CHAPTER 7

PETROGENESIS OF THE NANDEWAR SUITE

Many of the conclusions reached in the preceding chapter are also pertinent to the genesis of the Nandewar suite. The applicability of each of the genetic controls already discussed will now be evaluated in view of the field, petrographic, mineralogical and chemical data presented in Chapters 2 to 5.

FRACTIONAL CRYSTALLIZATION

Field, Petrographic and Mineralogical Evidence

The predominance of rhyolitic lavas and the absence of basalts *s.s.* from the Nandewar eruptives appears inconsistent with a genetic model involving closed-system crystal fractionation of transitional basaltic magma. However, the advanced state of erosion of the Nandewar Volcano, indicated by the outcrop of intrusive plugs on the highest peaks, suggests that significant quantities of volcanics of unknown composition have been removed. Even if most of this material were basaltic (which does not seem likely because of the trend towards increased acidity of the later eruptives), there would still probably be an excess of felsic types.

The inferred order of eruption and mineralogical characteristics of the various eruptive types are also difficult to reconcile with closed-system low to moderate pressure fractionation models. Field and geochronological evidence indicates that the voluminous alkali rhyolites were erupted first, followed by the main shield-forming sequence which appears to have been erupted in a restricted time interval (possibly within 1 Ma). Heat balance calculations (Usselman and Hodge, 1978) indicate that relatively large magma chambers will crystallize and solidify within approximately 10^5 years. Thus, if the older alkali rhyolites are cogenetic with the other eruptives (as is indicated by their trace element chemistries, discussed below), then age differences of up to 2 Ma indicated by the Rb/Sr and K/Ar data are unrealistically large.

The presence of aluminous orthopyroxene and clinopyroxene megacrysts and cumulate assemblages within the trachyandesites and hawaiites indicates periods of intratelluric crystallization of these magmas at approximately 6 to 8 kb, prior to the rapid movement of the host melts to the surface. On the other hand, the petrographic and mineralogical characteristics of the most evolved trachyandesites (e.g. 49012), tristanites and more felsic types indicate that, although they have generally experienced some intratelluric crystallization at low pressures, there is no evidence of crystallization at elevated pressures. To be internally consistent with a simple closed-system crystal fractionation model, it must be postulated that differentiation of 'parental' trachyandesite or hawaiite melts occurred at elevated pressures to give a tristanite melt (even though the volumes of high-pressure phases are trivial), which then migrated to a high-level magma chamber and subsequently fractionated to produce the trachytes, alkali rhyolites and comendites. According to this model, the 'parental' trachyandesites and/or hawaiites remained in a moderate pressure environment (without experiencing further fractionation) during removal of the tristanite magma, followed by a later residence period of the alleged tristanite derivatives in a high-level magma chamber necessary to produce the more evolved differentiates.

Thus constraints imposed by the order of eruption, apparent depth of origin and volumetric relationships require an unnecessarily complicated and probably quite unrealistic sequence of events to be consistent with crystal fractionation models.

Chemical Evidence

The role of fractional crystallization in the development of the Nandewar suite can be tested quantitatively by mass-balance calculations utilizing major and trace element data from natural phenocryst/host assemblages.

Major Elements

Evaluation of the major element mass-balance requirements for a number of proposed fractionation steps in the Nandewar series has been performed using the generalized least-squares mixing method of Le Maitre

(1979). The technique involves determination of a best fit linear combination of the proposed daughter composition and an appropriate crystal extract with the composition of the proposed parent. The relative success of a particular 'mixing model' is assessed mathematically from the sum of the squares (Σr^2) of the differences between oxide contents in the actual and computed parent magma compositions. Estimates of a 'good fit' range from $\Sigma r^2 < 0.1$ (le Roex and Erlank, 1982) to $\Sigma r^2 < 1$ (Baker *et al.*, 1977). Rigorous statistical evaluation of the relationship between the size of Σr^2 and the degree of fit requires information on the variances and covariances of the input data (Bryan *et al.*, 1969; Zielinski, 1975) which is rarely available. In the absence of a single definitive criterion for an acceptable fit, the solution should be scrutinized with due regard to the likely magnitude of analytical errors in the input data. In addition, the Σr^2 value may be quite low for a particular solution but the differences for one element within that solution may be quite significant.

A reasonable fit for all oxides between parent and daughter compositions plus the alleged extract demonstrates that their interrelationship via fractional crystallization is feasible although not proven. Acceptance of the fractionation model also depends on internal consistency of field, petrographic, mineralogical and other chemical data.

The mixing calculations were performed in a stepwise fashion. Initially the most primitive composition was selected as the parent and slightly more evolved compositions were tested as potential daughter products. One of these daughter products was then used as the parent for the next fractionation step. Computed and actual parent compositions together with the weight fraction of the calculated extracts and daughter compositions for the major fractionation steps are given in Table 7.1. Crystal extract compositions were based on microprobe analyses of the core zones of phenocrysts in the parent, with the exception of peralkaline trachyte 49098. However, phenocryst compositions used in transitions for this parental composition were from compositionally similar hosts. Solutions for the remaining lava compositions are summarized in Table 7.2 and are based on the same parent and phenocryst compositions as the calculations shown in Table 7.1. All analyses were normalized to 100

TABLE 7.1

Major element fractionation models for the Nandewar series

Fractionation Step	Hawaiite (49001)	to	Hawaiite (49003)	Hawaiite (49001)	to	Trachyandesite (49008)	Trachyandesite (49000)	to	Trachyandesite (49008)
	49001 Observed		49001 Calculated	49001 Observed		49001 Calculated	49000 Observed		49000 Calculated
SiO_2	48.35		48.35	48.35		48.16	48.61		48.55
TiO_2	2.29		1.98	2.29		2.08	2.74		2.14
Al_2O_3	14.35		14.33	14.35		14.17	15.05		14.78
ΣFeO	11.22		11.32	11.22		10.86	10.85		10.52
MnO	0.16		0.14	0.16		0.13	0.13		0.13
MgO	10.02		10.03	10.02		9.99	8.46		8.43
CaO	8.68		8.78	8.68		8.62	9.28		9.23
Na_2O	3.23		3.61	3.23		3.46	2.90		3.52
K_2O	1.09		0.87	1.09		1.55	1.48		1.63
P_2O_5	0.62		0.59	0.62		0.99	0.49		1.05

Solution (Wt. Fraction)		Solution (Wt. Fraction)		Solution (Wt. Fraction)	
49003	0.824	49008	0.663	49008	0.706
Oliv. (Fo_{81})	0.063	Oliv. (Fo_{81})	0.122	Oliv. (Fo_{82})	0.074
Cpx ($Ca_{49}Mg_{43}Fe_8$)	0.043	Cpx ($Ca_{49}Mg_{43}Fe_8$)	0.110	Cpx ($Ca_{47}Mg_{43}Fe_{10}$)	0.118
Plag. (An_{52})	0.070	Plag. (An_{52})	0.105	Plag. (An_{61})	0.102
Σr^2	0.311	Σr^2	0.651	Σr^2	1.279
				Fp	0.706

Fractionation Step	Trachyandesite (49008)	to	Trachyandesite (49012)	Trachyandesite (49012)	to	Tristanite (49076)	Tristanite (49076)	to	Trachyte (49083)
	49008 Observed		49008 Calculated	49012 Observed		49012 Calculated	49076 Observed		49076 Calculted
SiO_2	48.82		51.45	52.27		52.45	56.98		56.75
TiO_2	2.73		2.20	2.36		1.99	1.73		1.73
Al_2O_3	15.76		15.14	16.32		16.29	16.21		16.41
ΣFeO	11.74		10.78	10.46		10.77	9.06		8.91
MnO	0.16		0.14	0.14		0.19	0.17		0.16
MgO	5.07		5.77	3.35		3.07	1.85		2.00
CaO	7.64		6.86	6.70		6.98	4.53		4.59
Na_2O	4.32		4.19	4.58		4.69	5.49		4.89
K_2O	2.26		2.32	2.55		2.35	3.28		4.16
P_2O_5	1.49		1.15	1.27		1.21	0.70		0.40

Solution (Wt. Fraction)		Solution (Wt. Fraction)		Solution (Wt. Fraction)	
49012	0.909	49076	0.697	49083	0.731
Oliv. (Fo_{80})	0.050	Oliv. (Fo_{50})	0.040	Oliv. (Fo_{56})	0.023
Cpx ($Ca_{41}Mg_{47}Fe_{12}$)	0.041	Cpx ($Ca_{44}Mg_{44}Fe_{12}$)	0.053	Cpx ($Ca_{45}Mg_{40}Fe_{15}$)	0.064
Σr^2	9.70	Plag. (An_{53})	0.161	Plag. (An_{46})	0.142
Fp	0.642	Timt. (Usp_{61})	0.032	Timt. (Usp_{71})	0.037
		Apatite	0.017	Apatite	0.003
		Σr^2	0.475	Σr2	1.384
		Fp	0.447	Fp	0.327

TABLE 7.1 (continued)

Major element fractionation models for the Nandewar series

Fractionation Step	Trachyte (49083) to	Trachyte (49088)	Trachyte (49088) to	Trachyte (49098G)	Trachyte (49098G) to	Comendite (49162)
	49083 Observed	49088 Calculated	49088 Observed	49088 Calculated	49098G Observed	49098G Calculated
SiO_2	61.17	61.27	63.97	63.61	63.51	63.64
TiO_2	0.95	1.02	0.65	0.42	0.55	0.76
Al_2O_3	16.79	16.61	16.48	16.81	15.37	15.47
ΣFeO	6.37	6.41	4.83	5.21	6.62	6.65
MnO	0.12	0.15	0.12	0.23	0.20	0.20
MgO	0.67	0.56	0.33	0.13	0.16	0.45
CaO	2.43	2.47	1.68	1.75	1.62	1.57
Na_2O	5.51	6.30	6.56	6.74	6.68	5.36
K_2O	5.58	4.77	5.25	5.04	5.22	5.90
P_2O_5	0.40	0.43	0.13	0.05	0.06	0.01

Solution (Wt. Fraction)		Solution (Wt. Fraction)		Solution (Wt. Fraction)	
49088	0.783	49098	0.774	49162	0.389
Oliv. (Fo_{21})	0.015	Anorth. (Or_{28})	0.226	Oliv. (Fo_{13})*	0.029
Cpx. ($Ca_{47}Mg_{40}Fe_{13}$)	0.012	Σr^2	0.579	Cpx. ($Ca_{46}Mg_{18}Fe_{36}$)*	0.049
Anorth. (Or_{24})	0.161	Fp	0.198	Anorth. (Or_{43})	0.503
Timt. (Usp_{66})	0.021			Timt. (Usp_{65})**	0.025
Apatite	0.008			Σr^2	2.376
Σr^2	1.344			Fp	0.077
Fp	0.256				

Fractionation Step	Trachyte (49098G) to	Comendite (49161)	Comendite (49161) to	Comendite (49163)	Comendite (49161) to	Comendite (49164)
	49098G Observed	49098G Calculated	49161 Observed	49161 Calculated	49161 Observed	49161 Calculated
SiO_2	63.51	63.67	69.10	69.13	69.10	68.55
TiO_2	0.55	0.80	0.36	0.67	0.36	0.65
Al_2O_3	15.37	15.36	14.42	14.60	14.42	15.01
ΣFeO	6.62	6.64	4.30	4.23	4.30	3.77
MnO	0.20	0.18	0.11	0.08	0.11	0.09
MgO	0.16	0.45	0.02	0.07	0.02	0.34
CaO	1.62	1.52	0.48	0.58	0.48	0.84
Na_2O	6.68	5.55	5.89	5.81	5.89	6.17
K_2O	5.22	5.81	5.29	4.82	5.29	4.58
P_2O_5	0.06	0.01	0.03	0.01	0.03	0.00

Solution (Wt. Fraction)		Solution (Wt. Fraction)		Solution (Wt. Fraction)	
49161	0.422	49163	0.646	49164	0.946
Oliv. (Fo_{13})*	0.027	Cpx. ($Ca_{47}Mg_8Fe_{45}$)	0.019	Cpx. ($Ca_{47}Mg_8Fe_{45}$)	0.032
Cpx. ($Ca_{46}Mg_{18}Fe_{36}$)*	0.054	Anorth. (Or_{35})	0.311	Timt. (Usp_{67})	0.022
Anorth. (Or_{43})	0.471	Timt. (Usp_{67})	0.024	Σr^2	1.823
Timt. (Usp_{65})**	0.026	Σr^2	0.382	Fp	0.080
Σr^2	1.816	Fp	0.054		
Fp	0.084				

