

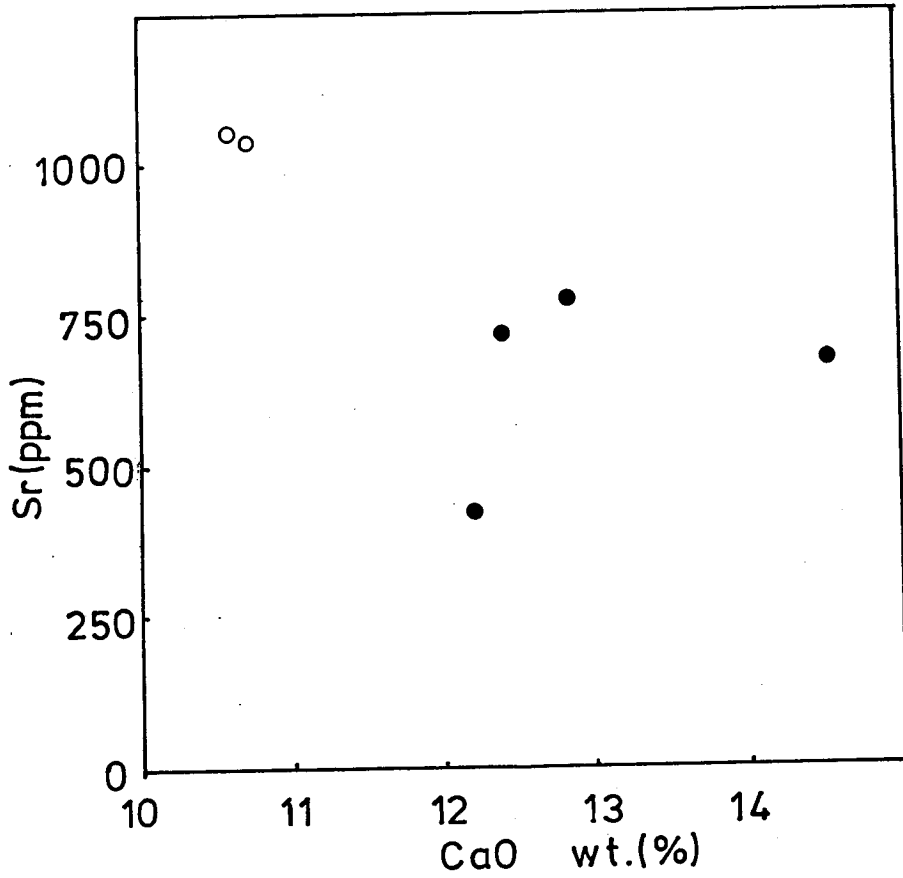


Figure 4.6. Sr(ppm) plotted against CaO weight per cent for the Mapanza amphibolites.

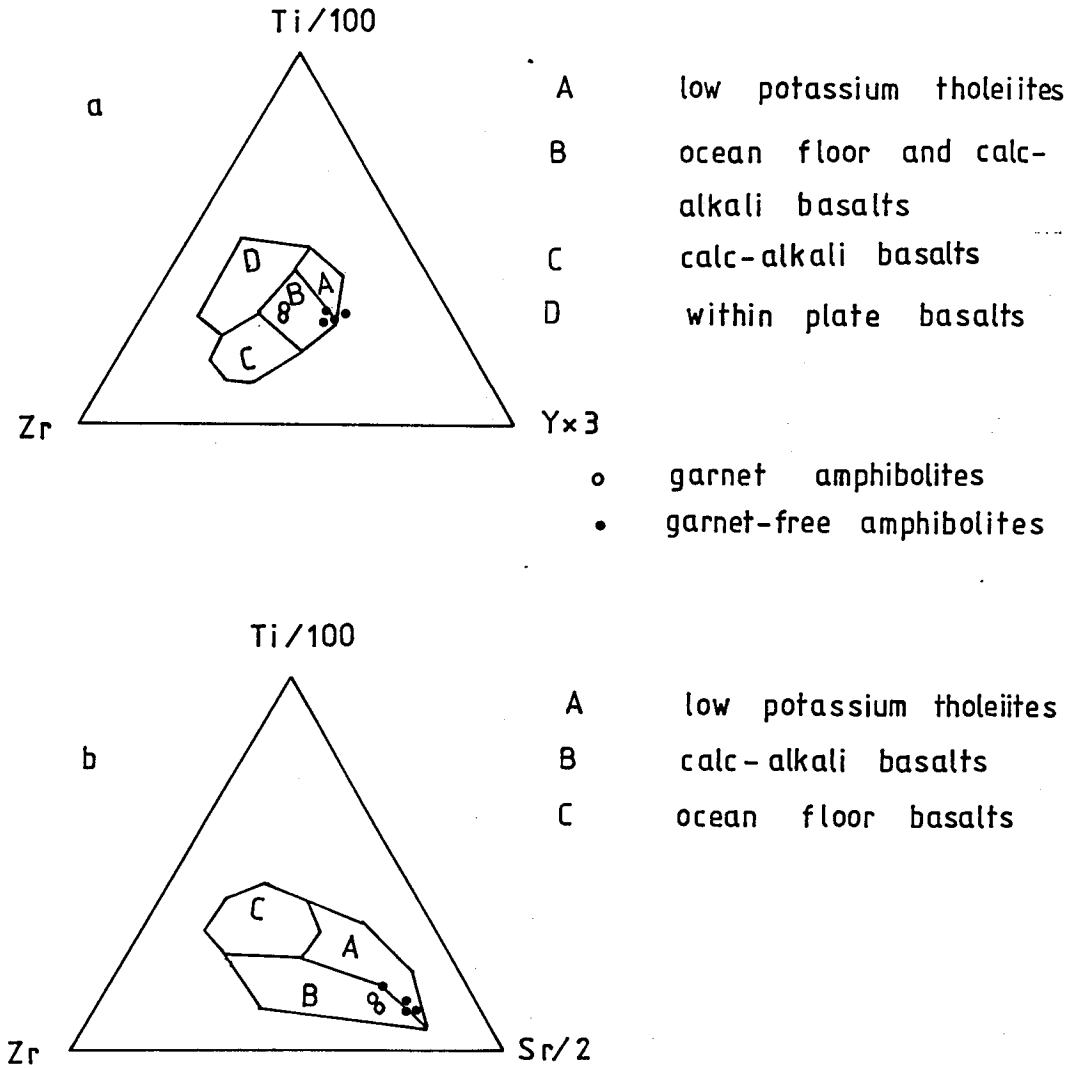


Figure 4.7. (a) Ti/100 - Zr - Y x 3 and (b) Ti/100 - Zr - Sr/2 ternary plots for the Mapanza amphibolites. Basalt fields after Pearce and Cann⁵³.

CHAPTER FIVE

MINERAL CHEMISTRY

5.1 Introduction

Analyses of plagioclase, hornblende; biotite and garnet from the Mapanza amphibolites and calcite and dolomite from marbles in the Muzuma Calc-silicate Formation are presented here. Details of the analytical procedures are outlined in Appendix II.

The chemical data for these minerals have a significant bearing on the discussion on metamorphism to follow. Many of the conclusions on metamorphic conditions are based on this information. The mineral analyses are relevant because they may also be used to indicate the nature of reactions taking place during metamorphism.

5.2 Hornblende

Microprobe analyses of hornblende within the Mapanza amphibolites are listed in Table 5.1. The minerals show a marked variation in their Fe/(Fe+Mg) mole ratios, which range from 0.32 to 0.53. Hornblendes with high Fe/(Fe+Mg) ratios (>0.5) are contained in the garnet amphibolites, which also have relatively high whole-rock Fe/(Fe+Mg) ratios (>0.5), whereas the hornblendes with low Fe/(Fe+Mg) ratios occur in the garnet-free amphibolites, which have correspondingly low whole-rock Fe/(Fe+Mg) ratios. Similarly K_2O and TiO_2 are higher in hornblende of the garnet amphibolites, which also have higher whole-rock content of these oxides.

Table 5.1 Microprobe analyses of hornblende in the Mapanza amphibolites

<u>garnet-free amphibolite (MA14)</u>			<u>garnet amphibolite (MA19)</u>			
	1	2	3	4	5rim	5core
SiO ₂	49.10	45.32	43.71	43.29	43.09	42.90
TiO ₂	0.28	0.61	0.59	0.77	0.75	0.58
Al ₂ O	7.85	9.79	10.44	12.97	10.69	11.03
*FeO	12.14	13.23	17.86	18.06	17.79	
MnO	0.16	0.17	0.18	0.25	0.28	0.31
MgO	14.81	12.80	12.76	8.93	10.11	9.57
CaO	12.78	12.42	12.44	11.58	11.69	11.49
Na ₂ O	0.82	1.61	1.62	1.45	1.40	2.16
K ₂ O	0.14	0.26	0.26	0.38	0.42	0.47
Cl	0.01	0.02	0.04	0.01	0.11	0.03
F	0.07	n.d	n.d	0.18	0.07	0.13
Total	98.15	96.23	95.51	97.69	96.67	96.46
Atoms per formular unit based on 23 (O)						
Si	7.08	6.76	6.60	6.50	6.57	6.57
Aliv	0.92	1.24	1.40	1.50	1.43	1.43
Alvi	0.42	0.48	0.46	0.79	0.49	0.56
Ti	0.07	0.07	0.07	0.09	0.09	0.07
Fe	1.46	1.66	1.70	2.24	2.20	2.28
Mn	0.02	0.02	0.02	0.03	0.04	0.04
Mg	3.18	2.84	2.87	2.00	2.30	2.18
Ca	1.97	1.98	2.01	1.86	1.91	1.88
Na	0.23	0.47	0.48	0.42	0.41	0.64
Cl	0.02	0.02	0.01	0.002	0.03	0.01
K	0.03	0.05	0.05	0.07	0.08	0.09
F	0.03	-	-	0.09	0.03	0.06

Cont'd

Table 5.1 Cont'd

Fe/ (Fe+Mg)	0.32	0.37	0.37	0.53	0.50	0.51
Sum (Y+X+A)	7.38	7.57	7.66	7.50	7.62	7.74
Sum (X+Y+Z)	15.12	15.05	15.13	15.01	15.13	15.01

total iron as FeO

n.d = not detected

These chemical variations in the hornblendes clearly indicate that the compositions of this mineral were influenced by the bulk chemical composition of the host rock. In contrast, Al_2O_3 is relatively high in the hornblendes within the garnet amphibolites, although these rocks have lower whole-rock Al_2O_3 content.

The structural formulae of the hornblendes have been calculated on an anhydrous basis of 23 oxygen ions. This is the normal procedure in amphibole analyses where no H_2O^+ determinations are made (71).

Taking the general formula of amphiboles as $\text{AX}_2\text{Y}_5\text{Z}_8\text{O}_{22}(\text{OH})_2$, cations have been allotted to structural positions as follows (72,73):

1. Tetrahedral site, Z: all Si, then sufficient Al, designated Al IV, to sum to 8.0.
2. Octahedral site (M1,M2,M3) Y: remaining Al, designated Al VI, then Ti, Mg, Fe and Mn to sum to 5.0. However, the total obtained for Y in these minerals is always slightly over this theoretical value of 5.0. This is commonly the case in analyses of amphiboles.
3. Site (M4) X: Ca first, then sufficient Na to sum to 2.0.
4. A site: remaining Na and K.

In all the hornblendes, the sum of the X- and A-group cations ($\text{Ca}+\text{K}+\text{Na}$) exceeds the theoretical maximum of 2.0 cations per formula

unit in the M⁴ site, which suggests partial occupation of the A sites.

The structural formulae for all of the analyzed grains have Si values of less than 7.2, making them true hornblendes⁽⁷⁴⁾. They also have $(Ca+Na) > 2.0$ and may further be classified as magnesio - and ferro - hornblendes according to the classification developed by Leake⁽⁷¹⁾. Those in the garnet amphibolites with higher Fe/(Fe+Mg) ratios are ferro-hornblendes whereas those in garnet-free amphibolites with low Fe/(Fe+Mg) ratios are magnesio - hornblendes.

5.3 Biotite

Microprobe analyses of biotite from the amphibolites are listed in Table 5.2. The biotites have low K₂O and SiO₂ compared to analyses given by Deer et al⁽⁷⁵⁾, which causes the low total oxides for these minerals. In particular, biotite grain 12 has abnormally low K₂O compared to the other two analyses. Low K₂O in biotites has been ascribed to chloritization, which lowers both the K₂O and the total oxide wt. %⁽⁷⁶⁾. Biotite grain 2 is in fact partly replaced by chlorite which clearly accounts for the low K₂O. It is possible that SiO₂ was also removed during chloritization since K₂O loss alone cannot account for the low total oxide wt%. Secondary chlorite is not present on the other two grains.

Table 5.2. Microprobe analyses of biotite and garnet in the Mapanza garnet amphibolite (MA19)

	Biotite			Garnet	
	1	2	3	1	2
SiO ₂	32.27	32.60	33.82	37.07	37.67
TiO ₂	1.30	1.14	1.63	0.13	0.11
Al ₂ O ₃	16.92	17.40	15.28	21.84	22.04
* FeO	23.72	24.25	19.08	25.66	25.36
MnO	0.15	0.18	0.10	2.85	2.69
MgO	11.01	11.47	13.64	2.50	2.52
CaO	0.12	0.12	0.15	8.54	8.76
Na ₂ O	0.11	0.19	0.11	0.05	0.08
K ₂ O	6.00	3.90	6.55	0.03	0.04
Cl	n.d	n.d	n.d	n.d	n.d
F	1.32	0.98	0.79	0.03	0.03
Total	92.92	92.23	91.15	98.70	99.29
Atoms per formula unit					
	based on 22(O)			based on 24(O)	
Si	5.19	5.20	5.39	5.94	5.98
Aliv	2.81	2.80	2.61	0.06	0.02
Alvi	0.40	0.47	0.26	4.06	4.10
Ti	0.16	0.14	0.19	0.02	0.01
Fe	3.19	3.23	2.54	3.44	3.37
Mn	0.02	0.02	0.01	0.39	0.36
Mg	2.62	2.73	3.24	0.60	0.60
Ca	0.02	0.02	0.03	1.47	1.49
Na	0.03	0.06	0.03	0.01	0.02
K	1.24	0.79	1.33	0.01	0.01
Cl	-	-	-	-	-
F	0.67	0.49	0.40	0.01	0.01
Fe/(Fe+Mg)	0.55	0.54	0.44	0.85	0.85

Molecular percentages

Phlogopite	45	54	44	Almandine	58	58
				Grossularite	25	26
Annite	55	46	56	Pyrope	10	10
				Sperssatine	7	6

* Total Fe as Feo

MgO, FeO total, Na₂O and Al₂O₃ contents of all the biotites are closely comparable to those given by Deer et al⁽⁷⁵⁾ and in particular to unaltered biotites from amphibolites of similar metamorphic grade⁽⁶⁴⁾. This suggests that these elements were not significantly affected by retrograde events.

