

## Stable oxygen and carbon isotope compositional fields for skeletal and diagenetic components in New Zealand Cenozoic nontropical carbonate sediments and limestones: a synthesis and review

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**Abstract** The stable oxygen isotope composition ( $\delta^{18}\text{O}$ ) of a precipitated carbonate depends mainly on the isotope composition, salinity, and temperature of the host fluid, whereas the stable carbon isotope composition ( $\delta^{13}\text{C}$ ) reflects the source of  $\text{CO}_2$  for precipitation, such as meteoric or sea water, shell dissolution, or various biochemical origins, including microbial oxidation of organic matter and methane. Despite the potentially complex array of controls, natural waters tend to show a characteristic range of isotope values which in turn are mimicked or tracked by the carbonate minerals precipitated from them. Consequently, plots of  $\delta^{18}\text{O}$  versus  $\delta^{13}\text{C}$  for carbonate materials can help identify their depositional and/or diagenetic environment(s).

Here we compile isotope results for about 800 samples of carbonate skeletons, bulk sediments, fossils, limestones, cements, concretions, and veins spanning a range of ages (latest Cretaceous to modern) and locations in temperate-region New Zealand. Despite some overlap, the isotope values for 21 defined categories of carbonate materials tend to group in discrete regions of the  $\delta^{18}\text{O}$ – $\delta^{13}\text{C}$  diagram, thereby providing important insights about their origin. New Zealand modern skeletal shelf carbonates plot in a distinctly different field from their tropical counterparts because of their heavier  $\delta^{18}\text{O}$  and narrower range of  $\delta^{13}\text{C}$  values, in accord with their nontropical bryomol skeletal facies. Cements in New Zealand temperate limestones are predominantly of burial or, more rarely, meteoric origin, but their nontropical heritage based solely on isotope composition becomes blurred and eventually lost as diagenesis proceeds. In common with many other global examples, siderite, calcite, and dolomite concretions have developed during shallow burial in a range of freshwater to marine depositional settings, the carbon originating mainly from early diagenetic, bacterially mediated reactions involving the decomposition of organic matter in bottom sediments. A summary  $\delta^{18}\text{O}$ – $\delta^{13}\text{C}$  diagram showing mean and standard-deviation isotope values for the various New Zealand carbonate categories will form a basis for comparing and interpreting other carbonate materials and deposits.

**Keywords** oxygen isotopes; carbon isotopes; New Zealand; Cenozoic; nontropical carbonates; limestones; skeletons; fossils; cements; concretions; calcite; siderite; dolomite

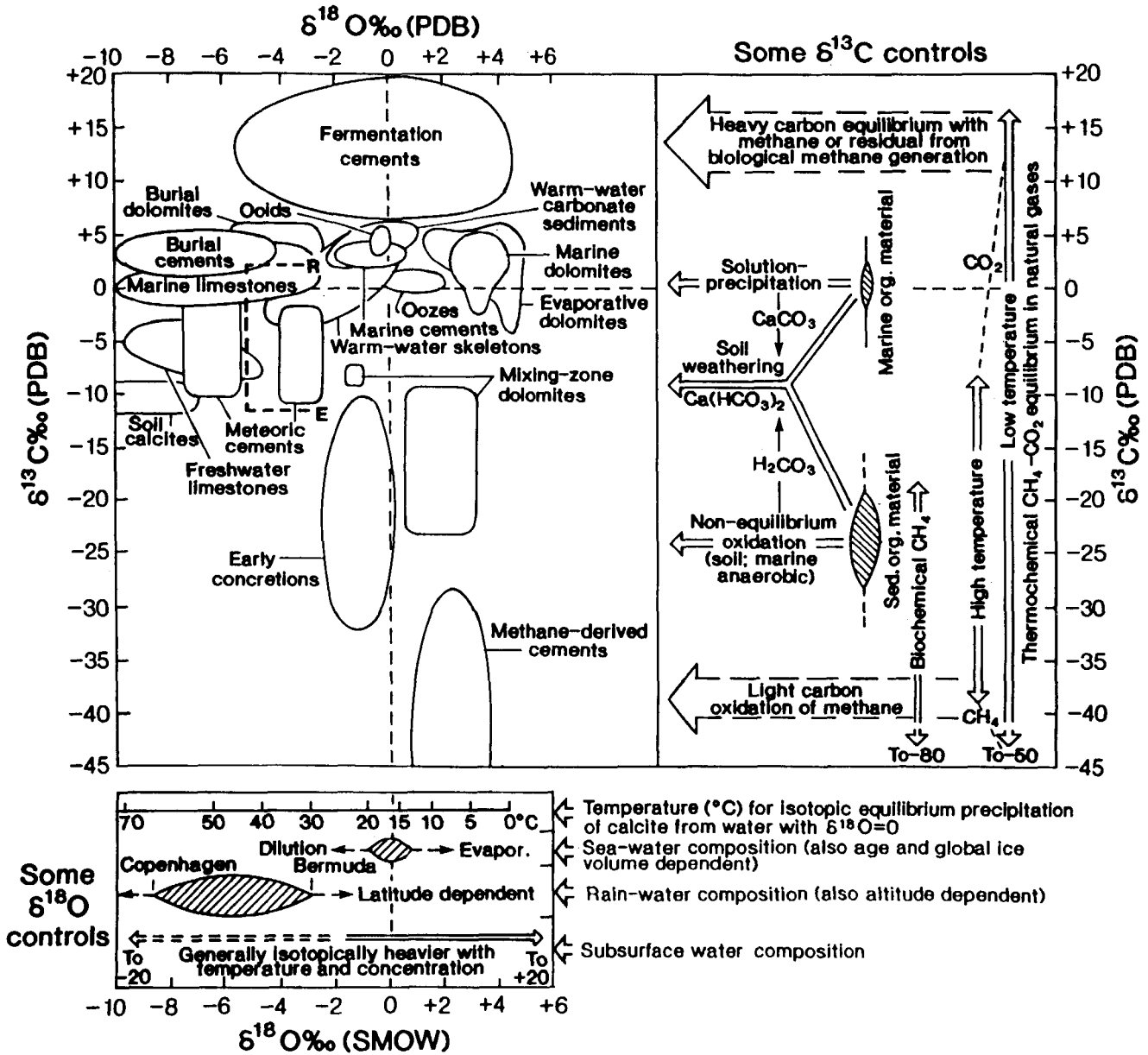
### INTRODUCTION

The majority of modern carbonate sediments are biological in origin and are forming under marine conditions in shallow to deep water. Their nature and distribution are controlled by environmental parameters favourable for the growth of the carbonate-secreting organisms, which include temperature, salinity, depth, substrate, and the relative abundance of siliciclastics (e.g., Lees 1975). Clues to interpreting the growth environment of the organisms come from identification of the taxonomic groups and species involved, their relative abundances, their morphological characteristics, and their associated sediment facies.

Environmental interpretations can be aided, and sometimes refined, by analysing the geochemistry of the skeletons, because this tends to reflect the physico-chemical properties of the environmental waters in which the organisms grew (e.g., Keith et al. 1964; Dodd & Stanton 1981; Morrison & Brand 1986). Moreover, in conjunction with standard petrographic techniques, geochemical investigations provide a powerful tool for helping to recognise and interpret the subsequent diagenetic processes and environments associated with the conversion of skeletal sediments into limestones. They may also shed light on the processes associated with the selective alteration or dissolution of certain carbonate components, such as metastable aragonite grains, and the growth of others, such as calcite cements or dolomite concretions (e.g., Hudson 1977). Again, such a relationship exists because the diagenetic processes are largely driven by the chemical and hydrological characteristics of sediment pore waters, which can be specific to each of the major diagenetic environments, including the subaerial, submarine, and subsurface realms (James & Choquette 1983; Moore 1989).

