ECORD Research Grant Final Report

Sea surface temperature changes in the Gulf of Alaska (IODP Expedition 341) during the Mid Pleistocene Climate Transition

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1) Background

IODP Expedition 341 (May - July 2013) in the Gulf of Alaska (NE Pacific) succeeded in drilling a remarkable sedimentary record that extends from the late Miocene to the Holocene (Expedition-341-Scientists et al., 2013). Sediments recovered from the distal deepwater site U1417 (Fig. 1) provide an unrivalled opportunity to generate a continuous record of the sea surface conditions in the subpolar North Pacific during the Mid Pleistocene Transition (MPT) 1.25 Ma - 0.7 Ma ago, when a shift from a 100 ka to a 41 ka periodicity in glacial-interglacial variations occurred (Elderfield et al., 2012). Most reconstructions of the Pleistocene palaeoceanographic and environmental development in the Pacific are confined to the tropical or NW Pacific. Data from the Gulf of Alaska thus help to address how the subpolar NE Pacific responded and/or contributed to the MPT and allow an examination of potential interactions between ocean conditions and continental ice-sheet dynamics. To fully exploit the climate information archived in U1417 sediments, a multi-proxy approach drawing on organic geochemical, sedimentological and micropalaeontological studies has been applied. Organic geochemical biomarker analyses were performed to gain insight into climate driven palaeoenvironmental changes during the MPT. Variability in the distribution and abundance of alkenones, C_{25}-highly branched isoprenoids (HBIs), and short- and long-chain *n*-alkanes, for example, is interpreted to reflect changes in sea surface temperature (SST), marine primary productivity, and the input of terrigenous organic matter via iceberg, sea ice, meltwater or aeolian transport. These data also enable an indirect assessment of the behaviour of the Cordilleran Ice Sheet (Fig. 1) in response to the MPT.

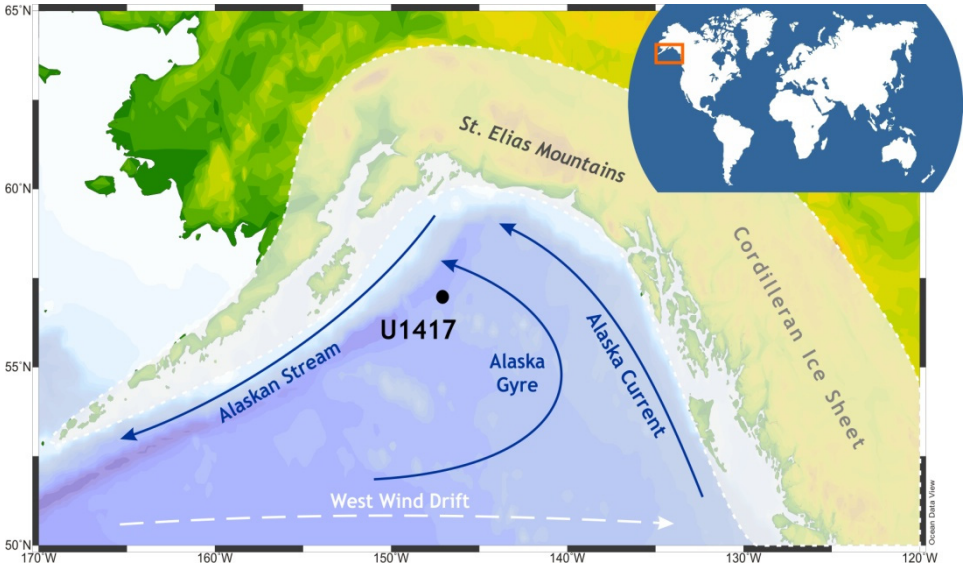

Fig. 1. Ocean currents and location of IODP drill site U1417 in the Gulf of Alaska. The approximate extent of the Pleistocene Cordilleran Ice Sheet is indicated.

During a 6 months research stay at the Department of Geography at the University of Durham (UK; Jan. - July 2014) a set of U1417 sediment samples covering the MPT and the late Pleistocene was extracted and purified to yield hydrocarbon and polar lipid fractions. The close cooperation with Dr Erin McClymont (University of Durham) was of essential help to avoid duplication of efforts and ensured the generation of a comprehensive biomarker record. Preliminary alkenone data produced during this research stay, however, revealed some major inconsistencies in the ocean temperature record of site U1417. The occasional occurrence of co-eluting compounds hampered a proper quantification of $C_{37:2}$, $C_{37:3}$ and $C_{37:4}$ alkenones and resulted in a significant overestimate of SSTs (Figs. 2, 3). The ECORD Research Grant allowed us to address these difficulties during a second research visit of the applicant at the University of Durham in November 2014.

