Discriminating cool-water from warm-water carbonates and their diagenetic environments using element geochemistry: the Oligocene Tikorangi Formation (Taranaki Basin) and the dolomite effect

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Abstract Fields portrayed within bivariate element plots have been used to distinguish between carbonates formed in warm- (tropical) water and cool- (temperate) water depositional settings. Here, element concentrations (Ca, Mg, Sr, Na, Fe, and Mn) have been determined for the carbonate fraction of bulk samples from the late Oligocene Tikorangi Formation, a subsurface, mixed dolomite-calcite, cool-water limestone sequence in Taranaki Basin, New Zealand. While the occurrence of dolomite is rare in New Zealand Cenozoic carbonates, and in cool-water carbonates more generally, the dolomite in the Tikorangi carbonates is shown to have a dramatic effect on the "traditional" positioning of cool-water limestone fields within bivariate element plots. Rare undolomitised, wholly calcitic carbonate samples in the Tikorangi Formation have the following average composition: Mg 2800 ppm; Ca 319 100 ppm; Na 800 ppm; Fe 6300 ppm; Sr 2400 ppm; and Mn 300 ppm. Tikorangi Formation dolomite-rich samples (>15% dolomite) have average values of: Mg 53 400 ppm; Ca 290 400 ppm; Na 4700 ppm; Fe 28 100 ppm; Sr 5400 ppm; and Mn 500 ppm. Element-element plots for dolomite-bearing samples show elevated Mg, Na, and Sr values compared with most other low-Mg calcite New Zealand Cenozoic limestones. The increased trace element contents are directly attributable to the trace element-enriched nature of the burial-derived dolomites, termed here the "dolomite effect". Fe levels in the Tikorangi Formation carbonates far exceed both modern and ancient cool-water and warm-water analogues, while Sr values are also higher than those in modern Tasmanian cool-water carbonates, and approach modern Bahaman warm-water carbonate values. Trace element data used in conjunction with more traditional petrographic data have aided in the diagenetic interpretation of the carbonate-dominated Tikorangi sequence. The geochemical results have been particularly useful for providing more definitive evidence for deep burial dolomitisation of the deposits under the influence of marine-modified pore fluids.

Keywords carbonate geochemistry; trace elements; cool-water limestone; dolomite; Tikorangi Formation; Oligocene; Taranaki Basin; New Zealand; reservoir

INTRODUCTION

Over the past two decades, a variety of facies characteristics have been documented to distinguish between shelf limestones deposited in warm (tropical) sea water from those formed in cool (temperate) water (e.g., Nelson 1988; James 1997) (Table 1). Rao (1996) in particular has advocated that the element geochemistry (Ca, Mg, Sr, Na, Fe, Mn) of limestones may also be used to differentiate these depositional settings, as well as to help elucidate their subsequent diagenetic evolution (e.g., Morse & Mackenzie 1990; Winefield et al. 1996). Here we document the trace element geochemistry of the non-tropical Oligocene Tikorangi Formation carbonates from Taranaki Basin, western North Island of New Zealand, partly to increase our understanding of their diagenesis from that gained from previous petrographic study (Hood et al. 2003b, 2004), but mainly to gauge the influence of their dolomite content on the usefulness of trace elements for discriminating between warm-water and cool-water carbonate facies.

PETROLOGICAL BACKGROUND FOR TIKORANGI FORMATION

The latest Oligocene Tikorangi Formation is a subsurface (c. 3 km depth), fractured carbonate reservoir in Taranaki Basin (King & Thrasher 1996; Hood et al. 2003a,b). Rocks comprise a spectrum of siliciclastic through carbonate dominated facies formed at temperate latitudes in shelf to basin paleoenvironments (Hood et al. 2003c). Compared with other well-studied New Zealand occurrences of mid-Tertiary cool-water calcitic limestones (e.g., Nelson 1978), the Tikorangi carbonates are distinctive because they include small to moderate quantities of diagenetic dolomite (Hood et al. 2004).

Tikorangi Formation rocks were cemented during burial diagenesis by ferroan low-Mg calcite (1–3 mol% $MgCO_3$) having slightly to moderately depleted $\delta^{18}O$ values (–2 to –4.3‰, av. –3.2‰) and $\delta^{13}C$ values (–0.2 to –0.9, av. –0.45‰) (Hood et al. 2003b). Pressure-dissolution during burial to several hundred metres produced tight rock fabrics with essentially zero porosity. Original intermediate to high Mg calcite skeletal fragments (echinoderms, benthic foraminifers, calcareous red algae, some bryozoans) were transformed to more stable low-Mg calcite forms via incongruent dissolution, while rare undissolved aragonitic skeletal fragments (bivalves) were neomorphically transformed to low-Mg calcite (Hood et al. 2003b).

The Tikorangi carbonates include ubiquitous, but generally small quantities (typically <15%, rarely up to 50%) of very fine (20–90 μm) euhedral rhombs of ferroan dolomite. The rhombs have dull luminescent Fe-rich cores, and often concentrically zoned bright/dull outers (Fig. 1). The dolomites are non-stoichiometric Ca-rich (av. 58 mol% $CaCO_3$) and Fe-rich (av. 13 mol% $FeCO_3$) varieties suggested to have formed

Table 1 Some contrasting environmental, compositional, and diagenetic features of the Tikorangi Formation in comparison to cool-water (non-tropical) and tropical shelf carbonates (modified after Hood & Nelson 1996).

