LIMESTONE

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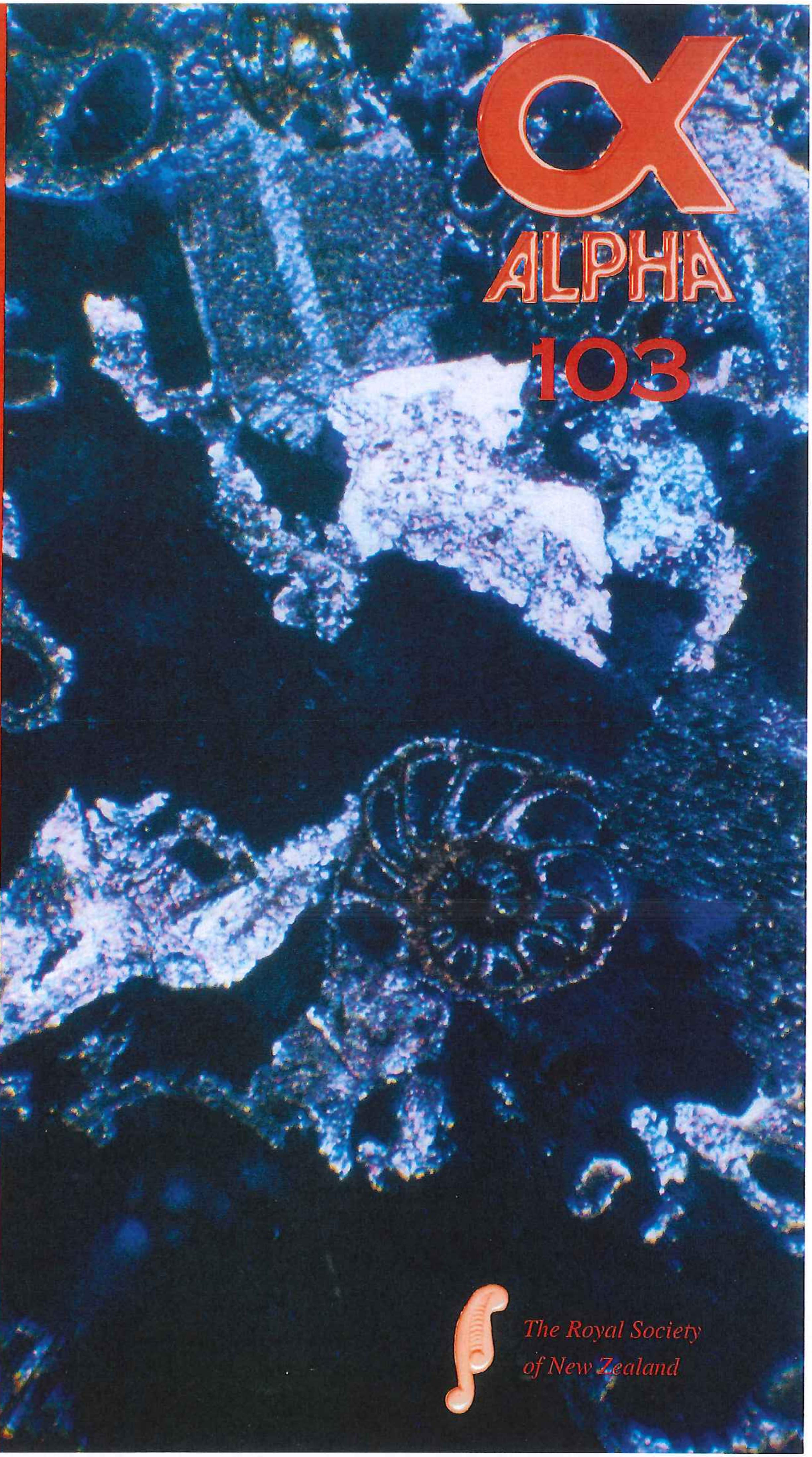


The Royal Society of New Zealand

LIMESTONE

Limestone is a sedimentary rock made up of more than 50% calcium carbonate ($CaCO_3$) minerals. It is distinct from other rocks because it is made up of the shell remains of once-living marine life. The two main forms of $CaCO_3$ are calcite and aragonite. Some shells consist of aragonite, others are calcite, and a few comprise both minerals. However, aragonite is unstable and over geological time will convert to calcite.

Limestone is a sedimentary rock. For geologists, limestone is a window into past climate, geography, and life forms. For farmers, it is the substance that can neutralise acidic soils. For the adventurous, limestone country is a caver's heaven, whether abseiling down deep, dark sink-holes or squeezing through narrow gaps to enter underground caverns spiked with stalactites and stalagmites. Many moa tumbled to their death as they ran through luxuriant bush only to stumble into a sink-hole, a natural limestone trap, with smashed bones being discovered centuries later by cavers. Fast-flowing rivers and streams in limestone country carve spectacular gorges, form majestic arches, and seemingly disappear into dry riverbeds.

