Onset and Termination of the Messinian Salinity Crisis: constraining variation of bottom water temperatures, ice volume and sea level.

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Introduction and original objectives

During the Messinian Salinity Crisis (MSC - 5.95-5.33 Ma), the present-day Mediterranean sea was isolated from the Atlantic Ocean and became an enclosed, desiccated basin. The isolation was driven by a combination of tectonic uplift and sea level fall (Krijgsman et al. 1999). Tectonic uplift was probably the main driving force of the initial isolation; however, there is still uncertainty surrounding the exact contribution of glacio-eustatic change to the crisis (Krijgsman et al. 2010). Past investigations of Messinian glacio-eustasy have not established whether there was a direct causal relationship between global sea level change and the onset or termination of the Messinian Salinity Crisis (Vidal et al. 2002; Hodell et al. 2001).

The project's main objective was to better understand the role of glacio-eustatic variations in the onset and termination of the Messinian Salinity Crisis by reconstructing ice volume fluctuations from ~6.0 to 5.2 Ma. We aimed to approximate ice volume variations using a multiproxy geochemical approach that combines calcification-temperature-dependent trace element ratios (Mg/Ca; Li/Ca) with stable isotope ($\delta^{18}O$) measurements on benthic foraminifera that reflect both calcification temperature and ice volume fluctuations.

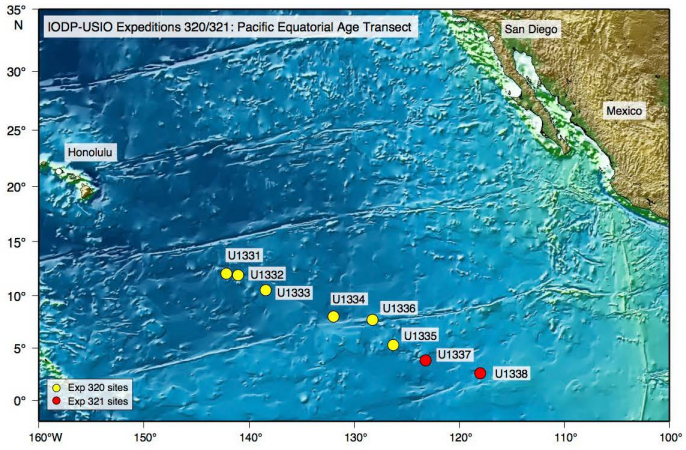

Figure 1. Location of IODP Site U1338 in the eastern equatorial Pacific.

Samples from IODP Site U1338 in the eastern equatorial Pacific were selected for this study (Figure 1). Site U1338 was chosen because high sedimentation rates occurred there throughout the late Miocene (Expedition 320/321 Scientists 2010; Palike et al. 2010). By using samples from the deep Pacific Ocean, glacio-eustatic variation during the MSC could be approached with a "far-field" view, thereby avoiding issues that occur when reconstructing eustacy in coastal settings. Site U1338 was initially chosen, as it could be dated using multiple biostratigraphies and shipboard investigations of the benthic foraminifera at the site showed the species were generally well preserved (Expedition 320/321 Scientists 2010).

Current Project Update

Whilst generating the benthic foraminiferal $\delta^{18}O$ and $\delta^{13}C$ stable isotope records that underpin this project, we found that quantifying benthic foraminiferal preservation using reflected light microscopy alone was not possible. We also found that the benthic foraminifera were less widespread than expected in the targeted interval, and not sufficiently abundant to enable the original trace element sampling strategy at 6 – 8 kyr resolution. A new sampling strategy was devised that focussed solely on the onset (5.96 ± 0.1 Ma) and the termination (5.33 ± 0.1 Ma) of the MSC.

A high-resolution age model was crucial to successfully target the onset and termination of the MSC for sampling. Generating an orbitally tuned age model was beyond the scope of this project; however, a high-resolution age model was generated using stratigraphically correlation of Site U1338 isotopes to an orbitally tuned target.

As a result of preservation and time-scale concerns raised during the initial stable isotope investigations, the project scope was extended beyond the original objective of investigating glacio-eustatic variation during the MSC. The project was expanded with the following objectives:

1. To assess the preservation of the benthic foraminifera *Cibicidoides mundulus* at Site U1338 during the MSC using scanning electron microscopy (SEM).
2. To generate a high-resolution age model to determine the location of the onset (5.96 ± 0.1 Ma) and the termination (5.33 ± 0.1 Ma) of the MSC in the Site U1338 sediments. The age model was created by stratigraphically correlating the high-resolution stable isotope records from Site U1338 to the published orbitally-tuned stable isotope records from ODP Site 982 (Hodell et al. 2001) using the automated-correlation software Match (Lisiecki & Lisiecki 2002; Lisiecki & Herbert 2007).

By including these additional objectives, the original aim of this proposal has not yet been achieved. This final report focuses on the outcomes of the additional two objectives, and looks at how these results impact work on the original objective.

