CLIMATE AND EARTH-OCEAN-ATMOSPHERE SYSTEMS

H. Elderfield, M.J. Bickle, D. Hodell, I.N. McCave, A. Galy, N. Hovius, A.M. Piotrowski, A.V. Turchyn & L. Skinner.

Research in global change is increasingly important and involves a wide range of disciplines – geochemistry, sedimentology, micropalaeontology, palaeoclimatology and tectonics. We are particularly interested in the Quaternary with a number of programmes involving different aspects of glacial-interglacial change. Research also extends across the whole of the Tertiary, including the roles of tectonics in global climatic change, the long term evolution of ocean chemistry and solid Earth-hydrosphere-atmosphere interactions.

Current research includes: -

- Calibrations of astronomical forcing of climate change records in oceanic sediments.
- Multi-proxy studies of abrupt climate change in the oceans.
- Sedimentological and geochemical tracers of past deep sea circulation vigour and sediment supply.
- Use of foraminiferal metal chemistry and the stable isotopic composition of biogenic sediments in palaeochemical studies of ocean temperature and nutrient variations.
- Processes and geochemical fluxes associated with earth-atmosphere interaction in chemical weathering.
- Isotopic studies of siliceous and calcareous microfossils for palaeoproductivity and environmental variations.
- Biogeochemical cycling of stable isotopes and elements in marine and terrestrial systems.

We are also interested in supervising research students in the general fields of seawater and sediment geochemistry particularly using isotope geochemistry to understand water and chemical budgets of the oceans, particularly in linking understanding of the chemistry of the modern rivers and oceans to weathering history and palaeoceanography. Studies of modern sedimentation also provide a link to understanding past ocean dynamics.

We have well equipped laboratories with a multi-collector ICP mass-spectrometer, three solid-source and four gas-source mass spectrometers, atomic-emission spectrometer, ICP-MS, C-H-N analyzer, atomic absorption, sedigraph, a coulter counter, magnetic susceptibility, X-radiography, cathodoluminescence. Thus, we offer topics which incorporate training in geochemical and sedimentological techniques, into research on major current problems in global change and global biogeochemical cycles.

CLIMATE AND EARTH-OCEAN-ATMOSPHERE SYSTEMS

C1 **Orbital and Millennial-Scale Climate Variability across the Middle Pleistocene Transition from the "Shackleton site" on the SW Iberian Margin.**
David Hodell & Luke Skinner.

C2 **Deep Ocean Circulation Changes during the last glacial cycle inferred from Gardar Drift (North Atlantic)**
David Hodell, Nick McCave & Alex Piotrowski.

C3 **A New Tool for Paleoenvironmental Reconstruction Using Mineral Hydration Water.**
David Hodell & Alexandra (Sasha) Turchyn.

C4 **Ocean circulation and carbon cycling since the last glacial maximum.**
Luke C. Skinner.

C5 **Oxygenation of the past ocean interior: novel methods and new insights into carbon cycle implications**.
Luke C. Skinner, David Hodell, Harry Elderfield.

C6 **Stable isotope tracers of microbial processes in estuarine sediments.**
Alexandra (Sasha) Turchyn.

C7 **Reconstructing hydrothermal circulation through geochemical analysis of ophiolites.**
Also see P7
Mike J. Bickle, Alexandra (Sasha) Turchyn & John Maclennan.

C8 **Evolution of the sulphur cycle in the aftermath of the K/T boundary.**
Also see Q3
Alexandra (Sasha) Turchyn.

C9 **Temporal relations between ocean circulation, dust inputs, and nutrient cycling during the last ice age.**
Alex Piotrowski, Albert Galy, Nick McCave & David Hodell.

C10 **Reconstructing glacial Atlantic deep water circulation and sediment sourcing using radiogenic isotopes.**
Alex Piotrowski & Nick McCave.

C11 **Past changes in Pacific-Southern Ocean deep water exchange from Nd isotopes.**
Alex Piotrowski, Harry Elderfield, Nick McCave & Helen Bostock (NIWA, New Zealand)

C12 **Geological carbon storage reservoirs: Reactions between CO_2 , brines and minerals in reservoirs.**
Also see P16
Mike Bickle.

C1

TITLE: ORBITAL AND MILLENNIAL-SCALE CLIMATE VARIABILITY ACROSS THE MIDDLE PLEISTOCENE TRANSITION FROM THE "SHACKLETON SITE" ON THE SW IBERIAN MARGIN.

SUPERVISORS: DAVID HODELL & LUKE SKINNER.

Importance of the area of research concerned: Millennial-scale climate variability has been well documented for the last glacial cycle in the North Atlantic, but relatively little is known about the nature of such variability during older glacial periods of the Pleistocene [Margari *et al*., 2010]. Shackleton's work on the Iberian Margin demonstrated the potential of this region for providing high-fidelity records of millennial-scale climate variability for the last glacial cycle [Shackleton *et al*., 2000, 2004]. Drilling during IODP Expedition 339 (http://iodp.tamu.edu/scienceops/expeditions/mediterranean_outflow.html) will extend this remarkable sediment archive through the Middle Pleistocene. This project provides an opportunity for a student to work on sediment cores recovered from Site SHACK-04, which will provide a continuous high-resolution record with which to evaluate the character of millennial-scale variability for the Pleistocene. The focus will be on documenting changes across the Middle Pleistocene Transition (MPT), which occurred between ~1250 and 650 ka and represented a shift in the spectral character of the climate signal from dominantly 41-kyr power before 1250 ka to the emergence of a quasi 100-kyr cycle at 650 ka (for review, see Clark *et al*., [2006]).