### Stable oxygen and carbon isotopes

Of the various geochemical techniques employed for assisting with the interpretation of sedimentary and diagenetic conditions and environments, analysis of the stable isotopes of oxygen and carbon in carbonate samples has found particular favour (e.g., Hudson 1977; Anderson & Arthur 1983; Marshall 1992; Corfield 1995). The two most naturally abundant isotopes of oxygen,  $^{18}\text{O}$  and  $^{16}\text{O}$ , and of carbon,  $^{13}\text{C}$  and  $^{12}\text{C}$ , are normally used, variations in  $^{18}\text{O}/^{16}\text{O}$  and  $^{13}\text{C}/^{12}\text{C}$  ratios between samples being measured by high-precision mass spectrometry (e.g., Fairchild et al. 1988). The abundance of  $^{18}\text{O}$  and  $^{13}\text{C}$  in a sample is conventionally reported as the per mil (= mg/g or ‰) difference in delta ( $\delta$ ) notation ( $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ ) between the



**Fig. 1** Reference  $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$  diagram showing generalised isotope fields for a selection of carbonate components, sediments, limestones, cements, dolomites, and concretions, and some of the factors that control the  $\delta^{18}\text{O}$  (bottom) and  $\delta^{13}\text{C}$  (right) compositions of precipitated carbonates. SMOW = Standard Mean Ocean Water, the international standard used for reporting oxygen isotope variations in natural waters. Based on Hudson (1977, fig. 1), and adapted using several isotope compilation figures in Moore (1989). The heavy dashed vertical line corresponds to the meteoric calcite line of Lohmann (1988, fig. 2.11A), with oxygen-enrichment trends related to evaporation (towards E) and increasing rock-water interaction (towards R).

isotope ratios in the sample and those in the international Pee Dee Belemnite (PDB) standard which, by definition, has  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values of 0‰ (Hudson 1977). Increasingly negative, or more depleted,  $\delta$  values with respect to PDB imply a relative increase in the lighter isotopes ( $^{16}\text{O}$ ,  $^{12}\text{C}$ ) in the analysed samples, while more positive, or enriched, values indicate a relative increase in the heavier isotopes ( $^{18}\text{O}$ ,  $^{13}\text{C}$ ).

The  $\delta^{18}\text{O}$  of a carbonate precipitated from water depends chiefly on the  $\delta^{18}\text{O}$  composition and temperature of the water. Increasingly lighter (more negative) values tend to be associated with decreasing salinity and with increasingly higher temperatures (Hudson 1977). The  $\delta^{13}\text{C}$  composition of precipitated carbonates primarily reflects the source(s)

of bicarbonate dissolved in the waters, which can include sea water ( $\delta^{13}\text{C}$  near 0‰), marine shell dissolution ( $\delta^{13}\text{C}$  near 0‰), soil weathering processes ( $\delta^{13}\text{C}$  near -10‰), bacterial oxidation or sulphate-reduction of organic matter ( $\delta^{13}\text{C}$  near -25‰), bacterial methanogenic fermentation ( $\delta^{13}\text{C}$  near +15‰), oxidation of methane ( $\delta^{13}\text{C}$  from -50 to -80‰), or abiotic reactions associated with thermal cracking and decarboxylation ( $\delta^{13}\text{C}$  from -10 to -25‰) (Hudson 1977; Irwin et al. 1977; Coleman 1993; Mozley & Burr 1993). Thus, carbonates precipitated at or near isotopic equilibrium from natural waters tend to show a characteristic range of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  isotope values that reflects reasonably closely their genetic environment. However, amongst some skeletal carbonates there exists the potential

problem of so-called “vital effects” and disequilibrium precipitation, the stable isotope compositions being strongly affected by biological and metabolic processes (see later; Hudson 1977; Swart 1983).

### $\delta^{18}\text{O}$ – $\delta^{13}\text{C}$ diagrams

Bivariate plots involving  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  are a common and convenient way of distinguishing the depositional and/or diagenetic (paleo)environments responsible for carbonate formation. A particularly informative  $\delta^{18}\text{O}$ – $\delta^{13}\text{C}$  cross-plot was prepared by Hudson (1977), who distinguished a number of characteristic isotope fields for carbonates having different origins. His diagram has been followed, adapted, and extended by many subsequent workers (e.g., see  $\delta^{18}\text{O}$ – $\delta^{13}\text{C}$  plots in Bathurst 1981; Choquette & James 1987; Moore 1989; Morse & Mackenzie 1990). A modified version of Hudson's plot is reproduced here as Fig. 1, and forms a basis for the discussion and preliminary interpretation of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  data from carbonate sediments and rocks generally. Moreover, by plotting the isotope composition of individual limestone components, such as fossils and cements or cement zones, it is sometimes possible to trace in detail the diagenetic evolution of whole rock samples (e.g., Dickson & Coleman 1980; Lohmann 1983; Meyers & Lohmann 1985; Rao & Wang 1990).

In this paper we use  $\delta^{18}\text{O}$ – $\delta^{13}\text{C}$  diagrams to summarise the isotope analyses of a large number and diverse array of New Zealand carbonate materials of mainly Cenozoic (including modern) age to: (1) gauge their range of isotope compositions; (2) note whether or not samples of similar type tend to occupy unique areas of the isotope diagram; (3) compare any such fields with the “reference” plot (Fig. 1); and (4) interpret in general terms the trends and genetic significance of the isotope plots, particularly in regard to their potential for assisting with the paleoenvironmental analysis of carbonate samples.

### NEW ZEALAND DATABASE AND METHODS

We have assembled New Zealand carbonate  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  data from a variety of published and unpublished sources into 10 major categories: modern marine skeletons; modern nonmarine otoliths; bulk skeletal marine carbonate sediments; fossil skeletons; bulk skeletal limestones; spar cements; bulk micrites; bulk dolomitic micrites; calcite veins; and calcite, siderite, and dolomite concretions (Table 1). A 13-page tabulation of all isotope results, including locality (Fig. 2), source references, and other sample information, is available on request. Out of the total 799 sample analyses reported here, generating about 1600  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values, 90% were processed at the University of Waikato Isotope Laboratory (UWIL; Table 1). Excluded from this database are the large number of isotope analyses generated at UWIL on microfossil shells from deep-sea cores about New Zealand; these are recorded elsewhere (Nelson et al. 1993a) and provide a basis for high-resolution records of Quaternary oxygen- and carbon-isotope stratigraphy in the Southwest Pacific region (e.g., Nelson et al. 1993b).

Isotope analytical methods used at UWIL are detailed in the references cited in Table 1 and, despite small procedural changes over the years associated with equipment improvements, are more or less as follows. Samples are thoroughly cleaned of any extraneous material, vacuum

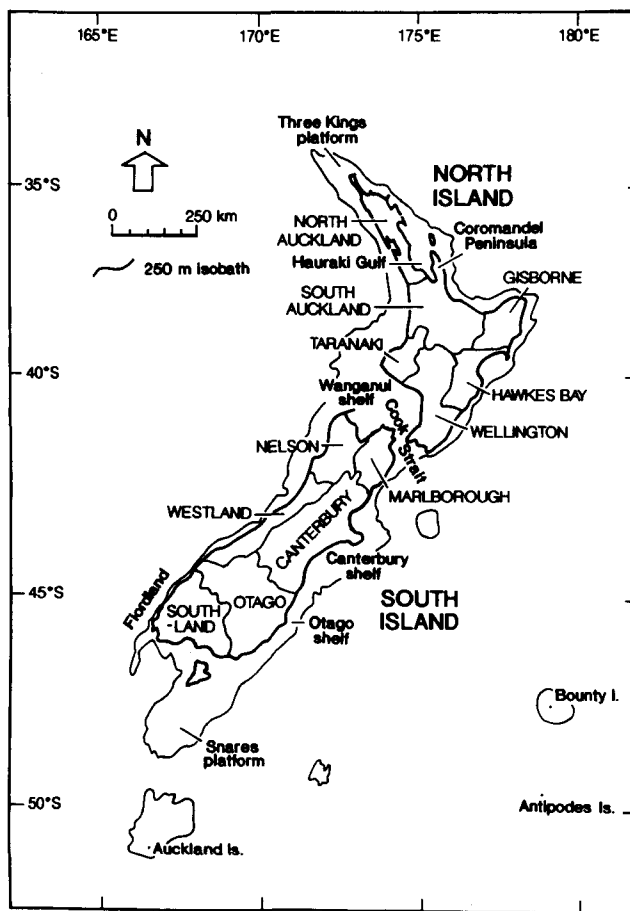


Fig. 2 Locality map for New Zealand place names mentioned in the text and in the available tabulation of all sample isotope results.

roasted for 2.5 h at 400°C to remove organic contaminants, finely ground, and reacted completely with 100% orthophosphoric acid at either 25°C or, in more recent years, 50°C (for siderite samples, acidification was at 100°C for 24 h with subsequent correction of the oxygen isotope data using the fractionation factor of Rosenbaum & Sheppard (1986)). Evolved  $\text{CO}_2$  is separated from other condensibles at  $-110$  to  $-100^\circ\text{C}$  and transferred directly into a VG Micromass 602E (originally C) mass spectrometer to be compared with an internal  $\text{CO}_2$  reference gas, usually either TKL (Blattner & Hulston 1978) or WLS (Burns 1980). This in turn is calibrated daily against the international standard carbonate NBS-19 (Coplen et al. 1983). Isotope results are reported in conventional delta ( $\delta$ ) notation as per mil (‰) deviations from the Pee Dee Belemnite (PDB) standard. Replicate analyses indicate a reproducibility of better than  $\pm 0.1\text{‰}$  for  $\delta^{13}\text{C}$ , and typically  $\pm 0.1$  to  $0.2\text{‰}$  for  $\delta^{18}\text{O}$  (up to  $\pm 0.7\text{‰}$  for siderites).

