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## Origin of quartz in selected soils and sediments, North Island, New Zealand

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**Abstract** Quartz from two marine shales has  $\delta^{18}\text{O}$  values indicative of low-temperature crystallisation. In a Mangakahia Group shale, the low-temperature quartz is confined to the silt fraction and is a result of diagenesis; in the Whangai Shale, it occurs as clastic chert in a range of grain sizes. Quartz in soils formed from andesitic and basaltic parent materials is of eolian rather than pedogenic origin. However, quartz in the sand fractions of soils formed from a range of parent materials, including volcanic, has a  $\delta^{18}\text{O}$  value indicative of high-temperature formation and was probably a component of rhyolitic tephra from central North Island. Similar  $\delta^{18}\text{O}$  values for quartz in beach sands from the west coast of Northland indicate a predominantly rhyolitic source, and higher  $\delta^{18}\text{O}$  values of quartz in east coast beach sands indicates the presence of additional locally derived sediment. Only one example of low-temperature quartz was found in the soils investigated but this was found to be of eolian origin. Quartz from albic horizons of three podzols had  $\delta^{18}\text{O}$  values which clearly indicated that the quartz was not of pedogenic origin.

**Keywords** quartz; oxygen; isotopes; soils; sediments; genesis; podzols

### INTRODUCTION

Quartz is common in New Zealand soils formed from parent materials ranging from volcanic ash to sediments (New Zealand Soil Bureau 1968). Quartz in soils formed from basic and intermediate volcanic ash has been shown to be of eolian origin (Campbell 1971; Mokma et al. 1972; Stewart et al. 1977, 1984), and in rhyolites the quartz may also be a primary constituent (Mokma et al. 1972). In

soils developed on sedimentary rocks, quartz is likely to be inherited from the parent material but the formation of pedogenic quartz has been postulated, particularly as a result of intense podzolisation (Fieldes et al. 1956; Smidt et al. 1977). Quartz from the albic horizons of these podzols may have been subsequently reworked to comprise some of the Northland beach sediments (Schofield 1970).

This paper has two objectives: (1) to determine if quartz present in a range of North Island soils was of pedogenic origin; (2) to examine selected materials which may have been a source of eolian quartz in the region.

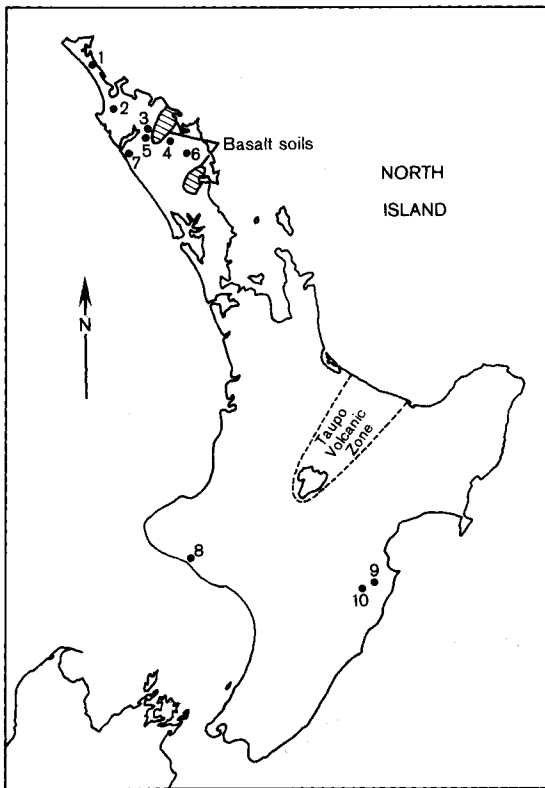
### MATERIALS

Quartz-rich sediments, tephra, and soil parent materials covering a range of compositions were examined (Fig. 1). Cretaceous and Tertiary marine siltstones are widespread in North Island and contain substantial amounts of quartz. Two examples were selected for examination, one from the Cretaceous Whangai Formation (near Waipawa, Central Hawke's Bay) and the other from the Lower Tertiary Mangakahia Group (near Pakaraka, Northland). Limestones are also common throughout North Island, and the oxygen isotope composition of quartz in the insoluble residue of Te Aute Limestone, Central Hawke's Bay, was included in this study.

In Northland, highly quartzose beach sands occur on both eastern and western coasts and are a potential source of eolian quartz in adjoining soils. Thus, beach sands were sampled from both the west (Waimamaku locality) and east (Rarawa locality) coasts.

Three podzols from the region were then examined to determine if the highly quartzose albic horizons in each resulted from pedogenic quartz formation or were a result of concentration by podzolisation. The soils examined were two kauri podzols (the Wharekohe soil developed on Tertiary sandstone and siltstone, and the Te Kopuru soil developed on late Pleistocene beach sands) and a grey podzol (the Kara soil developed on silty lacustrine sediments).

