On the significance of CO₂ inclusions in plagioclase microphenocrysts in tholeiite from Moeraki, New Zealand

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Abstract. Liquid plus vapour inclusions of CO₂ are widespread in plagioclase microphenocrysts in small tholeiitic intrusions and tephra of the Moeraki and adjacent areas of northeast Otago, New Zealand. They imply the presence of immiscible CO₂ droplets in the magma at depths of about 7–14 km. Their presence within 5 µm of the edges of microphenocrysts as little as 35 µm thick and 118 µm long indicates minimal feldspar crystal growth during the final ascent and quenching of the magma. Delicate branching clusters of lath-like microphenocrysts escaped disruption during this ascent. Such CO₂ inclusions are a potential source of ‘excess argon’ perturbing K-Ar age determinations.

Key words: carbon dioxide – fluid inclusions – plagioclase – tholeiite magma – Moeraki (NZ)

Introduction

Fluid inclusions of CO₂ were shown by Roedder (1965) to be virtually ubiquitous in the mafic to ultramafic nodules commonly found in alkaline basaltoid rocks. Inferred pressures indicate depths of entrapment of these generally secondary inclusions of 10–15 km, which is within the upper mantle where continental crust is absent. The apparent absence in most cases of primary inclusions containing higher pressure CO₂ may reflect the limited tensile strength at magmatic temperatures of the host minerals, mainly olivine, pyroxene, and sometimes garnet, though Murck et al. (1978) have reported CO₂ fluid densities up to 1.14 g cm⁻³, corresponding to pressures of more than 10 kbar for an entrapment temperature of 1200°C. Moore et al. (1977), Harris (1981), Jambon and Zimmermann (1987), and other workers have further shown that CO₂ is the dominant component of vesicles in ocean-floor basalts. Degassing of CO₂ from basaltic magmas evidently comprises in the mantle, and CO₂ remains the dominant exsolved gas component until the magma reaches shallow depths, perhaps less than 500 m, where water may dominate, especially if CO₂ has been able to escape during storage in high-level magma chambers (Greenland et al. 1985; Gerlach 1986).

Although CO₂ inclusions are often reported from the phenocrysts of basaltic rocks, most examples are in olivine and pyroxene, and in many cases these are probably crystals detached from nodules or cumulates of deep-seated origin. Examples of CO₂ inclusions in plagioclase from lavas are more rarely reported (Berman and Dubessy 1984; De Vivo et al. 1987; McInnes 1990; Solovova et al. 1990; Wang et al. 1990).

We here describe liquid CO₂ inclusions in plagioclase microphenocrysts in tholeiites of the South Island of New Zealand as briefly recorded by Coombs et al. (1986) and Roedder and Coombs (1987). Using the methods described in Roedder (1983) and Belkin et al. (1985) we place some constraints on the crystallization history of the rocks containing them. We present evidence that very small lath-like crystals of plagioclase (lengths ≥ 100 µm; thickness ≥ 30 µm) in glassy chilled margins and tephra have formed at depths of 7–14 km before final ascent and emplacement into and onto sediments of a shallow continental shelf. This is contrary to a common assumption that sub-millimetre crystals of plagioclase in fine-grained basaltic rocks formed by crystallization in place during and after high-level intrusion or extrusion.

Geological setting

In northeast Otago, New Zealand, the quartzofeldspathic Haast Schist is overlain by a veneer of quartz sands and quartz conglomerates of Late Cretaceous age followed by a transgressive sequence, some hundreds of metres thick, of shallow-water glauconitic mudstones of Late Cretaceous to Late Eocene age. The Waireka–Deborah volcanics, which contain the CO₂ inclusions here described, were emplaced in Late
Eocene and Early Oligocene times, partly as piles of tephra resulting from Surtseyan eruptions on a shallow continental shelf, partly as pillow lavas, and partly as minor intrusions in the underlying muds and associated Early Oligocene limestones (Coombs et al. 1986; Cas et al. 1989).

