

Evaluation of the CaCO₃ dissolution proxies in the sediment cores from above the lysocline

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Abstract:

Calcium carbonate analyses were carried out from two size fractions (<63µm and >63µm) from the Ocean Drilling Program Sites 752 and 715 collected from above the lysocline depth in the Indian Ocean, to evaluate the calcium carbonate size index as paleocarbonate ion proxy in these cores. Size index values varied from 69 to 81 at Site 752 and showed a similar pattern with that of total carbonate content at this site. But high values of size index and the location of this site, far from any landmass, suggest that, only changes in productivity of overlying waters are responsible for the observed variations.

Low values of size index at Site 715 suggest supralysocline dissolution, the inverse relation between size index variations and the total CaCO₃ content shows that the total carbonate variations are controlled by the finer fraction composed of juvenile foraminifera, foraminifera fragments and coccolithophores. This further confirms the observed variations of CaCO₃ content of the <63µm fraction, which follows the trend of total CaCO₃ content. This study demonstrates that apart from factors such as breakup of shells after burial due to organic matter respiration and dilution due to terrigenous material, changes in surface water productivity and coccolithophores might be a constraint to use size index as a paleocarbonate ion proxy for sediments from above the lysocline.

Keywords: Lysocline, carbonate ion, size index, dissolution, coccolithophores.

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1. Introduction:

Studies of the distribution and preservation of calcium carbonate in marine sediments are important because carbonate depositional patterns are tied to the regulations of atmospheric CO₂. Three main factors govern the calcium carbonate content of marine sediments: (1) dilution by non-carbonate material, (2) productivity of calcareous planktonic organisms, and (3) carbonate dissolution (Volat et al, 1980). The proportional contribution of each factor controlling total carbonate varies from place to place.

Calcite dissolution in marine sediments is driven by saturation state of the overlying waters and/or responds to sedimentary organic matter respiration and the resulting acidification of pore waters that results from that (Emerson and Bender, 1981; Archer and Maier-Reimer, 1994). Specifically, differences in the carbonate ion concentrations of bottom water are believed to be responsible for the first-order variations in the depth of the lysocline between and within oceans (Peterson and Prell, 1985). This would mean that only the calcite deposited in sediments below the lysocline is subjected to dissolution. On the contrary, it has been reported that about 25% of CaCO₃ produced above the lysocline also undergoes dissolution (Milliman, 1993). Significant dissolution could occur above the lysocline as a result of metabolic CO₂ release from decaying organic matter into sediment pore waters (Emerson and Bender., 1981; Jahnke et al., 1997). de Villiers, (2005) suggests that in addition the respiratory dissolution flux in shallower sediments is not necessarily the pore waters but rather the benthic fluff layer. It has been reported that sedimentary organic carbon respiration is most rapid when a fluff layer is present (Martin and Sayles, 1999). The CaCO₃ must pass through this layer before burial. The exposure time of foraminifera to under saturation in the fluff layer will be a function of sedimentation rate as well as the frequency of phytodetrital input (de Villiers., 2005).

The extent of CaCO₃ dissolution in sediments above the lysocline is therefore very significant from a mass balance perspective. However, the extent of dissolution above the lysocline is still a matter of debate and its role in the global carbon cycle is unresolved (de Villiers, 2005).

Various indicators have been used to reconstruct the changes in carbonate ion concentrations and hence the records of dissolution of carbonate constituents from deep-sea sediments. Some of these are, ratio of dissolution prone to dissolution resistant planktonic foraminifera shells (Ruddimann and Heezen, 1967; Berger, 1970); ratio of foraminifera fragments to whole shells (Peterson and Prell, 1985; Wu and Berger,

1989), shell weight of foraminifera (Lohmann, 1995) and percentage of coarse fraction (Broecker and Clark, 1999, 2001a-c).

