about 0·5% of the volume of the baryte. Now, if we assume that the density of the inclusion fluids is about 1 g/cm^3, a scratch even as small as 1 cm × 0·1 cm × 0·1 cm (10^{-2} cm^3 in volume) would release 5×10^{-5} cm^3 of inclusion fluid. This is equivalent to 3×10^{-8} cm^3 of H_2S at S.T.P., or about $0{\cdot}5 \times 10^{-10}$ g for the sample containing the *lowest* amount of this gas (NP1, 600 ppm). Even this minute quantity can easily be detected by the human nose, which according to Roedder (1972) can detect as little as 10^{-10} g in a litre of air, or 10^{-11} g in 10^2 cm^3 of air.

As expected the 'odourless' remobilized baryte contains the lowest proportion of H_2S. It also contains the lowest proportion of CO_2. It is not possible to assess whether these two gases are components of type I inclusions or whether they are contained within type II and type III inclusions not readily apparent under the microscope. The former seems more likely.

Several authors (for example, Palache *et al.*, 1951; Dons, 1956; Deer *et al.*, 1963) have also recorded the fetid odour of H_2S when baryte from other localities is heated or rubbed. It is probable that these samples also contain H_2S-bearing inclusions, although it is apparent from this present study that such inclusions need not be rich in H_2S. As little as 600 (by volume) ppm of this gas in inclusion fluids is sufficient to cause this distinctive odour provided the inclusions, as in the case of the North Pole barytes, are present in abundance.

One most useful observation in connection with the origin of the H_2S-bearing type II and type III inclusions is the occasional presence of sphalerite (and calcite) as captured mineral phases within these two inclusion types. Because sphalerite (and calcite) are considered to be primary inclusions themselves, it follows that at least some of the type II and type III inclusions are also primary. This implies that both free H_2S and sphalerite (reduced sulphur species) were present during the growth of the baryte (oxidized sulphur species) and that the sulphur in these three species is of the same origin. Either H_2S was produced by the reduction of sulphate and reacted with traces of zinc in the baryte-forming fluid, or oxidation of reduced sulphur species (H_2S and ZnS) in a barium-rich fluid resulted in the formation of baryte. Sulphur isotope studies are needed to test the merits of these two alternatives and to investigate the unusual redox conditions prevailing during the formation of baryte from the North Pole deposit.

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Clinoptilolite pseudomorphs after calcitic and aragonitic Miocene fossils, Kaipara Harbour, New Zealand

CLINOPTILOLITE, analcime, chabazite, erionite, and phillipsite have been recorded as replacement products of volcanic glass in marine, volcano-clastic-rich beds of the Waitemata Group—an early Miocene sedimentary sequence (Sameshima, 1978). For a number of years, palaeontologists of the Geology Department have recognized that many of the fossil tests collected from one rich locality of this Group at Bushy Point on the Kaipara Harbour (36° 15′ S. 174° 13′ E.) are no longer calcareous. Subsequent investigations have shown that most of the specimens in the Departmental fossil collection from this locality are clinoptiolite pseudomorphs, after both calcite and aragonite—the perfection of replacement being very high.

A wide variety of both calcitic and aragonitic shells have been totally pseudomorphed. These include species of gastropods (*Polinices*, *Magnatica*, *Tropicolpus* (*Amplicolpus*), *Struthiolaria*, *Austrofusus*, *Amalda*, *Austrotoma*, *Latirogona*), bivalves (*Glycymeris*, Ostreacea, *Miltha*, *Maoricardium*, *Varicardium*), colenterates (*Lobophyllia*, *Plesiastrea*, and *Tubinaria*), bryozoa, and annelids. In some instances patches of calcium-carbonate remained, e.g. some tests of *Latirogona*. In others not all specimens of a particular species were replaced, e.g. *Plesiastrea*. With others, e.g. *Oculina virgosa* and solitary corals such as *Balanophyllia alta* and '*Flabellum*' *sphenodeum*, no zeolitized tests were found. Although epifaunas were usually altered along with any host occasional examples were found of non-zeolitized bryozoa epiphytic on a replaced host. Some zeolitized tests were contained in rock rich in unaltered calcareous bioclastic hash. No consistent pattern of replacement has been observed at the outcrop nor within or between individuals while no zeolitized fossils have been found among specimens collected from additional rich localities immediately to the north and south.

The rocks at Bushy Point are part of a widespread, shallow water, cyclical sequence consisting of andesitic agglomerates, conglomerates, tuffs, pumiceous sandstones, and breccias. Numerous small volcanic bodies are intimately associated with these sediments and indicate that the eruptive centres lay close to the site of deposition.