In Quaternary time, rhyolitic tephra from the central North Island have influenced soils over much of the North Island and northern South



**Fig. 1** Location of materials investigated in this study. Most soils in central North Island have been influenced by additions of rhyolitic tephra from the Taupo Volcanic Zone. 1, Rarawa; 2, Te Kopuru; 3, Kara; 4, Mangakahia Group shale; 5, Parahaki; 6, Wharekohe; 7, Waimamaku; 8, Egmont; 9, Te Aute Limestone; 10, Whangai Shale. Data for Egmont have been published in detail by Stewart et al. (1977).

Island. One of the quartz-bearing eruptives, Ohinewai Tephra, was selected as a representative example of a source of quartz of rhyolitic origin.

Soils developed from volcanic parent materials in Northland have been previously examined. In this study, a soil developed from weathered rhyolite (the Parahaki soil, previously reported by Mokma et al. 1972) was reinvestigated.

The origin of quartz in six basaltic soils from Northland is reported in Stewart et al. (1984).

## METHODS

Soil samples were treated with 1M NaOAc-HOAc (pH 5) and  $H_2O_2$  to remove carbonate and organic matter (Jackson 1956). The Te Aute Limestone sample was treated with 1M HCl to dissolve shelly material. The two marine shales were disaggre-

gated by gentle crushing. The beach sands were treated with 6M HCl to remove carbonate and any iron oxide coatings, dried and sieved, and quartz grains were hand picked for analysis. All other samples were separated into size fractions by sieving, sedimentation, and centrifugation (Jackson 1956). Quartz was isolated from the samples by  $Na_2S_2O_8$  fusion and  $H_2SiF_6$  digestion (Jackson 1956; Sridhar et al. 1975).

For oxygen isotope analysis, oxygen was liberated from quartz by reaction with  $BrF_3$  (Clayton & Mayeda 1963). Isotope ratios were determined with a double collecting mass spectrometer and are reported as  $\delta^{18}O$  in parts per thousand (‰) relative to Standard Mean Ocean Water, SMOW (Craig 1961).

## RESULTS AND DISCUSSION

### Sediments

Oxygen isotope analysis results are summarised in Tables 1 and 2.  $\delta^{18}O$  values of quartz from the 63–20  $\mu m$  size fraction of the Mangakahia Group shale of 12.0‰ is similar to that of quartz in the same size fraction in Northland soils (Table 2). In scanning electron microscope (SEM) and optical microscope examination, quartz grains appear as angular, monocrystalline, detrital fragments. However, the  $\delta^{18}O$  values of quartz in the 5–2  $\mu m$  size fraction of this shale of 25.7‰ indicates a large component of low-temperature quartz. SEM examination of this size fraction showed grains to be irregular aggregates of small, euhedral quartz crystals (Stewart et al. 1984). Thus, detrital, monocrystalline quartz dominates the coarser size fractions but recrystallisation is occurring in the finer size fractions, probably as a result of diagenesis. Comparison with other data in the literature suggests a minimum temperature of 68–70°C (Murata et al. 1977).

In contrast, quartz from the 63–20  $\mu m$  and 5–2  $\mu m$  size fractions of Whangai Shale has  $\delta^{18}O$  values of 25.6‰ and 26.6‰ respectively, indicating low-temperature quartz in both size fractions (Table 1). Optical microscope examination of thin sections of the Whangai Shale show it to comprise some detrital quartz but the remainder is predominantly clastic chert grains, hence the consistently high  $\delta^{18}O$  values across the size fractions examined.

The high  $\delta^{18}O$  values of quartz in the Whangai Shale could arise in two ways, either through substantial whole-rock recrystallisation or from inheritance of grains from a source area containing cherts. The presence of both detrital quartz and chert grains suggests the latter; the cherts are responsible for the high  $\delta^{18}O$  values (Churchman et al. 1976).

Ohinewai Tephra Formation is a rhyolitic tephra deposit erupted from the central North Island c.

150 000 years B.P. (Vucetich et al. 1978). A  $\delta^{18}\text{O}$  value of 8.4‰ in the 500–100  $\mu\text{m}$  and 63–20  $\mu\text{m}$  quartz size fractions is typical of a high-temperature origin (Churchman et al. 1976). Only a small amount of quartz occurs in the < 63  $\mu\text{m}$  size fraction, a distribution which also appears to occur in other rhyolitic tephra. This suggests that rhyolitic tephra are not a major source of silt-sized quartz in North Island soils. However, central North Island acid volcanism has been the indirect source of much quartzose sediment transported down rivers to accumulate as coastal sediments.