Here an attempt has been made to study the calcite dissolution above the lysocline by using an indirect and less labor intensive method of Broecker and Clark (1999) for determining progressive breakup of foraminifera shells. This method is based on measuring the size index i.e. the ratio of coarse calcite to total calcite [$(>63\mu\text{m CaCO}_3/\text{Total CaCO}_3) \times 100$]. It has been shown by them that in today's tropical ocean the percentage of CaCO_3 contained in grains $>63\mu\text{m}$ in size is closely tied to the pressure-normalized carbonate ion of water bathing the sea floor. The idea being that, since the $>63\mu\text{m}$ fraction is dominated by foraminifera shells and the lesser fraction contains coccoliths, juvenile foraminifera and foraminiferal fragments, this size index actually is the ratio of CaCO_3 contained in whole foraminifera shells to CaCO_3 contained in total sediments. This index gained a substantial value as a paleocarbonate ion proxy for deep-sea sediments from the equatorial region when applied to Holocene period (Broecker et al., 1999). However, this proxy can not be applicable for various reasons to glacial age sediments (Broecker and Clark, 2001c). In this communication we apply this size index to two sediment cores recovered from above the lysocline. to assess the suitability of this proxy in understanding supralysocline calcite dissolution in the Indian Ocean.

2. Methods:

Ocean Drilling Program (ODP) Site 752 was drilled in the eastern Indian Ocean near the crest of Broken ridge ($30^\circ 53.475'S$ and $93^\circ 34.652'E$) at a water depth of 1086 m, (Fig.1). The ODP Site 715 was drilled from northern equatorial Indian Ocean on the eastern margin of Maldives Ridge ($5^\circ 04.890' N$ and $73^\circ 49.879' E$) at a water depth of 2266 m (Fig.1).

The ODP Site 752 was sub-sampled at 4cm to a length of 101cms. The ODP Site 715 was sub-sampled at 7cm intervals up to 200cm. All the samples were oven dried at 50°C ; a portion of the sample was weighed and disaggregated by soaking in distilled water and then wet sieved through a $>63\mu\text{m}$ sieve. The residue was collected carefully and dried, and both the size fractions, $>63\mu\text{m}$ and $<63\mu\text{m}$ were weighed separately.

The content of CaCO_3 in the sediment sample as a whole, $< 63\mu\text{m}$ and in the $>63\mu\text{m}$ fractions were determined using coulometric titration method. The size index was calculated as the percentage of CaCO_3 content in the $>63\mu\text{m}$ fraction compared to the CaCO_3 content in the bulk sediment (Broecker and Clark, 1999).

Chronology of these Sites was based on calcareous nanofossil datum's established (Duncan et al., 1990) to the ODP Site 715 by (Rea et al., 1990) to the ODP Site 752.

Data from the GEOSECS stations from the Indian Ocean was used to calculate *in-situ* carbonate ion profiles of water column close to our core sites (St. Nos: 418 and 437; Fig.1, 2a and b). Carbonate ion concentrations were calculated using a programme designed by Taro Takahashi of Lamont Doherty Earth Observatory. The following parameters were the inputs for the programme: Depth (dB), Temperature (°C), Salinity (‰), Alkalinity ($\mu\text{Eq kg}^{-1}$), Total CO_2 ($\mu\text{mol kg}^{-1}$), Silicate ($\mu\text{mol kg}^{-1}$) and Phosphate ($\mu\text{mol kg}^{-1}$).

It is necessary to take into account the increase in calcite solubility with pressure and hence water depth. Following the method of Broecker and Clark, (1999), The $\text{CO}_3^{=}$ concentrations were normalized to a depth of 4km as follows:

$$\text{CO}_3^{=*} = \text{CO}_3^{=} + 20(4-h) \mu\text{mol kg}^{-1}$$

Where h is the water depth in km at the core site and $20 \mu\text{mol kg}^{-1}$ is the increase with water depth of the solubility of calcite. $\text{CO}_3^{=*}$ is used to avoid the necessity of selecting a value for the solubility of calcite.

3. Results and Discussion:

Pressure-normalized $\text{CO}_3^{=*}$ calculated from in-situ $\text{CO}_3^{=}$ for ODP Site 752 is $135 \mu\text{mol kg}^{-1}$ whereas that calculated for ODP Site 715 is $112 \mu\text{mol kg}^{-1}$. Broecker and Clark (1999) have shown that dissolution occurs in the pressure normalized $\text{CO}_3^{=}$ ion concentration range of $105\text{-}70 \mu\text{mol kg}^{-1}$. In the present study the $\text{CO}_3^{=*}$ values obtained at both the ODP Sites are higher than $105 \mu\text{mol kg}^{-1}$ and hence suggest that no dissolution takes place at these Sites. The lysocline in the equatorial Indian Ocean sector lies at about 3400m water depth (Schulte and Bard, 2003). In the Central Indian Ocean Basin the lysocline is placed at about 4400m water depth (Banakar et al., 1998). These pieces of evidence indicate that both the ODP Sites 752 and 715 lie well above the present day lysocline in the Indian Ocean and can be proved to be useful in investigating the supralysocline calcite dissolution.