2) Methods and results

In the original application for the ECORD Research Grant, financial support was requested to re-visit the University of Durham to conduct additional chemical treatments such as urea adduction to yield clean alkenone fractions. On account of the overall low concentrations of biomarkers (and alkenones) gas chromatography-chemical ionization-mass spectrometry (GC-CI-MS) was performed instead. This analytical method provides enhanced sensitivity and selectivity when compared to the conventional gas chromatography-flame ionization detection (GC-FID) technique used for alkenone identification and quantification (Rosell-Mele et al., 1995). GC-CI-MS is based on the specific reaction of ammonia with unsaturated target compounds and selected ion monitoring (SIM) mass spectrometry. The selective ionization of alkenones by means of ammonia produces characteristic pseudo-molecular ions of C_{37} methyl alkenones (m/z $[M+NH_4]^+$), which are determinable via SIM mass spectrometry. GC-CI-MS thus allows a significantly improved and reliable identification of alkenones. A comparison of two chromatograms showing alkenone peaks obtained via GC-FID and GC-CI-MS analysis (Fig. 2) highlights the advantage of the latter technique, which permits a more accurate integration of alkenone peak areas to calculate the U^K_{37} temperature index (Brassell et al., 1986). Temperature estimates derived from both conventional GC-FID and GC-CI-MS analyses of U1417 samples differ substantially (up to 15°C) with GC-CI-MS data

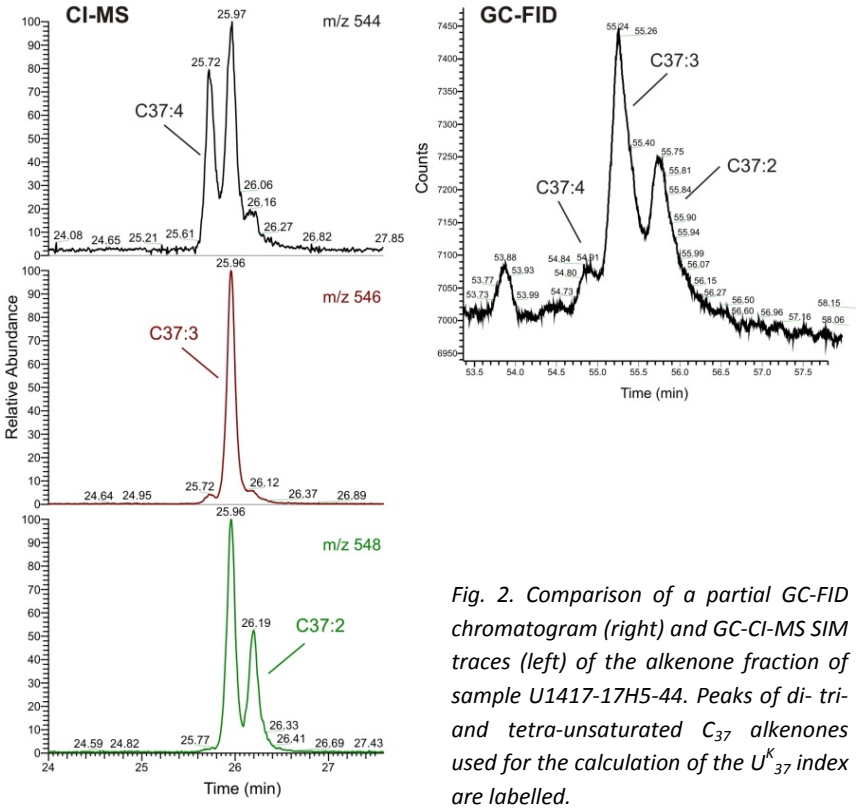

Fig. 2. Comparison of a partial GC-FID chromatogram (right) and GC-CI-MS SIM traces (left) of the alkenone fraction of sample U1417-17H5-44. Peaks of di- tri- and tetra-unsaturated C_{37} alkenones used for the calculation of the U^K_{37} index are labelled.

resulting in generally lower temperatures (Fig. 3). This is mainly due to an improved identification of the $C_{37:4}$ alkenone reflective of cold surface waters and separation of the $C_{37:2}$ alkenone from co-elutants.

