Reconstructing southeastern Mediterranean bottom and surface water environments during Sapropel S1 using laser-ICPMS elemental ratios on foraminiferal shells

Meryem Mojtahid, R. Hennekam, Lennart Jan de Nooijer, Gert-Jan Reichart, G.J. Jorissen, Gert de Lange

Reconstructing southeastern Mediterranean bottom and surface water environments during Sapropel S1 using laser-ICPMS elemental ratios on foraminiferal shells

M. MOJTAHID[1], Hennekam, R.[2,3], De Nooijer, L.[3], Reichart, G.J.[2,3], Jorissen, F.[1], de Lange, G.[2]

[1] LPG-BIAF UMR-CNRS 6112, University of Angers, UFR Sciences, [2] bd Lavoisier 49045, Angers Cedex 01, France (meryem.mojtahid@univ-angers.fr; frans.jorissen@univ-angers.fr); [2] Department of Earth Sciences-Geochemistry, Faculty of Geosciences, Utrecht University, P.O. Box 80.021, 3508 TA Utrecht, The Netherlands. F.M.Hennekam@uu.nl; G.J.Reichart@uu.nl; G.J.deLange@uu.nl.; 3 Marine Geology and Chemical Oceanography, Royal Netherlands Institute for Sea Research, Landsdiep 4, 1797 SZ 't Horntje Texel, The Netherlands. Lennart.de.Nooijer@nioz.nl.

Figure 1. Core location PS009PC (32°07.7'N, 34°24.4'E; 552 m water depth. SW: Mediterranean Surface Waters. The red arrows show modern surface water circulation. Photograph of the core with the location of S1 (Mojtahid et al., 2015).

Salinity ?

Quantitative estimates of salinities (Na/Ca = (0.22*Salinity)-0.75; [4]) (Fig. 2):

- Unrealistic values compared to the litterature (Figs. 2a-c; f-h).
- The difference of ~2.9 units between the max and min Na/Ca$_{G. ruber}$-surface salinities during S1 (Fig. 2f) is coherent with the litterature (Fig. 2h) > the general trend of salinity variation is correctly described.

The possible factors leading to low salinity values using Wit et al. calibration :

1) Calcification rate and ontogenetic effect: In Wit et al. (2013), Na/Ca ratios measured on *A. tepida* (<200 µm) correlated negatively with test size (Fig. 2e). This size effect is absent in our samples (>200 µm) (Fig. 2e) > As the test grows larger, calcification rates slow down leading to lower E/Ca ratios in the larger tests? This pattern is not found in the different life stages of the measured specimens (Fig. 3; b).
2) Diagenesis and dissolution effects: Na+, due to the charge difference, is not directly substituting for Ca^{2+} during calcite precipitation.
3) Inter-species effect (Fig. 2b): Faster growing individuals have partition coefficients closer to the abiotic seawater than slower growing individuals [5].

Past deep and surface salinity variations during S1:

Two specific periods (↔ S1a and S1b; [2]) with an interrruption at ~8.1 ka (Fig. 2a) :