At the ODP Site 752, total CaCO_3 content ranges from 91% to 96% over the last 442 kyrs (Fig. 3a). Very high CaCO_3 content and minor variation in the CaCO_3 content at site 752 suggests that dilution plays a very insignificant role here. This site is situated relatively far away from landmass and hence not significantly affected by terrigenous material. Basically the minor variations observed in the carbonate content at site 752 may be due to changes in productivity of the overlying waters and/or minor

dissolution. Present day productivity of the surface waters at ODP 752 is $0.48\text{gCm}^{-2}\text{d}^{-1}$ (Kabanova, 1968).

At Site 715, total CaCO_3 content varied from 59% to 77% over last 45kyr (Fig.3b). Larger variations at Site 715 are possibly attributed to its proximity to the Indian sub-continent and hence influence by terrigenous material derived from the landmass. Similarly it has been reported the influence of terrigenous dilution derived through Indus River on the CaCO_3 in the eastern Arabian Sea (Naidu, 1991). Present day productivity of the surface waters at ODP 715 is $0.31\text{gCm}^{-2}\text{d}^{-1}$ (Kabanova, 1968).

As stated earlier, it has been estimated that about 25% of CaCO_3 produced above the lysocline undergoes dissolution (Milliman, 1993). Therefore, other than the dilution and productivity factor, the third factor, i.e. dissolution could play an important role for sediments from above the lysocline. We therefore employ the size index to possibly figure out the role of dissolution at these sites.

The size index shows variation from 69 to 81 with a core top value of 78 at Site 752 (Fig. 3a) and values of 23 to 41 with core top value of 34 for the Site 715 (Fig. 3b). There has been a significant variation in the size index for both the cores. Broecker and Clark (1999), showed that in the pressure normalized $\text{CO}_3^{=}$ ion concentration range of $105\text{-}70\mu\text{mol/kg}$, a linear decline occurs in the ratio of CaCO_3 in the $>63\mu\text{m}$ fraction to the total CaCO_3 from 55 to 0 occurs in the bulk sample. These results suggested that the size index could be used as a paleocarbonate ion proxy. The results implied that the initial size composition of the CaCO_3 deposited throughout the tropics is quite uniform and that influence of variations in the ratio of the flux of organic carbon to that of CaCO_3 must be small. Depth transect of shallower cores on the Ceara Rise suggest that for $\text{CO}_3^{=*}$ values higher than $105\mu\text{mol kg}^{-1}$ the index values stand no longer valid ($\text{CO}_3^{=*} = \text{CO}_3^{=} + 20(4\text{-}h)$, where 'h' is the water depth in kilometers and $20\mu\text{mol kg}^{-1}\text{ km}^{-1}$ is the increase with water depth of solubility of calcite) (Broecker et al., 1999). For water depths above 4000 m the index is nearly constant at a value of 52 ± 2 (Broecker et al., 1999), suggested that the size fraction index validated for the water depths below 4000 m does not continue for water depths above. It has been observed that higher values of the index i.e. around 55 to 75 are to be found in tropical Indian Ocean cores from between 2000m and 3000m depth (Peterson, 1984). By contrast, results from Sites 752 and 715 showing core top size index values of 77 and 34 respectively are at odds with the findings by Broecker and Clark (1999) and Peterson (1984).

The size fraction index and total CaCO_3 percentage for Site 752 and 715 show contrasting results (Fig. 3a and 3b). At Site 752 the variations in size index and total CaCO_3 percentage show a similar trend

which could be due to $\text{CO}_3^{=}$ ion concentrations of waters bathing the sediment or due to variations in foraminifera versus coccolith productivity. But, the values are substantially higher to those proposed by Broecker and Clark, (1999), in pressure normalized $\text{CO}_3^{=}$ ion concentration range of 105-70 $\mu\text{mol/kg}$, ruling out any dissolution at this Site. This suggests that the minor variations observed in the carbonate content at site 752 could be only due to changes in productivity of the overlying waters. As stated earlier both cores lies above the lysocline. The differences in core top size index values between the cores used in the present study and other cores from the Indian Ocean (as mentioned earlier from the studies of Peterson, 1984 and Broecker and Clark, 1999) may be attributed to rain rates of non-calcareous material and/or calcite and organic carbon to the sediments, which depend on the surface-water productivity.

