Dr Carme Huguet - Visiting professor (2014-2015)

Report of activities at Stellenbosch University, South Africa.

The visit took place from 10th of November to 2nd of December 2014 in order to accommodate both the visitor's (Dr Huguet) and the host's (Dr Fietz) schedules. During the visit I helped Dr Fietz to set up the sample preparation and extraction technique for alkenones and GDGTs in the general Geochemistry Lab, Department of Earth Sciences. Dr Fietz is starting the first organic biomarker research lab in Africa and has ready access to samples from the Southern Ocean (SANAP; R/V SA Agulhas II) austral summer and winter cruises 2015.

With the support of staff scientist Dr. Marietjie Stander at the Stellenbosch University, Central Analytical Facility, MS-Lab (http://academic.sun.ac.za/saf/services/services1.html) we started setting up the analytical procedures using the UPLC-MS (Utra High Pressure Liquid Chromatograph coupled to a Mass Spectrometer; Figure 1). The method proposed by Becker et al., (2013; 2015) was strictly followed at the beginning. After running test samples and standards, it was modified considerably to improve the sensitivity to be able to detect compounds in Southern Ocean waters. For instance, measurements were done initially using a positive APCI (Atmospheric Pressure Chemical Ionization) source and results were promising (see Figure 2 for examples of peak detection and integration and Table 1 for example samples' outcome); however, sensitivity using the routine amount of sample available for this kind of work was low. A series of changes was made, e.g., replacing the APCI by an ESI (Electron Spray Ionization) source as well as temperature changes and source adjustments. The changes resulted in a satisfactory set-up for some applications. For instance, sediment core standard samples used in an intercalibration on indices used for paleo-reconstructions (Schouten et al., 2009) gave the correct, published index values (e.g., Table 1), and hence, the UPLC-qTOF-MS with ESI interface set-up could be used as long as sufficient sediment material is available; an estimated >2g dry sediment is currently needed for reliable pale-reconstructions. However, the target compounds in Southern Ocean water samples (one of the main aims for Dr Fietz' current research) were below detection limit. This hinders current objectives to provide a Southern Ocean calibration for the cold- or polar-water indicating OH-GDGTs.

For this reason a new machine (ACQUITY UltraPerformance Convergence Chromatography, UPC²) was tested following the recommendation of the staff scientist Dr. Marietjie Stander. This is a new type of chromatography that uses CO₂ in a critical state as the liquid phase to separate the compounds. This set-up has a much lower critical abundance for detection. Preliminary results using our Crenarchaeol standard and test samples were promising, as we detected all major targeted compounds, but we did not have time to complete the tests and I hope to be able to work remotely during 2016 together with Dr Fietz and Dr. Stander on further tuning of the method.

I also participated in the evaluation of the B.Sc. Honors' student projects, particularly in the examination of the written research thesis and evaluation of the oral defense of Ms Gillian Trollope's thesis on "The distribution and abundance of hydroxylated GDGTs and their use as a paleo-environmental proxy in the Southern Ocean". A new B.Sc. Honors student, Mr. Johan

Viljoen, will continue the set-up of the UPLC system during 2016 and a new PhD candidate, Mr. Arnaud Nicolas, shall develop the new UPC2 methodology and publish the new method.

The visit was also used to i) polish/finish two papers started early in 2015 on molecular dynamics of cold or polar-water indicating OH-GDGTs and Southern Ocean paleo-temperature reconstruction ii) prepare proposal on future Colombian-SA collaboration using GDGTs as paleo-thermometer.



Figure 1. Complete set-up of UPLC-MS using an auxiliary pump system for improved compound detection; Stellenbosch University, Central Analytical Facilities, MS-Lab.

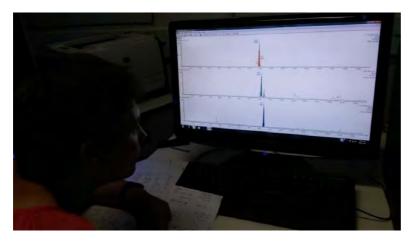


Figure 2. Example of compound detection and quantification for GDGTs of terrestrial origin (so called branched GDGTs, Hopmans et al., 2004) in peat bog samples.

Table 1. Examples samples used for compound detection and index calculation (TEX_{86} and BIT, see Schouten et al., 2013 for index review) using an early set-up of the UPLC-qTOF-MS with ESI interface. Header row represents m/z of respective target GDGTs (common abbreviations are given in the second row). See Schouten et al., (2013 for a review). Values represent relative integrated peak areas (dimensionless) or index values (for TEX_{86} and BIT indices).

	1302	1300	1298	1296	1292	1292r	1022	1020	1018	1036	1034	1032	1050	1048	1046	TEX86	BIT
	isoGDGT	isoGDGT	isoGDGT	isoGDGT	isoGDGT	isoGDGT	brGDGT										
sample ID	0	1	2	3	5	5reg	la	lb	lc	lla	IIb	IIc	Illa	IIIb	IIIc		
Colombian peat							1400	155	63	1007	32	31	193	7	14		
Colombian peat							2061	200	145	1376	35	69	248	10	17		
Colombian peat							439	24	12	177	7	3	22		6		
Ocean (warm)	138	58	53	9	157	32	17	8	2	12	7	3	22			0.62	0.25
Pond (temperate	13	5	5		4		68			45			14			0.50	0.97
Southern Ocean	46	11	4		35											0.27	