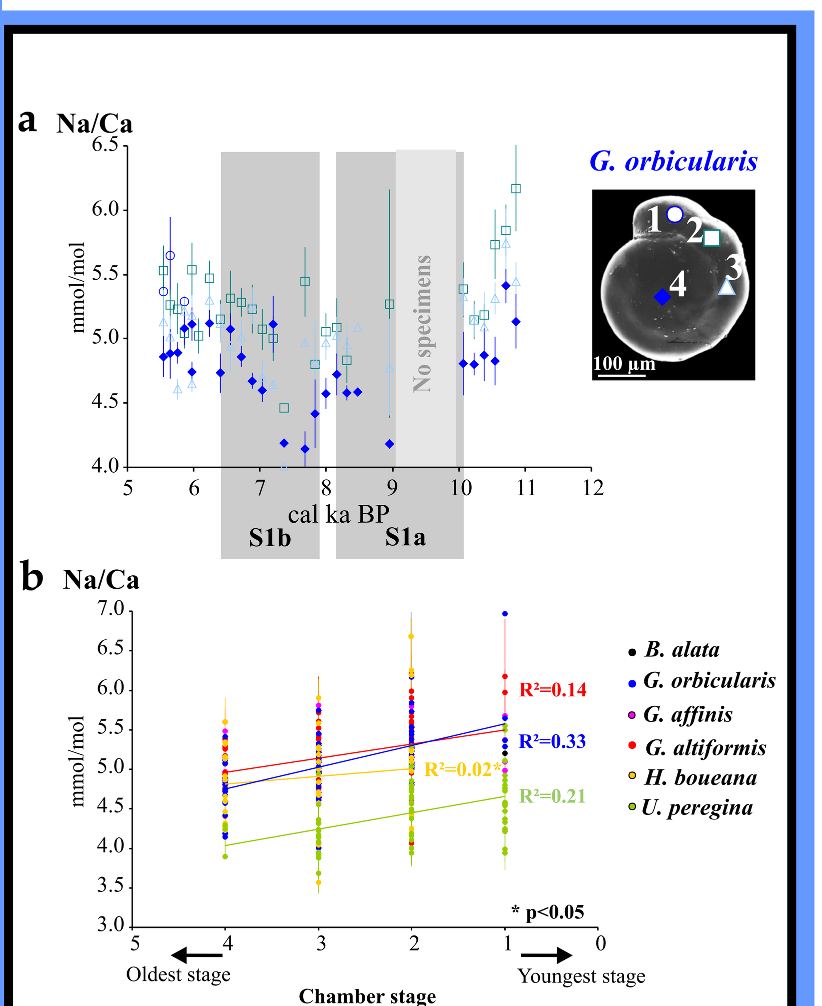

Figure 3. a) Ba/Ca ratios measured in four chambers of *G. orbicularis* during Sapropel S1. b) Ba/Ca ratios in the six benthic foraminiferal species plotted against chamber stages from the oldest to the youngest stage.

Period 1: A rise in bottom water salinities during S1a → Hypothesis: a strong halocline at ~450 m separated stagnant old saline and anoxic waters (see the low abundances of benthic foraminifera (Fig. 2d) and the dominance of low oxygen indicative species (Fig. 2p)) from the well-ventilated upper ocean circulation ↔ the stop of LIW formation?

Period 2: Bottom water salinities raised shortly during S1b before an abrupt drop around 7.6-7.0 ka, followed by a gradual increase (Fig. 2a) → Hypothesis: weakening of the halocline due to decreasing freshwater discharges (as recorded by Na/Ca$_{G. ruber}$; Fig. 2f) → vertical mixing and freshening of deep waters → the LIW gradually formed again in the Aegean leading to the subsequent increase in bottom water salinities as recorded by Na/Ca$_{benthics}$ (Fig. 2a).

Productivity ?

- Enhanced (Ba/Al)$_{sed}$ ratios indicate that more $BaSO_4$ was reaching the seafloor during S1 (Fig. 2i). Enhanced $BaSO_4$ fluxes are a function of both productivity and preservation.

- Ba/Ca$_{benthics}$ ratios recorded during S1 (Fig. 2k) are well correlated to the PFAR (Fig. 2j) often used as a paleoproductivity proxy.

- In surface waters, Ba is usually depleted through the precipitation of Barite [6]. However, runoff of tropical rivers (e.g., Nile) is highly enriched in dissolved Ba and may serve as an additional local source of Ba^{2+} to the Levantine (Fig. 2n). This explains the high Ba/Ca$_{G. ruber}$ values during S1 (Fig. 2m).

- Even though the described feature by Ba/Ca$_{benthics}$ ratios is coherent with the literature when considering all species together (Fig. 2k), some species-specific differences are noted (Fig. 2l) ↔ combination of several effects which are not yet well constrained (e.g., calcification rate and ontogenetic effects, diagenesis and dissolution effects, microhabitat effect).

Study Context

We explore the potential of using Na/Ca, Ba/Ca, and Mn/Ca in benthic and planktic foraminiferal species as proxies for reconstructing past changes in sea water salinity, productivity, and oxygenation. The eastern Mediterranean is a perfect natural laboratory to perform such study as it is the theatre of one of the most spectacular climatic phenomena that led to the formation of Sapropels. Two prerequisites have been suggested for their formation: (a) freshwater flooding leading to stagnant bottom waters with reducing conditions, and (b) high primary production. The present study focuses on the most recent Sapropel (S1; ~10 to 6 cal ka BP) from a sediment core PS009PC located in the southeastern Levantine Basin (Fig. 1). Core PS009PC was earlier studied for its inorganic geochemical properties (Ti/Al, Ba/Al, V/Al), $\delta^{18}O_{G. ruber}$ and $\delta^{13}C_{G. ruber}$ and planktic foraminiferal assemblages [1; 2; 3]. This study presents a unique dataset in the Mediterranean and during such a big environmental change of laser-ICPMS elemental ratios performed on six benthic foraminiferal species and one planktic species.

