# Carbonate dissolution/preservation history

## Pacific Carbonate Cycles

Since the discovery (*e.g.* Arrhenius, 1952) of periodic cycles in the Quaternary carbonate record of eastern equatorial Pacific sediments, a number of studies relating to the nature and cause of what is now called "Pacific Carbonate Cycles" have subsequently followed (*e.g.* Luz and Shackleton, 1975; Thompson and Saito, 1976; Shackleton, N., 1977; Moore *et al.*, 1977, Berger, 1979, 1992; Pisias and Prell, 1985; Farell and Prell, 1989, 1991; Snoeckx and Rea, 1994; Oba, 1994; LaMontagne *et al.* 1996). In many Pleistocene to Recent deep-sea core sequences from depths between the lyscoline and the carbonate compensation depth (CCD), glacial intervals are carbonate rich relative to the interglacial intervals. Commonly invoked mechanisms driving these cycles often revolve around either increased surface water productivity during glacial times (increased carbonate supply) or changes in deepwater corrosiveness during interglacials. Although far from resolved, there is a growing body of evidence pointing to the latter as the primary cause (Broecker, 1971; Berger *et al.*, 1973; Thompson and Saito, 1976; Emerson, 1985; Farell and Prell, 1989; Wu *et al.*, 1991; Le and Shackleton, 1992; Karlin *et al.*, 1992; Stephens and Kadko, 1997). Because a change in deep-water corrosiveness involves a change in the chemistry of the oceans, it is often linked to changes in atmospheric $CO_2$ concentrations. An alternative hypothesis was recently proposed by Oba (1994) citing the role of glacial/interglacial changes in carbonate eolian dust particle supply in regulating seawater alkalinity.

Many of the studies made on carbonate cycles in the Pacific are based on sedimentary sequences from the equatorial central Pacific. Because the sea floor in the North Pacific is almost everywhere bathed with $CO_3$ under-saturated waters (below present day CCD), there have been very few and often conflicting reports on this subject. Karlin *et al.*(1992) observed a strong linkage between the carbonate stratigraphy in the northeast Pacific sediments of their study and that of the central equatorial Pacific records. Almost similar results are observed in the mid to high latitude northwestern Pacific (Zahn *et al.* 1991, Hovan and Rea, 1991) although the "Atlantic Type" of carbonate pattern has also been suggested to occur in this region (Keigwin *et al.*, 1992; Haug *et al.*, 1995).

## Results

The time series profiles of FDX, FRAG and planktic foraminiferal number for the three cores are here compared. In core NGC 102, these three indices broadly covary down-core exhibiting distinct periodicity in the order of 100 kyr cycles (Figure 7). The same is observed for NGC 108 and NGC 106, although the relationship between planktic foraminiferal number and the two other indices is not as distinct (Figures 8 and 9). In all three cores, however, FDX and FRAG are tightly coupled (Figures 7e, 8e, and 9e) indicating that the signals generated by these two indices are not mere artifacts of laboratory processing or counting. FDX and FRAG values recorded for the deepest core NGC 106 (3,713 m water depth) are generally higher than NGC 102 (2,612 m water depth) and NGC 108 (3,390 m water depth).

The FDX and FRAG records of the cores are compared with the carbonate records (Figure 10) of NGC 102 and a nearby core V21-146 (Hovan *et al.*, 1991). Core V21-146 was also taken from Shatsky Rise (37°41'N, 163°02'E, water depth of 3,968 m) but at a slightly northern position and at a deeper depth relative to the three cores. As previously emphasized, the different dissolution indices here measured and $CaCO_3$ content, although related, do not necessarily have a linear relationship (Figure 10). The carbonate record of core V21-146 and the two indices (FDX and FRAG) broadly covary down-core suggesting that carbonate dissolution have significantly affected %CaCO3 at least for this depth. In contrast, the carbonate record of NGC 102 does not exhibit any clear glacial-interglacial pattern and only partially correlates with the two dissolution indices. In addition, the increased carbonate dissolution (increasing FRAG and FDX values) observed in the three cores during the Holocene interval (oxygen isotope stage 1) is not accompanied by any corresponding decrease in %CaCO3 in core V21-146 and NGC 102. Clearly carbonate contents of the sediments are influenced by other factors such as dilution by non-carbonate materials. During glacial periods, there is a marked increase in both biogenic opal and eolian derived sediments in core V21-146 (Hovan et al., 1991) and core NGC 102 (Kawahata *et al., in press*).