For all of us limestone and its products are an integral part of our technological world; from concrete to glass, steel to toothpaste, limestone is a most valuable and useful natural resource. Perhaps most significant of all is the role limestone plays in the global carbon cycle. Life on planet Earth is intrinsically linked to this remarkable rock.

Above: Moa fossil bones, Honeycomb Caves, Karamea. PHOTO: IGNS
Left: Limestone formations, Aranui Cave, Waitomo. PHOTO: IGNS

CHEMICAL ORIGIN OF LIMESTONES

CHEMICAL COMPOSITION OF SEA WATER

The chemicals needed to make limestone are found in sea water. Oceans cover about 71% of planet Earth's surface, making a total volume of about 1.4 billion cubic kilometres. The oceans are a chemical solution made up of dissolved salts and gases (Table 1).

Table 1 Salt composition of sea water (modified from Strahler & Strahler 1973).

Salt	Chemical formula	Grams/litre of water
Sodium chloride	$NaCl$	23
Magnesium chloride	$MgCl_2$	5
Sodium sulphate	Na_2SO_4	4
Calcium chloride	$CaCl_2$	1
Potassium chloride	KCl	0.7
Total salt		33.7

The salts are the weathered products of the rock-forming minerals. They are transported to the sea by rivers and streams. The **calcium ion (Ca^{2+})** originates mainly through the chemical weathering of limestones. Weathering of the same rocks also produces great quantities of the **bicarbonate ion (HCO_3^-)** which, along with the calcium ion, is dissolved in water and transported by rivers to the ocean, adding to the sea salt mixture. Both these ions are the major constituents of shell material.

Sea water also contains dissolved gases. These include oxygen, essential for the respiration of marine organisms, and **carbon dioxide**.

Most carbon dioxide is supplied to the oceans by the out-gassing of undersea volcanoes. This occurs at sites of sea-floor spreading where new lava is erupted and vast quantities of volatile gases are emitted. Atmospheric carbon dioxide can also be dissolved in the upper layers of the ocean. However, most oceanic **carbon** (in all its forms) has originated from the weathering and erosion of carbonate rocks (Broecker 1983).

MAKING SHELLS

Marine invertebrate organisms are able to biochemically combine the dissolved bicarbonate and calcium ions and secrete a new insoluble compound, calcium carbonate, in the making of their shells.

The food eaten by a mollusc, for example, contains the minerals that form the shell. The blood stream of the animal carries the minerals to a fleshy, skin-like tissue called the mantle. Here glands produce the liquid substance that makes the shell. Another gland in the mantle adds a hardening material to the liquid so that it becomes the hard shell with which we are familiar.

Marine organisms that have calcite or aragonite shells include molluscs, corals, echinoderms, bryozoans and barnacles, microscopic animals (mainly foraminifera) and some algae (Figs. 1 and 2).

When these organisms die, their remains settle to the bottom of the sea floor where the soft parts decompose leaving behind accumulations of carbonate or calcareous sediment. Limestones are the remains of marine organisms!