The Site 715 shows an exactly opposite variation pattern of CaCO_3 % and size index. The size index in this case may not reflect the dissolution pattern. Two possible explanations are offered for the observed variations.

i) Breakup in foraminifer's shells can continue for thousands of years after burial due organic matter respiration which is a likely driving mechanism for dissolution in sediments overlain by supersaturated bottom waters (Adler et al., 1989; Cai et al., 1995; Hales and Emerson, 1997). The $>63\mu\text{m}$ size fraction is related to the percentage of whole foraminifera. During dissolution whole foraminifera break into fragments, coarse fragments break into finer fragments, and fine fragments then become completely dissolved (Le and Shackelton, 1992). In this case the size index will underestimate the $\text{CO}_3^{=}$ concentration of the waters bathing the sea floor.

ii) The $<63\mu\text{m}$ fraction CaCO_3 for Site 715 shows large CaCO_3 variations over a range of 30% (Fig.4b). There is a striking resemblance of $<63\mu\text{m}$ fraction CaCO_3 with the total CaCO_3 content which is not seen for the $<63\mu\text{m}$ fraction CaCO_3 of site 752 (Fig.4a). Hence it can be interpreted as $<63\mu\text{m}$ fraction controls the total CaCO_3 content of sediment at this site. McCave et al. (1995) using a more sophisticated method of sediment characterization has shown that the sediment $<10\mu\text{m}$ is dominantly coccoliths and the 10-63 μm fraction contains mainly foraminiferal fragments. In the present scenario the size index expresses predominantly the ratio of whole adult foraminifera to coccoliths and foraminiferal fragments and juvenile foraminifer species, respectively. If one considers that no breakup takes place after deposition, this index directly reflects the variations in calcareous nannofossils productivity.

4. Summary and Conclusion:

We applied the size index proposed by Broecker and Clark (1999), to two ODP Sites located in different oceanic regimes raised from above the lysocline depth in the Indian Ocean. The size index as measured at ODP Sites 752 and Site 715 shows significant variations, though both the sites are located well above the lysocline. High values of size index at Site 752 and since the site is located far from any landmass the observed variations are due to changes in productivity of the overlying waters. Low values of size index at Site 715 suggest significant dissolution has occurred throughout the core. But based on the size index alone we are unable to ascertain the reasons for the observed behavior.

The reasonably synchronized mismatch between size index and CaCO_3 occurring at Site 715 is a unique result and observed for the very first time. The Size index variations at this Site mirror the total CaCO_3 content. From the $<63\mu\text{m}$ variations it is evident that the finer fraction which is composed of juvenile forams, foraminiferal fragments and coccoliths dominates the carbonate content and holds the key to the observed variations.

In order to understand, whether juvenile foraminifera or the coccoliths dominate the sediment at this Site, size fraction studies of the $<63\mu\text{m}$ fractions of Site 715 will be worthwhile in future. It has already been concluded by Broecker, (2003) that the value of size index must be demoted to the status of a qualitative indicator of dissolution intensity and applied within intervals of more uniform climate (like the Holocene). In addition we conclude here that the size index does not give a correct estimation of the carbonate ion content of bottom waters for sediment lying above the lysocline mainly due to breakup of shells after burial as a result of organic matter respiration. In regions dominated by coccolithophores, as encountered in the present study, the size index will present a totally inverse picture. Changes in surface water productivity and dilution due to terrigenous material will also cause an incorrect estimation of the carbonate ion content. This index coupled with certain other proxies would possibly give an indication of factors affecting the carbonate variations above the lysocline.

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6. References:

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7. Figure legends:

Fig. 1. Location of ODP Site 715 and 752 in the Indian Ocean. Plus signs indicate GEOSECS stations.

Fig. 2. Profiles of *in-situ* $\text{CO}_3^{=}$ concentrations calculated from a) GEOSECS Station 437 and b) Station 418.

Fig. 3. Fluctuations of a) total CaCO_3 and size index values at ODP Site 752 and b) total CaCO_3 and size index values at ODP Site 715.