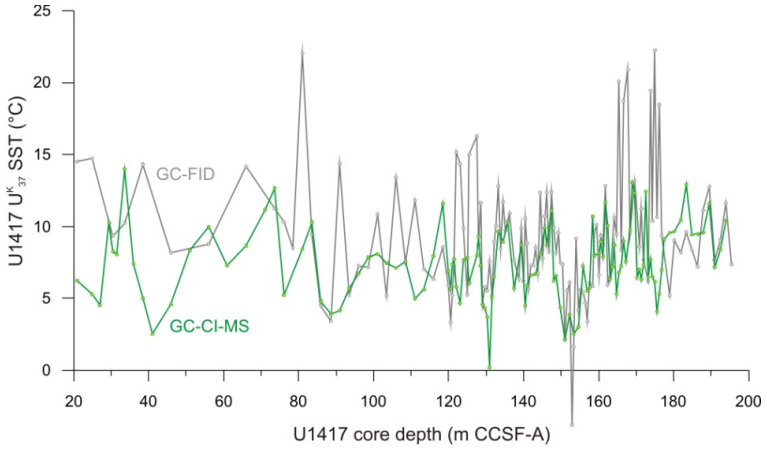

Fig. 3. Alkenone-based sea surface temperatures determined via GC-FID analyses (grey) and via GC-CI-MS measurements (green).

A comparison of U1417 data with published SST records from ODP site 983 in the North Atlantic (McClymont et al., 2008) and ODP site 882 in the NW Pacific (Martínez-Garcia et al., 2010) supports the reliability of the distinctly lower temperatures determined via the GC-CI-MS technique. All three records reveal significant temperature fluctuations throughout the past 1.5 Ma and a pronounced cooling and an expansion of polar water (indicated by maximum $C_{37:4}$ alkenone contents) at about 1 Ma ago (Fig. 4). This synchronous Northern Hemisphere ocean cooling seems to be associated with the relatively weak interglacials during Marine Isotope Stages 29 and 27. Interestingly, compound specific $\delta^{13}C$ data obtained from a land-plant biomarker (n-C_{31} alkane) point to an increase in precipitation during this cooling event. A higher precipitation (i.e. snowfall) during an interval of colder climate certainly promoted the expansion of the Cordilleran Ice Sheet during the MPT.