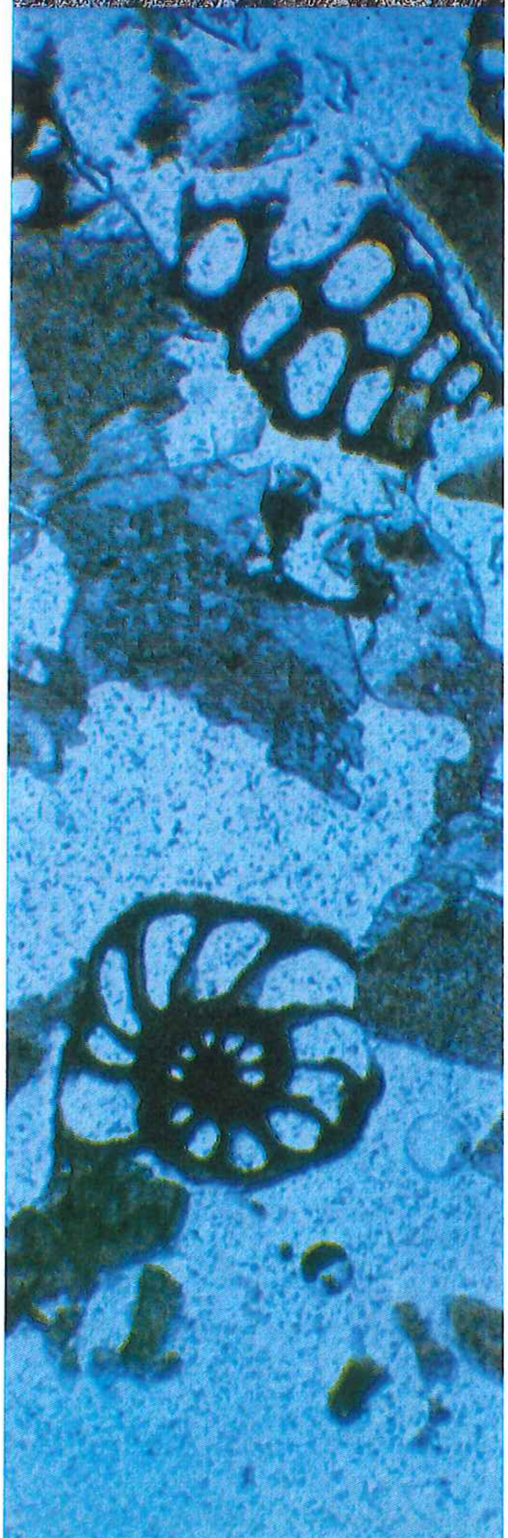


Fig. 1 (*above*) Scallop fossil, Johnston's Farm, Waikato. PHOTO: IGNS
Fig. 2 (*below, and front cover*) Photomicrograph of thin sections of limestone with foraminifera (cellular shells) and ehinoderm remains in clear calcite cement. PHOTO: Sue Courtney, University of Auckland.

Scale: scallop 10 cm across; foraminifera about 0.5 mm across.

CALCAREOUS OOZE AND WATER DEPTH

Scientists have discovered that the carbonate ion in sea water decreases with depth (Table 2). The solubility of calcite increases with pressure. Deepest ocean basins (abyssal plains) will have no calcareous sediments whereas shallower ones and most continental slopes above the critical depth of complete carbonate dissolution (usually 4–5 km depth) will accumulate these foraminiferal sediments, called calcareous ooze.

This is well illustrated in the relationship between New Zealand's sea floor sediments and bathymetry (Fig. 4). Vast quantities of calcareous ooze are accumulating offshore at depths between 500 and 4000 m. At depths greater than 4000 m only very small amounts of calcite exist and only deep ocean clays are being deposited. Note also that calcareous ooze is not being deposited in troughs, steep slopes, or within close proximity to the New Zealand land mass, although locally in the latter area of shallow water coarse-grained shelly carbonate sediments can be conspicuous (e.g., about Stewart Island and Three Kings Islands).

Table 2 Carbon and its dissolved compounds in warm and deep water (modified from Broecker (1983)).

Ion	Warm surface water (10^{-6} mol L^{-1})	Average deep water (10^{-6} mol L^{-1})
Bicarbonate ion HCO_3^-	1764	2140
Carbonate ion CO_3^{2-}	223	90
Carbon dioxide gas CO_2	13	45
Total carbon	2000	2275

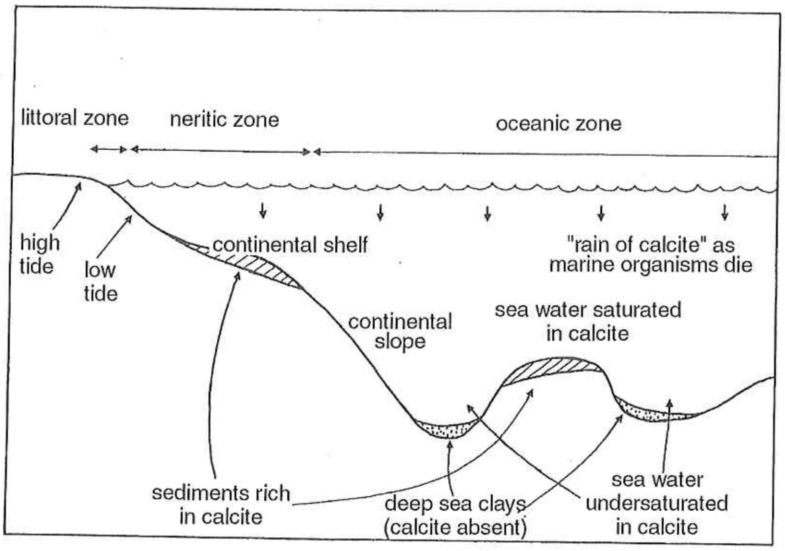


Fig. 3 Water depth and the solubility of calcium carbonate.

