



## STABLE ISOTOPE STUDY OF CALCITE CEMENT AND VEINS FROM NORTHLAND ALLOCHTHON AND BASAL WAITEMATA GROUP ROCKS, NEW ZEALAND

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This paper provides stable isotope studies of calcite cement and vein calcite from units of Northland Allochthon rocks and the lower part of the overlying Miocene Waitemata Group of New Zealand to establish the source of C and O in the sediments. Veins in Cretaceous claystones beneath the Miocene rocks have  $\delta^{18}\text{O}_{\text{PDB}}$  of -4.5 to -5.94, and  $\delta^{13}\text{C}_{\text{PDB}}$  of +2.8 to +14.94. Veins in Oligocene Mahurangi limestone have  $\delta^{18}\text{O}_{\text{PDB}}$  of -1.11 to -10.14 and  $\delta^{13}\text{C}_{\text{PDB}}$  of +1 to +1.84. Veins in basal Waitemata Group have  $\delta^{18}\text{O}_{\text{PDB}}$  of -9.18 to -10.62, and  $\delta^{13}\text{C}_{\text{PDB}}$  of -10.5 to -17.15. Results indicate that the depositing solutions were probably less saline than seawater; however, the wide variation in C values suggests different sources of carbon in the three samples. Calcite cement in the concretions of Cretaceous age, sandstones has  $\delta^{18}\text{O}_{\text{PDB}}$  of 7.6 to -10.6, and  $\delta^{13}\text{C}_{\text{PDB}}$  of -20 to -23.6. More negative of O values than the veins in the Cretaceous rocks suggest formations at different time when pore solutions were even further from marine composition. The strongly negative C values indicate origin from oxidation of organic matter. The difference from the veins in the Cretaceous rocks supports the evidence of different source waters. Calcite cements of sandstone concretions from basal Miocene have  $\delta^{18}\text{O}_{\text{PDB}}$  of -4.3 to -3.5, and  $\delta^{13}\text{C}_{\text{PDB}}$  of -7.1 to +1.3. Both O and C values support an early diagenetic origin, indicated by slightly modified seawater source.

**Keywords:** Northland allochthon, Stable isotope, Miocene, Waitemata group, Diagenesis

### 1. Introduction

In sedimentary basins, pore waters responsible for diagenesis may have disappeared from the system. However, pore water may have left a record of its isotopic composition in solid phases which formed or exchanged at that stage of diagenesis. The isotopic composition of such minerals can be used to reconstruct pore water evolution in a sedimentary basin throughout its geological history [1-3].

Calcite which has crystallised in equilibrium with pore water is enriched in  $^{18}\text{O}$  and depleted in  $^{16}\text{O}$  relative to ocean water [4]. The exact extent of fractionation depends on temperature at which the calcite formed. The oxygen isotopes were redistributed between the calcite and pore water according to an isotope exchange reaction of the system. The  $^{18}\text{O}/^{16}\text{O}$  ratio in nature shows variations ranging upto 10%. These variations results from both equilibrium and kinetic fractionation effects. Equilibrium fractionation derives from small but significant differences in the thermodynamic properties between compounds containing an isotope with higher  $^{18}\text{O}$  versus lower mass number  $^{16}\text{O}$  [5, 6].

Another important kind of isotope fractionation encountered during diagenesis is carbon isotope.

During photosynthesis,  $\text{CO}_2$  gas is preferentially selected during the production of organic matter. The resultant of fractionation of  $\text{CO}_2$  gives organic matter a characteristic isotopic signature that points to its biological origin. This fractionation is controlled by kinetic processes [7].

### 2. Northland Allochthon-Study Area

The Northland Allochthon is present both NE and SW of a structural high located between the Three Kings Island and Mt. Camel (Figure 1) in northern North Island of New Zealand. This is a thick widespread displaced allochthon rock unit contains rocks of Late Cretaceous to Early Miocene age [8]. Lithologically the allochthonous rocks are mostly composed of sandstone, siltstone, greensand, siliceous mudstone, argillaceous micritic limestone and rare coal measures alongwith dispersed organic matter. It overlies the autochthonous, paleogene non-marine to marine transgressive sediments [9]. It is unconformably overlain by the Waitemata and correlative groups of Upper Oligocene-Lower Miocene age.

