# Mineralogy and Proposed P - T Paths of Basaltic Lavas from Rabaul Caldera, Papua New Guinea

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**Abstract.** Rabaul caldera is a large volcanic depression at the north-east tip of New Britain, Papua New Guinea. The lavas range in composition from basalt to rhyolite and have a calc-alkalic affinity but also display features typical of tholeiites, including moderate absolute iron enrichment in flows cropping out around the caldera. The basalts contain phenocrysts of plagioclase and clinopyroxene with less abundant olivine and titanomagnetite. In the basaltic andesites olivine is rare, while orthopyroxene and titanomagnetite are common along with plagioclase and clinopyroxene. Orthopyroxene is also found mantling olivine in some of the basalts while in both rock types pigeonitic augite is a fairly common constituent of the groundmass. Plagioclase in both basalt and basaltic andesite often exhibits sieve texture and analysis of the glass blebs show them to be of similar composition to the bulk rock. Phenocrystic clinopyroxene is a diopsidic augite in both basalt and basaltic andesite. Al<sub>2</sub>O<sub>3</sub> content of the clinopyroxene is moderately high (~4%) and often shows considerable variation in any one grain. Calculations show that the microphenocrysts probably crystallised near the surface, while phenocrysts crystallised at around 7 kb (21 km). Neither the basalts nor the basaltic andesites would have been in equilibrium at any geologically reasonable P and T with quartz eclogite. Equilibration between mantle peridotite and a. typical Rabaul basaltic liquid could have occurred around 35 kb and 1270 °C. A basaltic andesite liquid yields a temperature of 1263 °C and a pressure of 28 kb for equilibration with mantle peridotite.

Partial melting of sufficient volumes of mantle peridotite at these P's and T's requires about 15%  $H_2O$ , but there is no evidence that these magmas ever contained large amounts of water. It is proposed that the Rabaul magmas were initially generated by partial melting of subducted lithosphere and subsequently modified by minor partial melting as they passed through the overlying mantle peridotite.

## Introduction

Rabaul caldera, situated at the northeast tip of New Britain, lies at the eastern end of the New Guinea-New Britain volcanic arc. The caldera is the result of two closely spaced periods of construction and collapse, each collapse being accompanied by the eruption of dacitic pumice ash-flows. Presently, volcanic activity is confined to small cones within the caldera. The geology and petrology of Rabaul caldera is described elsewhere (Heming, 1974) and the mineralogy and geochemistry of the ash-flows is treated by Heming and Carmichael (1973).

Basalt and basaltic andesite lavas of the caldera display a mild absolute iron enrichment trend and contain occasional groundmass pigeonite while the basalts display a reaction relationship between olivine and liquid. Their trace element geochemistry has strong similarities to calc-alkalic series (Jakeš and Gill, 1970), especially in the high abundance of Rb, Ba and Sr and moderate to low K/Rb (529-282) and high Rb/Sr (0.03-0.05). In some other respects however, particularly Ti/Zr and the relative abundance of Ti, Zr and Sr, the Rabaul rocks have close affinities to low-potash tholeiites (Pearce and Cann, 1973). The potassium to sodium ratios vary from 0.25 to 0.52 and overlap the range displayed by the lavas of Tonga which lie between 0.25-0.40 (Ewart et al., 1973). Yet in strong contrast to the flat rare-earth element pattern displayed by low-potassium tholeiites and island arc tholeiites the Rabaul rocks are all enriched in light rare-earth elements ( $\sum La - Eu/Gd - Lu = 2.32 - 1.13$ ) (Heming and Rankin, unpub. data). The lack of an iron enrichment trend in the lavas of some parasitic cones suggests that this effect is some artifice of the magma chamber below the caldera. This, combined with the generally alkalic character of the suite and the high alumina contents of the basalts suggest a calc-alkalic affinity. Basalt and basaltic andesite constitute about 53% of the volume of lava erupted, andesite 30%, dacite 15% and rhyolite about 2%. The chemical variation from basalt to rhyolite can be readily explained by crystal fractionation of the observed phenocryst phases (Heming, 1974).

In this paper, the mineralogy of the basalts, basaltic andesites and andesites is described and P-T paths for the lavas are calculated.

### Mineralogy

### Feldspar

Zoned plagioclase is a ubiquitous phenocryst and groundmass mineral in basic and intermediate lavas from Rabaul; however, a potassium feldspar is absent from the series. Analyses of feldspar are shown in Figure 1. In both the basalts and basaltic andesites the composition ranges from  $An_{95}$  to  $An_{40}$ , with a slightly more restricted range in the groundmass plagioclase ( $An_{80}$  to  $An_{45}$ ). Plagioclase compositions in the andesites and dacites also cover a considerable range ( $An_{85}$ to  $An_{35}$ ) but most lie between  $An_{60}$  and  $An_{40}$ . Rarely, xenocrysts of anorthite are found in coarse-grained clots in the andesites. Groundmass feldspar is relatively rare in the more siliceous rocks, most rocks of andesite and dacite composition having a glassy base. When a groundmass feldspar is present it is usually less sodic than the coexisting phenocrysts.