LIMESTONE AND THE CARBON CYCLE

Essentially, carbon is recycled through the atmosphere, hydrosphere, and lithosphere by the processes inherent to the carbon cycle (Fig. 5).

The greatest amount of carbon on Earth lies in storage, trapped in calcareous sediments on land and on the sea floor. Limestone rocks contain the equivalent of 20 times more carbon dioxide than the Earth's atmosphere. Calcareous sediments and sedimentary rocks are often referred to as carbon sinks (or fixed carbon), a place where carbon remains for geologically significant lengths of time.

Once in storage, carbon is by no means buried for good. The processes of **plate tectonics** can bring the carbonate sediments to the Earth's surface where they are weathered and eroded. As limestone dissolves during weathering it releases carbon dioxide gas. Release of carbon dioxide can also occur as carbonate sediment is dragged beneath continental crust in subduction zones. Here melting and ensuing volcanic eruption can bring the carbon dioxide back to the atmosphere.

Consider these carbon cycle scales of time:

- as most oceanic crust is no older than 200 million years before it is consumed at subduction zones some carbon atoms have remained in this carbon sink for this length of time before rejoining the carbon cycle.
- a single carbon atom may have made the journey from sediment to atmosphere to water 20 times in Earth's history (Pearce 1989).
- calculations suggest that all of the CO_2 in the atmosphere passes through the oceans once every 7 to 8 years (Strahler & Strahler 1973).
- the movement of a carbon atom from soil to plants to air to water and back takes about 100 000 years (Pearce 1989).

Carbon and its chemical family, the bicarbonate and carbonate ions as well as carbon dioxide, are in constant movement between atmosphere, oceans, lithosphere, and living things. Limestone is a critical link in the carbon cycle, a cycle that maintains life on planet Earth.

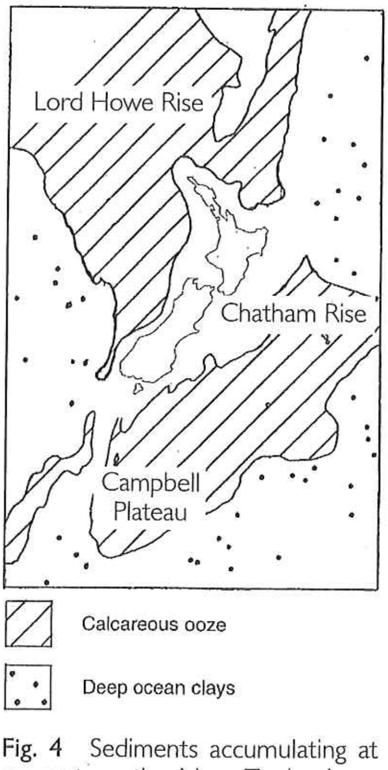


Fig. 4 Sediments accumulating at present on the New Zealand sea floor (modified from *New Zealand Region, Sediments*, 1989 New Zealand Oceanographic Institute DSIR).

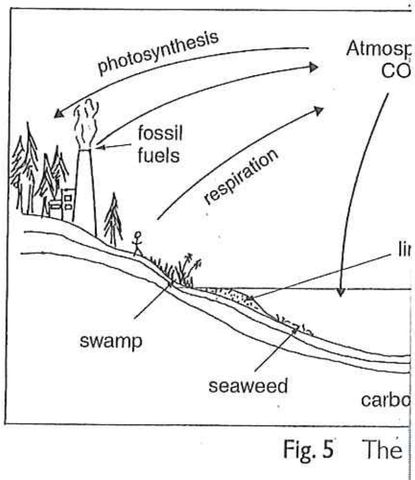


Fig. 5 The

WHAT ARE LIMESTONES MADE OF?

The types of limestone formed depend on a number of inter-related factors including:

- the species and numbers of marine organisms present;
- water depth;
- ocean temperature;
- proximity to land and the contribution of sand, silt and clay to the limestone mix; and
- energy of the depositional environment.

The following marine organisms have in their own way contributed to the manufacture of most of the limestones found on Earth:

- **shells**, complete or broken remains of organisms including molluscs, brachiopods, corals, bryozoans, echinoderms and many others.
- **faecal pellets**, the waste product produced by carbonate mud-ingesting organisms.
- **benthonic algae** (seaweed).

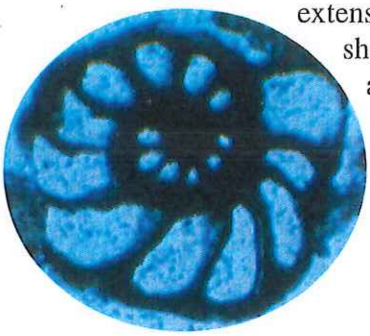
Some algae act like sticky surfaces that can trap fine carbonate particles, forming layers upon layers of sediment. These algae are also thought to be the origin of **stromatolites.** Stromatolites are believed to represent some of the earliest life forms on Earth with some specimens in Australia being as old as 3.5 billion years. They are interpreted as ancient algal reefs and may have had an enormous influence on the evolution of the Earth's atmosphere.

