Dissolved organic matter in two thermal springs of East African rift valley

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1) Introduction and gaps in knowledge

Recent investigations on the C cycle in aquatic ecosystems have been focusing on the role of hydrothermal systems in the synthesis, processing and transformation of dissolved organic matter (DOM). Several looked at how marine DOM is reworked and degraded when it recirculates through sub-aquatic hydrothermal vents at oceanic ridges (Rossel et al., 2017), deep water volcanic mud (Brogi et al., 2019) or, in shallow hydrothermal systems (Gomez-Saez et al., 2016); at the same time however, *very little is known about DOM chemodiversity in continental hot springs/geyser*

2) Questions and Objectives

The main goal of this study consists in enhancing our knowledge about DOM molecular properties in continental hot springs.

We focus on two sites located in the East African Rift, a region with well-known volcanic activity where dozens of hot springs border highly productive saline-alkaline lakes. Results from the present study were compared with data from a smalls volcanic soda lake in the region (Sonachi, Butturini et al., 2020) and placed within a larger context to compare them with other hydrothermal systems studied elsewhere.

Study sites

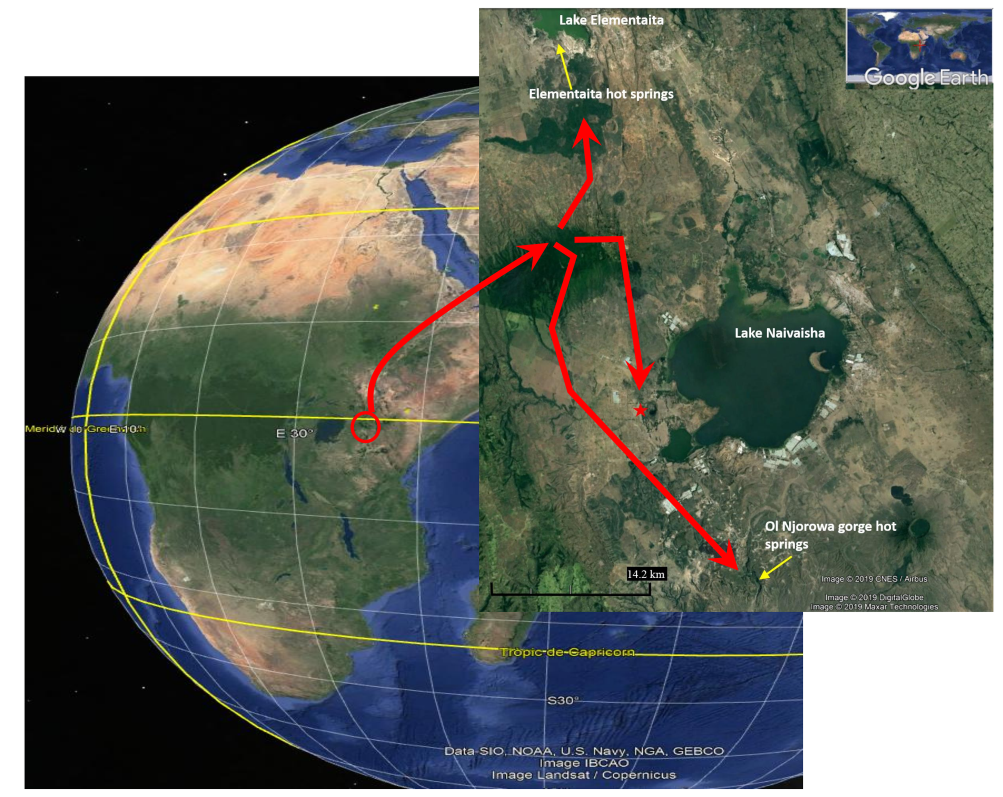

Figure 1. Study site locations (yellow arrows). Red star indicates the position of Lake Sonachi (a meromictic soda lake (Butturini et al., 2020).