* Composition of microphenocrysts in trachyte 49103

** Composition of microphenocrysts in trachyte 49102

Σr^2 = sum of the squares of the residuals

Fp = the weight fraction which a derivative liquid represents of the 'parental' trachyandesite (49000)

TABLE 7.2

Summary of major element mass-balance calculations for the Nandewar suite

Fractionation Step	Weight Fraction of Crystal Extracts							
	Olivine	Clinopyroxene	Plagioclase	Titanomagnetite	Apatite	Anorthoclase	F	Σr^2
Hawaiite 49001								
→ 49000	0.053	-	0.016	-	-	-	0.931	0.473
→ 49002	0.065	0.034	-	-	-	-	0.901	0.430
→ 49004	0.099	0.067	0.015	-	-	-	0.819	0.625
→ 49007	0.119	0.115	0.003	-	-	-	0.763	2.409
Trachyandesite 49000								
→ 49005	0.060	0.104	0.102	-	-	-	0.734	0.954
→ 49009	0.069	0.114	0.088	-	-	-	0.729	1.536
→ 49011	0.111	0.135	0.148	-	-	-	0.606	5.351
→ 49012	0.109	0.148	0.107	-	-	-	0.636	6.845
→ 49013	0.107	0.147	0.105	-	-	-	0.641	5.923
Trachyandesite 49008								
→ 49011	0.033	0.044	-	-	-	-	0.923	8.075
→ 49013	0.048	0.039	-	-	-	-	0.913	7.956
→ 49018	0.065	0.146	-	-	-	-	0.789	32.139
Trachyandesite 49012								
→ 49018	0.025	0.053	0.093	0.025	0.011	-	0.793	0.658
→ 49075	0.031	0.067	0.104	0.036	0.017	-	0.745	0.339
→ 49077	0.044	0.047	0.163	0.034	0.018	-	0.694	0.394
→ 49078	0.039	0.070	0.160	0.029	0.017	-	0.685	0.500
→ 49079	0.038	0.066	0.139	0.036	0.020	-	0.701	0.244
→ 49080	0.038	0.072	0.127	0.043	0.019	-	0.701	0.413
Tristanite 49076								
→ 49080	-	0.031	-	0.018	-	-	0.951	0.300
→ 49081	0.008	0.029	0.059	0.040	0.008	-	0.856	0.304
→ 49082	0.029	0.026	0.098	0.036	0.006	-	0.805	0.255
→ 49097	0.015	0.057	0.100	0.035	0.007	-	0.786	0.336
→ 49084	0.029	0.074	0.148	0.047	0.007	-	0.695	1.325
Trachyte 49083								
→ 49084	0.007	0.020	-	0.013	0.005	0.036	0.919	0.121
→ 49085	0.008	0.005	-	0.021	0.009	0.107	0.850	0.943
→ 49086	0.010	0.011	-	0.021	0.008	0.121	0.829	1.162
→ 49087	-	0.036	-	0.018	0.008	0.091	0.847	0.489
→ 49119	0.014	0.017	-	0.043	0.016	0.423	0.487	2.265
→ 49120	0.012	0.026	-	0.038	0.015	0.346	0.563	1.376
→ 49121	0.009	0.027	-	0.037	0.014	0.321	0.592	1.273
→ 49122	0.016	0.016	-	0.043	0.016	0.476	0.433	2.067
→ 49123	0.018	0.017	-	0.044	0.017	0.418	0.486	1.821
→ 49124	0.031	0.015	-	0.046	0.017	0.352	0.539	1.933

TABLE 7.2. (continued)

Summary of major element mass-balance calculations for the Nandewar suite

Fractionation Step	Weight Fraction of Crystal Extracts						
	Olivine	Clinopyroxene	Titanomagnetite	Apatite	Anorthoclase	F	Σr^2
Trachyte 49088							
→ 49090	-	0.039	0.006	-	0.230	0.725	0.625
→ 49089	-	0.014	0.005	-	0.096	0.885	0.222
→ 49091	0.033	0.042	-	-	-	0.925	2.663
→ 49102	-	0.012	0.008	-	0.145	0.835	0.127
Peralkaline trachyte 49098G							
→ 49103	0.026	0.014	0.003	-	-	0.957	0.554
→ 49099	0.023	0.042	0.011	-	0.287	0.637	0.822
→ 49100	0.008	0.050	0.024	-	0.300	0.618	0.780
→ 49104	-	0.056	0.017	-	0.130	0.797	0.584
→ 49107	0.008	0.047	0.015	-	0.052	0.878	0.458
→ 49101	0.016	0.056	0.025	-	0.398	0.505	0.932
→ 49105	0.021	0.054	0.024	-	0.314	0.587	0.934
→ 49106	0.015	0.055	0.017	-	0.090	0.823	0.463
→ 49108	0.028	0.058	0.025	-	0.324	0.565	1.380
→ 49160	0.023	0.043	0.026	-	0.439	0.469	1.558
Comendite 49161							
→ 49165	-	0.029	0.036	-	0.249	0.686	1.071
Alkali rhyolite 49121							
→ 49119	-	-	0.017	-	0.258	0.725	0.581
→ 49120	-	-	0.007	-	0.077	0.916	0.286
→ 49122	-	-	0.020	-	0.358	0.622	0.334
→ 49123	-	-	0.023	-	0.239	0.738	0.379
→ 49124	-	-	0.036	-	0.065	0.899	0.602
→ 49125	-	-	0.045	-	0.239	0.716	1.139
→ 49126	-	-	0.045	-	-	0.955	1.407
→ 49127	-	-	0.048	-	0.257	0.695	1.090
→ 49128	-	-	0.042	-	0.049	0.909	0.601
→ 49129	-	-	0.052	-	0.364	0.584	0.919
→ 49130	-	-	0.055	-	0.412	0.533	1.051
→ 49131	-	-	0.052	-	0.238	0.710	1.476

F = weight fraction of liquid remaining

Σr^2 = sum of the squares of the residuals percent anhydrous with total Fe as FeO for the calculations.

It was noted in Chapter 5 that the marked variation in Na_2O/K_2O ratios of the Nandewar mafic rocks may be difficult to explain by a closed-system fractional crystallization model. Poor fits between actual and calculated Na_2O, K_2O, P_2O_5 and TiO_2 values in the modelling calculations (Tables 7.1 and 7.2), which test the possible derivation of hawaiite from trachyandesite and vice versa, confirmed these suspicions. Similarly, the considerable variation of Na_2O/K_2O ratios amongst the hawaiites (2.13 to 3.88) results in poor agreement between computed and actual alkali contents. TiO_2 also often exhibits poor agreement, suggesting that if the hawaiites were related in some way by fractionation controls, the alleged crystal extracts were at variance with observed phenocryst phases.

Poor fits for TiO_2,Na_2O and P_2O_5 are evident in the transitions trachyandesite 49000 → 49008 and trachyandesite 49008 → 49012. In the latter example poor agreement also exists between calculated and observed SiO_2, ΣFeO, MgO and CaO contents. Compositions of plagioclase phenocrysts and orthopyroxene megacrysts in trachyandesite 49008 were initially used in the calculations, but both gave unrealistically large negative solutions and were omitted from subsequent calculations. The marked disparity in the calculated and observed P_2O_5 contents for the transition trachyandesite 49008 → 49012 exists, because, although apatite was not observed as a phenocryst phase in the alleged parent, P_2O_5 nevertheless decreases in the more evolved types.

Many of the solutions for the fractionation steps involving the more evolved trachyandesites → tristanites and tristanites → mafic trachytes are acceptable. However, the generally aphyric nature of the most evolved trachyandesites seems at variance with the quite significant amounts of crystal extracts (~30 wt. percent) which are required to have been removed to generate the tristanites. The poor fits for Na_2O and K_2O evident in several solutions for the fractionation step tristanite → mafic trachyte may be partly explicable by Na_2O loss from the trachytes during crystallization, but K_2O contents in some of the proposed daughter products are higher than expected by concentration resulting from loss of Na.

An analogous fractionation step to the derivation of mafic trachyte from tristanite is provided by monzonite (49070) and its schlieren. The results of mass-balance calculations for these compositions are listed in Table 7.3. There are two interesting features of these solutions. Firstly, alkali feldspar and biotite, which are relatively abundant phases in the host monzonite gave negative solutions in initial calculations. Secondly, the calculated weight fraction of schlieren (59.8 percent) contrasts strikingly with the generous volumetric estimates of 1 to 5 percent at the outcrop. However, the latter feature may have resulted from only localized segregation of residual liquids, the major portion remaining interstitial to early crystallized phases.

TABLE 7.3

Monzonite (49070) calculated as a linear combination of its schlieren composition and its constituent minerals

	Host Observed	Host Calculated	Schlieren		Solution (Wt. Fraction)
SiO_2	57.78	57.68	65.22		
TiO_2	1.78	1.72	0.57	Schlieren	0.598
Al_2O_3	16.13	16.06	17.18	Cpx	0.052
ΣFeO	8.55	8.50	3.28	Plag.	0.205
MnO	0.15	0.15	0.05	Amph.	0.083
MgO	1.95	1.90	0.79	Timt.	0.049
CaO	4.62	4.64	1.40	Ilm.	0.004
Na_2O	5.29	5.48	6.33	Apat.	0.009
K_2O	3.11	3.24	5.04		
P_2O_5	0.63	0.46	0.15	Σr^2	0.108

There is reasonable agreement for most elements in the fractionation step mafic trachyte to peralkaline trachyte although quite significant amounts of anorthoclase (~20 wt. percent) must be extracted. Production of the comendites from a peralkaline trachyte parent requires removal of even larger amounts of anorthoclase (~40 to 48 wt. percent) and the solutions generally display poor fits for Na_2O, K_2O, TiO_2 and

P_2O_5. The discrepancies in P_2O_5 contents arise, because, although apatite ceases to occur as a phenocryst phase in lavas more evolved than the mafic trachytes, P_2O_5 continues to decrease to very low levels in the peralkaline trachytes and comendites.

Generation of the most evolved comendites by fractionation of comendite 49161 seems feasible in some cases (e.g. 49163) and most unlikely in others (e.g. 49164), where there are significant discrepancies for most elements in the solution.

The feasibility of deriving the metaluminous to peraluminous alkali rhyolites from mafic and peralkaline trachyte parents was tested, even though the latter case is precluded on experimental grounds (Bailey and Schairer, 1964). Removal of anorthoclase, the dominant phenocryst phase in the peralkaline trachytes, should result in increased peralkalinity in the derivative liquids. In this regard, it is of interest to note that the transition from peralkaline trachytes to comendites (see Fig. 5.2a) is accompanied by a trend of *decreasing* peralkalinity. Solutions for the derivation of the alkali rhyolites from a mafic trachyte parent (Table 7.2) are generally characterized by poor fits and do not support a simple relationship of the volcanics by fractional crystallization.

The compositional variation amongst the older alkali rhyolites, albeit somewhat restricted, was also considered in terms of crystal fractionation models. Solutions based on removal of anorthoclase and titanomagnetite from the least evolved variant commonly resulted in poor fits for Na_2O, K_2O, TiO_2 and ΣFeO in the proposed daughter products.

Inspection of the Fp values in Table 7.1, which give the weight fraction that a particular derivative melt represents of the 'parental' trachyandesite (49000), indicates that approximately 90 to 95 percent crystallization of the proposed parent is required to produce a comenditic liquid. The trivial volumes of cognate cumulates which occur as inclusions in the volcanics and the rarity of phenocrysts in many types do not support the production of the more evolved variants by such large degrees of crystallization. Nevertheless, the estimated weight fractions of crystal extracts in each transition can be used as a basis to evaluate the consistency of trace element variations in the suite with major element fractionation models.