Fig. 4. Fluctuations of a) $<63\mu\text{m}$ fraction at ODP Site 752 and b) $<63\mu\text{m}$ fraction at ODP Site 715.

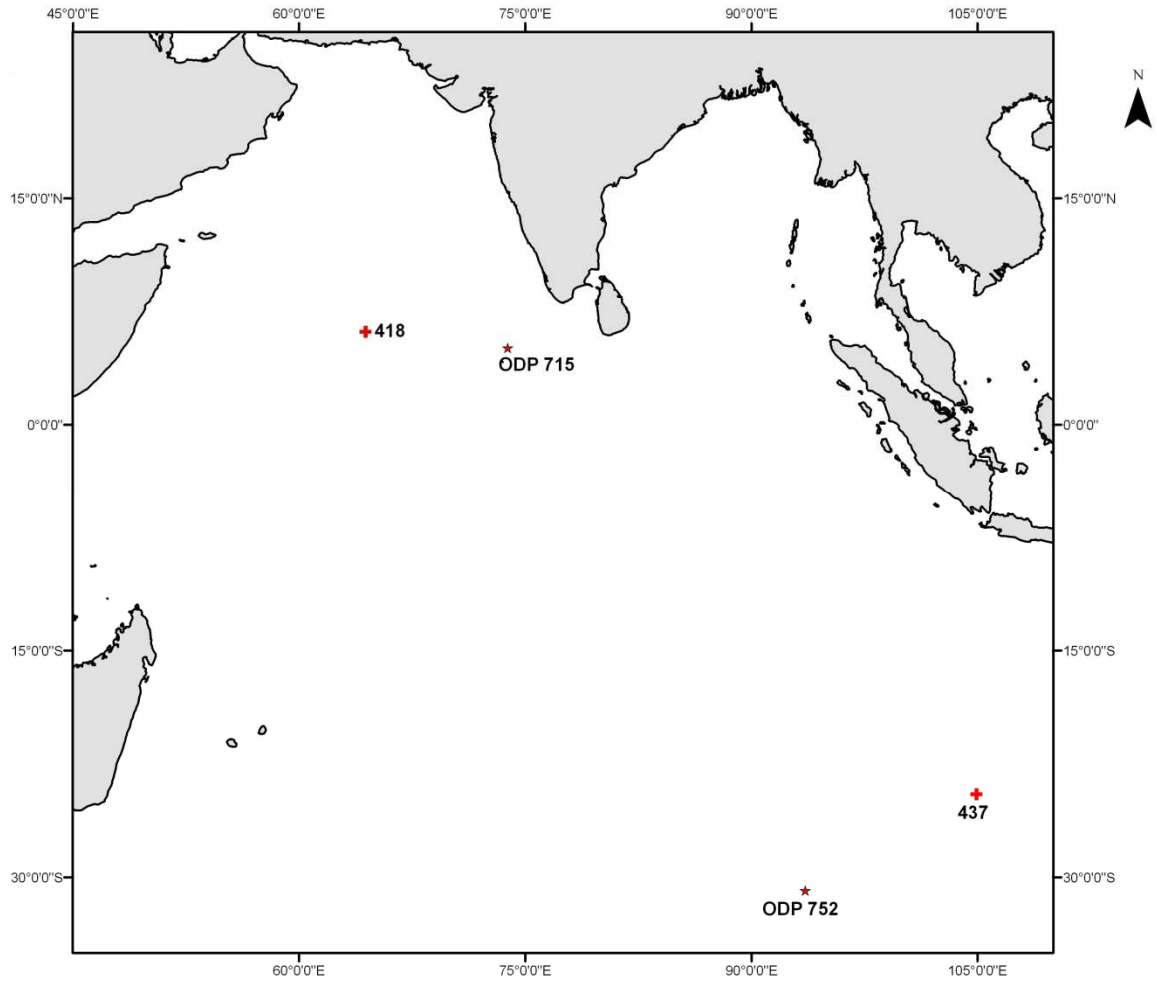


Fig.1

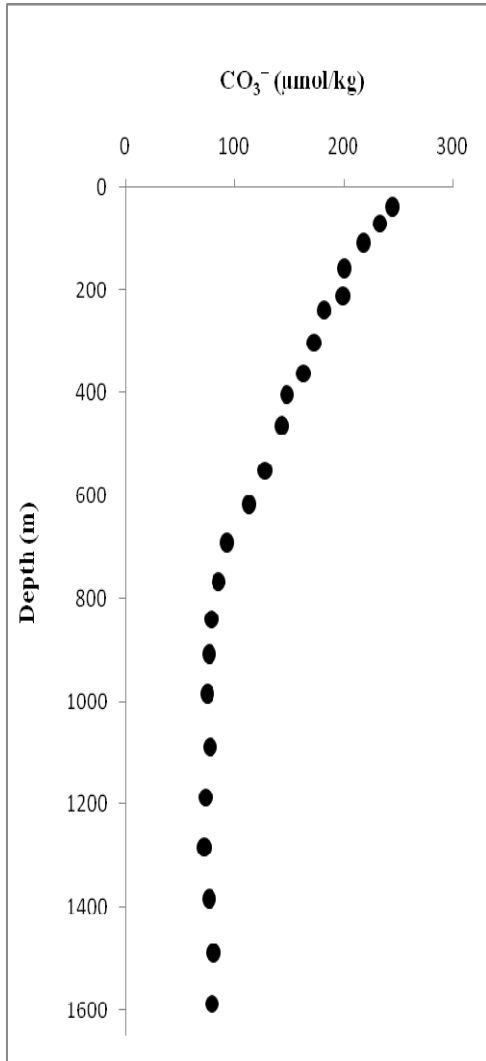


Fig. 2a