The project: The specific objectives will be to:

i. Define the nature of millennial-scale and orbital climate variability change across the MPT.

ii. Derive a marine sediment proxy record for the Greenland Ice Core for the MPT and examine the amplitude and pacing of Dansgaard-Oeschger-type variability across this period.

iii. Determine interhemispheric phase relationships (leads/lags) by comparing the timing of proxy variables that monitor surface (Greenland) and deep-water (Antarctic) components of the climate system. Did the bipolar seesaw exist prior to the MPT when glacial ice volume was reduced?

iv. Study how changes in orbital forcing and glacial boundary conditions across the MPT affected the character of suborbital-scale climate variability and, in turn, how millennial-scale variability interact with orbital geometry to produce the observed glacial-to-interglacial patterns of climate change.

What the student will do: The student will produce high-resolution proxy records of climate variability mainly by measuring stable isotopes (e.g., $\delta^{18}O$ and δD) and trace metals (e.g., Mg/Ca, B/Ca, U/Ca) in foraminifer shells and integrate these results with core scanning XRF, core logging, and colour reflectance data. Although the shipboard phase of IODP Expedition will have been completed by the start of the project, the student will participate fully in post-cruise activities, including organized sampling parties at the IODP repository in Bremen, Germany, and post-cruise science meetings. There will be ample opportunity to collaborate directly with other IODP scientists working on complementary proxies from the same core.

Training which will be given: The student will receive training in the Godwin Laboratory for Palaeoclimate Research which provides state-of-the-art analytical facilities. Research methods will include stable isotope and trace element geochemistry as well as sedimentological, micropalaeontological, and XRF techniques.

References:

Clark, P. U., D. Archer, D. Pollard, J. D. Blum, J. A. Rial, V. Brovkin, A. C Mix, N. G. Pisias, and M. Roy (2006), The middle Pleistocene transition: characteristics, mechanisms, and implications for long-term changes in atmospheric CO_2, *Quat. Sci. Rev*, **25**, 3150-3184.

Margari, V., Skinner, L.C., Tzedakis, P.C., Ganopolski, A., Vautravers, M., Shackleton, N.J., 2010. The nature of millennial-scale climate variability during the past two glacial periods. *Nature Geoscience*, **3**, 127-131.

Shackleton, N. J., M. A. Hall, and E. Vincent, 2000. Phase relationships between millennial-scale events 64,000–24,000 years ago, *Paleoceanography*, **15**, 565–569.

Shackleton, N. J., R. G. Fairbanks, T.-C. Chiu, and F. Parrenin, 2004. Absolute calibration of the Greenland time scale: Implications for Antarctic time scales and for Δ14C, *Quat. Sci. Rev.*, **23**, 1513–1522.

C2

TITLE: DEEP OCEAN CIRCULATION CHANGES DURING THE LAST GLACIAL CYCLE INFERRED FROM GARDAR DRIFT (NORTH ATLANTIC)

SUPERVISORS: DAVID HODELL David Hodell, NICK MCCAVE & ALEX PIOTROWSKI.

Importance of the area of research concerned: The leading hypothesis to explain millennial-scale climate variability (Dansgaard-Oeschger events) during the last glacial period is reorganization of ocean circulation via fresh water forcing. That is, freshening of North Atlantic surface waters led to a slowdown in Atlantic meridional overturning circulation (AMOC), sea ice expansion, and coupled atmospheric changes. There is little direct evidence, however, that D-O events were associated with changes in the vigour of deep ocean circulation. To test this hypothesis, it is necessary to determine the phase relationships between deep flow speeds and temperature change in Greenland and Antarctica.

The project: The research will involve measuring sortable silt (SS) (McCave & Hall, 2006) at IODP Site U1304 (Piston core JPC13) to reconstruct the history of Iceland Scotland Overflow Water (ISOW) and assess its role in millennial-scale climate variability for the past 130,000 yrs. IODP Site U1304 (JPC13) was drilled in 3082 m of water at the southern extremity of the Gardar Drift, and was formed by the interaction of ISOW with deep-sea sediments in the form of a Deep Western Boundary Current. Previous measurements of SS have demonstrated that the Gardar Drift contains a detailed record of past variations in ISOW flow (Hall *et al*., 1998; Bianchi and McCave, 2000; Kleiven *et al*., 2011). Some questions to be addressed include: What is the phase relationship between changes in ISOW production, ice rafted detritus events, and changes in surface/deep hydrography relative to Greenland and Antarctic temperature variations? Were D-O cycles and Heinrich events associated with mode changes in AMOC? Were changes in deep ocean circulation a cause of or response to abrupt climate change? Was ISOW production the same during the last interglacial (Marine Isotope Stage 5e) as the Holocene (Hodell *et al*., 2009)?

What the student will do: The student will produce a high-resolution (i.e. subcentennial) record of sortable silt at IODP Site U1304 (JPC13) as a proxy of ISOW variability for the last 130,000 yrs. The stable isotope record at this site has been completed and a precise chronology established by correlating millennial-scale features in the benthic $\delta^{18}O$ record to Portuguese Margin Core MD95-2042 (Hodell *et al*., 2010). With the alignment of benthic $\delta^{18}O$ of Site U1304/JPC-13 to MD95-2042, the relative timing of changes in sortable silt can be determined relative to Greenland and Antarctic climate change. The SS will also be interpreted in the context of other potential proxies of deep-water circulation to be generated by this study (e.g., benthic $\delta^{13}C$, K/Ti by scanning XRF, environmental magnetic properties) and a SS record for most of MIS 3 for Bermuda Rise (c.f. Hall *et al*., 1998). Because SiteU1304 contains a complete Pleistocene section, there is opportunity to extend the study of ISOW variability to older isotope stages of the Pleistocene when orbital and glacial boundary conditions differed.