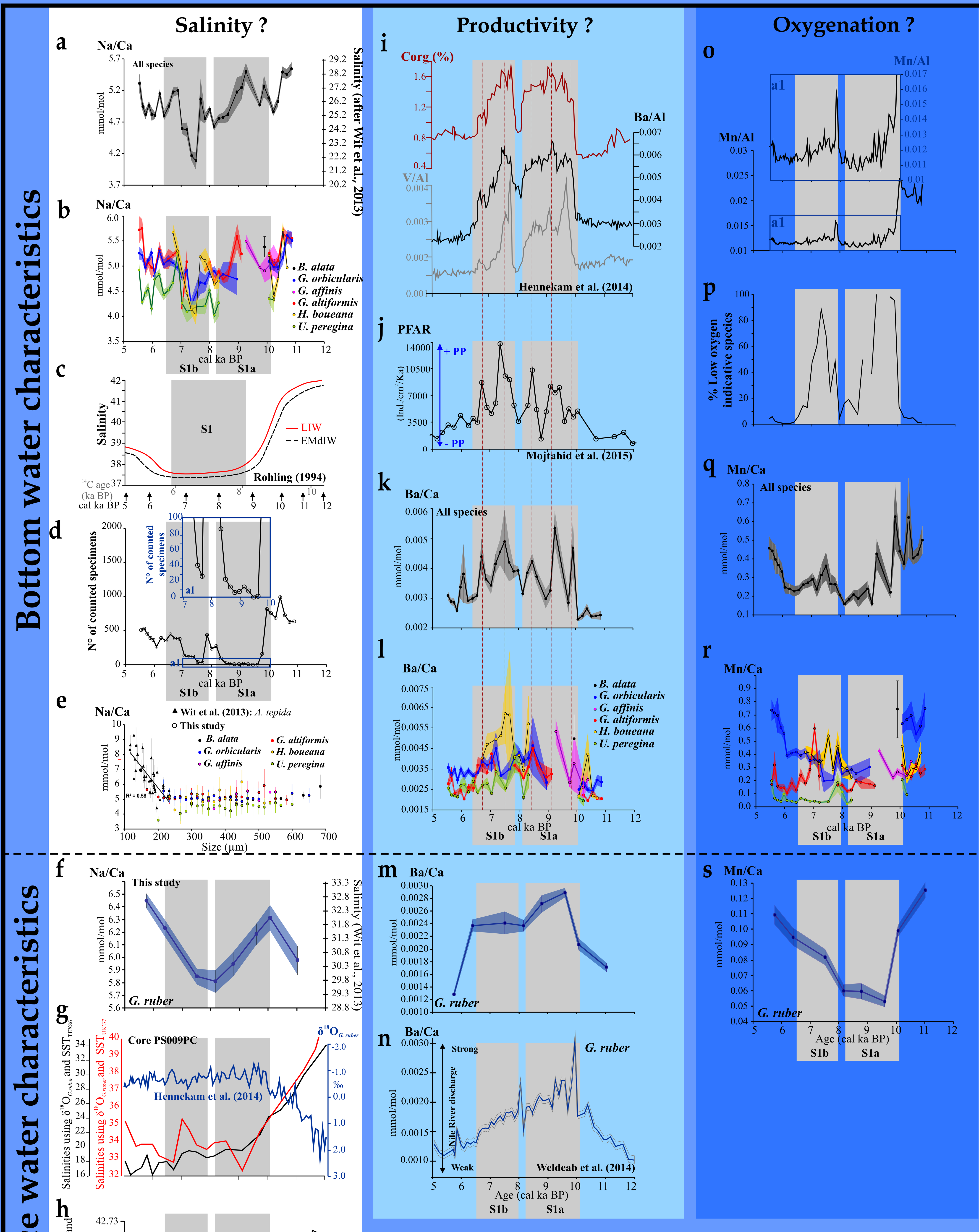

Figure 2. Bottom and surface water characteritics based on productivity, salinity and oxygenation proxies from this study (Ba/Ca, Na/Ca, and Mn/Ca respectively measured by LA-ICPMS on six benthic species (*B. alata*, *G. affinis*, *G. altiformis*, *G. orbicularis*, *H. boueana*, and *U. peregrina* and one planktic foraminiferal species *G. ruber*) and from the literature. PFAR: Planktic foraminiferal accumulation rates. LIW: Levantine Intermediate Waters. EMDW- Eastern Mediterranean Deep Waters. SST$_{UK'37}$ and SST$_{TEX86}$ data are from Castañeda et al. (2010) [8]. Corg, V/Al, Ba/Al, and Mn/Al were measured in the sediment. S1a and S1b: the two phases of Sapropel 1 as defined by Hennekam et al. (2014) [2] in the sediment from the same core.

Oxygenation ?

Several arguments favor the Mn/Ca recording primarily diagenetic processes; the redox signal being at the best drown in the diagenetic signal: a) Our Mn/Ca values are far higher than values of primary shell material (<0.001 mmol/mol; [7]) (Figs, 2q; s), although our study area is under the direct influence of Nile runoff which brought during S1 high C$_{org}$ fluxes to the seafloor (Fig. 2i). b) The absence of the usual anti-correlation between (Mn/Al)$_{sed}$ and (Mn/Ca)$_{benthics}$ (Figs, 3o; q). c) The high Mn/Ca$_{G. ruber}$ ratios (Fig. 3s) are also indicative of the presence of diagenetic Mn coatings as dissolved Mn in surface waters are nearly absent. Alternatively, within S1, there was a significant positive correlation between Mn/Ca$_{benthics}$ (Fig. 3q) and the percentages of low oxygen indicative species (Fig. 3p). This might be the only time where we could discriminate between the redox and the diagenesis signals using our (Mn/Ca)$_{benthics}$.

Conclusions

- Foraminiferal Na/Ca and Ba/Ca present undeniably a good potential for reconstructing paleosalinity and paleoproductivity variability during S1 whereas Mn/Ca is more likely to record primarily diagenetic processes rather than the redox signal.