3) Results. Bio-Geochemistry: alkaline hot springs

Sample ID	pH	CO_2 -----(µmol L^{-1})----	CH_4	$SUVA_{254}$	DOC ---------(mg L^{-1})---------	S^{2-}	SO_4^{2-}	Ca^{2+}	Na^+	K^+	F^-	Mn ------(µg L^{-1})------	Fe	Li	As
Sonachi (Soda lake*)	9.72	2.4	156	4.5	97	7.8	106	3.46	2496	327	130	5.3	30	161	45
Elementeita (Hot spring)	9.16	75	548	0.48	1.67	NA	69.1	10.6	784	29.4	79.8	5.0	63	253	28
Ol Njorowa (Hot spring)	8.38	>9000*	NA	3.3	0.97	2-18.5*	144	1.04	478.02	23.73	45-80*	70.22	1.8 10^3	590	87.03

3) Results. DOM Spectroscopy and SPE-DOM FT-ICR-MS

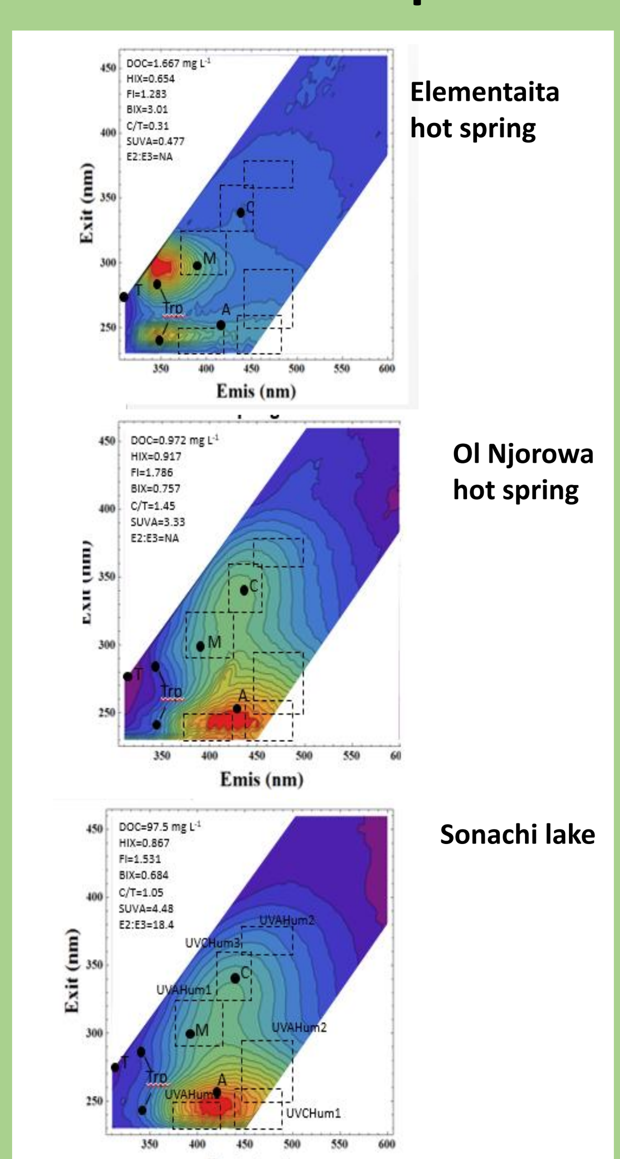

Figure 2. EEMs from Ol Njorowa, Elementaita hot springs and mixolimnion of Lake Sonachi. Black dots indicate the position of fluorophore peaks commonly detected in freshwater: A, C (high molecular weight humic-like) , M (low molecular weight humic-like), T and Trp (protein-like tyrosine and tryptophan peaks respectively).