The range of compositional zoning in individual plagioclase crystals from



Fig. 1. Plagioclase feldspar compositions (mole percent) from the basalts and basaltic andesites (top figure) and andesites, dacites and the rhyolite (lower figure). Compositions of the phenocrysts are plotted in the left-hand triangle and groundmass compositions in the right-hand triangle. Normative compositions are represented by large dots and the numbers refer to analyses published in previous papers (Heming and Carmichael, 1973; Heming, 1974). The dashed line is the trace of the boundary of the two feldspar field



Fig. 2. Variation in the iron content of plagioclase feldspars (cast as  $Fe_2O_3$ ). Iron plotted against Albite (wt percent). Top figure A depicts data from basaltic rocks while the lower figure shows basaltic andesites (triangles) and andesites and dacites (dots)

the basic rocks and the andesites is rather small being at most around 10 mole percent, much lower than in other orogenic lava suites such as the Cascades (Smith and Carmichael, 1968) or Talasea (Lowder, 1970). Potash is low and, recast as the orthoclase molecule, it varies between  $Or_{0.12}$  in the feldspars of a basalt and  $Or_{2.7}$  in a dacite, with rare values as high as 3.3 and 7.4. SrO reaches uniform values of between 0.10 and 0.15 in the feldspars of all rock types except dacites and rhyolite, and shows no systematic variation. Iron as  $Fe_2O_3$  is commonly between 0.6 and 1.4 wt percent and also shows a consistent pattern of variation (Fig. 2). The upper diagram in this figure shows that in the basalts there is a steady increase of  $Fe_2O_3$  with albite content of the feldspar to about  $Ab_{30}$ . No such simple curve is found in the basaltic andesites and andesites (lower diagram, Fig. 2) where the data seem to describe a curve with a maximum around  $Ab_{30}$ .

Such high values of  $Fe_2O_3$  are not uncommon, having been reported by Smith and Carmichael (1968) for Cascades lavas, and from Talasea (Lowder, 1970) where it varies from around 1.0 percent in the feldspars of the basalts to 0.3 wt percent in the rhyolite. Brown and Carmichael (1971) described a relationship between  $Fe_2O_3$  and the anorthite component in basanite and tephrite lavas of Lake Rudolph in the Central African Rift that is similar to the pattern observed at Rabaul, with  $Fe_2O_3$  increasing to a maximum at around  $An_{70}$  and then decreasing with increasing Ab content.

The variation of iron in feldspar may be characterised by this reaction:

plagioclase liquid plagioclase liquid  $CaAl_2Si_2O_8 + Fe_2O_3 = CaFe_2Si_2O_8 + Al_2O_3$ . anorthite Fe-anorthite

An increase in  $a_{\text{Fe}_2\text{O}_3}$  will favour the right-hand side of the equation and may be brought about by an increase in  $f_{\text{O}_2}$  which may be characterized by reactions such as:

$$2 \operatorname{FeO}^{\text{liquid}} + \frac{1}{2} O_2 = \operatorname{Fe}_2 O_3^{\text{liquid}}$$

and

 $4 \operatorname{Fe}_{3} \operatorname{O}_{4}^{\text{liquid}} + \operatorname{O}_{2} = 6 \operatorname{Fe}_{2} \operatorname{O}_{3}^{\text{liquid}}$ .

There is no means by which small fluctuations in  $f_{O_2}$  may be estimated during the early crystallisation history of these liquids; overall one could only predict a decrease in  $f_{O_2}$  with falling temperature. The  $a_{Fe_2O_3}$  however, is not simply dependent on oxygen fugacity. Paul and Douglas (1965) have shown that  $Fe^{3+}$ - $Fe^{2+}$  equilibria in alkali-silicate glasses is a function not only of  $f_{O_2}$  but the activity of the oxygen ion and that there is a correlation between higher  $Fe^{3+}/Fe^{2+}$  and an increase in alkali or feldspathic components. As the amount of alkalic components would increase during crystallization of the Rabaul magmas, this could account for an increase in  $Fe_2O_3$  and a consequent rise in the Fe-anorthite component of the plagioclase.

The termination of this trend of increasing  $Fe_2O_3$  may be caused by the increasing crystallisation of titanomagnetite, as shown for example by the reaction:

$$TiO_2^{liquid} + Fe_2O_3^{liquid} = Fe_2TiO_4^{Ti-magnetite} + \frac{1}{2}O_2.$$
  
ulvospinel

This is in accord with the petrographic observation that titanomagnetite is a more abundant phenocryst phase in the basaltic andesites than in the basalts.

In common with the feldspars of many other orogenic regions (e.g. Smith and Carmichael, 1968), the feldspars from basalts and basaltic andesites from Rabaul are often riddled with fine inclusions of dark brown glass (sieve texture). An attempt was made to analyse some of the larger glass inclusions; these analyses are presented in Table 1. Of the three feldspars, those chosen from lavas 7084 and 7007 have sieved cores, while that from 8082 has a marginal sieve zone. The poor totals are due to large fluctuations in composition across the inclusions, some of which are due to incipient crystallization of plagioclase and a pyroxene in the glass blebs.

Two hypotheses have been proposed to account for the appearance of sieve texture.

(a) Incomplete resorption of earlier formed phenocrysts, which break down to a more acidic feldspar and glass (Macdonald and Katsura, 1965).

(b) Increase in the concentrations of iron and magnesium at the crystal margins until coprecipitation of a ferromagnesium mineral occurs (Bottinga, et al., 1966).

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Table 1. Analyses of glass inclusions(sieve texture) in feldspars and theirC.I.P.W. norms

Sample No.	7084	7007	8082
SiO <sub>2</sub>	51.86	52.09	52.10
TiO <sub>2</sub>	0.92	1.31	1.45
$Al_2O_3$	20.50	16.52	16.42
FeO	9.72	11.03	13.71
MnO	0.28	0.30	0.30
MgO	3.77	7.28	6.05
CaO	11.30	9.67	8.90
Na <sub>2</sub> O	1.97	2.48	1.10
K <sub>2</sub> O	0.65	0.62	1.56
SO <sub>3</sub>	< 0.01	0.19	0.05
Cl	0.01	0.09	0.10
F	0.04	0.10	0.09
Total	101.36	101.60	101.83
Q	2.90	0.00	3.69
Or	3.84	3.66	9.22
Ab	16.53	19.00	8.24
An	45.25	33.17	35.82
HL	0.02	0.16	0.16
TH	0.02	0.34	0.09
Di	8.88	11.66	6.44
Hy	21.76	30.80	35.17
Ol	_	0.15	_
ilm	1.75	2.49	2.75
Fl	0.08	0.21	0.18
Sum	101.01	101.63	101.77

These and all subsequent analyses are by electron microprobe using analysed standards of similar composition to the unknown. Specimen numbers refer to collection 913 in the Department of Geology and Geophysics, University of California, Berkeley.