### RESULTS AND DISCUSSION

Summary statistics of the isotope data for the main categories of New Zealand carbonate materials are given in Table 2. In this section, the full isotope results for samples in the various categories are displayed in turn on appropriately scaled  $\delta^{18}\text{O}$ – $\delta^{13}\text{C}$  plots, followed by brief discussion of some of

the major features and trends, including their general (paleo)environmental significance in relation to the "reference"  $\delta^{18}\text{O}$ – $\delta^{13}\text{C}$  diagram (Fig. 1). More detailed descriptions and interpretation of specific data within the carbonate categories are given in the source articles cited, and are not elaborated upon here.

#### Modern marine skeletons (Fig. 3A)

The largest isotope database is for 202 specimens of marine skeletons picked from modern New Zealand shelf carbonate deposits from the Three Kings platform and Hauraki Gulf off northern New Zealand, and from the Snares platform off southern New Zealand (Fig. 2) (Nelson et al. 1988a). The skeletons comprise identified species from a number of taxonomic groups, including bryozoans ( $n = 113$ ), bivalves ( $n = 43$ ), gastropods ( $n = 11$ ), brachiopods ( $n = 9$ ), ahermatypic corals ( $n = 8$ ), barnacles ( $n = 6$ ), annelids ( $n = 6$ ), echinoderms ( $n = 4$ ), and benthic foraminifera ( $n = 2$ ). The abundance of bryozoans and bivalve molluscs in the collection reflects the overwhelming predominance of

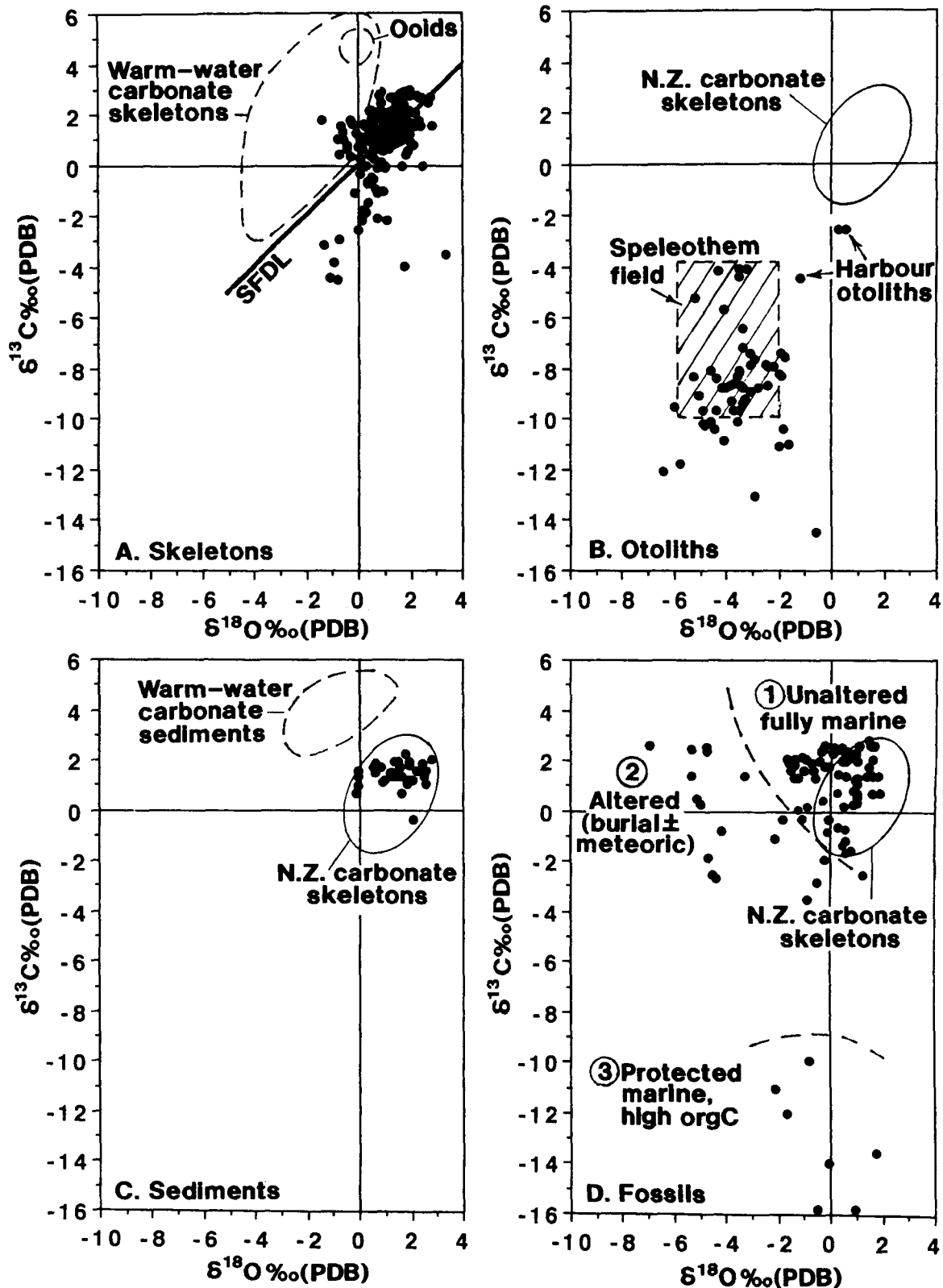
bryomol skeletal carbonate facies on the New Zealand shelf (Nelson et al. 1988a, b; Hayton et al. 1995).

The majority of the New Zealand skeletons cluster at small positive values (0 to +3‰) for both  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ , with rare extensions to small negative  $\delta^{18}\text{O}$  (to –2‰) and moderately negative  $\delta^{13}\text{C}$  (to –5‰) values (Fig. 3A). The grouping of a variety of skeletal taxa at small positive  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values is supportive of the premise that these organisms, dominated by bryozoans, bivalves, barnacles, and brachiopods, have mainly precipitated their shell carbonate close to isotopic equilibrium with ambient shelf waters (cf. Rao & Nelson 1992). Several of the more scattered of the nonclustered samples involve echinoderm and coral analyses, taxa known to exhibit large variations in their  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  compositions because of disequilibrium precipitation owing to prominent "vital" effects (e.g., Weber & Raup 1968; Weber & Woodhead 1970; Swart 1983). Other outlying values in the plot are associated with either very shallow water samples, where the environmental influences of freshwater runoff, warm temperatures, and algal activity

**Table 1** Categories and numbers of New Zealand carbonate samples for which  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  data have been compiled, including their source references and their analytical laboratories (UWIL, University of Waikato Isotope Laboratory; INS, (formerly) Institute of Nuclear Sciences, DSIR, Lower Hutt; AEPR, Arco Exploration and Production Research, USA; CSIRO, Commonwealth Scientific and Industrial Research Organisation, North Ryde, NSW).  $n$ , number of samples.

Carbonate category	$n$	Laboratory	Source references and $n$
Modern marine skeletons	202	UWIL	Smith (1992) – 112 Nelson (unpubl.) – 90
Modern nonmarine otoliths	63	UWIL	Nelson et al. (1989) – 26 Northcote et al. (1992) – 37
Bulk skeletal marine carbonate sediments	37	UWIL	Burns (1980) – 10 Rao & Nelson (1992) – 22 Nelson (unpubl.) – 5
Fossil skeletons	100	UWIL	Burns (1980) – 35 Harris (1986) – 10 Nelson (unpubl.) – 6
		INS	Devereux (1967a) – 29
		CSIRO	Haywick (1990) – 20
Bulk skeletal limestones	103	UWIL	Burns (1980) – 41 Harris (1986) – 3 Nelson (unpubl.) – 41
		INS	Devereux (1967a) – 8 Anderson (1984) – 10
Spar cements	94	UWIL	Harris (1986) – 54 Nelson (unpubl.) – 3
		CSIRO	Haywick (1990) – 37
Bulk micrites	29	UWIL	Burns (1980) – 4 Lawrence (1989) – 25
Bulk dolomicrites	33	UWIL	Lawrence (1989) – 33
Veins	22	UWIL	Harris (1986) – 19 Nelson (unpubl.) – 3
Concretions (a) calcite	52	AEPR	Thyne & Boles (1989) – 19
		UWIL	Middleton (1989) <sup>1</sup> – 26 Nelson (unpubl.) – 7
(b) siderite	37		Middleton (1989) <sup>1</sup> – 37
(c) dolomite	27	AEPR	Thyne & Boles (1989) – 1
		UWIL	Lawrence (1989, 1991) – 23 Nelson (unpubl.) – 2
		CSIRO	Haywick (1990) – 1

<sup>1</sup>See also Middleton & Nelson (in press).