Most of the more detailed observations which followed were made on the chilled glassy margin of the Tawhiroko intrusion on Moeraki Peninsula (Benson 1943, 1944; Nakamura and Coombs 1973). This is a rounded body 300 m long, 150 m wide, and perhaps 50 m thick. It was emplaced in soft muds and apparently reached to within a few metres of the top of these, though the muds may already have been buried by tephra at the time of emplacement of the intrusion. From the nature of the sediments, it is inferred that the depth of water during sedimentation of the mudstones at Moeraki and during the onset of volcanism is unlikely to have been more than a few tens of metres or at most 100–200 m. This is compatible with the absence of pillow lava on Moeraki Peninsula apart from a few very restricted pillow-like forms; various writers such as Kjartansson (1966) and Allen (1980) have reported cases of upward transition from subaqueously erupted tholeiitic pillow lava to the products of explosive fragmentation at water depths between 100 and 200 m or even less.

Inclusions of liquid CO$_2$ in plagioclase are also present in biostratigraphically coeval and petrographically related tephra at Lookout Bluff and Bridge Point–Aorere Point (Cas et al. 1989), respectively 10 and 15 km to the north of Moeraki Peninsula, and are relatively abundant in plagioclase crystals 0.2–1.5 mm long in a slightly younger olivine tholeiitic sheet of the Waiareka–Deborah volcanics intrusive into Early Oligocene limestone near Clark’s Mill, Maheno, 25 km north of Moeraki Peninsula (Benson 1943).

CO$_2$ inclusions have previously been reported by Roeadder (1965) in blocks of lherzolite and garnet pyroxenite and in various megacrysts in the Kakanui Mineral Breccia, an Early Oligocene nephelinitic member of the Waiareka–Deborah volcanics. These blocks and megacrysts are believed to be mantle-derived and are products of quite different physical conditions and magmatic parentage than the occurrences described in the present paper.

**Petrography**

The contact zone of the Tawhiroko and other minor intrusions on Moeraki Peninsula contains an outer selvage about 5–10 mm thick of dark sideromelane glass which is brown and translucent in thin sections, followed progressively inwards by tachylite and increasingly coarse-grained doleritic basalt (Benson 1944; Nakamura and Coombs 1973). Apart from about 12% vesicles, the glassy margin of specimen OU31407 has 53.5% SiO$_2$ and 7.9% MgO on a volatile-free basis and contains 71.1% glass with 55.8% SiO$_2$ and 4.63% MgO, 8.4% pseudomorphs of carbonate and smectite after olivine, 18.2% plagioclase An$_{64}$–$57$, and 2.3% augite averaging Ca:Mg:Fe=36:9:50:2:12.8 (Coombs et al. 1986). Inward from the contact margin, overgrowths on the augites become more iron-rich and include pigeonite in epitaxial growth, plagioclase becomes more sodic, olivine ceases to crystallize, magnetite and ilmenite appear, and highly siliceous residua are developed.

Typical plagioclase microphenocrysts in the glassy margin are less than 0.4 mm long and 0.03–0.1 mm

![Photo of fragile stellate aggregate of slender plagioclase laths and attached augite grain, OU31407. Width of field: 0.9 mm](image)

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1 Numbers prefixed OU refer to specimens in the collection of the Geology Department, University of Otago, see Table 1.

**Table 1.** Representative occurrences of tholeiitic rocks with CO$_2$ inclusions in plagioclase, Moeraki district, Otago, New Zealand