| Property	Tikorangi Formation	Cool-water (non-tropical) shelf carbonates	Warm-water (tropical) shelf carbonates
Setting	Unrimmed open shelf, foredeep basin (slope/bathyal depths), outer basin floor	Unrimmed open shelves and ramps	Shallow rimmed shelves, open shelves, ramps, reefs
Energy	High (shelfal; mass flows into foredeep) to low energy (foredeep and basinal pelagic settling)	High energy	High to low energy
Hermatypic reefs	Absent	Absence of hermatypic reefs (polewards of 30°N to 30°S)	Common hermatypic coral reefs (from 30°N to 30°S)
Skeletal assemblages	Heterozoan (foramol) skeletal types: complex mix of echinoderms, foraminifera, bivalve molluscs, bryozoans, barnacles, calcareous red algae	Heterozoan (foramol) skeletal types: bryozoans (bryomol), echinoderms (echinofor), bivalve molluscs (bimol), foraminifera (nannofor)	Photozoan (chlorozoan) skeletal types: corals, calcareous green algae, molluscs, benthic foraminifera
Sediment texture	Gravel (shelf) to sand/mud (foredeep) to mud (basinal)	Gravel and sand textures dominate	Sand and mud textures dominate
Water temperature	Cool water	Cool water (10–18°C bottom water)	Warm water (>22°C bottom water)
Carbonate saturation	Saturated/undersaturated	Saturated/undersaturated	Saturated/supersaturated
Non-skeletal grains	Absence of non-skeletal grains	Absence of non-skeletal grains	Common non-skeletal grains (ooids, aggregates)
Cementation	Early to late burial ferroan calcite cements, replacement dolomite rhombs	Minor early cementation; late burial cements dominate	Extensive early cementation by marine and meteoric cements
Carbonate mud	Minor to common (physical maceration, erosion resulting from mass redeposition)	Minor carbonate mud (bioerosion)	Abundant carbonate mud (micritisation, precipitation, bioerosion)
Mineralogy	Low-Mg calcite, dolomite	Low and intermediate Mg calcite dominate	Aragonite and high-Mg calcite dominate
Diagenesis	Destructive early diagenesis (dissolution, maceration), late burial cementation, partial replacement dolomitisation	Destructive early diagenesis (dissolution, maceration), late burial cementation	Constructive diagenesis (early cementation)
Sedimentation rates	Low to high (high in mass redeposited units)	Typically low accumulation rates	Typically high accumulation rates
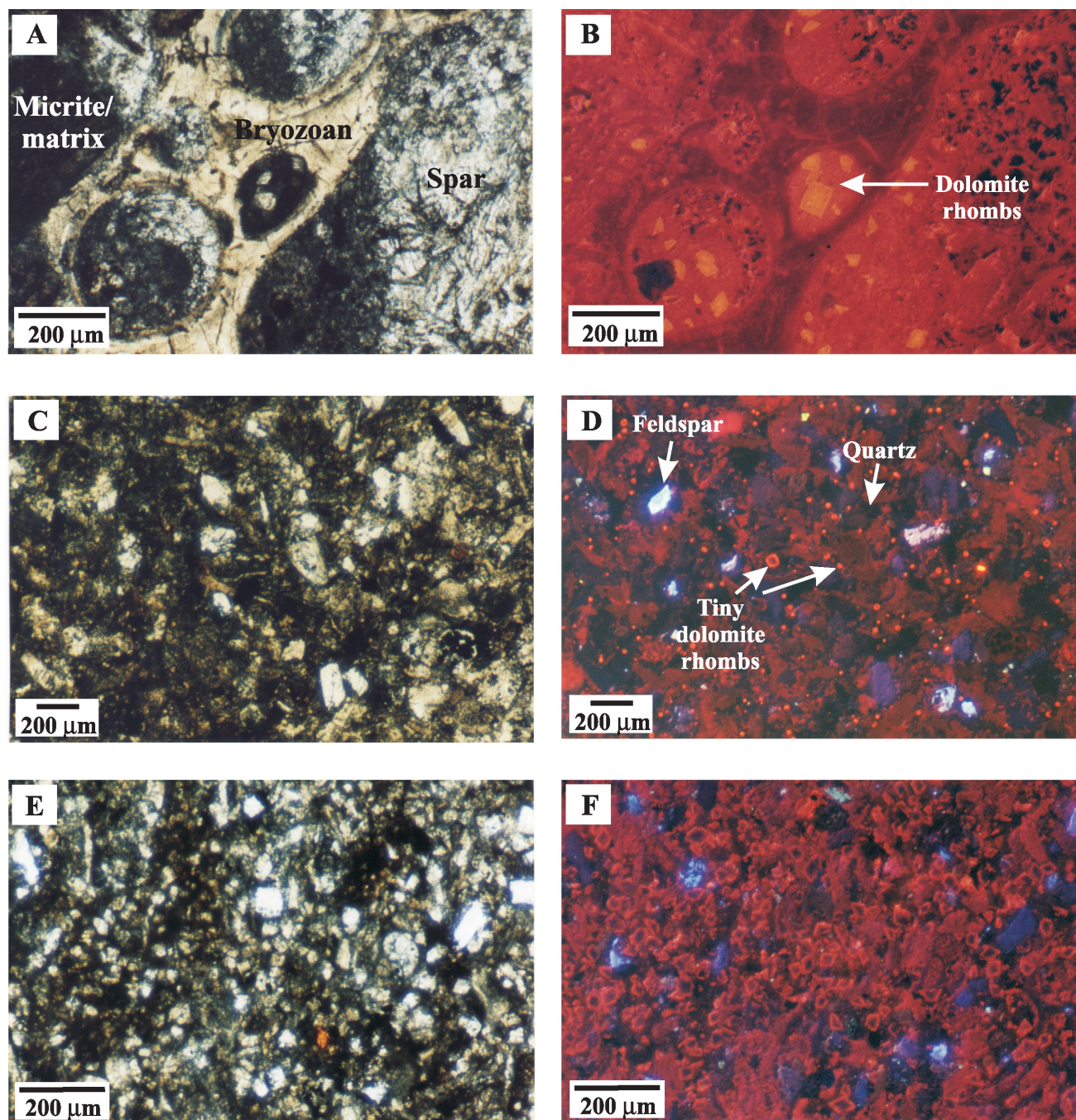
Fig. 1 Photomicrograph pairs under plane polarised light (left) and cathodoluminescence light (right) of selected thin sections of the Tikorangi Formation. **A**, **B**, Bryozoan-rich shelfal limestone with dolomite rhombs mimicking original micrite/microsparite fabrics and exhibiting in (B) bright yellow/orange cores and outer zones (W00503). **C**, **D**, Tiny scattered euhedral rhombs (C) within siliciclastic/matrix/micrite-rich areas exhibiting (D) dull luminescent cores enveloped by moderately bright outers (W00562). **E**, **F**, Dolomitised limestone showing abundant rhombs with non-luminescent cores and orange-red luminescent outers (W00709).

by selective replacement of micritic and argillaceous matrix materials during burial (Hood et al. 2003b).

The wider geological context of the latest Oligocene (New Zealand Waitakian Stage) Tikorangi Formation in Taranaki Basin is well described by King & Thrasher (1996), while the stratigraphy, detailed petrography, and fracture and vein mineralisation history of the Tikorangi deposits based upon study of core material from wells in the Waihapa-Ngaere and Maui-1 oilfields are detailed by Hood et al. (2003a,b,c).