Next, FRAG and FDX records of the three cores are compared with the composite carbonate record of the equatorial Pacific (Farell and Prell, 1989) where siliceous sedimentation is minimal. The correlation between the carbonate dissolution intensity recorded in the three cores from Shatsky Rise and the carbonate event scale constructed by Farell and Prell (1989) for the central equatorial Pacific is striking (Figure 10). There is a clear correspondence between dissolution maxima and minima (FRAG and FDX record) and the carbonate minima and maxima events in the equatorial Pacific. Between FDX and FRAG, FRAG appears to follow more consistently the central Pacific carbonate pattern. Combined FRAG curves clearly illustrate this relationship. Counterparts of the dissolution maxima (carbonate minima) events B 3m and B 5m identified in the central Pacific cores at approximately 100 kyr and 200 kyr respectively can be easily picked from the dissolution profile of the three northwestern Pacific cores. The short lived deglacial preservation pulse during the last glacial - Holocene transition reported throughout the world ocean at approximately 12 kyr (Berger, 1977, 1979; LaMontagne *et al.*, 1996) can similarly be observed. Precise age of this preservation peak in the three cores cannot be ascertained until a more reliable dating method is employed (*i.e.* $C^{14}$).

**Discussion**

The unequivocal occurrence of fragmentation in the core top samples of NGC 102, NGC 106, and NGC 108 (Plate 1, figures a & b) suggests that sediments on all three cores have been subjected to a certain degree of dissolution and are therefore most likely at depths between the present day foraminiferal lysocline and CCD. Theoretically, it is not possible to distinguish between dissolution as a result of high respiratory $CO_2$ production (oxidation of organic carbon) in the sediments and dissolution as a result of bottom water $CO_3$ under-saturation. The cores are located beneath a region of relatively high nutrient concentrations (Figure 2b) and organic carbon flux to the sediments should be significant. However, organic carbon as well as benthic foraminiferal data in NGC 102 (Ohkushi, 1998 MS) indicate increased glacial organic carbon flux to the sediments. In contrast, the dissolution profiles based on FDX and FRAG follow distinctly the Pacific carbonate cycles showing increased preservation (decreased dissoltuion) during glacial periods. Specifically, dissolution maxima tend to occur during glacial build-up and the dissolution minima (preservation maxima) tend to occur during deglaciation. In addition, timing and magnitude of the changes in the dissolution intensity are comparable with what is observed in the carbonate records of the central equatorial Pacific. This implies a linkage between these two spatially separate regions. They are presently linked by the Pacific deep water and the observed fluctuations in dissolution intensity are most likely due to changes in the depth of the lysocline/bottom water chemistry. In the equatorial Pacific, Farell and Prell (1987) estimated that the lyscoline deepened as much as 800 meters during glacial times. An almost equal magnitude of change in the foraminiferal lysocline depth can be approximated from the present samples. At present, cores NGC 102 and NGC 108 are separated by a depth of 788 m (2,612 m, 3,390m). Based on the state of foraminiferal preservation of the core top samples, it estimated that the present foraminiferal lysocline should be at least shallower than that of NGC 102 (2,612 m). During periods of minimum dissolution (*e.g.* deglacial preservation spike), however, both display a remarkable state of preservation (Plate 1, Figures c & d) suggesting depths above the foraminiferal lysocline.

Among FDX, FRAG, and planktic foraminiferal number, FRAG is a more faithful recorder of the carbonate dissolution signal. Its down-core profiles show more consistency between cores with the FRAG maxima and minima corresponding to carbonate lows and highs. FDX is assemblage based and is therefore also subject to changes in local ecology (Be *et al.*, 1975). The abundance of planktic foraminiferal test (planktic foraminiferal number) on the, other hand, should also respond to changes in surface water productivity. The two cores used in the study are situated very near the sub-polar frontal boundary (with NGC 108 being the closest) and it is thus expected that surface water ecology significantly varied in the past as a result of frontal boundary migration. This is evidenced by changes in *N. pachyderma* left-coiling abundance in NGC 106 and NGC 108. Closer inspection of FDX for both cores reveals that much of the signal is generated by the relative abundance of *Globigerina bulloides* (Figures 7d, 8d, 9d). High relative abundance of *G. bulloides*, a highly dissolution susceptible species, corresponds to low FDX values (low dissolution). Similarly, a significant proportion of the planktic foraminiferal number can be attributed to *G. bulloides* absolute abundance. Thus, FDX and planktic foraminiferal number, at least for the three cores studied, are closely linked to *G. bulloides* abundance. *G. bulloides* is found abundant in cold nutrient rich waters of high latitudes (Bradshaw, 1959; Be *et al.*, 1977 , Saito *et al.*, 1981) but is also found abundant in regions of upwelling (Be *et al.*, 1977; Hemblen *et al.*, 1989; Sauter and Thunell, 1991). This particular species is therefore closely associated with high productivity. Hence, FDX and planktic foraminiferal number have been potentially affected by both productivity and dissolution intensity changes. However, the tight coupling specifically between FRAG and FDX strongly favors dissolution intensity as the primary causal factor.