**Fig. 3**  $\delta^{18}\text{O}$ – $\delta^{13}\text{C}$  plots for some New Zealand carbonate biota and sediment samples. **A**, Modern marine skeletons (dominantly bryozoans and bivalves) from mainly shelf water depths. General fields for warm-water carbonate skeletons and ooids (dashed) are superimposed (from Fig. 1), as is the trend of the sea floor diagenesis line (SFDL; Milliman & Muller 1977; Rao & Nelson 1992). **B**, Modern otoliths from the common smelt *Retropinna retropinna* (Richardson) from freshwater lakes and rivers, and from harbours, in the South Auckland region (see Northcote et al. 1992), in relation to the core field for New Zealand marine carbonate skeletons (interpreted by eye from Fig. 3A). The hatched field includes the isotope composition of freshwater speleothems from modern South Auckland caves (Hendy 1969). **C**, Bulk skeletal marine carbonate sediments from the New Zealand shelf in relation to the general fields for shallow-marine tropical carbonate sediments (Fig. 1) and individual New Zealand carbonate skeletons (interpreted from Fig. 3A). **D**, Macrofossils from New Zealand Cenozoic formations, showing fields 1–3, in relation to the core field for modern offshore carbonate skeletons (interpreted from Fig. 3A).

are maximised, or deep samples, where coolest temperatures prevail. A more detailed account relating the modern skeletal isotope data to particular taxonomic groups and species, to mineralogy, and to environmental parameters, is in preparation.

The principal isotope field for New Zealand modern skeletons is displaced from that outlining the dominant skeletal grains in modern tropical carbonate sediments on the reference  $\delta^{18}\text{O}$ – $\delta^{13}\text{C}$  diagram, with little overlap (Fig. 1, 3A). There are several explanations for this. Firstly, the biotic assemblages of tropical carbonates differ substantially from their nontropical counterparts, with major contributions from groups that are absent or relatively uncommon in New Zealand waters, such as calcareous green algae and hermatypic corals, the so-called chlorozoan or chloralgal skeletal carbonate association (Lees 1975). The broad isotope field encompassing the warm-water skeletons reflects the widespread occurrence of isotopic disequilibrium during shell precipitation because of major "vital effects" associated especially with algal metabolic processes, symbiotic in the corals (Milliman 1974; Swart 1983). The New Zealand skeletal envelope is much tighter because it is dominated by a bryomol assemblage of marine skeletons (Hayton et al. 1995) that mainly precipitate shells close to isotopic equilibrium with sea water (Rao & Nelson 1992). Secondly, the tendency for  $\delta^{18}\text{O}$  to occur at low negative values in the chlorozoan skeletons, but low positive values in the New Zealand skeletons, reflects the temperature contrast between warm tropical and cool temperate shelf settings. Using the paleotemperature equation of Shackleton & Kennett (1975), the  $\delta^{18}\text{O}$  values for the New Zealand

skeletons suggest ambient water temperatures mainly in the range 4–18°C (Rao & Nelson 1992). Thirdly, the trend towards moderately positive  $\delta^{13}\text{C}$  values for many skeletons from tropical carbonate environments is contributed by the high algal population and photosynthetic activity (Milliman & Muller 1977). This fosters relative  $^{13}\text{C}$  enrichment in the shoal waters from which carbonate is precipitated, an explanation consistent also with the rather positive  $\delta^{13}\text{C}$  composition of inorganically formed carbonate grains, such as ooids (Fig. 1, 3A), which are widespread in tropical chlorozoan carbonates but absent in temperate-latitude bryomol ones (Nelson 1988). Fourthly, the isotope compositions of temperate-region skeletons tend to follow the trend line for seafloor diagenesis through the origin of the  $\delta^{18}\text{O}$ – $\delta^{13}\text{C}$  diagram (SFDL on Fig. 3A) because they are usually in equilibrium with upwelling and cool bottom waters, and not atmospheric  $\text{CO}_2$  and warm surface waters as are shoal-water tropical carbonates (Rao & Nelson 1992; Rao 1993).

#### Modern nonmarine otoliths (Fig. 3B)

Nelson et al. (1989) and Northcote et al. (1992) analysed the  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  composition of aragonitic otoliths (fish ear-bones) from the common smelt *Retropinna retropinna* (Richardson) collected from harbours, rivers, and lakes in the South Auckland region of central North Island (Fig. 2). The studies were undertaken to investigate the usefulness of stable isotope measurements for identifying habitat waters of the smelt, and for distinguishing between resident and migratory populations. Results indicated that the otolith  $\delta^{18}\text{O}$  values are similar to those of the smelt-rearing waters.

**Table 2** Summary of statistics for isotope composition of categories of New Zealand carbonates.

New Zealand carbonate category	No. of samples	$\delta^{18}\text{O}$ (‰)					$\delta^{13}\text{C}$ (‰)				
		Mean	SD	Min.	Max.	Range	Mean	SD	Min.	Max.	Range
Modern marine skeletons	202	1.02	0.83	-1.42	3.32	4.74	1.03	1.43	-4.50	2.97	7.47
bryozoans	113	0.92	0.81	-1.35	2.75	4.10	1.02	1.21	-4.50	2.81	7.31
bivalves	43	1.22	0.74	-0.80	3.32	4.12	1.33	1.44	-4.50	2.97	7.47
Modern nonmarine otoliths	63	-3.28	1.45	-6.40	0.60	7.00	-8.86	2.92	-17.97	-2.60	15.37
Bulk skeletal sediments	37	1.42	0.77	-0.17	2.78	2.95	1.39	0.47	-0.37	2.22	2.59
Fossil skeletons	100	-0.50	1.91	-6.95	1.90	8.85	0.00	3.94	-15.74	2.90	18.64
Group 1	76	0.22	0.96	-1.68	1.90	3.58	1.27	1.18	-2.52	2.90	5.42
Group 2	17	-3.75	1.95	-6.95	-0.20	6.75	-0.23	2.10	-3.50	2.58	6.08
Group 3	7	-0.38	1.37	-2.15	1.71	3.86	-13.13	2.27	-15.74	9.9	5.84
Bulk skeletal limestones	103	-1.89	1.52	-6.80	1.20	8.00	0.34	1.62	-4.83	2.97	7.80
Spar cements	94	-4.45	1.19	-9.33	-1.18	8.15	-2.62	3.90	-10.70	2.88	13.58
Group 1	58	-4.37	1.35	-9.33	-1.18	8.15	0.13	1.18	-1.90	2.88	4.78
Group 2	36	-4.82	0.81	-6.89	-3.19	3.70	-7.05	2.34	-10.70	-2.90	7.80
Bulk micrites	29	-4.08	1.74	-6.90	-1.09	5.81	1.34	1.12	-1.53	3.04	4.57
Bulk dolomicrites	33	-4.13	1.28	-6.82	-1.89	4.93	1.22	1.84	-5.82	3.35	9.17
Veins	22	-5.76	2.15	-11.36	-2.22	9.14	-1.74	4.95	-19.60	2.64	22.24
Group 1	17	-5.79	1.75	-9.32	-2.22	7.10	0.34	1.35	-2.25	2.64	4.89
Group 2	5	-5.64	3.46	-11.36	-2.67	8.69	-8.79	6.38	-19.60	-3.13	16.47
Calcite concretions	52	-3.36	3.37	-10.00	2.52	12.52	-16.19	11.25	-31.72	3.05	34.77
Group 1	23	-6.93	1.61	-10.00	-4.85	5.15	-9.52	7.06	-18.30	3.05	21.35
Group 2	29	-0.53	1.44	-3.79	2.52	6.31	-21.49	8.97	-31.72	0.65	32.37
Siderite concretions	37	-2.18	1.97	-5.68	1.88	7.56	3.63	7.14	-14.51	13.11	27.62
Group 1	27	-2.99	1.55	-5.68	-0.37	5.31	6.26	5.39	-8.48	13.11	21.59
Group 2	8	-0.45	0.70	-1.38	0.99	2.37	-0.72	3.71	-8.80	4.06	12.86
Group 3	2	1.84	0.06	1.79	1.88	0.09	-14.36	0.22	-14.51	-14.20	0.31
Dolomite concretions	27	-1.82	3.90	-6.79	6.34	13.13	-6.77	15.80	-46.89	8.36	55.25
Group 1	15	-0.63	1.66	-3.77	3.75	7.52	4.24	4.79	-8.64	8.36	17.00
Group 2	9	-6.23	0.32	-6.79	-5.66	1.13	-22.85	14.85	-46.89	-5.30	41.59
Group 3	3	5.44	0.93	4.49	6.34	1.85	-13.57	7.78	-21.80	-6.33	15.47

whereas the  $\delta^{13}\text{C}$  compositions are not in isotopic equilibrium with the environmental waters, but they do track the major differences between them (Northcote et al. 1992). Here we use the otolith  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  analyses as an example of predominantly freshwater skeletal carbonate precipitates in North Island. The data serve to emphasise the strong isotopic contrast that exists between skeletons from nonmarine and open-marine environmental habitats (Fig. 3B). As anticipated, the three otolith samples from harbour-resident smelt plot closer to the main New Zealand shelf carbonate skeletal field (Fig. 3B). The only other stable isotope data known to us for modern New Zealand fish otoliths are the  $\delta^{18}\text{O}$  values reported by Devereux (1967b) from open-ocean conditions, which range from +0.2 to +2.1‰; these are consistent with our fully marine carbonate skeletal values.

