reciprocal or direct lattice constant variance-covariance ma-subscripts m and n assume values 2 and 3 or 4 and 6 according is a function of the edges or of the unit cell angles. Furwhether thermore

 $\partial \Delta / \partial x = -(1/2A)(\partial B/\partial x) \pm [1/\sqrt{(B^2 - hAC)}][(B/2A)(\partial B/\partial x) - (\partial C/\partial x)]$ (11) ∂B/∂x=(A34-A12)(y4-y3-y2*y1)

2C/3x=124(y2-y1)+1222(y4-y3)-12234(y4-y3+y2-y1)

 $\partial \Delta / \partial y = -(1/2A)(\partial B/\partial y) \pm (1/\sqrt{B^2 - 4AC})[(B/2A)(\partial B/\partial y) - (\partial C/\partial y)]$ (12) ∂B/∂y=-(Δ34-Δ12)(x4-x3-x2+x1)

 $\frac{\partial C}{\partial y} = - \frac{\lambda_{34}^2}{(x_2 - x_1)} - \frac{\lambda_{12}^2}{(x_4 - x_3)} + \frac{\lambda_{12}\lambda_{34}}{(x_4 - x_3 + x_2 - x_1)}$

$$\begin{split} & 2G/\partial y = -\Delta_{3,1}^2(x_2-x_3) + \Delta_{1,2}^2(x_1-x_3) + \Delta_{1,2}\Delta_{3,4}(x_1-x_3+x_2-x_3)) \\ & \text{Equations (11) and (12) must be used with the positive sign or the negrative sign according to whether the value of A accepted has been obtained from (8) with the positive or negative square root of the discriminant. Variance and covariance terms required to solve equation (10) are unally available on the output of the lattice constant refinament programs. Incidentally, for correct utilization of (10) its bould be borne in mind that as this as the same conternal, covariance, in degree. If on applying (8) one assumes that the errors are uncorrelated, i.e. cov(x_0, x_0), then the subar root of the value os of 2(a) = (bA/bx)^2 \gamma_{min} (13) \\ & m_{10} = (b_1, b_1, b_2, b_2) = (b_1, b_2, b_1) = (b_1, b_2, b_2) = (b_1, b_2, b_3) = (b_1, b_2, b_3) = (b_1, b_3) = (b_2, b_3) = (b_1, b_3) = (b_2, b_3) = (b_3, b_3) = (b_1, b_3) = (b_1, b_3) = (b_1, b_3) = (b_2, b_3) = (b_1, b_3) = (b_1, b_3) = (b_1, b_3) = (b_2, b_3) = (b_1, b_3) =$$

Errors:

 $\sigma^2(\mathcal{O}r) = (\partial\mathcal{O}r/\partial x)^2 V_{mm} + (\partial\mathcal{O}r/\partial y)^2 V_{mn} + 2(\partial\mathcal{O}r/\partial x)(\partial\mathcal{O}r/\partial y) V_{mn}$

where V_{mm} , V_{mn} , V_{mn} , V_{mn} have been previously defined. In this case, the subscripts *m* and *N* of course assume values 2 and 3 in the reciprocal lattice constant variance-covariance matrix. Moreover:

 $\partial O_{F}/\partial x = -(1/2D)(\partial E/\partial x) \pm [1/\sqrt{(E^{2}-4DF)}](E/2D)(\partial E/\partial x) - (\partial F/\partial x)]$ (15)

 ${}^{\partial E/\partial x=(Or_{24}-Or_{13})(y_4-y_3-y_2+y_1)}$

 $\frac{\partial F}{\partial x} = Or_{24}^2 (y_3 - y_1) + Or_{13}^2 (y_4 - y_2) - Or_{13} Or_{24} (y_4 + y_3 - y_2 - y_1) \\ \frac{\partial Or}{\partial y} = -(1/2D) (\partial E/\partial y) \pm (1/\sqrt{(E^2 - 4DF)}) [(E/2D) (\partial E/\partial y) - (\partial F/\partial y)] (16)$

 $\partial E/\partial y = -(\partial r_{24} - \partial r_{13})(x_4 - x_3 - x_2 + x_1)$

 $\partial F/\partial y = -Or_{24}^2(x_3-x_1) - Or_{13}^2(x_4-x_2) + Or_{13}Or_{24}(x_4+x_3-x_2-x_1)$

When applying (14), it should be noted that double signs must be used in expressions (15) and (16) in a similar way to those used in calculating the errors in δ . If one assumes that the errors are uncorrelated the cross product of equation (14) becomes zero.

