Some aspects of petrification of Miocene wood from Kaipara Harbour, New Zealand

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Abstract   Silicified woods of probable Altonian (Lower Miocene) age occur in southeast Hukatere Peninsula, Kaipara Harbour, New Zealand. Pyroclastic flows, apparently flowing from a northerly direction, carried woods from a broadleaf-podocarp forest to mix with probable Avicennia (mangrove) growing in estuarine conditions close to the site of preservation. Many woods were partially or completely carbonized by the flow.

Thin section petrography, scanning electron microscope micrographs, and X-ray diffractograms indicate the woods were silicified by silica in solution, formed by devitrification of volcanic glass. The sequence of silicification is likely to have been either opal-A → opal-CT → α-quartz and chalcedony, or directly to α-quartz and chalcedony. The degree of crystallinity of the quartz is not time dependent. The mode of occurrence of α-quartz, chalcedony, cristobalite, tridymite, lussatite and amorphous opal is described. Other minerals present in the woods include goethite and members of the saponite group, as well as organic compounds.

Key words: wood, Miocene, New Zealand, silicification, petrification

INTRODUCTION

Pockets of petrified wood associated with late Cenozoic sub-aerial silicic volcanic rocks, are widespread throughout Northland, the Coromandel Peninsula and the Auckland region. The Miocene woods from southeast Hukatere Peninsula, Kaipara Harbour (Fig. 1), are generally well preserved, with the cell structure present and uncrushed, and the logs undistorted, making this locality suitable for a study of silicification of wood. There is a range of degree of silicification and the wood is plentiful and easy to collect. Jones (1966), Hayward (1976) and Brook (1983ms) extensively review the stratigraphy of the north Kaipara area. The woods are from a limited stratigraphic interval, the Tinopai Member of the Puketi Formation (Waitemata Group). Brook (1983ms) infers from stratigraphy that the wood-bearing Tinopai Member is probably early or mid-Altonian. Paleobotanic evidence suggests an Otaian or Altonian age (Sutherland 1985ms). There are no sub-aerial glass-rich deposits like those at north Kaipara known elsewhere in the Waitemata Group.

At Puketi Point there is a dominant orientation of logs at about 035° which suggests with sedimentological evidence (Brook 1983ms) that the pyroclastic flows are likely to have come from the northeast (although there are other logs at 060° and 172°). The Parahaki dacite domes are thus the most probable source. K-Ar dates for andesites on Hukatere Peninsula range from about 18 to 15 myrs and for the Parihaki dacites about 19 myrs (Doi 1993ms; Hayward 1993).

The wood preserved on the southern Hukatere Peninsula ranges from splinter-sized shards to large logs nearly a metre in diameter. They show a wide colour range from black, through greys and browns, to buff and white and many woods have an outer glossy strongly iron-stained zone. Some woods have a buff weathering rind up to 1 cm thick but with fresh surfaces showing a range of colours. The outer weathered layer is often fibrous and powdery, the fibres following the original grain of the wood.

Although most woods are incompletely silicified and partially porous, some are very dense and hard with all the spaces filled, and a few are glossy with conchoidal fractures. The more com-

