Geochemistry of Nummulites as a proxy for early Eocene paleotemperature evolution in the southern North Sea Basin

Article *in* Geologica Belgica · October 2019

4 authors:

Lise Martens
KU Leuven

Peter Stassen
KU Leuven

Robert P. Speijer
KU Leuven

Etienne Steurbaut
Royal Belgian Institute of Natural Sciences

Geochemistry of *Nummulites* as a proxy for early Eocene paleotemperature evolution in the southern North Sea Basin

LISE MARTENS[1,2,*], PETER STASSEN[1,2], ETIENNE STEURBAUT[1,2] & ROBERT P. SPEIJER[1]

[1]*Department of Earth and Environmental Sciences, KU Leuven, Celestijnenlaan 200E, B-3001 Heverlee, Belgium.*
[2]*Directorate Earth and History of Life, Royal Belgian Institute of Natural Sciences, Vautierstraat 29, B-1000 Brussels, Belgium.*
[*]*corresponding author.*

The early Eocene is characterized by sudden temperature peaks (hyperthermals), which are superimposed on a long term warming trend leading up to the Early Eocene Climatic Optimum (EECO). Our research assesses the usability of larger benthic foraminifera (LBF, i.e. *Nummulites*) as a proxy for long-term temperature change towards the EECO, as recorded in the Ypresian deposits of the southern edge of the North Sea Basin. We reconstruct paleotemperatures of this shallow marine setting by use of the Mg/Ca (mmol/mol) ratio of the calcareous tests of nummulites (Evans et al., 2018). Whereas nummulites are absent within the Ypresian clays of the Orchies and Aalbeke Members, they are present in the fine sands of the Mons-en-Pévèle Formation (i.e. pre-EECO assemblage of *N. involutus*; top NP11 to base NP12) and in the Egem sands of the Hyon Formation (i.e. EECO assemblage of *N. aquitanicus*; top NP12).

A detailed methodological study assesses the relationships between nummulite geochemistry and (a) preservation, (b) LBF test size and (c) foraminiferal cleaning techniques. Geochemical analysis using ICP-OES, together with SEM observations of different preservation states, indicates that increasing taphonomic alteration (i.e. partial dissolution of the outer test and recrystallization) results in a continuum of decreasing Sr/Ca and Mg/Ca in the tests, rendering unrealistically low paleotemperatures (Fig. 1). Well-preserved specimens without taphonomic bias are used to evaluate the effect of varying test size on the geochemistry of individual specimens (Egem/Ampe-F2 level). Smaller tests (radius < ± 3.5 mm) record a larger 'natural' variability, while the bigger specimens (radius > ± 3.5 mm) mostly record the upper range of Mg/Ca values. Thus, ontogenetic effects may bias towards higher paleotemperatures and must be taken into account. Traditional cleaning protocols for foraminifera remove elements associated with superficial sedimentary and diagenetic contaminations. Our results show that Fe and Mn are effectively removed during more intensive, chemical cleaning without considerable effect on the Mg/Ca ratio of the LBF tests. These results imply that Mg-contamination by sedimentary and diagenetic coatings is insignificant, and thus do not contribute to the presented paleotemperature estimates. Therefore, a simplified cleaning procedure of well-preserved specimens within a constrained size range is applied to verify mean annual temperature (MAT) changes towards the EECO.

Most nummulites from the Mons-en-Pévèle and Hyon Fms. (Steurbaut et al., 2016) are well-preserved and record reliable Mg/Ca ratios (± 60-85 mmol/mol) and high Sr/Ca ratios (> 1.75 mmol/mol). The MAT estimates reveal a gradual warming trend from 21-23 °C (top NP11) to 24-25 °C (base NP12) before the EECO, rising up to 28 °C during EECO peak warming (top NP12) (Martens, 2018). These MAT and the ± 7 °C warming trend are in agreement with other proxy data (Evans et al., 2018; Bijl et al.; 2009; Vanhove et al., 2011). We speculate that the LBF assemblage changes might be related to the crossing of temperature thresholds of the taxa.

Our observations indicate that nummulites provide useful proxies for the reconstruction of early Eocene temperature evolution in the studied shallow basin. Ongoing research will further reconstruct the temperature evolution of the Eocene and constrain the specific habitat preferences of the recorded nummulite taxa in the southern North Sea Basin and adjacent regions.