The structural formulae of the biotites have been calculated on the basis of 22 oxygen ions, as is usually the case in probe analyses of micas⁽⁶⁴⁾. Taking the general formula of biotite to be X₂ Y₆ Z₈ O₂₀ (OH,F)₄, cations have been assigned to various structural sites as follows:

1. Tetrahedral site, Z: all Si, and sufficient Al, designated Aliv, to sum to 8.0. In all three analyses, there is enough Al to fill the unoccupied tetrahedral site.
2. Octahedral site, Y: remaining Al, designated Alvi, then Mg, Fe and Ti to sum to 6.0. However, the sum obtained is always slightly over the theoretical maximum of 6.0
3. X site: all interlayer cations (K, Na and Ca) to sum to 2.0. The total obtained for X is however below 2.0 in all three analyses. This is probably due to secondary alteration as outlined above.

The average formula for the biotite crystals is Phl 0.49 Ann 0.51, where Phl is the phlogopite end member, and Ann is the annite end member. These compositions fall within the range of true biotites.

5.4 Garnet

Two garnet crystals coexisting with biotite in one sample were analysed. (Table 5.2) but no within - grain analyses were obtained for individual garnet grains. No significant chemical between -grain variation is shown by these analyses.

The structural formulae of the garnets have been calculated on the basis of 24 oxygen ions per unit cell⁽⁷⁵⁾ and all Fe has been taken to be Fe²⁺. The analyses show that the garnets are largely a solid solution of almandine (Fe₃ Al₂ Si₃ O₁₂) and grossularite (Ca₃ Al₂ Si₃ O₁₂) components, with minor amounts of pyrope (Mg₃ Al₂ Si₃ O₁₂) and sperssatine (Mn₃ Al₂ Si₃ O₁₂) components. The average formula is Alm₅₈ Gr₂₅ Py₁₀ SP₇.

5.5 Plagioclase

Analyses of plagioclase crystals in the Mapanza amphibolites by electron microprobe are tabulated in Table 5.3. Their structurally formulae have been calculated on the basis of 32 oxygen ions per unit cell, as usually formulated⁽⁷⁵⁾.

The plagioclases are all andesine in composition, with an average formula of Ca 0.44 Na 0.58 Al 1.47 Si 2.53 O₈, and contain insignificant amounts of the orthoclase component. Grain to grain compositional variation is significant (An33-An49), whereas within-grain

Table 5.3 Microprobe analyses of plagioclase in the Mapanza amphibolites

	Garnet amphibolite (MA19)				Garnet-free amphibolite (MA14)			
	* rim ¹	core	rim ²	core	rim ¹	core	rim ²	core
SiO ₂	55.62	54.76	59.09	60.07	55.72	56.25	55.25	55.18
Al ₂ O ₃	28.15	29.42	27.28	26.41	28.27	28.62	28.54	27.48
CaO	9.41	9.79	7.14	7.50	9.75	9.74	10.37	9.31
Na ₂ O	6.51	6.52	7.87	7.86	6.27	6.06	5.82	6.63
K ₂ O	0.04	0.09	0.06	0.05	0.11	0.09	0.09	0.06
Total	99.73	100.60	101.40	101.90	100.10	100.80	100.10	98.65
Atoms per formular unit based on 32 (O)								
Si	10.03	9.82	10.40	10.53	10.02	10.03	9.94	10.07
Al	5.98	6.22	5.66	5.99	5.46	6.02	6.06	5.91
Ca	1.82	1.88	1.35	1.41	1.98	1.86	2.00	1.82
Na	2.27	2.27	2.69	2.67	2.19	2.10	2.03	2.35
K	0.01	0.02	0.01	0.01	0.02	0.02	0.02	0.01
Sum (Si+Al)	16.01	16.04	16.06	15.99	16.01	16.05	16.00	15.98
Sum (Ca+Na+K)	4.10	4.17	4.17	4.09	4.19	3.98	4.05	4.18
Molecular percentages								
An	44.40	45.10	33.30	34.50	47.20	46.70	49.40	43.50
Ab	55.40	54.40	66.40	65.30	52.30	52.80	50.10	56.20
Or	0.20	0.50	0.30	0.20	0.50	0.50	0.50	0.30

*Individual plagioclase grains probed in the garnet-free amphibolite (MA14) and garnet amphibolite (MA19)

chemical zonation generally lies in a narrow range, compositional variation showing a slight increase in anorthite content from rim to core is evident in analyses 1 and 2. Reverse zonation, in which anorthite content increases towards the rim is seen in analyses 3 and 4 and is most pronounced in analysis 4.

Morteani and Rease⁽⁷⁷⁾ have proposed two processes to explain reverse zoning and the abrupt increase in An (anorthite) content from core to rim in grains of metamorphic plagioclase:

1. by mineral reactions due to an increase in grade of metamorphism, causing the growth of more calcic plagioclase.
2. by an abrupt increase in temperature (or pressure) while other minerals coexisting with plagioclase change their composition in a similar manner.

5.6 Calcite and dolomite

Analyses of calcite and dolomite from the marbles in the Muzuma Calc-silicate Formation by atomic absorption spectrometry are tabulated in Table 5.4. A small amount of secondary post-metamorphic dolomite is present in sample FO21B (Chapter 2), but not in amounts large enough to significantly perturb the analyses. All Fe in calcite and dolomite was assumed to be ferrous iron. This is based on the fact that Fe^{2+} substitute for Mg with which it has a similar ionic radius and to some extent Ca.

Table 5.4. Chemical analyses of dolomite and calcite in marbles of the Muzuma Calc-silicate Formation.

	Dolomite					Calcite				
	FO13A*	FO22*	FO21B*	FO13B*	FO16	FO4	FO13B*	FO22*	FO13*	FO21B*
CaO	30.80	28.94	30.03	29.94	29.66	52.72	50.80	51.15	53.14	52.45
MgO	20.95	21.61	22.00	21.36	21.43	0.560	2.110	0.760	1.230	2.040
FeO	0.185	0.345	0.174	0.113	0.161	0.117	0.165	0.117	0.314	0.355
SrO	0.007	0.014	0.041	0.042	0.004	0.220	0.014	0.350	0.137	0.210
MnO	0.022	0.028	0.021	0.070	0.021	0.189	0.021	0.018	0.033	0.260
Mg/Mg+Ca	0.49	0.51	0.51	0.50	0.50	0.02	0.06	0.02	0.03	0.05

* coexisting calcite and dolomite

Dolomite generally has higher Fe and lower Sr contents than calcite but in some cases has similar Mn values. It is stoichiometrically close to ideal dolomite, with Mg mole per cent ranging from 49 to 51 per cent, compared to 50 per cent for ideal dolomite.

Calcite has variable amounts of MgO, SrO, FeO and MnO. It is also generally close to ideal calcite, although F013B and F021B differ in having slightly higher CaO. The MgO content of calcite coexisting with dolomite is higher than that from the calcite marbles (F04) which does not contain any dolomite.

Due to overlap in the specific gravity between dolomite (2.86-2.93) and calcite (2.72-2.94), it is possible that mineral fractions obtained using the float and sink method were not pure fractions. In general, however, the analyses compare well with those obtained by Kretz⁽²⁷⁾ for dolomite and calcite in upper amphibolite to lower granulite facies marbles in the Grenville Province. However, calcite coexisting with dolomite in the present case has lower Mg contents than in the Grenville Province.

CHAPTER SIX

METAMORPHISM

6.1 Introduction and general comments

The calc-silicate rocks, marbles and amphibolites have mineralogical imprints of the Late Proterozoic Pan-African regional metamorphism. Their presumed equilibrium assemblages based on textural relationships, such as the absence of reaction rims and the presence of simple, well-defined grain-to-grain contacts, are listed in Table 6.1. Where possible, mineral-forming reactions occurring during metamorphism have been inferred from these assemblages and to some extent from the textural relationships of the individual minerals.

Analyses of biotite and garnet in the amphibolites and calcite coexisting with dolomite in the carbonate rocks have been utilized in the garnet-biotite and calcite-dolomite geothermometers to obtain temperature estimates of regional metamorphism. Analyses of plagioclase and hornblende in the amphibolites have also been used in the recently calibrated hornblende - plagioclase geothermobarometer to estimate both T and P conditions.

6.1.1 Calcite marbles

The mineral assemblages of most calcite marbles in the Muzuma Calc-silicate and Mapanza Carbonate Formations (Table 6.1) show that these rocks generally did not generate the characteristic minerals (tremolite, diopside, etc) normally expected during metamorphism of impure carbonate rocks. This is due to inappropriate bulk composition.

Table 6.1. Characteristic equilibrium mineral assemblages for the calc-silicate rocks, marbles and amphibolites (listed in order of decreasing abundance)

Rock type	Mineral assemblages*	number of specimens
Calc-silicate gneisses	Dio + Scp + Hbl + Qt _z + Cal	3
"	Bio + Plg + Qt _z + Cal	6
"	Bio + Plg + Hbl + Qt _z	4
"	Dio + Scp + Qt _z + Cal	3
Calc-silicate schists	Bio + Plg + Qt _z + Cal	6
"	Bio + Plg + Hbl + Qt _z + Cal	2
"	Bio + Scp + Qt _z + Cal	2
Massive calc-silicate rocks	Qt _z + Scp + Dio + Gro + Plg + Hbl +	
	Kfs + Cal + Sph	3
"	Qt _z + Plg + Dio + Cal + Sph	6
"	Qt _z + Dio + Scp + Cal + Sph	4
"	Qt _z + Act + Gro + Dio + Sph + Zoi + Plg + Cal	1
"	Qt _z + Dio + Act + Plg + Cal + Sph	1
"	Qt _z + Dio + Act + Scp + Cal + Sph	2
Calcite-marbles	Cal + Qt _z + Bio + Scp	3
"	Cal + Qt _z + Bio + Scp + Plg	2
"	Cal + Qt _z + Sph + Ru + Plg	1
"	Cal + Qt _z + Tr	1
Dolomite marbles	Dol	2
"	Dol + Dio	1
"	Dol + Phl	5
"	Dol + Tr + Cal	4

Dolomite marbles	Dol + Cal + Tr + Phl	2
Amphibolites	Hbl + Plg + Qt _z + Zoi + Czo +	
	Alm + Bio	2
"	Hbl + Plg + Qt _z + Zoi/Czo	6
"	Hbl + Plg + Dio + Qt _z + Zoi/Czo	2

* Dol, dolomite; Hbl, Hornblende, zoi, zoisite; Czo Clinozoisite; Plg, Plagioclase; Scp, scapolite; Dio, diopside; Qt_z, quartz; Gro, grossularite aml, amlmandine; Cal, /Calcite; Phl, phlogopite; Sph, sphene, Ru rutile Act, actinolite, Kfs, K-feldspar; mineral symbols and compositions are also indicated in section on mineral reactions.

Upon metamorphism, most calcite simply recrystallized, resulting in a coarsening of grain size, accompanied by crystallization of impurities and reaction with carbonate to form plagioclase or scapolite.

These rocks, however, do contain plagioclase that is uniformly andesine in composition (An₃₆₋₄₀) suggesting metamorphism under amphibolite facies conditions. In the greenschist facies, the stable plagioclase is commonly albite regardless of bulk CaO content⁽⁷⁴⁾. The presence of scapolite of mizzonite composition (Me₆₀₋₆₅) in these rocks also suggests amphibolite facies metamorphism. Kwak⁽⁷⁸⁾ and Heitane n⁽⁷⁹⁾ have found that the meionite content of scapolite increases with increasing grade of metamorphism irrespective of the composition of the host rocks. Marialite-rich scapolite is characteristic of the greenschist facies whereas more calcic scapolite of mizzonite composition is found in amphibolite facies calc-silicate rocks, impure marbles and scapolite schists.⁽⁷⁸⁾

Effects of retrograde metamorphism to greenschist facies in the calcite marbles are reflected by sporadic partial replacement of biotite by secondary chlorite and muscovite, and plagioclase by sericite.

6.1.2 Dolomite Marbles

The presence of tremolite in the mineral assemblages of the dolomite marbles is consistent with amphibolite facies conditions⁽⁸⁰⁾. The assemblage dolomite + quartz is not present in these rocks,

indicating that the greenschist facies has been exceeded. The assemblage diopside + dolomite found in one sample is also characteristic of amphibolite facies conditions.

6.1.3 Calc-silicate Rocks

Mineral parageneses of the calc-silicate rocks contain diopside, scapolite (Me 60-55), plagioclase (An32-40), hornblende and grossularite-rich garnet (Table 6.1). These assemblages are diagnostic of amphibolites facies^(74,80). Primary actinolite in some of the massive calc-silicate rocks is also consistent with amphibolite facies metamorphism. In Al_2O_3 -poor rocks, this mineral persists into the amphibolite facies⁽⁷⁴⁾.

ACF diagrams for the various assemblages are not presented. These show numerous crossing tie lines, and in light of the petrographic evidence for textural equilibrium within the assemblages, this is interpreted to reflect the presence of more than three true components within the bulk compositions. That is, constituents such as MgO and FeO in these rocks cannot be treated as a single component, as is required in the construction of the ACF diagram^(29,63).

Partial retrogression of these rocks to greenschist facies is widespread. This is indicated by partial replacement of biotite by chlorite and muscovite and by partial replacement of plagioclase by

sericite in the calc-silicate schists. In the massive calc-silicate rocks and calc-silicate gneisses, it is indicated by the presence of secondary actinolite pseudomorphing diopside, and by the partial alteration of grossularite and scapolite by zoisite.

6.1.4 Amphibolites

The Mapanza amphibolites all contain the assemblage andesine (An33-49) + hornblende which is diagnostic of amphibolite facies metamorphism. Diopside in MA7 is obviously of metamorphic origin, reflecting conditions near the higher temperature limits of the amphibolites facies⁽⁷³⁾

An "A" FM diagram (Fig. 4.1) has already been presented in Chapter 4. There, it was shown that the appearance of garnet within the amphibolites is a reflection of the bulk rock composition and not of metamorphic grade.

Retrogression to greenschist facies is also present in the amphibolites. This is indicated by partial replacement of hornblende and biotite by chlorite + sphene, and by partial replacement of plagioclase by calcite and sericite.