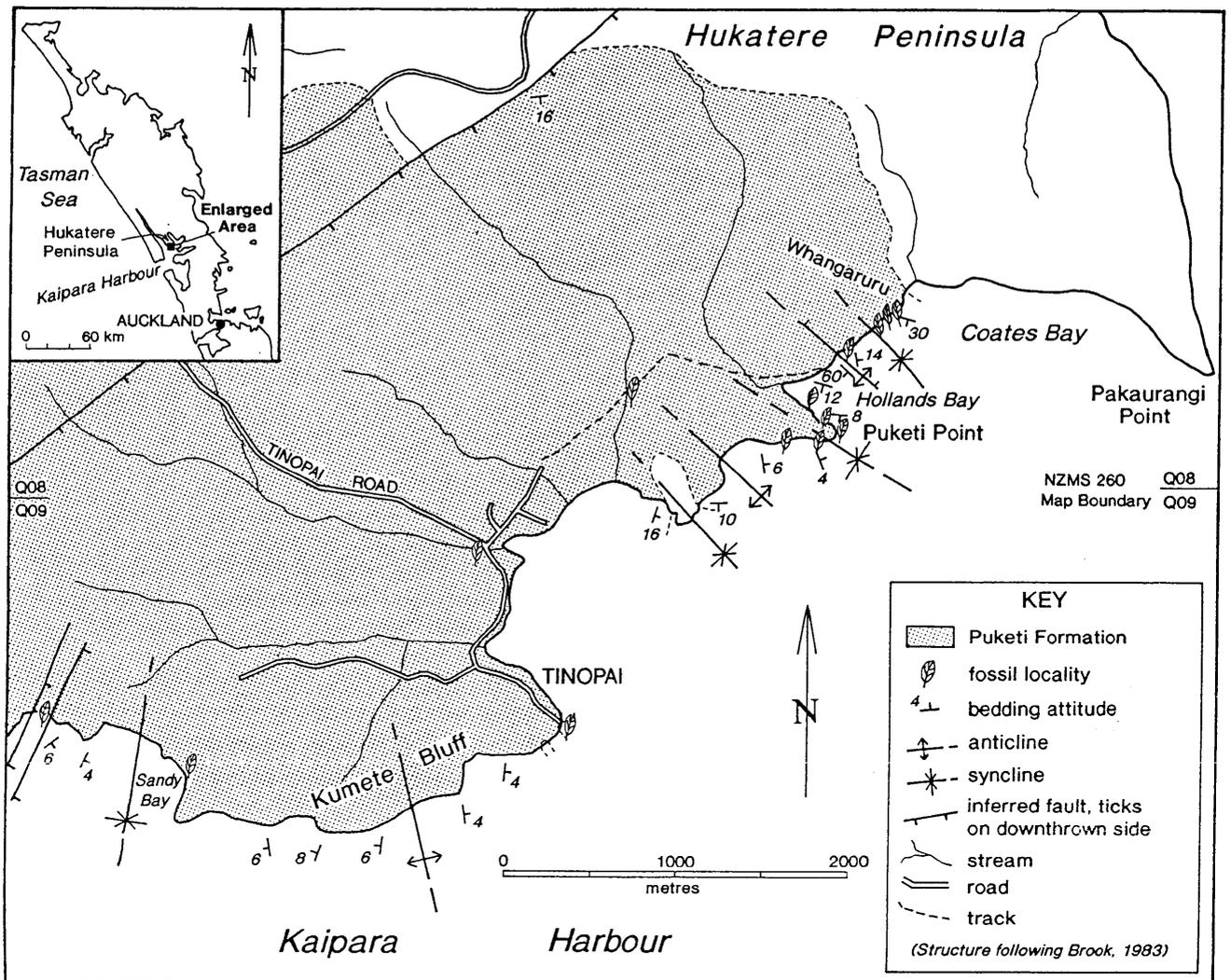[1]Department of Geology, University of Auckland, Private Bag 92019, Auckland, New Zealand.

Fig. 1   Southeast Hukatere Peninsula, Kaipara Harbour, New Zealand.

pletely silicified portions show excellent preserva-
tion of cellular structure (Fig. 2a) and some show
a mineral framework which has almost completely
replaced the organic structures. Although in most
of the Kaipara wood the cell walls are still rela-
tively intact, in some the cell lumena have been
silicified and the organic structure has been re-
placed with quartz crystals. The crystals may be
less than 1 mm in length, and mixed with frag-
ments of organic material (Fig. 2b), or up to 3
mm long radiating into open spaces in the wood.