Training which will be given: The interdisciplinary nature of the project will provide opportunity for the student to pursue a diverse set of analytical and stratigraphic techniques. The student will specifically be trained in the use of core scanning XRF and sortable silt analysis (coulter counter and Sedigraph), but will also utilize stable isotope, micropaleontology, and rock magnetic proxies for interpretation.

References:

Bianchi, G.G. & McCave, I.N. 2000. Hydrography and sedimentation under the deep western boundary current on Björn and Gardar Drifts, Iceland Basin, *Mar. Geol*., **165**, 137-169.

Hall, I.R., McCave, I.N., Chapman, M.R. & Shackleton, N.J. 1998. Coherent deep flow variation in the Iceland and American basins during the last interglacial, *Earth and Planetary Science Letters*, **164**, 15–21.

Hodell, D.A., Minth, E.K., Curtis, J.H., McCave, I.N., Hall, I.R., Channell, J.E.T., Xuan, C., 2009. Surface and deep-water hydrography on Gardar Drift (Iceland Basin) during the last interglacial period. *Earth Planet*. Sci. Lett., *Earth Planetary Science Letters*. **288**: 10-19.

Hodell, D.A., Evans, H.F., Channell, J.E.T., and Curtis, J.H., 2010. Phase relationships of North Atlantic ice-rafted debris and surface-deep climate proxies during the last glacial period. *Quat. Sci. Rev*. **29**, 3875-3886.

Kleiven, H.F., Hall, I.R., McCave, I.N., Knorr, G., & Jansen, E., Deep-water formation and climate change in the North Atlantic during the Mid-Pleistocene. *Geology*, **39**, 343–346.

McCave I.N. and I.R. Hall, 2006. Size sorting in marine muds: Processes, pitfalls and prospects for palaeoflow-speed proxies. *Geochem. Geophys. Geosyst*., **7**, Q10N05, doi:10.1029/2006GC001284, 37

C3

TITLE: A NEW TOOL FOR PALEOENVIRONMENTAL RECONSTRUCTION USING MINERAL HYDRATION WATER.

SUPERVISORS: DAVID HODELL & ALEXANDRA (SASHA) TURCHYN.

Importance of the area of research concerned: The quintessential problem in oxygen isotope paleoclimatology is that the temperature equation is under constrained. The $\delta^{18}O$ of calcite or aragonite can be measured on fossil shell material but a unique temperature solution is not possible without knowing the $\delta^{18}O_{water}$ from which the carbonate precipitated. Hydrated minerals (e.g., gypsum) that co-occur with carbonate offer the potential for solving the paleotemperaure equation provided that (i) the fractionation factors between mother water and hydration water are known; and (ii) no further exchange has occurred between environmental and hydration water after deposition.

The project: Tandem $\delta^{18}O$ measurements of both carbonate and mineral hydration water in the same samples offer a potential tool for quantifying past changes in temperature. The project will build upon our on-going research utilizing co-occurring gypsum and biogenic carbonate in lake sediment cores to quantitatively derive changes in temperature and lake water oxygen isotopic composition. Several research directions are possible at this point, including analytical experimentation, theoretical mineral physics and/or increased development of the paleoclimate application.

What the student will actually do:

- Improve the precision of the isotopic fractionation factors between mineral hydration water and mother water as a function of temperature;
- Experimentally and theoretically evaluate the kinetics of post-crystallization isotope exchange of mineral hydration water and ambient environmental water;
- Test the application of mineral hydration water to reconstruct paleoenvironmental change in marine, lake and continental sediments and soils.
- Develop an analytical method and equipment for stepped heating to liberate hydration water with on-line measurement of $\delta^{18}O$ and δD using cavity ringdown laser spectroscopy.
- Collaborate with Earth Science Mineral Physics Group to determine how hydration water is structurally bound in the mineral lattice and calculate theoretical fractionation factors and exchange kinetics.

Training:

Chemical and mineral preparation techniques (e.g. wet chemistry lab work).
Analytical methods:
Solution and isotopic geochemistry
Isotope Ratio Mass Spectrometry (TCEA-DeltaV)
Cavity Ringdown Laser Spectroscopy (Picarro)
Thermal Gravimetry, Resonant Ultrasound Spectroscopy

References:

Rohrssen M., Brunner B., Mielke R.E., and Coleman M. 2008. Method for simultaneous oxygen and hydrogen isotope analysis of water of crystallization in hydrated minerals. *Analytical chemistry*, **80**, 7084-7089.

Hodell *et al*., 2008. An 85-ka record of climate change in lowland Central America. *Quaternary Science Reviews*. **27**. 1152-1165.

Gonfiantini R. and Fontes J.C. 1963. Oxygen Isotopic Fractionation in the Water of Crystallization of Gypsum. *Nature*. **200**. 644-646.

Hodell, D.A., Turchyn, A.Y., et al., inpress. Late Glacial temperature and precipitation changes in the lowland Neotropics by tandem measurement of $\delta 18O$ in biogenic carbonate and sypsum hydration water. Geochimica, Cosmochimica. Acta

C4

TITLE: OCEAN CIRCULATION AND CARBON CYCLING SINCE THE LAST GLACIAL MAXIMUM.

SUPERVISOR: LUKE C. SKINNER.

Importance of the area of research: The atmospheric greenhouse gas concentration is a key regulatory parameter in the Earth's total heat budget. Changing concentrations of carbon dioxide (CO_2) are known to have played a central role in both the long-term and the more abrupt climate changes of the past. The mechanisms by which changing CO_2 levels can affect climate are reasonably well known; it is the mechanisms that regulate the atmospheric CO_2 budget (in particular those that operate via changes in the biosphere and the physical overturning of the ocean) that remain incompletely characterised. Bridging this gap in our knowledge of the climate system has become a pressing concern.