Trace Elements

Trace element modelling calculations may be performed assuming either equilibrium between the surface of the crystallizing phases and the melt (equation 1; Gast, 1968), or, equilibrium between the total solid and the melt (equation 2; Arth, 1976)

$$\frac{C_L}{C_o} = F^{(D_s-1)} \tag{1}$$

$$\frac{C_L}{C_o} = \frac{1}{F+D_s(1-F)} \tag{2}$$

where C_o is the concentration of the element in the original melt, C_L is the concentration of the element in the differentiated liquid, F is the weight fraction of liquid remaining and D_s is the bulk distribution coefficient given by:

$$D_s = W_A K^{A/liq} + W_B K^{B/liq} + \ldots\ldots,$$

where $K^{A/liq}$ and $K^{B/liq}$ are the solid/liquid partition coefficients and W_A and W_B represent the weight fractions of A and B in the crystal extract, respectively.

Arth (1976) suggested that the surface-equilibrium model may be more applicable to rapidly cooled high-level magma bodies, whereas the total-equilibrium model is likely to more closely approximate slowly cooled plutonic magmas. Most trace element modelling studies (e.g. Baker *et al.*, 1977; le Roex and Erlank, 1982) assume Rayleigh fractionation or surface equilibrium (i.e. equation 1). This assumption is not unreasonable in view of trace element zoning observed in natural volcanic phenocrysts (Shimizu and le Roex, 1982). Slow cationic diffusion rates in crystals compared to crystallization rates (Margaritz and Hofmann, 1978a), coupled with natural convective processes likely to occur in magma chambers (Bartlett, 1969), probably results in a relatively homogeneous liquid and surface-equilibrium conditions. Decreased diffusion rates in relatively dry granitic magmas may result in significant departures from a homogeneous melt in a boundary layer adjacent to crystal surfaces (Margaritz and Hofmann, 1978a). However, such effects are unlikely to be important in peralkaline melts with moderately high F and Cl contents.

Meaningful application of trace element modelling calculations depends strongly on the availability of partition coefficients which are appropriate to the particular system under consideration. Partition coefficients are generally determined by analysis of phenocrysts and matrix separated from porphyritic lavas (e.g. Onuma *et al.*, 1968; Berlin and Henderson, 1969; Philpotts and Schnetzler, 1970), or by experimental studies, reviewed by Irving (1978).

Both approaches are subject to a number of uncertainties which makes selection of appropriate partition coefficients very difficult. Since phenocrysts may commonly be zoned with respect to major and trace elements, bulk separation of the phenocrysts will not provide partition coefficients appropriate to the surface-equilibrium model. In addition, the very techniques of mineral separation and purification discriminate against phenocryst rims with adhering matrix fragments which further biases the partition coefficients (Alberede and Bottinga, 1972). Other problems with partition coefficients based on phenocryst/matrix data relate to the presence of inclusions in phenocrysts and the purity of separated mineral and matrix fractions. Whilst these difficulties can generally be overcome by careful scrutiny of the separated materials, the rarity or absence of phenocrysts in certain lava types often precludes the determination of partition coefficients appropriate to those compositions.

The problems associated with experimentally-determined partition coefficients include: (1) the attainment of equilibrium in the experiments (Irving, 1978); (2) the possibility that the relatively high concentrations used in 'doped' experimental runs results in non-Henry's law behaviour (Mysen, 1976,1978); and (3) that simple synthetic systems may not produce results appropriate to natural systems.

Factors which may affect partition coefficients include pressure (Mysen and Kushiro, 1978), temperature (Watson, 1977; Lindstrom and Weill, 1978), bulk composition of the liquid and solid phases (McIntyre, 1963; Lindstrom and Weill, 1978), rate of crystal growth (Alberede and Bottinga, 1972; Long 1978; Henderson and Williams, 1979) and melt structure (Henderson, 1977; Watson, 1977; Ryerson and Hess, 1978;

Mysen and Virgo, 1980; Mahood, 1981a). Variations of partition coefficients with temperature are difficult to isolate from compositional effects and are as yet incompletely understood. However, a common trend observed in both natural and experimental systems is that partition coefficients increase with Si/O atomic ratio of the liquid (Irving, 1978) and with increasing degree of melt polymerization, as indicated by the ratio of non-bridging to bridging oxygens (Mysen and Virgo, 1980). Factors which tend to depolymerize the melt, such as increased (Na+K)/Al ratio (Larsen, 1979) and addition of volatiles (i.e. H_2O, Cl, F) will result in a reduction of crystal/liquid partition coefficients (Mysen and Virgo, 1980). The increased availability of anionic volatile constituents probably also results in a greater degree of complex formation with the incompatible elements, thereby reducing the likelihood of their incorporation in crystalline phases and effectively reducing the solid/liquid partition coefficients. In view of these factors, the considerable increases in partition coefficients which occur in subalkaline to mildly peralkaline high-SiO_2 rhyolites (Mahood, 1981a) are unlikely to be as marked in the more evolved members of many transitional alkaline suites due to the inferred relatively high F (and ?Cl) contents and their more obvious peralkaline character.

Partition coefficients used to evaluate fractionation models for the Nandewar suite (Table 7.4) have been determined where possible from natural phenocryst matrix compositions. In spite of the potential constraints on these values, discussed above, it is considered that these are likely to most closely approximate the actual partition coefficients at the time of crystallization. Olivine was sufficiently abundant in only the more mafic trachyandesites to permit its separation, and olivine, clinopyroxene and plagioclase partition coefficients for the tristanites and mafic trachytes must be inferred from the trachyandesite data since the scarcity of these phases as phenocrysts in the more evolved rocks precluded their separation. However, errors in the calculated trace element abundances resulting from incorrect partition coefficients for these phases should be relatively small because of the small amounts of these phases which are indicated to have been fractionated in the more evolved variants (see Tables 7.1 and 7.2).

REE data were unfortunately not obtained for the separated olivine,

TABLE 7.4

Phenocryst/groundmass partition coefficients
used in trace element modelling calculations

	Ol./Gdmss* (49002)	Cpx/Gdmss (49002)	Plag./Gdmss (49002)	Cpx/Gdmss (49010)	Plag./Gdmss (49010)	Timt./Gdmss** (49010)	Apat./Gdmss (49076)	Anor./Gdmss (49086)	Anor./Gdmss (49098)
Sc	-	4.64	-	2.24	-	0.289	0.132	-	-
V	0.092	1.34	-	1.83	-	22	-	-	-
Cr	0.377	5.47	-	8.00	-	246	-	-	-
Ni	9.32	1.33	-	6.28	-	50	-	-	-
Cu	0.792	0.417	0.396	1.03	-	62	-	1.25	1.13
Zn	1.59	0.414	0.172	0.690	0.359	3.86	-	0.152	0.120
Rb	-	0.028	-	0.013	-	-	-	0.234	0.482
Sr	-	0.148	2.32	0.109	3.71	-	2.85	7.23	0.700
Y	-	0.254	-	0.722	-	-	-	-	-
Zr	-	0.261	-	0.215	-	0.103	-	-	-
Nb	-	0.067	-	0.083	-	-	-	-	-
Ba	-	0.104	0.416	0.058	0.667	-	2.48	5.78	4.90
La	0.010†	0.100	0.109	0.134	0.096	0.298	5.90	-	0.037
Ce	0.010	0.244	0.038	0.277	0.047	0.252	6.61	-	0.028
Nd	0.011	0.375	0.023	0.500	0.041	0.369	9.02	-	0.028
Sm	0.011	0.500	0.046	0.627	0.082	0.264	7.34	-	0.026
Eu	0.010	0.500	0.273	0.537	0.244	0.200	6.84	-	1.46
Tb	0.013†	0.600	0.020	0.615	0.015	0.269	10.83	-	0.33
Yb	0.023†	0.565	0.013	0.577	0.014	0.226	5.48	-	0.021
Lu	0.025†	0.606	0.012	0.579	0.011	0.226†	4.02	-	0.017

[*] REE partition coefficients from Schnetzler and Philpotts (1970)

[†] Values estimated by interpolation and extrapolation

[**] REE partition coefficients for Sm, Eu, Tb, Yb from Schock (1979)

but published REE partition coefficients based on olivine phenocryst/matrix data and experimental investigations (Irving, 1978) are uniformly low, and olivine/groundmass values for a basalt measured by Schnetzler and Philpotts (1970) have been used in the modelling calculations. Similarly, complete REE analyses were not obtained for the titanomagnetite separate, and partition coefficients used in the calculations are for a basalt from the Azores (Schock, 1979). These were selected because partition coefficients for La, Ce and Nd correspond quite closely with values determined by XRF analysis of the Nandewar trachyandesite titanomagnetite/groundmass pair. REE partition coefficients for the major crystallizing phases used in the calculations are plotted versus atomic number in Fig. 7.1.

Remaining partition coefficients from the Nandewar phenocryst/matrix data are comparable to and generally within the range of published values for similar rock types. The broad range of published values, especially for $D_{Sr}^{Plag/liq}$ and $D_{Ba}^{Kfsp/liq}$ (Berlin and Henderson, 1969; Higuchi and Nagasawa, 1969; Philpotts and Schnetzler, 1970; De Pieri and Quareni, 1978; Leeman and Phelps, 1981) reaffirms the necessity to carefully select these values.

A simple and limiting case for the trace element models is provided by the incompatible trace elements (i.e. $D_x^{Sol/liq} \sim 0$). For these elements $\frac{C_L}{C_O} \sim \frac{1}{F}$ and hence the maximum possible enrichment from the proposed parent to the most evolved derivative can be simply calculated. Inspection of the partition coefficient data (Table 7.4) indicates that none of the elements are perfectly incompatible, although U (Dostal and Capedri, 1975) and Th, Ta, Hf and Nb (Ferrara and Treuil, 1974) most closely approximate this behaviour.

Assuming perfect incompatibility (i.e. $D_x^{Sol/liq} = 0$) the maximum possible enrichment of any element in the most evolved comendites (e.g. 49163 and 49164) with respect to the proposed parental trachyandesite (49000) is of the order of 10 to 20 times. Although enrichment levels for many of the elements are within this range La is enriched ~23 times in comendite 49164. Since the partition coefficient data (Table 7.4) indicate that La cannot be regarded as an incompatible element, this level of enrichment must be attributable to some process other than, or, in addition to closed-system fractional crystallization.