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J.F.W.Bowles : History of Fe₃O₄-FeTiO₃ grains (App.)

An estimation of the probable errors of the method of tracing the cooling history of complex magnetite-ilmenite grains and a discussion of the results produced by using different methods of treatment of the minor elements contained in these minerals when using the Buddington and Lindsley (1964) geothermometer.

(Appendix to "A method of tracing the temperature and oxygen-fugacity histories of complex magnetite-ilmenite grains", this vol. pp 103-109)

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Estimation of errors in the method of calculation used by Bowles (1977)

The formation of ilmenite from titanomagnetite frequently shows separate generations of exsolved ilmenite. Bowles (1977) used microprobe analyses of host magnetite and two generations of ilmenite with an estimate of the volume of each phase to derive compositions representing different stages in the cooling history of a complex magnetite ilmenite grain. Use of the Buddington and Lindsley (1964) geothermometer provided two points in the temperature and oxygen-fugacity history of the specimen. In this appendix a comparison of the errors of measurement is used to determine the likely errors in the result, to check the validity of that result.

The quantity of TiO, in the titanomagnetite is directly related to the quantity of ulvospinel that is calculated. One standard deviation of the microprobe X-ray counts leads to an estimated error of ± 0.12 % TiO₂ on the measured value of 8.07% ${\rm Ti0}_2^{}.$ This error encompasses the X-ray statistical variation and the mineralogical variation between 20 measured localities on 5 adjacent magnetites. Only minor amounts of TiO₂ are subtracted when the minor elements are expelled to give 23.7 \pm 0.35% ulvöspinel. Since the magnetite-ulvöspine? contours on the Buddington and Lindsley (1964) diagram are the most steeply inclined they have the greatest influence on the horizontal, temperature axis. At the condition of equilibrium of the magnetite with the ilmenite lamellae a variation of 10% ulvospinel results in a temperature variation of 25⁰C, hence the calculated error of 0.35% ulvospinel gives a temperature error of + 0.88°C and a value

of $\pm 1^{\circ}$ C is adopted here.

The quantity of total Fe0 contained in the ilmenite lameliae is 41.19% with an error of + 0.33% estimated from one standard deviation of the 20 microprobe measurements on limenite lamellae within the five adjacent magnetite grains. Only a small proportion of the measured Fe forms the 3.02% hematite but since a subtraction is involved the whole of the error has been loaded onto the hematite. The less steeply inclined ilmenitehematite lines of the Buddington and Lindsley diagram indicate a greater influence on oxygen fugacity and at the lower temperature equilibration 2% hematite represents a change of about 1 log f02 in oxygen fugacity. Thus an error of 0.33% hematite represents an error of 0.17 log f0, oxygen fugacity and a value of <u>+</u> 0.2 is taken here.

At the condition of equilibrium of the granular ilmenite the influence of errors in the microprobe results for the granular ilmenite is less, since the lines on the Buddington and Lindsley diagram are spaced more closely and reasoning similar to the above leads to -11.5 \pm 0.04 log f0₂ for the oxygen fugacity measurement. In the determination of the earlier magnetite composition, errors introduced by other techniques must be considered. The change in cell size of the magnetite with composition is small, so the effect of errors in composition on cell size may be neglected. However the influence of the less precise point counting technique must be considered here. The same five adjacent magnetite grains for which microprobe results were obtained, were covered by point counting on equally spaced linear traverses and 1019 points were counted. The five grains in different orientations show wide variation in the width of the ilmenite lamellae at their intersection with the polished surface. However, since for each grain the relative orientation of the magnetite to the ilmenite is preserved, the measured value of the ratio of area is little affected by changes in orientation. The proportion of ilmenite lamellae determined In this way is 16.1 + 2.03% with the error determined at the 95% confidence limit. This figure is used (Bowles, 1977) to determine that the number of atoms of Fe and Ti within the ilmenite is $(6.12 \pm 0.76) \times 10^{21}$ and $(33.60 \pm 0.84) \times 10^{21}$ within the magnetite. A total of $(39.72 \pm 1.14) \times 10^{21}$ atoms, of which $(5.61 \pm 0.16) \times 10^{21}$ are Ti, are calculated for the magnetite producing a Ti/(Ti + Fe) ratio of 0.141 ± 0.004 and leading to a molecule containing 42.3 ± 1.12% ulvospinel. At the conditions of equilibration of the granular ilmenite a change of 10% ulvospinel corresponds to a 29⁰C change in temperature and leads to a temperature of $930 \pm 3.2^{\circ}$ C. Because the lines on the Buddington and Lindsley diagram intersect at a low angle,an error on one set of lines influences estimates of error on the other axis