The Project: This project will make use of radiocarbon measurements performed on the fossil shells of both surface- and deep- dwelling foraminifera in order to investigate past changes in the 'age' of the deep ocean, and therefore the carbon sequestration capacity of the deep sea. Depth transects will be generated in the Northeast Atlantic, the eastern and western low-latitude Atlantic and the Southern Ocean for five key time-slices: the late Holocene, the Younger Dryas, the Bølling-Allerød, Heinrich Stadial 1 and the Last Glacial Maximum). In addition to radiocarbon, auxiliary geochemical proxies, including stable carbon isotopes and authigenic uranium content, will also be measured in order to provide insights into the causes of local deep-water radiocarbon ventilation changes across the last deglaciation. The goal will be to generate firm constraints on the character and causes of whole-ocean radiocarbon budget changes over the last ~ 30,000 years. This in turn will provide a basis for assessing the role of the physical ocean circulation in the deglacial rise in atmospheric CO_2, in particular through the use of simple numerical ocean models.

What the student will do: The student will be responsible for the selection of fossil material for radiocarbon dating and geochemical measurement in over 20 sediment cores, and will also be responsible for the preparation of samples for analysis. An important component of this project will involve the development of methods (and possibly equipment) for the graphitisation of very small carbonate samples.

Training: The student will receive training in micropalaeontological (microscopy) methods, clean lab procedures, graphitisation (AMS target preparation) methods and mass spectrometry techniques. There will be a possibility of participating in a research cruise, and there will be many opportunities for collaboration and interaction with research partners abroad, including in particular collaborators at the Australian National University radiocarbon facility.

References:

Skinner, L. C., Fallon, S., Waelbroeck, C., Michel, E., and Barker, S. 2010. Ventilation of the deep Southern Ocean and deglacial CO_2 rise. *Science*, **328**, 1147-1151.

Broecker, W., and Barker, S. 2007. A 190 permil drop in atmosphere's Delta-^{14}C during the "Mystery Interval" (17.5 to 14.5 kyr). *Earth and Planetary Science Letters*, **256**, 90-99.

C5

TITLE: OXYGENATION OF THE PAST OCEAN INTERIOR: NOVEL METHODS AND NEW INSIGHTS INTO CARBON CYCLE IMPLICATIONS.

SUPERVISORS: LUKE C. SKINNER, DAVID HODELL & HARRY ELDERFIELD.

Importance of the research: The distribution of dissolved oxygen in the ocean interior is intimately connected to the biological cycling of organic carbon and atmosphere-ocean gas exchange. As such it has a direct bearing on the marine carbon cycle, including in particular the balance of pre-formed versus remineralised nutrients in the ocean interior, which is expected to exert a primary control on atmospheric CO_2 on millennial- and glacial-interglacial timescales [*Ito and Follows*, 2005; *Sigman et al.*, 2010]. Methods for the reconstruction of past oxygenation have typically relied on the abundance of redox-sensitive metals incorporated into marine sediments [*Rosenthal et al.*, 1995]. However, palaeo-oxygenation reconstructions that are based on these methods are often hampered by the difficulties of distinguishing between pore-water and seawater oxygenation impacts on benthic chemistry [*McManus et al.*, 2005]. A refinement of our palaeo-oxygenation proxies, through careful modern process studies based on core-top sediments and pore-water chemistry analyses is required if advances are to be made. If new insights into the past oxygenation of the ocean interior can indeed be obtained, our understanding of the ocean's role in past atmospheric CO_2 variability may be greatly improved.

The project: This project will make use of a set of newly recovered and pristine multi-core and gravity/piston core sediments and pore-water samples from the Iberian Margin (Northeast Atlantic) to investigate modern controls on a set of key palaeoceanographic proxies. These will include proxies for deep-water temperature and carbonate ion concentration [*Elderfield et al.*, 2006; *Yu and Elderfield*, 2007], but will focus primarily on a set of complimentary 'ventilation' and oxygenation proxies (i.e. benthic fauna; bulk sediment and dispersed phase redox chemistry; benthic foraminifer stable isotope ratios; and benthic-planktic radiocarbon offsets).

Using sediment cores from a range of water depths on the Iberian and Namibian Margins, these proxies will also be used to reconstruct the evolution of North Atlantic and South Atlantic water-column hydrography and oxygenation across the last deglaciation. The project thus seeks to derive new insights into our proxies for past ocean interior properties, and to investigate the implications of novel palaeo-oxygenation reconstructions for our understanding of the glacial-interglacial carbon cycling.

What the student will do: Using core-top and down-core material from the Iberian Margin and the Namibian Margin, the student will perform bulk sediment and foraminiferal geochemistry measurements, for comparison with parallel pore-water geochemistry analyses and hydrographic data. It may be possible for the student to join the Iberian Margin cruise, and to participate in the sediment recovery and pore-water chemistry analyses. The student will also assess the microhabitat preferences and variable abundances of key benthic foraminifer species. The student will need to consider a range of water-column and pore-water processes that may affect the oxygenation proxies under consideration, as well as microhabitat effects on benthic foraminifer geochemistry. The student's project will thus draw on a range of complimentary techniques and approaches, and will target our understanding of modern processes as well as the implications of these processes for our ability to shed new light on the operation of the carbon cycle in the past.

Training: The student will receive training at the Godwin Laboratory for Palaeoclimate Research in all necessary micropalaeontological, geochemical and analytical techniques, including clean-lab sample preparation and analysis by ICP-OES and ICP-MS analysis. The student will also receive training in the graphitization of small carbonate samples for radiocarbon analysis. It may be possible for the student to gain shipboard experience, where training will be provided in sediment core handling and processing, water column profiling and sampling, and pore-water extraction and analysis techniques. Opportunities will exist for exchanges with international collaborators based in Europe, Australia and the United States.