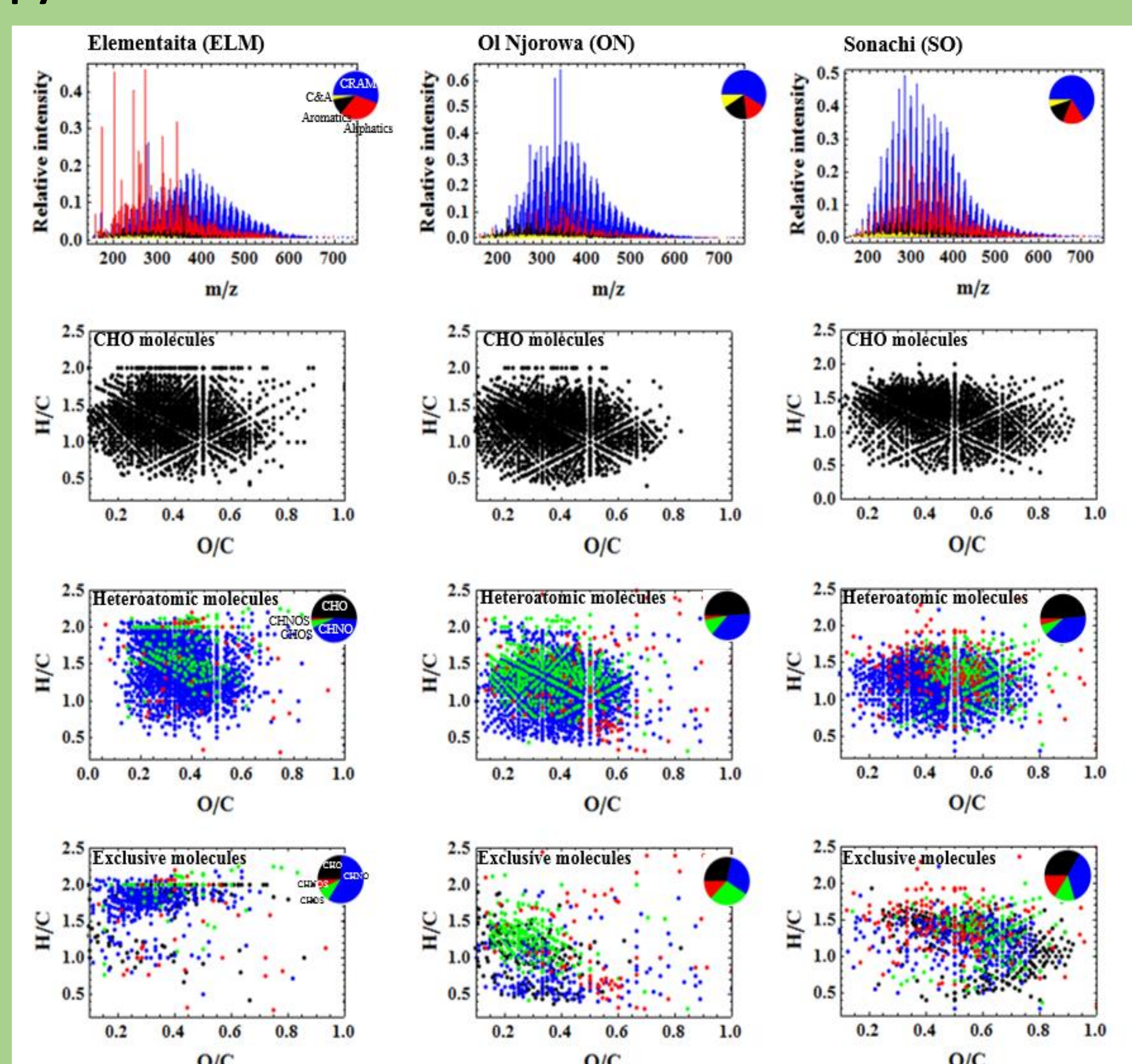

Figure 3. SPE-DOM FT-ICR-MS spectra and associated van Krevelen diagrams for Lake Sonachi, ELM and ON samples and their exclusive molecular footprints. Pie plots indicate the frequency of CHO and CHOx molecules.

