Fluid flow through carbonate platforms: constraints from $^{234}$U/$^{238}$U and Cl$^-$ in Bahamas pore-waters

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Abstract

The geometry, timing, and rate of fluid-flow through carbonate margins and platforms is not well constrained. In this study, we use U concentrations and isotope ratios measured on small volumes of pore-water from Bahamas slope sediment, coupled with existing chlorinity data, to place constraints on the fluid-flow in this region and, by implication, other carbonate platforms. These data also allow an assessment of the behaviour of U isotopes in an unusually well constrained water–rock system. We report pore-water U concentrations which are controlled by dissolution of high-U organic material at shallow depths in the sediment and by reduction of U to its insoluble 4+ state at greater depths. The dominant process influencing pore-water ($^{234}$U/$^{238}$U) is alpha recoil. In Holocene sediments, the increase of pore-water ($^{234}$U/$^{238}$U) due to recoil provides an estimate of the horizontal flow rate of 11 cm/year, but with considerable uncertainty. At depths in the sediment where conditions are reducing, features in the U concentration and ($^{234}$U/$^{238}$U) profiles are offset from one another which constrains the effective diffusivity for U in these sediments to be $1-2 \times 10^{-3}$ cm$^2$ s$^{-1}$. At depths between the Holocene and these reducing sediments, pore-water ($^{234}$U/$^{238}$U) values are unusually low due to a recent increase in the dissolution rate of grain surfaces. This suggests a strengthening of fluid flow, probably due to the flooding of the banks at the last deglaciation and the re-initiation of thermally-driven venting of fluid on the bank top and accompanying recharge on the slopes. Interpretation of existing chlorinity data, in the light of this change in flow rate, constrain the recent horizontal flow rate to be 10.6 (±3.4) cm/year. Estimates of flow rate from ($^{234}$U/$^{238}$U) and Cl$^-$ are therefore in agreement and suggest flow rates close to those predicted by thermally-driven models of fluid flow. This agreement supports the idea that flow within the Bahamas Banks is mostly thermally driven and suggests that flow rates on the order of 10 cm/year are typical for carbonate platforms where such flow occurs. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: fluid dynamics; carbonate platforms; U-238/U-234; pore water
1. Introduction

The flow of pore-waters through continental-margin and platform sediments has been recognised as a widespread but poorly understood phenomenon. This flow is important as it is responsible for geochemical fluxes of material between seawater and margin sediments and therefore influences seawater chemistry; the chemistry and diagenesis of the sediment; and the microbial environment of the sediment [1]. The specific examples of carbonate margins and platforms are of particular interest because fluid flow is required to explain the large volume of dolomite formed in these environments.

Several mechanisms may drive margin and platform fluid flow including differences in elevation head; compensation for freshwater flow; heating of fluid within the margin; and salinity contrasts caused by evaporation [2,3]. Previous studies have recognised fluid-flow from pore-water chemistry and have investigated the driving mechanisms e.g. [3,4]. But estimating the timing and rate of fluid flow has proved more difficult. A lower limit has been derived for the Australia margin at 0.2 cm/yr [5] but the best estimates of flow rates come from modelling studies [2] rather than observations. Modelling, unsurprisingly, predicts different rates depending on the mechanism driving fluid flow with <1 cm/yr for salinity-driven flow and as high as 7.5 cm/year for thermally driven flow.

Improving our understanding of the driving mechanism and the rate of fluid flow for margin sediments was a major objective of two recent drilling programs in the Bahamas — The Bahamas Drilling Project [6] and ODP Leg 166 [1,7]. These programs uncovered clear evidence for fluid flow from pore-water chemistry and from temperature measurements [1,7]. In particular, ODP Leg 166 unearthed considerable evidence for active flow of seawater into the slopes of the Bahamas (Swart et al. manuscript in preparation).

In this study, we investigate the timing and rate of fluid flow in Bahamas slope sediments in order to gain a better understanding of the mechanism driving flow and the fluxes of material into and out of the sediment. To achieve this, we have measured \(^{234}U/^{238}U\) ratios in pore-water samples from ODP Leg 166. \(^{234}U/^{238}U\) ratios in pore water are a potentially powerful tool as they are influenced by radioactive decay and by alpha recoil of \(^{234}U\). Both these processes happen at known rates and \(^{234}U/^{238}U\) may therefore provide information about the rates and timing of fluid flow not attainable from more commonly measured pore-water species.