Also shown on Fig. 3B is the field range for the typical isotopic composition of modern calcitic speleothems in the South Auckland region (based on data in Hندی 1969). The substantial overlap between speleothem and river/lake smelt isotope data confirms the freshwater heritage of both these carbonate precipitates.

#### Bulk skeletal marine carbonate sediments (Fig. 3C)

The  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  composition of bulk samples of marine skeletal sediments from the modern Three Kings, Snares, and Hauraki Gulf regions (Fig. 2) (Nelson et al. 1988a) are plotted on Fig. 3C in relation to the main fields for the individual New Zealand skeletons and their tropical carbonate equivalents. The bulk New Zealand carbonates cluster tightly at small positive values of  $\delta^{18}\text{O}$  (0 to +2‰) and  $\delta^{13}\text{C}$  (+1 to +2‰) inside the New Zealand skeletal envelope, reflecting the modal isotope compositions of the dominant skeletal contributors to samples, especially bryozoans and bivalves (Table 2). The New Zealand whole sediment isotope field is distinct from that for warm shallow-marine carbonate sediments (Fig. 3C), the former reflecting near-equilibrium isotope precipitation of skeletal components from cool bottom and upwelling waters, the latter a spectrum of equilibrium through disequilibrium precipitates of skeletal and inorganic carbonate grains from warm surface waters (Rao & Nelson 1992; Rao 1993). The New Zealand bulk skeletal carbonate isotope field overlaps with that for deep-sea carbonate oozes (Fig. 1) and, like the plot for the component skeletal grains (Fig. 3A), is bisected by the seafloor diagenesis trend line (Rao & Nelson 1992).

#### Fossil skeletons (Fig. 3D)

Available macrofossil  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  analyses are almost exclusively of bivalve shells, including fresh-looking calcitic oysters and pectens, and recrystallised or rather chalky specimens of (formerly) aragonitic bivalves, together categorised as "altered bivalves". The fossils come mainly from North Island limestone (and some siliciclastic) formations that range in age from Eocene to Pleistocene, but are mainly Oligocene–Miocene. The isotope plot shows a wide scatter of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values that are separated into three fields (Fig. 3D).

Field 1 is centred on  $\delta^{18}\text{O}$  values of  $0 \pm 2\text{‰}$  and small positive  $\delta^{13}\text{C}$  values (0 to +2.5‰), overlapping with, and closely similar to, the main cluster of modern New Zealand skeletons and whole carbonate sediments. Field 1 fossils are typically fresh and unaltered, dominantly calcitic, and come

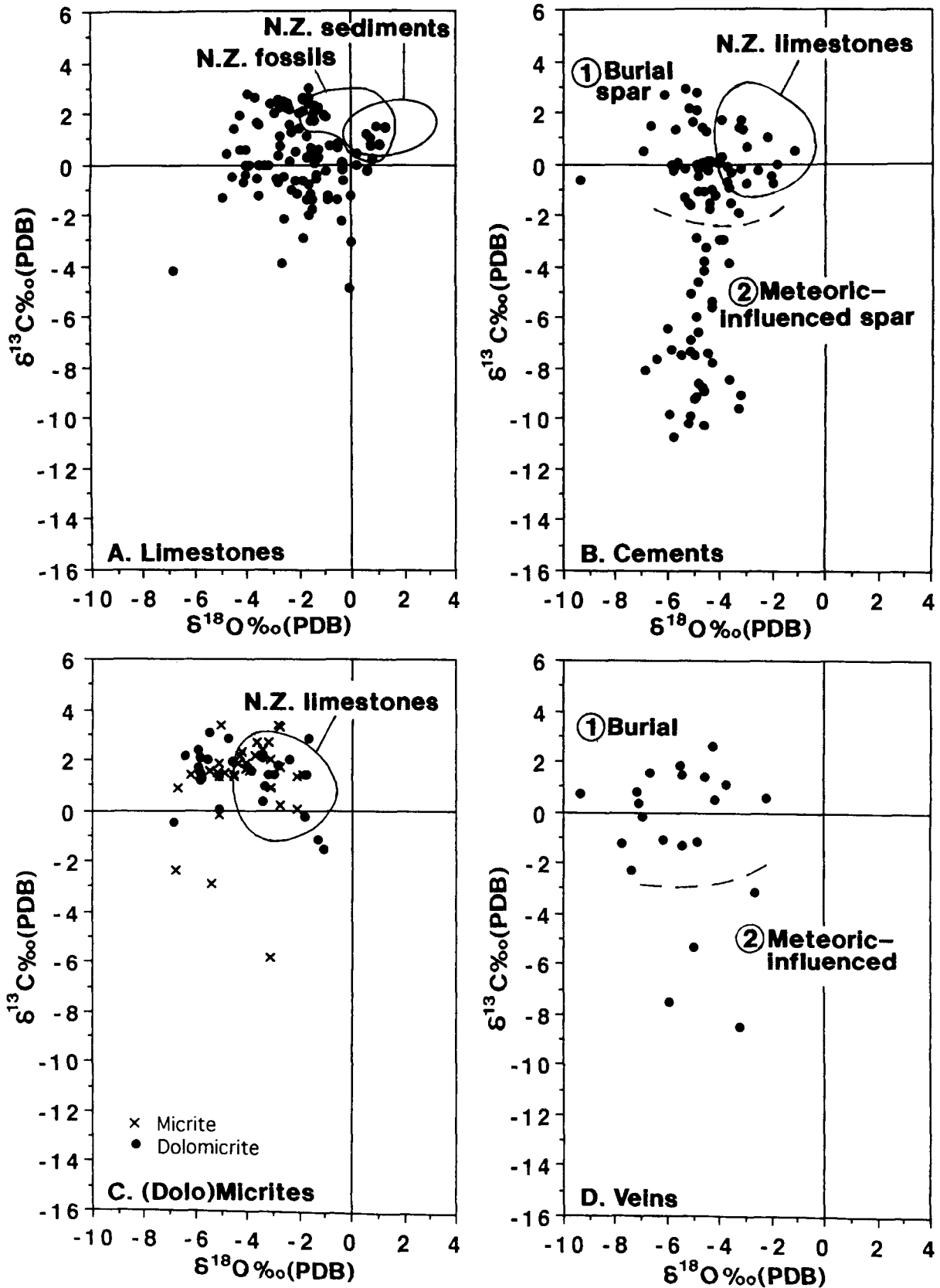
from fully marine formations. The small negative shift towards lighter  $\delta^{18}\text{O}$  values for the field as a whole compared to the modern New Zealand skeletons may reflect the dominance of mid-Tertiary age fossils in the database, since these specimens grew at a time when the global ice budget was less than present and sea water had correspondingly lighter  $\delta^{18}\text{O}$  values and was possibly relatively warmer (e.g., Renard 1986; Railsback 1990).

Fossils in field 2 also come from formations deposited under fully marine conditions. Their isotope plots are scattered and, compared to field 1, are characterised by more negative  $\delta^{18}\text{O}$  values (typically –2 to –6‰) and a wider range of  $\delta^{13}\text{C}$  compositions towards slightly more depleted values. In most fossils there is hand-specimen evidence that shells in this group have been diagenetically altered or recrystallised, and thus field 2 fossils are interpreted as showing isotopic re-equilibration of their shell carbonate within either the burial (increasing temperature and  $^{18}\text{O}$  depletion) or meteoric (both  $^{18}\text{O}$  and  $^{13}\text{C}$  depletion) diagenetic realms (e.g., Haywick 1990). The spread of isotope values can be related to variations in the rate, timing, and environment of alteration, and the extent of shell/water interaction.

Fossils in field 3 are mainly large calcitic oysters characterised by marine  $\delta^{18}\text{O}$  values near 0‰, but having strongly negative  $\delta^{13}\text{C}$  values from –10 to –16‰. They occur in muddy, often organic matter rich, formations (e.g., Mangakotuku Formation) whose depositional paleoenvironments were probably sheltered, shallow-marine gulfs or estuaries that experienced locally anaerobic conditions (e.g., Nelson et al. 1983). The strongly depleted  $\delta^{13}\text{C}$  values of fossil shells are interpreted as due to incorporation of isotopically light  $\text{CO}_2$  from decomposition of marine and/or terrestrial organic matter ( $\delta^{13}\text{C}$  from c. –10 to –30‰) in the shallow-subsurface sulphate-reducing zone that has mixed and equilibrated to varying extents with sea-water bicarbonate in a low-energy marine depositional setting (cf. Coleman & Raiswell 1981).