It is difficult to draw any conclusions about ei-
ther the occurrence of silicified wood or the de-
gree of silicification as the area has been selec-
tively collected for many years. Park (1886) de-
scribed "silicified trees of large dimensions and
finely preserved" at Coates Bay. Ferrar (1934) de-
scribed silicified trunks of trees and stems of tree
ferns. Wood of this size and tree ferns are not
found in the area anymore. There is a sugges-
tion from the limited sample available from the
western   coast   that   the   glassy   conchoidally

fracturing type of preservation is more common in
the west of southern Hukatere Peninsula, particu-
larly Sandy Bay. The abundance of silicified wood
in Coates Bay may also reflect the lower desirabil-
ity to collectors of the more porous woods as
well as the difficulty of access through a man-
grove swamp or across private property.

Carbonized woods are found in the pumiceous
horizons and associated paleosols of the Tinopai
Member and on the evidence of "fluid" escape
pipes (Brook 1983ms) are believed to have been
carried in hot pumiceous pyroclastic flows. The
flows have incorporated the vegetation growing at
the sites they passed over and may have carried
woods from a broadleaf-podocarp forest some dis-
tance to deposit them amongst probable Avicennia
(mangrove), the dominant species in Coates Bay
(Sutherland 1985ms).

Many of the larger trunks at Coates Bay have
a thick outer layer of carbonized wood and non-
carbonized silicified wood on the inside. Some
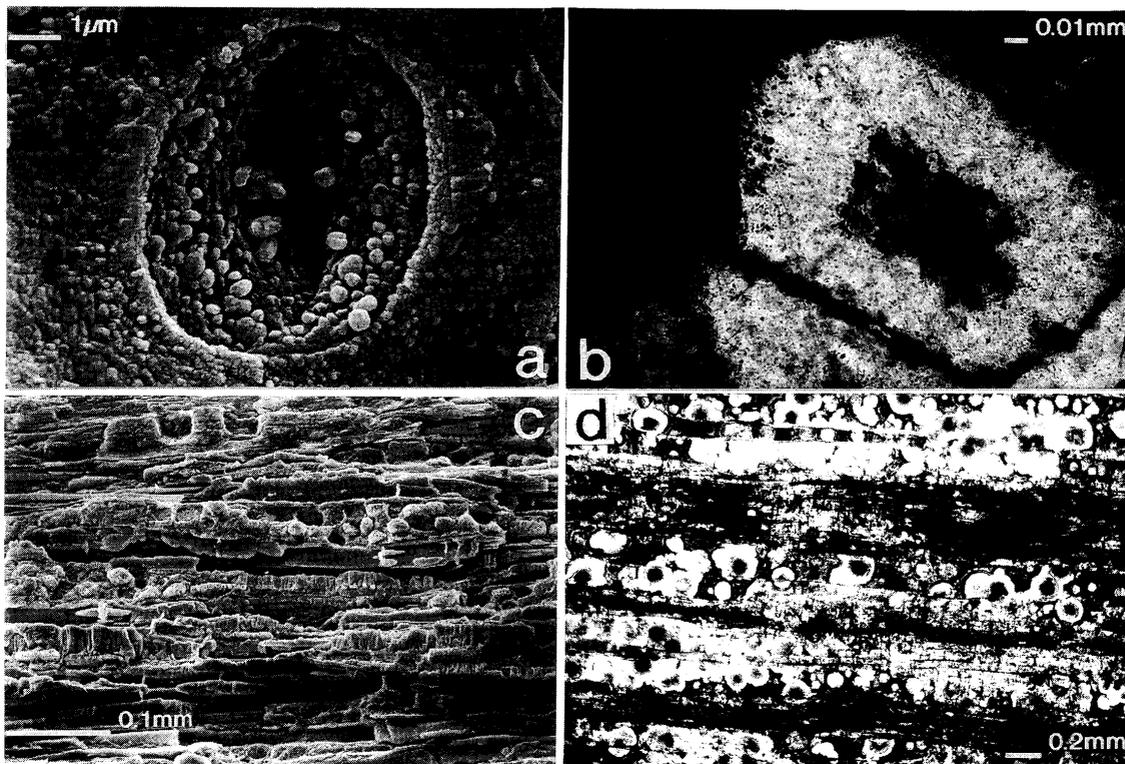smaller logs are totally carbonized and silicified.