The segregation of re-precipitated calcite into certain horizons and accretions of calcareous cements about a siltstone nucleus within some sandstone beds has led to the formation of very prominent concretionary bodies and layers in Northland Allochthon and basal Waitemata Group

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rocks in North Island of New Zealand (Plates A & B). Concretion growth can span a large time period, from burial of mudstone to depth of 1 km or more. In North Auckland in the North island of New Zealand, Late Cretaceous sediments of Mangakahia group have been mapped as concretionary sandstone and siltstone, overlying and interbedded with siliceous shales of varying form and mineralogy (Plate-A). These concretions are highly indurated and weathered resistant, thus occur as approximately spherical in shape, ranging to a meter in diameter. Induration is due to calcite cement. No macrofossils were observed.

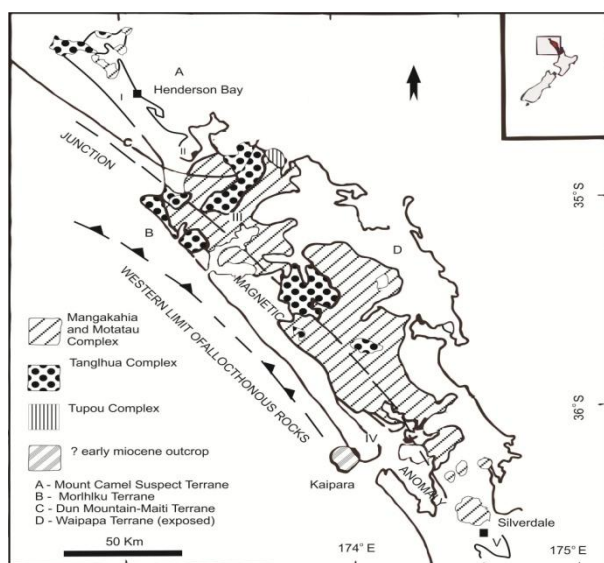


Figure 1. Outcrop distribution of the Northland Allochthon rocks and inferred basement terrane in Northland Basin, New Zealand.

At Motutapu Island, calcareous concretions are common in some thick sandstone beds near the base of Waitemata group rock units. They occur in a variety of shapes and forms. More often, concretions form discontinuous bodies. They may occur as thin disc like structures upto three inches thick. The concretions at Motutapo differ from those described by the above authors, firstly, in that they occur in sandstone, secondly, in that they are not formed in a markedly reducing environment (most likely, the conditions were slightly oxidising), thirdly, in that the concretions in this area form mainly elongated, almost continuous bodies along certain horizons of a bed (Plate-B), rather being distributed at intervals through the bed. It is clear from the very extensive occurrence of these concretions, that alkaline conditions in these sediments were not confined to small, isolated localities as in the case of concretions that occur in reducing environments.

**Calcite vein** samples were collected from basal Waitemata group and Northland Allochthon (Ngatuturi claystone and Mahurangi limestone) rocks. Veins are thin and lenticular range in thickness from 0.5 to 5 cm.