References:

Elderfield, H., *et al*. (2006), Calibrations for benthic foraminiferal Mg/Ca palaeothermometry and the carbonate ion hypothesis, *Earth Planet. Sci. Lett.*, ***250***, 633-649.

Ito, T., and M. J. Follows (2005), Preformed phosphate, soft tissue pump and atmospheric CO_2, *Journal of Marine Research*, ***63***, 813-839.

McManus, J., *et al*. (2005), Authigenic uranium: relationship to oxygen penetration depth and organic carbon rain, *Geochimica et Cosmochimica Acta*, ***69***(1), 95-108.

Rosenthal, Y., *et al*. (1995), Glacial enrichments of authigenic Cd and U in Sub-Antarctic sediments - a climatic control on the elements oceanic budget, *Paleoceanography*, ***10***, 395-413.

Sigman, D. M., *et al*. (2010), The polar ocean and glacial cycles in atmospheric CO_2, *Nature*, *466*, 47-55.

Yu, J., and H. Elderfield (2007), Benthic foraminiferal B/Ca ratios reflect deep water carbonate saturation state, *Earth Planet. Sci. Lett.*, ***258***, 73-86.

C6

TITLE: STABLE ISOTOPE TRACERS OF MICROBIAL PROCESSES IN ESTUARINE SEDIMENTS.

SUPERVISOR: ALEXANDRA (SASHA) TURCHYN.

Importance of the area of research: In the absence of oxygen, microbial communities in the subsurface exploit electron potential gradients to obtain energy for growth, replication, and cell maintenance. These communities respire electron acceptors such as oxidized iron and manganese, nitrate, and sulphate, using residual organic carbon as food. These microbial processes are responsible for all organic carbon oxidation in the subsurface. A better understanding of how these microbial communities interact, both among themselves and with the surrounding minerals and environment, is essential for resolving redox processes in the deep biosphere.

The project: Stable isotope ratios provide a unique tool for exploring and resolving these processes. The coupled use of nitrogen isotopes in nitrate or sulphur isotopes in sulphate, for example, with oxygen isotopes in either nitrate or sulphate can expose both the net flow of carbon through the system as well as the gross rates of redox cycling within the system. In this case the nitrogen or sulphur isotopes expose the net reduction of nitrate or sulphate while the oxygen isotopes expose cycling of nitrate or sulphate between reduced and oxidized states. Taken together, coupled isotopes can approach a complete picture of energy flow through the environment.

What the student will do: The student will build flow-through reactors and collect sediments from local esturaries, which will be incubated in the Laboratory for Marine Biogeochemistry at Cambridge University. Carefully designed microbial experiments with the collected sediments, along with measurement of input and output isotope ratios (on either side of the flow through reactor) will allow the student to understand the coupled behavior of the various microbial communities and the impact of changing mineralogy on the total community behaviour.

Training which will be given: The student will work on a variety of mass spectrometers (measuring sulphur, nitrogen, oxygen isotopes) in the Godwin Laboratory. The student will also learn numerical tools associated with reactive-transport modeling for modeling flow through the built reactors. The student will design and build the flow through reactors and work in an anaerobic chamber necessary for laboratory incubations. This project will be of interest to students who wish to work at the forefront of the field of geomicrobiology.

References:

Pallud C., Melle C., Laverman A.M., Abell J., Van Cappellen P. 2007. The use of flow-through sediment reactors in biogeochemical kinetics: Methodology and examples of applications. *Marine Chemistry* **106,** 256-271.

Pallud C. and Van Cappellen P. 2006. Kinetics of microbial sulfate reduction in estuarine sediments. *Geochim. Cosmochim. Acta* **70**, 1148-1162.

C7

TITLE: RECONSTRUCTING HYDROTHERMAL CIRCULATION THROUGH GEOCHEMICAL ANALYSIS OF OPHIOLITES.
Also See P7

SUPERVISORS: MIKE J. BICKLE, ALEXANDRA (SASHA) TURCHYN & JOHN MACLENNAN.

Importance of the area of research: Hydrothermal circulation at mid-ocean ridges circulates the entire volume of the oceans through the ocean crust within a few tens of millions of years and plays a major role in buffering the chemistry of the oceans. However the structure of the hydrothermal systems, ocean ridge igneous processes and the magnitude of the hydrothermal fluid fluxes are all controversial. Ophiolites are sections of ocean crust that have been obducted onto the continents. Their structure is important for understanding magmatic and hydrothermal processes at active spreading ridges. The composition of hydrothermal minerals constrains past ocean chemistry.

What the project will involve: The project will take advantage of the 3D exposures in the best exposed ophiolites to map fossil ocean ridge hydrothermal systems. Concentrated high temperature flow locally converts basaltic rocks to distinctive epidosite assemblages which can be traced from the reaction zones at the top of the gabbros, through the sheeted dykes and into the lava sequence and are also found within the gabbros. The highly altered epidosites are buffered close to the composition of the infiltrating ocean waters for the more rapidly transported tracers and the project will investigate their use in reconstructing the oxygen isotope composition of the oceans over the last 2 Ga.

What the student will be doing: The student will work on material in Cambridge and sample hydrothermal material in ophiolites including the ~2 Ga Purtuniq ophiolite in Canada and the 93 Ma Semail ophiolite in Oman. A range of petrological observations, study of mineral reactions, fluid inclusions and geochemical and isotopic measurements may be used to understand the pressure-temperature evolution, map fluid pathways and quantify fluid fluxes.