Although \(^{234}U/^{238}U\) has been measured in many groundwater studies [8] it has not often been measured in sediment pore-waters, due largely to the problem of getting large enough samples of pore-water to analyse. But thermal-ionisation techniques [9] now enable isotopic analysis on samples of the size routinely collected for pore-water studies. Four previous studies have reported \(^{234}U/^{238}U\) measurements on sediment pore-waters [10–13]. Together, these studies have demonstrated that the ratio is similar to sea-water in rapidly accumulating sediments but increases above the seawater value for slowly accumulating red clays. To date, no \(^{234}U/^{238}U\) measurements exist on samples from >1 m below the sediment surface and a full assessment of the processes that control the ratio in sediment pore-waters is still lacking.

2. Regional setting and samples

The Bahamas are a series of Mesozoic basement features swathed in a thick sequence of carbonate-dominated sediment [14]. These sediments have responded sensitively to sea-level change, prograding rapidly basinward during episodes of high sea-level. During the Pleistocene, with its rapid and cyclical sea-level changes, this responsiveness manifests itself as a series of discrete packages of rapidly accumulating highstand sediment, separated by layers of more slowly accumulating lowstand sediment [15]. During highstands, the flooding of the Bahamas Banks increases production of aragonite leading to increased sedimentation rates of aragonite-rich sediment on the slopes. During lowstands, when the banks are exposed, more slowly accumulating slope sediments contain higher percentages of calcite (Fig. 1).

ODP Leg 166 drilled into the prograding wedge of sediments on the western slope of the Great Bahamas Bank with the principal goals of elucidating sea-level change through the Cenozoic and the nature
Fig. 1. Stratigraphy of ODP Leg 166 Site 1009. The first panel indicates mineralogical variations with depth (shipboard measurements [1]) and shows repeated variations in the aragonite content of the sediment reflecting sea-level changes. The second panel shows porosity (shipboard measurements [1]), with arrows representing sampling horizons of pore-waters analysed in this study. The fourth panel shows oxygen-isotope measurements made on bulk sediment at 50 cm intervals on a Finnigan 251 with a Keil II automated carbonate reaction system (Slowey et al. in preparation). The thin glacial sediment packages cause these to be under-sampled but some glacial values are observed. The sedimentary and isotope data enable marine isotope stages (MIS) to be assigned to the core, shown in the third panel. The inset map shows the location of this Site, together with the other samples discussed in this paper.

of fluid-flow through passive margins [1,7]. For the latter goal, pore-waters were extracted from each of the seven sites drilled, of which two have been used for this study: Site 1005 (24°33.772' N, 79°14.141' W, 362 m water depth); and Site 1009 (23°36.84' N, 79°3.00' W, 320 m water depth) (Fig. 1).

Pore-waters were separated from the core on ship. Protocols were similar to those routinely used for ODP pore waters [16] except that, for samples from Site 1009, most of the sediment handling was performed under a nitrogen atmosphere in a disposable glove bag. Sections were capped quickly after core retrieval and transferred rapidly to the geochemistry laboratory. Sediment extrusion, surface scraping, and packing into holders for squeezing was performed in the glove bag. Squeezing was performed immediately upon removal from the glove bag and samples were filtered [16] into acid-washed storage bottles. Sub-samples of pore-waters between 2.4 g and 15.9 g were used for the U analyses of this study.
Fifteen samples ranging to a depth to 122 m were analysed from Site 1005 and 16 samples to a depth of 192 m analysed from Site 1009. In addition, several 4-ml samples of Bahamian seawater were analysed to assess the precision of the analytical techniques, and to ensure that seawater U in the region is similar to that elsewhere. These seawater samples were from offshore Lee Stocking Island (23°47.1’N, 76°5.0’W) and are taken from three depths: surface; 15.2 m; and 30.4 m. The latter was measured three times to assess reproducibility.