Lowder (1970) analysed similar inclusions and found the Fe: Mg ratio to be about the same in both inclusions and residual glass in the groundmass. He therefore discounted Bottinga's hypothesis and instead favoured an origin involving incomplete resorption of early formed crystals. Neither of the above explanations is favoured by the data in Table 1 which because of their similarity to the bulk rock compositions instead suggest inclusion of small amounts of the magmatic liquid into the growing crystal. This may happen in the following way. If the feldspar began to grow in a skeletal fashion, perhaps in response to a more rapid nucleation rate, small amounts of liquid would either be enclosed by or form embayments within the growing crystal. As crystallisation proceeded the crystal would not only enlarge itself by growth on the outer boundaries but also by encroaching on the pools of enclosed liquid. If this process were to continue these pools would be consumed forming plagioclase, or more likely olivine or pyroxene would begin to crystallise as the entrapped liquid is progressively depleted in the plagioclase component. This is in agreement with the common observation that small olivines, pyroxenes or even opaque phases occur within sieved zones (Bottinga, et al., 1966). Eruption of the lava would result in a rapid

Sample	7084	8082	7007	6982	8015
SiO <sub>2</sub>	36.08	38.31	38.38	38.31	37.60
FeO	27.84	25.97	25.84	26.87	26.64
MnO	0.63	0.69	0.56	0.60	0.85
MgO	35.49	35.35	34.79	33.32	34.29
CaO	0.22	0.24	0.24	0.17	0.17
Total	100.26	100.51	99.81	99.28	99.55
Molecula	ar Composi	tion			
Fa	26.9	29.1	29.9	30.5	30.5
La	0.3	0.3	0.3	0.2	0.2
Fo	72.7	70.6	69.7	69.2	69.3

### Table 2. Analyses of olivines

increase in the cooling rate and quenching of any of the liquid inclusions that had not previously crystallised.

#### Olivine

Olivine is commonly found as phenocrysts and microphenocrysts in the basalts and some basaltic andesites. In lavas from the North Daughter and Watom Island, they are often replaced by iddingsite and serpentine. Olivine also occurs in some coarse-grained clots in the andesites, along with pyroxene and plagioclase. Analyses of olivine are shown in Figure 3 and average analyses of olivine from basalt, basaltic andesite and glomeroporphyritic clots within andesite are listed in Table 2.

Within individual phenocrysts iron increases toward the rims but there is rarely a steady increase and more often it is a rapid jump near the edge of the crystal, by as much as 6% FeO. MnO shows no consistent pattern of variation, but is noticeably lower in the slightly more iron-rich olivines of the basaltic andesite. NiO could not be detected on the electron microprobe. Compared to olivines from basalts at Talasea (Lowder, 1970) which had NiO values ranging from 0.1 to 0.25, the virtually nickel-free olivines from Rabaul are unusual. Olivine crystals in the andesites are always associated with Ca-rich plagioclase and diopsidic augite in coarse-grained glomeroporphyritic clots and are thought to be xenocrysts because of the close compositional similarity to phenocrysts within the basaltic andesites.

### Pyroxene

Two pyroxenes are commonly found throughout the suite with calcic pyroxene by far the most abundant. Orthopyroxene is a common phenocryst in the intermediate and acid rocks, but it is rather scarce as phenocrysts or groundmass in the basalts and basaltic andesites, though it is often found as rims around olivine and clinopyroxene.

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Fig. 3. Olivine (diamonds) and pyroxene compositions (dots) in mole percent. As in Figure 1, data from basalts and basaltic andesites are plotted in the top figure and from andesites, dacites and rhyolite, in the lower figure. Phenocryst and groundmass compositions are differentiated in this figure. Dashed line represents pyroxene trends from the Skaergaard intrusion (Brown and Vincent, 1963)

Average analyses of representative pyroxenes are given in Table 3 and the range in composition of individual crystals is shown in Figure 3. The range in composition of clinopyroxene phenocrysts is remarkably small and unlike clinopyroxenes from other orogenic lava suites (Lowder, 1970; Smith and Carmichael, 1968) which are more iron-rich in andesites than in basalts, those from Rabaul are all of virtually the same composition and show restricted zonation within individual rocks.

Of the minor elements,  $Al_2O_3$  is highest with average values of 4 wt percent or more being common in the basalts; within individual crystals some zones have much higher amounts. Comparable values are noted by Lowder (1970) but clinopyroxenes from both suites are notably higher in alumina than the 1-2%measured by Ewart et al. (1973) in clinopyroxenes from the younger Tongan lavas. In the case of one phenocryst from basalt 8080, three traverses were made across the grain to determine the distribution of Ca, Si and Al. The results of these traverses are shown in Figure 4. There is a tendency for Al to be concentrated in the rims, so that  $Al_2O_3$  may be as much as 1 percent higher there than in the core. Alumina concentration shows one maximum near the core, another anywhere from 30 to 80 microns from the core and a final peak near the rim. The total



**Fig. 4.** Variation in  $Al_2O_3$  (small dots), CaO (open circles) and SiO<sub>2</sub> (diamonds), all in weight percent, across an individual clinopyroxene phenocryst. The respective scales are marked on the side of the figure. Three traverses were made from the core region to the rim (left to right in diagram) with analyses at approximately 10 micron intervals

variation within the crystal is over 3.5 wt percent  $Al_2O_3$ . Silica tends to behave antipathetically to alumina as would be expected if alumina is entering the tetrahedral site, whereas calcium generally behaves sympathetically.