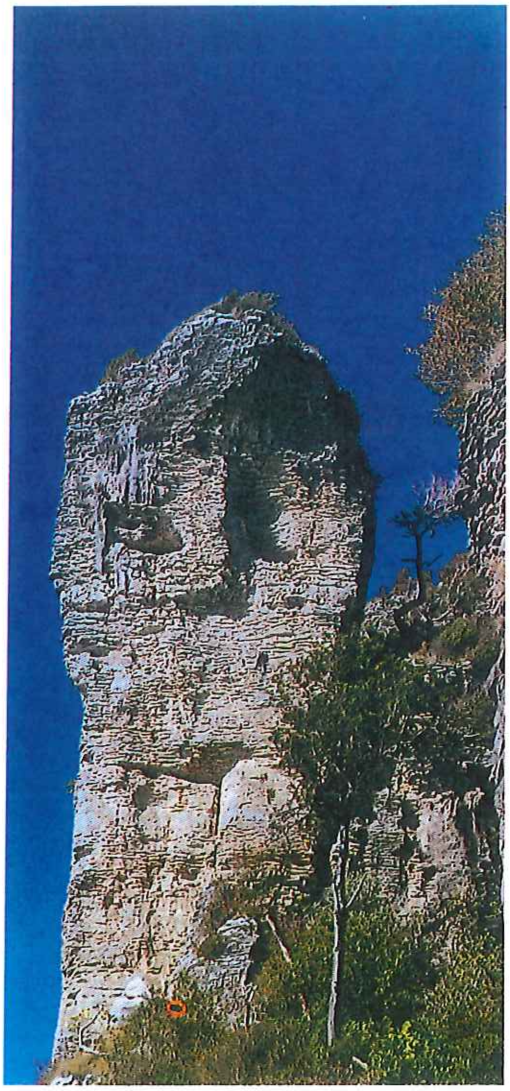
- **Planktonic algae**

Some planktonic algae called **coccoliths** are able to secrete tiny calcium carbonate structures while they drift freely around surface waters. In the past they have contributed greatly to the fossil record. Their most famous occurrence is in the chalk cliffs of southeastern England, known as the "White Cliffs of Dover".

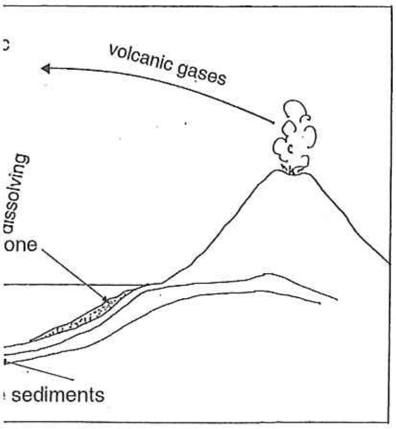
- **Foraminifera** (Forams)

Forams are single-celled animals with a calcareous shell or **test**. They are hugely abundant in the sea and can form deposits called **oozes**. Oozes are found extensively in waters deeper than about 200 m, but shallower than 4000 m. New Zealand has a huge area of calcareous ooze at present being deposited on the Lord Howe Rise, Campbell Plateau, and about the Chatham Rise (Fig. 4).





Limestone outcrops, Tarakohe, Golden Bay.
PHOTO: Graeme Partridge.



on cycle.

Pancake Rocks, Punakaiki, West Coast.
PHOTO: Graeme Partridge.

INORGANIC PRECIPITATES

Inorganic precipitates are compounds directly precipitated from sea water. A precipitate occurs when two oppositely charged ions meet and combine in water to form an insoluble compound.

In your science class you will have most likely blown through a straw into limewater. The cloudy or milky appearance formed in the test-tube is a precipitate of calcium carbonate formed from the reaction between the calcium hydroxide solution (limewater) and the carbon dioxide of your breath.

A similar reaction occurs in sea water. It is thought to be partly responsible for the formation of ooids (or oolites), spherical sand-sized particles that have concentric rings of calcium carbonate precipitated about some other grain, and common in shallow tropical seas.

Over thousands and millions of years great thicknesses of calcareous sediment build up on the sea floor. If these accumulations occur on continental shelves away from the muddying contribution of terrestrial sediments (land-derived sediments), then the sediment is composed almost entirely of calcium carbonate.