3. Chemical and analytical methods

Pore-waters were decanted into clean Teflon beakers and weighed. They were spiked with a mixed 233U-235U-236U-Th spike with a 233U/236U ratio close to unity. The U was co-precipitated with iron and concentrated from a mixed HCl-acetone solution on two sequential 100-μl anion-exchange columns. Chemical yields were 87% (±3% 2 s.d.; n = 4) and total procedural blanks were 6.3 pg (±5.5 pg 2 s.d.; n = 4). The U samples were analysed as the metal using a VG Sector 54-30 mass spectrometer. All peaks were measured using ion-counting and collected in the following sequence: 233U (2 s); 234U (8 s); 235U (2 s); 236U (2 s). 30–100 cycles were collected at 234U+ count rates of 20–100 cps. Mass fractionation was corrected using the known 233U/236U ratio in the spike. A correction to the measured 234U/235U ratio was necessary for 234U contained in the spike but this correction was typically only about 1% and the 234U concentration of the spike is known well enough that the uncertainty introduced to the final isotope ratio by this correction is always less than 1.5%.

Corrected 234U/235U ratios were converted to (234U/238U) (where round brackets signify an activity ratio) using a 238U/235U ratio of 137.88; λ234 of 2.835×10^-6 [18]; and λ238 of 1.551×10^-10 [19]. No age correction has been made to the measured values.

Mass-spectrometer performance was assessed by repeated measurement of the NIST standard, U-500, interspersed between sample analyses. Eight filaments were loaded with 0.1 ng of U-500. This mass of U-500 contains 235U and 234U equivalent to that in ≈7 ng of natural U. These loads were run with the 234U+ beam at 50–100 cps for 60 cycles in order to mimic the sample runs. These runs yield an average 235U/234U of 95.72 ± 0.41 (2 s.d.), within error of the certified value.

4. Results

The seawater samples have U concentrations of 3.34±0.07 ppb (2 s.d.; n = 5) (Table 1). Normalising to a salinity in the region of Lee Stocking Island of ≈36 permil yields U concentrations of 3.24 ppb, in agreement with the concentration of open-ocean Pacific and Atlantic water [20]. Seawater (234U/238U) is 1.143 ± 0.004 (2 s.d.; n = 5), again in agreement with existing measurements [20].

Two sampling artefacts have been recognised for pore-water U measurements. First, on exposure to air of even a few minutes, sediment pore-waters rapidly change their redox state which can result in dramatic release of any reduced U from the solid phase into pore-waters [10,17,21]. As samples from Site 1005 were exposed to air during squeezing, results from this core must be treated with caution, particularly in the deeper, reducing portions. Discussion for the remainder of the paper will therefore focus on the samples from Site 1009 for which the main sampling was performed under nitrogen to minimise this artefact.

The second sampling artefact is due to sample decompression [22–24]. When sediment is brought to the surface, the decrease in pressure causes precipitation of carbonate from pore-waters which can change the U concentration for deep-water samples. In the shallow waters of the Bahamas this effect is expected to be small, however, and should not have reduced U concentrations enough to change any of the interpretations of this paper. If minor amounts of U are precipitated during decompression, this removal will not fractionate the U isotopes and will not alter the pore-water (234U/238U) values.

Results from Site 1009 are illustrated in Fig. 2, together with other pore-water results on these samples collected during ODP Leg 166 [1]. U concentrations of the uppermost samples are up to 8.7 ppb. Beneath this depth, there is a general decrease in the U concentration to reach values consistently below 1 ppb.
Fig. 2. Pore-water results from ODP Leg 166 Site 1009. The upper two panels are results of this study, and the lower two are shipboard measurements [1]. These shipboard measurements also extend to greater depth but are not shown here because of the lack of accompanying U data. \(^{(234\text{U}/238\text{U})}\) values are not age corrected. Errors are within symbol size. Sedimentary features for this core are shown in Fig. 1. The thin horizontal line on each panel represents the seawater value for that species and shaded bars represent the thin glacial packets of sediment representing stages 2, 6, 8, 10, and 12. Arrows on the chlorinity figure represent interpretation of the features: between the core top and 1 advection dominates, between 2 and 3 diffusion is dominant, and between 1 and 2 advection and diffusion are in balance. The latter interval is used in the text to derive a flow rate.
by $\approx 50$ m. At depths greater than 50 m, two broad peaks are seen in the $U$ concentration at 50–100 m and 100–145 m. $(^{234}\text{U}/^{238}\text{U})$ in Site-1009 samples show a wide range between 1.051 and 2.874 (Table 1). Samples from the Holocene sediment package, 0–20 m, are characterised by $(^{234}\text{U}/^{238}\text{U})$ values which are slightly above the seawater value. Beneath this, from 20–60 m, $(^{234}\text{U}/^{238}\text{U})$ is variable but lower than seawater and exhibits an inverse correlation to the $U$ concentration. Beneath 60 m $(^{234}\text{U}/^{238}\text{U})$ is higher than seawater and rather variable. Two broad peaks are visible and occur at slightly greater depth than those seen for $U$ concentration, the shallower from 50–95 m and the deeper from $\approx 95–140$ m (Fig. 2).