#### Bulk skeletal limestones (Fig. 4A)

Samples come from a wide range of marine limestone formations throughout New Zealand, particularly from western North Island, and are of mainly Oligocene or early Miocene age, the dominant period of widespread shallow-marine carbonate deposition in New Zealand (Nelson 1978). Their  $\delta^{13}\text{C}$  compositional range (+3 to –1.5‰) is broadly similar to values for New Zealand modern carbonates and field 1 fossils (Fig. 3D), but their  $\delta^{18}\text{O}$  composition has shifted to noticeably more depleted values, falling between c. –1 and –4.5‰ (Fig. 4A). The negative shift in  $\delta^{18}\text{O}$  of the limestone field is in response to diagenetic transformation of unconsolidated skeletal sediment into limestone, involving mainly the precipitation of carbonate cement into pore spaces. Thus, the most porous and least cemented of the New Zealand Oligocene limestones, the "Oamaru" limestones of southeastern South Island (Gage 1957), have the heaviest  $\delta^{18}\text{O}$  compositions (0 to +1‰) of all the analysed samples. Those Oligocene limestones with the largest amounts of calcite cement, however, have some of the lightest  $\delta^{18}\text{O}$  values (–4 to –5‰) (Nelson et al. 1988c, fig. 5). The range of moderately depleted  $\delta^{18}\text{O}$  values in most limestones is supportive of cementation under mainly burial and/or meteoric conditions (see next section) rather than by syndimentary marine cements as occurs in many



**Fig. 4**  $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$  plots for some New Zealand limestones and cements. **A**, Bulk skeletal limestones of Cenozoic age in relation to the core fields for modern New Zealand shelf carbonate sediments and for fossils, interpreted by eye from Fig. 3C and D, respectively. **B**, Calcite spar cements, showing groups 1 and 2, in relation to the core field for New Zealand skeletal limestones interpreted from Fig. 4A. **C**, Micrites and dolomicrites, mainly from the Late Cretaceous - early Tertiary Amuri Limestone (Lawrence 1989), in relation to the core field for New Zealand skeletal limestones (interpreted from Fig. 4A). **D**, Calcite spar veins, showing groups 1 and 2 (cf. Fig. 4B).



tropical carbonate deposits (Fig. 1). As diagenesis advances, there is a gradual loss of the former clear “isotopic expression” for the nontropical heritage of the New Zealand skeletal carbonates (Fig. 3C) as the deposits shift towards, and enter, the “global marine limestone” field (Fig. 1).

#### Spar cements (Fig. 4B)

The dominant cements in the majority of New Zealand's nontropical limestones are calcite spar and microspar having equant granular or, about echinoderm particles, syntaxial rim fabrics (Nelson 1978). Data on the isotope composition of cements drilled from limestone samples is presently available only for Oligocene–Miocene formations from western North Island (Harris 1986; Nelson et al. 1988c, 1994) and Pliocene–Pleistocene formations of eastern North Island (Haywick 1990). However, the limestones in these two regions are broadly representative of the spectrum of coarser grained skeletal limestones characterising the New Zealand Cenozoic record, both in terms of their skeletal make-up (bryomol and barnamol, respectively; Hayton et al. 1995) and tectonic setting (passive and convergent margins, respectively) (e.g., Nelson 1978; Kamp & Nelson 1988; Kamp et al. 1988).

The  $\delta^{18}\text{O}$ – $\delta^{13}\text{C}$  plot separates carbonate cements into two broad groups on the basis of  $\delta^{13}\text{C}$  composition: group 1 retains “normal-marine”  $\delta^{13}\text{C}$  values of  $0 \pm 2\text{‰}$ , and group 2 is characterised by moderately to strongly depleted  $\delta^{13}\text{C}$  values from c.  $-3$  to  $-11\text{‰}$  (Fig. 4B). Group 1 cements have moderately to strongly depleted  $\delta^{18}\text{O}$  values ( $-2$  to  $-9\text{‰}$ ), always lighter than the bulk limestones from which they were derived, and accounting for the depletion shift between the isotope field for New Zealand fossils and their associated lithified limestones, as noted above (Fig. 4A). By integrating the isotope data represented by group 1 cements with field, petrographic, and elemental information for the host limestones, Nelson et al. (1988c) showed that the bulk of these cements were of burial origin. It was suggested that pressure-dissolution of calcitic skeletal fragments in the deposits became widespread after a few 100 m of burial, and that the dissolved carbonate was reprecipitated as calcite spar in nearby pore spaces. The  $\delta^{13}\text{C}$  composition of the cements remained similar to that in the dissolved marine skeletons ( $\delta^{13}\text{C}$   $0 \pm 2\text{‰}$ ), but the  $\delta^{18}\text{O}$  values of the cements became progressively more depleted in  $^{18}\text{O}$  compared to the original marine shells because of temperature-related fractionation with increasing burial depth. From graphical relationships established by Nelson et al. (1988c, fig. 6), it was estimated that  $\delta^{18}\text{O}$  values between c.  $-3$  and  $-8\text{‰}$  would have formed in cements at subsurface depths between c. 500 and 1500 m, respectively, corresponding to burial temperatures in the range of  $30$ – $60^\circ\text{C}$ . Thus, group 1 cements are inferred to be dominantly burial spar cements.

The roughly constant, but moderately depleted  $\delta^{18}\text{O}$  composition (mainly  $-4$  to  $-6\text{‰}$ ) of group 2 spar cements, coupled with their range of moderately to strongly depleted  $\delta^{13}\text{C}$  values ( $-3$  to  $-11\text{‰}$ ), closely matches the trend of the idealised meteoric calcite line deduced by Lohmann (1988) to be characteristic of meteoric carbonate precipitation (Fig. 1). The range of  $\delta^{13}\text{C}$  values can be explained by different amounts of isotopic buffering of meteoric waters from dissolution of the host marine limestone and its components, with the least rock-water interaction at the more depleted end of the  $\delta^{13}\text{C}$  range. Group 2 cements are particularly well developed in several of the Pliocene–Pleistocene limestones

of eastern North Island, where Haywick (1990) demonstrated that the strongest meteoric signal typically occurs in the later formed cements that were precipitated as carbonate formations came under an increasing influence from freshwater recharge during periods of basin shallowing associated with uplift in the hinterland and glacio-eustatic lowering of sea level.

#### Bulk micrites (Fig. 4C)

Dense fine-grained limestones (calcilutites or micrites) are a conspicuous carbonate facies in many Late Cretaceous – early Tertiary sequences in New Zealand (Nelson 1978), and are especially prominent in southeastern North Island and northeastern South Island where they have been assigned the regional name “Amuri Limestone” (Browne 1987). The limestones are coccolithophorid-planktonic foraminiferal biomicrites whose paleodepths of deposition are problematic (Lewis 1993), but probably ranged from outer shelf to deep-ocean basin (Nelson 1968; Carter 1969; Lewis 1993). Their isotope composition (Fig. 4C) overlaps the field for the coarser grained skeletal limestones, but includes several samples with lighter  $\delta^{18}\text{O}$  values, from  $-5$  to  $-7\text{‰}$ .

Pressure-dissolution during burial and tectonic movements is probably the major source of the cryptocrystalline calcite spar cement in the micrites, demonstrated by common stylolite seams in the direction of bedding and along low-angle intersecting joint sets (Lawrence 1989; Nicol 1992). The more depleted  $\delta^{18}\text{O}$  compositions may relate to the associated temperature-dependent fractionations accompanying increased burial pressures and tectonic stresses, and varying amounts of calcite recrystallisation. However, they probably also reflect the very wide age range of the Amuri Limestone and the warmer and more  $\delta^{18}\text{O}$ -depleted nature of ocean water in the Late Cretaceous – early Paleogene compared to later in the Cenozoic (e.g., Renard 1986; Railsback 1990). These imparted correspondingly lighter  $\delta^{18}\text{O}$  compositions to the primary planktonic microfossil elements comprising the micrites.

#### Bulk dolomicrites (Fig. 4C)

Dolomites, or dolostones, are rare in New Zealand Cenozoic carbonate sequences (Nelson 1978), the only significant development being in the stratigraphically lower part of some of the Amuri Limestone micrites described in the previous section. Some  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  data for the Amuri dolomicrites, which plot within the same isotope field as the Amuri micrites (Fig. 4C), were interpreted by Lawrence (1989, 1991) to support early diagenetic dolomitisation of microfossil ooze close to the seafloor under conditions of very slow sediment accumulation, the  $\text{Mg}^{2+}$  being supplied from sea water.