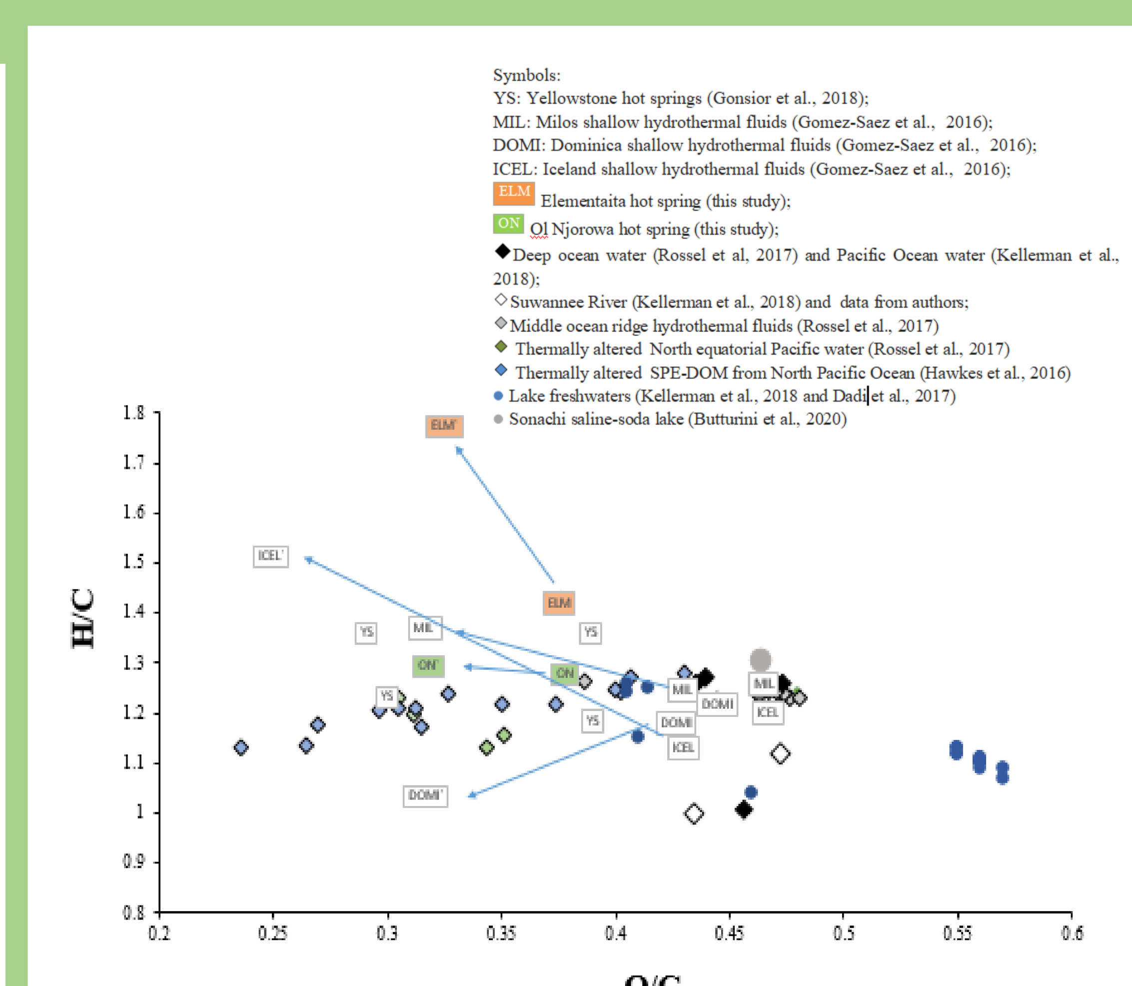

Figure 4. Plot of weighted H/C *vs* O/C values in different SPE-DOM samples collected in different hydrothermal systems or altered by heat experiments. Values from freshwater lakes are provided for comparative purposes. Arrows highlight the difference between weighted O/C and H/C ratios in SPE-DOM from a sample and the same ratios estimated by considering the molecules detected exclusively in that sample.

4) Conclusions

1) The DOC concentrations estimated at ELM and ON were within the same range of those reported in Yellowstone (Ball et al., 2002), suggesting that samples were not in contact with lixiviates derived from terrestrial vegetation and/or soils (the case of ON sample), nor with waters of Lake Elementaita that have extremely high DOC concentrations.
2) In a spectroscopic context, the two samples showed opposite signatures; the ELM sample had an unusual protein-like signal, which is missing in ON and in Yellowstone hot springs (Gonsior et al., 2018).
3) SPE-DOM from ELM and ON were strongly reduced with an O/Cw ratio in the range of that reported for the Yellowstone hot springs (O/C<0.4), which in turn, were lower than values typically reported for freshwaters (O/C>0.45).
4) SPE-DOM from ELM and ON were strongly reduced with an O/Cw ratio in the range of that reported for the Yellowstone hot springs (O/C<0.4), which in turn, were lower than values typically reported for freshwaters (O/C>0.45).
5) The H/Cw value of ELM`is the highest reported so far for SPE-DOM in hydrothermal waters. The ELM hot spring is the only example, among those included in Figure 4, which is located in proximity of a lake. Elementaita hot springs perfuse through organic-rich sediments reintroducing buried organic carbon (mainly aliphatic) into the lacustrine system. The presence of high amounts of dissolved CH_4 measured at ELM provides a clue to the presence of an active subsurface prokaryote community.
6) At ON, the most prominent property of DOM-SPE was the abundance of sulfur-bearing molecules. Evidencing that at ON the hydrothermal system acts as a remarkable source of S-bearing reduced DOM, which in turn might reflect DOM sulfurisation together with dehydration

5) Literature

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