<table>
<thead>
<tr>
<th>Specimen no.</th>
<th>Locality and grid reference</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>OU5875</td>
<td>Te Paitu Head J42 425365</td>
<td>Dike of olivine augite plagioclase tholeiite with quenched groundmass</td>
</tr>
<tr>
<td>OU31407</td>
<td>Tawhiroko Point J42 428353</td>
<td>Glassy chilled contact of pudding-shaped dolerite intrusion in soft mudstone; phenocrysts of olivine, plagioclase, augite</td>
</tr>
<tr>
<td>OU39371</td>
<td>Moeraki Point J42 421369</td>
<td>Lower contact of irregular intrusion against porcellanitized mudstone; phenocrysts of olivine and plagioclase in glass; CO$_2$ inclusions relatively abundant</td>
</tr>
<tr>
<td>OU52303</td>
<td>Shore, north side of Lookout Bluff J42 420469</td>
<td>Lapilli tuff with phenocrysts of olivine, plagioclase (to 0.75 mm) and augite in pale brown glass</td>
</tr>
<tr>
<td>OU55062</td>
<td>Clark’s Mill, Maheno J42 410588</td>
<td>Olivine basalt sill; dolerite basalt with olivine and plagioclase to 1 mm and finer-grained augite, CO$_2$ in inner zones of plagioclase</td>
</tr>
</tbody>
</table>
wide, and the smallest are no more than 1.5 \, \mu m \text{ wide. Very few exceed 0.75 mm in length. In many cases they form delicately branching stellate clusters which may be attached to a central granule of olivine or pyroxene (Fig. 1). In the tachylite zone, approximately 10 mm from the outer contact, a new generation of plagioclase of very high aspect ratio appears as \{010\} plates less than 1 \, \mu m \text{ thick and as whisker-like overgrowths on the corners of existing crystals, an observation compatible with the undercooling expected at this stage. Augite occurs in the glassy margin as microphenocrysts and as aggregates of small equidimensional grains mostly 40 to 300 \, \mu m \text{ in diameter. Many augite and larger plagioclase crystals enclose silicate melt inclusions, now glass, with small shrinkage bubbles. Larger bubbles in some such inclusions may result from the trapping of an immiscible droplet of CO}_2 \text{ as well as silicate melt. Many cases of augite partially moulded on plagioclase, and vice versa, provide clear textural evidence that the two minerals crystallized together. Microprobe analyses from the same chilled contact as OU31407 show that these augites contain about 0.4–1\% Cr_2O_3 and higher Al_2O_3 contents than the essentially Cr-free augites that crystallized after emplacement of the intrusion (Nakamura and Coombs 1973). Augite is lacking in the chilled margins of some of the other minor intrusions and tephra in the area. }

Rounded primary inclusions of liquid CO_2 and vapor, 1–8 \, \mu m \text{ in diameter, are found in many of the plagioclase crystals and may be present in augite as well. Most CO}_2 \text{ inclusions occur towards the centres of the crystals, but inclusions up to 4 \, \mu m \text{ in diameter have been observed less than 5 \, \mu m \text{ from the euhedral edges of their host crystals. Most inclusion-bearing grains are strictly euhedral laths, although the ragged forms of some suggest skeletal growth or resorption (Nelson and Montana 1992). }

Lengths and widths of all the larger plagioclase crystals in a randomly chosen area of a double-polished section, about 60 \, \mu m \text{ thick, of specimen OU31407 were measured, and they were then examined for CO}_2 \text{ inclusions under oil immersion at 1500 \times \text{ magnification. Of the 32 crystals measured, 14 contained recognizable CO}_2 \text{ liquid-plus-vapor inclusions (Figs. 2, 3). The seven smallest crystals examined (140 \, \mu m \text{ long and } 25 \, \mu m \text{ wide) contained no inclusions, and a cursory check of the abundant still smaller plagioclase laths (minimum thickness 1.5 \, \mu m) revealed no CO}_2 \text{. However, some crystals as short as 118 \, \mu m \text{ and others as thin as 35 \, \mu m did contain CO}_2 \text{ inclusions. Microprobe studies have not revealed any compositional difference between crystals with and without inclusions and we assume that their presence of absence results from vagaries in the inclusion-trapping process. In the coarser-grained interiors of the intrusions similar CO}_2 \text{ inclusions occur in the labradorite cores of some plagioclase crystals, but they are lacking in the more albitic outer zones and in crystals which grew in situ after high-level emplacement. }

Most of the CO}_2 \text{ inclusions were not suitable for microthermometry, and for several reasons the few numerical data obtained (all on OU31407, Tawhiroko Point) are not high in precision or accuracy. Three inclusions, in three different plagioclase microphenocrysts, homogenized in the liquid phase in the range 26.5–26.7\,^\circ\text{C. One large inclusion homogenized in the liquid phase at 29.6\,^\circ\text{C. }