#### Veins (Fig. 4D)

The isotope composition of some vein calcites in Oligocene–Miocene limestones from western North Island only are plotted on Fig. 4D. All the veins are tectonic in origin and formed following lithification of the limestones. The more  $^{18}\text{O}$ -depleted nature of several of the vein calcites (group 1) compared to the limestone cements is consistent with their formation under higher temperatures during post-lithification basin subsidence to burial depths  $>1$  km (Harris 1986). However, other vein calcites (group 2) with moderately depleted  $\delta^{13}\text{C}$  values have been precipitated under the

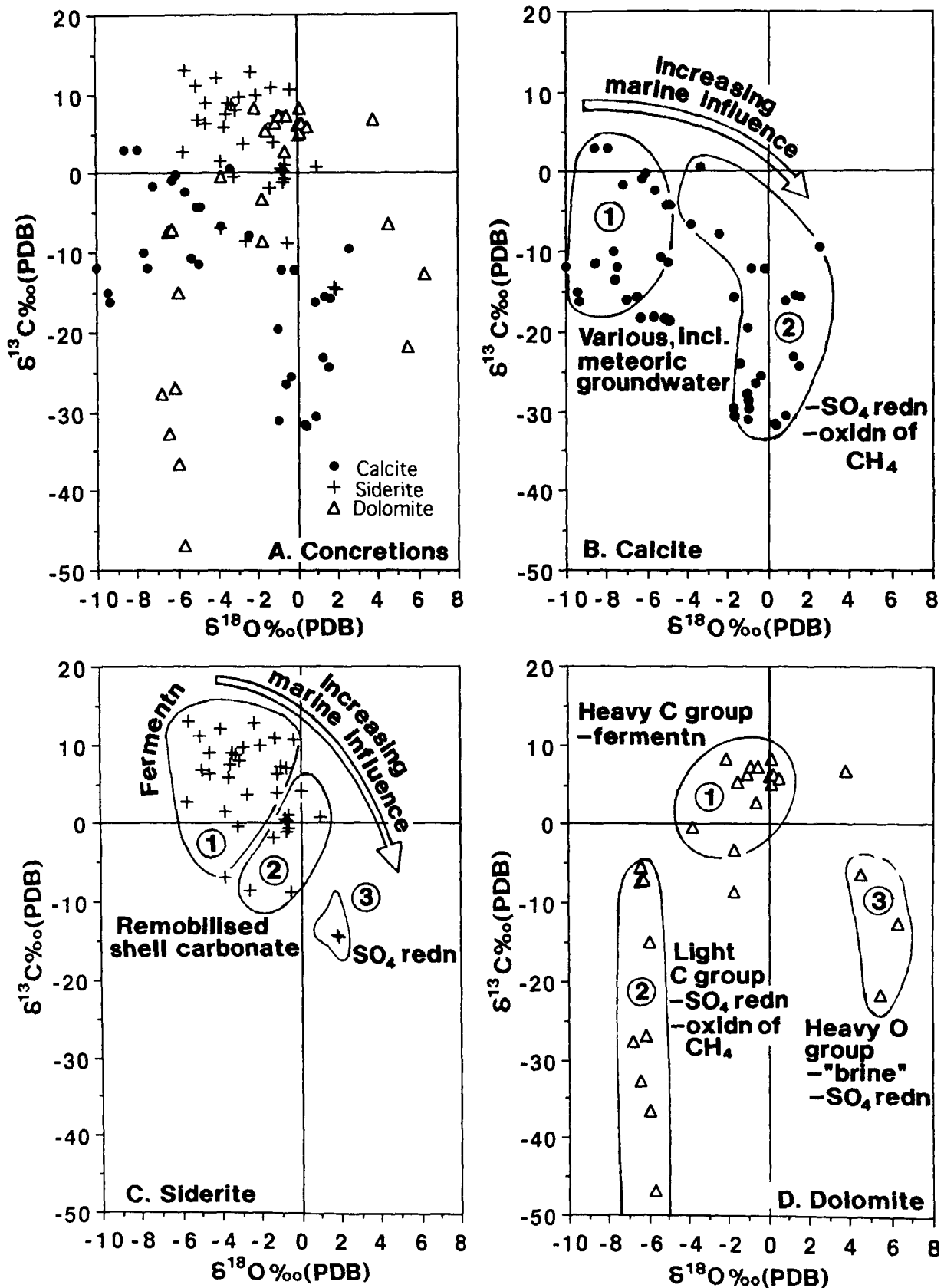
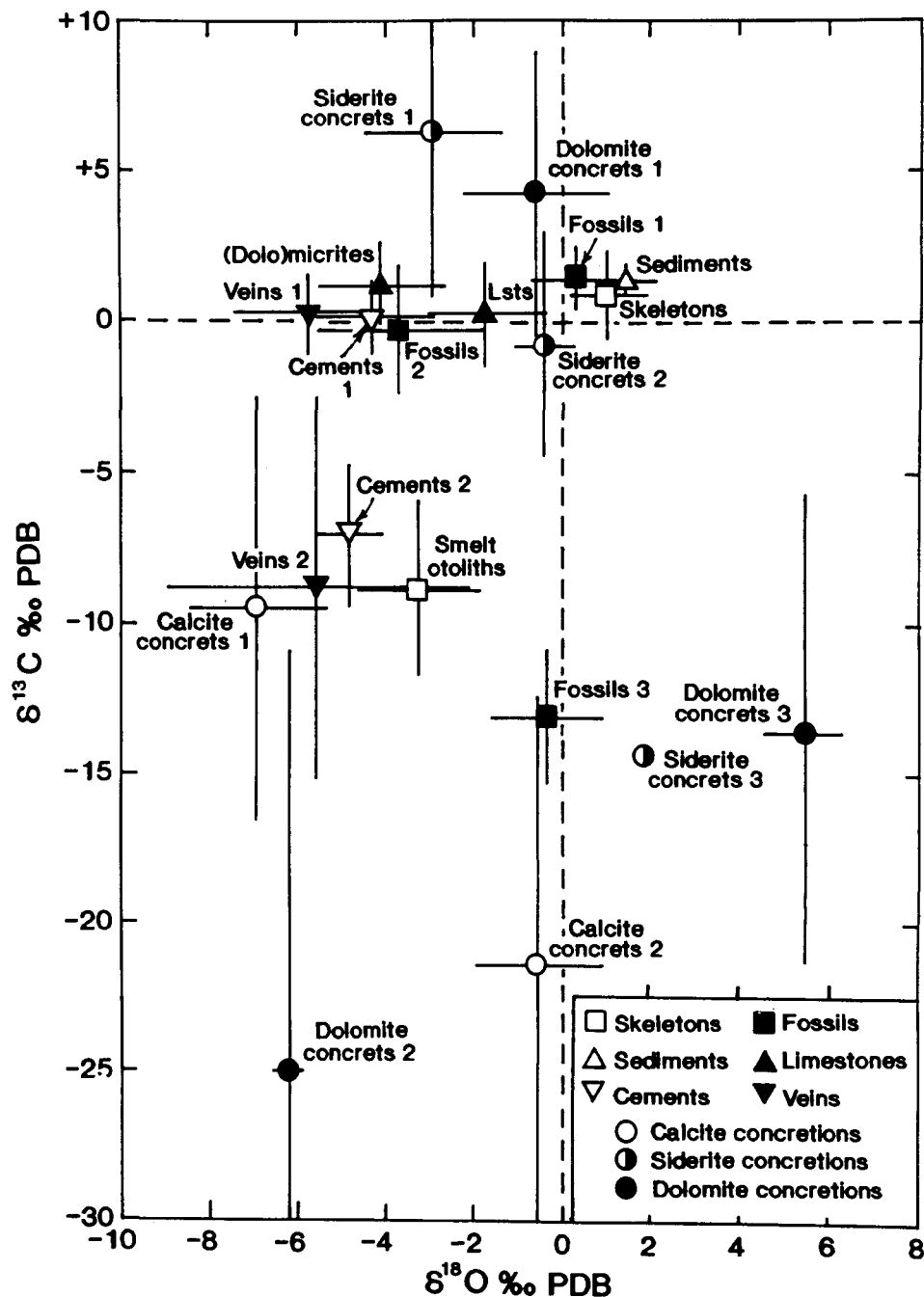


Fig. 5  $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$  plots for some New Zealand concretions. A. All concretions. Note change in scales of  $\delta^{18}\text{O}$  and particularly  $\delta^{13}\text{C}$  axes compared to Fig. 3 and 4. B. Calcite concretions, showing groups 1 (nonmarine) and 2 (marginal marine to marine), and possible sources of their carbonate carbon (see Middleton 1989; Middleton & Nelson in press). C. Siderite concretions, showing groups 1 (nonmarine), 2 (marginal marine), and 3 (marine), and possible sources of their carbonate carbon (see Middleton 1989; Middleton & Nelson in press). D. Dolomite concretions, showing groups 1-3 (all marine), and possible sources of their carbonate carbon (see Lawrence 1991).