TRACE ELEMENTS AS DISCRIMINATORS OF CARBONATE ENVIRONMENTS

Skeletal differences between shelf carbonates forming in cool water beyond 30°N and °S and those forming in warm waters of the tropics have been well documented (e.g., Lees & Buller 1972; Nelson 1988; Hayton et al. 1995; James 1997) (Table 1). These skeletal differences typically manifest themselves in contrasting primary carbonate mineralogies
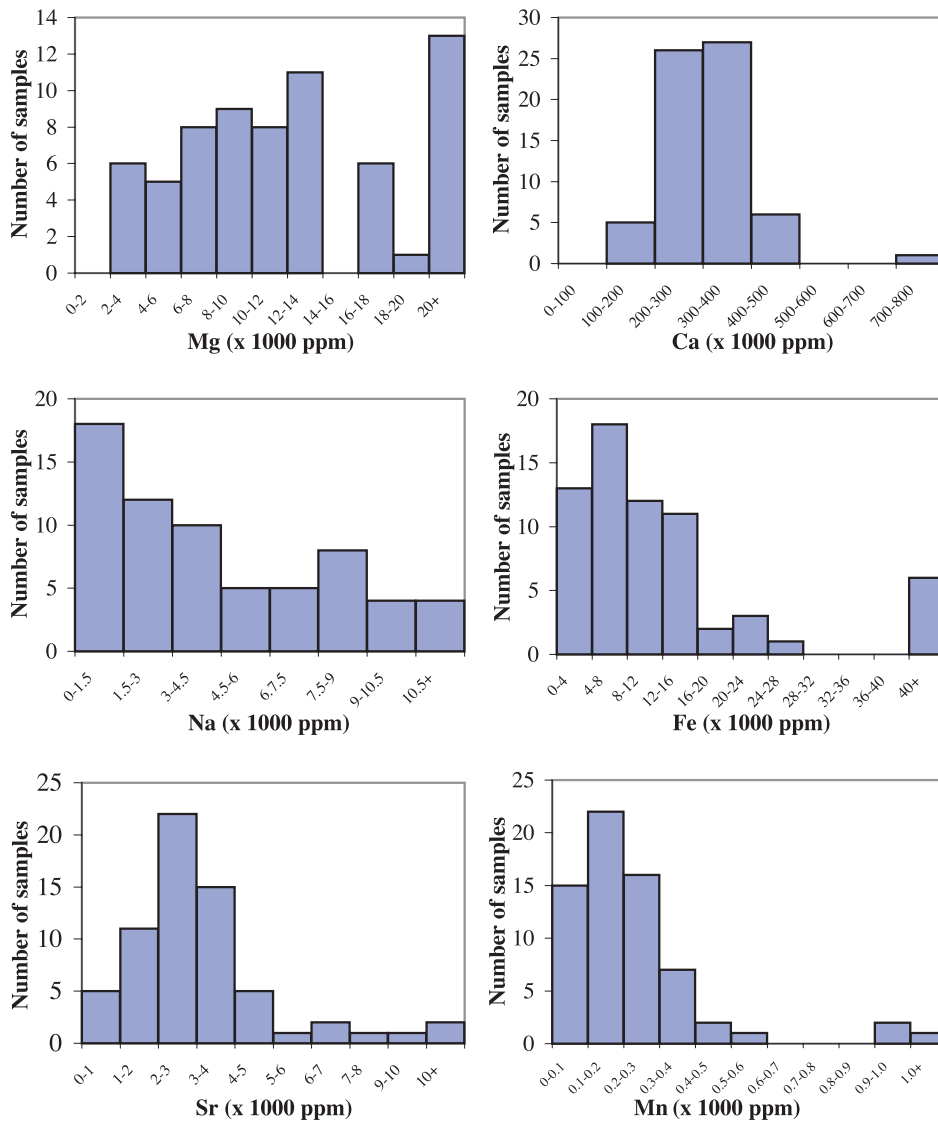
Fig. 2 Histograms displaying the range of trace element concentrations in the carbonate fraction of representative Tikorangi Formation samples.

(Rao 1996). High-Mg calcite (HMC; >12 mol% MgCO$_3$) and aragonite are the primary mineralogies in the warm-water (or tropical) skeletal and inorganically precipitated carbonates, while intermediate-Mg calcite (IMC; 4–12 mol% MgCO$_3$) and low-Mg calcite (LMC; <4 mol% MgCO$_3$) mineralogies more typically dominate cooler water (temperate) carbonates. Inevitably, these mineralogical contrasts manifest themselves in trace element differences between the warm-water and cool-water carbonates, and thus potentially provide a geochemical approach for distinguishing between these settings in ancient limestones.

Studies of cool-water carbonates are far outnumbered by studies of their warm-water counterparts, and consequently our present understanding of cool-water carbonates is still developing. While cool-water carbonates are beginning to receive greater recognition worldwide (Nelson 1988; James 1997), there is a long way to go to establish their spectrum of origins, including the vexed question of superimposed dolomitisation at temperate latitudes (James et al. 1993; Nicolaides 1997; Kyser et al. 2002). Due largely to the work of Rao (1981, 1986, 1990a,b, 1991, 1996), but also others (e.g., Veizer 1983; Morrison & Brand 1986; Brand & Morrison 1987; Morse & Mackenzie 1990; Winefield

et al. 1996), a geochemical approach has evolved to help differentiate calcitic cool-water carbonates from their warm-water counterparts based on trace element composition.

Chemical discrimination between cool-water and warm-water carbonates has been suggested on the basis of characteristic fields within bivariate element plots (Rao 1981, 1986, 1990a,b, 1991; Winefield et al. 1996). Rao (1991) noted that the concentrations of Na, Sr, and Mn differed between subtropical, cool-temperate, and subpolar Tasmanian limestones and that element-element plots could be used to discriminate between them. Winefield et al. (1996) found that for New Zealand Cenozoic cool-water limestones, the Mg and Sr contents are mainly lower than occur in many warm-water carbonates, while Na, Fe, and Mn are relatively higher. In particular, for element-element plots involving Na and Sr, they noted that the New Zealand limestones plotted well outside the field for warm-water carbonates and within a cool-water field having Sr values of 100–1000 ppm and Na values of 500–5000 ppm.

Differences in the trace element content of cool-water and warm-water carbonates may not only reflect their paleolatitudinal depositional setting, but also their subsequent diagenetic history. Diagenetic alteration and

cement formation generally lower the concentrations of Sr, Mg, and Na, but increase the Fe and Mn contents (Al-Aasm & Veizer 1986; Winefield et al. 1996; Al-Aasm & Packard 2000). Combinations of element-element plots and summary element matrices have been used to help infer diagenetic environments (e.g., Brand & Veizer 1980; Al Aasm & Veizer 1986; Brand & Morrison 1987; Rao 1990a, 1991), including for cool-water limestones in New Zealand (Winefield et al. 1996; Nelson et al. 2003).

METHODOLOGY

Following standard and cathodoluminescent (CL) thin-section petrography, representative powders of 65 Tikorangi Formation samples (see Hood et al. 2003d) were prepared using a ringmill with a tungsten-carbide head to prevent any iron contamination. Samples were then subject to acid digestion following the procedures of Robinson (1980) and Winefield (1995). Following appropriate dilution, the sample solutions were analysed for Ca, Mg, Na, Fe, Sr, and Mn using a GBC909AA double beam atomic absorption spectrophotometer. Winefield (1995) provides more specific analytical details. Errors are ±1% for Ca and Mg, and ±5 ppm for Sr, Na, Mn, and Fe. The predominantly fine-grained nature of the rocks negated the ability to extract microspar cements or individual dolomite rhombohedra from samples, a problem noted for other partially dolomitised fine limestones (Török 2000). The extremely thin (<5 μm) CL zonations in the Tikorangi dolomites negated the possibility of obtaining meaningful microprobe data for specific crystal zones, prompting the bulk geochemical approach adopted here.

X-ray diffraction (XRD) of unoriented powder mounts was used to determine the amount of Mg substitution in calcite and dolomite lattices (Tucker 1988), and of Fe in the dolomite lattice. Mounts were slow scanned at 0.25°2θ/min, with the addition of an analytical grade NaCl (halite) spike for accurate determination of peak positions. Calibration curves for estimating dolomite percent in the presence of calcite were taken from Al-Hashimi & Hemingway (1974) and Lumsden (1979). Displacement of the d_{104} peak of calcite with increasing mol% $MgCO_3$ to dolomite is based on the calibration curve of Goldsmith et al. (1961). Displacement of the d_{104} spacing of dolomite relative to $FeCO_3$ wt% uses the calibration curve of Al-Hashimi & Hemingway (1974).

