogeochemical processes in Monticchio maar lakes, Mt Vulture volcano (southern Italy): New geochemical constrains of active degassing of mantle derived fluids

A. Caracausi, P.M. Nuccio, R. Favara, and F. Grassa
INGV, Palermo, Palermo, Italy (a.caracausi@pa.ingv.it)

Since the catastrophic releases of carbon dioxide from the African volcanic lakes Nyos and Monoun in the 1980s, the scientific community draw attention towards all those crater lakes able to accumulate massive amount of CO_2, which could be catastrophically released following overturn of their deep waters. This implies a quantification of the gas accumulation rate into the lakes and the knowledge of recharge processes and their evolution in time. In fact the gaseous recharge in a lake occurs at alarming rates, when an active degassing of hazardous nature volatiles occurs into the lakes and the structure and dynamic of the lake permit the accumulation of gases into the water.
The Monticchio lakes, LPM and LGM, occupies two maar craters formed during the last volcanic activity of Mt. Vulture occurred [U+F07E] 140 000 years ago. LPM is a permanently stratified lake, with a thick deep volume of stagnant water and a shallower layer affected by seasonal overturn. On the contrary LGM is a monomittic lake with a complete overturn of the water during winter time.
The major dissolved volatiles are methane and CO_2. Dissolved helium is in trace amounts and its isotopic signature ranges between 6.1 and 5.3 Ra (Ra is the atmospheric 3He/4He isotopic ratio). These values are within the range of those measured in the olivine fluid inclusions (both of mantle xenoliths and dispersed in the pyroclastics) of LPM maar ejecta.
During three years of investigations we observed that dissolved methane in the deep waters of LGM drastically decreases in wintertime as consequence of the complete overturn of the water. The isotopic signature of methane in the deepest portions of LGM (both sediment and water) is quite stable with time and highlights a biogenic origin, being produced both by acetate fermentation and by CO_2-reduction in variable proportions. In contrast, a higher contribution of methane produced via CO_2 reduction characterizes sediments at shallower depths.
At LPM, there is a great difference in methane contents between shallower (< 14m) and deep water, being CH4 concentrations higher in the stagnant volume of waters. Nonetheless the large gradient in methane contents (CH4 increases with depth) observed in the deep waters both C and H isotopes of methane remain constant with depth. In contrast, in the shallow waters the changes in dissolved CH4 contents are accompanied with modifications in the isotope signature of methane thus indicating that oxidation processes seem to be relevant only at a depth lower than 14 m. It is striking that in this lake, CO_2-reduction is thought to be the main methanogenesis pathway for methane dissolved in the waters, while in the sediments methane is mainly produced by acetate fermentation.
As methanogenesis processes leads to both bacterial consumption and production of CO_2, the quantification of these becomes fundamental in inferring the nature and the quantitative releasing of carbon dioxide of magmatic origin and estimation of its isotopic signature. The re-calculated isotopic compositions (-7 ‰ [U+F064]13C<-1 ‰ fall within typically magmatic values, furthermore they fall also in the range of Mt. Vulture carbonatites. The computed values of C/3He (2-8 x 109) are in the range of sub-continental mantle. As the Monticchio lakes can be view as natural geological reservoirs subjected to injection of bio and a-biogenic gases, this study shows that amounts and isotopic signature of methane coupled to total dissolved inorganic carbon is a sensitive tool to evaluate the amount of mantle-derived fluids carried into groundwater feeding the lakes.