### Table 1

Uranium concentrations and isotope ratios from Bahamas seawater and pore-waters

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<th>Depth (m)</th>
<th>Sample mass (g)</th>
<th>$(^{234}\text{U}/^{238}\text{U})$</th>
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<th>$238\text{U}$ (ppb)</th>
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5. Discussion

5.1. Controls on U behaviour

5.1.1. U concentration

Uranium concentrations in pore-waters are changed from the initial seawater value by sediment dissolution and precipitation (Fig. 3). The uranium concentrations of the upper samples of Site 1009 are up to 2.6 times that of seawater due to dissolution. Evidence for aragonite dissolution in these sediments comes from pore-water Sr concentrations which are \( \approx 7\% \) higher than seawater. But U concentrations are \( \approx 160\% \) higher than seawater and, as Sr and U are incorporated into aragonite at about the same ratio as they occur in seawater, these high values require the dissolution of a phase with a much higher U/Sr ratio than aragonite. The most likely candidate is organic material which is being oxidised close to the sediment/water interface. A relationship between organic material and U has been reported before for anoxic sediments [25,26] but, in these studies, the relationship may be explained by a post-depositional flux of U into the sediment by pore-water diffusion [21]. More convincing evidence that organic material can contain very high concentrations of U is provided by measurements of algal organic material which yield U concentrations up to \( 10^5 \) times those of the water from which they were filtered [27]. From high values close to the sediment–water interface, the U concentration decreases with depth to values significantly lower than seawater, indicating an active removal mechanism. This removal is probably due to the reduction of U to the insoluble U(IV) form and precipitation within the sediment. Such precipitation has been the subject of several studies e.g. [10,28,29] and the reduction from U(VI) to U(IV) has been found to occur at a reduction potential close to NO\(^3\)- reduction and Fe reduction [10,28]. Shipboard pore-water data do not allow an assessment of the depth in the sediment at which this reduction potential is reached, but pore-water sulphate data (Fig. 2) indicate that some sulphate reduction is occurring in these sediments, so the reducing potential in the sediment is high enough to support the removal of U by this mechanism.

![Fig. 3. Plot of U-isotope ratio against concentration showing schematically the impact of various processes on pore-water values. The open square represents the seawater values at which pore waters start. Alpha recoil and decay change the isotope ratio without changing the concentration. Reduction of U to its insoluble state decreases the concentration without fractionating the isotopes. And dissolution causes an increase of U concentration which may be accompanied by a lowering of \( \left( ^{234}\text{U}/^{238}\text{U} \right) \) due to dissolution of \(^{234}\text{U}\)-impoverished grain surfaces if the grains are old.](image-url)
5.1.2. Alpha recoil

If pore-waters do not interact with the sediment, (234 U/238 U) will decrease with age due to the decay of excess 234 U (Fig. 3). But interaction does occur because, during alpha decay of 238 U, a fraction of the daughter 234 Th is expelled from a layer close to the surface of mineral grains into the pore water, where it rapidly decays to give 234 U. Assuming that the recoil layer is thin relative to the grain size, then at the surface of the grain the fraction of 234 Th ejected is 0.5 simply because the chance of an atom being moved towards the centre of the grain is equal to that of it being moved outwards. At equilibrium, therefore, the edge of the grain will have (234 U/238 U) = 0.5. The approach towards this equilibrium value with time from an initial (234 U/238 U) is analogous to the approach towards 1.0 in a closed system and is given by:

\[
\frac{234 \text{U}}{238 \text{U}}_i = \left( \frac{234 \text{U}}{238 \text{U}} \right)_{\text{init}} - 0.5 \times e^{-\lambda t} + 0.5 \quad (1)
\]

where (234 U/238 U)_init equals the activity ratio at time t, and initially. Averaging for the whole of the surface layer from which recoil loss occurs, geometry suggests that 25% of the 234 Th will be lost. A value of 0.75 should therefore be inserted in place of 0.5 in Eq. 1 in order to assess the evolution of the isotope ratio of the whole layer.