All trace element and mineralogical data are contained in Hood et al. (2003d), and are available on request.
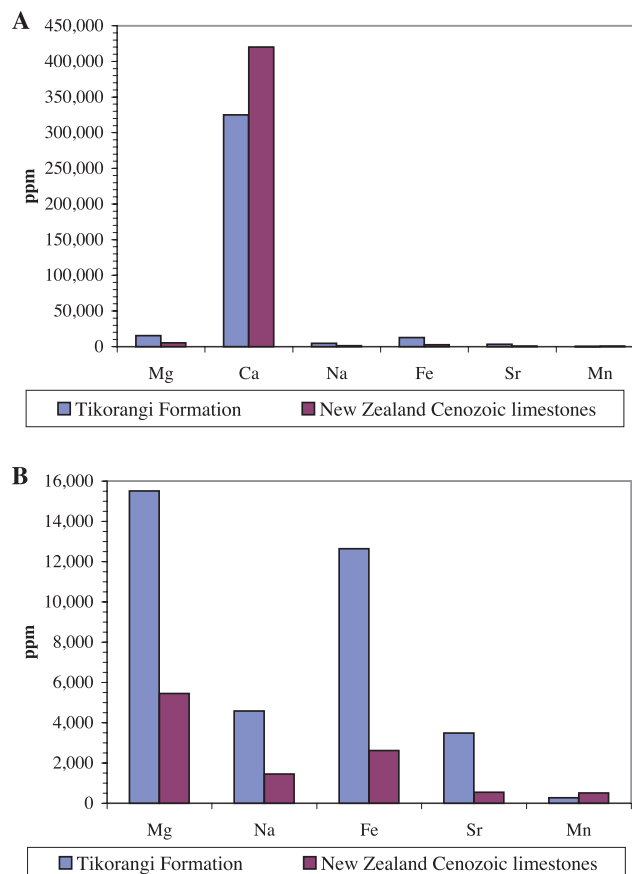

Fig. 3A, B Comparison of average trace element concentrations in the Tikorangi Formation with those for New Zealand Cenozoic limestones (Table 2) showing (A) the Tikorangi Formation is relatively depleted in Ca, and (B), considerably enriched in Mg and Fe, with lesser enrichment in Na and Sr.

ELEMENT GEOCHEMISTRY

Raw trace element data for the Tikorangi Formation samples are summarised in the histogram plots in Fig. 2. Comparison of the average trace element values for the Tikorangi Formation as a whole with those for the New Zealand Cenozoic cool-water limestone database of Winefield et al. (1996) shows that the Tikorangi carbonates exhibit moderately elevated Mg and Na values, and substantially elevated Fe and Sr values (Fig. 3; Table 2), despite both being of cool-water (temperate-

Table 2 Summary trace element data for Tikorangi Formation samples.

|	No. of samples	Mg	Ca	Na	Fe	Sr	Mn
Rock type							
Mudstone	2	51 108	196 011	10 987	35 425	3512	655
Wackestone	23	15 802	320 454	6676	16 901	4318	374
Packstone	15	12 157	292 216	4037	14 434	3491	209
Packstone/grainstone	14	18 856	305 963	2969	8169	2560	207
Grainstone	11	9446	380 267	1967	5751	2218	164
Tikorangi Formation average	65	15 515	325 040	4589	12 647	3483	273
Carbonate type							
Calcite (0% dolomite)	8	2769	319 139	836	6313	2432	343
Mixed calcite/dolomite (5–15% dolomite)	24	13 799	295 620	4996	10 796	3651	197
Dolomite-rich (>15% in sample)	8	53 431	290 374	4749	28 118	5419	503
New Zealand limestone average	548	5508	419 574	1392	2428	555	577
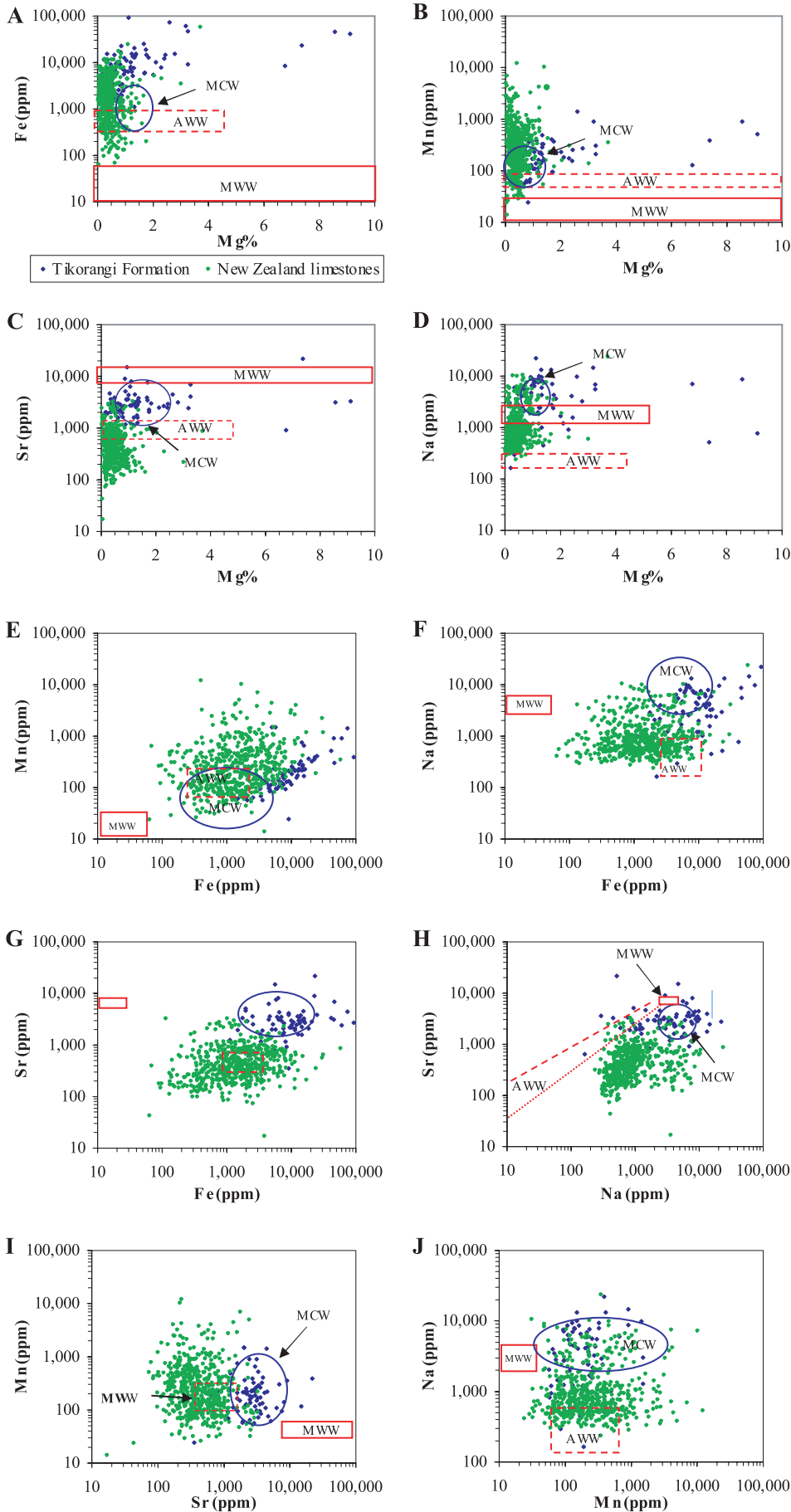
Fig. 4A–J   A selection of element-element plots comparing typical fields for modern warm-water (MWW), modern Tasmanian cool-water (MCW), and Ordovician Tasmanian subtropical shelf carbonates (AWW) with data points for bulk samples of the Tikorangi Formation (blue points) and New Zealand Cenozoic cool-water limestones (green points). Solid red box = modern warm-water Bahaman-type (aragonite + HMC) shelf carbonates; red dashed box = ancient (Ordovician) Tasmanian warm-water shelf limestones; blue ellipse = modern Tasmanian (IMC + LMC) cool-water shelf carbonates.