6.1.5 Spatial distribution of mineral assemblages

Figure 6.1 shows the distribution of diopside-bearing and primary

26°05'E
16°05'S

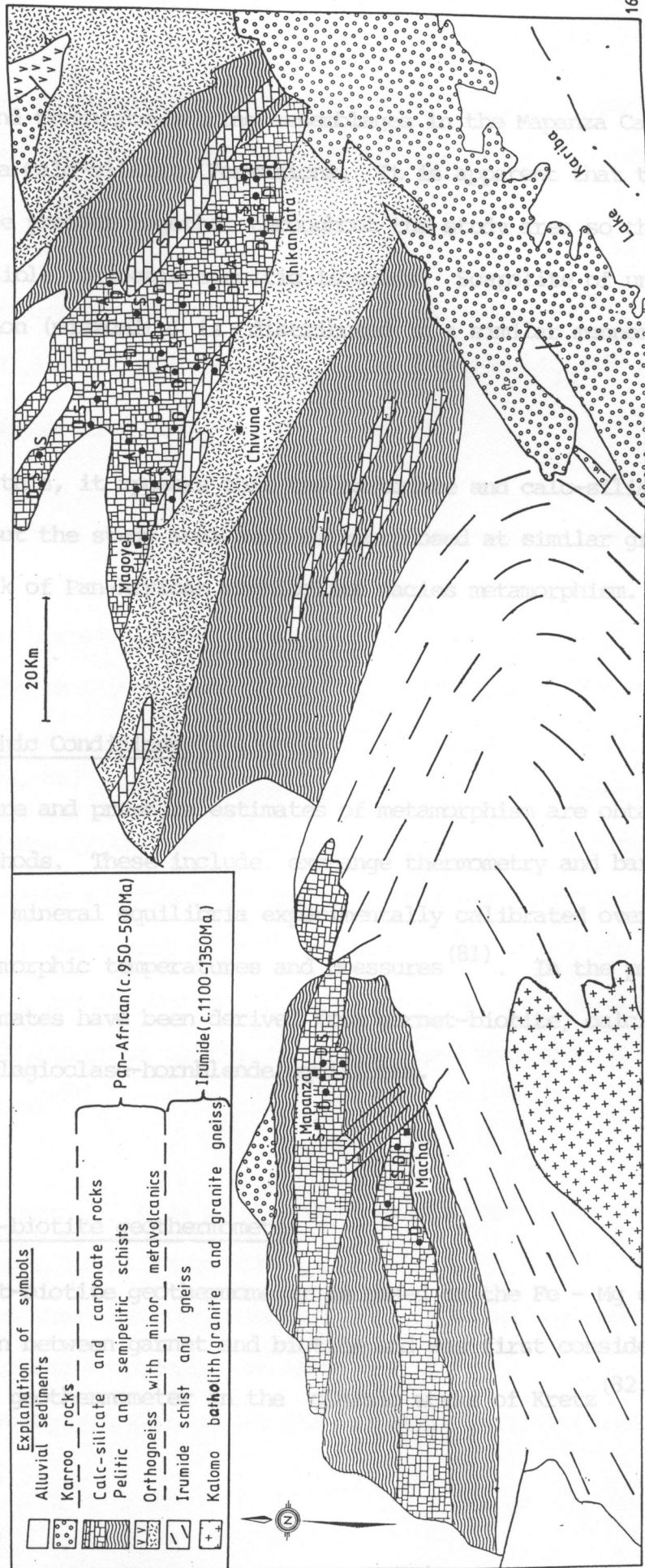


Figure 6.1. Metamorphic map showing the distribution of some of the mineral assemblages in the Mapanza Carbonate and Muzuma Calc-silicate Formations. D represents diopside-bearing assemblages; A, actinolite(primary)- and tremolite-bearing assemblages; S, scapolite(mizzonite)-bearing assemblages.

actinolite - and tremolite-bearing assemblages in the Mapanza Carbonate and Muzuma Calc-silicate Formations. It is apparent that these assemblages are present together throughout the study area so that it is not possible to locate specific isograds. Scapolite of uniform composition (mizzonite) is distributed in a similar manner (Fig. 6.1).

Based on this, it appears that the carbonate and calc-silicate rocks throughout the study area were metamorphosed at similar grade during the peak of Pan-African amphibolite facies metamorphism.

6.2 Metamorphic Conditions

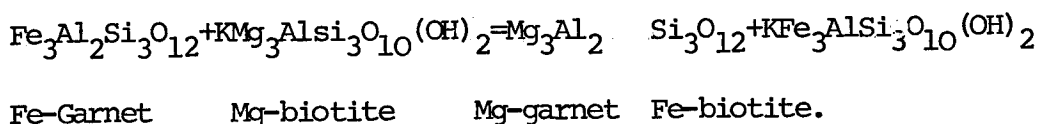
Temperature and pressure estimates of metamorphism are obtained by various methods. These include exchange thermometry and barometry based on mineral equilibria experimentally calibrated over a range of metamorphic temperatures and pressures⁽⁸¹⁾. In the present case, T/P estimates have been derived from garnet-biotite, calcite-dolomite and plagioclase-hornblende equilibria.

6.2.1 Garnet-biotite geothermometer

The garnet-biotite geothermometer is based on the Fe - Mg exchange reaction between garnet and biotite and was first considered as a potential geothermometer in the classic works of Kretz^(82,83).

It has since been calibrated by field observations⁽⁸⁴⁾, by comparison with results obtained from oxygen isotope geothermometry⁽⁸⁵⁾ and by laboratory experiments⁽⁸⁶⁾.

The geothermometer is based on the exchange reaction⁽⁸⁶⁾:



The distribution coefficient, KD, for this exchange reaction is given as :

$$\text{KD} = (\text{Mg/Fe})_{\text{garnet}} / (\text{Mg/Fe})_{\text{Biotite}}$$

and is a function mainly of temperature and of the amount of other components in solid solution such as Ca and Mn in garnet and Ti and Al in biotite^(85, 86). Pressure has little effect on the distribution coefficient because of the small volume variations in the minerals during the exchange reaction⁽⁸⁷⁾. Another factor that affects the geothermometer is the amount of Fe^{3+} present in the garnet and biotite. This is a problem because probe analyses can only determine total Fe and the effect of this on the temperature estimates is not commonly evaluated⁽⁸¹⁾.

Ferry and Spear⁽⁸⁶⁾ have calibrated the geothermometer over a restricted compositional range with a precision of $\pm 50^\circ\text{C}$. They have recommended that their experimental results be applied without correction for other components, at least for

$(\text{Ca}+\text{Mn})/(\text{Ca}+\text{Mn}+\text{Fe}+\text{Mg}) \leq 0.2$ in garnet and $(\text{AlVI}+\text{Ti})/(\text{AlVI}+\text{Ti}+\text{Fe}+\text{Mg}) \leq 0.15$ in biotite.

Garnets in the Mapanza amphibolites have significant grossularite and spessartine components (Table 5.2), with an average $(\text{Ca}+\text{Mn})/(\text{Ca}+\text{Mn}+\text{Fe}+\text{Mg})$ value of 0.32. Biotites, however, have low Ti contents with an average $(\text{AlVI}+\text{Ti})/(\text{AlVI}+\text{Ti}+\text{Fe}+\text{Mg})$ value of 0.08, and thus the second condition for the application of the geothermometer is fulfilled.

Temperatures of 'equilibration' between garnet and biotite estimated from the calibration curve given by the expression:

$$\ln KD = (2109/T^{\circ}\text{K}) + 0.782,$$

which also includes a small pressure correction⁽⁸⁶⁾, are shown in Table 6.2. These values are probably somewhat low due to the presence of the grossularite and spessartine components in the garnet. The effect of higher Ca and Mn content in garnet is to reduce the value of KD, so that it indicates a temperature value that is lower than the 'true' value (Kretz, 1984, Pers. Commun). It is not possible, however, to state by how much these values are lower.

Another possible complicating factor that may affect the geothermometer in the present case is the alteration of the biotite (see chapter 5). Pattison et al⁽⁷⁶⁾ have pointed out that chloritization of biotite may raise the temperature given by the geothermometer. In the present case, however, the Mg/Fe ratios of the analyzed biotites do not differ markedly from those of unaltered biotites in amphibolites and other rock types obtained in other studies (see chapter 5), so that it is assumed that alteration has not affected the geothermometer results significantly.

Table 6.2 Temperature estimates by the garnet - biotite geothermometer in Mapanza amphibolite (MA19)

<u>garnet biotite</u>			<u>garnet biotite</u>		
	1	1		2	2
X _{Mg}	0.149	0.453		0.151	0.458
X _{Fe}	0.851	0.547		0.849	0.542
K _D		0.211			0.210
Temp(°C)					
**FS		630			630
***GA		655			660

* numbers refer to coexisting biotite and garnet analysed (Table 5.1)

** FS - ferry and spear (85) calibration

*** GA - Goldman and Albee (84) calibration

Because of the significant amounts of Ca and Mn in the garnets, the calibration of the garnet-biotite exchange reaction given by Goldman and Albee⁽⁸⁵⁾ was also applied. The resulting temperature values (using eqn. 9 and the expression on P. 756 of Goldman and Albee⁽⁸⁵⁾) are 25-30°C higher than those obtained with the Ferry and Spear calibration (Table 6.2). The Goldman and Albee values are probably more reasonable, as their empirical calibration takes into account the presence of Ca and Mn components in the garnet.

Temperature estimates determined from garnet-biotite geothermometry have mainly been obtained in pelitic rocks, where biotite and garnet lie reasonably close to their respective binaries. Most of the determinations⁽⁸⁸⁾ have yielded reasonable temperatures by the Ferry and Spear calibration, whereas the Goldman and Albee calibration has commonly yielded relatively low temperatures in these cases.

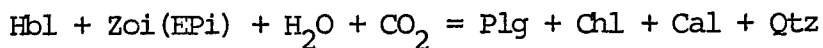
The present study suggests that the Goldman and Albee calibration may be more appropriate for amphibolites, a conclusion also reached by Watkin⁽⁸⁹⁾ for semi-pelitic compositions.

6.2.2. Hornblende - plagioclase geothermobarometer

In most world-wide occurrences of metabasic rocks, the assemblage amphibole + chlorite + epidote + plagioclase is common and persists from the greenschist to the amphibolite facies, with considerable changes in phase compositions⁽⁹⁰⁾. With increasing grade of metamorphism, chlorite and epidote decrease in modal abundance, while

amphibole increases. Concomitantly, pargasite and tschermackite components in amphibole increase and the anorthite content of plagioclase increases.

Based on this, Plysunina ⁽⁹¹⁾ has used the Al content of Ca-amphibole and the anorthite content of plagioclase coexisting with amphibole to construct an experimental geothermobarometer. This is based on the reaction.



and was calibrated for a wide range of temperatures (450-650°C) and pressures (2-8kb). Use of the geothermobarometer requires the following:

1. The rocks should contain either zoisite or epidote.
The paragenesis hornblende + plagioclase + zoisite is the limiting assemblage.
2. The amphibole must contain more than 1.5 Ca and less than 1.0 Na, in atomic proportions.

Both these conditions are fulfilled for the Mapanza amphibolites (Tables 5.1 and 6.1). Compositions of coexisting plagioclase and hornblende in the amphibolites are plotted on Fig. 6.2, yielding temperatures of 560-630°C and pressures of 3.5-6 Kbars (Table 6.3).

These results are in accord with experimental results on metamorphic phase equilibria for basic rocks ⁽⁹²⁾. These experiments show chlorite to totally disappear above 575°C at a fluid pressure of 5 Kbars, which is consistent with the absence of primary chlorite in

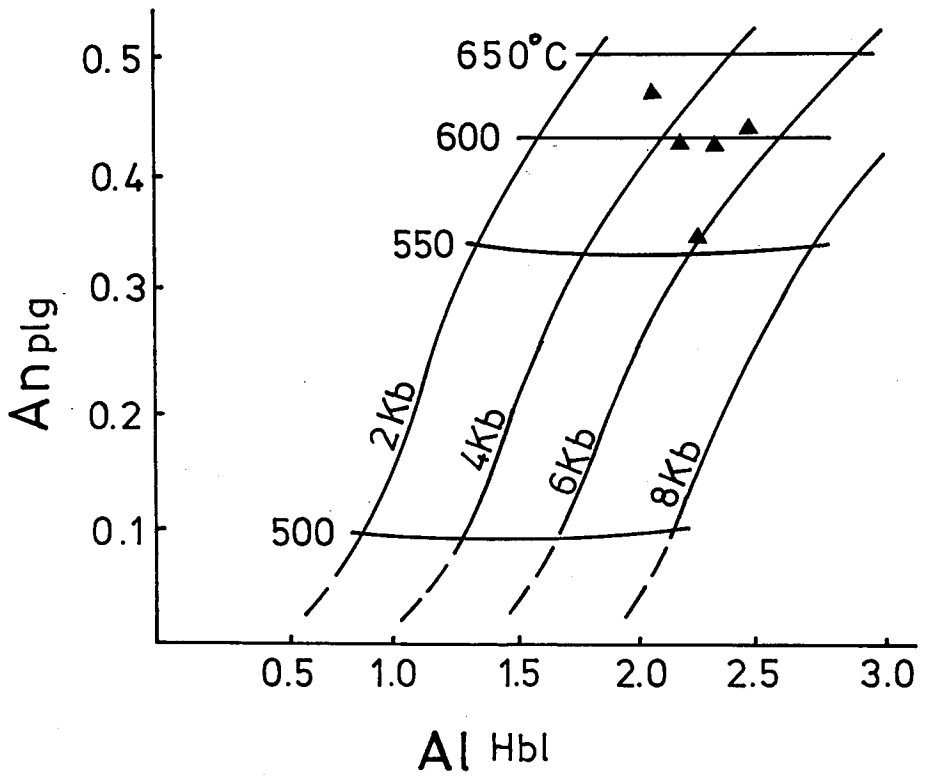


Figure 6.2. Anorthite and Aluminum content of coexisting plagioclase and hornblende in the Mapanza amphibolites plotted on the diagram of Plysunina⁹¹.

Table 6.3 Temperatures and pressures determined from coexisting hornblende and plagioclase in the Mapanza amphibolites using the method of Plyusina (91)

* Sample No.	Anorthite content in plagioclase (%)	Al content in hornblende (atomic proportion)	T°C	P (Kbars)
MA 19 (1)	47.2	1.72	630	3.5
MA 19 (2)	43.5	1.86	600	5.0
MA 14 (1)	44.4	1.99	600	4.5
" 14 (1)	45.1	1.92	610	6.0
" 14 (2)	34.5	2.29	560	6.0

* MA 19garnet amphibolite

MA 14garnet - free amphibolite

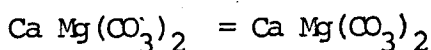
number in parenthesis correspond to numbers of analysed plagioclase grains in Table 5.3.

the Mapanza amphibolites. The temperatures are also comparable with those obtained from the garnet-biotite geothermometer.

The variations in the T and P values derived from the hornblende - plagioclase geothermobarometer are not regarded as an indication of variation in metamorphic grade, because the samples come from spatially close amphibolite bodies. It seems possible that these variations may reflect variability in the precision of the electron microprobe analyses and/or various degrees of re-equilibration during retrogression to lower temperatures.

6.2.3 Calcite-dolomite geothermometer

The calcite-dolomite geothermometer is based on the well established fact that the Mg content of calcite coexisting with dolomite increases with increasing temperature^(93,94) according to the exchange reaction:



dolomite in solid solution

in calcite

Calibration of this exchange reaction has revealed that it is mainly a function of temperature⁽⁹⁴⁾. Pressure effects are insignificant. For example, on increase of 10 Kbars causes a corresponding increase of only 1 per cent MgCO_3 in calcite coexisting with dolomite⁽⁹⁴⁾.

Significant amounts of Fe and Mn in solid solution in calcite have a profound influence on the geothermometer, but these effects have been thermodynamically evaluated⁽⁹⁵⁾. It should be noted, however, that in some cases the geothermometer has yielded inconclusive results and has thus been questioned⁽⁹⁶⁾.