Lithification is the term used to describe the transformation of sediment into sedimentary rock. Calcareous sediment is lithified to form limestone. As sediment builds up on the sea floor, older sediment becomes increasingly buried. Circulating water causes precipitation of calcite cement in pore spaces (between shells) which changes the sediment into limestone (Fig. 2).

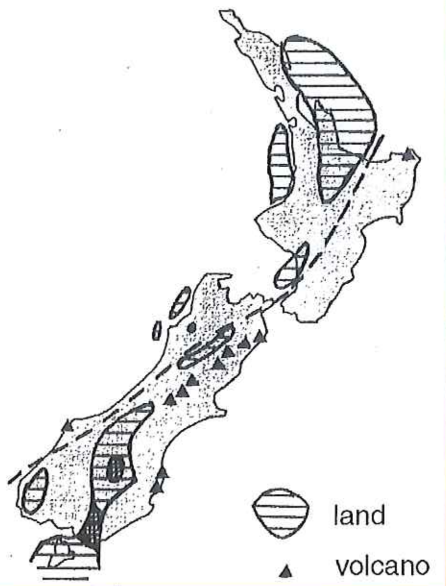


Fig. 6 A paleogeographic map of New Zealand during the Oligocene 37–25 million years ago. The present coastline is shown shaded for reference (modified from Stevens 1980).

"By Oligocene times, 35 million years ago, the slow weathering of New Zealand had reached its climax when virtually the entire land was worn down to a very low level. Some two-thirds of the area of modern New Zealand was now covered by sea and the remaining remnants of land consisted of an elongated, narrow-gutted archipelago and a few scattered islands. Deep seas covered the entire eastern flank of New Zealand from East Cape to Southland, and extended at least as far as National Park in the North Island. Most of the South Island was virtually under water and a deep marine trough occupied the Waiau-Hollyford region. Except for the eroded stumps of land in central and northern North Island and in inland Marlborough, south Canterbury, Otago and Fiordland, the only land poking out of the sea was small chains of volcanic islands in inland Canterbury and Marlborough, and at East Cape and Oamaru."

(Excerpt from Stevens et al., *Prehistoric New Zealand*, 1988. See Fig. 6 for the paleogeographic map of this time.)

WHAT DO THE LIMESTONES IN NEW ZEALAND REVEAL OF OUR GEOLOGICAL PAST?

PALEOGEOGRAPHY

Paleogeography is the study of ancient land and sea arrangements.

The description from *Prehistoric New Zealand* sets the ideal scene for accumulation of great quantities of limestone on New Zealand's Oligocene continental shelf. In comparison, New Zealand today is tectonically active. Precipitous mountain ranges are rapidly weathering and eroding. Fast-flowing rivers and streams transport great quantities of land sediment to the sea. Earthquakes trigger huge under-sea debris avalanches on steep continental slopes and in canyons enabling terrestrial sediment to reach far out into ocean basins. This present-day situation is a far cry from the low-lying tectonically stable New Zealand of 35 million years ago (Fig. 6).

PALEOCLIMATOLOGY

Paleoclimatology is the study of ancient climate. This can be done by using oxygen isotopes to interpret past temperatures.

Right: Oamaru Stone wall, Civic Square, Wellington.

A LITTLE NUCLEAR CHEMISTRY

Most oxygen atoms have a mass number of 16, 8 protons and 8 neutrons in the nucleus. A few oxygen atoms have a mass number of 18, 8 protons and 10 neutrons. The extra two neutrons give this oxygen more mass. These two forms are called isotopes of oxygen. The most common is the lighter isotope, oxygen 16; the less common is the heavier isotope, oxygen 18.