The 234 Th ejected from the mineral grains is added to pore-waters and increases their (234 U/238 U). The rate of addition of 234 U to the pore waters in mol/cm^3/a is given by:

\[
\text{Porewater } \frac{234 \text{U}}{238 \text{U}} \text{ gain } = \frac{r^3 - (r - \alpha)^3}{4r^3} \times 238 \text{ U_solid} \times \lambda 238 \times \rho_{\text{solid}} \times (1 - \phi) \quad (2)
\]

where r is the effective radius of grains in the sediment; \( \alpha \) is the 234 Th alpha-recoil distance (\( \approx 550 \) Å [30]); 238 U_solid is in mol/g, \( \rho_{\text{solid}} \) is the dry density of the sediment, and \( \phi \) is the porosity. The first term describes the fraction of daughter 234 U which is expelled from the mineral grains (assuming they are spherical). Other terms describe the amount of 238 U decay per year in terms of mol/cm^3 of bulk sediment.

This gain of 234 U to the pore waters is counteracted by loss of excess 234 U by decay. The rate of this excess 234 U loss (mol/cm^3/a) is given by:

\[
\text{Porewater } \frac{234 \text{U}}{238 \text{U}} \text{ loss } = 238 \text{ U_p.w. } \times \lambda 238 \times \frac{[\left( \frac{234 \text{U}}{238 \text{U}} \right) - 1]}{\rho_{\text{p.w.}} \times \phi} \quad (3)
\]

For old pore-waters, the rate of gain of 234 U will eventually equal the rate of loss of excess 234 U. Then, from Eqs. 2 and 3, the equilibrium pore-water (234 U/238 U) is given by:

\[
\left( \frac{234 \text{U}}{238 \text{U}} \right)_{\text{Equil.}} = \frac{r^3 - (r - \alpha)^3}{4r^3} \times \frac{238 \text{U}_\text{solid}}{238 \text{U}_{\text{p.w.}}} \times \frac{\rho_{\text{solid}}}{\rho_{\text{p.w.}}} \times \frac{(1 - \phi)}{\phi} + 1 \quad (4)
\]

and is therefore dependant largely on the effective grain-size of the sediment and the ratio of solid to pore water U concentrations. The approach of pore-water (234 U/238 U) towards this equilibrium value is given by a similar equation to Eq. 1:

\[
\left( \frac{234 \text{U}}{238 \text{U}} \right)_i = \left[ \left( \frac{234 \text{U}}{238 \text{U}} \right)_{\text{Equil.}} - \left( \frac{234 \text{U}}{238 \text{U}} \right)_{\text{init}} \right] \times [1 - e^{-\lambda t}] + \left( \frac{234 \text{U}}{238 \text{U}} \right)_{\text{init}} \quad (5)
\]

In environments where the (234 U/238 U)_init is known, pore-water measurements of the U isotope ratio might therefore be used to give an age of that pore-water and this value used to assess the rate of fluid flow. This can be done for the Holocene samples from Site 1009 in this study. Taking (234 U/238 U)_init as 1.143 (the measured seawater value); r as 20 \( \mu m \) (the average grain size based on sieving); 238 U_solid as 4 ppm for these aragonite-rich sediments [31]; 238 U_p.w. as 8 ppb (based on the upper two concentration measurements); \( \rho \) as 2.8 for aragonite; \( \phi \) as 0.6 (Fig. 1); and (234 U/238 U), as 1.151 (from the 17.2 m sample) gives an age of the pore water of 1.7 ka. Pore-water and seawater (234 U/238 U) measurements are not clearly resolved so no minimum age can be assessed by this method. But maximising the difference between the seawater and pore-water values within the measurement errors allows a maximum age for the pore water to be calculated at 3.7 ka. These ages will be discussed further in Section 5.2.
5.1.3. Grain-surface dissolution

Samples from 25 to 52 m in both Sites 1005 and 1009 have \(^{234}\text{U}/^{238}\text{U}\) values which are significantly lower than seawater and, in most cases, are lower than can be explained by decay of excess \(^{234}\text{U}\). For instance, the 26.7 m sample from Site 1009 is from the Stage 5 sediment package which, in a closed system would yield a \(^{234}\text{U}/^{238}\text{U}\) of \(\approx 1.102\), but which has a measured value of 1.061. And the 32.9 m sample from Site 1005 is actually lower than 1.0, which cannot be explained by decay regardless of age. The only source of \(\text{U}\) with \(^{234}\text{U}/^{238}\text{U}\) significantly lower than seawater in these sediments is the outer layer of the sediment grains which have lost \(^{234}\text{U}\) by alpha-recoil. The low values seen at this depth in the sediment, therefore, must reflect dissolution of the surface of mineral grains in the sediment.