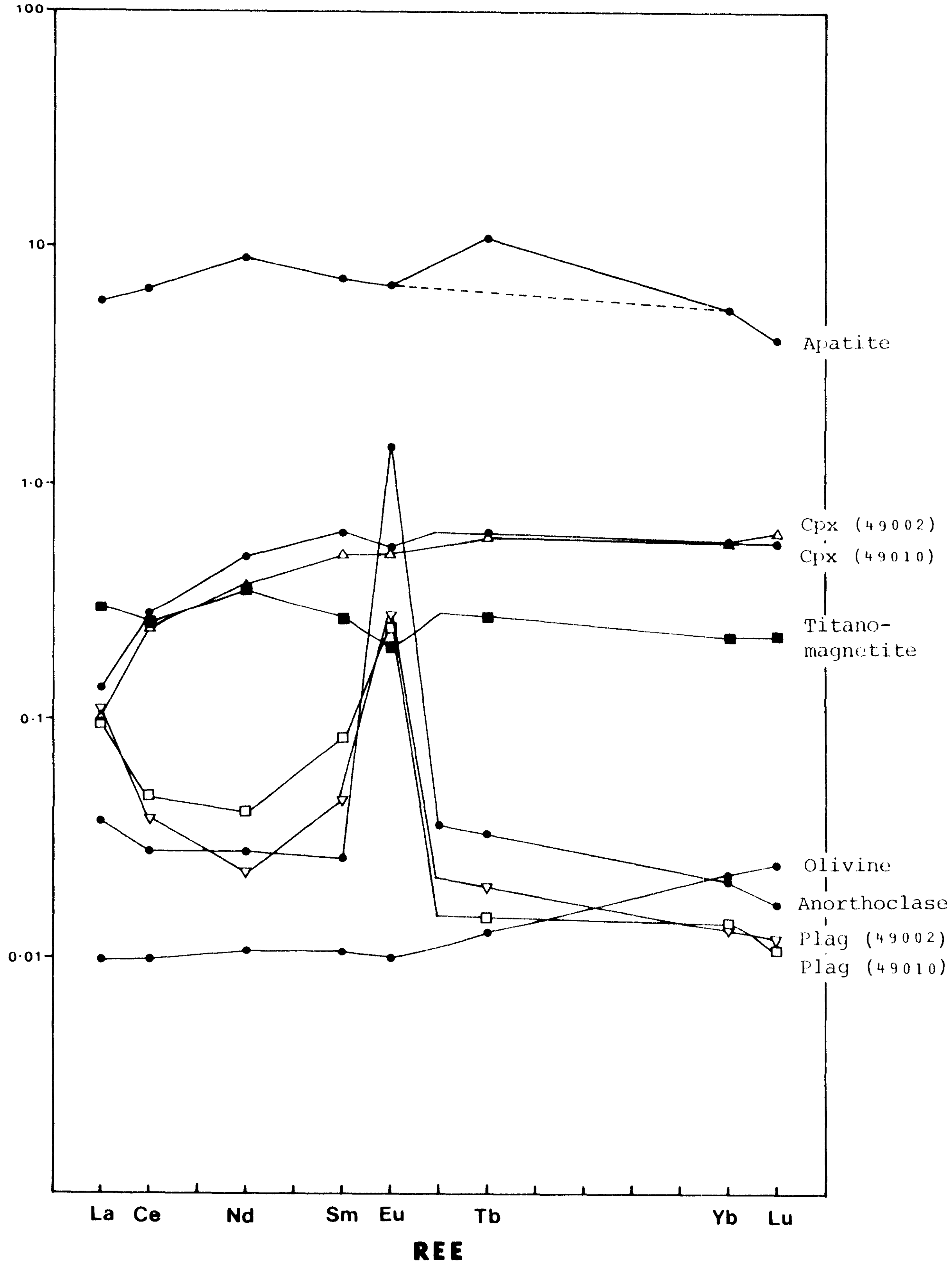

Fig. 7.1: A log-normal plot of REE partition coefficients versus atomic number for the phases used in the trace element modelling calculations.

Furthermore, the major element calculations (Table 7.2) indicate the necessity for significant anorthoclase fractionation to produce comendite 49163 from comendite 49161, whereas minimal feldspar removal is apparently required to generate comendite 49164 from the same parent. This is inconsistent with the fact that both alleged derivatives have identical Sm/Eu ratios since $D_{Eu}^{Anor/liq}$ is considerably larger than $D^{Anor/liq}$ for the other REE (see Table 7.4).

Plots of elements which are commonly regarded as incompatible against Nb and Ta (Figs. 7.2 and 7.3) display considerable variation in their degree of colinearity. Nb and Ta were selected as the x ordinates because they display a strong correlation with each other (r = 0.985) and the crystal/liquid partition coefficients for Nb in the major crystallizing phases are very low, thus indicating their approximate incompatible behaviour. Th and Hf are also strongly correlated with Nb and Ta (r = 0.971 to 0.990) and regression lines for these plots generally pass through the origin at the 95 percent confidence level.

These strong inter-element correlations provide compelling evidence for derivation of this suite of volcanics from a common source. It does not seem plausible that certain members of the suite (e.g. the older alkali rhyolites) could have been generated from an independent (? lower crustal) source, since this source would be unlikely to have almost identical incompatible trace element ratios.

Trace element modelling calculations for the major fractionation steps are presented in Table 7.5. Although the correlation between calculated and trace element abundances for some transitions appear reasonable for some elements, the calculated values for many elements diverge significantly from the observed abundances.

Depletion of V, Cr, Ni and Cu does not occur rapidly enough in the calculated values for the transition from the parental trachyandesite (49000) to the more evolved trachyandesites (49008 and 49012). The observed depletion could be generated in the calculated values by inclusion of titanomagnetite in the crystal extract but this phase is not present as a phenocryst phase in trachyandesites less evolved than or similar to 49008, and hence cannot be regarded as a plausible crystal extract.

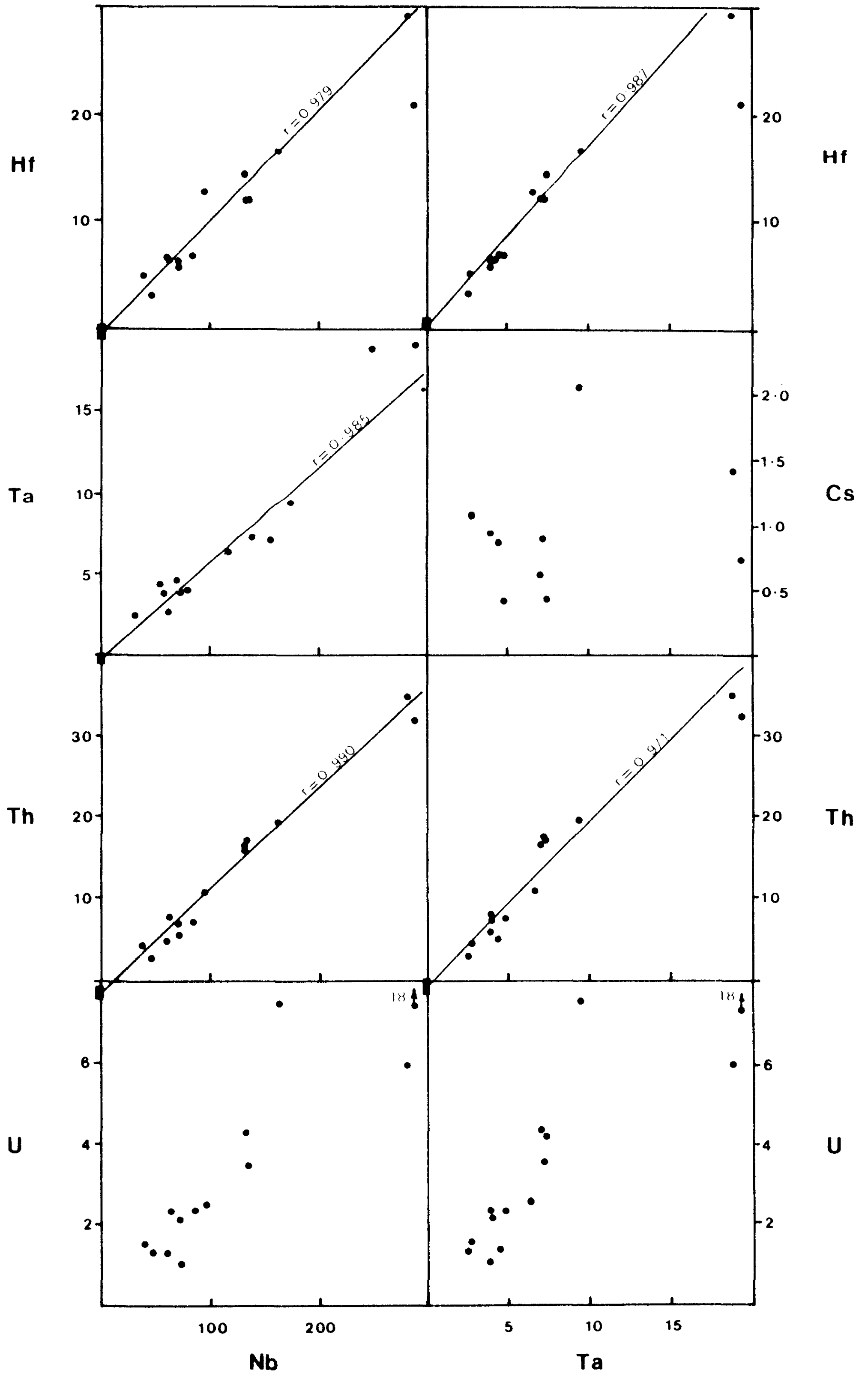

Fig. 7.2: Plots of pairs of 'residual' trace elements for the Nandewar volcanics. Correlation coefficients (r) and regression line intercepts (at the 95 percent confidence level) are indicated for element pairs which display reasonable correlations.

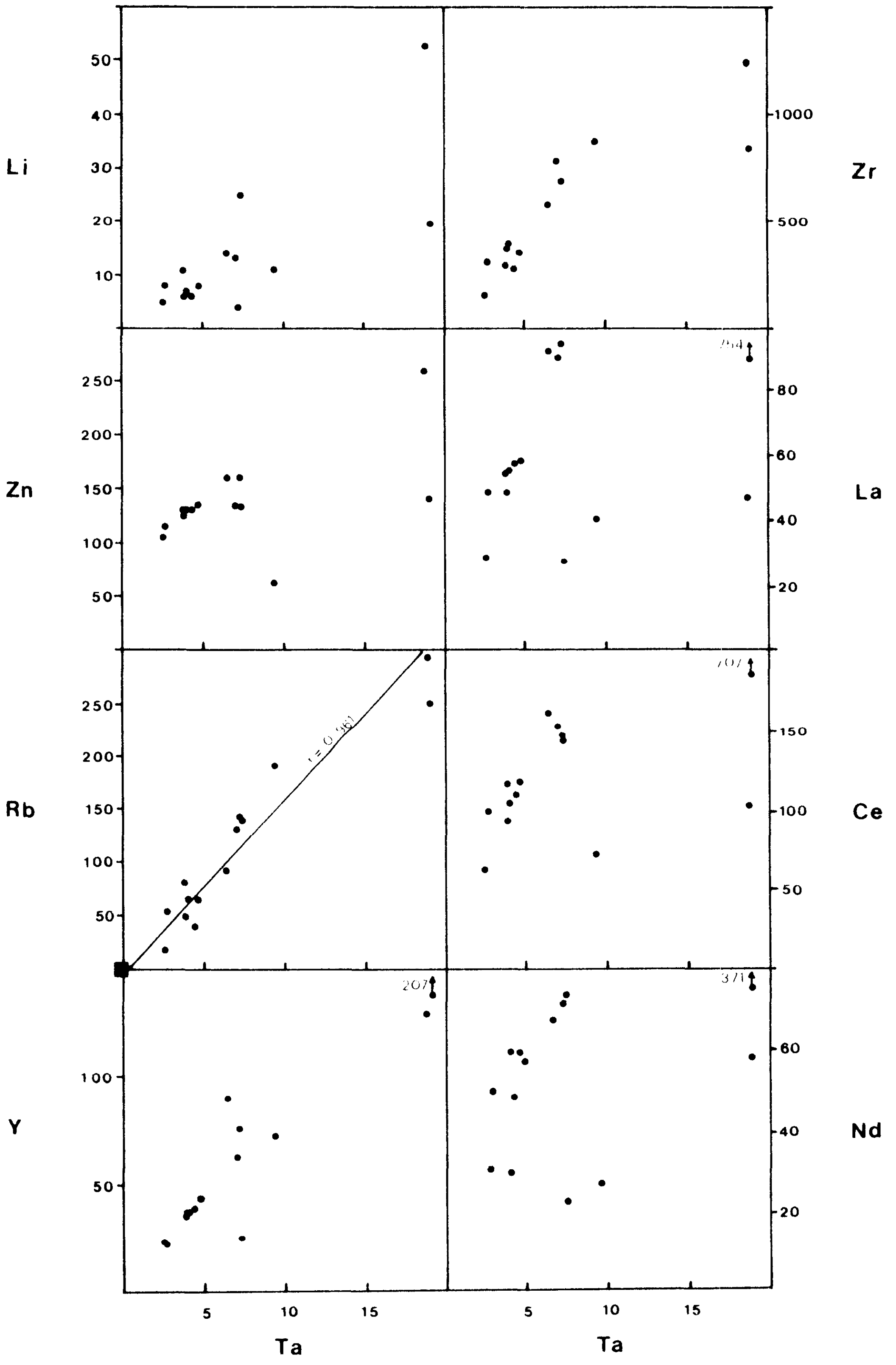

Fig. 7.3: Plots of pairs of 'residual' trace elements for the Nandewar volcanics. Correlation coefficients (r) and regression line intercepts (at the 95 percent confidence level) are indicated for element pairs which display reasonable correlations.