Experimental studies (Kushiro, 1969; Cohen, et al., 1967; Green and Ringwood, 1967) have suggested that the  $Al_2O_3$  content of clinopyroxene increases with pressure at the expense of anorthite component in the coexisting plagioclase. Silica activity of the magma however, is also an important influences as pointed out by Verhoogen (1962). The role of  $Al_2O_3$  in calcium-rich pyroxenes can be shown in the following reaction:

plagioclase		clinopyroxene		liquid
CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	_	CaAl <sub>2</sub> SiO <sub>6</sub>	+	SiO <sub>2</sub> .
anorthite		Ca-Tschermaks		

Thus fluctuations in  $a_{CaAl_2SiO_6}$  could be caused by a change in  $a_{SiO_2}$ , possibly due to changes in the diffusion rates around a growing crystal, or by variation in *P* and *T*.

The few orthopyroxene phenocrysts in the basalts have a very limited range in composition from about  $En_{74}$  to  $En_{68}$ . In both andesites and dacites the amount of zoning is much larger, from  $En_{75}$  to  $En_{60}$  with occasional compositions around  $En_{50}$ . Three orthopyroxene analyses from the andesites and dacites are shown in Table 3. Al<sub>2</sub>O<sub>3</sub> decreases from around 1 percent in the basaltic orthopyroxene to 0.5 percent in the dacite. CaO is low and shows no particular tendency to increase with FeO.

Pigeonite and sub-calcic augite are found together, mainly in the groundmass of a few basaltic andesites where they possibly represent a disequilibrium quenching similar to the quench scatter noted by Evans and Moore (1968) in groundmass pyroxenes of the Makaopuhi lava lake in Hawaii.

#### Table 3. Analyses of pyroxenes

Clinopy	roxene p	henocr	ysts				_					Ortho pheno	pyroxe ocrysts	ne
	8014	8080 cores	8080 rims	8081	6985	7066 cores	7066 rims	8015	8087	8016	8046	8016	8087	8046
SiO <sub>2</sub>	50.00	49.88	49.21	49.62	50.79	51.09	50.44	50.94	50.92	51.88	51.00	54.22	54.32	54.09
TiO <sub>2</sub>	0.47	0.58	0.51	0.66	0.46	0.49	0.46	0.47	0.46	0.45	0.36	0.31	0.02	0.26
$Al_2O_3$	4.33	3.78	4.31	4.01	2.63	2.18	3.06	2.08	2.52	1.96	1.92	0.91	0.93	0.43
FeO	8.92	8.53	8.80	8.51	10.50	8.20	10.19	9.24	9.84	9.23	9.95	16.90	17.36	18.61
MnO	0.24	0.21	0.22	0.22	0.43	0.45	0.33	0.47	0.42	0.48	0.79	0.81	0.87	1.36
MgO	15.61	14.95	14.44	15.35	15.83	15.51	16.15	14.83	14.60	15.00	13.66	24.14	22.97	23.27
CaO	20.15	21.05	21.20	21.03	18.45	20.56	19.61	20.56	19.94	19.21	19.25	1.43	1.79	1.56
Na <sub>2</sub> O	0.26	0.30	0.30	0.26	0.21	0.29	0.29	0.24	0.27	0.23	0.31	0.03	0.03	0.03
Total	100.00	99.28	98.99	99.66	99.30	98.77	100.53	98.83	98.27	98.44	97.24	98.74	98.28	99.61
Cr <sub>2</sub> O <sub>3</sub> v	vas belov	w the li	mit of s	ensitiv	ity in al	ll speci	mens e	cept 80	014 (0.0	2%). F	ormula	based o	on six o	xygens.
Si	1.862	1.874	1.859	1.858	1.909	1.923	1.878	1.926	1.922	1.956	1.959	1.998	2.015	1.998
Al <sup>IV</sup>	0.138	0.126	0.141	0.142	0.091	0.077	0.122	0.038	0.078	0.044	0.041	0.002	_	0.002
Al <sup>vi</sup>	0.052	0.041	0.051	0.035	0.026	0.020	0.012	0.055	0.035	0.043	0.046	0.038	0.041	0.017
Ti	0.013	0.016	0.014	0.019	0.013	0.014	0.013	0.013	0.013	0.013	0.010	0.009	0.001	0.007
Mg	0.866	0.837	0.812	0.856	0.886	0.870	0.896	0.835	0.821	0.842	0.782	1.315	1.269	1.281
Fe <sup>2</sup> +	0.278	0.268	0.278	0.266	0.330	0.258	0.317	0.292	0.311	0.291	0.320	0.521	0.538	0.575
Mn	0.008	0.007	0.007	0.007	0.014	0.014	0.010	0.015	0.013	0.015	0.026	0.025	0.027	0.043
Ca	0.804	0.847	0.858	0.843	0.743	0.829	0.782	0.832	0.806	0.776	0.792	0.056	0.071	0.062
Na	0.019	0.022	0.022	0.019	0.015	0.021	0.021	0.018	0.020	0.017	0.023	0.001	0.001	0.002

### Iron-Titanium Oxides

Titanomagnetite is the only oxide phase found in the basalts and basaltic andesites. Ilmenite, though rare, joins magnetite in the groundmass of the andesites, dacites and rhyodacites. Analyses of one-phase titanomagnetites are presented in Table 4. When both phenocryst and groundmass titanomagnetites are analysed those from the groundmass are invariably enriched in ulvospinel. Al<sub>2</sub>O<sub>3</sub> is particularly high in some of these titanomagnetites, especially 7066 and 7084. Vanadium decreases steadily from basalt through the andesites, otherwise the minor elements show little variation throughout the series. The range in ulvospinel content for the entire series is  $Usp_{22}$  to  $Usp_{46}$ , about the same as Talasea (Lowder, 1970), but much higher than in basalts and basaltic andesites from Manam Island at the western end of the New Guinea–New Britain arc (Heming, 1974).