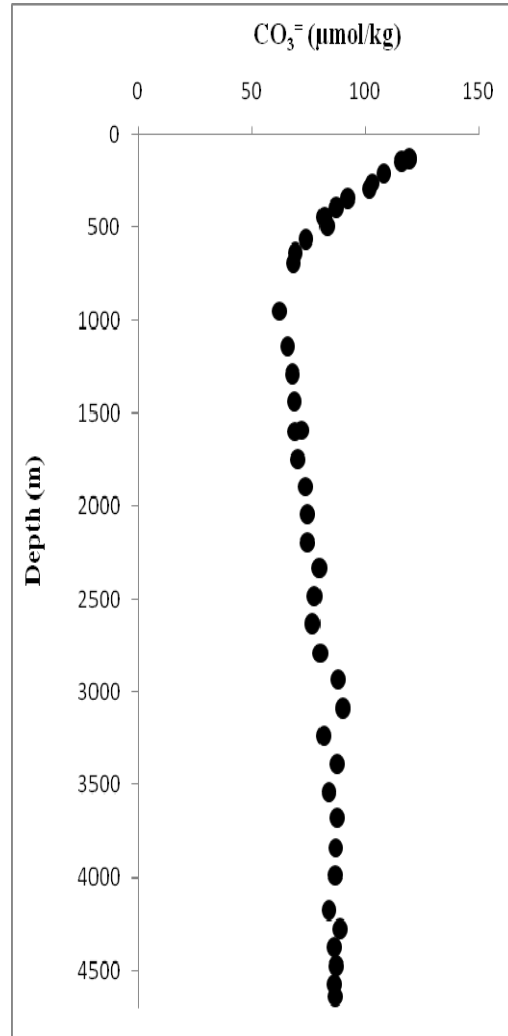


Fig. 2b

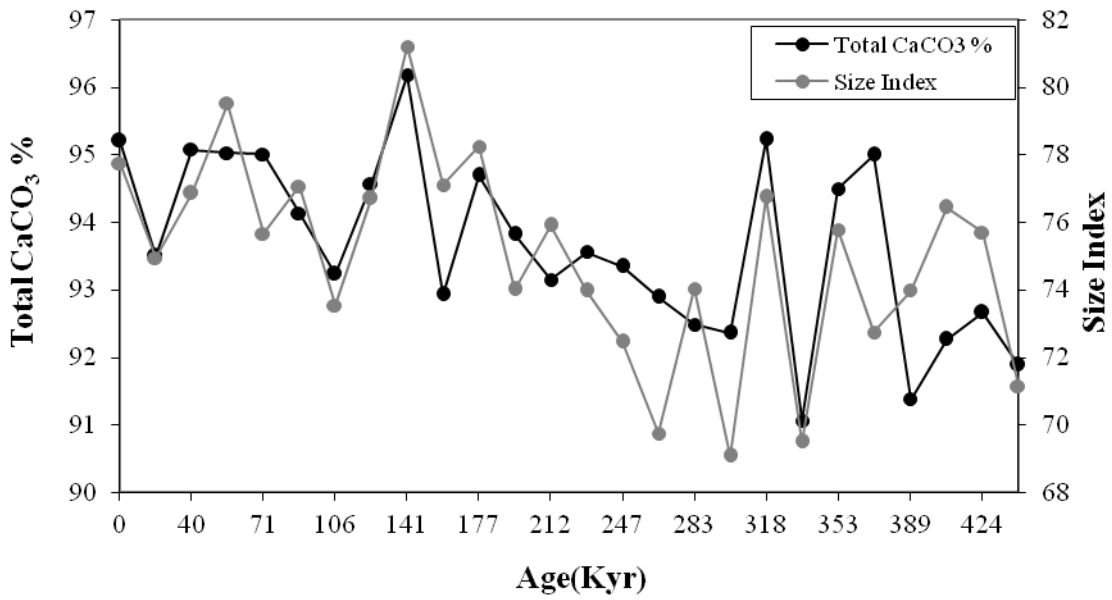


Fig. 3a

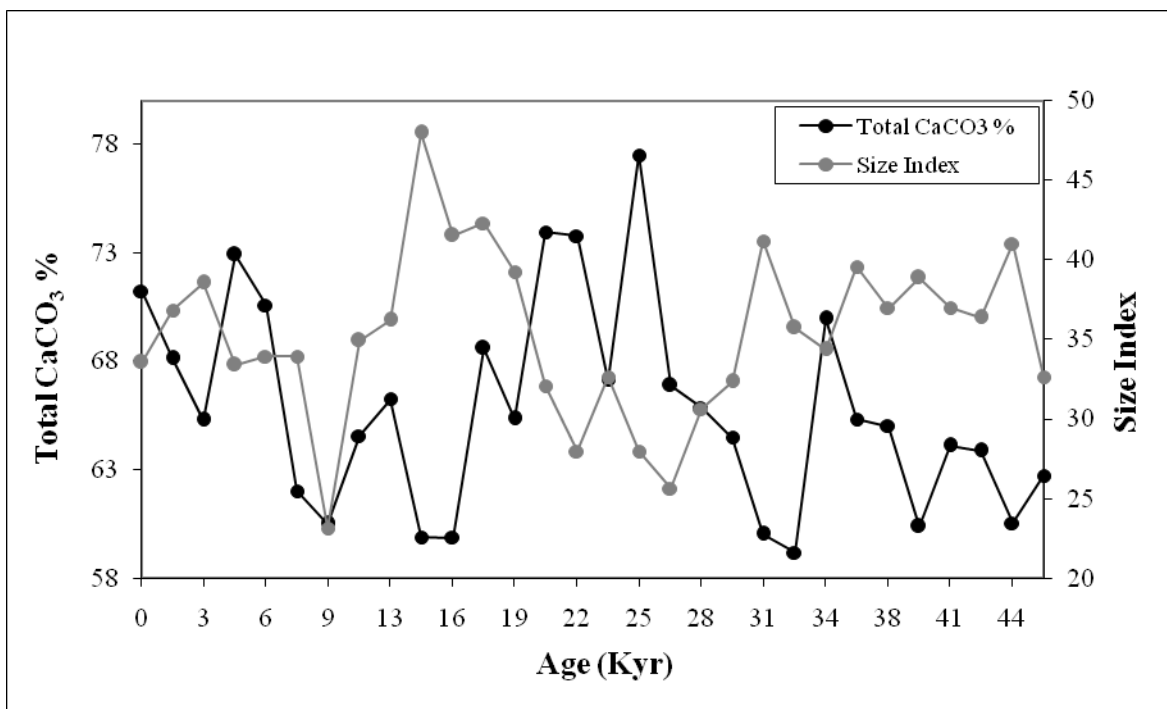