and the error in oxygen fugacity due to the microprobe results is masked by the larger error (0.1 log $f0_{2}$) measured from the diagram.

The 16.1% of the second generation ilmenite lamellae changes the magnetite composition by 18.6 Mol %. The third generation of ilmenite lamellae occupy less than 0.1% of the specimen. These lamellae can only change the molecular percentage of the ulvöspinel in the magnetite by less than one third of the 0.35% error of the microprobe results, so that they have not been considered in the calculation.

Mineralogical measurements can clearly be placed on the Buddington and Lindsley diagram with a good precision but the accuracy of the whole set of results is governed by the error limits of $\pm 30^{\circ}$ C and $\pm 1 \log f0_{2}$ laid down by Buddington and Lindsley for their experimental work.

Discussion of the method of treatment of minor elements used by Bowles (1976, 1977)

Complete analyses of naturally occurring iron-titanium oxides often show appreciable concentrations of other elements. A number of methods of dealing with these impurities are in common use. One method is proposed by Chevallier, in Vincent, Wright, Chevallier, and Mathieu (1957), whilst another method, due to D. R. Wones, is described by Buddington and Lindsley (1974). The methods appear similar in that divalent elements are gathered together as \underline{R} , trivalent elements appear as $\underline{R}_2 \boldsymbol{0}_3$, and tetravalent form 102. However, the use of these groupings by various authors is very different. In the method of Chevallier, magnetite and magnetite-like molecules (eg MgO. Al₂O₂) are grouped together and taken as magnetite. TiO₂ and SiO₂ are equated to form ulvöspinel by the addition of 2 Fe0, and the ulvospinel is taken to include ulvöspinel-like molecules such as 2 Mg0. Ti0₂, where some of the TiO_2 in the entire group is in fact SiO_2. Remaining $\underline{R0}$ and $\underline{T0}_2$ are associated to form an ilmenite suite of minerals. Molecular proportions of magnetite, ulvospinel and ilmenite are calculated and thus contain the impurities distributed between them in an arbitrary manner. A similar treatment has been described by Carmichael (1967a). The method of Buddington and Lindsley groups and discards $\underline{R0}$, $\underline{R_20}_3$ and $\underline{2R0}$, $\underline{Si0}_2$ but in this method R0 and $\frac{R}{2}$ 03 do not contain iron oxide. Either RO or R_03 are left, and these are grouped with small amounts of iron oxide and TiO_2 as Fe0. \underline{R}_20_3 or as equal amounts of $\underline{R}0$, Fe_20_3 and $\underline{2}\underline{R}0$. Ti0₂, and discarded from the system. Remaining iron and titanium oxides are grouped so as to lie on the appfopriate solid solution series,

Anderson (1968) has proposed a variation on this method in which the treatment of the minor elements in the magnetite is changed, following the work of Speidel (1967), so that $2\underline{R}0.TiO_2$ is preferred to $\underline{R}0.Fe_2O_3$, and RO.R20, contains a proportion of FeO as RO. A more comprehensive discussion of the reasons why Anderson made this change is contained in a later paper by Speidel (1970).