### Accessory Minerals

Apatite is found in the basaltic rocks. It forms small euhedral crystals, usually within the groundmass or sometimes enclosed by a phenocryst. Apatites from the basalts and basaltic andesites were not analysed, but considering the similarity in the analyses of apatites from the andesites and rhyolites (Heming and Carmichael, 1973) it might be expected that apatites from the basalts have similar composi-

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	7084 Micro- pheno- cryst	8082 Micro- pheno- cryst	8080 Pheno- cryst	8080 Ground- mass	7007 Micro- pheno- cryst	7066 Pheno- cryst	7066 Micro- pheno- cryst	7066 Ground- mass	6982 Pheno- cryst	6982 Micro- pheno- cryst	6982 Ground- mass	8015 Pheno- cryst	8087 Micro- pheno- cryst	8087 Ground- mass	8046 Pheno- cryst
SiO <sub>2</sub> TiO <sub>2</sub>	0.13 10.67 3.50	0.11 10.91 375	0.13 15.20	0.26 15.78 1 37	0.18 13.37 7 37	0.09 8.62 4.47	0.20 8.56 3.84	0.24 11.67 2.44	0.13 9.08 3.58	0.21 10.60 3.06	0.23 12.29 2.58	0.08 10.32 2.91	0.12 10.15 3.08	0.23 15.20 2.22	0.15 12.88 2.46
М2О3 V2O3 FeO	1.05 1.05	0.74	1.00 74.94	0.78	0.94 0.94 78.54	0.74 0.74 77.94	0.77 78.20	0.84 78.00	1.00 78.12	1.03 78.25	0.90 0.90 77.23	0.62	0.58 77.40	0.60 73.60	0.62 77.01
MnO	0.49	0.53	0.48	0.56	0.45	0.40	0.40	0.50	0.37	0.41	0.46	0.57	0.51	0.58	0.96 2.07
CaO NiO	0.03 n.d.	0.05	0.11 0.11 0.05	0.27 0.06	0.05 0.08 0.08	0.01 0.05 0.05	0.06 0.04	0.07 0.06 0.06	0.01 0.04 0.04	0.06	0.03 0.03	0.02	0.01	0.11	0.02 0.04
Total	95.50	95.63	95.73	95.00	96.52	94.94	93.46	94.25	94.59	95.16	94.43	95.76	93.39	93.54	95.92
Recalculat Fe <sub>2</sub> O <sub>3</sub> FeO	ed analys <sup>,</sup> 43.52 38.83	es. UlvosF 45.25 38.60	sinel basis 36.13 42.43	s (Carmich: 35.08 43.31	ael, 1967) 39.63 42.88	) 47.32 35.36	46.11 36.71	41.28 40.85	46.61 36.18	43.88 38.77	40.01 41.23	46.17 37.60	44.73 37.15	34.35 42.69	41.72 39.47
Total	99.86	100.16	99.35	98.52	100.49	99.68	98.08	98.39	99.26	99.56	98.44	100.39	98.27	96.98	100.10
Mole % ulvospinel	30.13	30.83	43.03	45.85	38.02	24.05	24.99	34.25	25.76	30.41	35.87	28.85	29.11	44.62	36.28

Table 4. Analyses of Titanomagnetites

Basaltic Lavas from Rabaul Caldera, Papua New Guinea

tions. Pyrrhotite, which is often found in the siliceous rocks, has not been identified in any of the basalts. In analyses of the trace elements in these rocks (Heming, 1974) it was noted that Cu was enriched in basalts 8080 and 8082, and this may be due to the presence of pyrrhotite as those from the dacites contain as much as 1.37 Cu wt percent.

### **Plagioclase Temperatures**

The empirical plagioclase geothermometer derived by Kudo and Weill (1970) and modified by Mathez (1973), was applied to the basalts and basaltic andesites from Rabaul. Plagioclase temperatures vary as a function of  $pH_2O$  and therefore cannot be used to estimate quenching temperatures if  $pH_2O$  is unknown, which is the case in these rocks. But temperature estimates can be made for the equilibration of phenocryst phases in some rocks by using either the orthopyroxene clinopyroxene geothermometer (Wood and Banno, 1973) or olivine-clinopyroxene (Powell and Powell, 1974). These estimates can then be used to calculate the range of  $pH_2O$  during crystallisation of the lava.

The results for three rocks are listed in Table 5. No temperature estimate is available for number 7084, while number 7007 has a phenocryst equilibration temperature of  $1040^{\circ}$ - $1060^{\circ}$  C (olivine-clinopyroxene) and 6985 a temperature of  $1050^{\circ}$  C (orthopyroxene-clinopyroxene).

