Biogeochemical processes involving dissolved CO_2 and CH_4 at Albano, Averno, and Monticchio meromictic volcanic lakes (Central-Southern Italy)

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Meromictic lakes hosted in non-active volcanoes may store large amounts of gases, mainly CO2 and CH4, produced by: (i) sub-lacustrine hydrothermal vents or (ii) microbial activity. The occurrence of a gas reservoir in the deep layers favours a clear vertical chemical and isotopic stratification.

This study focuses on the chemical and isotopic features of dissolved CH4 and CO2 in four meromictic lakes hosted in volcanic systems of Central-Southern Italy: Albano (Alban Hills), Averno (Phlegrean Fields) and Monticchio Grande and Piccolo (Mt. Vulture). The δ13C-CH4 and δD-CH4 values of dissolved gases from the maximum depths (from -66.8 to -55.6‰V-PDB and from -279 to -195‰V-SMOW, respectively) suggest that CH4 is mainly produced by microbial activity. The δ13C-CO2 values of Grande, Piccolo and Albano (from -5.8 to -0.4‰V-PDB) indicate a significant CO2 contribution from sub-lacustrine vents originating from (i) mantle degassing and (ii) thermometamorphic reactions involving limestone, i.e. the same CO2 source feeding the regional thermal and cold CO2-rich fluid emissions. In contrast, the relatively low δ13C-CO2 values (from -13.4 to -8.2‰V-PDB) of Averno seem to indicate prevalent organic CO2, although preliminary δ13C values in CO2 discharged from nearby thermal springs (Stufe di Nerone), consistent with those of Averno, support the idea that this restricted area is characterized by an isotopically anomalous carbon source. On the whole, the chemical and isotopic compositions of dissolved CO2 and CH4 at different depths in the four investigated lakes mainly depend on (i) CO2 inputs from external sources, (ii) CO2-CH4 isotopic exchange and (iii) methanogenic and methanotrophic activity. In the epilimnion, vertical water mixing, free oxygen availability and photosynthesis cause the dramatic decrease of both CO2 and CH4 concentrations. In the hypolimnion, where the δ13C-CO2 values progressively increase with depth and the δ13C-CH4 values show an opposite trend, biogenic CO2 production from CH4 tends to counteract the methanogenesis process which is particularly efficient at the water-sediment interface. Theoretical δ13C-TDIC values, calculated on the basis of δ13C-CO2 values, are not consistent with those measured, indicating a lack of equilibrium between CO2 and the main C-bearing ion species (HCO3-) likely due to the fast kinetics of biochemical processes involving both CO2 and CH4.

This research demonstrates that the vertical patterns of (i) CO2/CH4, (ii) δ13C-CO2 and (iii) δ13C-CH4 can be regarded as promising tools to detect perturbations possibly affecting aerobic and anaerobic layers of meromictic volcanic lakes, such as changes in the CO2 input from sub-lacustrine springs.