Fig. 5 Correlation trends for each of mudstone through grainstone rock types in the Tikorangi Formation based on the average trace element value for each rock type (Table 2). With the exception of Ca, there is a significant decreasing trend in element concentration from mudstone to grainstone. Mst., mudstone; Wst., wackestone; Pst., packstone; Pgst., packstone/grainstone; Gst., grainstone.
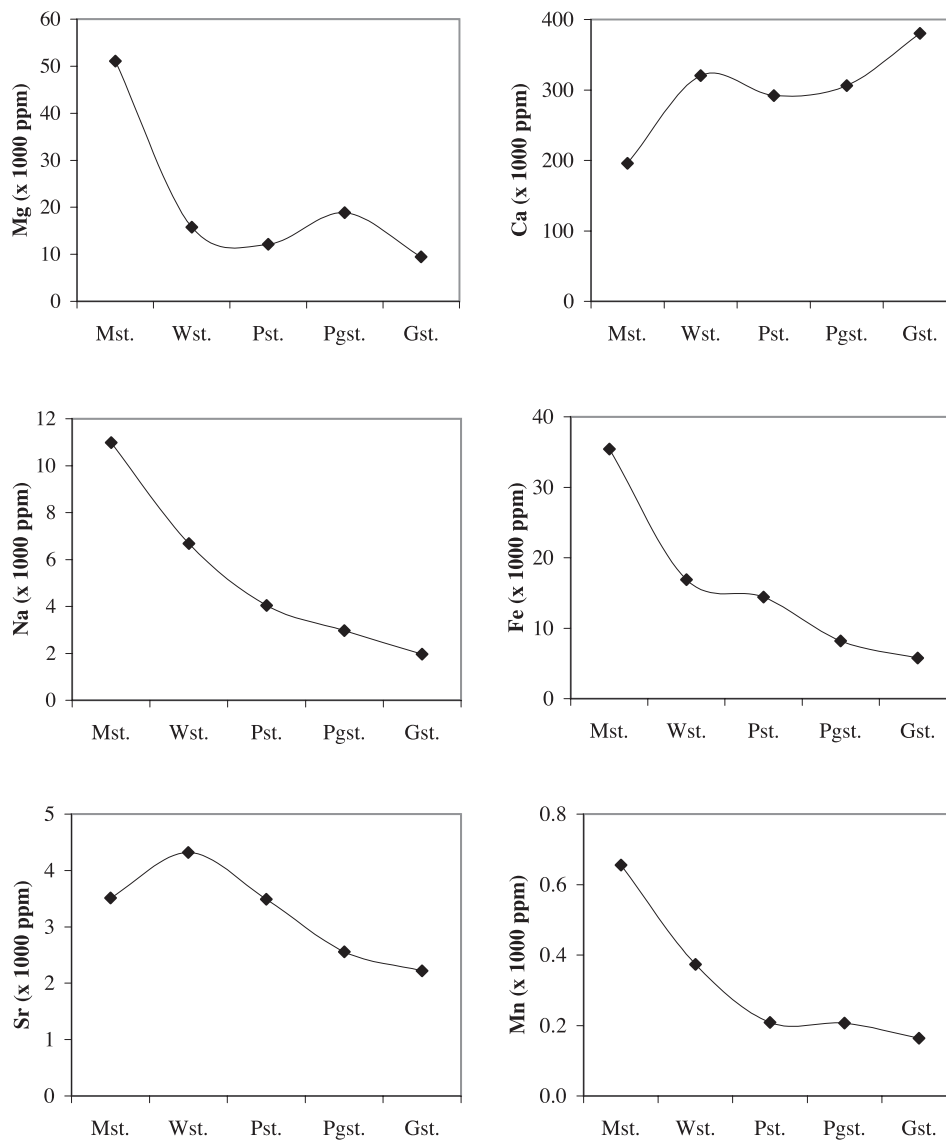
latitude) origin (Hood et. al. 2003a,b,c). Conversely, Ca and Mn values are reduced in the Tikorangi Formation in relation to the New Zealand average.

Comparative plots

Bivariate trace element plots have been constructed (Fig. 4A–J) to graphically compare the entire Tikorangi Formation trace element database with the entire available New Zealand limestone database, as well as previously suggested fields (Rao 1996) for both modern and ancient warm-water and cool-water carbonates. Display of the entire data as opposed to calculated averages affords a better appreciation of the overall differences in the element distributions. It is evident that the Tikorangi Formation samples commonly have elevated Mg, Na, Fe, and Sr trace element concentrations compared to the New Zealand Cenozoic limestones, and are nearer to the fields for modern Tasmanian (IMC + LMC) cool-water carbonates and modern warm-water Bahaman (aragonite + HMC) carbonates.

Trace elements versus rock composition

Comparison of average trace element data for the five main petrographic facies previously identified in the Tikorangi Formation by Hood et al. (2003b) (Table 2) is shown in Fig. 5. This indicates a generally declining Mg, Na, Fe, Sr, and Mn content, but increasing Ca content, with passage from matrix/micrite-rich mudstones to sparry grainstones. This facies control on trace element composition has been further investigated by determining the correlation trends between trace element values and various petrographic properties from the same samples (data in Hood et al. 2003d), as summarised in Fig. 6. Correlations between total carbonate percent and each of Mg, Na, Fe, Sr, and Mn are all negative. However, positive correlations between dolomite percent and these same elements, suggest a likely strong influence by the burial-derived diagenetic dolomite in the Tikorangi Formation (Hood et al. 2004). Similar correlations between micrite/matrix and siliciclastic percent and Mg, Na, Fe, Sr, and Mn result from dolomite being more prevalent in the relatively micrite/clay-rich and carbonate-poor facies (Fig. 1).