- Our study also shows that several effects certainly hamper the direct use of the equation Na/Ca = 0.22S-0.75 [4] for quantitative estimates of past salinities → Further calibration studies are needed, for instance, using deep-sea benthic formainifera under a larger range of salinity variation.

References [1] Hennekam and de Lange, 2012: X-ray fluorescence core scanning of wet marine sediments: methods to improve quality and reproducibility of high-resolution paleoenvironmental records, Limnol. Oceanogr. Methods, 10, 991–1003; [2] Hennekam et al., 2014: Solar forcing of Nile discharge and sapropel S1 formation in the early- to mid-Holocene eastern Mediterranean, Paleoceanography, 2013PA002553; [3] Mojtahid et al., 2015: 13,000 years of southeastern Mediterranean climate variability inferred from an integrative planktic foraminiferal-based approach, Paleoceanography, 2014PA002705; [4] Wit et al., 2013: A novel salinity proxy based on Na incorporation into foraminiferal calcite, Biogeosciences, 10(10), 6375–6387; [5] A biomineralization model for the incorporation of trace elements into foraminiferal calcium carbonate, Earth Planet. Sci. Lett., 142(3–4), 409–423; [6] Lea, 1999: Trace elements in foraminiferal calcite, in Modern Foraminifera, pp. 259–277, B. K. Gupta, UK., 1999; [7] Lee et al., 2004: Ontogenetic trace element distribution in brachiopod shells: an indicator of original seawater chemistry, Chem. Geol., 209(1–2), 49–65. Castañeda et al., 2010: Millennial-scale sea surface temperature changes in the eastern Mediterranean (Nile River Delta region) over the last 27,000 years, Paleoceanography, 25(1), PA1208, doi:10.1029/2009PA001740.

Aknowledgments This study makes part of a project MADHO (MediterraneAn Deltas in the Holocene) financed by the international program MISTRALS PaleoMEX. NWO is acknowledged for financial support to PASSAP cruise, PASS2- and PALM-projects. Special thanks to Wim Boer from the NIOZ for his technical support for LA-ICPMS analyses.