Fig. 2 a: A bordered intervessel pit from sample AU 9493 (*Avicennia*) preserved in silica. Quartz crystals are scattered over the pit area. Scanning electron micrograph. The scale bar is 1 μm. AU numbers are from the Paleontology Register of the Geology Department of Auckland University.
b: Carbonaceous material included within a quartz crystal from sample AU 9494.4. Transmitted light. The scale bar is 0.01 mm.
c: Parallel bands of fibrous chalcedony in specimen AU 7302.6. Scanning electron micrograph. The scale bar is 0.1 mm.
d: Spherical chalcedony showing agate-like banding from specimen AU 7644.15. Transmitted light. The scale bar is 0.2 mm.

A few well silicified logs have irregular areas of carbonization in the centre of the log. Such patchy carbonization is difficult to interpret as there is no evidence of rotting wood or hollow logs. At one site on Puketi Point there are a number of holes lined by carbon, probably left by the complete combustion of wood. Much of the wood on Puketi Point is carbonized and associated with lignite bands of very low rank and tree roots in growth position. There is no evidence for upright transport of trees at Kaipara as has been recorded in the Yellowstone National Park deposits (Coffin 1976) and at Mt St Helens (Coffin 1983; Fritz 1980).

The movement of pyroclastic flows rapidly abrades the softer bark and cambium layers and removes branches, as happened at Mt St Helens, where a number of logs were also splintered and eroded by the blast (Lipman & Mullineaux 1981). However, no splintered logs have been found at Kaipara, although the large number of fine shards on Puketi Point may have been formed in this way before being rounded by wave action on the beach.

SILICIFIED WOODS

Scurfield & Segnit (1984) discuss in detail the petrification of wood by silica minerals, and their findings can in general be applied to Kaipara woods (Fig. 3). They found four forms of silica: opal-A, which is highly disordered, nearly amorphous; opal-CT, which is a poorly crystalline disordered interlayering of tridymite and cristobalite units; chalcedony, which is microcrystalline quartz, often in porous fibrous aggregates; and crystalline quartz. Chalcedony also occurred with both quartz and opal. The petrographic criteria for distinguishing forms of silica are shown in Fig. 4.

Opal-A: Buurman (1972) defined wood-opal as a silicification with an opaline lustre and noted that it shows excellent structure preservation. Such a definition is too loose, and in general the "opaline" forms from Kaipara have poorer preservation of detail than do the fine grained quartz and chalcedony woods, and some "opaline" wood has an outer quartz-rich layer in which cell structure is best preserved. The term "opal" is thus of dubious value when used for these woods and is used by some authors for opal-CT or tridymite (e.g., Mitchell & Tufts 1973). All samples from
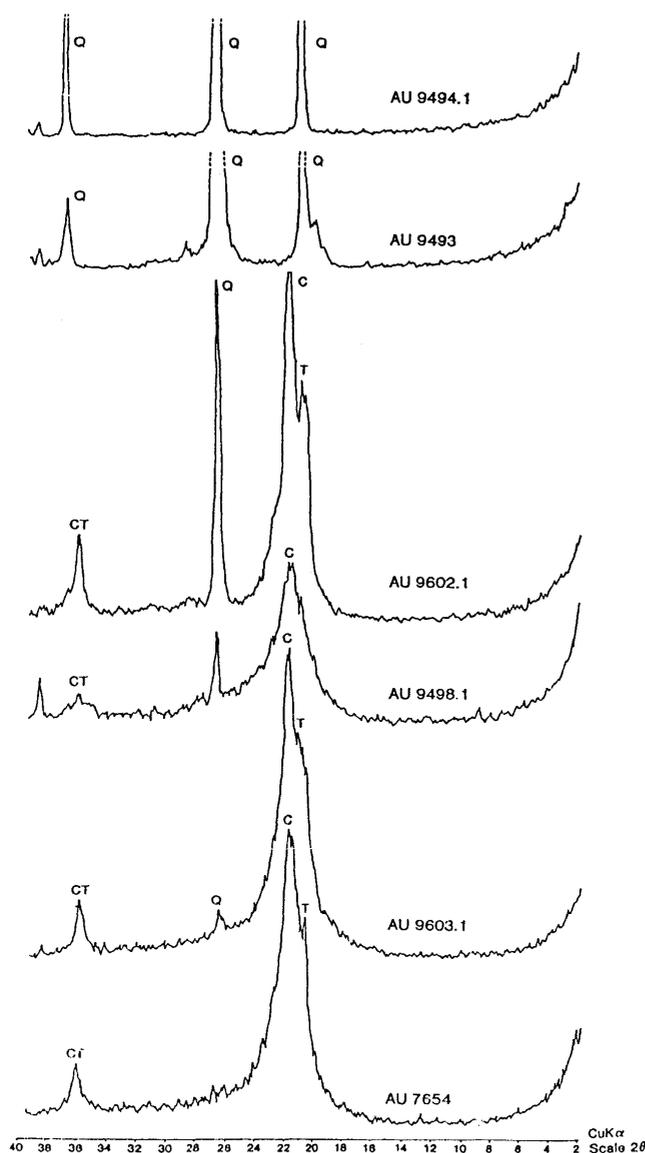
Fig. 3 Comparison of X-ray diffractograms of siliceous woods from Kaipara. Samples were X-rayed using a Phillips X-ray diffractometer fitted with a graphite monochromator and a copper target. The samples were mounted on an aluminium plate using the acetone slurry method.