The temperatures for 0, 0.5 and 1.0 kb are very high, much higher than the equilibration temperatures for the ferromagnesian phenocrysts. Assuming the plagioclase temperatures to be correct, equilibration temperatures for the ferromagnesian phenocrysts would mean partial pressures of water of 3-4 kb. Also, as the temperature difference between core and rim and core and groundmass is very small, the only way to get a sensible temperature difference between liquidus and solidus is to assume that pH<sub>2</sub>O in these lavas has increased with crystallisation. Such a high pH<sub>2</sub>O in these lavas is hard to accept when no hydrous

	Tempera	ture at various	s $P_{\rm H_2O}$ (T in de	grees centigrade)
	0	0.5	1	5 K-
7084				
basalt groundmass	1237	1291	1238	907
phenocrysts	1255	1395	1261	1015
7007				
basalt groundmass	1211	1258	1205	870
phenocrysts, rim	1216	1266	1213	964
phenocrysts, core	1201	1245	1193	916
6985				
basaltic andesite groundmass	1197	1242	1187	822
phenocrysts, rim	1185	1225	1172	886
phenocrysts, core	1195	1239	1185	843

Table 5.	Plagioclase	temperatures	for	selected	rocks
1 4010 01	1 14 10 01 400	tomporator.	101	00100104	100000

phase appears as a phenocryst or in the groundmass and deuteric alteration of olivine has not been observed in many of the lavas.

#### Proposed Crystallization Paths in the Basaltic Lavas

Nicholls and Carmichael (1972), Bacon and Carmichael (1973) and Carmichael et al. (1976) have demonstrated a means of calculating temperature and pressures at which phenocrysts may have been in equilibrium with their host liquid or that liquid with some source material. At Rabaul, the lack of coexisting ilmenite and magnetite precludes estimation of a surface quenching temperature for the lavas and consequently any reliable calculation along the lines of those suggested by Bacon and Carmichael (1973). This is a problem faced by many petrologists working with island arc lavas but as most basaltic rocks quench at temperatures between 950° C and 1050° C, it is possible to estimate the range of temperature and pressure over which phenocrysts and magma may have been in equilibrium. Estimates were attempted for both phenocrysts and microphenocrysts of six lavas; four basalts and two basaltic andesites, and the results are shown in Table 6. Specimen numbers refer to Heming (1974). For a fuller discussion of the theoretical basis of these calculations and the development of the equations the reader is referred to Bacon and Carmichael (1973), Nicholls et al. (1971), Nicholls and Carmichael (1972) and Carmichael et al. (1976).

These papers also present a full discussion of the estimation of the activities of both liquid and solid components and mole fractions of the liquid components. Thermodynamic data for the various components used in the equations may be found in Bacon and Carmichael (1973) and Carmichael et al. (1976) and additional thermochemical data was culled from Kelley (1960), Robie and Waldbaum (1968) and Stull and Prophet (1971).

The basalts for which calculations have been made contain phenocrysts of plagioclase, clinopyroxene and titanomagnetite along with olivine in 7007 and orthopyroxene in 7084. Basaltic andesites 7066 and 6985 contain all the above minerals except olivine.

#### Method of Calculation

In this paper the more rigorous method of calculation proposed by Carmichael et al. (1976) is used in which the compressibility and thermal expansion of the phases in the reaction are taken into account while  $\Delta H^0 f_{298}$ ,  $S^0_{298}$  are taken to the temperature of interest by using the appropriate heat capacity power function.

In the case of the Rabaul lavas the mineralogy allowed the liquid components  $CaMgSi_2O_6$ ,  $NaAlSi_3O_8$ ,  $KAlSi_3O_8$ , and  $Fe_2SiO_4$  to be used along with  $SiO_2$  and  $Al_2O_3$ .

Estimation of the  $a_{SiO_2}^{liquid}$  is difficult because of the absence of olivine-orthopyroxene pairs in the groundmass of the basalts. Carmichael et al. (1976) however, noted that  $RT \ln_{yTiO_2}^{liquid}$ , for a number of lavas embracing the range basalt to rhyolite, depended on both temperature and amount of TiO<sub>2</sub> in the lava. Hence given  $X_{\text{TiO}_2}$ , from an analysis of the rock,  $RT \ln_{\gamma \text{TiO}_2}^{\text{liquid}}$  may be calculated which upon rearrangement and insertion of a plausible value for T gives  $\ln_{\gamma \text{TiO}_2}^{\text{liquid}}$ . This value was then put into the following equation:

$$\begin{array}{rcl} & \text{Olivine} & \text{Ti-magnetite} \\ \text{TiO}_2 + & \text{Fe}_2\text{SiO}_4 &= & \text{Fe}_2\text{TiO}_4 &+ & \text{SiO}_2, \\ \text{liquid} & \text{fayalite} & & \text{ulvospinel} & & \text{glass} \end{array}$$
(1)

whence

$$\ln \gamma_{\text{TiO}_2}^{\text{lava}} = \frac{\Delta G^0}{RT} + \ln a_{\text{Fe}_2\text{TiO}_4}^{\text{titanomagnetite}} + \ln a_{\text{SiO}_2}^{\text{lava}} - \ln x_{\text{TiO}_2}^{\text{lava}} - \ln a_{\text{Fe}_2\text{SiO}_4}^{\text{olivine}}$$
(2)

from which  $a_{SiO_2}$  can be calculated.

Given a value for  $a_{SiO_2}$  the equation,

$$\begin{array}{rcl} CaMgSi_2O_6 &+ & Al_2O_3 &+ & \frac{1}{2}SiO_2 \end{array} \rightleftharpoons & CaAl_2Si_2O_8 &+ & \frac{1}{2}Mg_2SiO_4 \\ solid & & liquid & glass \end{array}$$
(3)

can then be used as follows to give an estimate of  $a_{Al_2O_3}^{lava}$ ,

$$\ln a_{\text{Al}_2\text{O}_3}^{\text{lava}} = \frac{\Delta G^0}{RT} + \ln a_{\text{CaAl}_2\text{Si}_2\text{O}_8}^{\text{plagioclase}} + \frac{1}{2}\ln a_{\text{Mg}_2\text{Si}_4}^{\text{olivine}} - \frac{1}{2}\ln a_{\text{Si}_2}^{\text{lava}} - \ln a_{\text{CaMg}}^{\text{pyroxene}} .$$
(4)

### Equilibration with a Solid Residue

Equilibration was attempted with four kinds of solid residue; microphenocrysts, phenocrysts, mantle peridotite and quartz eclogite.