Training that will be provided: The student will be trained in appropriate analytical tools in petrology, geochemistry, light stable isotope geochemistry and solid source mass spectrometry and in fieldwork on one or more well preserved ophiolites. The training will include modelling of reactive transport by fluid flow through the ocean crust to better understand the structure of the hydrothermal systems and resolve seawater signals in ancient hydrothermal systems.

References:

Bickle, M. J., Teagle, D. A. H., Beynon, J., and Chapman, H. J., 1998, The structure and controls on fluid-rock interactions in ocean ridge hydrothermal systems: constraints from the Troodos ophiolite: *Geological Society London, Special Publication*, **148**, 127-152.

Davis, A., Bickle, M. J., and Teagle, D. A. H., 2003, Imbalance in the oceanic strontium budget: *Earth and Planetary Science Letters*, **211**, 173-187.

Maclennan, J., Hulme T., and Singh, S. C., 2005. Cooling of the lower oceanic crust: *Geology*, **33**,357–366.

Teagle, D. A. H., Bickle, M. J., and Alt, J. C., 2003, Recharge flux to ocean-ridge black smoker systems: a geochemical estimate from ODP Hole 504B: *Earth and Planetary Science Letters*, **210**, 81-89.

Scott, D. J., Helmstaedt, H., and Bickle, M. J., 1992, Purtuniq ophiolite, Cape Smith Belt, northern Quebec, Canada: a reconstructed section of Early Proterozoic oceanic crust: *Geology*, **20**, 173-176.

C8

TITLE: EVOLUTION OF THE SULPHUR CYCLE IN THE AFTERMATH OF THE K/T BOUNDARY.
Also See Q3

SUPERVISOR: ALEXANDRA (SASHA) TURCHYN.

Importance of the research: Understanding the temporal evolution of the sulphur cycle can provide insight into the causes of variability in the paleo-carbon cycle. The first 20 million years of the Cenozoic exhibited interesting carbon cycle dynamics, including a 3-million year recovery of the biological pump after the K/T boundary and an increase and subsequent decrease in the $\delta^{13}C$ of carbonate skeletons. Sulphur isotopes measured decrease from the K/T boundary then show a dramatic increase. What drove these changes in the marine carbon and sulphur cycles, and how they might be related remains a major puzzle.

What the project involves: This project aims to explore changes in the marine biogeochemical sulphur cycle through the Paleocene and Eocene through the analysis of sulphur and oxygen isotopes in carbonate skeletons, marine barite, pyrite, bulk carbonate and possibly organic-bound sulphur. These analytical measurements will be complemented by a modeling component where the student will build a coupled carbon and sulphur isotope model to ascertain how a delayed recovery of the carbon cycle in the aftermath of the K/T boundary could impact the sulphur cycle. Analysis of coexisting oxidized and reduced sulphur pools in sediments may help constrain marine sulphate concentrations.

What the student will do: The student will obtain samples both from Ocean Drilling Program cores from different locations as well as through collaboration with a colleague in Italy. The student will chemically extract the various sulphur fractions and perform the isotope analysis at Cambridge University. The student will build a numerical model to explore the behaviour of the sulphur cycle and how it relates to the carbon cycle, particularly during and after carbon cycle perturbations such as the K/T boundary.

Training: The student will measure sulphur isotopes at Cambridge University on the Delta V Plus, aiding in our analytical development of samples down to 5ug of sulphur. The student will build coupled biogeochemical box models to explore the co-variation of the carbon and sulfur cycles after perturbations and particularly the impact on carbon and sulfur isotopes in various geochemical reservoirs. The student will have some basic fieldwork associated with obtaining the samples in Italy from across the K/T boundary. The student will learn chemical extraction techniques for a variety of sulphur minerals and help build and establish these procedures at Cambridge.

References:

D'Hondt S., Donaghay P., Zachos J.C., Luttenberg D., & Lindinger M. 1998. Organic Carbon Fluxes and Ecological Recovery from the Cretaceous-Tertiary Mass Extinction. *Science*, **282**, 276-279.

Paytan A., Kastner M., Campbell D., & Thiemens M.H. 1998. Sulphur Isotopic Composition of Cenozoic Seawater Sulphate. *Science*, **282**, 1459-1462.

Kurtz A.C., Kump L.R., Arthur M.A., Zachos J.C., and Paytan A. 2003. Early Cenozoic decoupling of the global carbon and sulfur cycles. *Paleoceanography* **18** No. 4. doi:10.1029/2003PA000908.

C9

TITLE: TEMPORAL RELATIONS BETWEEN OCEAN CIRCULATION, DUST INPUTS, AND NUTRIENT CYCLING DURING THE LAST ICE AGE.

SUPERVISORS: ALEX PIOTROWSKI, ALBERT GALY, NICK MCCAVE & DAVID HODELL.

Importance of the area of research: The study of the link between atmospheric and ocean circulation is critical to our understanding of rapid changes in the Earth's climate system. In the modern global circulation, deep water masses that are formed in the Atlantic basin ventilate much of the deep ocean. Wind-forced mixing and upwelling is an important component of global thermohaline ocean circulation because it brings nutrient-rich sub-thermocline intermediate waters to the surface ocean. Carbon is transferred to the deep ocean via the biological pump, which is especially active in upwelling regions of the ocean. It is also returned to the surface ocean and atmosphere via upwelling and air-sea gas exchange. Wind-blown dust is also a source of nutrients for surface ocean biological activity. Climate studies suggest that ocean circulation, wind strength and dust, as well as oceanic primary productivity may have different temporal forcing and lead-lag relationships during recent glacial cycles. Better constraints of the links and feedbacks of these climate variables are necessary for our understanding of how the ocean-climate system operates.