TABLE 7.5

Trace element modelling calculations for the Nandewar suite

Fractionation Step	Trachyandesite (49000) to Trachyandesite (49008)		Trachyandesite (49008) to Trachyandesite (49012)		Trachyandesite (49012) to Tristanite (49076)		Tristanite (49076) to Trachyte (49083)		Trachyte (49083) to Trachyte (49088)	
	49008 Observed	49008 Calculated	49012 Observed	49012 Calculated	49076 Observed	49076 Calculated	49083 Observed	49083 Calculated	49088 Observed	49088 Calculated
Sc	15	-	12	16	13	16	14	17	9	18
V	148	274	120	162	31	129	10	32	8	11
Cr	106	197	1	113	2	<1	<1	<1	2	<1
Ni	68	126	<1	70	<1	<1	<1	<1	8	<1
Cu	30	67	18	33	11	12	9	7	8	8
Zn	130	126	130	142	135	169	130	170	160	161
Rb	40	37	49	44	64	70	66	88	93	84
Sr	831	854	755	914	516	856	102	596	42	97
Y	39	28	37	43	44	52	38	59	91	48
Zr	278	249	293	306	355	418	395	483	585	504
Nb	60	62	72	66	85	103	71	116	95	91
Ba	676	413	591	744	865	802	802	1145	2213	812
La	58	46	55	64	59	75	56	79	94	71
Ce	110	88	117	121	118	159	105	159	162	132
Nd	60	45	60	66	58	80	49	77	68	61
Sm	12.3	-	11.8	13.5	12.8	15.9	8.5	17.1	7.6	10.7
Eu	3.7	-	3.3	4.1	3.8	4.4	3.3	5.0	3.8	3.9
Tb	1.1	-	1.3	1.2	1.2	1.7	1.1	1.6	2.0	1.4
Yb	2.5	-	2.6	2.7	3.1	3.6	3.0	4.2	7.6	3.8
Lu	0.36	-	0.36	0.40	0.48	0.50	0.43	0.64	1.3	0.54

TABLE 7.5 (continued)

Trace element modelling calculations for the Nandewar suite

Fractionation Step	Trachyte (49088) to	Trachyte (49098G)	Trachyte (49098G) to	Comendite (49162)	Trachyte (49098G) to	Comendite (49161)	Comendite (49161) to	Comendite (49163)	Comendite (49161) to	Comendite (49164)
	49098G Observed	49098G Calculated	49162 Observed	49162 Calculated	49161 Observed	49161 Calculated	49163 Observed	49163 Calculated	49164 Observed	49164 Calculated
Sc	-	11.6	2.9	-	3.0	-	0.37	4.6	0.23	3.2
V	<1	10	3	<1	<1	<1	<1	<1	4	<1
Cr	2	3	<1	<1	3	<1	2	<1	<1	2
Ni	6	10	7	3	<1	3	12	<1	15	<1
Cu	15	10	4	5	7	5	7	5	8	7
Zn	200	205	160	411	133	386	260	193	145	140
Rb	110	119	143	224	141	214	294	204	255	149
Sr	6	36	6	11	1	11	2	1	5	1
Y	62	118	76	154	25	142	130	39	207	26
Zr	719	756	696	1824	693	1683	1245	1070	844	732
Nb	119	123	135	304	132	281	282	204	289	140
Ba	10	2047	44	3	<4	<4	4	<4	10	<4
La	76	121	96	189	28	175	48	43	754	30
Ce	136	209	147	338	144	313	103	221	707	152
Nd	60	88	74	147	23	136	59	35	371	24
Sm	13.0	9.8	17.8	31.8	5.2	29.4	14.5	8.0	78	5.5
Eu	1.1	4.5	0.78	1.4	0.43	1.4	0.18	0.54	0.97	0.45
Tb	1.5	2.6	0.97	3.7	0.31	3.4	3.7	0.47	6.2	0.33
Yb	5.6	9.8	6.0	13.8	3.1	12.7	9.7	4.8	11.0	3.3
Lu	0.77	1.7	0.82	1.9	0.52	1.8	1.6	0.80	1.1	0.55

Similarly, the observed Sc depletion in the mafic trachytes and comendites is not apparent in the calculated products. The relatively high $D_{Sc}^{Cpx/liq}$ values (Table 7.4) indicate that clinopyroxene fractionation is the dominant control on Sc abundances in derivative liquids produced by fractional crystallization. While it is plausible that $D_{Sc}^{Cpx/liq}$ may increase in the more evolved variants (cf. Mahood, 1981a), the partition coefficient data in Table 7.4 appear to suggest the reverse in this case.

Correlations between observed and calculated values for Zn are acceptable for most transitions. However, calculated Zn values for the derivation of comendites 49161 and 49162 from peralkaline trachyte 49098G are considerably higher than observed abundances. This is in fact the case for most moderately incompatible trace elements (e.g. Rb, Y, Zr, Nb and the REE) in this transition because of the large quantities of anorthoclase which are required to have been fractionated to satisfy the major element mass-balance constraints.

Calculated Rb and Y values are in reasonable agreement with observed abundances for transitions spanning the compositional range trachyandesite to tristanite, and the calculated Rb values correspond quite well with the observed values for the transitions from the mafic trachytes to the peralkaline trachyte (49098G). For most other transitions the calculated Rb and Y values depart significantly from the observed values.

Sr, Zr and Nb values calculated for the transitions trachyandesite 49012 → tristanite 49076 and tristanite 49076 → trachyte 49083 are considerably higher than the observed values and the calculated values for Zr and Nb depart markedly from the observed abundances in the transitions involving the derivation of comendites 49161 and 49162 from peralkaline trachyte 49098G.

The agreement between calculated and observed Ba values in the mafic and intermediate members, where Ba is most abundant, is generally quite poor. The most notable disparity occurs in the transition from mafic trachyte 49088 to peralkaline trachyte 49098G where the extreme depletion in the latter cannot be explained by the amount of anorthoclase fractionation indicated from major element mass-balance calculations.

Calculated REE abundances depart significantly from observed values in all transitions except that involving production of trachyandesite 49012, and perhaps trachyandesite 49008. Chondrite-normalized REE plots for each of the calculated derivatives are shown in Fig. 7.4 and can be compared with similar plots of the observed abundances (Fig. 5.13). It is interesting to note the absence of negative Eu anomalies in the calculated REE patterns for the tristanite and mafic trachytes. This may in part have resulted from the use of published partition coefficients for titanomagnetite/liquid which are characterized by a slight negative Eu anomaly (Fig. 7.1), and which may or may not have been appropriate.

The typically poor correlation between calculated and observed trace element abundances, particularly in alleged derivatives more evolved than mafic trachyte 49088, does not support their development by closed-system fractional crystallization.

Isotopes

The relatively restricted range of initial $^{87}Sr/^{86}Sr$ ratios supports the notion that all members of the Nandewar suite were derived from a common source, a conclusion which is also required by the incompatible trace element data. The variation in initial $^{87}Sr/^{86}Sr$ ratios is probably due to slight contamination by radiogenic crustal Sr, although liquid fractionation involving thermogravitational diffusion may conceivably be responsible for some of the variation (Hildreth, 1981). The available isotopic data cannot be used to discriminate between genetic models involving fractional crystallization or partial melting and thus are of little further use.

Experimental Evidence

Experimental evidence relevant to the genesis of the comendites is available from studies in the systems K_2O-Al_2O_3-SiO_2 and Na_2O-Al_2O_3-SiO_2 at 1 atmosphere (Schairer and Bowen, 1955,1956) and the system Ab-Or-Q-Ac-Ns-H_2O at 1 kb P_{H_2O} (Carmichael and MacKenzie, 1963). The Nandewar peralkaline trachyte and comendite analyses are plotted (Fig. 7.5) in terms of molecular SiO_2-Al_2O_3-Na_2O+K_2O, following Bailey and Macdonald 1969,1970), and are compared with the quartz-feldspar cotectic zone and

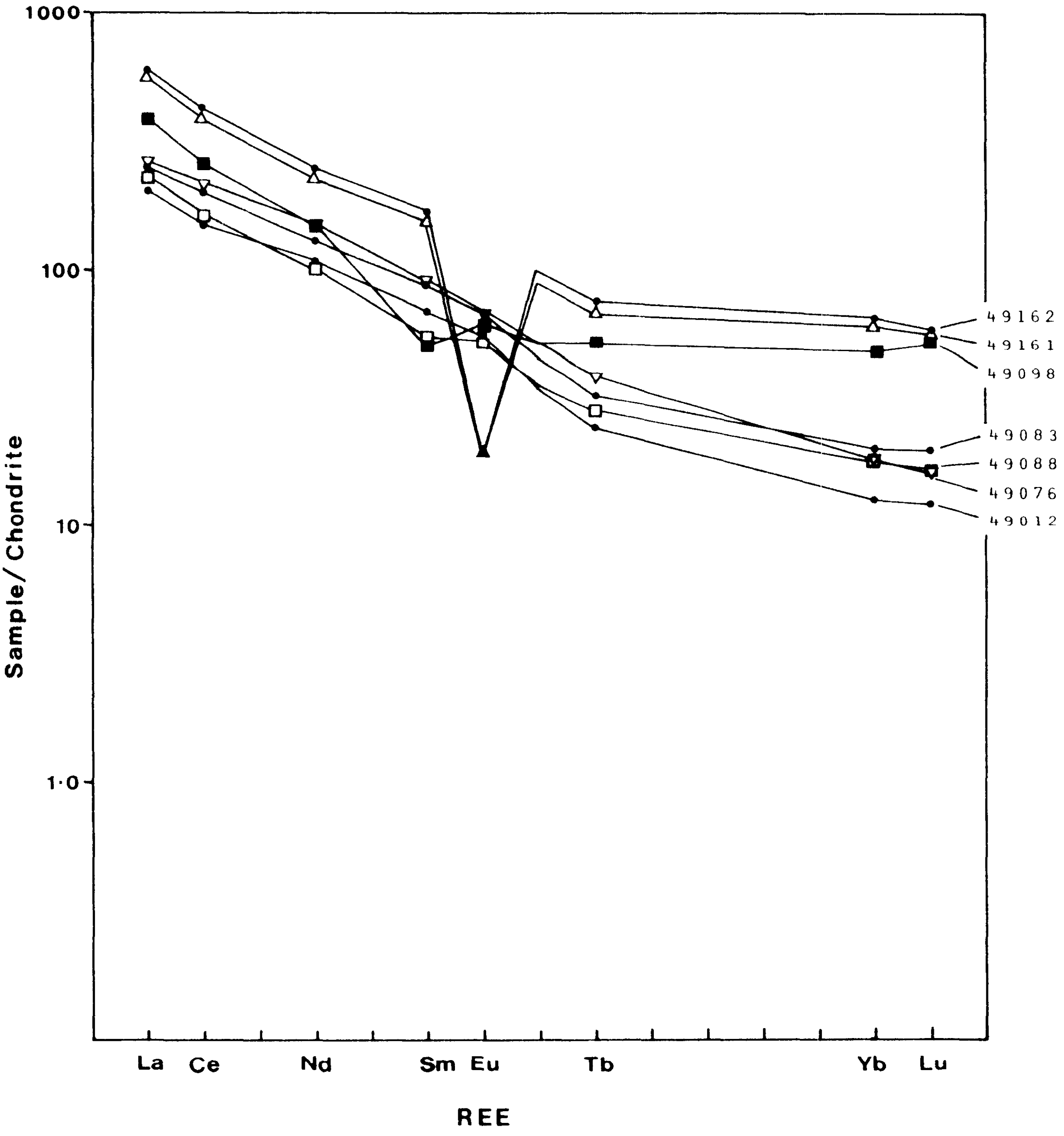

Fig. 7.4: Chondrite-normalized REE plots of the calculated values for the proposed Nandewar derivatives from Table 7.5.