#### Microphenocrysts

No reasonable solutions for P and T were obtained for the microphenocrysts probably because of the sensitivity of the equations to variations in composition. All of the solutions gave small negative pressures and temperatures less than the quench temperatures, suggesting near surface equilibration.

### Phenocrysts

For the phenocryst phases solutions were obtained for six rocks using the components  $CaMgSi_2O_6$ ,  $NaAlSi_3O_8$  and  $Fe_2SiO_4$ . As there is no estimate of the actual quench temperature for each rock a possible pressure of equilibration is given for each of the assumed quench temperatures. For three of the rocks however, one can calculate an independent equilibration temperature for the phenocrysts. In samples 7007 and 8082 the presence of olivine and orthopyroxene phenocrysts allows use of the olivine-clinopyroxene geothermometer calculated by Powell and Powell (1974) which has a slight pressure dependence. For 6985, which contains orthopyroxene and clinopyroxene phenocrysts, the orthopyroxene-clinopyroxene geothermometer suggested by Wood and Banno (1973) was employed. This geothermometer is independent of pressure. For each quenching temperature

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Sample No.	Quench	Equilib	ration	Liquid components used	
	Temp. °C	<i>P</i> ⋅ kb	$T^{\circ}$ C	_	
7007 basalt	950	11.5	1077	diopside + albite with	
	1000	8.2	1082	Ol-Cpx geothermometer	
	1050	4.3	1083		
7066 basaltic andesite	950	9.7	1040		
	1000	9.5	1085	diopside + albite	
	1050	10.1	1140		
8080 basalt	950	8.7	1025		
	1000	8.8	1075	diopside + albite	
	1050	9.0	1125	-	
8082 basalt	950	10.9	1055	diopside + albite with	
	1000	6.8	1050	Ol-Cpx geothermometer	
	1050	3.2	1045		
6985 basaltic andesite	950	9.9	1058	diopside+albite with	
0,00 000000 000000	1000	7.3	1072	Opx-Cpx geothermometer	
	1050	5.2	1086	· · · ·	

Table 6. Calculated equilibration P's and Ts for phenocrysts

the results (ie the intersections of the equilibration curves) were averaged and they are presented in Table 6. Without an independent method of fixing a quench temperature it is difficult to choose between the three solutions, but in some cases a close agreement between three curves gives a favoured result, e.g. 6.8 kb and 1050° for 8082. The best agreement between curves suggests equilibration pressures of 7 to 11 kb and temperatures that are around 100° above quenching.

An additional estimate of an equilibration pressure for the phenocrysts in sample 6985 may be made using the silica geobarometer of Nicholls et al. (1971). The chosen quench temperature in this case was  $1000^{\circ}$  C and the equilibration temperature for the phenocrysts was taken as being equal to the opx-cpx temperature of  $1050^{\circ}$  C.

#### The reactions

and,

olivine liquid orthopyroxene  

$$Mg_2SiO_4 + SiO_2 \rightleftharpoons 2MgSiO_3$$
 (6)  
forsterite glass enstatite

were used to fix  $a_{SiO_2}$  for the phenocrysts at some unknown pressure. Although olivine is not present in rock 6985 it is found in sample 6982 which is very similar in composition and age to 6985 (Heming, unpublished data). Therefore it was

decided to attempt a solution in this case as an additional estimate. The two solutions, 5.7 kb and 4.2 kb are lower than the equilibration pressure of 7.3 kb (Table 6). The results indicate equilibration pressures in the range 3 to 11 kb with a clustering of solutions around 8 to 10 kb. The result for 8082 given above and those using the silica geobarometer suggest lower pressures of the order of 7 kb or less. All of the pressures indicate depths above the Moho which lies at 32 km beneath Rabaul (Finlayson and Cull, 1973).

Whether the calculated equilibration pressures indicate the depth of a magma chamber or chambers beneath the caldera is debatable. Attempts by Kubota and Berg (1967) to identify magma chambers beneath the Katmai Range by seismic methods suggested that chambers may be located over a range of depths, with clusters around 10 to 20 km related to overlying valcanoes and a second more random grouping between 20 km and the Moho. Hence the range of depths suggested by the data in Table 6 may in part be real. The basaltic phenocrysts yield no evidence of crystallisation in shallow (< 5 km) magma chambers as may have occurred in the case of phenocrysts in the rhyolites (Heming and Carmichael, 1973).

### Mantle Peridotite and Quartz Eclogite

Green and Ringwood (1967, 1968) proposed a quartz eclogite parent for the derivation of island-arc magma series. More recently Marsh and Carmichael (1974) present evidence to suggest that partial melting of quartz eclogite in a descending lithosphere slab can account for the origin of island-arc magmas and also for the depth:  $K_2O$  relationship noted in particular by Hatherton and Dickinson (1968). An alternative origin for the tholeiitic magmas in island arcs involving partial melting of hydrous peridotite mantle has been suggested by Nicholls and Ringwood (1973), Nicholls (1974) and Kushiro (1972, 1973) amongst others. Both sources were examined in this study.