Compositions of coexisting calcite and dolomite in marbles within the Muzuma Calc-silicate Formation are given in Table 5.4. These show insignificant amounts of Fe and Mn so that no correction for these components is necessary. Temperature estimates have been computed using the expression.

$\text{LOG mole \% MgCO}_3 \text{ in calcite} = 1.727 \times 10^{-3} T^{\circ}\text{C} - 0.223$ derived by Scheppard and Schwarz⁽⁹⁷⁾ from the calcite-dolomite solvus of Goldsmith and Newton⁽⁹⁴⁾. The resulting temperatures are given in Table 6.4

Table 6.4. Temperatures determined from the calcite-dolomite geothermometer⁽⁹⁴⁾ for marbles in the Muzuma Calc-silicate Formation.

Sample number	FO13A	FO13B	FO22	FO21B
MgCO ₃ wt.% in calcite	4.41	2.57	1.59	4.27
T °C	500	< 400	< 400	490

These temperatures are markedly lower than those determined from the garnet-biotite and hornblende - plagioclase geothermometers and are not consistent with the presence of the amphibolite facies assemblages in the calc-silicate rocks with which the marbles are closely associated. The following reasons may be advanced to account for these low temperature values:

1. Magnesium may have exsolved as dolomite from calcite during cooling following amphibolite facies metamorphism. No exsolution lamellae of dolomite within calcite were observed in stained samples, but it is possible that exsolved dolomite may have moved completely out of the calcite crystals to form discrete dolomite crystals (Kretz, Pers. Commun. 1984). Petrographic evidence for this is not present.
2. Retrograde metamorphism caused re-equilibration between coexisting calcite and dolomite subsequent to the peak of amphibolite facies metamorphism. This is taken as the most likely explanation, in light of the petrographic evidence for retrogression in the Muzuma Calc-silicate Formation. The calcite-dolomite geothermometer is known to be easily reset by retrograde events (80,81).

6.2.4 Summary

The estimated T/P conditions of metamorphism are summarized in Table 6.5. It is likely that during the amphibolites facies metamorphism, temperatures were in the range 600-660°C with pressures

Table 6.5 Summary of temperatures and pressures estimated from geothermobarometry

Equilibria*	T (°C)	P (Kb)	Lithology	Locality
Plg-Hbl	560-610	4.5 - 6.0	Amphibolite (MA14)	Mapanza area
Plg-Hbl	600-630	3.5 - 5.0	Amphibolite (MA19)	Mapanza area
Grt-Bio	630-650	-	Amphibolite (MA19)	Mapanza area
Cal-Dol	500	-	dolomite marble (FO13A)	East of Magoye
"	490	-	dolomite marble (FO21B)	West of Chikankata Mission

*Plg plagioclase, Cal calcite

Hbl hornblende, Dol dolomite

Grt garnet, Bio biotite

probably in the range from 5 to 6 Kbars, corresponding to a depth of about 18-20 Km. These conditions are characteristic of intermediate pressure (Barrovian type) metamorphism⁽⁸⁰⁾. They are also consistent with general estimates of the T/P limits for the amphibolites facies and with the presence of diopside in the amphibolites⁽⁷³⁾.

The estimated pressures are consistent with the presence of kyanite in the associated metapelites in this part of the Zambezi belt (see Chapter 1).

6.3 Mineral reactions in the calc-silicate and carbonate rocks

6.3.1 Definitions

In the discussions on mineral reactions to follow, the minerals have been written in terms of their ideal phase compositions. The following abbreviations are used as usually formulated⁽⁹⁸⁾:

<u>Mineral</u>	<u>Abbreviation</u>	<u>Composition</u>
Quartz	Qtz ...	SiO_2
Calcite ...	Cal ...	CaCO_3
Dolomite ...	Dol ...	$\text{CaMg}(\text{CO}_3)_2$
Talc ...	Tal ...	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$
Tremolite ...	Tr ...	$\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$
Diopside ...	Dio ...	$\text{CaMgSi}_2\text{O}_6$
Forsterite ...	Fo ...	Mg_2SiO_4
Phlogopite ...	Phl ...	$\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$

Grossularite ...	Gr ...	$\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$
K- feldspar ...	Ksp ...	KAlSi_3O_8
Zoisite ...	Zo ...	$\text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}\text{OH}$
Meionite ...	Me ...	$3\text{Ca Al}_2\text{Si}_2\text{O}_8 \cdot \text{CaCO}_3$
Marialite ...	Ma ...	$3\text{NaAlSi}_3\text{O}_8 \cdot \text{NaCl}$
Sphene ...	Sph ...	CaTiSiO_5
Rutile ...	Ru ...	TiO_2
Anorthite ...	An ...	$\text{CaAl}_2\text{Si}_2\text{O}_8$

6.3.2 Phase equilibria

Mineral-forming reactions in carbonate and calc-silicate rocks are known to a large extent and most have been experimentally calibrated. Abundant experimental data exists for reactions involving carbonate and calc-silicates in the system $\text{CaO-MgO-SiO}_2\text{-CO}_2\text{-H}_2\text{O}$ (99,100,101, 102,103,104), and also to some extent in the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-CO}_2\text{-H}_2\text{O}$ (105). Mineral phases included in the above systems are quartz, calcite, dolomite, talc, tremolite, diopside, forsterite, grossularite, zoisite, anorthite and wollastonite.

In laboratory experiments designed to study carbonate-silicate equilibria, normally a well-defined gas phase is present, of known composition and pressure, and mineral phases of fixed compositions are used. In nature, however, these mineral phases may contain significant amounts of other components in solid solution. For instance, dolomite, forsterite, amphibole and diopside may contain Fe^{2+} in solid solution with Mg, amphibole may contain variable

amounts of Al substituting for Si and some of the OH in amphibole may be replaced by F and /or Cl. Further more, the composition of the fluid phase during metamorphism of impure carbonate rocks may not be a simple $\text{H}_2\text{O}-\text{CO}_2$ binary as is normally the case in laboratory experiments. This is commonly evidenced by the presence of graphite, pyrite and oxide phases in natural carbonate rocks. This indicates the presence of appreciable amounts of other species in the fluid phase during metamorphism, such as SO_2 , CH_4 , and O_2 .

Consequently, equilibria in these systems, even if they are experimentally calibrated, do not form sensitive geological temperature indicators ⁽²⁷⁾. The mineral reactions presented below are only approximations to the equilibria occurring in natural systems.

6.3.3 Nature of reactions

Fig. 6.3 is an isobaric temperature versus fluid composition ($\text{T}-\text{XCO}_2$) for some important reactions calibrated by experimental studies. A similar diagram for the reactions 8,9,10,12 and 14 is given by Winkler ⁽¹⁰⁶⁾. Where possible, reactions will be discussed in relation to this diagram. A pressure value of 5 Kbars has been chosen from the results of the hornblende - plagioclase geothermobarometer and is consistent with the ubiquitous presence of kyanite in associated pelitic rocks within the Zambezi belt. The numbers of the curves in Fig. 6.3 correspond to those used in the discussion below.

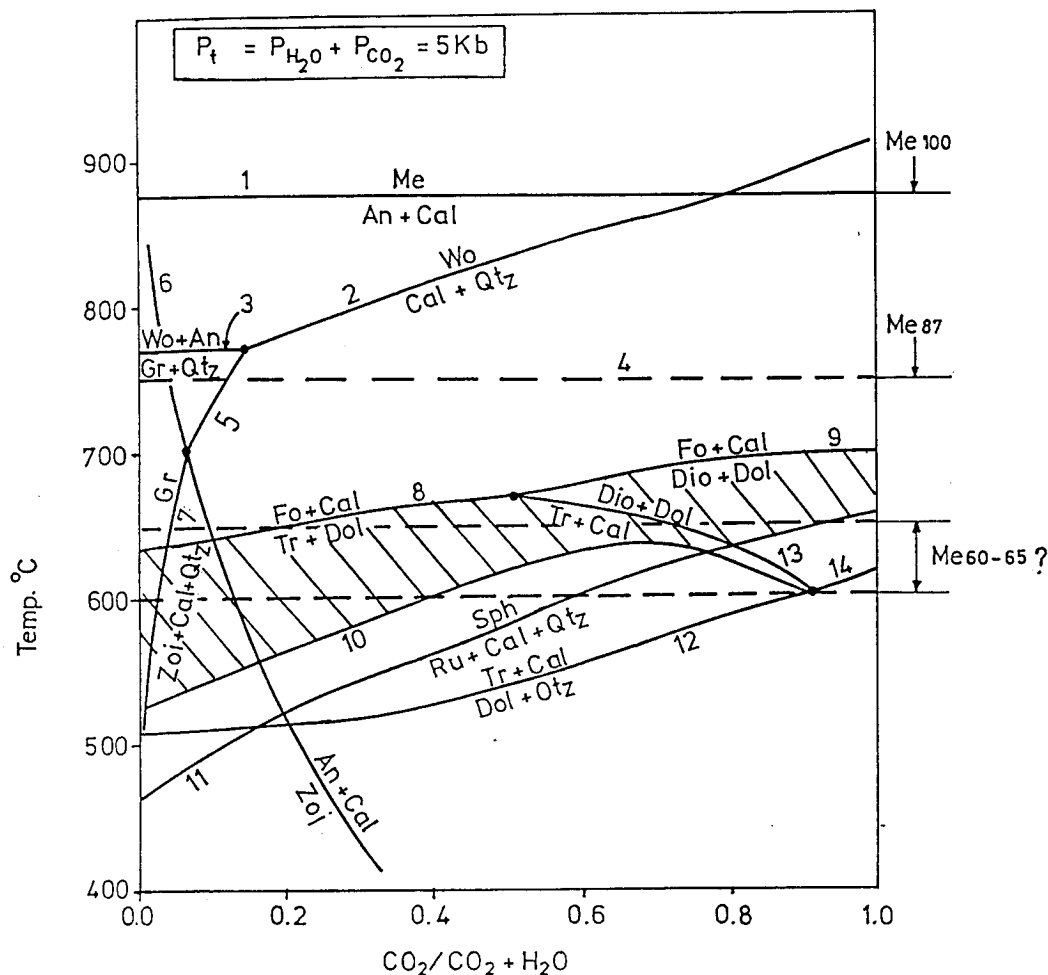
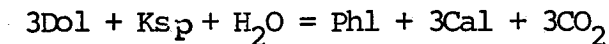
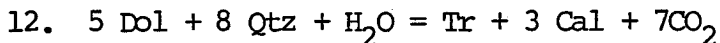


Figure 6.3. Isobaric T-XCO₂ diagram at 5Kbar fluid pressure constructed for the calc-silicate rocks and marbles. Reaction curves are discussed in the text and are from: 1, Goldsmith and Newton¹¹²; 2, 3, 5, 6 and 7, Gordon and Greenwood¹⁰⁵; 4, Ellis¹¹³; 8, Metz¹⁰³; 9, Kase and Metz¹⁰⁴; 10, 12 and 14, Hewitt¹¹⁴; 11, Hunt and Kerrick¹⁰⁸; 13, approximately located by Winkler¹⁰⁶. The temperature for mizzonitic scapolite (Me60-65) has been deduced from temperature estimates from garnet-biotite and hornblende-plagioclase equilibria in the Mapanza amphibolites. Shaded region represents approximate T-XCO₂ conditions in the calc-silicate rocks and marbles during regional amphibolite facies metamorphism.

In impure dolomite marbles, dolomite begins to react with quartz in the greenschist facies. Talc is the first mineral to form in this way during prograde metamorphism if the mole fraction of H_2O in the fluid phase is high⁽¹⁰⁶⁾. If the formation of talc is inhibited due to high mole fraction of CO_2 in the fluid phase, then tremolite forms instead as dolomite begins to react with quartz. Gordon and Greenwood⁽¹⁰⁰⁾ have shown that the presence of minor amounts of Al_2O_3 and K_2O in the system $CaO-MgO-SiO_2-CO_2-H_2O$ is sufficient to inhibit the formation of talc, because the mole fraction of CO_2 in the fluid phase is raised when phlogopite crystallizes from these components according to the reaction:

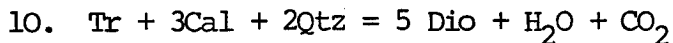


In the marbles, discussed here, the presence of the assemblage dolomite + phlogopite + Calcite suggests that the above reaction did occur. Therefore, tremolite would have been the first phase to form by the reaction between dolomite and quartz as follows:



This is supported by the presence of the assemblage dolomite + tremolite + calcite and the absence of quartz in the dolomite marbles. Also by calcite + quartz + tremolite in calcite marble.

The assemblage diopside + calcite + quartz is widespread in the calc-silicate rocks, which suggests that diopside crystallized according to the reaction.



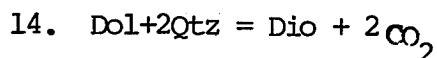
In a few samples (e.g, MA16), all the solid participants in this reaction (calcite + quartz + diopside + actinolite with tremolite in solid solution) are present as primary phases in apparent textural equilibrium. The presence in a rock of both reactants and products which participate in a fluid - dependent reaction suggests that the fluid composition was locally controlled or internally buffered by the mineral assemblage⁽¹⁰⁷⁾, but this would be rigorously true only if the solid phases had pure end-member compositions.

In most of the calc-silicate rocks, however, diopside is commonly mantled by actinolite. This suggests that during retrogression, with introduction of fluids rich in H_2O and CO_2 reaction (10) reversed to produce secondary amphibole.

The absence of forsterite and the presence of the assemblage tremolite + dolomite in the Zambezi belt carbonate rocks is of interest in relation to experimental studies conducted by Metz⁽¹⁰³⁾. During metamorphism of siliceous dolomitic limestones, forsterite first appears by the reaction:

8. $Tr + 11Dol = 8 Fo + 13 Cal + 9CO_2 + H_2O$ (101,102,103).
Therefore in the dolomite marbles where tremolite coexists with dolomite, temperature conditions were apparently below curve 8 in Fig. 6.3.

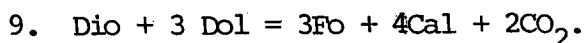
The assemblage diopside + dolomite was only found in one sample and could have been produced by either:



or

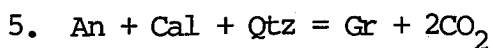


The absence of either tremolite or calcite associated with this assemblage suggests that reaction 14 is more likely to have occurred. This reaction takes place only in the presence of a very high CO_2 mole fraction in the fluid phase (Fig. 6.3)^(101,102). Such conditions probably existed locally in the massive dolomite marbles during metamorphism. The upper temperature limit of the diopside + dolomite assemblage is constrained by the reaction:



Grossularite-rich garnet occurs in minor amounts in a few calc-silicate rocks in the Muzuma Calc-silicate Formation but is abundant in the Calc-silicate rocks which form bands in the predominantly pelitic Nega Formation. In the Muzuma Calc-silicate Formation, the grossularite-bearing rocks are spatially associated with calc-silicate schists. Grossularite was also reported from calc-silicate rocks in the Mapanza Carbonate Formation⁽⁹⁾, but its association with other rock types is not known.