Optical examination under oil immersion at 1250 \times \text{ showed that other inclusions in plagioclase microphenocrysts in this same sample had a similar range of degree of fill when the slide was warmed until the measured inclusions were near to homogenization. Inclusions showing homogenization in the liquid phase were also found in OU5875 (dike, Te Paitu), OU39371 (lower contact, Moeraki Point intrusion), and OU52303 (tephra, Lookup Bluff). However, other microphenoc-
crysts in OU31407, OU39371, and OU52303 had CO2 inclusions that were of lower density, as they homogenized near the critical point, using the microscope illumination as a qualitative but sensitive temperature control. Primary CO2 inclusions in OU5062 (Clark’s Mill) are also of relatively low density. Whether any of these have homogenization temperatures higher than the one measured at 29.6°C is not known. When several inclusions were found in the same microphenocryst, they usually showed similar degrees of fill. Only one inclusion (in OU52303) showed homogenization to vapor; it may have leaked.

A feature of all the observed CO2-bearing rocks, and of the Waiakea–Deborah volcanics in general, is the presence of tiny clots, rarely as much as 3 mm long and mostly less than 1 mm long, consisting of loosely aggregated small plagioclase crystals of blocky habit typically 40–150 µm in diameter. These are distinct from the plagioclase microphenocrysts of lath-like habit, though overgrowths of this habit are often seen on the outer surfaces of the more granular aggregates. Microprobe studies show compositions An59Ab41Or1 for the blocky plagioclase, essentially identical to those of the lath-like microphenocrysts. They contain inclusions of bluish-grey spinel normally less than 10 µm in diameter, and CO2 fluid inclusions which tend to be unusually abundant and in the same density range as those in the microphenocrysts. The overgrowths lack the spinel inclusions and tend to contain conspicuously fewer CO2 inclusions than that part of the crystal attributed to the initial clot. The origin of these clots is obscure; the margin and roof regions of the Moeraki dolerites often contain extraordinary concentrations of schist-derived refractory quartzose xenoliths up to decimetres in diameter, but larger xenolithic representatives of the plagioclase-spinel clots have not been found.

 Depth of entrapment

The temperature of homogenization of CO2 inclusions is a measure of the density of the CO2 phase present. If the CO2 is essentially pure (as it is in almost all such basaltic environments) and the temperature of entrapment can be estimated, the pressure and hence depth of trapping can be estimated. Kirby and Green (1980) showed that olivine crystals may be stretched around high-pressure CO2 inclusions; in such cases, these pressure and depth estimates would be minima, but we have no evidence of stretching in these plagioclase crystals.

Consideration of various geothermometers including the glass geothermometers developed for Kilauea and MORB glasses by Helz and Thornber (1987) and the olivine, plagioclase activity geothermometers of Glazner (1984) suggests that final temperatures of OU31407 before chilling were somewhere in the range 1110–1160°C. Initial saturation of the melt in olivine may have occurred about 70°C higher than the quenching temperature, with most plagioclase crystallization in the mid to lower part of the crystallization interval. Using the calculated data for CO2 of Kerrick and Jacobs (1981), and assuming trapping of CO2 inclusions to have occurred at 1150°C under a column of rock and basalt magma of average density 2.7 (Roedder 1983), homogenization at 26.6°C corresponds to 13.8 km depth and 29.6°C corresponds to 11.3 km. CO2 with critical density (homogenizing at 31.1°C) corresponds to about 7±2 km depth. This lower limit is at best a very rough estimate, as the top of the two-phase field on the T–V plot for CO2 is so flat that a wide range of densities yields almost identical homogenization behaviour. If the trapping temperature was 1100°C or 1200°C rather than 1150°C, inferred depths would be decreased or increased respectively by about 0.4 km.

Partial leakage from high-pressure CO2 inclusions is common in olivine of ultrabasic rocks (Roedder 1965), but seems unlikely here in view of the uniformity of apparent density for groups of more than one inclusion in a given microphenocryst. Thus the range of depths inferred for the trapping of CO2 in different crystals in the same and related samples suggests crystal growth in this range of depths.