At Bushy Point itself, the sediments dip gently to the south-west. A conglomerate rests on a scoured sandstone surface and grades into the fossiliferous bed, which contains a variety of coarse sediment types. Dominant are breccias and conglomerates with a tuffaceous sandy matrix, which pass laterally into an agglomeratic phase containing numerous blocks of pumice. Fossils in the coarser facies are frequently broken or well worn, apart from the sturdier bioclasts, e.g. the glycymerids; but in the finer tuffaceous phases, such as the matrix, well-preserved zeolitized and non-zeolitized tests abound, admixed with wood and pumice fragments. Similar, poorly sorted, thick, volcanoclastic, marine horizons are well known in the Waitemata Group and have been interpreted as resulting from mass deposition by lahar or volcanic mudflow action (e.g. Brothers, 1954; Arlidge, 1955) particularly where they rest on scoured surfaces. At Bushy Point the fossiliferous horizon is succeeded by some 20 m of tuffs, lapilli-breccias, and andesitic pumice breccia probably deposited by ash-shower.

Both the manner and quality of the replacement of individual specimens varies. In some instances the entire volume of shell material has been replaced. In other cases a porous interior is enclosed in a solid sheath of zeolite giving the specimen a fragile, brittle quality but preserving in fine detail shell surface features. Quite commonly, a crystal-lined cavity appears to be impressed into a corroded portion of a test and may penetrate deeply into the interior of the shell wall.

X-ray diffraction of the pseudomorphs showed not only the characteristic clinoptilolite–heulandite pattern but also a small, distinct quartz peak at 3·34 Å (cf. Mumpton, 1960) and a larger unidentified reflection at 3·18 Å (?feldspar). Cell dimensions varied a little between several of the specimens examined: a = 17·68–17·70 Å, b = 17·92–17·94 Å, c = 17·40–17·42 Å, β = 116·3–116·4°. Mean refractive index, n = 1·49. Differential thermal analysis failed to yield any endotherm near 360 °C and the general pattern was consistent with that of clinoptilolite as given by Mason and Shand (1960) and Mumpton (1960). After heating at 450 °C for 16 hours, the X-ray diffraction reflections of the mineral were partially but not totally destroyed, the 020 and some of the other more intense reflection persisting, although in a greatly reduced state, and the mineral would appear to correspond to Group 2 of Boles (1972) in terms of thermal stability.

Chemical analyses, Table I, showed the replacement mineral to be a high-potash variety of clinoptilolite but to be significantly low in silica with $Si/(Al+Fe^{3+}) \approx 3{\cdot}4$. A comparable low-silica variety has been noted by Sameshima (1978) from basic volcanics occurring at Cape Reinga, New Zealand, although his specimen was high in lime. Both analyses given in Table I vary considerably in the weight per cent of alkalis and alkaline earths

TABLE I. *Analyses and calculated unit cell content, on a basis of 72 oxygens, of clinoptilolites from Kaipara, New Zealand*

	1	2		1	2
SiO_2	60·44	60·51	Si	27·855	28·310
TiO_2	0·01	0·01	Ti	0·004	0·004
Al_2O_3	14·75	14·71	Al	8·015	8·135
Fe_2O_3	0·16	0·22	Fe^{3+}	0·055	0·077
MgO	2·54	0·66	Mg	1·745	0·461
CaO	0·30	1·23	Ca	0·147	0·616
Na_2O	2·81	1·98	Na	2·509	1·794
K_2O	3·50	3·61	K	2·060	2·153
H_2O+	15·42	16·65			
Total	99·93	99·58	$Si/(Al+Fe^{3+})$	3·45	3·44

1. Clinoptilolite pseudomorphous after calcite forming *Glycymeris* test; University of Auckland, Geology Department, sample no. 26437, a = 17·682 ± 0·005, b = 17·942 ± 0·001, c = 7·421 ± 0·001, β = 116·37 ± 0·02, a c area = 117·57 Å^2, cell volume = 2109·4 Å^3, n = 1·491 ± 0·002.

2. Clinoptilolite pseudomorphous after aragonite forming *Plesiastrea* colony; 26438.

but the relative proportions of Na:K:(Ca+Mg) are not too dissimilar and are comparable to clinoptilolite described from the Ricardo Formation (Sheppard *et al.*, 1965). Certainly, the sum of the divalent cations in 26437 ($\Sigma = 1{\cdot}89$) is consistent with this specimen being a member of Boles's thermal stability group 2 although 26438 ($\Sigma = 1{\cdot}0$) is more typical of his group 3. However, in both instances the Si/Al ratio is much lower than that which Boles found necessary in these groups to resist some or all of the thermally induced contraction. Both chemically and thermally each of the analysed specimens would plot as a heulandite type 2 according to the scheme of Alietti (1972).

Sameshima (1978) regards the extensive zeolitization of the volcanoclastic materials of the Waitemata Group rocks as the result of hot-spring activity that accompanied hydrothermal alteration at shallow depth (probably $<$ 1000 m) both during and in post-Miocene times. In so far as the Bushy Point laharic deposit contains both an admixture of zeolitized and calcareous material it seems likely that the thanatocenose is derived from at least two biocenoses, one of which could have provided not only the means of alteration but the source of the laharic transport event. Sameshima regards the alteration of his volcanic glasses as occurring after deposition but in the present instance it would appear that alteration occurred prior to transport.

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