Gordon and Greenwood⁽¹⁰⁵⁾ have shown that grossularite is stable only in the presence of H_2O -rich fluids. Under these conditions, the mineral may crystallize according to the reaction:

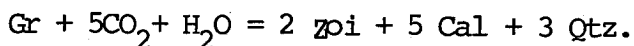


The calculated curve for the reaction (Fig. 6.3) at 5 Kbars⁽¹⁰⁵⁾, however, lies at higher temperatures than those inferred for the present case. A second possible grossularite-forming reaction is

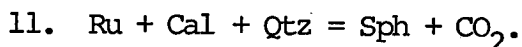


This occurs only at very low X_{CO_2} values in the fluid phase. The spatial association of grossularite-bearing assemblages with pelitic rocks or calc-silicate schists suggests that the fluid phase may have been quite rich in H_2O during metamorphism, due to dehydration reactions occurring in the pelitic rocks. Thus grossularite may have formed by reaction 7.

In most grossularite-bearing samples in the Muzuma Calc-silicate Formation, the mineral is commonly mantled by zoisite, clearly indicating retrogression. With introduction of fluids containing some CO_2 , the mineral may be replaced according to the reaction



Sphene is common in all the calc-silicate rock types. The low temperature stability limit of this mineral is represented by the reaction



The ubiquitous presence of sphene in the calc-silicate rocks and calcite marbles suggests that conditions were generally above curve 11 in Figure 6.3 during the amphibolite facies metamorphism. The presence of all four minerals participating in reaction 11 in apparent textural equilibrium in one calcite marbles suggests that during metamorphism, the fluid composition was locally buffered by this assemblage (105). However, in a few specimens of the calc-silicate rocks, the minor amount of rutile present is mantled by sphene. Two possible explanations for this texture may be advanced:

1. It may reflect retrogression according to the reaction:
$$5 \text{ Dio} + 3 \text{ Ru} + \text{Qtz} + \text{H}_2\text{O} = \text{Act/Tr} + \text{Sph}^{(108)}$$
2. The texture may indicate a prograde reaction that has not gone to completion possibly due to fluctuation in the composition of the fluid phase or due to kinetic factors.

The above reaction would imply that rutile reappeared during prograde metamorphism after reaction 11 had occurred, in order to undergo later retrogression. The assemblage diopside+rutile + quartz has been documented in granulite facies rocks⁽²⁹⁾. Such high temperature conditions were clearly not attained in the present case, so that the second possibility is considered more likely.

6.3.2.1 Formation of scapolite

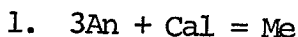
Scapolite is quite widespread in the Muzuma Calc-silicate and Mapanza Carbonate Formations (Fig. 6.1). In almost all these rocks, the mineral is commonly in apparent textural equilibrium with other calc-silicate minerals formed during amphibolite facies metamorphism, which suggests that it is also a product of regional metamorphism.

Scapolite is also widely distributed in the Katangan rocks of the Copperbelt and the Central Province and also in rocks of older ages in Zambia^(109,5). Ramsay and Ridgway⁽³⁾ have pointed out that 'scapolite is rarely found in such abundance and Zambia must be one of the major scapolite provinces in the world'.

Two main models for the origin of scapolite in metamorphic rocks are often advanced. The first involves metasomatic introduction of the necessary constituents such as F_2 , Cl_2 , SO_2 and CO_2 ⁽¹¹⁰⁾. This model is often invoked in geological environments where scapolite-bearing rocks are in proximity to an igneous intrusion. However, it has also been proposed that regional metasomatic introduction of these volatiles with a mantle source may take place ⁽¹¹¹⁾. The second model involves regional metamorphism of sedimentary rocks containing appreciable amounts evaporitic minerals. Dissolution of the latter provides the necessary constituents required to form scapolite.

The second model best accounts for the widespread occurrence of scapolite in the carbonate and calc-silicate rocks of the Zambezi belt. Anhydrite is present in parts of the Katangan succession on the Copperbelt ⁽¹⁰⁹⁾, perhaps suggesting the original presence of evaporites in the Katangan succession elsewhere in Zambia.

Experiments conducted by Goldsmith and Newton ⁽¹¹²⁾ have shown that the calcic end member of scapolite, meionite, is stable only above $875^{\circ}C$ independent of pressure and is related to anorthite and calcite by the reaction:



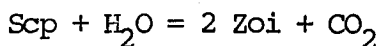
Na is found to stabilize scapolite to lower temperatures ^(78,79). For example, at $750^{\circ}C/4 \text{ Kb}$, scapolite coexisting with plagioclase and calcite is Me 87 in composition ⁽¹¹³⁾.

In the calc-silicate rocks and marbles, scapolite, calcite and plagioclase are occasionally found together in apparent textural equilibrium, and scapolite is uniformly mizzonite in composition (Me 60-65). It is thus possible that the scapolite in these rocks crystallized according to reaction (1), but taking place at a lower temperature than 750°C due to the presence of the marialite $(3 \text{ NaAlSi}_3\text{O}_8 \cdot \text{NaCl})$ component.

The probable temperature of formation of mizzonite with a composition of Me 60-65 are indicated in Figure 6.3, assuming that the temperature estimates obtained by geothermometry for the Mapanza amphibolites pertain to the calc-silicate and carbonate rocks considered here.

It is also interesting to note that in the Copperbelt and Central Provinces where the grade of metamorphism is relatively lower, the mineral also has lower meionite content. In the Copperbelt the composition varies from Me 0 to Me 50⁽¹⁰⁹⁾, whereas in Central Province in the calcareous rocks of the Cheta Formation the composition of scapolite Formation, is Me 55⁽¹¹⁵⁾.

In a few specimens of the calc-silicate rocks of the present study, zoisite develops rims around the scapolite crystals indicating retrogression. This can be accounted for by the reaction:



This reaction has also been documented in certain retrogressed marbles in the Grenville Province of the Canadian shield⁽²⁷⁾ and in certain Precambrian calc-silicate rocks in India⁽⁴⁰⁾.

6.3.4 Conclusions

Conclusions drawn from the above discussions may be summarized as follows:

1. Temperatures of metamorphism were in excess of those required for reactions 10 and 11 but below those required for 8 and 9, which is indicated on Figure 6.3 by the shaded region. It therefore seems clear that the temperature estimates obtained from garnet-biotite and hornblende - plagioclase geothermometry are consistent with experimentally determined mineral equilibria for assemblages in both the Muzuma Calc-silicate and Mapanza Carbonate Formations. These two lines of evidence point to the conclusion that the two formations were both metamorphosed under similar conditions within the amphibolite facies.

2. Widespread occurrence of scapolite of uniform composition (Me 60-65) in the Calc-silicate rocks and marbles is further evidence of uniform grade throughout the Muzuma Calc-silicate and Mapanza Carbonate Formations.

3. During amphibolite facies metamorphism, fluid composition varied from one point to another. The assemblage diopside + dolomite in one of the dolomite marbles requires very high mole fraction of CO_2 in the fluid phase. The presence of tremolite + calcite in other marbles, however, requires lower to intermediate mole fraction of CO_2 in the fluid phase, as otherwise these phases would have reacted

to form diopside + dolomite at the temperatures indicated (reaction 13, Fig. 6.3). The presence of grossularite (and also primary zoisite, see reaction 6 in Fig. 6.3) in some of the massive calc-silicate rocks, requires very low mole fraction of CO_2 (X_{CO_2}) in the fluid phase. These variations probably reflect the relative dominance of dehydration or decarbonation reactions occurring in nearby rock masses.

4. Retrograde effects observed in thin section (e.g., alteration of diopside to actinolite, mantling of grossularite and scapolite by zoisite) can be accounted for by a decrease in T possibly occurring together with influx of H_2O and CO_2 .

CHAPTER SEVEN

DISCUSSION AND CONCLUSIONS

Significant conclusions that have emerged from the petrographical, geochemical, and petrological study of the calc-silicate rocks, marbles and amphibolites may be summarized as follows:

1. The Muzuma Calc-silicate and Mapanza Carbonate Formations within the Pan-African Zambezi belt consist of texturally and mineralogically diversified calc-silicate rocks. These are represented by calc-silicate gneisses, calc-silicate schists, massive calc-silicate rocks and a few mottled varieties with scapolite porphyroblasts. The associated carbonate rocks occur as calcite marbles and dolomite marbles with simple mineralogical compositions.

2. Whole-rock major and trace element contents of the calc-silicate schists and fine-grained, biotite-rich layers of the calc-silicate gneisses suggest that calcareous argillite was the probable protolith for these rocks. The coarse-grained layers of the calc-silicate gneisses were derived from interbeds of carbonate rich sediment. The massive calc-silicate rocks were probably derived from calcareous sands. The marbles were originally relatively pure limestones and dolostones. The banding in the calc-silicate gneisses reflects original sedimentary bedding.

3. General trends in whole-rock chemical composition and various inter-element correlations indicate that most of the

elements were relatively immobile during metamorphism of the calc-silicate rocks and marbles. Instead the chemical variations in these rocks largely reflect admixture of detrital phases with carbonate in the original sediment. In particular the elements Al, K, Na, Fe, Cr, Rb, Ba, Zn, Ni and Nb were incorporated largely in the original sediment in the clay mineral fraction and in detrital micas. Zr and Y were mainly added to the sediment as detrital zircon, whereas Ti was probably added partly as detrital rutile but was also carried in the clay mineral fraction. Si was added partly as detrital quartz. Sr was largely concentrated in the carbonate fraction of the sediment, with the possibility that during metamorphism it suffered metasomatic movement to some extent.

4. Amphibolites in the Mapanza Carbonate Formation occur as relatively large, discrete bodies showing relict intrusive relations against the host rocks, and as smaller boudins and bands. They have an igneous parentage, with a possible minor sedimentary component for the boudins and bands. The appearance of almandine - rich garnet and biotite within the amphibolites was controlled by bulk chemical composition.

5. The rocks were deformed and progressively metamorphosed under intermediate pressure (Barrovian type) amphibolite facies conditions. Application of the garnet-biotite geothermometer and the hornblende - plagioclase geothermobarometer for the Mapanza amphibolites indicates metamorphic temperatures of $600-660^{\circ}\text{C}$ and pressures of 5-6 Kbars. These estimates are consistent with published experimental

data for the mineral assemblages in the calc-silicate rocks, marbles and amphibolites. The temperature estimates are also consistent with the presence of scapolite of uniform mizzonite composition, uniform occurrence of diopside, tremolite and andesine throughout the study area. Additionally, the T/P estimates of metamorphism of calc-silicate rocks, marbles and amphibolites are consistent with the mineralogy of the adjacent pelitic rocks. In particular, the presence of kyanite in the pelitic phase assemblages is in accord with the P estimates⁽¹¹⁶⁾. It thus seems likely that metamorphism of this part of the Zambezi belt took place at somewhat lower pressures than in those parts where talc-kyanite-quartz assemblages developed.

6. During metamorphism, the composition of the fluid phase in the calc-silicate and carbonate rocks varied spatially from CO₂ - rich to H₂O-rich. This variation of fluid phase composition was dictated by the bulk rock chemical composition and by the nature of mineral reactions occurring during regional metamorphism of adjacent rock masses.

7. The rocks were later partly downgraded to greenschist facies, which may be related to uplift and cooling after the peak of amphibolite facies metamorphism. This is reflected by the relatively low temperature estimates obtained from the calcite-dolomite geothermometer and by the petrographic evidence of partial replacement of earlier amphibolite facies assemblages.

CHAPTER EIGHT

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APPENDIX I

STRUCTURAL ANALYSIS

Small-scale structural mapping was conducted in the calc-silicate gneisses of the Muzuma Calc-silicate Formation along the Munyameshi and Kalya Rivers and in an area 10 Km northeast of the Chikankata turn-off (Figs. A.1.1. and A.1.2). These areas were chosen because of almost continuous exposures along the streams. No structural mapping was conducted in the Mapanza Mission area (Fig. A.1.3).

The mapping involved taking measurements of attitudes of foliations, lineations and axial surfaces and hinge lines of folds. The results are summarized in equal angle stereonet plots (Figs. A.1.4 through A.1.7.) and discussed below.

So and S1 Foliations

The main foliation in the Muzuma Calc-silicate Formation is defined by compositional layering in the calc-silicate gneisses (Fig. A.1.4) and is designated as So. Geochemical evidence presented in Chapter 3 indicates that the compositional layering reflects original sedimentary bedding. The layering trends uniformly in a northwest-southeast direction, dipping to the northeast along the Munyameshi River (Fig. A.1.4I) and to the southwest along the Kalya River and northeast of the Chikankata turnoff (Fig. A.1.4II). Near Mazabuka, the foliation also dips steeply to the southwest.

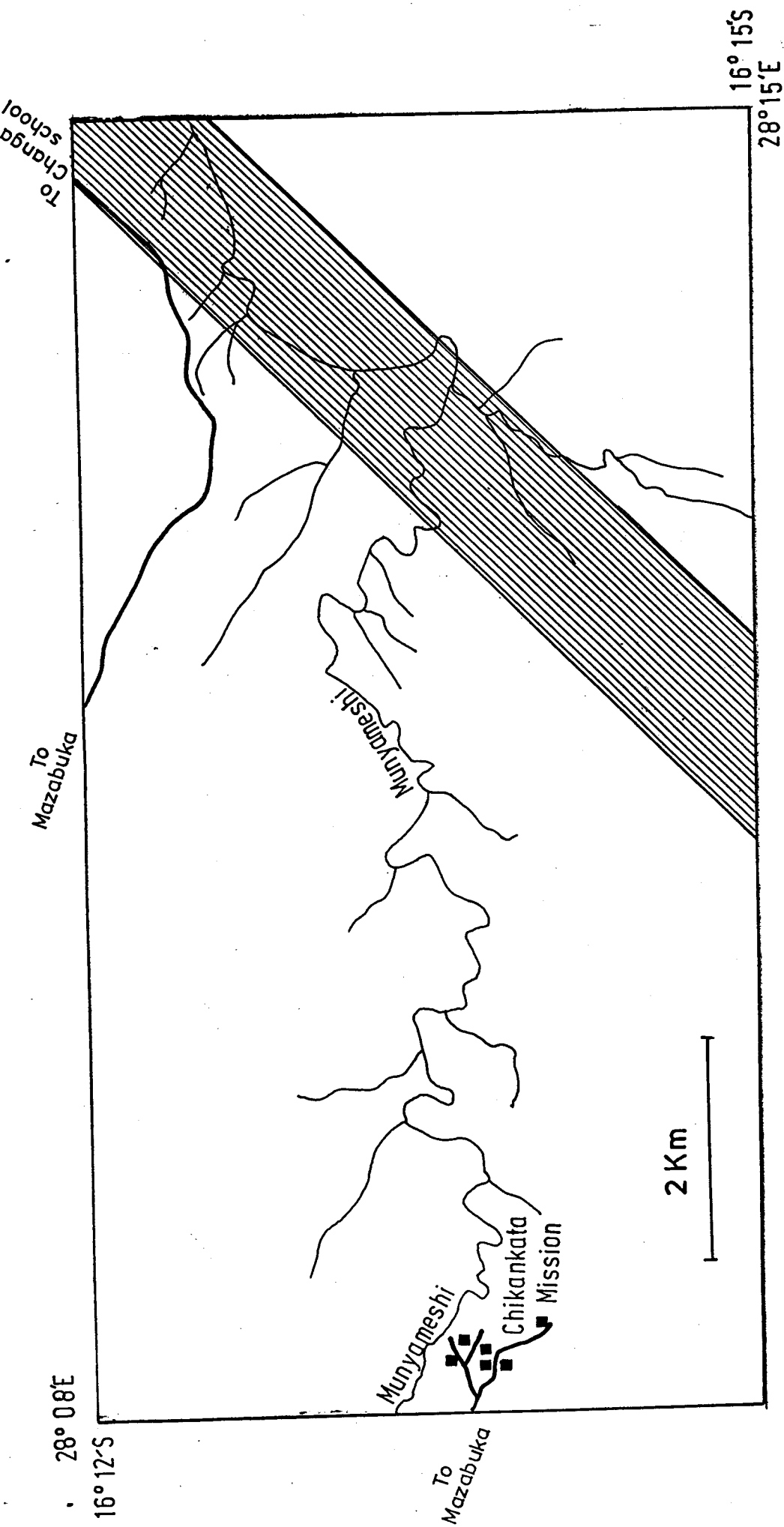


Figure A.1.1. Locality of the area along the Munyameshi River (shaded) where structural mapping was conducted.