Kaipara which could be called opal from their lustre and fracture in hand specimen were X-rayed but no opal-A was recognised in the X-ray diffractograms of any of these samples, some of which were opal-CT and others were highly quartzose. The low curve of any opal-A present would be masked by peaks of opal-CT and/or quartz. Opal-A was recognised in 7 thin sections by its isotropic nature.

Opal-CT: Opal-CT is the most common form of opal in woods according to Scurfield (1979) but this is not so for the Kaipara wood samples. Of the 30 samples of wood X-rayed from Kaipara, opal-CT was the dominant constituent in 9 samples and present to a lesser extent in a further 3

samples. In one that showed strong opal-CT peaks from brown portions of the wood, the outer white rim and inner black portions showed small quartz peaks as well as the opal-CT peaks. In the Kaipara woods, in general, the best cellular detail is preserved in samples that have a high proportion of opal-CT or fibrous chalcedony.

Opal-CT is built up of a disordered interlayering of α-cristobalite and α-tridymite units but can sometimes have a massive appearance. The boundary between massive opal-CT and opal-A is not sharp and Raman & Jayaraman (1953) have suggested from a study of X-ray powder photographs of opal-A that a periodic interstratification of α-cristobalite and β-cristobalite may be present. Opal-CT in the fibrous form of lussatite was recognised optically in only one section. Jones & Segnit (1971) found that optically many of the opals in the CT group contain fibrous lussatite although many samples which may show identical X-ray diffraction signatures do not show this fibrous structure and are optically isotropic. For Kaipara woods opal-CT was found to be very weakly anisotropic (as determined by using a λ compensation plate).

It is likely that most of the woods have some opal-CT as in even the well crystallised quartz samples the X-ray trace shows some broadening at the base suggesting the presence of opal-CT. None of the Kaipara woods contained only tridymite and frequently the tridymite portion of the opal-CT peak was not well developed. Mitchell & Tufts (1973) described 32 samples of fossilised wood where all but two of the samples were disordered tridymite either alone or with quartz. The tridymite structure approached β-tridymite in Mitchell and Tuft's samples but in the Kaipara samples the tridymite was all α-tridymite. No high temperature β-cristobalite or β-tridymite was found.

Jones & Segnit (1972) discussed the genesis of cristobalite and tridymite at low temperatures, suggesting that the observed metastable formation of cristobalite in the stability field of quartz could be explained by the topology of these silica polymorphs and the resulting energies at the time of formation. No opal-C has been detected in any of the woods from Kaipara, the woods X-rayed showing only broader opal-CT peaks. In the literature opal-C is associated with lava flows.