Buddington and Lindsley suggest that, if the impurities have not been measured, then the iron-titanium oxides can be rounded up to 100%. This method is occasionally used (Duchesne 1972) where the impurities have been measured and then discarded. However, this method can only be applied where and Fe $^{3+}$ have been determined, and the major phases can be computed without recourse to the minor elements. If this ratio has not been determined, as with microprobe analyses, it is necessary to associate the minor elements with small amounts of the major elements before the major phases can be assembled by distributing total Fe between ${\rm Fe}^{2+}$ and ${\rm Fe}^{3+}$ to form ilmenite and hematite or ulvöspinel and magnetite. If the results are to be used in conjunction with the Buddington and Lindsley geothermometer, it is essential to decide which method should be used. Since the experimental system of Buddington and Lindsley involved only the pure FeO ~ TiO_2 - Fe_2O_3 system, the methods of Chavallier and Carmichael are inappropriate here. The methods of Chevallier and of Buddington and Lindsley require that the Fe²⁺ to ${\rm Fe}^{3+}$ ratio is known and as such are inappropriate for microprobe results. The method of Wones acknowledges the minor elements, yet gives the pure system as the final result. This method, as modified by Anderson, appears to be the most satisfactory and is the method selected here and used elsewhere (Bowles 1976, 1977). A specimen previously described (Bowles 1977) is used in Table I to illustrate the difference in the results produced by the various methods.

By adopting different methods of calculation of the distribution of trace elements, significantly different results may be obtained. This is Illustrated by the work of Elsdon (1972) in which he has made a comparison between iron-titanium oxides of the Kap Edvard Holm layered gabbro calculated according to Anderson, and the same phases from Skaergaard as calculated by Buddington and Lindsley, from the analyses of Vincent and Phillips (1954). Table II shows one of Elsdon's analyses (No 2) recalculated by these methods and it is seen that the method of Anderson gives a result some $80^\circ C$ lower and with an oxygen fugacity about 1.5 to 2.5 more negative on the log $\mathrm{f0}_2$ scale. Eldson's comparison showed that the Kap Edvard Holm series equilibrated at a temperature 200 to 300⁰C lower than Skaergaard but it is

seen that a proportion of this temperature difference i different method of calculation of the results. However the change in the oxygen fugacity caused by the change in calculation is twice as large and in the opposite direction to the comparison made by Elsdon. As it happens this does not detract from Elsdon's argument, since the change brought about by changing the method of calculation has the effect of sliding the results along the buffered cooling curve.

It is therefore worth noting that analytical results can, in some cases, be affected quite strongly by the method of calculation of the minor elements, and if comparisons are to be made they should clearly be between results calculated in the same manner. The method due to Wones (Buddington and Lindsley, 1964) as modified by Anderson (1968) is preferred for calculations based on microprobe results destined for use on the Buddington and Lindsley geothermometer. Analyses should contain minor elements which are used to subtract a proportion of the Fe and Ti, to leave a result which may be compared with the pure experimental system of Buddington and Lindsley. Comparison of the remaining Fe and Ti with appropriate formulae enables the total Fe to be allocated to Fe $^{2+}$ and Fe $^{3+}$.

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TABLE I A comparison of the results obtained for the molecular composition of a single specimen of magnetite and ilmenite lamellage after the minor element distribution has been calculated using several published methods.

The analysis of these phases was given by Bowles (1977 p. 107).

Method of					
calculation of minor elements	Chevallier	Wones	Buddington & Lindsiey	Carmichael	Anderson
Reference	Vincent <u>et</u> <u>al</u> .(1957)	Buddington <u>et al</u> . (1964)	Buddington <u>et al</u> . (1964)	Carmichae) (1967a)	Anderson (1968)
Method					
adopted in	Vincent <u>et</u>		Buddington	Carmichael	Anderson
papers by:	<u>al</u> . (1957)		et al.	(1967a)	(1968)
			(1964)	Carmichael	Elsdon
			Duchesne	(1967ь)	(1972)
			(1972)	Nicholls	Czamańske
				(1971)	<u>et al</u> . (1972).
finnen ite %	96.0*	96.6	87.6	96.0*	96.6
Hematite %	4.0*	3.4	12.4**	4.0+	3.4
Magnetite %	72.9	74.0	73.5	72.9	76.3
ülvöspinet %	27.1	26.0	26.5	27.1	23.7
Temperature (°C)		678		675	662
Log f0,	-	18.2		-18.5	-19.0

* RO. R203 *R203 *TIO2

(Table II overleaf)

M 18

TABLE II Comparison of calculations of results given by Elsdon (1972) for his specimen No. 2.