If dissolution is continuous, it will tend to counteract the alpha-recoiled \(^{234}\text{U}\) and therefore decrease the pore-water value from that predicted from Eq. 3. But continuous dissolution will not be able to reduce the \(^{234}\text{U}/^{238}\text{U}\) beneath that predicted for closed-system decay. In order to do this, and therefore to get values as low as those seen here, the dissolution rate must have increased recently. This implies either that the fluid flowing past these sediments became more corrosive, perhaps by reversing flow direction, or that the rate of flow of the fluid increased [32]. During slow flow, sediment grain surfaces become impoverished in \(^{234}\text{U}\), and this ejected \(^{234}\text{U}\) is carried away, either out of the sediment or to greater depth depending on the flow direction. Then, when flow rates increase or flow reverses, dissolution of the sediment grain surfaces occurs which releases \(\text{U}\) with unusually low \(^{234}\text{U}/^{238}\text{U}\) to the pore-waters. Increased dissolution also results in higher pore-water \(\text{U}\) concentrations as evidenced by the inverse correlation between \(^{234}\text{U}/^{238}\text{U}\) and \(\text{U}\) concentration in this depth interval (Fig. 2, Table 1). This scenario argues strongly that fluid flow through the Bahamas banks is not constant but has changed recently, most probably due to changing sea-level (Section 5.2).

5.1.4. Exchange with reduced \(\text{U}\)

Beneath 52 m, alpha-recoil is the dominant control on pore-water \(^{234}\text{U}/^{238}\text{U}\) values. Because of the changing flow rate and/or the possibility that flow has reversed in the past, using the high \(^{234}\text{U}/^{238}\text{U}\) values here to deduce past flow rates is difficult. This problem is exacerbated by the fact that chemical exchange of \(\text{U}\) appears to occur between the pore-waters and the solid phase.

Evidence for this exchange come from \(^{234}\text{U}/^{238}\text{U}\) values which do not increase monotonically with depth as expected from Eq. 3 but show structure related to the composition of the sediment. The upper peak visible in both \(\text{U}\) concentration and \(^{234}\text{U}/^{238}\text{U}\) corresponds to Stage 7 and the lower peak to Stage 11 (the thin Stage 9 packet is not sampled). Highstand sediment contains more \(\text{U}\) than the intervening lowstand sediment and is finer grained, both of which serve to increase the \(^{234}\text{U}/^{238}\text{U}\) in the pore-waters. The correspondence of high pore water \(^{234}\text{U}/^{238}\text{U}\) with highstand sediment packages suggest that the alpha-recoiled \(\text{U}\) has not been advected far in the sediment and has been chemically retarded. This is also shown by the two peaks in \(\text{U}\) concentration which have been moved only a small distance by the fluid flow.

An assessment of the retardation of \(\text{U}\) in the sediment can be made from the slight offset between the \(\text{U}\) concentration and \(^{234}\text{U}/^{238}\text{U}\) peaks caused by the opposite diffusional gradients for these tracers: \(\text{U}\) concentrations decrease down the core while \(^{234}\text{U}/^{238}\text{U}\) increases. Although sampling density is not high enough to do this accurately, the troughs between the two peaks at \(\approx 100\) m are clearly offset. This offset is about 6 m so each peak has moved \(\approx 3\) m in the \(\approx 250\) ka since the stage 8 sediment in which they are found. Using the approximate relationship \(T = L^2/D_{\text{eff}}\), where \(T\) = time and \(L\) = distance [33], gives a \(D_{\text{eff}}\) of \(\approx 1 \times 10^{-8}\) cm\(^2\) s\(^{-1}\). Similarly, for the troughs at around 140 m, the offset is \(\approx 10\) m, or 5 m in either direction, and the age is \(\approx 420\) ka, giving \(D_{\text{eff}}\) \(\approx 2 \times 10^{-8}\) cm\(^2\) s\(^{-1}\). These values of \(D_{\text{eff}}\) are only approximate but are within the range found by Ku [34] who reported values of \(1.5-4.5 \times 10^{-8}\) cm\(^2\) s\(^{-1}\) from a variety of sediment types. Other workers have reported values still lower in highly-reducing turbidites of the Madeira plane (<5 \(\times 10^{-13}\) cm\(^2\) s\(^{-1}\) [35]; 0.1–1 \(\times 10^{-14}\) cm\(^2\) s\(^{-1}\) [36]).