Chalcedony: In the Kaipara silicified woods no sample was composed totally of chalcedony. The chalcedony tended to be a vessel filling phase and in thin section and under the SEM fibrous parallel chalcedony is an important component of veins (Fig. 2c). Fibrous chalcedony in the Kaipara woods had a length-fast sign of elongation which is the usual direction (Frondel 1962) although length-slow forms have been reported (Folk & Pittman 1971). A number of cell lumina contain
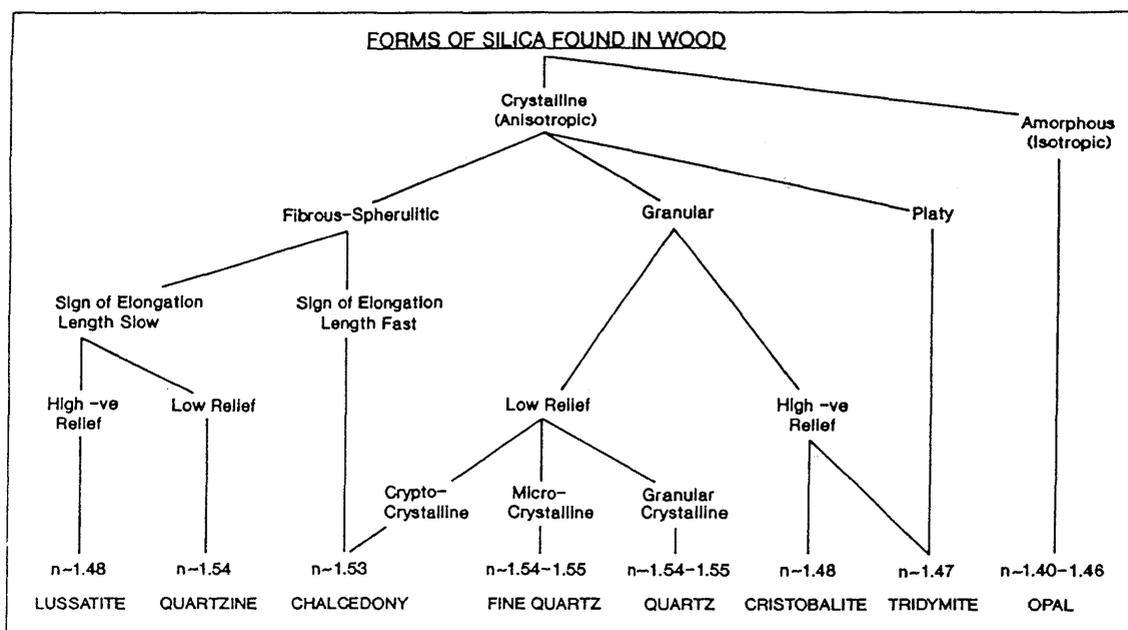
Fig. 4 Identification in thin-section of forms of silica found in wood. The boundary between micro-crystalline and granular crystalline quartz is arbitrarily defined as whether or not crystals are readily visible under low power of the microscope.

fan-like, radiating fibrous chalcedony which mostly shows agate-like banding (Fig. 2d). Scurfield & Segnit (1984) illustrate spherical fibrous structures with markings like the banding of agate on a fine scale which they identify as opal-CT. The microbotryoidal forms noted by Scurfield & Segnit (1976) were not seen in Kaipara woods. In some samples spheres of chalcedony with coarser fibrous structure are emplaced in fine fibrous chalcedony. Some spheres are composed of fibrous intergrowths of silica and goethite and show high dispersion and good parting, and the characteristic cross extinction of chalcedony. Such close-packed aggregates of silica spheres of uniform size are more typical of opal-A or amorphous opal than chalcedony. Other samples contain hollow spherical structures where the chalcedony projecting into the hollow is ragged — possibly corroded as might result where the micro-environment inside the sphere lay close to the boundary on the solubility curve where chalcedony is formed or dissolved. Many veins of parallel or massive microcrystalline chalcedony throughout the wood probably preserve original cracks in the wood. A network of fine lines may preserve original cracks from volume change in the gel from which the chalcedony crystallized. Fine cracks are also present in some cells which are infilled with chalcedony and may represent incipient devitri-fication.