What the project will involve: Using geochemical and sedimentalogical proxies, this study will compare changes in inferred glacial and deglacial ocean circulation and how this relates to wind strength, as reconstructed from dust properties. It will also seek to examine the link between dust input and chemical inputs to the ocean with a focus on understanding its link to nutrient cycling and primary productivity.

What the student will be doing: The student will work with geochemists and paleo-climate scientists at Cambridge measuring radiogenic isotopes and particle size on the silicate fraction of marine sediment cores. Marine sediment cores located proximal to and distal from dust sources and local sediment sources will be examined, initially from Pacific Ocean but later perhaps in the Atlantic and Indian Oceans. Coupled grain size spectrum and radiogenic isotopes on the silicate fraction will be used to constrain the wind-blown component. Geochemical work on terrestrial loess samples will also constrain the radiogenic isotopic compositions in potential source areas. Neodymium and lead isotopes on authigenic foraminiferal coatings and benthic foraminiferal $\delta^{13}C$ from deep sites will be used to constrain past changes in deep ocean water mass mixing, chemical inputs, and biological activity.

Training: The project will be lab-based, and the student will learn marine sediment processing including isolation and measurement of grain-size. In order to constrain sourcing, the student will measure Sr, Nd, and Pb isotope proxy on specific grain size silicate-fraction and foraminiferal coatings from sediment cores. Ion exchange chromatographic elemental separation, analysis of elemental concentrations by ICPMS, and radiogenic isotopes by MC-ICPMS will take place at Cambridge. Carbon isotopes will be measured by the student in the Godwin Laboratory for Palaeoclimate Research at Cambridge.

References:

Parkin, D.W., (1974) Trade-winds during the glacial cycles, *Proc. R. Soc. London Ser.A*, **337**, 73-100.

Jones, C.E., Halliday, A.N., Rea., D.K., and Owen, R.M., (1994) Neodymium isotopic variations in North Pacific modern silicate sediment and the insignificance of detrital REE contributions to seawater, *Earth and Planetary Science Letters* **127**, 55-56.

Banakar, V.K., Galy A., Sukumaran N.P., Parthiban G., and Volvaiker A.Y., (2003) Himalayan sedimentary pulses recorded by silicate detritus within a ferromanganese crust from the Central Indian Ocean, *Earth and Planetary Science Letters*, **205**, 337-348.

Piotrowski, A.M., Banakar, V.K., Scrivner, A.E., Elderfield, H., Galy, A., Dennis, A., (2009) Indian Ocean circulation and productivity during the last glacial cycle, *Earth and Planetary Science Letters*, **285**, 179-189.

C10

TITLE: RECONSTRUCTING GLACIAL ATLANTIC DEEP WATER CIRCULATION AND SEDIMENT SOURCING USING RADIOGENIC ISOTOPES.

SUPERVISORS: ALEX PIOTROWSKI & NICK MCCAVE.

Importance of the area of research: In seeking to predict how climate may change in the future, we need to understand the natural mechanisms which influenced large-scale climate changes in the past. The role which ocean circulation plays in forcing and amplifying climate change is one of the most intensely debated topics in earth science research. Lateral flow of deep water masses are important variables necessary for reconstructing the physical circulation states of the ocean through time.

What the project will involve: Most transport of deep water in the ocean occurs in deep western boundary currents. It has been shown that sediment mean grain size in the silt range is controlled by bottom water flow speed, making it a proxy of deep water circulation strength. Radiogenic isotopes can be used to trace sediment source, which in deep western boundary settings effectively traces bottom water flow direction and source, and also inputs of sediment along deep water flow paths. Understanding how ocean circulation strength and source changed during the last glacial cycle will greatly improve our understanding of the link between ocean circulation and climate change.

What the student will be doing: Samples from cores along the Atlantic deep western boundary current will be measured for grain size and radiogenic isotopes at specific climatologically-important time intervals. Radiogenic isotopes will be measured on specific size fractions, and the student will integrate this with grain size data in both a geochemical and sedimentalogical perspective to infer changes in deep water flow speed and source.

Training that will be provided: The project will be lab-based, and the student will learn marine sediment processing including isolation and measurement of grain-size. In order to constrain sourcing, the student will measure Sr, Nd, and Pb isotope proxy on specific grain size silicate-fraction. Ion exchange chromatographic elemental separation, analysis of elemental concentrations by ICPMS, and radiogenic isotopes by MC-ICPMS will take place at Cambridge.

References:

Hall, I.R., McCave, I.N., Shackleton, N.J., Weedon G.P., and Harris S.E., (2001) Intensified deep Pacific inflow and ventilation in Pleistocene glacial times, 2001, *Nature*, **412**, 809-812

Kissel. C., Laj, C., , Piotrowski, A.M., Goldstein, S.L., and Hemming S.R., (2008) Millennial-scale propagation of Atlantic deep waters to the glacial Southern Ocean, *Paleoceanography* **23**, PA2102, doi:10.1029/2008PA001624.

C11

TITLE: PAST CHANGES IN PACIFIC-SOUTHERN OCEAN DEEP WATER EXCHANGE FROM ND ISOTOPES.

SUPERVISORS: ALEX PIOTROWSKI, HARRY ELDERFIELD, NICK MCCAVE & HELEN BOSTOCK (NIWA, NEW ZEALAND)

Importance of the area of research: The deep western boundary current inflow to the Pacific Ocean, near New Zealand, is one of the key locations for inter-basin exchange of deep water in the global ocean. The large volume of the deep Pacific means that it has the potential to be a large carbon reservoir, and changes in its ventilation may play an important role in controlling atmospheric carbon dioxide on glacial-interglacial timescales.