The value of \(D_{\text{eff}}\) of \(\approx 10^{-8}\) found for the Bahamas sediments is two to three orders of magnitude lower than for conservative species in marine sediments [37]. This suggests that, in the reducing portions
of the sediments of this study, exchange with the sediment will cause U advection or diffusion to be 100–1000 times slower than the advection or diffusion of the fluid phase and of non-reactive species within this fluid [34]. It is interesting to note that the maximum pore-water U concentration measured from Site 1009 is just over 100 times higher than the minimum value. This implies that all the U removed from the pore-waters as they become reducing remains in a form that exchanges and equilibrates with the pore-waters. If so, then it might, in the future, prove possible to use the distance moved by the U peaks, and the measured \(^{234}\text{U}/^{238}\text{U}\) in the pore-waters, to calculate long-term fluid fluxes through the sediment.

5.2. Constraints on fluid flow

One of the principal objectives of ODP Leg 166 was to investigate the nature of fluid flow in a carbonate platform [1,7]. Pore-water \(^{234}\text{U}/^{238}\text{U}\) results provide two insights into this fluid flow. First, the \(^{234}\text{U}/^{238}\text{U}\) values measured from the Holocene sediment package provide information directly about the age of the pore-waters there. And second, the unusually low \(^{234}\text{U}/^{238}\text{U}\) values in older sediments immediately below the Holocene provide strong evidence that the fluid flow has changed through time which must be taken into account when interpreting other tracers.

The shipboard pore-water data (Swart et al. manuscript in preparation) suggest that present-day flow is into the slope sediments. A recent increase or reversal of this fluid flow, as suggested by the \(^{234}\text{U}/^{238}\text{U}\) measurements, is most easy to explain by strengthened thermally-driven circulation [38] when the Bahamas Banks flood at the end of the last lowstand. During the lowstand, freshwater flow would have occurred through the exposed banks and caused compensatory flow of seawater through the slopes [39]. Then, when the banks flood, upward venting of warmed pore-waters onto the banks can occur. Thermally-driven recharge becomes the dominant flow mechanism on the slopes, drawing seawater into the sediments as suggested by ship-board pore-water data [1], and increasing flow rates. Modelling studies of such thermally-driven flow suggest that recharge flow on the slopes is close to horizontal [2].

The \(^{234}\text{U}/^{238}\text{U}\) value of pore waters in the Holocene suggest an age for these pore waters of 1.7 ka. In order to convert this to a flow rate, we need to know how far the pore-waters have moved. The Holocene sediment package is 20.4 m thick and formed since the flooding of the banks at 6 ka [40] giving it a sedimentation rate of 3.4 m/kyr. In 1.7 kyr, therefore, the pore-water has moved from 5.8 m to its present depth of 17.2 m. Assuming horizontal flow and a slope of the banks at this site of 3.5° [41] the horizontal distance travelled is 187 m yielding a flow rate of 11 cm/year. The minimum flow rate, calculated from the maximum possible age of these pore-waters, is 2 cm/year.

The pore-water measurement used to make this calculation is close to that of seawater leading to large uncertainties in the flow rate. And, unfortunately, deeper samples with more extreme \(^{234}\text{U}/^{238}\text{U}\) are not easy to interpret in this way due to the changing flow rate and possibly direction with time, and to the retardation of U advection in the reducing sediment. But we can gain more precise estimates of the flow rates from an interpretation of the ship-board Cl– data [1] in the light of conclusions drawn from \(^{234}\text{U}/^{238}\text{U}\) measurements. The Cl– profile (Fig. 2) exhibits generally high values at depths greater than 110 m with a linear decrease upward to 35 m and a constant value equal to that of seawater in the interval 0–22 m. High-chlorinity at depth is probably caused by diffusion of material from evaporites deeper in the sediment [1]. On its own, this profile could be interpreted as reflecting continuous channelised flow focused in the upper portion of the profile. But the \(^{234}\text{U}/^{238}\text{U}\) measurements presented here suggest that, instead, the Cl– reflects two phases of flow. The upper portion of the profile is due to rapid advection of seawater into the sediment at the present, while the linear increase below that reflects a relict diffusional profile formed during the last lowstand when fluid-flow was slower.