Quartz in a medium to coarse beach sand from the west coast of Northland (Waimamaku) has a  $\delta^{18}\text{O}$  value of 8.7‰ (Table 1), consistent with a high-temperature origin. The similarity of this  $\delta^{18}\text{O}$  value

with that of quartz from the Ohinewai Tephra Formation strongly suggests a similar source. The beach sand was probably transported from the central North Island by the Waikato River and subsequently dispersed northward by coastal currents (Schofield 1970).

$\delta^{18}\text{O}$  values of quartz in two size fractions (250–125  $\mu\text{m}$  and 125–63  $\mu\text{m}$ ) of a beach sand from Northland's east coast (Rarawa) were 11.7‰ and 11.5‰ respectively (Table 1) and indicate a greater component of lower temperature quartz compared with the west coast beach sands. By assuming a  $\delta^{18}\text{O}$  value of 8.7‰ for high-temperature quartz (as in the Waimamaku sample) and 15.0‰ for locally derived quartz from weathered Mesozoic greywacke (Mokma et al. 1972), a resultant  $\delta^{18}\text{O}$  value

**Table 1** Oxygen isotope abundance of quartz from selected size fractions of siliceous sediments, a rhyolitic tephra, and a coquina limestone.  $\delta^{18}\text{O}$  values are expressed in parts per thousand (‰) relative to Standard Mean Ocean Water, SMOW (Craig 1961).

Sample	Type	Age	Size fraction ( $\mu\text{m}$ )	$\delta^{18}\text{O}/^{16}\text{O}$
Mangakahia Group	Shale	Early Tertiary	63–20	12.0
			5–2	25.7
Whangai Formation	Shale	Cretaceous	63–20	25.6
			5–2	26.6
Te Aute Limestone	Coquina	Late Tertiary	63–20	13.9
			5–2	15.3
Waimamaku	Beach sand	Recent	500–250	8.7
Rarawa	Beach sand	Recent	250–125	11.7
			125–63	11.5
Ohinewai Tephra	Rhyolite tephra	Pleistocene	1000–500	8.4
			63–20	8.4

**Table 2** Oxygen isotope abundance of quartz from selected size fractions of some North Island, New Zealand, soils developed in a range of parent materials.

Soil series	Parent materials	Depth (m)	Horizon	Size fraction ( $\mu\text{m}$ )	$\delta^{18}\text{O}/^{16}\text{O}$
Parahaki	Rhyolite	0–0.1	Ap	63–20	9.0
				5–2	9.3
		0.1–0.2	Bw	63–20	9.2
				5–2	9.1
Wharekohe	Tertiary sandstone		E	63–20	12.8
				5–2	13.4
Te Kopuru	Pleistocene sands		E	> 63	8.9
				63–20	10.9
				5–2	14.2
Kara	Lacustrine silts	0.2–0.3	E	63–20	12.1
				5–2	15.6
		0.35–0.45	Btg	63–20	12.0
				5–2	15.1
Basaltic soils	Basalt		mean values from a sequence of six soils	> 125	8.2
				63–20	12.0
				5–2	13.9
Ruatangata		0.2–0.3	Bt	2–1	13.6

of 11.5‰ would require a 45% local component. This is consistent with the observations of Ricketts (1979) who suggested that east coast beach sands had multiple sources with a probable local component of the order of 40%.

The late Cenozoic Te Aute Limestone crops out through much of the Hawke's Bay region of North Island. Quartz from the acid-insoluble residue of the limestone had  $\delta^{18}\text{O}$  values indicative of a detrital origin (Table 1). The grain-size characteristics of the residue (well-sorted coarse silt to very fine sand) are similar to those of residues from other North Island limestones (Nelson 1977). Quartz in the 5–2  $\mu\text{m}$  size fraction has a  $\delta^{18}\text{O}$  value of 15.3‰ which is similar to values for quartz in the same size fraction in marine sediments at this latitude. The combination of this grain size and oxygen isotope composition has been interpreted to indicate derivation from tropospheric aerosolic dust (Rex & Goldberg 1958; Clayton et al. 1972; Jackson et al. 1973).

### Soils

The Parahaki soil, developed in rhyolite, contained quartz with  $\delta^{18}\text{O}$  values of 9.0–9.3‰ in both the 63–20  $\mu\text{m}$  and 5–2  $\mu\text{m}$  size fractions, confirming the results of Mokma et al. (1972) that little or no eolian addition of quartz to this soil has occurred. However, while indicative of a high-temperature origin (Mokma et al. 1972; Churchman et al. 1976), consistent with parental rhyolite, these  $\delta^{18}\text{O}$  values are significantly higher than those obtained for Ohinewai Tephra of 8.4‰. Either the quartz has crystallised in equilibrium with isotopically different fluid phases or crystallisation has occurred at different temperatures. If the latter, the temperature difference could have arisen through the rapid cooling of tephra compared with the slower cooling of a rhyolitic dome which allowed isotope equilibration at lower temperatures.