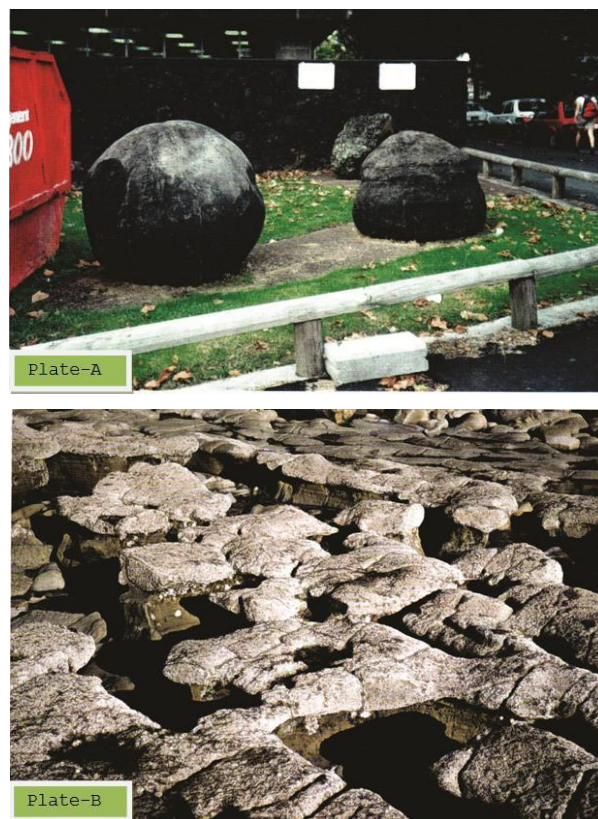


Figure 2. Plates – (A) shows spherical shape of carbonate concretions in Cretaceous sandstone, Silverdale area, Northland, New Zealand, (B) continuous elongated calcareous concretions bodies in the basal Waitemata Group rocks from Motatau Island, Auckland, New Zealand.

### 3. Sample Preparation and Measurements

Twenty one samples of calcite cement and veins, separated from sandstone concretions, limestone and claystone of Cretaceous and Miocene age were processed and analysed to get the  $^{18}\text{O}$  and  $^{13}\text{C}$  isotope presence at the Institute of Geological Science and Nuclear Sciences, Wellington.  $\text{CO}_2$  and water vapours were extracted from about 20 or 30 mg of pure calcite samples after reacting with 100%  $\text{H}_3\text{PO}_4$  in Rittenberg tubes that were placed in the water bath at  $25^\circ\text{C}$ . When the reaction was completed, the gases mainly  $\text{CO}_2$  and water vapours were transferred to a coiled trap immersed in a liquid nitrogen dewer. The next stage was to separate the water vapours and to transfer  $\text{CO}_2$  to a small tube attached to the

manometer. It was carried out by increasing the manometer "finger" in a liquid nitrogen Dewar and exchanging the liquid nitrogen Dewar of the coiled trap with a dry ice in alcohol Dewar. The CO<sub>2</sub> got frozen in the manometer finger leaving behind frozen water in the coiled trap. CO<sub>2</sub> was collected in sample bottles after measurements.

All CO<sub>2</sub> samples extracted from the calcite veins and whole rock samples were analyzed on a NAA-6-60RMS 15 cm radius, 60° sector mass spectrometer. The isotopic composition results

were given in terms of PDB scale. Isotopic standards for carbon and oxygen and correction factors for mass spectrometric analysis of CO<sub>2</sub> are reported by Craig [10].

#### 4. Results

Isotope data of calcite veins and cements from Northland Allochthon rocks, New Zealand is listed in Table 1. This illustrates a range of variable in the isotopic composition of the calcite cements and veins.

Table 1. Stable isotope data from calcite veins and cements from the Northland Allochthon and basal Waitemata Group rocks, Northland. Symbols M, O, C, C.st., and Lst indicate Miocene, Oligocene, Cretaceous, Claystone and limestone respectively.