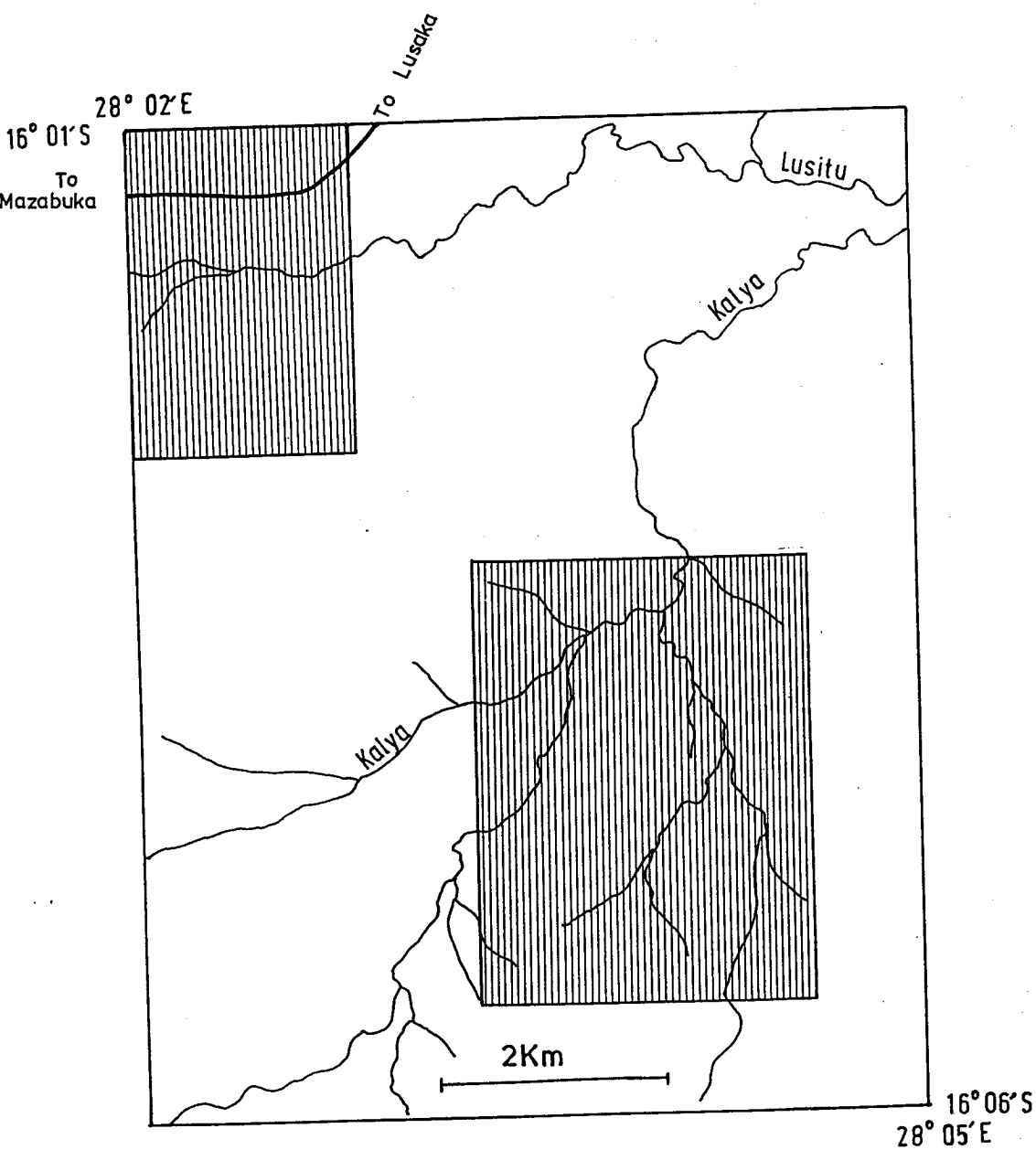


Figure A.1.2. Locality of the areas along Kalya River and along the Great North Road where structural mapping was conducted.

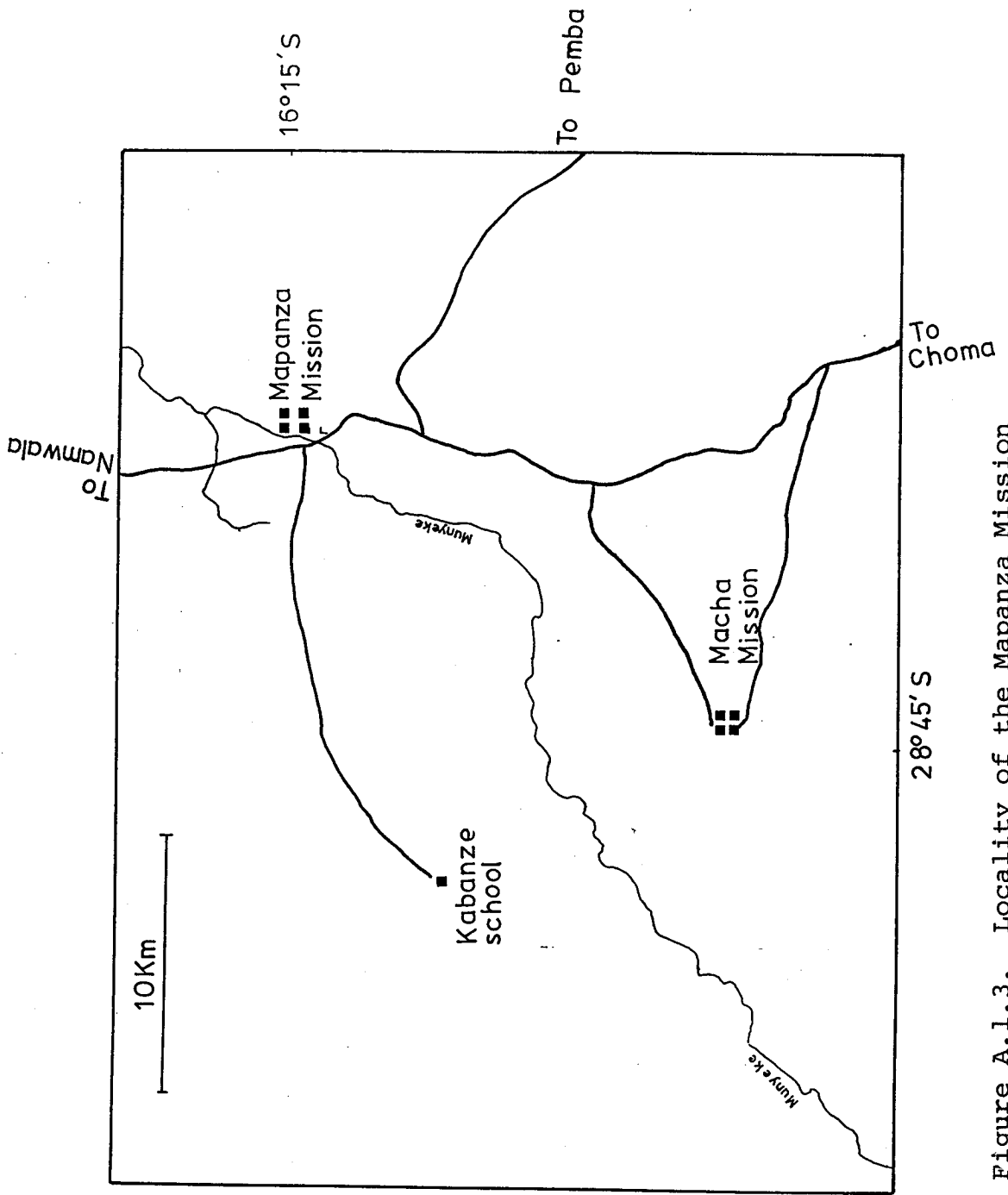


Figure A.1.3. Locality of the Mapanza Mission area.

At many exposures, this compositional layering is sheared, boudinaged and tightly to isoclinally folded as described below. At a few outcrops along the Great North Road, after the Chikankata turn-off towards Mazabuka intrafolial folds and pseudocross-bedding structures are developed within the calc-silicate bands. The presence of these structures together with the widespread occurrence of tight to isoclinal folds of the layering suggests that this foliation represents transposed foliation, reoriented into the regional northwest trend during deformation.

A foliation (S₁) has developed axial planar to the minor folds of S₀. It is defined by orientated biotite and is better developed in the fine-grained layers where it is expressed as a schistosity than in the coarse-grained layers of the calc-silicate gneisses. The foliation is parallel to S₀, where the latter is not folded on outcrop scale or where layering is folded isoclinally. Excellent examples of the S₁ foliation may be seen along the Munyameshi River but no attitude measurements were taken.

F₁ minor Folds

Tight to isoclinal folds of the S₀ banding in the calc-silicate gneisses are widespread in the calc-silicate terrane. These are generally parallel folds with rounded hinges and wavelengths varying from 20 to 150 cm and with amplitudes of up to 30cm. Locally the folds are disharmonic. They have 'S', 'Z', or 'M' symmetries and variation in symmetry within a single outcrop also occurs in the field. In

some cases, smaller isoclinal folds are present locally as parasitic folds of more open, larger folds. This suggests that the minor folds in general are related to larger scale folds.

In some exposures, the limbs of the folds are attenuated, boudinaged and sheared apart, the sheared limbs being brought into parallelism with the regional northwest trending foliation (Fig. A.1.8).

The hinge lines of most of these minor folds plunge at moderate or occasionally at steep angles to the northwest. Along the Munyameshi River, fold hinge lines plunging both to the northwest and southeast were measured (Fig. A.1.5.). At some exposures, folds plunging in opposite directions are present on the same outcrops.

Axial surfaces of the minor folds are generally parallel to the fold hinge lines and dip to the northeast at steep angles along the Munyameshi River (Fig. A.1.5I). Along Kalya River and northeast of the Chikankata turnoff, only a few measurements were taken but there the axial surfaces of the minor folds dip steeply to the southwest, opposite to those measured along the Munyameshi River (Fig. A.1.6).

Lineations

Where the compositional layering is tightly folded, a distinct intersection lineation formed by the intersection of S_1 and S_0 occurs. This plunges to the northwest at moderate angles (Figs. A.1.7_I and II).

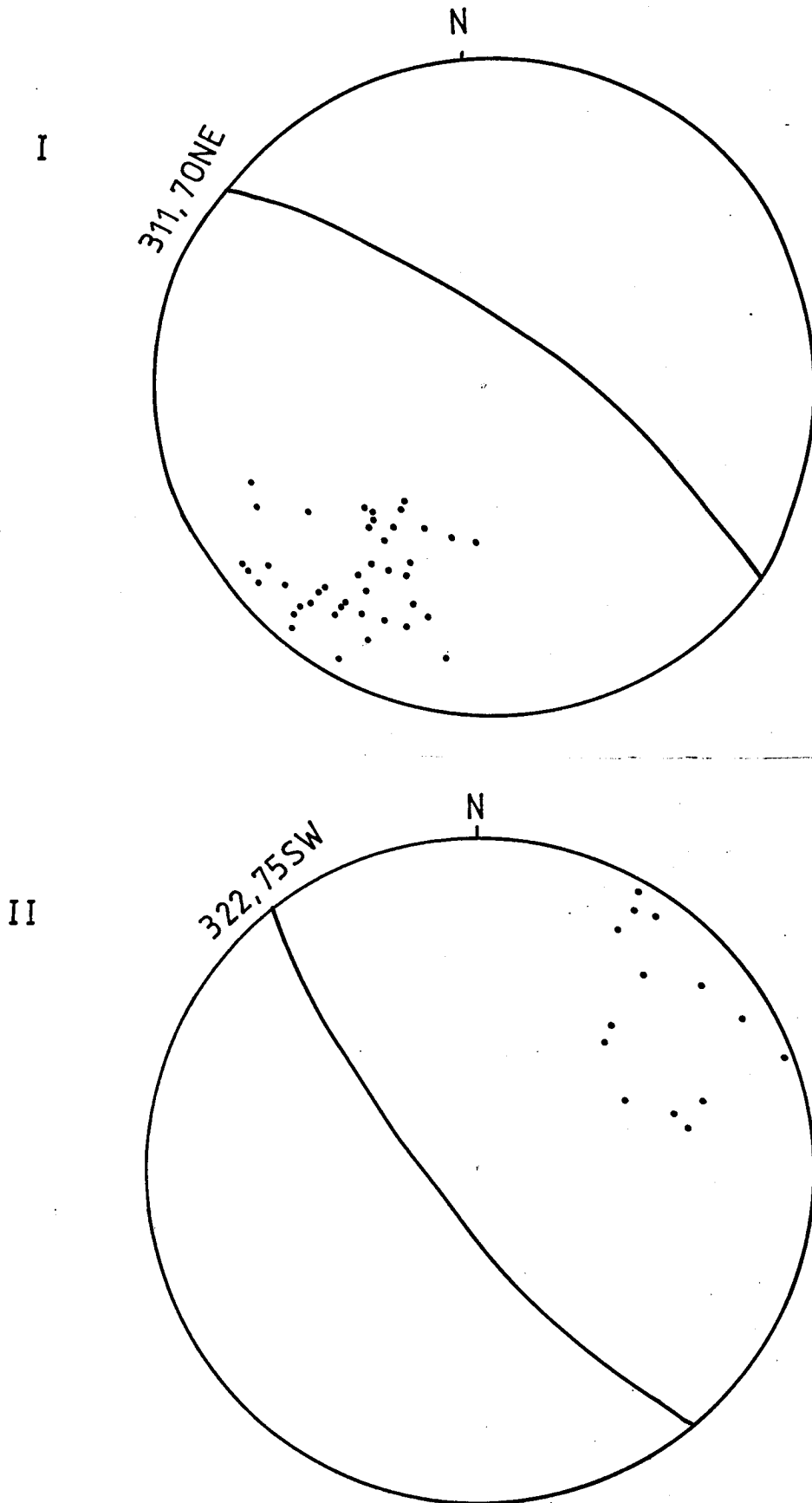
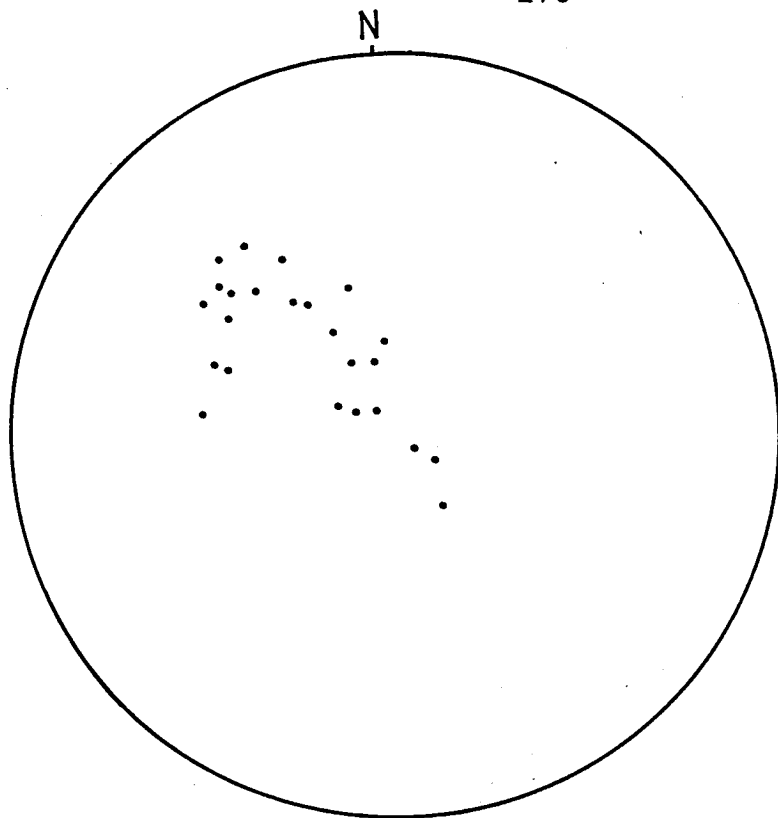