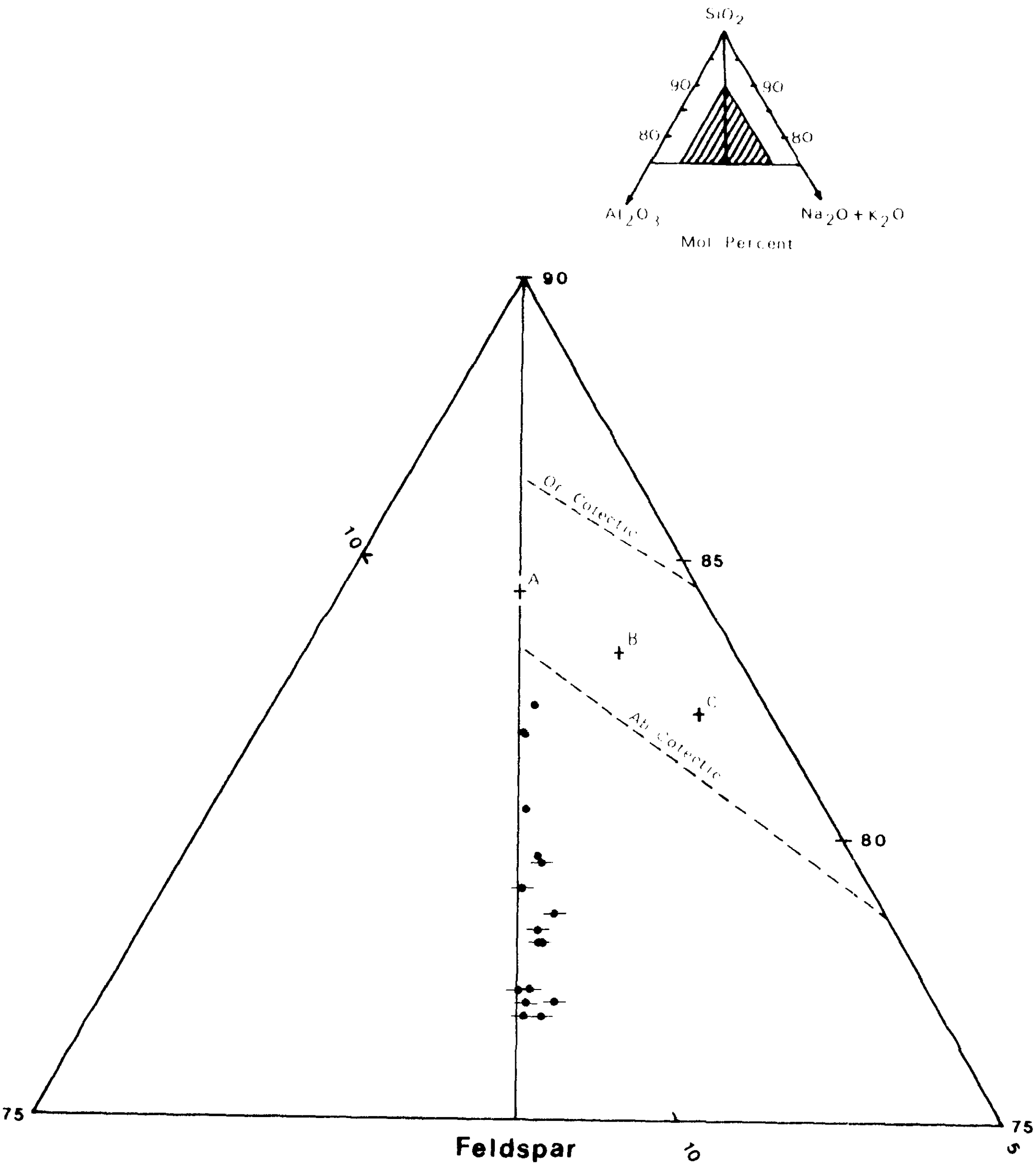

Fig. 7.5: Plot of the Nandewar comendites (circles) and peralkaline trachytes (circles with bars) in terms of SiO_2-Al_2O_3-Na_2O+K_2O (mol. prop.) following Bailey and Macdonald (1969, 1970). The positions of the quartz-feldspar cotectic zone and the quartz-feldspar minima (A,B,C) are reproduced from Bailey and Macdonald (1970) for comparison.

quartz-feldspar minima determined in the above systems.

In contrast to the continental comendites plotted by Bailey and MacDonald (1970), the Nandewar comendites do not plot in the quartz-feldspar cotectic zone. Instead, they are spread along a rough trend with the peralkaline trachytes extending from the feldspar point towards the cotectic zone and comparable in some respects to the trend displayed by oceanic comendites (Bailey and Macdonald, 1970). However, the decreasing peralkalinity in the transition from the peralkaline trachytes to comendites noted previously is also evident in this plot, and is at variance with a trend of increasing peralkalinity which should result from fractionation of alkali feldspar from peralkaline trachyte magma.

Selective loss of volatiles and alkalies is not considered to be responsible for this trend since the most evolved comendites are intrusive and are less likely to have been affected by this process than extrusive peralkaline trachytes.

Thus, interpretations based on the available experimental data are consistent with major and trace element modelling calculations, which do not support an origin for the Nandewar comendites by fractionation of alkali feldspar from peralkaline trachyte melts.

Physical Conditions of Fractionation

The difficulties associated with the mechanics of the crystal fractionation process which relate to crystal settling, convection and the general paucity of cognate cumulates were discussed in Chapter 6. The feasibility of crystal/liquid separation, which is fundamental to crystallization differentiation models, can be assessed by reference to relevant viscosity and density data.

Densities (Bottinga and Weill, 1970) and viscosities (Shaw, 1972) have been calculated for several Nandewar lavas at approximate magmatic temperatures (estimated from geothermometric data, Chapter 4), and for dry and for reasonable H_2O contents. The results are presented together with calculated feldspar densities in Table 7.6. Coefficients of expansion for the feldspars were taken from Clark (1966) and applied to density data (determined at $20^\circ C$) on appropriate compositions from Deer *et al.* (1963). Calculated viscosities for the trachyandesites and

TABLE 7.6

Calculated densities and viscosities for
Nandewar lavas and feldspar densities

	Melt Density ($g\ cm^{-3}$)	Feldspar Density ($g\ cm^{-3}$)	Viscosity (poise)
Trachyandesite (49000)			
1100^oC (Dry)	2.77	2.66 (An_{59})	5.4×10^2
1100^oC (1% H_2O)	2.70		-
1100^oC (2% H_2O)	2.64		1.1×10^2
Trachyandesite (49012)			
1100^oC (Dry)	2.60	2.64 (An_{48})	3.9×10^3
1100^oC (2% H_2O)	2.48		5.7×10^2
Tristanite (49076)			
1000^oC (Dry)	2.57	2.62 (An_{44})	7.1×10^5
1000^oC (1% H_2O)	2.45		2.2×10^4
Trachyte (49088)			
1000^oC (Dry)	2.28	2.54 (Or_{28})	1.7×10^6
1000^oC (1% H_2O)	2.23		3.0×10^5
Peralkaline Trachyte (49098)			
1000^oC (Dry)	2.31	2.54 (Or_{30})	1.4×10^6
1000^oC (1% H_2O)	2.25		5.2×10^4
Comendite (49161)			
1000^oC (Dry)	2.25	2.54 (Or_{30})	8.9×10^6
1000^oC (0.5% H_2O)	2.23		2.5×10^6

comendites are comparable to measured values on rocks of similar composition (Scarfe, 1977).

The calculated liquid densities indicate that in the absence of significant convection olivine, clinopyroxene and Fe-Ti oxides should have settled in all compositional variants. Plagioclase is also likely to have settled in trachyandesite 49012 and the tristanites. However, if trachyandesite 49000 contained 1 weight percent H_2O or less, the calculations suggest that plagioclase (An_{58}) would have floated. Increasing the H_2O content of the melt to 2 weight percent at 1100°C reduces the melt density to a value fractionally below that of the feldspar, which may then permit it to settle out. The uncertainties regarding the initial H_2O content of the melt preclude a definitive solution to this problem.

The calculated density data do not preclude fractionation of alkali feldspar from any of the trachytic or comenditic melts. However, calculation of settling velocities from Stokes Law (assuming perfect spherical crystals of 0.5 cm radius) indicates settling rates of ~2 to 90 m yr^{-1} under optimum conditions of minimum viscosity and maximum density contrast. These settling rates are small and probably ineffectual when convection processes are considered. Calculated Rayleigh numbers for the trachytic and comenditic melts utilizing data from Bartlett (1969) are $>> 10^5$ for magma bodies of ~100 m thick. Strong eddying motions and active convection are expected when Rayleigh numbers exceed 10^5 (Elder, 1976).

Therefore fractionation of ~48 to 50 weight percent alkali feldspar from peralkaline trachyte melts to produce the comendites does not seem plausible by crystal settling. The absence of essentially monomineralic anorthoclase cumulates as inclusions within any of the lavas further weakens the crystal fractionation model.

PARTIAL MELTING

It has been established that the members of the Nandewar suite are cogenetic and were derived from a common source with constant isotopic and incompatible trace element ratios. Since the results of mass-balance calculations in the preceding section indicate that the members (at least spanning the compositional range trachyandesites 49000 to trachyandesite 49012) are unlikely to be related by closed-system fractional crystallization, alternative genetic models must be considered.

General Characteristics of the Source

It was concluded in Chapter 6 that progressive partial fusion of a lower crustal source is not plausible because P-T constraints preclude generation of the more mafic variants. Therefore an upper mantle source is the only viable alternative. Since the silicic members of the suite are at present generally regarded as unlikely products of partial melting of an upper mantle source, a model involving partial melting followed by liquid or crystal fractionation (or both) may be appropriate for their genesis.

Clearly, if lavas as evolved as trachyandesites and perhaps tristanites are to be considered as 'primary' products of partial melting in the upper mantle, the composition of the source must differ significantly from the popular 'pyrolite' model of Ringwood (1975). Since we have no *a priori* knowledge of the composition of undepleted upper mantle, it is considered reasonable to test alternative potential source compositions within the broad constraints imposed by geophysical data (Ringwood, 1975) which indicate a peridotitic mineralogy.

Attempts to estimate the composition of undepleted upper mantle material are severely constrained by the lack of model-independent information concerning the percentage of partial melting required to produce the various lava types. Estimates based on trace element abundances of lavas and near-cosmic abundances for the upper mantle (Kay and Gast, 1973) require very small degrees of partial melting (<3 percent) to produce nephelinites and other strongly alkaline and LREE-enriched volcanics. It was noted in Chapter 6 that such small quantities of melt may be difficult to separate from the source. Frey *et al.* (1978) concluded that most basaltic lavas are probably produced by larger degrees of melting (i.e. 10 to 25 percent for alkali basalts to olivine tholeiites), and they based their estimates on the K_2O and P_2O_5 contents of the lavas in conjunction with the abundance of these constituents in 'pyrolite'. This model assumes uniformity of K_2O- and P_2O_5-bearing phases (presumably phlogopite, amphibole and apatite) in the source region. However, xenoliths from kimberlites and other alkaline rocks containing these phases (e.g. Dawson and Smith, 1973; Lloyd and Bailey, 1975; Francis, 1976; Wass *et al.*, 1980) typically display considerable modal variation, which presumably reflects heterogeneity in the source region. Thus, estimates of the degree of partial melting based on the concentration of K_2O and P_2O_5 in the resultant melts are subject to uncertainties from this variable as well as the uncertainty regarding the assumed composition of the source.

Constraints on the Nandewar Source

The compositions of the Nandewar lavas permit several constraints to be placed on the likely nature of the source material. 1) Experimental investigations on the solubility of apatite in basaltic liquids (Watson, 1979b) indicate that apatite should not be a residual phase during the relatively large degrees of melting required to produce the more mafic (lower SiO_2) variants of the suite. This is supported by the absence of apatite as a liquidus phase in all trachyandesites and hawaiites less evolved than 49012 and its general absence from refractory lherzolitic xenoliths. If all of the apatite is partitioned into early-formed melts the P_2O_5 content should decrease by dilution as melting proceeds. A plot of M versus P_2O_5 (Fig. 7.6) shows that this is true for all of the Nandewar trachyandesites except 49005, 49008 and 49009. The higher P_2O_5 contents of these lavas for similar M values suggests their derivation from a source with slightly higher modal apatite. The trend of increasing P_2O_5 with M in the range tristanite to trachyandesite is consistent with the presence of apatite as a liquidus phase indicating their saturation in this component. Moreover, this suggests that if these more evolved lavas were also formed by partial melting, apatite was a residual phase in the source region to this stage of melting.

2) The relatively high K/Rb ratios of the Nandewar mafic and intermediate rocks (generally in the range 450 to 460) appears to require the presence of amphibole in the source region. Menzies and Murthy (1980c) showed that the probable range of K/Rb ratios in lavas produced by 5 to 25 percent partial melting of an anhydrous mantle source is 220 to 400. The range of K/Rb ratios is considerably extended (449 to 794) by the addition of 5 percent pargasite to the source.