Calcite Veins						
Sample	Age	Rock Type	Locality	$\delta^{13}\text{C}_{\text{PDB}}$	$\delta^{18}\text{O}_{\text{PDB}}$	$\delta^{18}\text{O}_{\text{SMOW}}$
25	M	Waitemata	Matheson Bay	-12.4	-10.1	20.5
26	M	Waitemata	Matheson Bay	-17.1	-10.6	19.9
27	M	Waitemata	Matheson Bay	-10.4	-9.2	21.4
21	O	Mahurangi Lst.	Redvale Q	1	-3	27.8
28	O	Mahurangi Lst.	B. Lime Q	1.8	-1.1	29.7
29	O	Mahurangi Lst.	East Coast Rd	1.8	-10.2	20.4
30	O	Mahurangi Lst.	John Walker's Q	1.8	-4.9	25.8
22	C	Ngatuturi Cst.	Snell's Beach	14.9	-5.9	24.7
23	C	Ngatuturi Cst.	Snell's Beach	13.9	-4.6	26.1
24	C	Ngatuturi Cst.	Snell's Beach	2.9	-5.8	24.9
Calcite Cements						
Sample	Age	Rock Type	Locality	$\delta^{13}\text{C}_{\text{PDB}}$	$\delta^{18}\text{O}_{\text{PDB}}$	$\delta^{18}\text{O}_{\text{SMOW}}$
4	M	Sst. Conc.	Motutapu Is.	1.4	-4.4	26.3
14	M	Sst. Conc.	St. Hellier's Bay	-5.3	-3.5	27.2
15	M	Sst. Conc.	St. Hellier's Bay	-7	-3.4	27.4
8	O	Mahurangi Lst.	Silverdale	1.6	-5	25.7
12	C	Sst. Conc.	Silverdale	-20	-9.6	20.9
5	C	Sst. Conc.	Silverdale	-23.6	-10.6	20.2
6	C	Sst. Conc.	Silverdale	-21.6	-7.6	23.6
7	C	Sst. Conc.	Silverdale	-22.5	-8.6	22.4
10	C	Sst. Conc.	Silverdale	-18.2	-10.1	20.5
11	C	Sst. Conc.	Silverdale	-18.8	-8.1	22.5
13	C	Sst. Conc.	Silverdale	-22.5	-9.3	21.3

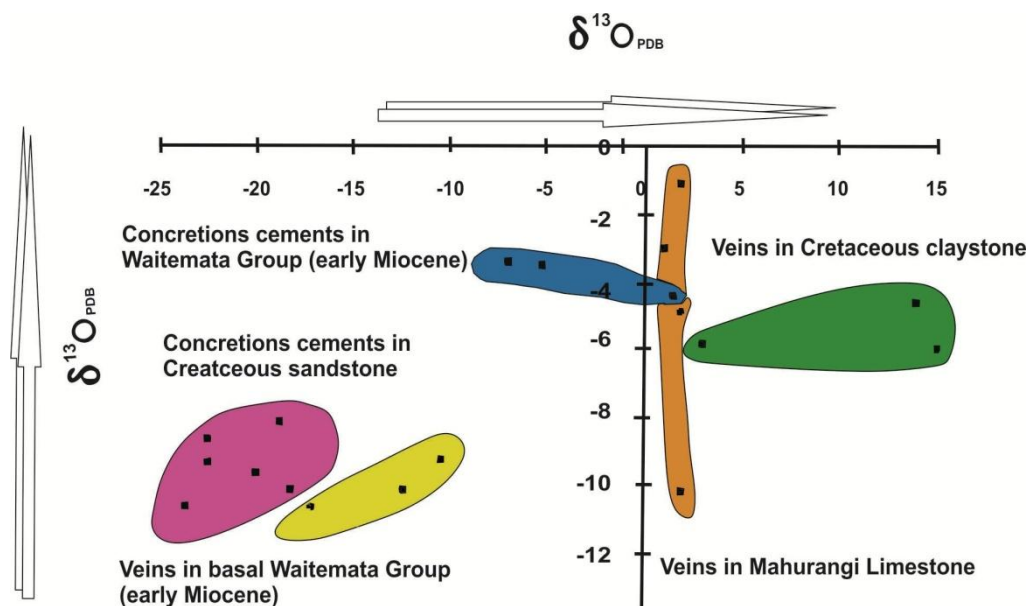


Figure 3. Scatter Diagram showing the distribution of stable isotope ( $^{13}\text{C}$  &  $^{18}\text{O}$ ) of calcite cement and veins from Northland Allochthon and basal Waitemata Group rocks, New Zealand.

#### 4.1. Carbon Isotope Data

The Carbon isotope data ranges from +14.95‰ to -23.6‰. High negative values (-18.2‰ to -23.6‰) encountered in concretions than calcite cement in basal Miocene concretions (-7‰ to +1.4‰). Like oxygen isotope values, three groups of Carbon isotope data range from 2.9‰ to 14.95‰ in Cretaceous Ngatuturi claystone, +1‰ to +1.8‰ in veins from Oligocene Mahurangi limestone and -17.14‰ to -10.4‰ in veins from Miocene waitemata group sediments.

