Active but hidden role of DOC in the C cycle of Precambrian analogs stratified lakes: an isotopic study

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The dissolved organic carbon (DOC) reservoir holds a critical role in past and modern Earth's surficial biogeochemical cycles both because of its size (*e.g.* oceanic DOC equals the amount of atmospheric CO_2) and involvement in many biogeochemical reactions. Indeed, much of primary fixed organic C is released as DOC, which is then at the start of food chains and fundamental microbial reactions. Isotopic analyses are powerful tracers of such phenomena, either at a global or local microbial scale, and have been widely used in laboratory and natural environments studies for most C-containing phases (dissolved inorganic and particulate organic carbon - DIC/POC, carbonates minerals, *etc.*). However, DOC isotopic data remain scarce in the literature.

Here, we measured the DOC concentrations and isotope compositions through the water columns of four Mexican volcanic crater lakes exhibiting seasonal oxygen stratification, diverse planktonic communities, and deprived of allochthonous DOC sources. In parallel, we analyzed DIC and POC reservoirs, sedimentary organic carbon and carbonate phases in order to constrain the specific role of DOC within the C cycle of these environments (production, recycling, accumulation) and its possible impact on sedimentary records.

The four lakes have high DOC concentrations (representing ~70 times the amount of POC, averaging 2 ± 4 mM; 1SD, n=28) with important variability between and within the lakes. All lakes exhibit peaks of DOC (up to 21 mM), found in the oxic or anoxic zones, or both. $\delta^{13}C_{DOC}$ also cover a broad range of values from -29.3 to -8.7 ‰ (with as much as 12.5 ‰ variation within a single lake).

DOC peaks in depth profiles and associated isotopic variability seem related to oxygenic and/or anoxygenic primary

productivity through the release of excess fixed C in three of the lakes, while in the last one they could be explained by partial degradation and accumulation in anoxic waters. Our results show that DOC records metabolic reactions that would not have been detected if only DIC and POC reservoirs were analyzed. However, despite the prominent role of DOC in the lakes C cycle, variations of $[DOC]/\delta^{13}C_{DOC}$ are not necessarily reflected in the sedimentary organic carbon record.