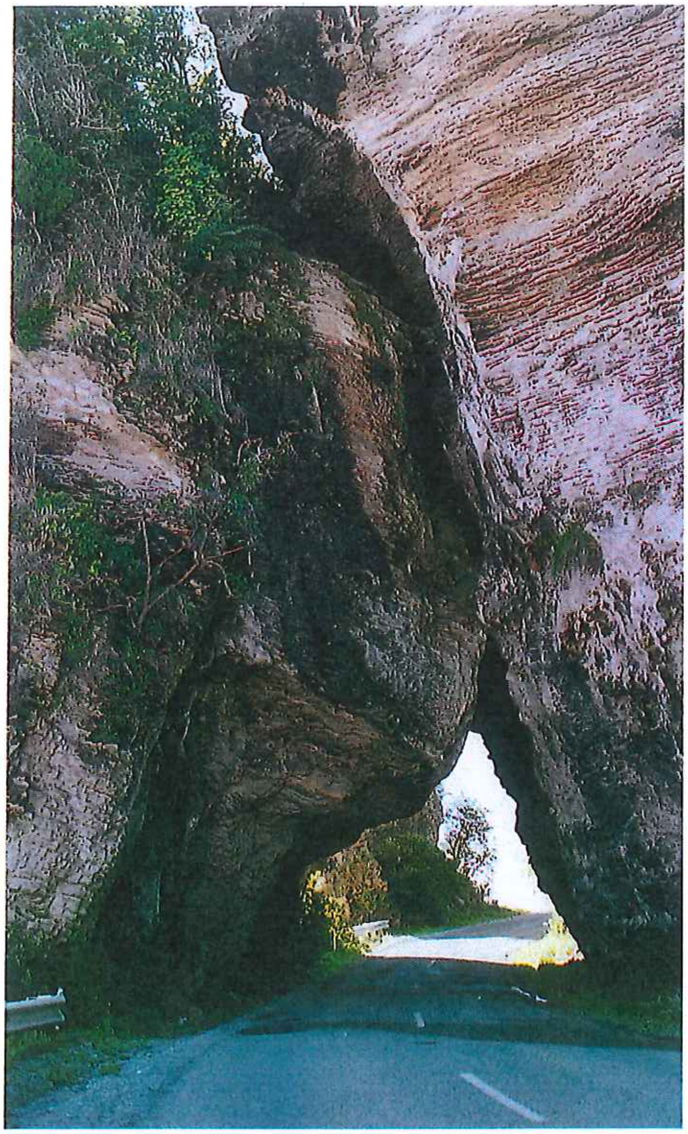
ICE AGES AND THE WATER CYCLE

Scientists have discovered that the ratio of the heavy isotope oxygen 18 to the lighter isotope oxygen 16 in ocean sediments and calcite shells of marine organisms provides evidence for global temperatures. During an ice age, evaporation preferentially removes the lighter oxygen 16 isotope from the ocean as water vapour. This water vapour is transported by global circulation patterns poleward where it cools and falls as snow in cold, high latitudes. In an ice age, the snow remains trapped in polar ice masses and is not recycled back to the oceans.

FOSSIL THERMOMETERS

Two consequences of this are the lowering of global sea level, e.g., in the last ice age sea level was reduced by about 120 m below present, and the relative enrichment of the heavy oxygen 18 isotope in the oceans. As discussed earlier, some marine organisms make shells by converting the bicarbonate ion into calcite. As you can see from these chemical formulae CO_2 and HCO_{3-} contain oxygen atoms. Therefore, the calcite shell contains a record of the O18/O16 ratio for the time of its existence. The shell can be thought of as a "fossil thermometer."

Analysis of oxygen isotopes from the fossil record results in paleoclimate interpretations such as the one shown in Fig. 7.



Tilted limestone blocks, Tarakohe, Golden Bay.
PHOTO: Graeme Partridge.