Solutions involving a number of components including KAlSi<sub>3</sub>O<sub>8</sub>, SiO<sub>2</sub> and CaMgSi<sub>2</sub>O<sub>6</sub> for the quartz eclogite and SiO<sub>2</sub>, CaMgSi<sub>2</sub>O<sub>6</sub> and Al<sub>2</sub>O<sub>3</sub> for mantle peridotite, were attempted. Activities of solid components in the quartz eclogite were taken as  $a_{SiO_2} = 1$ ,  $a_{KAISi_3O_8} = 1$ ,

 $a_{\text{CaMgSi}_2\text{O}_6} = 0.3$ ; and for mantle peridotite  $a_{\text{CaMgSi}_2\text{O}_6} = 0.5$ ,  $a_{\text{Mg}_2\text{SiO}_4} = 0.9$ ,  $a_{\text{MgSiO}_3} = 0.88$  and  $a_{\text{Mg}_2\text{AlO}_4} = 0.51$ .

In addition to the components  $CaMgSi_2O_6$ ,  $KAlSi_3O_8$  and  $SiO_2$ , the following equation was used to define  $a_{Al_2O_3}$  in the solid residue,

olivine orthopyroxene  

$$Mg_2SiO_4 + Al_2O_3 \cong Mg_2AlO_4 + MgSiO_3.$$
 (7)  
forsterite liquid spinel enstatite

The  $a_{Al_2O_3}$  in the liquid was calculated from the equation:

 $\begin{array}{ll} \text{clinopyroxene} \\ \text{CaMgSi}_2\text{O}_6 &+ \text{Al}_2\text{O}_3 &+ \frac{1}{2}\text{SiO}_2 \\ \text{diopside} & \text{liquid} & \text{liquid} \\ \end{array} \begin{array}{l} \text{plagioclase} \\ \text{CaAl}_2\text{Si}_2\text{O}_8 &+ \frac{1}{2}\text{Mg}_2\text{SiO}_4. \\ \text{anorthite} \\ \end{array} \begin{array}{l} \text{forsterite} \end{array} \tag{8}$ 

For the quartz eclogite no reasonable solutions were obtained. Equilibration pressures were either too high, i.e., greater than several hundred kilobars, nor no real solution to the equation was possible despite the use of a variety of eclogite compositions (e.g. Yoder and Tilley, 1962).

Equilibration with mantle peridotite compositions was attempted for three rocks; two basalts (7084, 7007) and one basaltic andesite (6985).

For the basalts, sample 7007 yielded a close intersection of equilibrium curves using four components (CaMgSi<sub>2</sub>O<sub>6</sub>, Mg<sub>2</sub>SiO<sub>4</sub>, Fe<sub>2</sub>SiO<sub>4</sub> and Al<sub>2</sub>O<sub>3</sub>;  $T_{quench} = 950^{\circ}$  C) at 1270° C and 34 kb. For 7084 the result using only two components (Fo, Fa) yielded a temperature of 36 kb at 1270° C. In the case of the basaltic andesite a close intersection for three components (Fo, Fa, Di;  $T_{quench} = 950^{\circ}$ C) gave a temperature of 1263° C and 28 kilobars.

The estimated equilibrium temperature for the basalts lies below the anhydrous liquidus for SiO<sub>2</sub>-saturated tholeiite (Nicholls and Ringwood, 1973) and near the liquidus curve for a 15% H<sub>2</sub>O content. The estimated equilibrium P and T for the basaltic andesite lies around 50° C beneath the basaltic andesite liquidus of Green (1972).

### Discussion

The results of the equilibrium calculations strongly favour mantle peridotite as a source composition for the basic magmas erupted at Rabaul and not quartz eclogite. Nicholls and Ringwood (1973) and Nicholls (1974) have shown that the addition of water to pyrolite compositions extends the stability range of olivine and upon partial melting results in the formation of SiO<sub>2</sub>-saturated tholeiitic fluids. Fractionation of olivine would produce liquids of quartz tholeiite and basaltic andesite composition.

The problem in applying such a model to the generation of the Rabaul magmas is the high water content, for there is no firm evidence to support a high  $p_{\rm H_2O}$  in these melts. The evidence yielded by the plagioclase geothermometer is difficult to interpret and at best is equivocal. If plagioclase, olivine and pyroxene crystallised over the same temperature range then the temperatures deduced from the ferromagnesian phenocrysts would indicate 3 to 4 kb  $p_{\rm H_2O}$ . The absence of any hydrous phase in the basaltic or indeed the andesitic lavas (only a welded andesite tuff contains amphibole and phlogopite, Heming and Carmichael, 1973) is also evidence against significant hydration of these magmas. It is also likely that the high plagioclase temperatures indicated for the dry melts (Table 5) did occur and that the ferromagnesian phenocrysts only began to crystallise at much lower temperatures.

Other arguments against a simple model of partial melting of mantle peridotite could be made based on the abundance of the compatible elements and the light REE enrichment found in these rocks. The solution must lie in a two-stage model involving melting of subducted lithosphere to produce calc-alkalic liquids which are then modified as they rise through the overlying mantle peridotite wedge. Nicholls and Ringwood (1973) proposed a model in which partial melting of quartz eclogite between 100 and 150 km produces melts which then react with the overlying mantle imprinting a highly fractionated trace element pattern and forming a wet garnet pyroxenite. This then rises to the surface undergoing partial melting resulting in calc-alkalic magmas. This model would still involve a hydrous magma for which there is no unequivocal evidence.

An alternative scheme proposed here involves the production of magmas by anhydrous melting of subducted lithosphere. These then rise through and promote partial melting of the mantle peridotite wedge beneath the island arc which causes dilution of the original fractionated trace- and minor-element chemistry and some modification of the major element chemistry. This results in a "masking" of the original source chemistry which equilibrium calculations like those outlined above cannot penetrate.

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