References

Bijl, P.K., Schouten, S., Sluijs, A., Reichart, G.J., Zachos, J.C. & Brinkhuis, H., 2009. Early Palaeogene temperature evolution of the southwest Pacific Ocean. Nature, 461/7265, 776–779. https://doi.org/10.1038/nature08399

Evans, D., Sagoo, N., Renema, W., Cotton, L.J., Müller, W., Todd, J.A., Saraswati, P.K., Stassen, P., Ziegler, M., Pearson, P.N., Valdes P.J. & Affek, H.P., 2018. Eocene greenhouse climate revealed by coupled clumped isotope-Mg/Ca thermometry. Proceedings of the National Academy of Sciences, 115, 1174–1179. https://doi.org/10.1073/pnas.1714744115

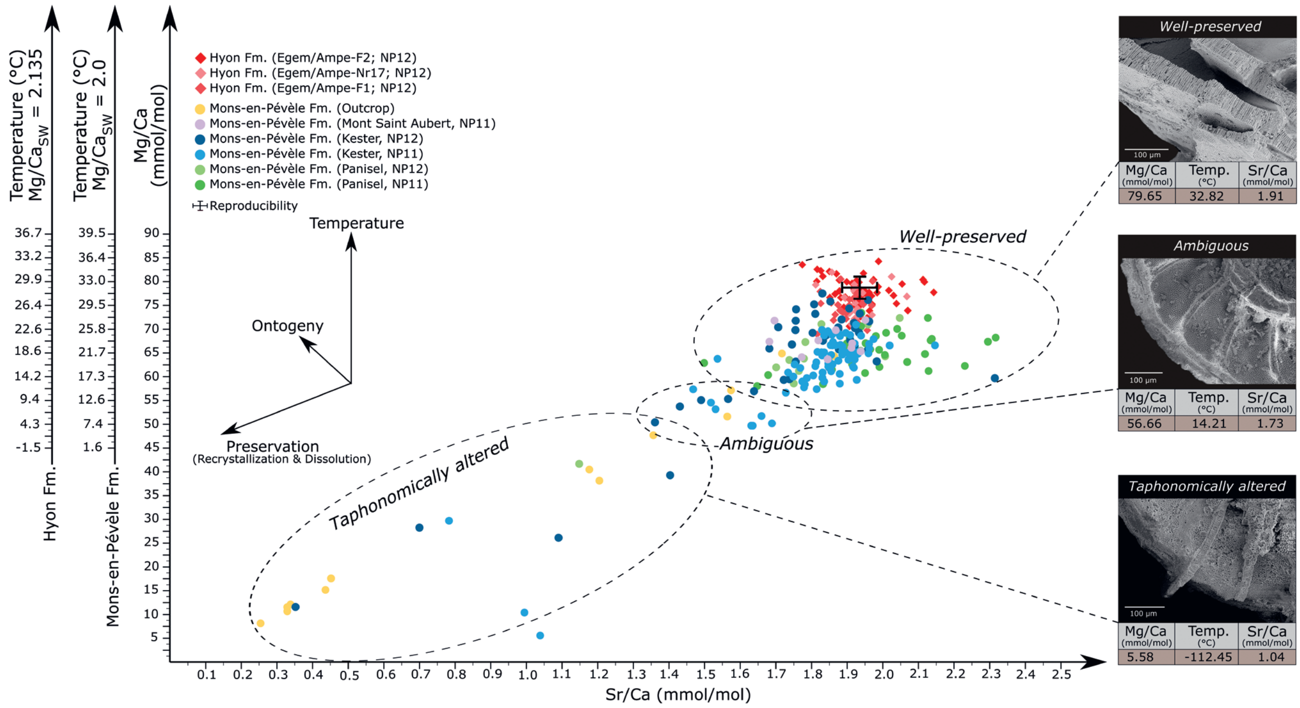

Figure 1. Effect of different preservation states of nummulites on the relationship between Sr/Ca (mmol/mol) and Mg/Ca (mmol/mol), with equivalent paleotemperatures (°C) following Evans et al. (2018). The three preservation classes are exemplified by SEM images.

Martens, L., 2018. Geochemistry of Nummulites as a proxy for Eocene paleotemperature evolution in the Southern North Sea Basin. Unpublished Master's thesis. KU Leuven, Belgium, 158 p.