**Fig. 6** Summary  $\delta^{18}\text{O}$ – $\delta^{13}\text{C}$  plot showing the interrelationships between the various New Zealand carbonate types according to their mean  $\pm 1$  SD values (Table 2). In this diagram the bulk micrite and dolomicrite categories are combined.

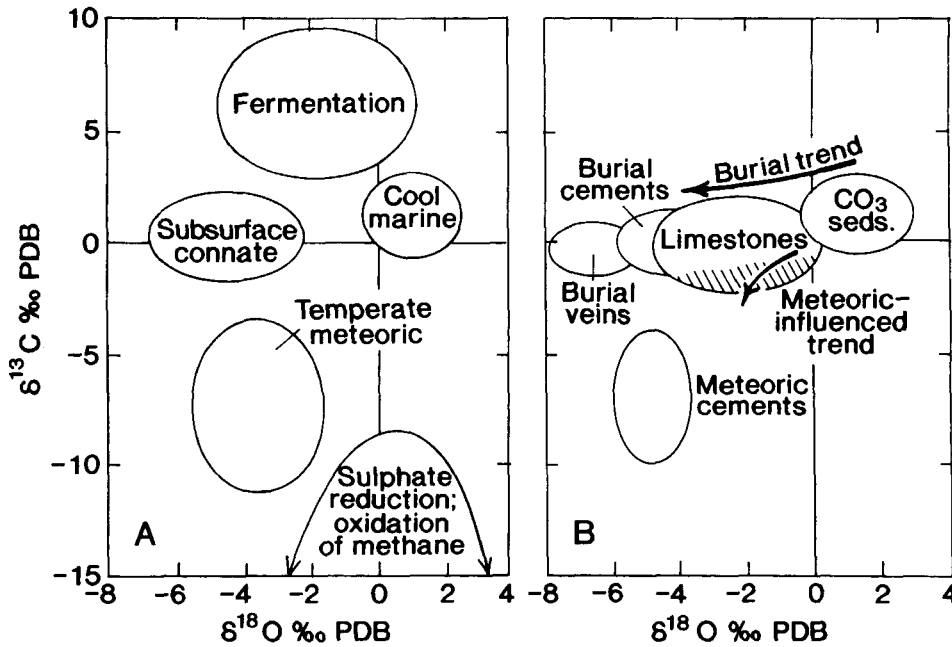


influence of circulating meteoric waters, variably buffered by water-limestone interaction, and formed during uplift of the limestone formations to the surface.

**Concretions** (Fig. 5)

Despite the common occurrence of concretionary structures in New Zealand Late Cretaceous–Cenozoic strata, there have been few studies of their  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  compositions. The stable isotope data available for calcite, siderite, and dolomite concretionary materials are from a restricted range of localities and formations, and are summarised in Fig. 5A. A prominent feature is the extreme variability in isotope composition of the concretions compared to the previously discussed carbonate categories, particularly in relation to their  $\delta^{13}\text{C}$  values (Table 2).

Carbonate concretions are typically early diagenetic structures, developing mainly within the first few metres or tens of metres below the sediment/water surface, and sometimes continuing to grow at a much reduced rate thereafter (e.g., Hudson 1977; Irwin et al. 1977; Coleman & Raiswell 1981; Coleman 1993). For the analysed New Zealand concretions, the source references (Table 1) all present convincing evidence for a predominantly early diagenetic origin (e.g., Thyne & Boles 1989; Middleton & Nelson in press). Consequently, the isotope composition of authigenic carbonate cements in the concretions should reflect mainly the isotope composition of their natural environmental waters, ranging from meteoric to marine, possibly modified to varying degrees (particularly the  $\delta^{13}\text{C}$  values) by microbiologically mediated metabolic reactions



**Fig. 7** A, Generalised isotope fields of the inferred environmental factors sourcing the main categories of New Zealand carbonate precipitates. The fermentation and sulphate reduction-methane oxidation fields relate principally to early diagenetic concretionary carbonates. B General isotope fields associated with the burial transformation of nontropical carbonate sediments into limestones, the main lithification process in the New Zealand deposits. Some of the limestones (hatched area) have also been influenced by subsequent meteoric diagenetic effects.

associated with the degradation of organic material during shallow burial of the host sediments (Fig. 1; Irwin et al. 1977; Coleman & Raiswell 1981; Coleman 1993; Mozley & Burns 1993). Diagenetic conditions under which the concretions originated thus tend to be site specific and dependent on a range of local environmental controls. The isotope fields for the different mineralogical types of New Zealand concretions suggest that the growth waters ranged from meteoric to marine, and that  $\text{CO}_2$  for carbonate precipitation was derived from a variety of mainly organic sources (Fig. 5B-D).

## SYNTHESIS

The  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  analyses reported in this New Zealand study come from a diversity of Cenozoic carbonate materials originating in a variety of depositional and diagenetic environments at widely different times and places. Given the potentially large number of controls on the  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  composition of carbonate minerals, including precipitation temperature, water chemistry, water-host sediment/rock ratio, mineral-water fractionation factors, biochemical reactions, degree of isotopic equilibrium, and post-formation isotopic exchange (e.g., Longstaffe 1983), it is perhaps surprising that the various New Zealand carbonate categories tend to cluster as much as they do on the  $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$  plots (Fig. 3-5). This clustering suggests that the isotope data preserve the dominant factors of isotope composition and temperature of the primary genetic waters, and that carbonate components have, in the main, not been significantly altered by subsequent isotope re-equilibration or exchange.

The isotope data for the New Zealand carbonate categories, in the form of mean  $\pm$  one standard deviation whisker plots, are summarised in Fig. 6. Several categories are tightly constrained and isotopically distinctive. Others, and particularly the various concretion types, occupy broader fields, but often in specific regions of the  $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$  plot. The kinds of environmental factors controlling the positions of the carbonate categories may be inferred from the

reference isotope diagram (Fig. 1), and have been noted on several of the individual  $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$  plots (Fig. 3-5).

The precipitation of the New Zealand carbonates can be generalised and related to a small number of "end-member" sources (Fig. 7A): cool shallow-marine bottom waters generating nontropical skeletons and carbonate sediments having low positive  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values; connate pore waters associated with sediment burial, compaction, and pressure-dissolution processes that provided burial cements (and veins) with moderately negative  $\delta^{18}\text{O}$  values, related closely to changing burial depth temperatures, and low positive or negative  $\delta^{13}\text{C}$  values inherited mainly from variably pressure-dissolved calcitic skeletons (Nelson et al. 1988c); temperate-latitude fresh waters providing meteoric precipitates (cements, speleothems, and nonmarine skeletons) with moderately negative  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values; and a range of fresh to saline waters (with variable  $\delta^{18}\text{O}$  values) precipitating localised concretionary carbonate sourced from the microbial degradation of sedimentary organic matter, including especially within the shallowest burial zones of sulphate reduction (moderately to highly negative  $\delta^{13}\text{C}$  values) and fermentation (moderately positive  $\delta^{13}\text{C}$  values), and from the oxidation of ascending methane gases (highly to extremely negative  $\delta^{13}\text{C}$  values).

The main sources identified for the New Zealand carbonates are little different from those elsewhere (Fig. 1), although the cool marine field associated with the modern nontropical skeletal carbonates contrasts significantly with the field for equivalent shelf carbonate deposits in tropical settings (Fig. 3A, C, 7A) (Rao & Nelson 1992). However, during the main diagenetic trend involving progressive burial and lithification of New Zealand nontropical carbonates into limestones, sometimes with the superimposed effects of meteoric diagenesis, this isotopic uniqueness is gradually lost (cf. Fig. 1, 4A, B, 7B).

We conclude that the New Zealand stable isotope data are a useful aid in categorising and interpreting the depositional and diagenetic settings and processes affecting carbonate materials, be they skeletons, sediments, cements,

limestones, dolostones, concretions, or veins. Inevitably, however, the isotope data must be integrated with other relevant information about the carbonates, such as elemental analyses, petrography, sedimentology, and field studies, in order to provide the fullest insight into their genesis and significance (e.g., Nelson et al. 1988c, 1994).

#### ACKNOWLEDGMENTS

We acknowledge the major contribution that Chris Hendy (Chemistry, University of Waikato) has made in maintaining for over 15 years the stable isotope mass spectrometer facility at University of Waikato, where the majority of analyses reported in this synthesis were performed. The paper benefitted considerably from review comments suggested to us by Chris Hendy, Peter Hodder (Earth Sciences, University of Waikato), Murray Gregory (Geology, University of Auckland), and Prasada Rao (Geology, University of Tasmania).

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