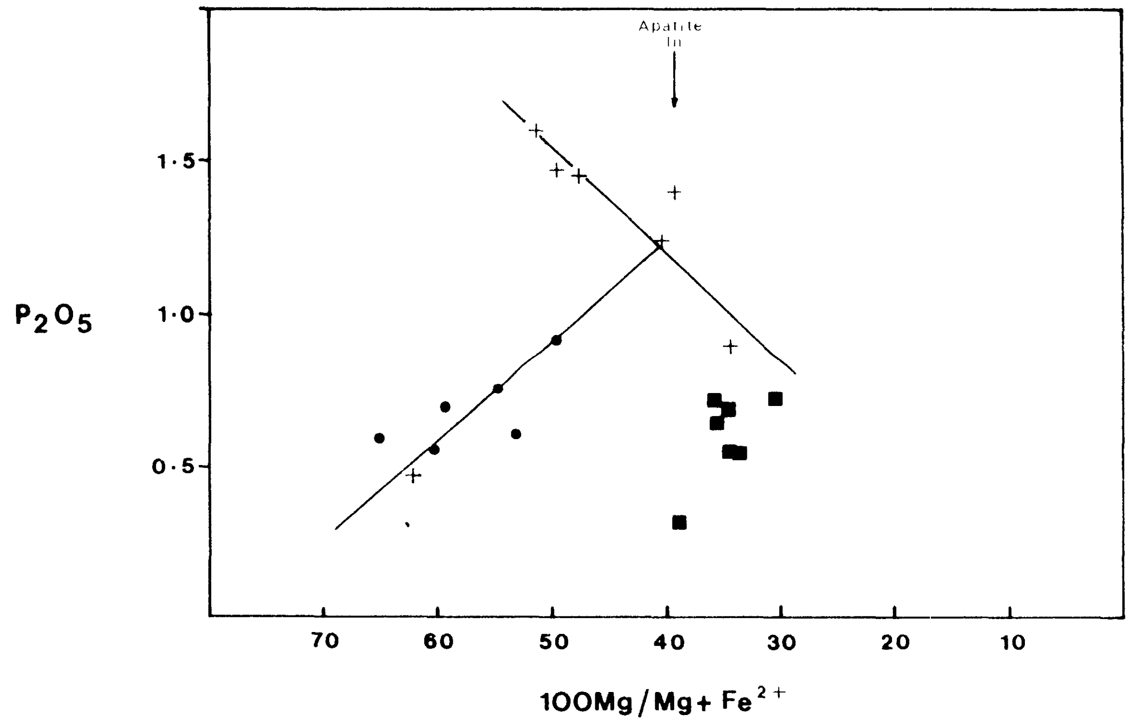

Fig. 7.6: Plot of *M* versus P_2O_5 for the Nandewar hawaiites (circles), trachyandesites (crosses) and tristanites (squares).

3) The relatively constant K/Rb ratios in the Nandewar mafic and intermediate lavas indicates that there could not have been significant variation in the modal amounts of phases with markedly different K/Rb ratios contributing to the melt. Amphibole and phlogopite would have the highest contents of K and Rb in any plausible upper mantle assemblage (Griffin and Murthy, 1969) and are likely to have had the greatest influence on K/Rb ratios of derivative melts. Phlogopite typically has quite low K/Rb ratios (~120, Dawson, 1972) whereas amphiboles typically have higher K/Rb ratios and commonly display a wide range of values (e.g. 336-3058; Menzies and Murthy, 1980c). If both of these phases contributed to the melt phase in variable proportions then a greater degree of variation in the K/Rb ratios of the melts would be expected. It therefore seems reasonable to conclude that the source for the Nandewar lavas contained some amphibole and apatite, whereas phlogopite was

probably absent.

4) Assuming amphibole and apatite were present in the source rocks of these lavas, it seems likely that they were completely consumed, at least for the highest degrees of partial melting, because of the general scarcity of amphibole-bearing inclusions amongst xenolith populations. Possible variations in melt composition resulting from the incongruent melting of amphibole (Holloway and Ford, 1975) are ignored, although this assumption may not be valid for small degrees of partial melting if amphibole is relatively abundant in the source (i.e. 5 to 10 percent).

Composition of the Residuum

The most obvious constraint on the composition of the residuum is provided by the *M* values of derivative melts with which it was in equilibrium. Experimental data (Roeder and Emslie, 1970; Cawthorn *et al.*, 1973; Thompson, 1974) indicate that the olivine-liquid Fe/Mg exchange partition coefficient at elevated pressures is ~0.33. The *mg* value of the peridotitic residuum is enhanced with increased degrees of melting (Mysen and Boettcher, 1975). Hence, trachyandesite 49000 (*M* = 62) should have been in equilibrium with a residuum with *mg* ~83. Descriptions of xenoliths with such low *mg* values are rare and the average of ~300 continental peridotite xenoliths (which would be 'depleted' relative to pristine upper mantle; Maaløe and Aoki, 1977) has *mg* = 90.1. If trachyandesites similar to the Nandewar trachyandesites and tristanites were indeed primary melts, the residua from these partial melting events is only rarely sampled. Further melting of a relatively Fe-rich residue (assuming it is undepleted in elements such as Al, Ca, Na, K, P) would probably yield basaltic melts, thereby leaving relatively Mg-rich residua more typical of the peridotitic inclusions in alkaline lavas.

A weight percent mode of the average spinel lherzolite (Maaløe and Aoki, 1977) is olivine 66.7, orthopyroxene 23.8, clinopyroxene 7.8 and spinel 1.7. Because clinopyroxene preferentially enters the melt with small degrees of partial melting (Mysen and Kushiro, 1975; Jaques and Green, 1980), undepleted 'pristine' Fe-rich lherzolites, and also Fe-rich residua persisting after only small degrees of melting, must be significantly enriched in this phase (and/or amphibole for hydrous assemblages) relative to the more common clinopyroxene-bearing harzburgite xenoliths.

Wilkinson and Binns (1977) used an average analysis (*mg* = 83.7) based on relatively Fe-rich lherzolite compositions as a potential upper mantle source composition from which moderately evolved hawaiites and tholeiitic andesites might be derived leaving harzburgitic and dunitic residua, respectively. However, even this relatively Fe-rich composition was depleted in important minor elements (Na_2O, K_2O, TiO_2 and P_2O_5) and consequently it was unable to satisfy mass-balance requirements for the production of the moderately evolved derivatives. As a first approximation it appears reasonable to use this relatively Fe-rich source composition as a possible residuum from a partial melting event which produced a trachyandesite (e.g. 49000) with *M* ~62. The compositions of the potential (already extracted) melt fractions are unknown. They may have possessed *M*-values similar to the Nandewar trachyandesite but could have differed significantly in other components (e.g. Otago mafic phonolite, *M* = 56; Price and Green, 1972). However, uncertainties of this type are inherent in all model upper mantle compositions formulated in this manner, including that of 'pyrolite'.

Composition of a Hypothetical Undepleted Source

Since the degree of partial melting required to produce trachyandesitic melts in equilibrium with the proposed residuum is unknown, various increments of trachyandesite 49000 (10,15,20,25 and 30 weight percent) were added to the residuum, thereby defining a range of *possible* source compositions (Table 7.7).

The respective modes (Table 7.7) were calculated using microprobe analyses of the anhydrous phases in an Fe-rich lherzolite (*M* ~80) from Spring Mount in north-eastern New South Wales (Wilkinson and Binns, 1977), and an apatite from a Victorian lherzolite xenolith (Frey and Green, 1974). Alternative modes were calculated adding amphibole (average analysis of pargasite from a lherzolite xenolith in a nephelinite from the Walcha district in north-eastern New South Wales; unpublished data of the author) to the anhydrous phases listed above. It was not possible to obtain a satisfactory solution using the least-squares

TABLE 7.7

Compositions and modes of a range of possible undepleted upper mantle materials

	Residuum* (A)	Residuum + 10% 49000	Residuum + 15% 49000	Residuum + 20% 49000	Residuum + 25% 49000	Residuum + 30% 49000
SiO_2	44.32	44.73	44.96	45.17	45.39	45.59
TiO_2	0.48	0.71	0.82	0.93	1.05	1.16
Al_2O_3	4.25	5.33	5.87	6.41	6.95	7.50
Cr_2O_3	0.31	0.31	0.26	0.25	0.23	0.22
ΣFeO	11.91	11.80	11.75	11.70	11.64	11.60
MnO	0.17	0.17	0.16	0.17	0.16	0.16
MgO	34.23	31.64	30.37	29.07	27.79	26.50
CaO	3.55	4.12	4.41	4.70	4.98	5.27
Na_2O	0.63	0.86	0.98	1.08	1.20	1.31
K_2O	0.09	0.23	0.30	0.37	0.44	0.50
P_2O_5	0.06	0.10	0.12	0.15	0.17	0.19
Total	100.00	100.00	100.00	100.00	100.00	100.00
mg	83.7	82.7	82.2	81.6	81.0	80.3
Anhydrous Modes (Wt. percent)						
Olivine	63.9	42.7	37.6	32.3	27.1	22.0
Orthopyroxene	15.9	33.5	36.0	38.7	41.3	43.8
Clinopyroxene	18.1	19.1	20.8	22.4	24.0	25.6
Spinel	2.1	4.3	5.2	6.1	7.0	8.0
Apatite	-	0.4	0.4	0.5	0.6	0.6
Σr^2	-	7.525	5.895	4.649	4.003	3.755
Hydrous Modes (Wt. percent)						
Olivine	-	42.3	38.0	33.6	29.3	25.0
Orthopyroxene	-	31.6	32.6	33.7	34.7	35.5
Amphibole	-	25.2	28.5	31.8	35.1	38.5
Apatite	-	0.9	0.9	0.9	1.0	1.0
Σr^2	-	3.614	1.823	0.672	0.229	0.462

*Analysis and volume % mode from Wilkinson and Binns (1977).

Σr^2 = Sum of the squares of the residuals.

mixing procedure by including clinopyroxene and spinel with amphibole in the hypothetical source composition. Better fits (i.e. lower Σr^2) were generally obtained for the amphibole-bearing assemblages but the amount of amphibole defined by the least-squares data generally appeared inordinately large (20 to 40 wt. percent, Table 7.7) and the olivine/orthopyroxene ratios appear too low.

Mass-balance calculations were carried out to test the feasibility of producing the Nandewar trachyandesites, hawaiites and tristanites from the range of proposed source rocks (Table 7.8). The best fits for the trachyandesites and hawaiites were achieved using a parent composition based on the addition of 15 percent trachyandesite 49000 to residuum A (Table 7.7). A less depleted residuum was adopted for the calculations involving the tristanites (i.e. residuum B, Table 7.8; calculated by adding 10 percent trachyandesite 49000 to residuum A) because the source will be relatively less depleted by the lower degrees of partial melting required for the production of the more 'evolved' primary melts. These calculations indicate that it is feasible in terms of major element mass-balance constraints, to produce the Nandewar tristanites, hawaiites and trachyandesites by 4 to 15 percent partial melting of the proposed source.

It is acknowledged that the existence of such a source is highly speculative, although it is supported to some extent by the compositions of some relatively Fe-rich lherzolites (Wilkinson and Binns, 1977; but see Irving, 1980). The possibility of deriving liquids with $M < 50$ by direct partial melting of a source similar to the one proposed is rather more speculative. Although many of the components can be satisfactorily balanced in least-squares mixing calculations, adopting a constant value of $K_D = 0.33$ for olivine-liquid equilibria appears to be a major constraint in parent-daughter relations. K_D depends on P, T and fO_2 (Mysen, 1975; Mysen and Boettcher, 1975) but Wilkinson and Binns (1977) suggested that opposing effects of P-T and fO_2 will probably be counterbalancing and $K_D \sim 0.3$ is likely to persist in relatively Fe-rich upper mantle source regions. Although this may be true for basaltic and hawaiitic melts, possible effects of higher alkali contents and variable bulk composition on K_D at elevated pressures are unknown and require more experimental data.