Preliminary Results and Discussions

Preservation of Cibicidoides mundulus at Site U1338

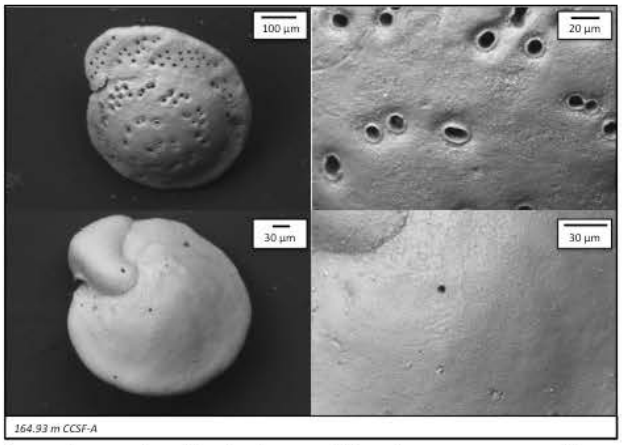

Figure 2. The umbilical and spiral view of a Cibicidoides mundulus from Site U1338. The preservation of this specimen is good and is representative for the other specimen examined.

The SEM study of the benthic foraminifera *Cibicidoides mundulus* was done to determine the preservation state of the calcite. 14 specimens from eight samples were investigated in the targeted interval. The specimens were mounted onto sticky carbon tape on a stub and were imaged using the Leo 1455 VP (variable pressure) SEM (working distance 15 – 16 mm; spot size 500; acceleration voltage of 15 kV) at the Natural History Museum (London, United Kingdom). The images were made at low vacuum using back-scattered electrons in topography mode (BSE-TOPO); therefore the samples were not coated. Figure 2 shows a representative example of a *Cibicidoides mundulus* from Site U1338. The SEM micrographs show that the *Cibicidoides mundulus* at Site U1338 generally show good preservation. Only minor calcite overgrowth was visible, and the original pore structure is well preserved. Apertures and individual chambers are still well defined. Considering the generally good state of preservation of the investigated *Cibicidoides mundulus* samples at Site U1338, this species is most likely suitable for later trace element analyses.

Establishing the timing of the onset and termination of the MSC

The high-resolution age model for the late Miocene to early Pliocene Site U1338 sediments was generated by using the automated-correlation software Match (Lisiecki & Lisiecki 2002) to stratigraphically correlate the high-resolution benthic foraminiferal $\delta^{18}O$ and $\delta^{13}C$ isotopes from Site U1338 to contemporaneous high-resolution benthic foraminiferal $\delta^{18}O$ and $\delta^{13}C$ records from North Atlantic ODP Site 982, which have previously been orbitally tuned (Hodell et al. 2001). This process has provided Site U1338 with a high-resolution, orbitally-based age model.

When using the new high-resolution age model to plot the high-resolution benthic $\delta^{18}O$ records from Sites U1338 and 982 across the MSC (Figure 3) it is apparent that there is an oxygen maximum that occurs around 5.96 Ma, coinciding with the onset of the MSC (red band – Figure 3). An oxygen minimum can also be identified around 5.33 at the termination of the MSC (green band – Figure 3).

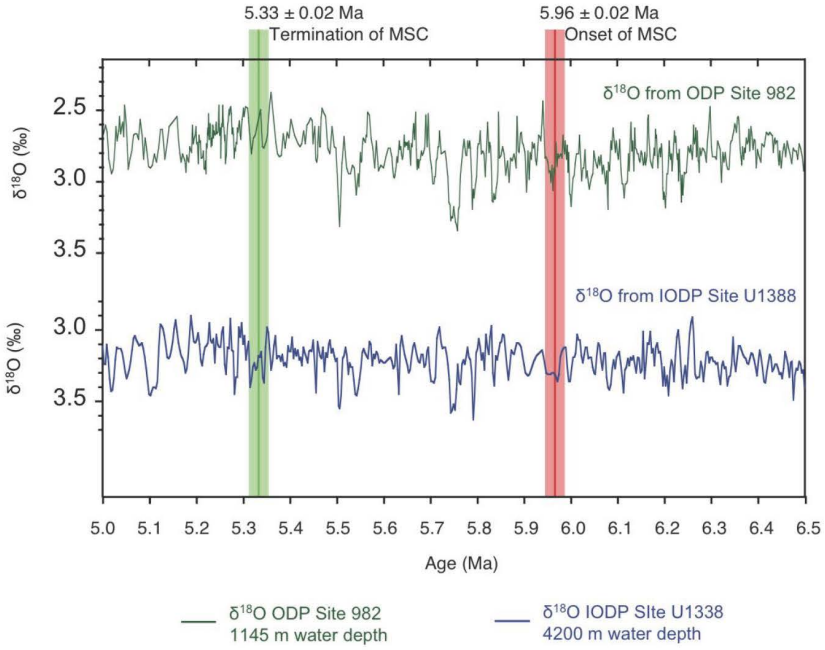

Figure 3. The benthic foraminiferal $\delta^{18}O$ records from ODP Site 982 (Hodell et al., 2001) and IODP Site U1338 (this study) on the high-resolution Match generated age model between 5.0 and 6.5 Ma. The MSC onset is highlighted with a red band (including age error) and the termination is indicated with a green band. An oxygen maximum can be found at the onset and a minima at the termination.