What the project will involve: This research builds upon the work of McCave *et al*. (2008), who used $\delta^{13}O$ and $\delta^{13}C$ measurements on benthic foraminifera to infer glacial to interglacial variations in water mass structure, observing that the water mass structure in the south-western Pacific remained broadly similar between the glacial and Holocene. We will bring a novel proxy, Nd isotopes, to examine whether the sourcing of deep water masses changed during the last glacial cycle. Nd isotope work from the South Atlantic and Indian Ocean shows large glacial-interglacial changes which are likely related to sourcing of deep waters, and should be propagated via the Southern Ocean to the south-western Pacific.

What the student will be doing: Samples from cores located in the Southern Ocean, along the southwestern Pacific deep western boundary current, and South Pacific, will be measured for foraminiferal radiogenic neodymium and stable carbon and oxygen isotopes. These will be integrated with other globally-distributed Nd isotope records from to understand large-scale changes in deep water mass exchange.

The role of boundary exchange on Nd isotopes along the New Zealand margin will also be examined, and may provide new insight into how the Nd isotope proxy works. Time-slice maps and cross sections will be produced from the southwestern Pacific to assess how well Nd isotopes follow hydrography and highlight potential inputs, thereby elucidating regional cycling of REE in seawater.

Training that will be provided: The project will be lab-based, and the student will learn marine sediment processing, working with foraminifera and other phases within marine sediments. Ion exchange chromatographic elemental separation, analysis of elemental concentrations by ICPMS, and radiogenic isotopes by MC-ICPMS will take place at Cambridge. Carbon isotopes will be measured by the student in the Godwin Laboratory for Palaeoclimate Research at Cambridge.

References:

McCave, I. N., L. Carter, and I. R. Hall. (2008) Glacial-interglacial changes in water mass structure and flow in the SW Pacific Ocean, *Quat. Sci. Rev*., **27**, 1886–1908, doi:10.1016/j.quascirev.2008.07.010.

Piotrowski, A.M., Banakar, V.K., Scrivner, A.E., Elderfield, H., Galy, A., Dennis, A., (2009) Indian Ocean circulation and productivity during the last glacial cycle, *Earth and Planetary Science Letters*, **285**, 179-189.

Piotrowski A.M., Goldstein S.L., Hemming S.R., Fairbanks R.G., and Zylberberg, D.R., (2008) Oscillating glacial northern and southern deep water formation from combined neodymium and carbon isotopes, *Earth and Planetary Science Letters* **272** (2008) 394–405.

McCave, I.N. and Carter, L., (1997) Recent sedimentation beneath the Deep Western Boundary Current off northern New Zealand. *Deep-Sea Research* I, **44**, 1203- 1237.

C12

TITLE: GEOLOGICAL CARBON STORAGE RESERVOIRS: REACTIONS BETWEEN CO_2, BRINES AND MINERALS IN RESERVOIRS.
Also see P16

SUPERVISOR: MIKE BICKLE.

Importance of the area of research: Geological carbon storage which involves separation of CO_2 from power station fuels or waste gases and injection and storage of the CO2 underground in geological formations offers one of the more economical and practical methods for society to manage its transition to a low-carbon economy. A key aspect of geological carbon storage is the need to ensure that the storage is safe and efficient and this requires the ability to model the fate of the CO_2 over the ~ 10000 year storage period.

What the project will involve: The CO_2 injected into geological formations will dissolve in saline brines which will then react with carbonate and silicate minerals. The research will use a combination of modelling, observations and analyses of fluids and minerals from natural CO_2-rich systems and on small scale CO_2 injection experiments or enhanced oil recovery sites to investigate the nature of the reactions and their kinetics.

What the student will be doing: The student will study existing and fossil CO_2 reservoirs in Colorado and sites of active CO_2 injection in Wyoming and Utah. Core from a research hole to be drilled in Utah should be available to study reservoir and caprocks which have interacted with natural CO_2-rich fluids. Depending on the student's specific interests, the work may include petrological study of CO_2 reservoirs, specific geochemical and isotopic analyses of fluids and minerals from the natural or anthropogenic injection sites and/or thermodynamic and transport modelling of reactive flow. The project will suit students trained in igneous or metamorphic petrology, geochemistry and/or thermodynamics with experience of field geology.

Training that will be provided: The student will take part in field work in Utah and Wyoming collecting rock samples, mapping possible fossil CO_2 reservoirs and collecting fluids and gases from seeps and drill holes into existing CO_2 reservoirs and from active injection sites. The student will be trained in thermodynamics, modelling of reactive transport and an array of geochemical and isotopic analytical techniques. They will join a group of 7 (faculty, post-docs and students) working on fluid-fluid and fluid-mineral reactions in CO_2 storage reservoirs, which is part of a larger consortium (CRIUS) involving Manchester and Leeds Universities and BGS. The student will also be encouraged to interact with workers in Cambridge researching other aspects of geological carbon storage including both modelling of multi-phase flow and seismic imaging of reservoirs.

References:

Bickle, M., Chadwick, A., Huppert, H. E., Hallworth, M., and Lyle, S., 2007, Modelling carbon dioxide accumulation at Sleipner: Implications for underground carbon storage: *Earth and Planetary Science Letters*, **255**, 164–176.

Bickle, M.J., Geological carbon storage. *Nature Geoscience* 2 (12), 815-818 (2009).

Kampman, N., Bickle, M., Becker, J., Assayag, N., and Chapman, H., 2009, Feldspar dissolution kinetics and Gibbs free energy dependence in a CO_2-enriched groundwater system, Green River, Utah: *Earth and Planetary Science Letters*, **284**, 473-488.