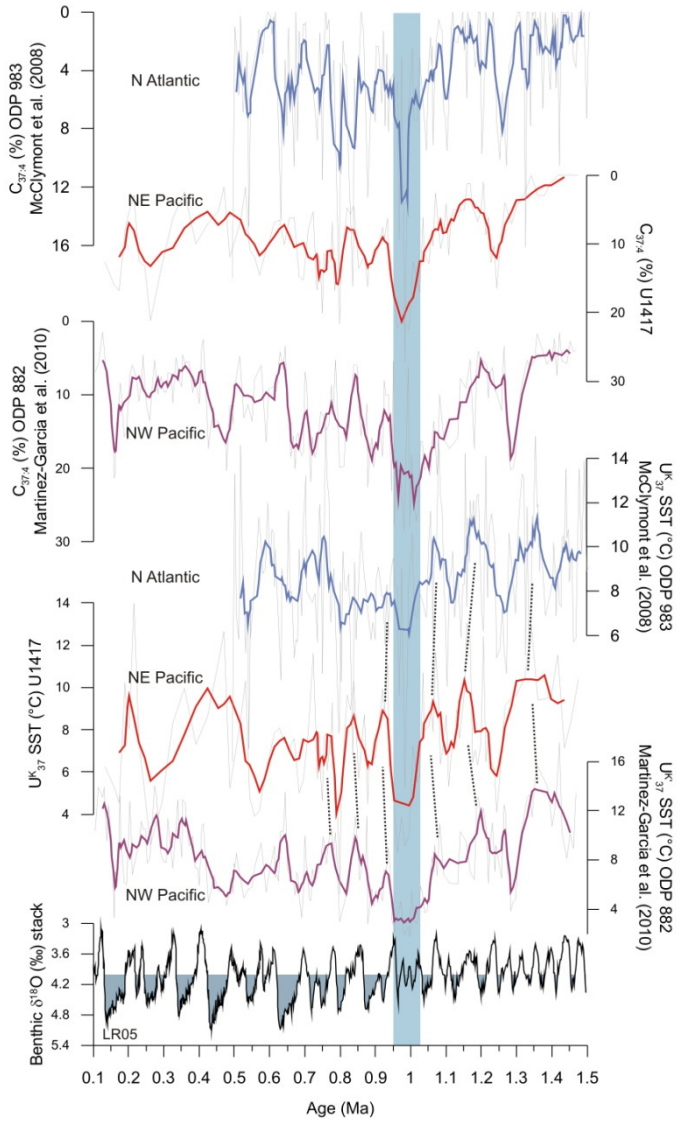

Fig. 4. Comparison of U1417 (red) and published (purple, blue) U^{K}_{37} sea surface temperature and $C_{37:4}$ records and the benthic $\delta^{18}O$ stack (Lisiecki and Raymo, 2005).

The final synthesis of biomarker, microfossil and sedimentological data will provide for a more detailed palaeoenvironmental reconstruction and the assessment of climatically controlled land-ocean-interactions (e.g. glacial-interglacial variability in the export of icebergs and ice rafted detritus, iron fertilization effects on primary productivity, etc.). These data will help to address the overall research objectives of the IODP research programme to understand the driving and feedback mechanisms of climate change.

3) Travel and laboratory expenses

The ECORD Research Grant has been used to cover the following expenditures:

Lab expenses at the University of Durham	
GC-CI-MS analyses (117 samples)	1260,54 €
Transport and Accommodation	
Public transport (Newcastle - Durham)	22,15 €
Flight costs (Berlin - Newcastle)	290,96 €
Accommodation costs	333,67 €
Total expenses	**1907,32 €**

4) Acknowledgments

The ESSAC Science Committee is gratefully acknowledged for their financial support. Many thanks go to Erin McClymont, Martin West and Amanda Hayton for indispensable discussions and their indefatigable technical assistance in the organic-geochemical laboratory at the University of Durham.

5) References

Brassell, S.C., Eglinton, G., Marlowe, I.T., Pflaumann, U., Sarnthein, M., 1986. Molecular stratigraphy: a new tool for climatic assessment. Nature, 320, (6058), 129-133.

Elderfield, H., Ferretti, P., Greaves, M., Crowhurst, S., McCave, I.N., Hodell, D., Piotrowski, A.M., 2012. Evolution of Ocean Temperature and Ice Volume Through the Mid-Pleistocene Climate Transition. Science, 337, (6095), 704-709.

Expedition-341-Scientists, Gulick, S.P.S., Jaeger, J., Mix, A., Asahi, H., Bahlburg, H., Belanger, C., Berbel, G.B.B., Childress, L., Cowan, E., Davies, M.H., Drab, L., Dottori, F., Forwick, M., Fukumura, A., Ge, S., Gupta, S., Kioka, A., Konno, S., LeVay, L., März, C., Matsuzaki, K., McClymont, E., Moy, C., Müller, J., Nakamura, A., Ojima, T., Ridgway, K., Romero, O., Slagle A., Stoner, J., St-Onge, G., Suto, I., Worthington, L., 2013. Southern Alaska margin: Interactions of tectonics, climate, and sedimentation. IODP Prel. Rept., 341. doi:10.2204/iodp.pr.341.2013.

Lisiecki, L.E. and Raymo, M.E., 2005. A Pliocene-Pleistocene stack of 57 globally distributed benthic d18O records. Paleoceanography, 20, (1), PA1003.

Martínez-Garcia, A., Rosell-Melé, A., McClymont, E.L., Gersonde, R., Haug, G.H., 2010. Subpolar Link to the Emergence of the Modern Equatorial Pacific Cold Tongue. Science, 328, (5985), 1550-1553.

McClymont, E.L., Rosell-Melé, A., Haug, G.H., Lloyd, J.M., 2008. Expansion of subarctic water masses in the North Atlantic and Pacific oceans and implications for mid-Pleistocene ice sheet growth. Paleoceanography, 23, (4), PA4214.

Rosell-Mele, A., Carter, J.F., Parry, A.T., Eglinton, G., 1995. Determination of the UK37 index in geological samples. Analytical Chemistry, 67, (7), 1283-1289.