Discussion

Like many tholeiitic bodies, the Tawhiroko intrusion differentiated into contrasting fractions containing 10–20% olivine on the one hand and relatively coarse-grained quartz dolerite on the other, together with quartz- and tridymite-bearing dikes and other late-stage segregations. The present observations demonstrate that immiscible droplets of CO2 existed in the melt and were being trapped by plagioclase at depths of about 14–7 km. We infer that these represent minimum depths for a crustal magma chamber which fed the Tawhiroko intrusion. Relatively (Al,Cr)-rich diopside augite and probably olivine crystallized in the same magma chamber in the same general pressure range. The Tawhiroko Point magma contained about 29% phenocrysts at the time of emplacement, largely or entirely the result of crystallization in this inferred magma chamber.

The relative abundance of CO2 inclusions in some of the plagioclase-spinel clots compared with the plagioclase overgrowths on these clots suggests an episode when CO2 droplets may have been especially abundant in the magma, perhaps as a result of falling pressure as the magma reached a crustal magma chamber, or perhaps as a result of reaction with wall rocks or xenoliths. However the magma remained saturated with CO2 until it left this magma chamber as shown by the presence of CO2 inclusions of similar density within 5–10 µm of the edges of some of the crystals. We see no reason to invoke unusually rapid feldspar growth to effect the trapping of the CO2 inclusions – in fact the mostly euhedral nature of the plagioclases suggests the contrary. Nucleation of the CO2 droplets is likely to take place on a solid surface, their density is relatively high ap-
proaching 1.0, and once nucleated there is expected to be little ten
dency for such minute droplets to detach and rise until they have grown much bigger than the observed dimensions of 1–8 μm.

Our data do not demonstrate the origin of the CO₂. It may have been of primary mantle origin, but it is also possible that it was released from wall rocks by contact metamorphism or assimilative reaction with xenoliths. The presence of the plagioclase-spinel clots might be evidence for this latter possibility, but carbonate-rich rocks are sparse in the Haast Schist base-
ment whereas rocks containing CO₂ inclusions are widespread amongst the Waiareka–Deborah volcanics.

As the CO₂ inclusions are as close as 5 μm to the edge of plagioclase laths as little as 35 μm thick, it is inferred that not more than about 5 μm of growth, and probably much less than that, took place on pinacoid faces during final ascent of the magma and during its quenching in the outer few millimetres of a body em-
placed in wet sediments. The associated drop in pres-
sure may have been as high as 5 kbar, and the lack of plagioclase growth contrasts sharply with the observation of Beard and Lofgren (1982) that in the case of hydrous high-alumina basalt (≥4% H₂O) plagioclase precipitates copiously during decompression from 3–1 kbar. On the other hand, the present observations acco-
dred well with the commonly observed lack of feldspar microcline growth in the relatively anhydrous MORB and Hawaiian tholeiite glasses.

During ascent, as pressure decreased, CO₂ droplets in the melt would have expanded, and increasing partition of volatiles, CO₂ and presumably H₂O, would have occurred into them. Inclusions of this lower den-
sity CO₂ or CO₂ + H₂O fluid have not been found in plagioclase of OU31407; their entrapment would have been precluded by the minimal feldspar growth inferred for this stage of ascent. It is remarkable that such delicately arranged clusters of crystals as are illustrated in Fig. 1 should have survived upward transport and emplacement. This behaviour contrasts sharply with the broken phenocrysts so typical of more viscous sili-
ceous magmas such as andesites and dacites, especially those in which the degree of crystallinity is higher than in the glassy rocks here described.

An important question arises as to why CO₂ does not appear to be trapped more commonly in the plag-
igioclases and other phenocrysts of basaltic rocks which have crystallized at crustal depths; the evidence of CO₂ microvesicles in glassy selvages of ocean-floor basalts suggests that basaltic magmas at crustal depths should normally be saturated with CO₂. Have CO₂ inclusions such as are here described been overlooked in routine petrographic studies?

It may also be noted that CO₂-rich fluid inclusions could well be enriched in magmatically derived argon. They are thus a potential source of ‘excess argon’ which would perturb K–Ar age determinations of any rocks containing them. A careful search should be made for any such inclusions in volcanic rocks to be used for K–Ar dating.

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