	Mg	Ca	Na	Fe	Sr	Mn
Total carbonate %	−	+	−	−	−	−
Dolomite %	+	−	+	+	+	+
Spar cement %	−	+	−	−	−	−
Micrite/matrix/clay %	+	−	+	+	+	+
Skeletal %	−	+	−	−	−	−
Siliciclastic %	+	−	+	+	−	

Fig. 6 Schematic summary of correlation trends in sample composition versus individual trace elements. Positive and negative values denote the sign of the slope of linear regression lines drawn through the composition versus trace element plots. For example, as total carbonate percent increases, Mg content decreases. Blank denotes no discernible trend.
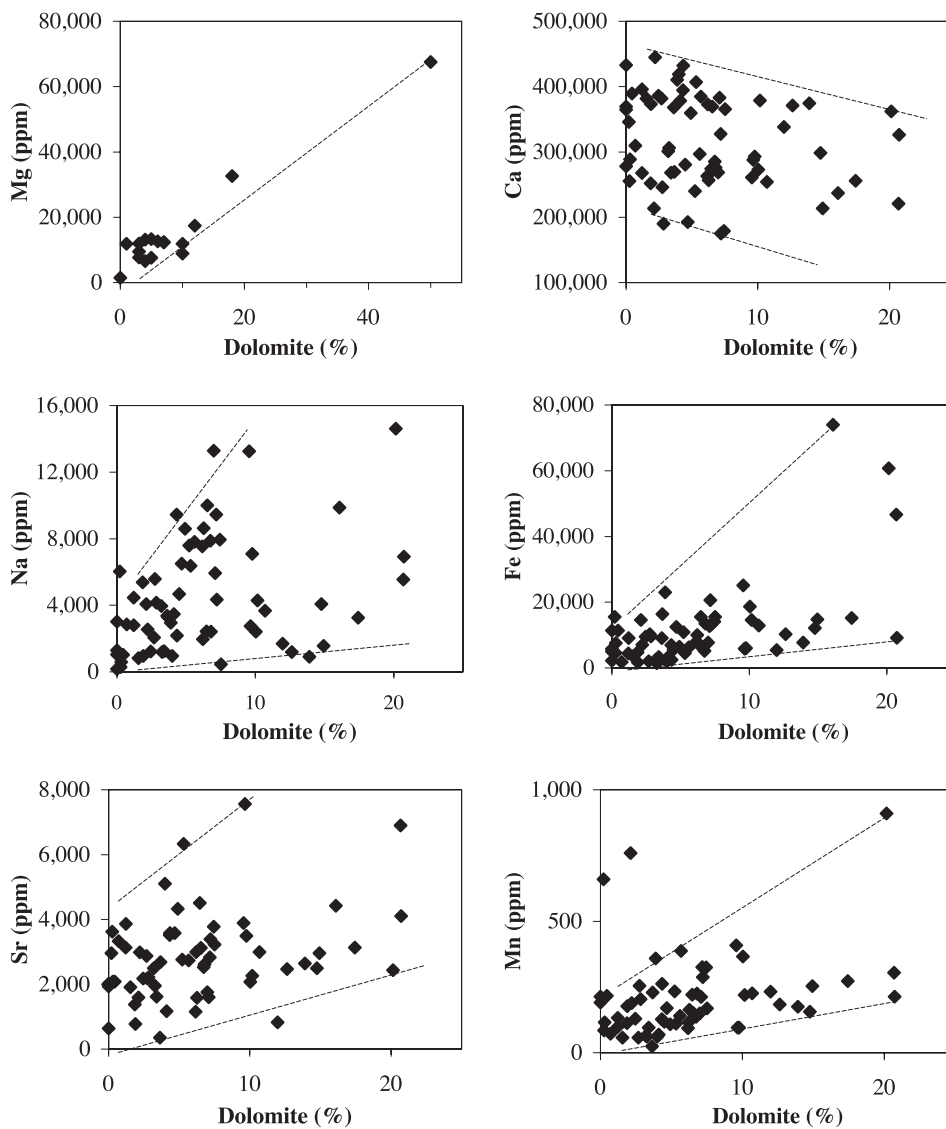

Fig. 7 Correlation fields of dolomite percent and average trace element values for the Tikorangi Formation rocks showing a general trend of increasing trace element concentration with increasing dolomite percent except for Ca.

Trace elements versus dolomite content

The dolomite content of Tikorangi Formation samples most commonly ranges from 5 to 10 wt%, and occasionally reaches as high as 20–50 wt%. Bivariate plots show the influence of dolomite content on trace element concentrations (Fig. 7). A negative correlation exists with Ca because of Mg substitution for Ca in the dolomite lattice. Na, Fe, and Mn, together with Mg, typically increase in concentration with increasing dolomite content. The Fe trend reflects the fact that the dolomite is iron rich. Mn, a major control in activating cathodoluminescence within the Tikorangi Formation dolomite rhombs (Fig. 1) (Hood et al. 2004), is present in higher quantities in the dolomite-rich rocks compared to the non-dolomite-bearing non-luminescent calcite cements.

Element geochemistry of carbonate mineral phases

Samples were segregated into three groups based on dolomite contents of 0, 5–15, and >15% to best ascertain the "dolomite effect" on trace element geochemistry within the Tikorangi Formation (Table 2). The element histograms in Fig. 8 indicate that variably elevated Mg, Na, and Fe contents are associated with the dolomitic groups, while the converse applies for Ca.

GEOCHEMICAL DISCRIMINATION OF DIAGENETIC ENVIRONMENTS

Diagenetic environments defined

Shallow burial diagenesis is considered here to involve pore fluids having "near normal" marine salinity (c. 35 ppt) and may involve sub-seafloor depths down to several tens of metres or more. This study uses the term deep burial diagenetic realm when burial depths were sufficient for the onset of chemical compaction as a result of increasing overburden pressure. For carbonate deposits this typically requires a few 100 m of burial (e.g., Hood & Nelson 1996; Nicolaides & Wallace 1997; Borre & Fabricius 1998). By this stage, pore fluid chemistry is usually influenced by increased temperatures and pressures, and possibly salinities, in a strongly reducing environment, involving marine-modified or connate fluids. Meteoric diagenesis is defined here as including meteorically derived fluids introduced into pore spaces in the subsurface, and does not necessarily have to have involved subaerial exposure. The postulated introduction of meteoric fluids into the deeply buried Tikorangi Formation would have necessitated a direct link into the deep subsurface from the upper levels experiencing meteoric circulation via extensive fracture networks within the formation (Hood et al. 2003b).