Steurbaut, E., De Ceukelaire, M., Lanckacker, T., Matthijs, J., Stassen, P., Van Baelen, H. & Vandenberghe, N., 2016. An update of the lithostratigraphy of the Ieper Group, 76 p. https://ncs.naturalsciences.be/sites/default/files/Text%20%20Version%209%20%20Revision%20Litho%20Ieper%20Group%20 15062016.pdf, accessed 08/20/2019.

Vanhove, D., Stassen, P., Speijer, R.P. & Steurbaut, E., 2011. Assessing paleotemperature and seasonality during the early Eocene climatic optimum (EECO) in the Belgian Basin by means of fish otolith stable O and C isotopes. Geologica Belgica, 14/3-4, 143–157.

Natural and artificial tracers in unsaturated zone. Application to Larzac karst

Aurélie MARTIN[1,2,*], Cédric CHAMPOLLION[2], Olivier KAUFMANN[1], Pascal GODERNIAUX[1]

[1]University of Mons, Faculty of Engineering, Geology and Applied Geology, Rue de Houdain 9, 7000 Mons, Belgium.
[2]University of Montpellier, Géosciences Montpellier, CNRS, UA, 34196 Montpellier, France.
[*]corresponding author: aurelie.martin@alumni.umons.ac.be.

The karstic aquifers are an important part of the world's freshwater resources and more particularly around the Mediterranean. These resources are vulnerable to pollution, but also to overexploitation or climate change. It is therefore important to understand better the transfers present in these environments and particularly in the epikarstic zone, the upper part of the unsaturated zone, the most vulnerable and the most recently studied. The unsaturated zone plays an important role in karstic aquifer dynamics, although its functioning is still poorly understood.

Geophysical methods allow imaging the structure of the epikarst. However, studying groundwater transfer in unsaturated zone is still a challenging task. Tracing is then used in this study to remedy this problem and to relate water flow with geological structures. Two tracing types are carried out on two different sites in Larzac (Massif Central, France): artificial tracing (Fluorescein and Sulforhodamine B) and natural tracing (temperature and water level).

The artificial multi-tracer experiment was initiated and interpreted in a calcareous epikarst. The chosen site (Tunnel of St Ferron, Campestre karstic plateau) has the advantage of providing access to the epikarst from the surface and at depth from an anthropogenic tunnel. This facilitates the implementation of this type of tracing. This multi-tracer experiment provides information on the type of transfer and the flow rate in the unsaturated zone. These results, related to the flow hypotheses deduced from the geophysical studies carried out on the zone (gravimetry, electrical resistivity), show the importance of using tracing in addition to geophysical methods to validate the hypotheses of flow and thus better know the epikarst and its functioning.

Natural tracers were studied in a dolomitic epikarst. The site (Observatory of 'GEK', Hospitalet karstic plateau) has boreholes of 20 and 50 m allowing the analysis of natural tracers such as water and temperature continuously for 5 years. A conceptual and numerical model has been deduced from these data. The temperature study provides information at global scale on climate change or the impact of the saturated zone on surface temperatures, as well as information at local scale such as the properties of the rock. Water levels provide information on transfer speeds.

In addition, this work has shown the importance of coordinated studies prior to any experimentation with tracers: geological analyzes, geophysical methods, knowledge of the material and its limits… It also showed the importance of the expected duration for such studies.

Finally, the joint study of artificial and natural tracers makes it possible to understand better the dynamics of water in the unsaturated zone. The continuation of joint studies of these tracers is therefore interesting to characterize other sites or karst regions. Especially, the impact of lithology on transfers could be deduced. These tracers can be used in numerical simulations, in parallel with geophysical measurements, in order to add constraints to the models.

Experiments on metal-sulphur-silicate melts equilibria under the reducing conditions of Mercury

Hadrien PIROTTE

University of Liège, Department of Geology, 12 allée du 6 Août B20, 4000 Liège, Belgium.