Fig. 3b

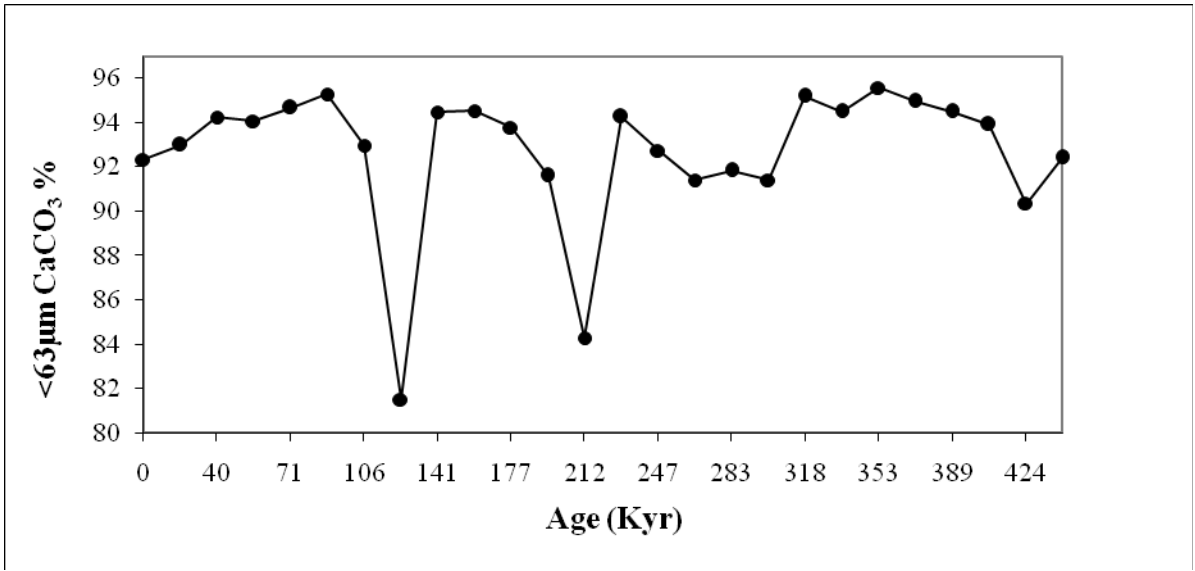


Fig. 4a

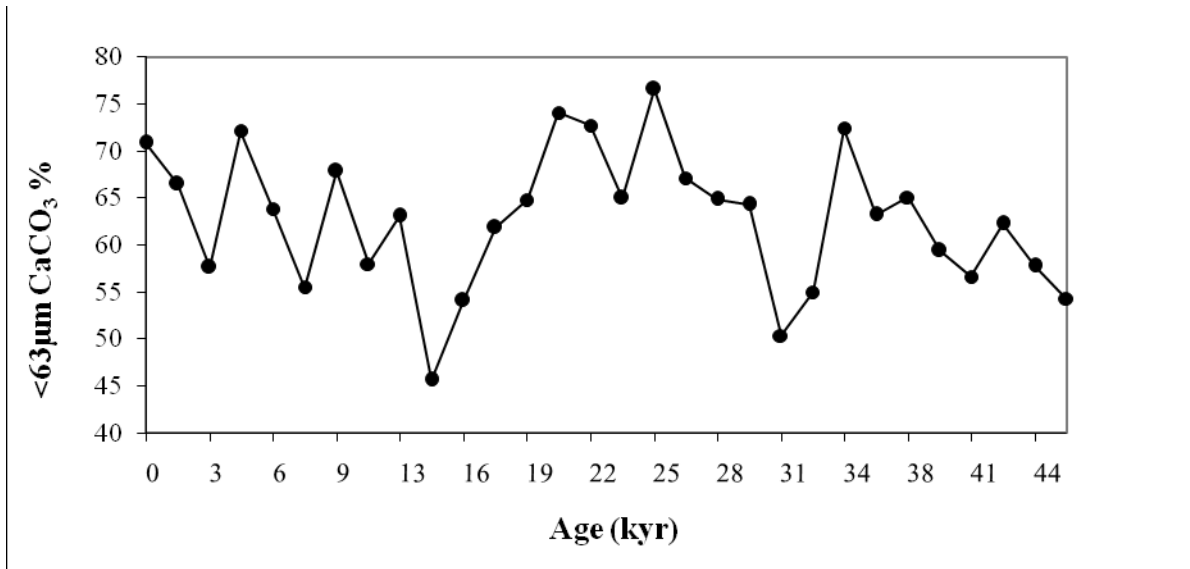


Fig.4b