$\delta^{18}\text{O}$  values for 63–20  $\mu\text{m}$  and 5–2  $\mu\text{m}$  quartz from the albic horizon of the Wharekohe soil indicate detrital quartz of mixed origin (Table 2). SEM examination shows both fractions to consist of angular quartz grains with no evidence of secondary quartz (Stewart 1982). The quartz is therefore not pedogenic, and the large amount present in the albic horizon most likely results from residual concentration from the parent material of the soil during podzolisation.

The Te Kopuru soil has an albic horizon that is often strongly cemented with silica. The  $\delta^{18}\text{O}$  values for selected size fractions from this albic horizon show the quartz in the sand fraction to be of high-temperature origin (Table 2), and affinities with present-day west coast beach sands are apparent.  $\delta^{18}\text{O}$  values increase with decreasing grain size (Table 2), indicating an increasing component of

locally derived eolian quartz in the silt fractions and a tropospheric aerosolic component in the 5–2  $\mu\text{m}$  fraction. Thin sections of an albic horizon from the Te Kopuru soil show it to include angular quartz grains surrounded by an isotropic material, probably silica, with no evidence of secondary quartz.

$\delta^{18}\text{O}$  values of quartz from a gley podzol (the Kara soil) are 15.1‰ and 15.6‰. This is higher than  $\delta^{18}\text{O}$  values for quartz in other soils in the same region (Table 2) but is similar to the highest values obtained for aerosolic quartz at similar latitudes (Mokma et al. 1972). Thus, the higher values could indicate a greater proportion of aerosolic dust in the Kara soil than in other Northland podzols. However, the Kara soil is developed in siliceous lacustrine sediments, eroded from Tertiary marine shales within the lake catchment, and the higher  $\delta^{18}\text{O}$  values may result from a component of low-temperature quartz inherited from the shales. Because the presence of detrital low-temperature quartz has been demonstrated elsewhere (Stewart et al. 1984), we favour the latter interpretation.

Evidence for the origin of quartz in andesitic and basaltic parent materials has been reported elsewhere. All quartz present in an Egmont soil developed in andesitic tephra was of eolian origin (Stewart et al. 1977). Detailed oxygen isotope analysis of quartz from six Northland basaltic soils also showed the quartz to be of a different origin from the basaltic parent material (Stewart et al. 1984). Quartz in the sand fractions of these basaltic soils is clearly of high-temperature origin ( $\delta^{18}\text{O}$  value of 8.2‰, Table 2) and is probably derived from airfall rhyolitic tephra. In contrast, the  $\delta^{18}\text{O}$  values for silt fractions are similar to values obtained for quartz in other soil and sediment silt fractions in New Zealand (Table 2), for which a detrital, eolian origin has been postulated (Mokma et al. 1972; Stewart et al. 1984). Even the 2–1  $\mu\text{m}$  size fraction of one of the strongly weathered basaltic soils (Ruatangata) contains quartz with a  $\delta^{18}\text{O}$  value of 13.6‰ (Table 2), indicating that the quartz is not of low-temperature (pedogenic) origin. It is similar to the mean  $\delta^{18}\text{O}$  value for quartz from the 5–2  $\mu\text{m}$  size fractions of the Ruatangata and other basaltic soils of 13.9‰, suggesting that the two size fractions have a common origin, possibly as part of a 10–1  $\mu\text{m}$  tropospheric aerosolic dust population (Rex et al. 1969; Syers et al. 1969; Mokma et al. 1972; Clayton et al. 1972). No quartz was found in the < 1  $\mu\text{m}$  size fraction of these soils, compatible with the lower limit for aerosolic dust.

In one of the basaltic soils there is clear evidence of low-temperature quartz in the 5–2  $\mu\text{m}$  size fraction. This has been shown to come from local additions of material from Mangakahia Group shale, indicating that the 5–2  $\mu\text{m}$  size fraction does not

consist exclusively of tropospheric aerosolic dust (Stewart et al. 1984).

## CONCLUSIONS

1. No evidence of pedogenic quartz formation was found in the soils examined. In particular, quartz in the albic horizons of podzols resulted from residual concentration rather than quartz crystallisation.
2. Low-temperature quartz forms in geological materials at pressures and temperatures higher than those of the soil environment and is therefore more properly considered to be a diagenetic process. Low-temperature quartz may, however, be subsequently incorporated in soil profiles by inheritance or as a result of eolian transport.
3. Quartz in North Island soils has a multiple provenance; it may be (1) inherited from underlying Cenozoic and Mesozoic sedimentary and igneous parent materials, (2) from Quaternary rhyolitic tephra as primary airfall material and as secondary retransported fluvial and marine sediments, or (3) eolian quartz from local Cenozoic and Mesozoic sedimentary rocks and tropospheric aerosolic dust transported in Quaternary time.

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