Figure A.1.4. Poles to foliation (So) measured along (I) Munyameshi River (n=42) and (II) Kalya River and 10Km NE of the Chikankata turn-off along the Great East Road (n=14). Equal angle projection. Visually estimated average trends shown by plotted planes.

I



II

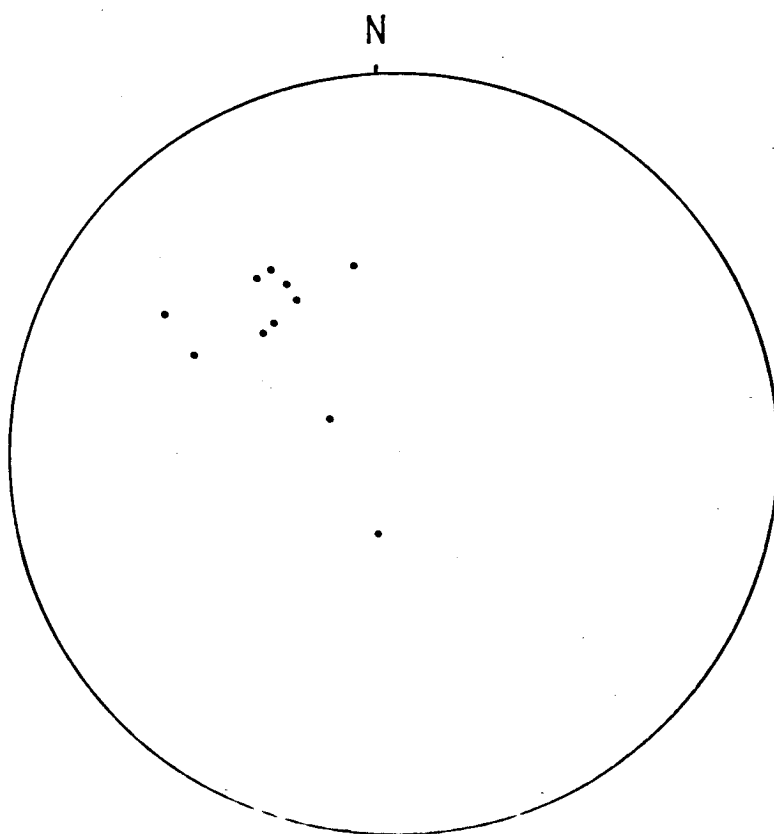


Figure A.1.5. Plunge of hinge lines in the calc-silicate gneisses along (I) Munyameshi River (n=25) and (II) Kalya River and 10Km NE of the Chikankata turn-off along the Great North Road (n=11). Equal angle projection.

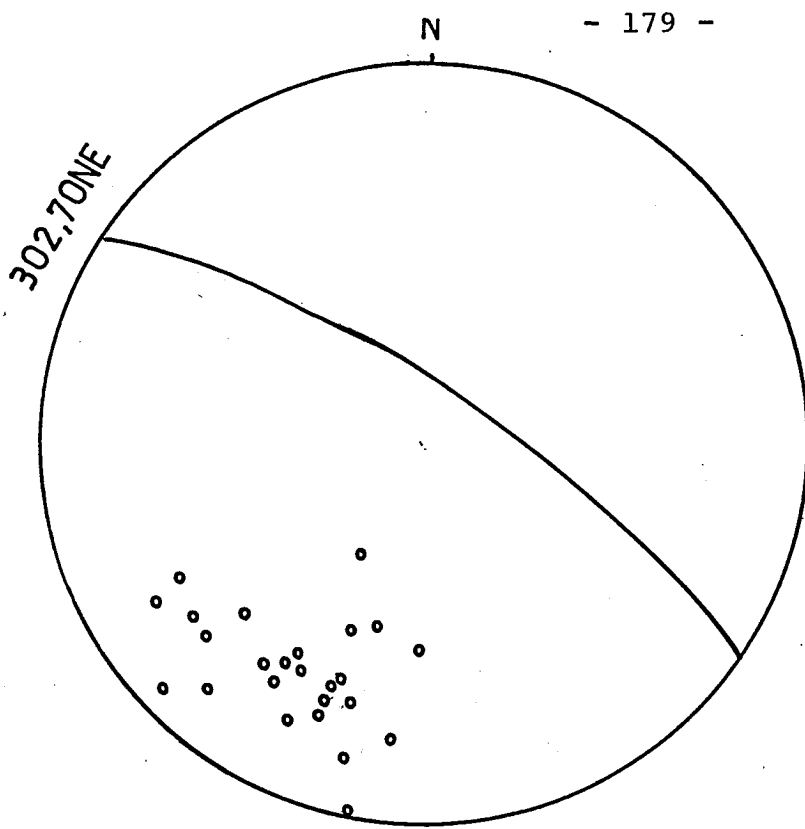
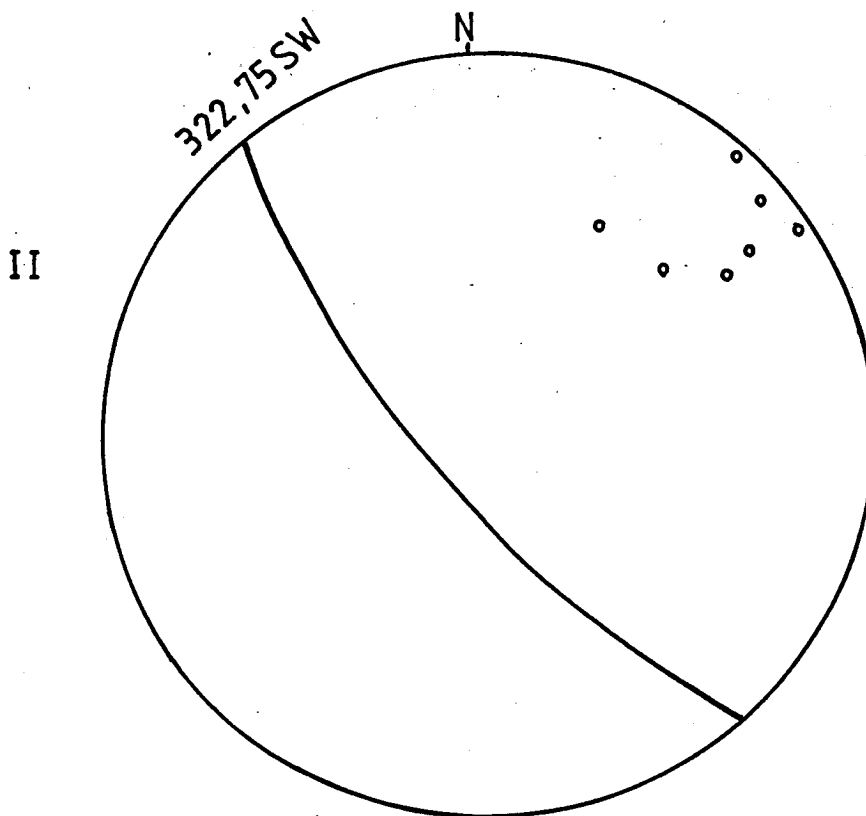
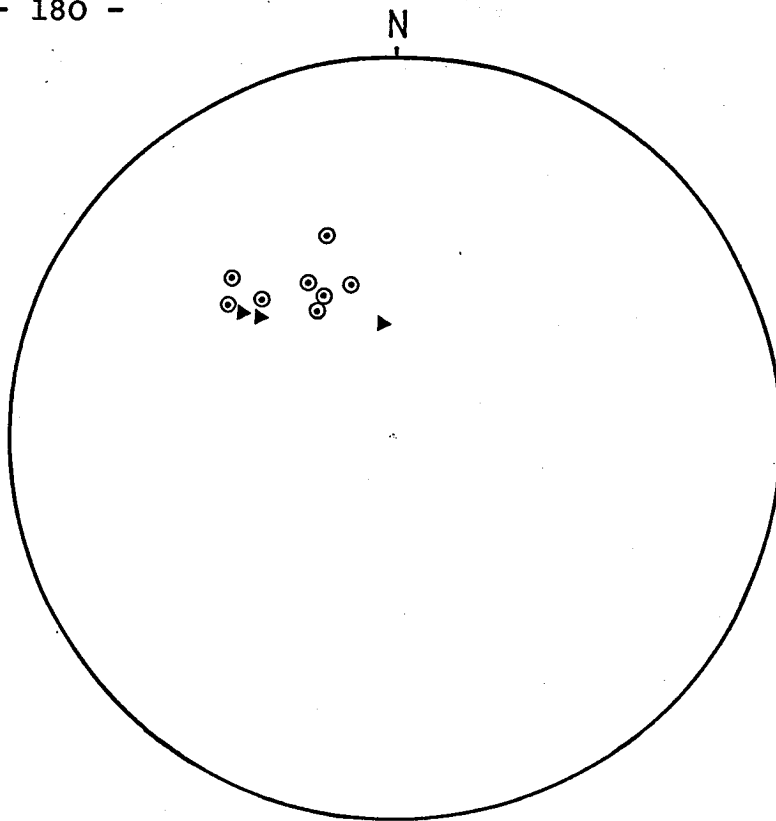


Figure A.1.6. Poles to axial surfaces of minor folds in the calc-silicate gneisses.

I



○ intersection lineation
▲ mineral lineation

II

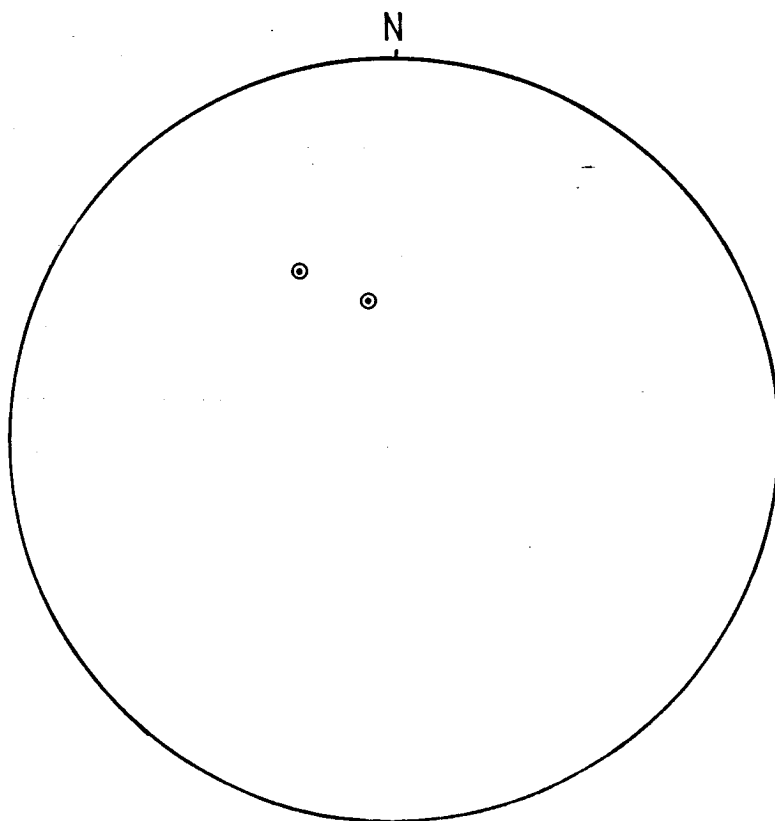


Figure A.1.7. Mineral stretching and intersection lineations measured along (I) the Munyameshi River (n=11) and (II) Kalya River (n=2).