The $\delta^{18}O$ maximum seen in both records could be due to a glacial stage, which would imply some glacio-eustatic control on the timing of the MSC onset. Similarly, the $\delta^{18}O$ minimum that coincides with the termination could reflect an interglacial stage, which would most likely have a corresponding sea-level increase, and may control the timing of the MSC termination. However, based on benthic foraminiferal $\delta^{18}O$ alone, the exact extent of ice volume variation cannot be separated from potential temperature control on the $\delta^{18}O$ records, therefore the association of a glacial stage at the onset and an interglacial stage at the termination cannot be confirmed until independent temperature control is established.

Outlook

The expanded objectives of this project have shown that preservation of the benthic foraminifera *Cibicidoides mundulus* is generally good, and that these specimens would be suitable for trace element analyses. In addition, the results have allowed the exact location of the onset and the termination of the MSC at Site U1338 to be determined. This has shown that there is a potential glacial stage present at the onset and a potential interglacial stage present at the termination. This $\delta^{18}O$ maximum and minimum are ideal targets for further trace element analyses. So, although at the time of writing, the original objective of this project has not yet been achieved, the work presented in this report will enable the original objectives to be completed as first planned.

Budget

Funding		
ECORD (€ 1200)	£ 975	
Supervisors Research Grant	£ 192	
Total funding	*£ 1167*	
Current Expenditure		
Item	*Total Cost*	
Sample storage vials for 185 samples (£0.23/vial)	£ 42.55	
Storage boxes for 185 samples (£13.25/box)	£ 66.25	
Microfossil slides for 185 samples (£0.75/slide)	£ 138.75	
Scanning Electron Analyses for 8 samples	£ 192	
Total expenditure	*£ 439.55*	
Outstanding expenditure		
Item	*Total Cost*	
Trace element analyses (using ICP-MS at UCL)	£ 590.55	
Analysis tubes	£ 40.70	
Tube racks	£ 22.40	
Hydrazine (for reductive cleaning protocol)	£ 39.00	
Sodium hydroxide (for reductive cleaning protocol)	£ 14.80	
Hydrogen peroxide (for reductive cleaning)	£ 8.00	
Nitric acid (for reductive cleaning)	£ 12.00	
Outstanding expenditure	*£ 727.45*	
Used budget		***£439.55***
Remaining budget		***£727.45***

Due to the addition of two objectives, the original budget had to be revised. Additional funding was required to cover the SEM study to assess preservation. These costs were covered by using remaining funds from the research grant available to do the original stable isotope measurements. The generation of the age model was achieved at no additional monetary cost. A few consumable items have also been used in preparation for the original objective; however, the bulk of the original budget assigned to trace element analyses is still available.

Resulting publications relating to this project:

The manuscripts listed below are related to the content discussed in this report and are submitted.

Drury, A.J., Lee, G.P., Pennock, G.M., John, C.M., *in review*, "Data report: late Miocene to early Pliocene coccolithophore and foraminiferal preservation at Site U1338 from scanning electron microscopy", submitted to Palike, H., Lyle, M., Nishi, H., Raffi, I., Gamage, K., Klaus, A. and Scientists, E. 320/321 (Eds.), *Proceedings of the Integrated Ocean Drilling Program, Scientific Results*.

References

Expedition 320/321 Scientists, 2010. Site U1338. In H. Palike et al., eds. *Proceedings of the Integrated Ocean Drilling Program, Volume 320/321*.

Hodell, D.A. et al., 2001. Correlation of late Miocene to early Pliocene sequences between the Mediterranean and North Atlantic. *Paleoceanography*, 16(2), pp.164–178. Available at: <Go to ISI>://WOS:000167693300003.

Krijgsman, W. et al., 1999. Chronology , causes and progression of the Messinian salinity crisis. *Nature*, 400(August), pp.652–655. Available at: <Go to ISI>://WOS:000082032900049 [Accessed April 5, 2014].

Krijgsman, W. et al., 2010. Rise and fall of the Paratethys Sea during the Messinian Salinity Crisis. *Earth and Planetary Science Letters*, 290(1-2), pp.183–191. Available at: <Go to ISI>://WOS:000274844700021.

Lisiecki, L.E. & Herbert, T.D., 2007. Automated composite depth scale construction and estimates of sediment core extension. *Paleoceanography*, 22(4). Available at: <Go to ISI>://WOS:000251693300001.

Lisiecki, L.E. & Lisiecki, P.A., 2002. Application of dynamic programming to the correlation of paleoclimate records. *Paleoceanography*, 17(4). Available at: <Go to ISI>://WOS:000180656400001.

Palike, H. et al., 2010. Expedition 320/321 summary. In H. Palike et al., eds. *Proceedings of the Integrated Ocean Drilling Program*. pp. 2–141.

Vidal, L. et al., 2002. Late miocene stable isotope stratigraphy of SE Atlantic ODP Site 1085: Relation to Messinian events. *Marine Geology*, 180(1-4), pp.71–85. Available at: <Go to ISI>://WOS:000174534900005.