During the Holocene, in the absence of any advection, the upward movement of the diffusional profile would keep pace with the sedimentation rate of 3.4 m/kyr to remain at the sediment–water interface. But instead, the base of the diffusional profile is found some 13 m below the base of the Holocene. Advection during the Holocene has therefore not
only prevented the diffusion of high-chlorinity into the Holocene sediment, but has been fast enough to deepen the end-point of the diffusional gradient.

By assuming that the Cl\textsuperscript{-} profile has reached steady-state, which is reasonable given the 6 yr of flow since the flooding of the banks [40], we can use the advection-diffusion equation to estimate the rate of flow during the Holocene:

\[ \frac{\partial C}{\partial t} = D_{\text{eff}} \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} \]  

(6)

where \( C \) = chlorinity, \( z \) = distance, \( v \) = linear advective fluid velocity, and \( D_{\text{eff}} \) = effective diffusivity for chlorinity e.g. [33]. We assume that advection dominates in the upper 22 m of the sediment, diffusion in the interval 35 to 108 m, and that the change between these states (which occurs over a distance, \( z \), of 13±2 m) reflects the steady-state balance between advection and diffusion. The temperature of the sediment at this site is \( \approx 19^\circ \text{C} \) [1] which equates to a \( D_{\text{eff}} \) for Cl\textsuperscript{-} in deep-sea red clay of \( 9 \times 10^{-6} \text{ cm}^2/\text{s} \) [37]. We take a value of \( 11 \pm 2 \times 10^{-6} \text{ cm}^2/\text{s} \) for the more porous carbonate sediments of this study and, by assuming steady state so that \( \partial C/\partial t = 0 \), calculate a flow rate of \( 0.86 \pm 0.28 \text{ cm/yr vertically.} \)

Given a slope angle of 3.5\(^\circ\) [41], this is equivalent to a horizontal flow rate of \( 10.6 \pm 3.4 \text{ cm/yr} \) (the error incorporates the range of \( z \) and \( D_{\text{eff}} \) quoted above).

This Cl\textsuperscript{-} estimate of flow rate is consistent with the looser constraints derived from the \((^{234}\text{U}/^{238}\text{U})\) measurements and both estimates of flow rate agree with a value of 7.5 cm/yr deduced from a model of thermally-driven fluid flow [2]. This agreement lends support to the idea that present-day fluid flow in Bahamas is thermally driven and suggests that flow rates of the order of 10 cm/year are typical of such flow in carbonate platforms.

6. Conclusions

\((^{234}\text{U}/^{238}\text{U})\) measurements on sediment pore-waters have potential to provide information about the timing and rate of fluid-flow. In this study, alpha recoil is found to be the dominant process, causing high \((^{234}\text{U}/^{238}\text{U})\) in pore-waters and low \((^{234}\text{U}/^{238}\text{U})\) in the surface layers of sediment grains. Values above seawater in relatively shallow pore-waters enable an estimate of the age of these waters and, by assuming a horizontal flow path, give a best estimate of the flow rate of 11 cm/year, but with considerable uncertainty. At greater depths, dissolution of the \(^{234}\text{U}\)-impoverished grain surfaces causes low pore-water \((^{234}\text{U}/^{238}\text{U})\). This must be caused by a recent increase in dissolution and probably reflects an increase in flow rate as the Bahamas Banks flooded at the end of the last glacial. Shipboard chlorinity data [1] can be interpreted, in the light of this recent increase in flow rate, to yield a horizontal flow rate of \( 10.6 \pm 3.4 \text{ cm/yr} \). The two independent estimates of the flow rate are in agreement with one another, and are also consistent with a thermally-driven model of fluid flow [2]. This agreement lends support to the idea that present-day fluid flow in Bahamas is thermally driven and suggests that flow rates of the order of 10 cm/year are typical of such flow in carbonate platforms.

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