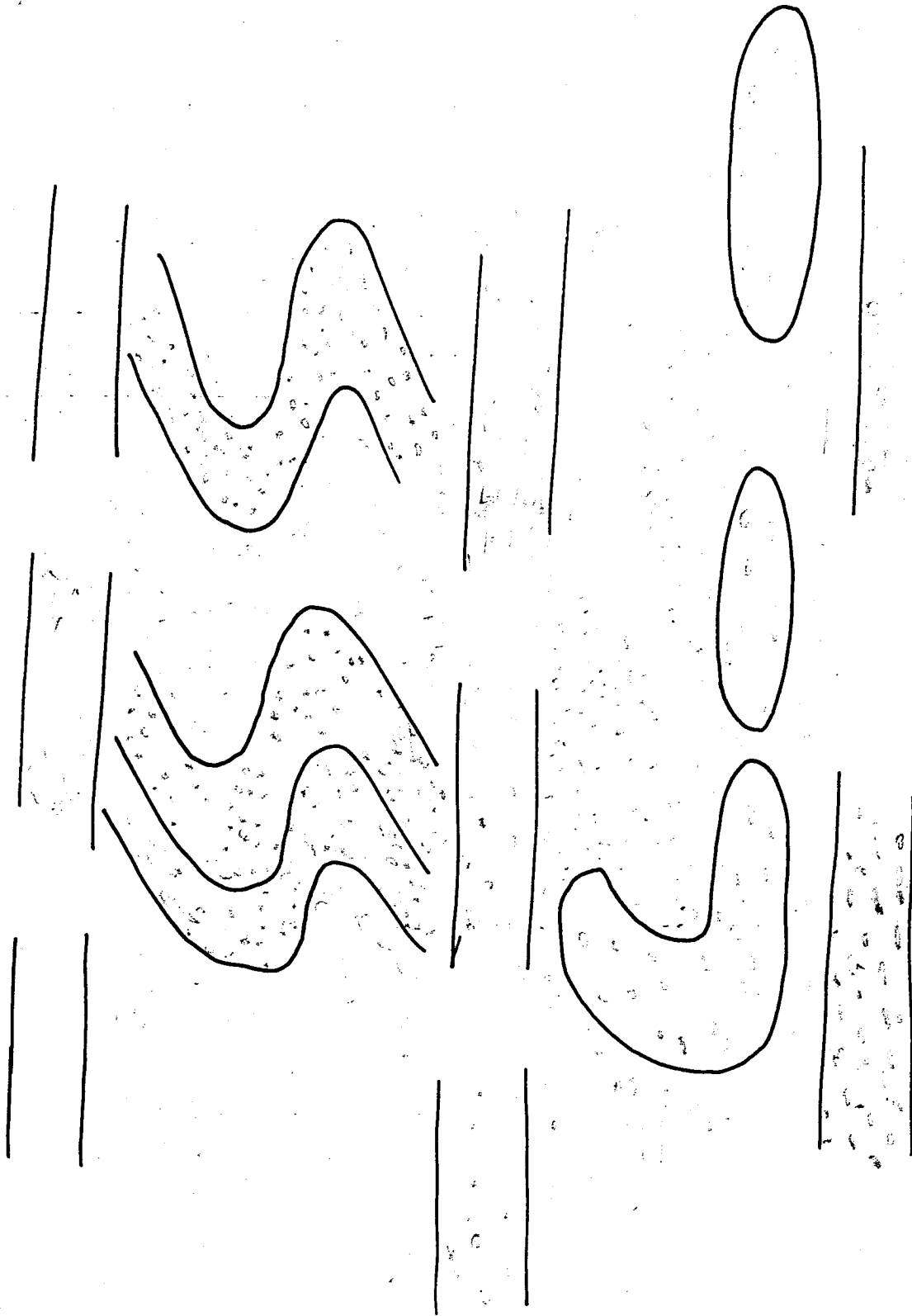


Figure A.1.8. Sheared calc-silicate layers and isolated fold closures of calc-silicate layers in the Muzuma Calc-silicate Formation (scale full size).

Mineral-stretching lineation is defined by elongate diopside and occasionally biotite crystals. Both minerals are streaked out on the S_0 foliation planes. This lineation plunges to the northwest at moderate to steep angles parallel to the intersection lineation (Figs. A.1.7 I and II) and to the hinge lines of the F_1 minor folds.

Later structures

A later and completely different style of folds (F_2) is sporadically seen in the field. This is defined by gentle, open folding of S_0 and S_1 . The later folds have northeast trending axial surfaces. The axial surface of one of these open folds along the Munyameshi River has an attitude of 245, 56 SE. In most cases, however, no attitude measurements were taken for these folds.

At two localities, along the Munyameshi and Kalya Rivers, F_2 folds refold isoclinal F_1 folds, and the foliation in the calc-silicate rocks definitely wraps around the F_2 fold noses.

A weakly developed and sporadically distributed northeast trending foliation (S_2) is also present in the calc-silicate terrane and is axial planar to the open folds. This occurs as a spaced foliation defined by fractures generally 5 to 10 mm apart.

Discussion of structural data

The structural data presented above is consistent with two phases of deformation, D_1 and D_2 . It is however also possible that these may belong to one progressive phase of deformation.

D_1 was more intense than D_2 , involving tight to isoclinal folding. This resulted in transposition of the compositional layering, which represents relict bedding into the regional northwest trend. This was accompanied by the development of axial planar foliation suggesting that the main-phase deformation accompanied the regional amphibolite facies metamorphism.

D_2 was an open folding event accompanied by the development of a weak, northeast trending axial planar foliation. This reoriented and locally folded minor folds formed during the earlier D_1 phase. As pointed out above, however, it may not represent an entirely different phases.

Smith⁽¹¹⁾ and Brown⁽¹³⁾ have suggested that the Muzuma Calc-silicate Formation is part of the northwest plunging Mazabuka synclinorium. The available structural data from the areas mentioned above is consistent with this interpretation. The minor folds are thus parasitic folds developed during the large scale folding. The attitudes of lineation and hinge lines are also generally consistent with those of Brown measured in the areas northwest of Chikankata, Chikankata south-east and around Changa School (see Brown,⁽¹³⁾).

Open folds with northeast axes were documented only in the Ngoma and Mpande Gneiss Formations by Brown⁽¹³⁾. These may be equivalent to those observed in the calc-silicate terrane in the present case.

The presence of minor folds with opposite plunges in some places within the calc-silicate gneisses suggests sheath-like geometry for these folds. In the same part of the Zambezi belt as discussed here, Wilson et al⁽¹⁵⁾ have also noted sheath folds, with a symmetry patterns indicating southward thrusting.

APPENDIX II

ANALYTICAL TECHNIQUES

Whole-rock and mineral analyses were conducted at the Ottawa Carleton Center for Geoscience Studies (OCCGS) in Canada. Whole-rock analyses were obtained using X-ray fluorescence (XRF) spectrometry, whereas mineral analyses were obtained by electron microprobe and atomic absorption spectrometry.

1. XRF Analysis

Forty-one rocks, including calc-silicate rocks, marbles and amphibolites, were selected for XRF analysis after careful petrographic study. Approximately 5 cm³ of each sample were crushed and ground to - 200 mesh.

Major and trace element analyses of the samples were carried out on a Phillips 1410 automated XRF spectrometer. The determinations were made on fused disks prepared with Li₂B₄O₇ and Li₂CO₃, using the technique described by De Jongh ⁽¹¹⁷⁾. Based on ANRT rock standard (D RN), the accuracy and precision of the analytical technique are summarized in Table I. Because of the analytical technique, the whole-rock analyses are presented on a volatile-free basis.

2. Atomic absorption analysis

Analyses of calcite and dolomite in the marbles were performed by atomic absorption spectrometry. Mineral separates were obtained with a heavy liquid medium (methylene iodide,), using a float and

Table 1 Precision and accuracy of XRF analysis of ANRT standard (DRN)

Major elements (wt.%)			
	Usable Value (Abbey, 1980)	Mean of 5 deter- minations	range
SiO ₂	52.88	52.99	52.86-53.16
TiO ₂	1.10	1.03	-
Al ₂ O ₃	17.56	17.61	17.59-17.65
FeO	8.72	9.73	9.71-9.76
MnO	0.21	0.21	-
MgO	4.47	4.22	4.14-4.41
CaO	7.09	6.98	6.96-7.02
Na ₂ O	3.00	2.95	2.89-3.00
K ₂ O	1.73	1.73	1.73-1.74
S	N.A	0.02	0.01-0.04
P ₂ O ₅	0.25	0.14	0.12-0.17
trace elements (ppm)			
Ba	380	372	368-379
Cr	45	43	40-47
Zr	125	129	127-132
Sr	400	386	381-391
Rb	75	70	69-71
Y	N.A	28	26-31
Nb	N.A	2	0-4
Zn	150	148	145-151
Ni	22	18	13-24

sink method at least twice as described by Kretz⁽²⁷⁾; Pers Commun., (1984). Hand Sorting was also applied after staining, for a few relatively coarse samples. These were simply crushed and stained.

Mineral separates were ground to powder with an alumina pestel and mortar, dissolved in 8% HCl and then filtered. The filtrate was then analyzed on a Techtron Instrument AAS 400 atomic absorption spectrometer. The precision of analyses on this spectrometer has been discussed by Kretz⁽²⁷⁾, who showed that the coefficient of variation, which is the standard deviation expressed as per cent of the amount present, is less than 10% for the elements Ca, Mg, Sr, Ba, Fe and Mn. The accuracy of the analytical method, obtained by co-analysing USGS rock standard (NBS-1a), was found to be generally within 12 per cent of the recommended value⁽²⁷⁾.

3. Electron Microprobe analysis

Carbon - coated polished sections of the Mapanza amphibolites were prepared for probe analysis. A Cambridge instrument Microscan -5 electron microprobe was used.

Analysis were conducted under an accelerating potential of 15 Kilo Volts and a specimen current of 50nA as measured on an albite standard. Beam diameter was 2 microns and counting periods were between 10-15s. Natural and synthetic minerals were used as standards.

The probe data was reduced to element concentrations by a computer program designed by Rucklidge and Gasperrini⁽¹¹⁸⁾

APPENDIX III

COMPUTATION OF NIGGLI PARAMETERS

Niggli parameters have been computed following the method outlined by Barth⁽³⁴⁾. This involves dividing Al_2O_3 , MgO , MnO , FeO total, Na_2O , K_2O , CaO in weight per cent by their respective molecular weights to give molecular proportions.

The molecular proportions are grouped together in the following way:

- (a) Al_2O_3 (including Cr_2O_3)
- (b) $\text{FeO} + \text{MgO}$ (+ $\text{MnO} + \text{NiO}$)
- (c) CaO (including $\text{BaO} + \text{SrO}$)
- (d) $\text{K}_2\text{O} + \text{Na}_2\text{O}$

The sum of those four quantities is recalculated to 100, and the resulting numbers designated al, fm, c and alk respectively.

The parameter si is calculated according to the equation:
 $\text{mol. prop. SiO}_2 : \text{mol. prop. Al}_2\text{O}_3 = x : \text{al}$
resulting x is called si

The molecular proportion of K_2O compared to the sum of the alkalies in alk is termed k, and the molecular proportion of MgO compared to the sum of the divalent elements in fm is termed mg.

These are computed as follows:

$$\underline{k} = \text{K}_2\text{O} / (\text{K}_2\text{O} + \text{Na}_2\text{O})$$

$$\underline{\text{mg}} = \text{MgO} / (\text{MgO} + \text{FeO} + \text{Mg})$$

APPENDIX IV

Sample localities of Calc-silicate rocks, marbles and amphibolites

Rock-type and sample number	Quarter Degree Sheet	Grid reference
Marble (FO4)	1628, NW	N284E 120
Marble (FO4A)	"	N284E 120
Marble (MA2)	1626, NE	N956E 885
Marble (MA4)	"	N024E 777
Marble (MA12)	"	N995E 920
Marble (FO13)	1628, NW	N082E 079
Marble (FO16)	"	N090E 073
Marble (FO20)	1627, NE	N105E 875
Marble (FO21)	"	N211E 790
Marble (FO22)	"	N211E 794
Marble (FO26)	"	N307E 923
Marble (MA18)	"	N033E 831
Marble (MA5)	"	N045E 776
Amphibolite (MA7)	"	N989E 670
Amphibolite (MA8)	"	N846E 714
Amphibolite (MA11)	"	N894E 714
Amphibolite (MA13A)	"	N984E 935
Amphibolite (MA14)	"	N974E 943
Amphibolite (MA15)	"	N968E 962
Amphibolite (MA13)	"	N984E 935
Amphibolite (MA19)	"	N027E 888
Amphibolite (MA19A)	"	N027E 888
Amphibolite (MA45)	"	N995E 712

Sample localities Cont'd

Rock-type and sample number	Quarter Degree Sheet	Grid reference
Calc-silicate (FO36)	1628, NW	N093E 283
Calc-silicate (FO37)	"	N298E 090
Calc-silicate (FO38)	"	N085E 299
Calc-silicate (FO40)	"	N800E 340
Calc-silicate (FO42)	"	N084E 346
Calc-silicate (FO43)	"	N082E 348
Calc-silicate (FO44)	"	N081E 348
Calc-silicate (FO47)	"	N094E 233
Calc-silicate (FO48)	"	N106E 224
Calc-silicate (FO49)	"	N105E 198
Calc-silicate (FO50)	"	N115E 164
Calc-silicate (FO51)	"	N135E 155
Calc-silicate (FO52)	"	N150E 128
Calc-silicate (FO53)	"	N172E 115
Calc-silicate (FO54)	"	N193E 099
Calc-silicate (FO55)	"	N222E 129
Calc-silicate (FO56)	"	N250E 119
Calc-silicate (FO57)	"	N267E 120
Calc-silicate (FO58)	1627, NE	N305E 650
Calc-silicate (FO59)	"	N275E 835
Calc-silicate (FO60)	"	N255E 884
Calc-silicate (FO61)	"	N259E 901
Calc-silicate (FO62)	"	N235E 935
Calc-silicate (FO64)	"	N193E 892

Sample localities Cont'd

Rock-type and sample number	Quarter Degree Sheet	Grid reference
Calc-silicate (MA1)	1626, NE	N035E 899
Calc-silicate (MA3)	"	N027E 888
Calc-silicate (MA16)	"	N895E 715
Calc-silicate (FO1)	1528, SW	N323 E 163
Calc-silicate (FO6)	1627, NE	N268E 040
Calc-silicate (FO7)	"	N223E 044
Calc-silicate (FO8)	"	N217E 034
Calc-silicate (FO9)	"	N187E 010
Calc-silicate (FO10)	"	N160E 028
Calc-silicate (FO11)	"	N135E 046
Calc-silicate (FO12)	"	N124E 048
Calc-silicate (FO18)	1528, SW	N320E 970
Calc-silicate (FO19)	"	N425E 835
Calc-silicate (FO23)	1627, NE	N239E 840
Calc-silicate (FO24)	"	N247E 847
Calc-silicate (FO25)	"	N281E 909
Calc-silicate (FO27)	1528, SW	N352E 921
Calc-silicate (FO28)	1627, NE	N275E 037
Calc-silicate (FO29)	"	N247E 058
Calc-silicate (FO30)	1628, NW	N214E 090
Calc-silicate (FO31)	"	N074E 245
Calc-silicate (FO32)	"	N078E 246
Calc-silicate (FO33)	"	N249E 092
Calc-silicate (FO34)	"	N248E 098
Calc-silicate (FO35)	"	N103E 270

Sample localities Cont'd

Rock-type and sample number	Quarter Degree Sheet	Grid reference
Calc-silicate (FO67)	1627, NE	N229E 948
Calc-silicate (FO68)	"	N258E 968
Calc-silicate (FO70)	1528, SW	N337E 921
Calc-silicate (FO71)	"	N395E 878
Calc-silicate (FO72)	"	N431E 878
Calc-silicate (FO73)	"	N442E 860 $\frac{1}{2}$
Calc-silicate (BA-N2)	15"	N431E 878
Calc-silicate (FO74)	"	N459E 834
Calc-silicate (CH3)	1628, NW	N084E 345
Calc-silicate (CH5)	"	N080E 333
Calc-silicate (CH16)	"	N224E 155
Calc-silicate (CH17)	"	N245E 158
Calc-silicate (LUI)	"	N281E 220
Calc-silicate (O51)	"	N059E 229