Summary element matrices

Element-element plots may be used to help infer the diagenetic environments that have influenced carbonate deposits (Veizer 1983; Morrison & Brand 1986; Brand & Morrison 1987; Morse & Mackenzie 1990; Winefield et al. 1996). The slope of linear regression lines drawn through element-element plots are delineated by positive and negative symbols forming summary element matrices (Fig. 9A). Schematic pie diagrams show the relative influence of each diagenetic regime for an unknown matrix. Summary element matrices were developed by Winefield et al. (1996) for idealised meteoric, marine, and burial diagenetic trends (in this case 100%).
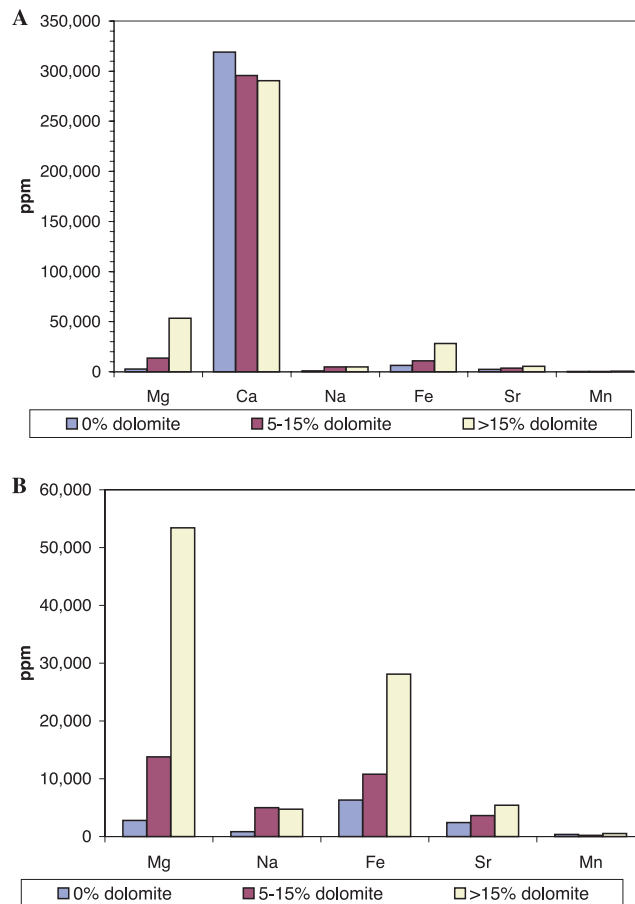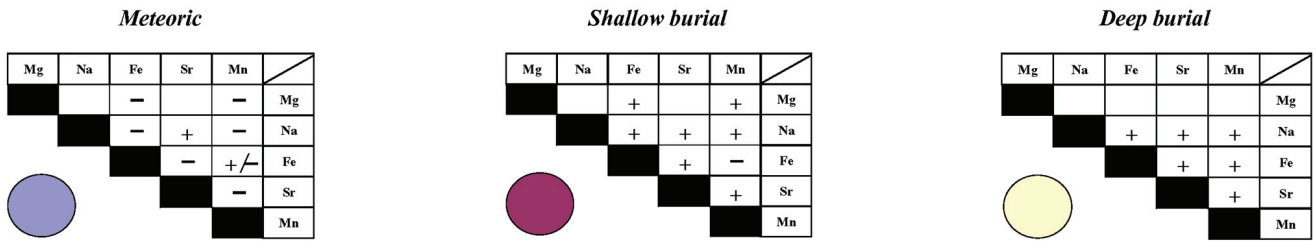

Fig. 8 **A**, Comparison of trace element concentrations in wholly calcitic, mixed calcitic/dolomitic (5–15% dolomite), and dolomitic-rich (>15% dolomite) limestone samples within the Tikorangi Formation. Note reduced Ca values in dolomitic samples in relation to calcitic ones. **B**, Trace element enrichment of Mg, Na, and Fe occurs in dolomitic samples in relation to calcitic ones, while Sr and Mn show similar levels across the groups.

The use of the term marine diagenesis by Winefield et al. (1996) was probably inappropriate because strictly it involves only alterations and cements formed in sea water at or very close to the sediment-water interface (Nelson & James 2000), and not a few to many metres below it. The suggestion of commonly occurring marine diagenesis in New Zealand Cenozoic carbonates by Winefield et al. (1996) is misleading because these limestones only rarely contain marine cements (Hood & Nelson 1996; Nelson & James 2000), and they are certainly absent from the Tikorangi Formation. It is suggested here that the bulk of the marine-influenced diagenesis in the Winefield et al. (1996) scheme formed in the shallow burial realm (Hood & Nelson 1996). Consequently, the concept of marine diagenetic trends inferred from element-element plots is here taken to reflect predominantly shallow burial diagenetic trends. Idealised summary element matrices are shown for meteoric (either within the subaerial or burial setting), shallow burial, and deep burial diagenetic realms in Fig. 9B. The extent of agreement of these "standard" matrices with individual matrices for the Tikorangi Formation rock types has been used to infer their diagenetic evolution, following the approach of Winefield et al. (1996).

A, Standard element matrices and pie diagrams

Meteoric

Mg	Na	Fe	Sr	Mn	
		−		−	Mg
		−	+	−	Na
			−	+/−	Fe
				−	Sr
					Mn

Shallow burial

Mg	Na	Fe	Sr	Mn	
		+		+	Mg
		+	+	+	Na
			+	−	Fe
				+	Sr
					Mn

Deep burial

Mg	Na	Fe	Sr	Mn	
					Mg
		+	+	+	Na
			+	+	Fe
				+	Sr
					Mn

B, Tikorangi formation element matrices

All Tikorangi rocks

Mg	Na	Fe	Sr	Mn	
	+	+	+	+	Mg
		+	−	+	Na
			+	+	Fe
				−	Sr
					Mn

0% dolomite

Mg	Na	Fe	Sr	Mn	
	+	+	−	+	Mg
		−	+	+	Na
			−	+	Fe
				−	Sr
					Mn

5-15% dolomite

Mg	Na	Fe	Sr	Mn	
	−	+	−	+	Mg
		+	−	+	Na
			−	+	Fe
				−	Sr
					Mn

>15% dolomite

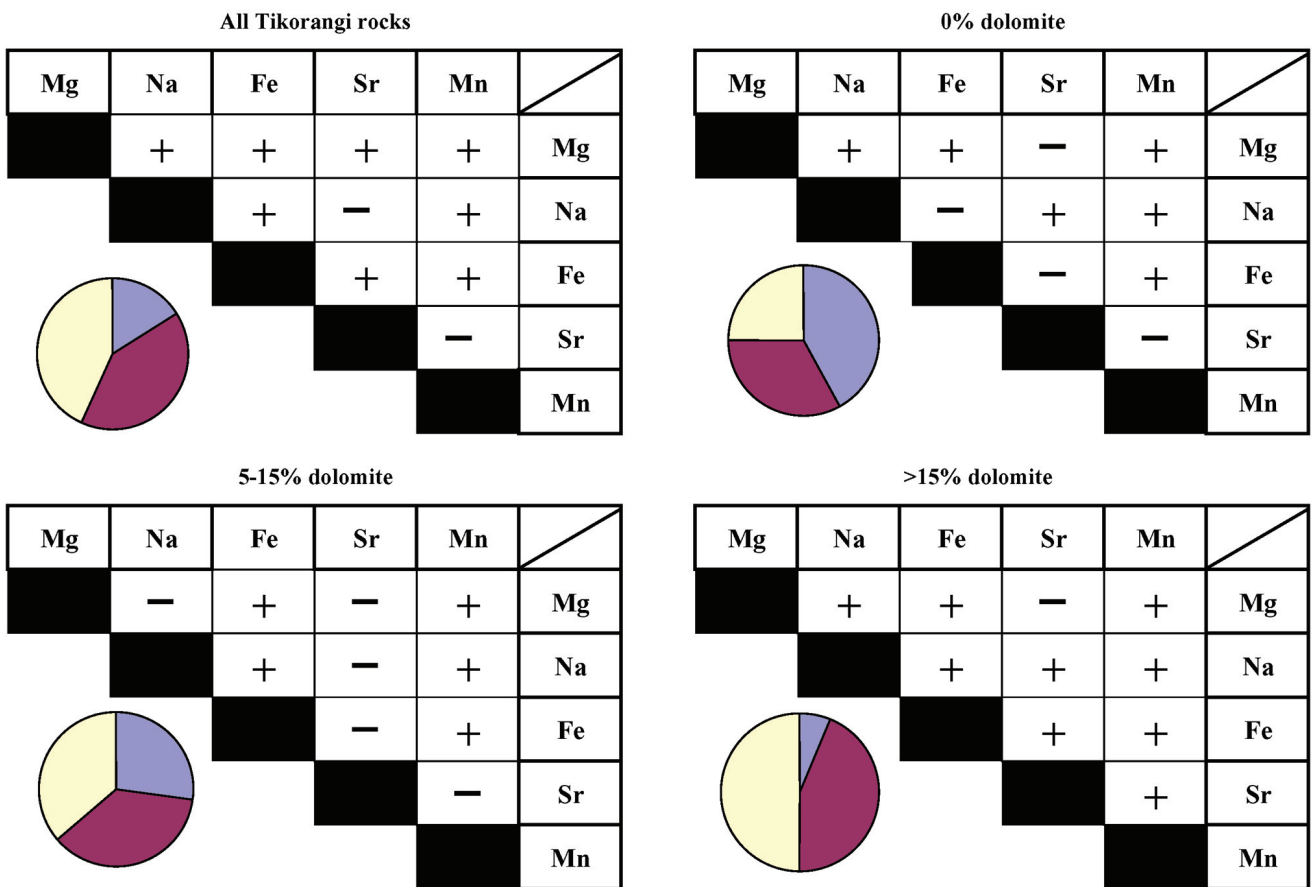| Mg	Na	Fe	Sr	Mn	
	+	+	−	+	Mg
		+	+	+	Na
			+	+	Fe
				+	Sr
					Mn