#### 4.2. Oxygen Isotope Data

There seems a consistent concentration of lighter isotopes in calcite phases but the degree of fractionation was variable (Table 1). The  $\delta^{18}\text{O}_{\text{PDB}}$  values of calcite cement range from -3.4‰ to -10.6‰. Cretaceous sandstone has  $\delta^{18}\text{O}_{\text{PDB}}$  of -7.6‰ to -10.6‰. Basal Miocene sandstone concretion has  $\delta^{18}\text{O}_{\text{PDB}}$  values of -4.4 to -3.4.

There is a general trend being observed that the Cretaceous concretions values are more negative than the younger concretions. While in Calcite veins, three set of  $\delta^{18}\text{O}_{\text{PDB}}$  values are noted. It ranges from -1.1‰ to -10.6‰. Veins in Ngatuturi claystone has  $\delta^{18}\text{O}_{\text{PDB}}$  values from -4.8‰ to -5.95‰ as compared to -9.2‰ to -10.61‰  $\delta^{18}\text{O}_{\text{PDB}}$  values in veins from basal waitemata group sediments. Third group is from veins of Mahurangi

limestone which range from -1.1‰ to -3‰. Only one sample (29) has value -10.15‰ much less than others in the group. Veins from younger sediments have more negative values than the veins from older sediments.

#### 5. Discussion

The stable isotope data when plotted on scatter diagram (Figure 3) fall into five distinct and well separated groups i.e. three groups of vein samples and two groups of calcite cements. A single sample of bulk Mahurangi limestone gives value similar to vein sample from Mahurangi limestone.

**Cretaceous Sandstone Cements:** The lightest  $\delta^{13}\text{C}$  values (-18.2 to -23.6‰, Table 1) may be due to present day anoxic conditions of the sediments at the base of the sulphate reduction zone which suggests a methane oxidation component. It suggests that concretions growth towards the base of the sulphate reducing zone, being diluted with marine carbonate from dissolved shell material with average  $^{13}\text{C}$  values of zero [11, 12]. The light sulphate reducing zone carbonate could equally be derived from the bacterial oxidation of organic matter or from the oxidation of methane at the base of the sulphate reducing zone or from the influx of meteoric water bearing soil derived  $\text{CO}_2$ . This trend is suggestive of an increase in input light carbon/light oxygen carbonate from the

decarboxylation zone which typically has  $\delta^{13}\text{C}$  values of -20‰ [13].

The lack of positive  $\delta^{13}\text{C}$  values argues mixing with methanogenic zone carbonate.  $\delta^{18}\text{O}$  values are more negative with increase in age (Table I) that may be due both to temperature effects and to mixing with migrating basinal pore waters and/or meteoric waters. The negative oxygen isotope composition for pore waters indicates marine environments. Light oxygen values indicate precipitation from either light waters at low temperatures or heavy waters at high temperatures [14].

It seems that  $\text{CO}_2$  component in the fluid had a much lower  $\text{C}^{13}$  i.e. had a major fraction of  $\text{CO}_2$  derived from organic source. The  $\text{C}^{13}$  composition suggest that  $\text{C}^{13}$  value of this fluid varied temporally as well as spatially during the calcite zone event depending on the quantitative influx of Juvenile  $\text{CO}_2$  [15].

**Early Miocene Sandstone Cements:** Meteoric water is also an important source of depleting water and ranges from -3 to -11‰. It seems that if the studied area is invaded by meteoric water, then it was a late stage event. Depletion of pore water during diagenesis may be due to formation of diagenetic minerals and ultrafiltration of clay minerals. Depletion of upto -3‰  $\delta^{18}\text{O}$  over a burial depth of 600 m due to formation of smectite from volcanic material was found during the Deep Sea Drilling Project.  $\delta^{13}\text{C}$  values ranging from -7 to 1.6‰ (Table 1) may be the values of  $\text{CO}_2$  from the methanogenic zone which is in accordance with the work by Curtis et al. [13].

**Veins in Cretaceous Claystone:**  $\delta^{13}\text{C}$  variation can be attributed to minor contribution from organogenic carbons in waters dominated by marine bicarbonate source. Dissolution of metastable fossils and early marine cements together with bicarbonate are likely source [11].