Crystalline quartz: Quartz crystals occur in cell lumina and also encrust the outside of some specimens or line open spaces in the wood. Of 30 samples X-rayed, 19 are dominantly crystalline quartz and 4 are a mixture of both α-quartz and opal-CT. Jones (1966) noted that the wood samples

which he X-rayed were dominantly fine grained crystalline quartz.

Conchoidal fracturing is present in SEM samples and may reflect step-like growth of the crystal from periods of multiple crystal growth and dissolution, or merely represent fresh breakage in the preparation of the sample for electron microscopy (c.f., Krinsley & Doornkamp 1973). Whalley (1978) illustrated a fracture surface showing well formed chalcedony in a vein in silcrete. The angles of breakage are sharper and less curved than in the Kaipara wood examples, but the resemblance is otherwise strong.

Murata & Norman (1976) proposed an index of crystallinity for quartz using standard X-ray powder diffraction procedure in the 2θ range of 67° to 69°. Five peaks in this range are fully developed only in diffractograms of well crystallised quartz. Using their method (Fig. 5), a wide range of crystallinity was found for samples from Kaipara. In their studies of 9 silicified plant remains Murata and Norman found these were generally poorly crystallised (>5.0) except when extensively recrystallised and permeated with drusy quartz. Stein (1982) added to the data of Murata and Norman and plotted the crystallinity index of silicified woods versus age of the sample. The values Stein obtained from silicified woods were generally low and in agreement with those of Murata & Norman (1976). The Kaipara data do not confirm Stein's evidence that a long period of time (i.e., many millions of years) is required to attain good crystallinity and point to factors other than just time being involved. Some Kaipara woods may have silicified directly as α-quartz without
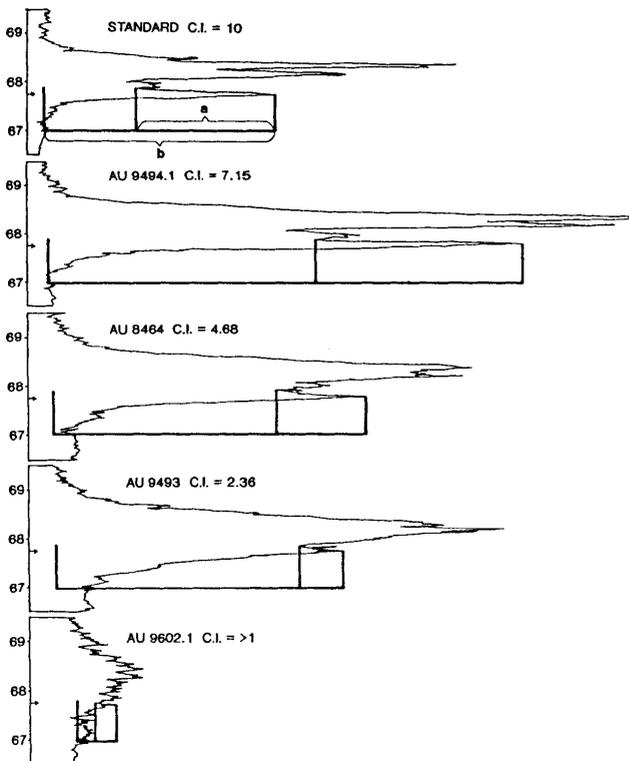
Fig. 5 The crystal index of silicified woods from Kaipara. The scale of the standard is half that of the other samples. Murata & Norman's (1976) index of crystallinity for quartz from the intensity of the (212) peak at 2θ of $67.74°$. Height of this peak (a) is first divided by its total height above background (b) in order to compensate for minor variations in the intensity of the pattern. The quotient a/b is further multiplied by 10 in order to convert fractions into numbers generally greater than 1.0. The highest value, calculated from clear euhedral crystalline quartz in this study, is raised to 10 and this scaling factor is used in the complete equation for all samples: Crystallisation index $= 10a\ F/b$ where F for this study was 1.63. The samples were mounted on an aluminium holder and were run 5 times from 67-$69°$ 2θ using a goniometer speed of $1°$ 2θ per minute a chart speed of 2 cm/minute, a time constant of 2 seconds and a range of 2×10^2 counts per second.