Fig. 9 **A**, Summary element matrices for idealised meteoric, shallow burial, and deep burial diagenetic trends. Positive and negative symbols delineate the sign of the slope of linear regression lines drawn through element-element plots. Schematic pie diagrams show the relative influence of each diagenetic regime for an unknown matrix (in this case 100%). **B**, Summary element matrices and pie diagrams for all samples of Tikorangi Formation, and those containing 0, 5–15, and >15% dolomite showing increased burial influence in the more dolomitic rich rocks.

Summary element matrices for samples containing 0, 5–15, and >15% dolomite have been derived for the Tikorangi Formation (Fig. 9A) to assess the effect that the presence of dolomite may have on each diagenetic regime (Hood 2000). On this basis, geochemical diagenetic signatures obtained across the range of non-dolomitic to dolomite-rich samples in the Tikorangi carbonates show that deep burial influences dominate in the dolomite-rich samples, but that this influence diminishes in the fully calcitic rocks and in the Tikorangi rocks treated as a whole (Fig. 9B). The element matrices imply that diagenesis in the Tikorangi Formation has experienced a persistent meteoric influence, especially so within the wholly calcitic rock types, but reducing to almost zero with dolomite content.

DISCUSSION

The trace element geochemistry of the Tikorangi Formation rocks has been shown using element-element plots to have many affinities with modern Tasmanian cool-water LMC and IMC carbonate sediments (Fig. 4, 10), involving elevated Mg,

Fig. 10 Schematic summary of relative abundances of trace elements in the Tikorangi Formation and comparison with other cool-water and tropical warm-water carbonates. The radius of the circles is roughly proportional to the average concentration of each element in the respective samples. Adapted from Winefield et al. (1996).

		Mg	Na	Fe	Sr	Mn
Temperate cool-water carbonates	*Tikorangi Formation (Oligocene)*	●	●	●	●	○
	New Zealand (Cenozoic)	●	○	●	○	○
	Tasmanian (Modern)	●	○	○	●	○
Tropical warm-water carbonates	*Tasmanian (Ordovician)*	●	∘	●	●	∘
	Bahaman (Modern)	●	●	∘	●	∘

Na, and Sr values in relation to ancient LMC New Zealand limestones. These elevated element data for Mg, Na, and Sr are therefore inconsistent with those derived from wholly calcitic cool-water limestones. Enriched trace element values are directly attributable to the presence of burial-derived dolomite in the Tikorangi Formation, which contrasts with the anticipated lowering of the element concentrations with progressive carbonate diagenesis in calcitic limestones. Indeed, the elevated Mg concentrations "falsely" overlap with modern and ancient warm-water carbonates. The anomalies are due to the presence of dolomite—"the dolomite effect"—in the Tikorangi Formation. Fe levels in the Tikorangi carbonates far exceed both modern and ancient cool-water and warm-water analogues (Fig. 4, 10), particularly so in the dolomite-rich samples (Table 2). The source of this Fe enrichment was probably from compaction in interbedded siliciclastic shale-like sequences (Hood et al. 2003a). Elevated Mn levels in the Tikorangi Formation in relation to the New Zealand database are similarly attributable to dolomite formation at considerable depths and elevated temperatures (Hood 2000). Sr values are enriched in dolomite-bearing facies and are slightly higher than average values for bulk Tasmanian cool-water modern carbonates, approaching values in modern Bahaman carbonates (Fig. 4, 10).

Given the modest proportion of tiny dolomite crystals with typically intricate CL zoning, the bulk geochemical approach can be defended as an evolving technique with the ability to provide perhaps more meaningful data than could have been derived from attempting to microprobe exceedingly thin specific crystal zones. Trace element data used in conjunction with more traditional petrographic data have aided in the diagenetic interpretation of the carbonate-dominated Tikorangi units. Results have been particularly useful for providing more definitive evidence for burial dolomitisation of the deposits and the general nature of associated pore fluids. The summary element matrices (Fig. 9B) suggest that burial influences dominate the diagenetic evolution of dolomite-rich samples while a meteoric influence dominates in the wholly calcitic rocks. Post-lithification fracturing is intensive in the Tikorangi rocks, so that the introduction of pore fluids including a meteoric component is tenable. This may imply dissolution and reprecipitation of small amounts of calcite which have taken on a meteoric diagenetic signature

reflected in trace element summary plots. In diagenetic studies of sandstones within Taranaki Basin, late (burial) calcite is thought to have formed in the underlying Eocene Kapuni Group from meteoric-derived fluids (Smale et al. 1999). In the Tikorangi, this may have occurred by slow diffusion of meteoric-tainted fluids, with dissolution and recrystallisation occurring on a micro-scale with no intervening void, after dolomitisation and tectonic fracturing events.

CONCLUSIONS

1. This study has contributed to the limited trace element database for carbonates generally, and for cool-water carbonates in particular, at the same time providing bulk trace element concentrations for a mixed dolomite-calcite cool-water sequence, the Oligocene Tikorangi Formation. The occurrence of dolomite is rarely reported in New Zealand Cenozoic carbonates, or from cool-water carbonates in general.
2. The "dolomite effect" in the Tikorangi samples is shown here to have had a dramatic influence on the bulk rock trace element geochemistry in comparison with most other cool-water calcitic carbonate occurrences.
3. Consequently, where dolomite is present, caution is needed if trace element data are to be used to help distinguish between ancient carbonates formed in cool-water versus warm-water shelf settings.
4. In the Tikorangi Formation, the trace element geochemistry supports a marine-modified, largely deep-burial origin for the dolomite.
5. Variables in the control of trace element sources within burial-derived dolomites, such as association with siliciclastics as key trace element providers, the openness of the diagenetic system, subsurface temperatures, pressures, and residency time, are all key factors worthy of future study.

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