Method of				
calculation of	Wones	Buddington	Ande	rson
minor elements		& Lindsley		
			Calculated for	Elsdon's
			this paper	Calculations
Ilmenite	87.7	87.7	87.7	87.7
Hematite	12.3	12.3	12.3	12.3
(Mo1 %)				
Nagnetite	75.2	73.4	79.3*	81.2
Uivöspinel	24.8	26.6	20.7	18.8
(Mo1 %)				
Temperature (^o C)	771	786	706	700
Log f0 ₂	-14.3	-14.0	-15.8	-16.5

* The difference in results for magnetite - ulvöspinel are probably due to difference in the Mg/Fe allocated in <u>R0</u> to form $\underline{R0}$, $\underline{R_2}$, $\underline{0}_3$.

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The reworked Proterosoic rocks in the inner tectoric bait, including the window zones of the Himalayse, are thought to have been derived through thrusting of a "accrocosticental" cover sequence, which lay between the land masses of India and Tibut (Sinha Roy, 1976a). The deep-rocted thrusts such as the present example, which are located to the south of the central crystalline axis and hence such to the south of the Indus-Tasagpo suture, represent a Terilary collidional interaction zone between the micro-continent and the Indian continent (Sinha Roy, 1976b). If as suggested, the moderate to high-present mean Bait to the Servoisan ecamorphism, then the former might be the result of such an interaction.

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 Myrahlro (A.), 1963. <u>Jan (J. L.)</u>, 2017. <u>Congr. 1981. Sci. 1064</u>, 199. 206 203.
 Nitsch (K. H.), 1965. <u>Mar. 111</u>, 297 211.
 Myrahlro (A.), 1963. <u>Jan (J. C. C.), 1963. Jan (J. C. C., 1963. Jan (J. C. C., 1963. Jan (J. C., 2032. 1973. <u>1973. Jan (J. C. C., 1963. Jan (J. C. C., 1963. Jan (J. C., 2032. 1973. Jan (J. C. C., 2033.
 Mitsch (K. H.), 1965. <u>Mar. 111</u>, 297 216.
 Mitsch (K. H.), 1965. <u>Mar. 166</u>, 126 166.
 Mitsch (K. H.), 1965. <u>Jan (J. C. C., 1963. Jan (J. C., 1963. Jan (J. C., 2045. 1974. 2067. 1975. 2081. 2097. 2081. 2097. 2081. 2097. 2081. 2097. 2081. 2097. 2081. 2097. 2081. 2097. 2081. 2097. 2081. 2097. 2081. 2097. 2081. 2097. 2081. 2</u></u></u></u></u>

D.R.Mason: Zoned amphibole from Papua



The Yirri Intrusive Complex (Jaques and Webb, 1975) of mid-Miocene age occupies about 200 mg. Em in the central and southern parts of Manus Tsland, about 400 km N of the Papua New Guinea mainland. The island forms the NW extremity of the Tertiary Outer Melanesian Arc.

High-K dioritic rocks (Gulaon et al., 1972) constitute the bulk of the Complex, and contain a typical calc-alkaline assemblage of plagioclase, K-feldepar, quartz, amphibole, biotite, magnetite, and accessory sphene and apatite. The amphiboles of dioritic rocks have usually been reported as being of 'magnesio-hornblende' type in the terminology of Leake (1968). Chemical analyses of a high-K diorite and a low- to normal-K diorite from the Mount Kren area are given in Table 1.