Fig. 6 Treatment of a sample of silicified wood to reveal the organic content and comparison of this sample with other organic compounds.

passing through transitional less crystalline phases of opal-A and opal-CT. As it is wood rather than the ash which has been silicified, the silica in solution may have passed into the wood by osmosis or diffusion from an area of high concentration of ions to one of lower concentration. Depending on the local pH conditions within the wood, quartz or a more amorphous form would be deposited. The larger crystals of quartz tend to be in open areas of the wood and these areas would be more exposed to the surrounding environment than would the interior of the wood.

Other compounds in silicified wood: A sample was treated with hydrofluoric acid to remove silica and then X-rayed to show other compounds present. The diffractogram showed so much iron fluoride that the background was still largely obscured. The sample was washed to remove the iron
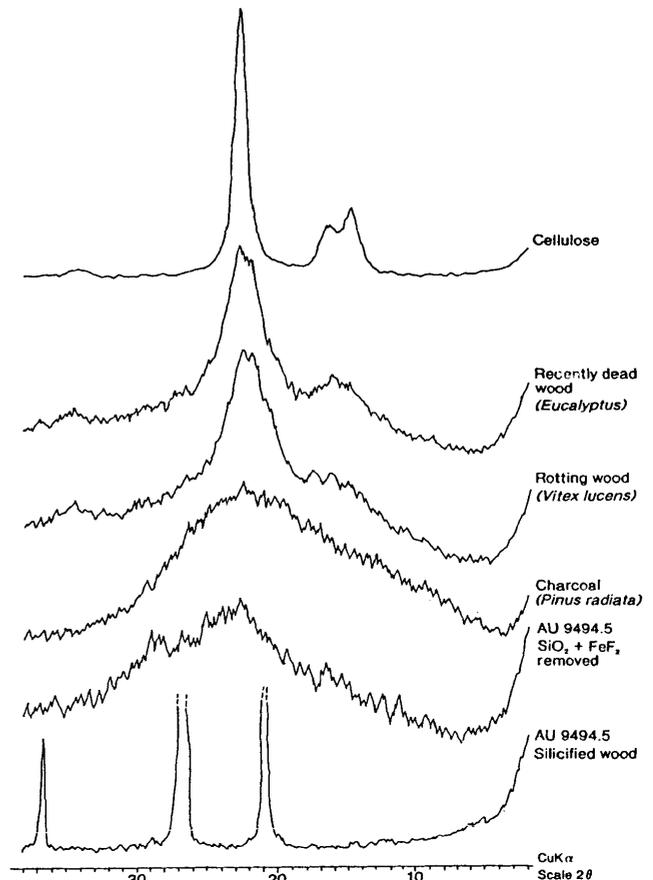
fluoride and X-rayed again (Fig. 6). This diffracto-gram shows a broad carbon "hump" similar to that shown by charcoal such as can be found in carbonized Pinus radiata. There is a suggestion of a sequence of decreasing cellulose content when recently dead wood, rotting wood and the fossil wood are compared with pure cellulose, but more woods would need to be examined to confirm this. Cellulose is present in most thin sections from Kaipara as a faint yellowing in the cell walls. To show lignin in an X-ray diffractogram all the cellulose would need to be removed, perhaps by heating in dilute acid or by enzyme decomposition. The chemistry of other relic organic compounds would be difficult to ascertain in this way.

The colour of Kaipara silicified woods appear to be related to the presence of Fe in minerals such as goethite, smectite and minerals of the saponite group. When pumice hydrolyses Al and Fe cations and alkalis are produced which may form clay minerals or zeolites. No zeolites were found in the wood.