Mercury has a very high bulk density, with an iron core that makes up for 80% of the planet's radius, and yet it has a very low FeO content on the surface. Very high sulphur content is observed at the surface (up to 4 wt%), making Mercury a surprisingly volatile rich planet. The planet was formed under highly reducing conditions, creating unique conditions that change the behaviour of elements. This study aimed at understanding the element partitioning between the silicate melt, the metallic melt and the sulphide melt. A piston-cylinder was used to produce high temperatures (1300-1700 °C) and high pressures (~1.2 GPa) conditions relevant for crystallization conditions during the magma ocean stage. The first aspect of the project was to setup the apparatus and establish an appropriate protocol to use it. Several days of testing and adjustments were necessary to obtain a fully functional device. The composition used for the experiment was similar to enstatite chondrites, as their silicate composition is close to the bulk silicate composition of Mercury. Sulphur was added to the powders to saturate the silicate melt in sulphur. FeS was also added in order to obtain a metallic phase (FeSi) and to measure the oxygen fugacity in the samples. The oxygen fugacity (fO_2) was controlled using silica metal in the starting compositions. Experimental products contain a silicate and a metallic (FeSi) melt. FeS globules were formed in 4 out of 14 samples, which implies that these experiments reached sulphur saturation. The composition for major and minor elements of the silicate, the metallic and the sulphide melts were acquired using the electron microprobe at the University of Hannover, Germany. Partition coefficients between the silicate melt and the metallic melt were concordant with other studies; Si become siderophile at highly reducing conditions, and Mn and Ti also show a siderophile behaviour with low oxygen fugacity. Temperature also has an influence on the behaviour of elements; at higher temperatures, Mn, Ti and Na show increasing siderophile behaviours. Phosphorus on the other hand become less siderophile with temperature. Concerning the partition coefficients between the silicate melt and the sulphide melt, Ti become increasingly chalcophile with decreasing fO_2. It appears clearly that a large amount of sulphur is lacking in the samples; approximately 23 wt% S were added to the powders and in non-saturated experiments, only ~5% S is left in the silicate melt. At high temperature, sulphur escaped and saturation was not obtained in most experiments. It appears that pure S is unstable and volatile, and is much stable bound to iron under the FeS form. The siderophile behaviour of Si at low oxygen fugacity could imply that significant amount of silicon partitioned into the core during the planet differentiation. This result has been confirmed by numerous studies. We propose that the chalcophile behaviour of Ti could form TiS (wassonite) as discovered recently in an enstatite chondrite. The stability of this mineral would have to be defined in future experiments, but, as the author of the discovery proposed, TiS could be the residue of evaporating Ti-bearing FeS. As space-weathering is an important phenomenon on Mercury, it would be interesting to study the partitioning of Ti in FeS and the evolution of FeS once exposed at the surface.

JONGERENDAG - JOURNEE DES JEUNES – 19.10.2018

Abstracts of communications presented at the 'Master Day' meeting, Liège

Differential radar interferometry and optical images analysis to study recent landslides evolution in the Maily-Say valley, Kyrgyzstan

Valentine PIROTON[1], Romy SCHLÖGEL[2] & Hans-Balder HAVENITH[1]

[1]*Department of Geology, University of Liège, Liège, Belgium; valentine@piroton.be; hb.havenith@uliege.be.*
[2]*ESA Climate Office, ECSAT, Didcot-Harwell, United Kingdom; romy.schlogel@gmail.com.*