In general, FRAG profiles for the three core show clear depth dependence with the deepest core exhibiting at an average higher FRAG values. The relationship between depth (and therefore dissolution intensity) and the degree of fragmentation is however, not necessarily linear. This is clearly manifested by the higher degree of fragmentation observed in NGC 108 (3,390 m) than in NGC 106 (3,713 m) during the dissolution maxima event at ~100 kyr. The higher degree of fragmentation in the shallower core during this period may either be due to errors associated with counting and/or splitting of sediment samples; or it can be explained by the dynamics of foraminiferal fragmentation and dissolution. According to Le and Shackleton (1992), the amount of fragments in the sediments varies as a result of three sequential processes: the breaking of individual foraminifera into fragments, the coarse fragments breaking into fine fragments, and the fine fragments completely dissolving. Thus, beyond a certain level of dissolution, the proportion of fragments may in fact start to decrease. It is here supposed that lower foraminiferal fragmentation recorded in NGC 106 relative to NGC 108 during dissolution maxima B 3m (~100 kyr) is due to this process. Additional proof can be seen by comparing foraminiferal fragment test walls during periods of strong dissolution (Plate 1, Figures e & f). The test walls of the foraminiferal fragments in NGC 106 and NGC 108 relative to NGC 102 are much thinner suggesting considerable etching and carbonate loss. It is thus highly probable that some of the original fragments had already been dissolved.

**Cross-spectral analysis**

Cross-spectral analysis between FRAG and $\delta^{18}O$ of the longest record (NGC 102) was carried out using the ARAND software package available at Brown University. Prior to analysis, time series data was re-sampled at 3 kyr intervals using simple linear interpolation. The confidence interval of phase estimates is at 80% significance level. Plots of the variance spectra, coherence, and phase angle are shown in Figure 11. The spectra of both FRAG and $\delta^{18}O$ are dominated by the 100 kyr cycle where significant coherence between these two occurs. FRAG lags behind $\delta^{18}O$ in the order of 26 degrees (~7 kyr) in the 100 kyr cycle. This falls within the range obtained by Le and Schackleton (1992) for western equatorial Pacific cores (6-20 kyr lag) using similar indices to track dissolution. Farell and Prell (1989), using %CaCO3 record as an index of carbonate preservation in central equatorial Pacific cores, estimate a 8-10 kyr lag between ice volume and carbonate dissolution. LaMontagne *et al.*(1996), also studying central Pacific cores, observed a similar phase relationship between $\delta^{18}O$ and the carbonate record (~ 7 kyr lag) but noted a decoupling of the carbonate record and the dissolution record. In their study, $\delta^{18}O$ leads dissolution by as much as ~37 kyr.

## Conclusions

1. The occurrence of a significant amount of fragmentation in the core top samples of NGC 102, NGC 108, and NGC 106 (at 2,612 m, 3,390 m, 3,713 m depth respectively) suggests all three cores are located at depths within the present carbonate compensation zone. The present foraminiferal lysocline must be shallower than 2,612 m.

2. Berger's (1968,1971) foraminiferal dissolution index (FDX) and the relative proportion of foraminiferal fragments (FRAG) co-vary down-core and follow the typical Pacific Carbonate Cycle. Specifically, dissolution maxima tend to occur during glacial build-up and the dissolution minima (preservation maxima) tend to occur during deglaciation. In addition, timing and magnitude of the changes in dissolution intensity as recorded by FDX and FRAG for these three northwestern Pacific cores closely follows Farell and Prell's (1989) carbonate event scale constructed for the central equatorial Pacific. This linkage between the dissolution/carbonate records of the northwestern Pacific and the central equatorial Pacific suggests a more regional cause for the observed changes in

the carbonate dissolution intensity: changes in the Pacific Deep Water corrosiveness.

3. Given the limitations of the age determinations used in the study, timing and magnitude of carbonate dissolution maxima and minima events appear to be regionally synchronous. This could prove useful for regional correlation and chronology of North Pacific deep-sea sediments located at depths within the carbonate compensation zone.

4. The relative proportion of foraminiferal fragments (FRAG) is a more robust and consistent index of dissolution than FDX as it is less subject to local ecological effects. FDX, and in fact the other indices commonly used, provides additional confidence in the use of FRAG as an index of dissolution when they are found to co-vary.

5. Cross-spectral analysis between $\delta^{18}O$ and FRAG suggests that dissolution lags ice volume by ~ 7 kyr in the 100 kyr cycle. This is in general agreement with values obtained by other workers (Farell and Prell, 1989; Le and Shackleton, 1992; LaMontagne *et al.* 1996).