Electron microprobe analyses (Ware, 1973; Reed and Ware, 1973) of discrete amphibole grains in these rocks reveal a wide range of composition (Table 1). In the high-K diorite, green amphibole is soned from magneto-hornblande in cores to actinuitic hornblande in rins. The zoning is not evident in thin section. In the low-to normal-K diorite, amphibole is zoned from ferroan pargamitic hornblande cores, through edenitic hornblande, to magneto-hornblande rins. In thin section the pargasitic cores can be discerned as sharply-edined, core subhedral grains up to 2 mm long. Fig. 1a shows a positive correlation between $A1^{20}$ and total Fe, a relationship attributed to high f_{0} during crystallisation by Camanake and Hones (1973). Such an interpretation is particularly acceptable when it is noted that hydrothermal alteration and porphyry copper mineralization are present in the Complex (Jaques and Webb, 1975). The negative correlation for the pargasitic cores sight imply that conditions of low f_{0} were operative at the time of formation of the core amphibole.

The pargasitic cores have compositions quite atypical of amphiboles from dioritic rocks. With about 43X $$30_2$, 37 $$10_2$, and 102 $$41_20_3$ they are more characteristic of amphiboles from gabbroic rocks and of high-pressure, high-temperature amphiboles from experimental work on basaltic rock compositions (Table 1). It might be suggested that the dioritic rocks of the Complex have assimilated basaltic country rocks, but the intrusive rocks are texturally homogeneous and mafic zenoliths are rare or absent.

The preferred interpretation is that the brown pargasitic cores represent relic material from a partially melted mafic source (possibly in the base of the crust), and the green magnesic-hornblende mantles represent amphibole

<u>Table 1</u>: Analyses of diorites and their amphiboles, Yirri Intrusive Complex, Manus Island, Papua New Guinea.

	1	2	3	4	5	6	7	8
\$10 ₂	61.58	59.91	48.9	52.9	43.7	51.5	42.1	40.2
T102	.48	.53	1.5	.4	3.0	.7	2.4	3.1
A1203	16.92	17.31	5.8	3,2	10.3	3.9	12.5	15.4
Fe ₂ 0	2.51	2,99						
Fe0	1.81	2.10	9.9*	9.5	10.8*	9.3*	13.8*	9.8
Mn0	.04	.05	.3	.4	.2	.3	.3	-
MgO	2.72	2.99	17.3	17.8	15.2	18.1	12.5	12.1
Ca0	5.18	6.63	11.4	12.3	11.6	11.9	12.1	11.8
Na ₂ 0	4.60	4.75	1.5	.7	2.5	1.2	2.0	1.8
к,0	2.49	,88	.5	.2	1.1	.3	.8	.3
P_05	.29	.29						
ร็	.03	.03						
н,0+	.83	.95						
н_о-	.20	.19						
cō,	.10	.09						
total	99.78	99.69	97.1	97.4	98.4	97.2	98.5	94.5

Explanation: * total Fe as FeO.

1: Specimen DEM110, high-X hornblende (biotite-clinopyroxene) diorite. 2: Specimen DEM112, low- to normal-K hornblende-quarte diorite. Both specimens from outcrops in Willie River, 2.5 Km SSW of Mount Kren. All elements by XRF except Na, PeO, and volatiles. Analyste: D.R. Mason and P.H. Bealey.

Probe analyses. 3, 4: green core and green rim respectively of amphibole in DRM10. 5, 6: brown core and green rim of amphibole in DRM112. Core and rim analyses for DRM110 and DRM112 were selected from totale of 25 and 27 spot analyses respectively to display the maximum amphibole compositional variation obtained for each specimen. 7: average of 6 spot analyses of brown hornblende in DRM054, a gabbro with granulitic texture from the Western Highlands of Papua New Guinea (Mason, 1975). 8: Amphibole in basaltic composition at 10 kb and 920°C (Green and Kingwood, 1966). Note that the brown core of DRM112 is similar to amphibole from mafic procks. which has crystallized from the melt. This interpretation supports theories which consider most granitoids to be composed initially of a melt plus solid refractory material from the source (Piwinskii, 1968; Chappell and White, 1974).

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<u>Fig. 1</u>: Compositional variation in amphiboles, using data from structural formulae (cations per half unit cell). (a) $A1^{12}$ <u>versus</u> total Fe. (b) Ca+Na+K <u>versus</u> 51. (c) $A1^{12}$ <u>versus</u> 71. (d) Mg <u>versus</u> total Fe. Small filled circles: green cores from DBM10. Large crosses: brown cores from DBM12. Small crosses: green rism from DBM12.