Landslides have catastrophic consequences in most mountainous areas of the world, representing a major problem for society. In Central Asia, and more specifically in Kyrgyzstan, landslides are recurrent due to the high seismicity of the region and as a consequence of intense rainfalls. In spring 2017, Kyrgyzstan suffered a massive activation event which caused 160 emergency situations. Koytash and Tektonik, located in the Mailuu-Suu Valley and part of the Fergana Basin, belonged to the numerous landslides which collapsed during this event. They represent a major threat to the local population of the small town of Maily-Say, as well as the villages downstream. In this region, risks related to landslide are accentuated by the presence of uranium tailings, remnants of the former nuclear mining activity. The rupture of the Koytash landslide, one of the largest in the area, led to the damming of the Mailuu-Suu River for several weeks. This deep-seated landslide is characterised by a rotational movement and extends on 1 km. Whilst Koytash collapsed in its entirety, the Tektonik landslide was only partially reactivated, rupturing in its upper part. The main goal of this study was to identify the geological, geomorphic and meteorological factors which contributed to the massive failure of Koytash and Tektonik in spring 2017. Different remote and proximal sensing techniques, combined with an extensive meteorological analysis, were applied to identify the conditions that triggered the collapse of these landslides. The meteorological analysis considered many variables (rainfall, temperature, and snow depth) which influence soil water saturation and thus sediment mobility, playing a major role in the landslide process. In parallel, radar and optical analyses were combined to monitor deformation zones. The computation of deformation time series by advanced differential synthetic aperture radar interferometry (D-InSAR) technique were used to generate interferograms allowing the identification of slow displacements and the estimation the evolution of displacement rates. The comparison of digital elevation models (DEMs; satellite and UAV imagery) enabled us to monitor changes in topography. Furthermore, we used optical imagery, through the difference of NDVIs (Normalized Difference Vegetation Index), to observe changes in landcover associated to sliding processes. The meteorological analysis revealed the important contribution of precipitations (rainfall combined with large snow accumulations linked to rapid melting) as triggers of the landslide movements in 2017. Indeed, despite a relative decrease in annual rainfall in 2017 compared to the preceding years, the month of April 2017 was characterised by heavy rains, including a major peak of rainfall the day of Koytash's failure. The D-InSAR analysis identified slow displacements during the months preceding the reactivation, indicating the long-term sliding activity of Koytash, well before the reactivation in April 2017. This was confirmed by the computation of deformation time series, showing positive velocity anomalies on the upper part of both landslides. The analysis of topography highlighted areas of depletion and accumulation, in the scarp and foothill zones respectively. Moreover, the presence of these deformations was confirmed by the optical analysis and showed the efficiency of land cover changes as indicators of ground displacements. The multidirectional approach used in this study, justified by the complementary nature of the techniques, enabled the gathering of complete and coherent results to monitor Koytash and Tektonik landslides activity.

Characterization of groundwater remediation using nanoparticles of zero-valent iron (nZVI)

Benjamin K. BLYKERS*, Tim DE KOCK & Veerle CNUDDE

PProGRess, Department of Geology, Ghent University, Krijgslaan 281/S8, 9000 Ghent, Belgium.
corresponding author: Benjamin.Blykers@ugent.be.

Introduction

Groundwater pollution is unfortunately omnipresent these days, and can be caused by a variety of industries, going from mining to even dry cleaning (Fayiga et al., 2018; Naghizadeh et al., 2011; Pous et al., 2018). One of the most recent and promising techniques for groundwater remediation is the injection of nanoparticles of zero-valent iron (nZVI) into the polluted aquifer. According to literature (Almeelbi & Bezbaruah, 2012; Lin et al., 2018; Stefaniuk et al., 2016), nZVI can reduce chlorinated hydrocarbons such as PCE (used as a dry cleaning fluid) and DDT (used as an insecticide) and transform a variety of dissolved metals into an insoluble phase, fixed to the rock, by several removal mechanisms: reduction, adsorption, oxidation and reoxidation, and (co-) precipitation (O'Carroll et al., 2013).

The purpose of this research is to investigate the transport behavior of nZVI through soils and its removal mechanisms of adsorption and (co)precipitation in a saturated soil sample. Barium was chosen for this specific study.

Material and methods

Batch tests were performed to quantify the decrease in barium concentration in a liquid phase upon application of nZVI. For this, eight different barium concentrations, four different amounts of a carboxymethylcellulose (CMC)-stabilized nZVI suspension and four grams of substrate consisting of quartz grains, were used. The total was shaken for 24 hours and the afterwards the liquid phase was analyzed chemically using inductively coupled plasma – optical emission spectrometry (ICP-OES).

The eight initial barium concentrations were 0.09 mg/L, 1.40 mg/L, 14.52 mg/L, 73.22 mg/L, 144.89 mg/L, 309.30 mg/L and 546.37 mg/L. The four amounts of nZVI were 0, 25, 50, and 100 mg of nZVI.

Results and discussion

The application of a higher amount of nZVI led to a higher amount of barium being sorbed to the substrate. However, in none of the samples barium was completely removed. The highest amount of removal occurred in the samples with a barium concentration of 73.22 mg/L and 100 mg of nZVI. After the experiment, the barium concentration was decreased to 14% of the initial concentration. It should also be noted that doubling the amount of nZVI from 50 to 100 mg did not lead to a double amount of barium being removed.