**Veins in Oligocene Limestone:** Isotope values of carbon and oxygen for veins Oligocene limestone show marine environments which are usually close to -5 to +3 per mil. The positive  $\delta^{13}\text{C}$  values (+1.0 to +1.8) indicate not mixing with methanogenic zone carbonate.

**Veins in Early Miocene Mudstone:** The oxygen isotope values (-1.1 to -10.61‰) corresponds to late diagenetic cements in limestone and sandstone [16]. The shift in  $\delta^{18}\text{O}$  from -10.6 to -5‰ indicates either decrease in pore water temperature or increase in pore water  $\delta^{18}\text{O}$ .

The reverse trend of oxygen isotope in veins suggests that the veins were not deposited during burial rather than in depositional waters. Reversals in isotopic composition than concretions could be because of temperature fluctuations during vein deposition, which is extremely unlikely under normal sedimentary burial conditions. The isotopic reversals are therefore probably due to changes in pore water composition.

Metamorphic vein calcite with  $\text{O}^{18}$  values of -4.2 to -10.61 permil and  $\text{C}^{13}$  values of -11 to -18 permil are reported from basal Miocene group rocks. The variation in  $\text{O}^{18}$  values may be due to mixing of meteoric water during the formation of the veins.

At Northland Allochthon, the  $^{13}\text{C}$  composition of calcite is dictated by temperature dependant fractionation effects of  $\text{CO}_2$ , however  $\text{HCO}_3$  plays a secondary role at lower temperature and in zones of mixing and  $\text{CO}_2$ -absorption.

The observed  $\delta^{13}\text{C}$  values may be explained by mixing  $\text{CO}_2$  derived from sedimentary and organic sources. The decomposition of the basement greywacke carbonate may provide high  $\delta^{13}\text{C}$   $\text{CO}_2$  (-2 to +2‰) [17]. In greywacke, carbonate occurs as metamorphic calcite with  $\delta^{13}\text{C}$  values of -10 to -20 ‰ [18] which are typical of organic carbon and not sedimentary as assumed by Lyon and Hulston [17]. In the absence of any known source of high  $\delta^{13}\text{C}$   $\text{CO}_2$  within the basement rocks and knowing that the contribution of organic  $\text{CO}_2$  is not significant ( $\delta^{13}\text{C}$  values are generally greater than -10‰), the "mixing" hypothesis may be ruled out.

## 6. Conclusions

The following conclusions are drawn on the basis of above discussion on isotope data available:

1. Calcite cement in concretions within Cretaceous sandstones has low  $\delta^{13}\text{C}_{\text{PDB}}$  values consistent with derivation of C from oxidation of organic matter in the sediment. Cretaceous sandstones in the Allochthon are quite rich in organic matter.
2. Calcite cement in concretions within the lower part of the Waitemata Group (Early Miocene), which overlies the Allochthon, has  $\delta^{13}\text{C}_{\text{PDB}}$  close to sea water, and negative  $\delta^{18}\text{O}_{\text{PDB}}$  values consistent with less increased temperature and a degree of dilution with meteoric water.
3. Calcite in veins in the basal Waitemata Group (Early Miocene) has low  $\delta^{13}\text{C}_{\text{PDB}}$  values

consistent with derivation of C from oxidation of organic matter. Basal Waitemata Group strata are fossiliferous.

4. Deposition of veins in the Oligocene Mahurangi limestone clearly accompanied localised deformation of the limestone. Otherwise the relative timing of these various calcite depositional events is not well constrained.
5. Veins in Cretaceous age claystone have high  $\delta^{13}\text{C}_{\text{PDB}}$  values which are consistent with the derivation of C from organic matter depleted in  $^{12}\text{C}$  by methanogenesis.
6. Calcite veins in the Oligocene Mahurangi limestone has uniform values of  $\delta^{13}\text{C}_{\text{PDB}}$  very close to marine carbonate values, and the same as our one bulk sample of the enclosing limestone. This suggests derivation of the calcite directly from the enclosing limestone.

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