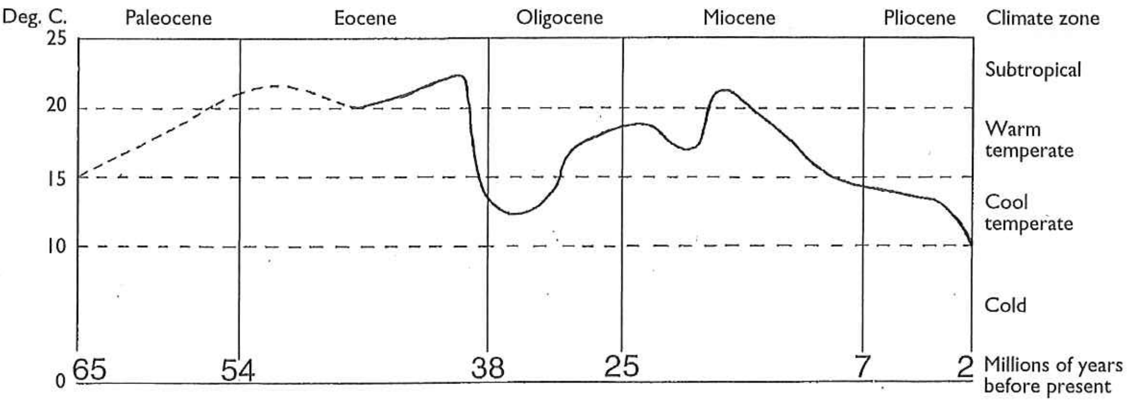
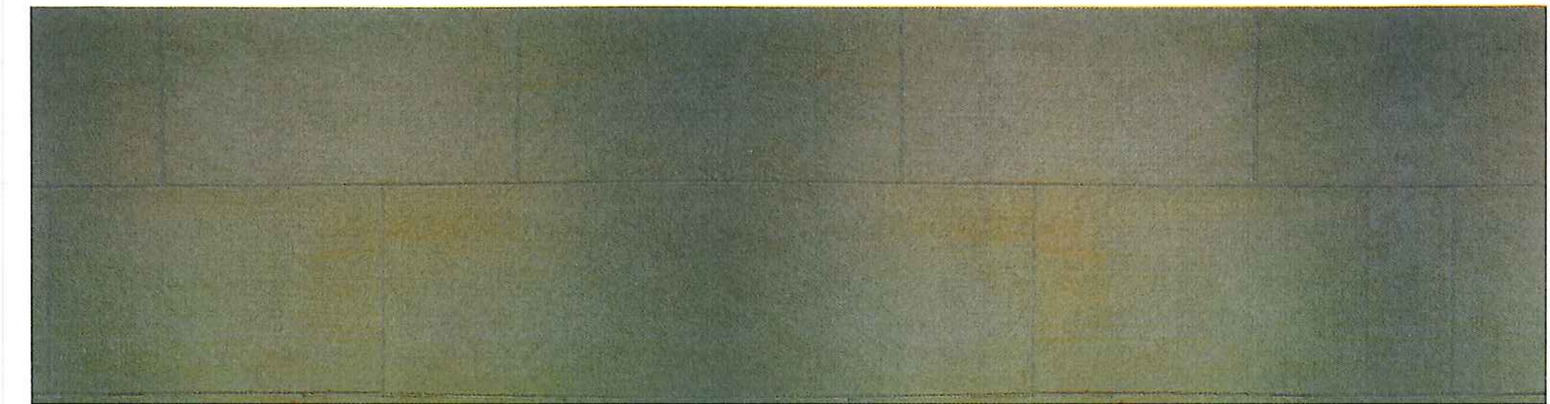
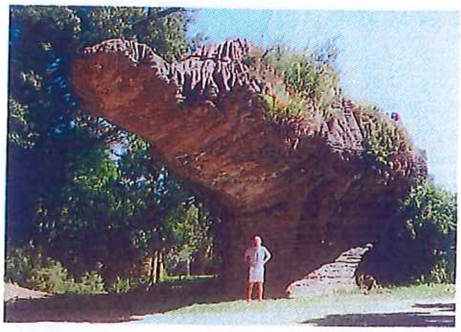


Fig. 7 New Zealand climates for the last 65 million years. Temperatures are based on oxygen isotope analysis (modified from Fleming 1979).





From above: Aorere River, Golden Bay; The Devil's Boot, Aorere Valley, Golden Bay; Marble (metamorphosed limestone) outcrops, Takaka Hill; Maori Leap Cave, Kaikoura. PHOTOS: Ruth Munro.

NEW ZEALAND LIMESTONE LOCALITIES

New Zealand limestone deposits are abundant throughout the country. Most limestones are Oligocene in age; however, there are much older marbles (metamorphosed limestone) such as the Ordovician marbles found in Northwest Nelson and Fiordland. The widespread occurrence of limestones has been most useful for the liming of our agricultural pastureland and for the manufacture of cement. Limestone is a remarkable rock.

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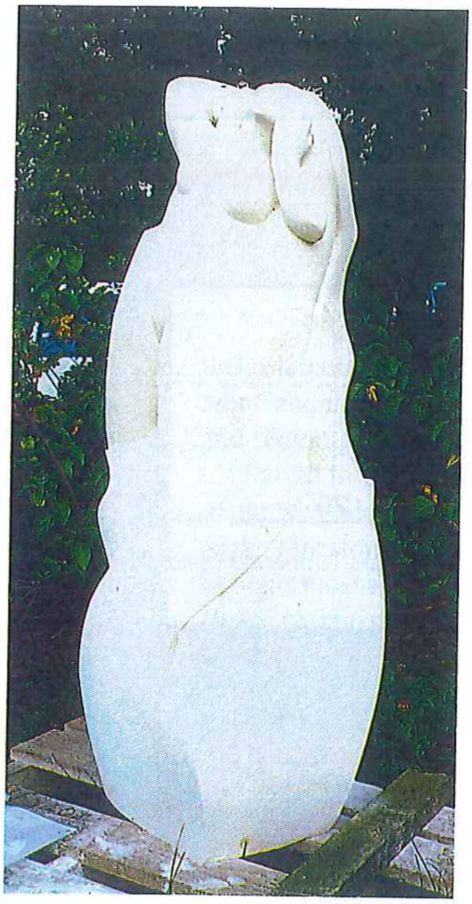

Oamaru Stone "Basking" by Island Bay sculptress Stephanie Jewell. PHOTO: Colin Walker.

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