TABLE 7.8

Mass-balance calculations relevant to partial melting models for the Nandewar mafic and intermediate lavas

	49001	Residuum[†] A	Proposed[*] Parent	Calculated Parent	49008	Proposed[*] Parent	Calculated Parent	49012	Proposed[*] Parent	Calculated Parent	49076	Residuum[**] B	Proposed[*] Parent	Calculated Parent
SiO_2	48.34	44.32	44.96	44.96	48.83	44.96	44.92	52.27	44.96	45.31	56.98	44.73	44.96	45.22
TiO_2	2.29	0.48	0.82	0.77	2.73	0.82	0.78	2.36	0.82	0.71	1.73	0.71	0.82	0.75
Al_2O_3	14.35	4.25	5.87	5.86	15.76	5.87	5.79	16.32	5.87	5.75	16.21	5.33	5.87	5.76
Cr_2O_3	-	0.31	0.26	0.26	-	0.26	0.27	-	0.26	0.27	-	0.31	0.26	0.30
ΣFeO[1]	11.22	11.91	11.75	11.80	11.74	11.75	11.89	10.46	11.75	11.73	9.06	11.80	11.75	11.69
MnO	0.16	0.17	0.16	0.17	0.16	0.16	0.17	0.14	0.16	0.17	0.17	0.17	0.16	0.17
MgO	10.02	34.23	30.37	30.36	5.07	30.37	30.32	3.35	30.37	30.39	1.85	31.64	30.37	30.45
CaO	8.68	3.55	4.41	4.37	7.64	4.41	4.10	6.70	4.41	3.94	4.53	4.12	4.41	4.14
Na_2O	3.23	0.63	0.98	1.05	4.32	0.98	1.13	4.58	0.98	1.12	5.49	0.86	0.98	1.04
K_2O	1.09	0.09	0.30	0.25	2.26	0.30	0.38	2.55	0.30	0.40	3.28	0.23	0.30	0.35
P_2O_5	0.62	0.06	0.12	0.15	1.49	0.12	0.25	1.27	0.12	0.21	0.70	0.10	0.12	0.12
mg	61.4	83.6	82.1	82.1	43.5	82.1	81.9	36.3	82.1	82.2	26.7	82.7	82.1	82.3
Wt.% melting	16.0				13.4			12.4			4.0			
Σr^2	0.015				0.172			0.405			0.176			

[1] - Total Fe as FeO

[†] - From Wilkinson and Binns (1977)

[*] - Calculated by adding 15 wt.% trachyandesite 49000 to residuum A

[**] - Calculated by adding 10 wt.% trachyandesite 49000 to residuum A

Σr^2 = sum of the squares of the residuals

Other alternative upper mantle sources might also be considered e.g. the metasomatized lherzolitic material described by Lloyd and Bailey (1975). The enrichment of Fe and incompatible trace elements, as well as the relative depletion in Cr and Ni which apparently accompanied metasomatism, indicates the potential for such a source to generate melts with very evolved major and trace element characteristics. Production of relatively siliceous upper mantle melts based on the incongruent melting of orthopyroxene (Mysen and Boettcher, 1975) appear to require further experimental data.

In view of the limited data defining the major element characteristics of pristine upper mantle there appears to be little profit in speculating on trace element compositions. Trace element models based on the equations for equilibrium or fractional melting (Shaw, 1970) depend heavily on information concerning the degree of partial melting, the nature and mode of the residual mineralogy of the source and solid/liquid partition coefficients, which are at present poorly known.

CONTAMINATION/HYBRIDISM/WALL-ROCK REACTION

The arguments outlined in the previous chapter regarding the general inapplicability of these processes to the production of transitional alkaline suites also pertain to the Nandewar suite. The general absence of xenoliths, partially digested igneous or sedimentary materials and disequilibrium phase assemblages argue strongly against the significant involvement of hybridism and contamination processes in the genesis of the Nandewar lavas.

However, the slightly higher initial $^{87}Sr/^{86}Sr$ ratios of several comendites (see Table 5.3) suggests that some contamination of these melts by radiogenic crustal Sr occurred. The very high Rb/Sr ratios of these rocks renders them very susceptible to such effects and the amount of contaminant may have been very small. This would indeed be the case if isotopic contamination occurred by direct exchange between magma and country rocks (Taylor, 1977) or by influx of groundwater (Lipman and Friedman, 1975).

VOLATILE TRANSFER

The conclusion in Chapter 6, that volatile transfer (especially volatile loss) is unlikely to have resulted in significant modification to the compositions of transitional mafic lavas, is also applicable to the Nandewar lavas. It was further suggested that loss of a volatile phase may be responsible for some of the compositional variation evident amongst the more evolved members of some suites.

Inspection of Tables 5.1 and 5.2 and Figs 5.4 to 5.11 reveals considerable scatter in the concentration of alkalies and several of the incompatible trace elements amongst the younger alkali rhyolites and comendites. Typically the alkali rhyolites are depleted in Na_2O, ΣFeO, Li, Zn, Rb, Y, Zr, Nb, HREE, Hf, Ta and Th relative to comendites of similar SiO_2 content. Since it has been established that these differences cannot be reasonably attributed to fractional crystallization, and their highly irregular nature appears inconsistent with thermo-gravitational diffusion processes (discussed below), chemical modification by loss of a volatile phase may be the most appropriate explanation.

The commonly vesicular character of the alkali rhyolites indicates that some loss of volatiles occurred, probably when the partly crystalline magma was extruded as exogenous domes. Evidence of alkali amphiboles having grown within the vesicles of some specimens was interpreted as indicating crystallization from an escaping volatile-rich fluid (see Chapter 4). Trace element data for the separated amphibole (Table 4.7) revealed that many of the elements (e.g. Li, Zr, Nb, HREE) depleted in the alkali rhyolites relative to the comendites are concentrated in this phase.

It is proposed therefore, that the magma which finally consolidated as the younger alkali rhyolites was originally comenditic in composition. The field occurrence of the comendites, principally as intrusive plugs, apparently prevented serious loss of volatiles and thus they more closely reflect original melt compositions. It is envisaged that the pressure release accompanying extrusion of the partially crystalline comenditic magma led to saturation of the interstitial melt fraction in a F-rich volatile phase and its subsequent loss from the system. Alkalies (principally Na) and many of the incompatible trace elements concentrated in the interstitial melt (probably in the form of fluoride complexes; see Chapter 6 for discussion) are also inferred to have been lost during the degassing process.

Whilst this process appears to have most seriously affected the alkali rhyolites, it may also have modified the compositions of some mafic and peralkaline trachytes. However, the generally non-vesicular character and higher Na_2O/K_2O ratios (usually >1) of these lavas suggests that such losses were probably less important.

The older alkali rhyolites also have relatively low Na_2O/K_2O ratios and irregularities in some trace element contents which suggests loss of a volatile phase during eruption. Specimen 49162 is slightly peralkaline (A.I. = 1.01) and hence was classified as a comendite, but it is regarded as a member of the older alkali rhyolites because of its close association in the field and similar mineralogy. These rocks are typically more Fe-rich than the younger alkali rhyolites and are compositionally similar to the most mafic extrusive comendites (e.g. 49160 and 49161; see Tables 5.1 and 5.2), the most notable discrepancy being lower Na_2O and higher Fe_2O_3/FeO ratios in the former. The older alkali rhyolites are depleted in Li relative to the comendites but many of the other incompatible trace element concentrations are comparable.

It is proposed that the older alkali rhyolites were also produced by degassing of a comenditic magma as it was extruded in the form of exogenous domes during the initial phases of volcanism. These magmas are thought to have been relatively H_2O-rich which permitted some loss of alkalies and trace elements and resulted in pervasive oxidation of the partially crystallized magma. The apparently minimal losses of Fe, Mn and incompatible trace elements, relative to those inferred for the younger alkali rhyolites, perhaps reflects different a_{H_2O} and a_{F_2} between the melts and the extent of complexing by halogen anions. The low partition coefficients for most elements between aqueous vapour and melt which support this interpretation were discussed in Chapter 6.

Whilst most of the chemical differences between the alkali rhyolites and comendites may be attributable to volatile-loss, one comendite (49164) is enriched in LREE beyond levels that can be reasonably attributed to fractional crystallization processes. Compared to comendite 49163, this particular specimen displays less enrichment in Zn, Rb, Zr, Hf and HREE, has almost identical Nb and Ta contents and Sm/Eu ratio, and is enriched in LREE by ~x 5 to 16 and U by ~x 3.

Specific enrichments of this magnitude are inconsistent with crystal fractionation involving alkali feldspar because the preferential concentration of Eu in this phase (see Table 7.4) would result in increased Sm/Eu ratios in derivative liquids. Also, the limited data available for magmas considered to be related by thermogravitational diffusion (cf. Hildreth, 1979,1981; Mahood, 1981a) suggests that Sm/Eu ratios do not remain unchanged during the operation of this process.

Therefore, some form of volatile transfer may be responsible for the strong enrichment in LREE and U evident in this comendite. Although this seems inconsistent with the tendency of the HREE to form complexes more readily than the LREE (Balashov and Krigman, 1976), the stability of metal complexes may be strongly dependent on the nature of the anionic species (e.g. Mitchell and Brunfelt, 1975; Balashov and Krigman, 1975), thereby creating the potential for selective cationic mobility in an evolving magma chamber. Volatile transfer could occur by exsolution of vapour from a saturated melt followed by its concentration in the upper part of the magma chamber. However, roofward migration and concentration of volatile species may also occur in the absence of a discrete vapour phase (Shaw, 1974).

MAGMA MIXING

Petrographic and mineralogical evidence of disequilibrium in the Nandewar lavas is sparse. Reaction rims on orthopyroxene megacrysts in several trachyandesites (considered to be moderate-pressure precipitates from their hosts) are explicable by their low-pressure instability. On the other hand, unusually magnesian olivine microphenocrysts (Fo_{88}) in trachyandesite 49008 (M = 47.6) constitute a disequilibrium assemblage. If a value of K_D ~0.3 for olivine-liquid equilibria is appropriate, it must be concluded that the euhedral olivine microphenocrysts crystallized from a melt with a higher M-value than their host (M ~70), and which is not currently represented in the volcanic pile. This melt could then have mixed with a more evolved trachyandesitic or hawaiite melt to produce the current host. There is, however, no evidence of two phenocryst populations which might support this proposal.

Sparse plagioclase phenocrysts (An_{57}) rimmed by anorthoclase in mafic trachyte 49082 also probably represent a disequilibrium assemblage.

Their presence could be interpreted in terms of mixing of a relatively Ca-rich (trachyandesitic) melt with a trachytic melt. The typically low MgO and CaO contents of the mafic trachytes indicate that if mixing with more Mg- and Ca-rich melts occurred, the relative volume of the latter was quite small. The absence of magnesian olivine and clinopyroxene phenocrysts, which usually accompany plagioclase phenocrysts in the trachyandesites, suggests that the calcic-plagioclase cores may be isolated accidental inclusions rather than the remnants of extensive magma mixing.

Although magma mixing may have occurred on a very restricted basis producing some of the localized disequilibrium mineral assemblages in the Nandewar lavas, it is not considered to have played a significant role in the development of the suite.

LIQUID IMMISCIBILITY

On the basis of the arguments outlined in Chapter 6, the process of liquid immiscibility is not considered to have been involved in the development of the major compositional variants comprising the Nandewar suite. There is no physical evidence of immiscibility in the volcanics or intrusive rocks and the essentially continuous chemical variation evident in the suite is inconsistent with such a process. Furthermore, the trace element characteristics of the more evolved representatives are at variance with those expected from partitioning relationships of immiscible liquids (Watson, 1976; Eby, 1980).

THERMOGRAVITATIONAL DIFFUSION

It was concluded from earlier discussions (see Chapter 6) that the process of thermogravitational diffusion seems incapable of producing the complete range of compositions represented in the Nandewar Volcano. Although the more mafic members of the suite may be 'primary' partial melts of a relatively Fe-rich upper mantle source region, it seems most unlikely that the salic types, especially the rhyolites, could have been formed in this manner. The apparent inadequacy of the crystal fractionation, liquid immiscibility, and other models so far considered to account for some of the compositions in this range, requires that the process of thermogravitational diffusion be considered as a possible alternative.

Appraisal of this model in the genesis of the more evolved Nandewar rocks is necessarily speculative since very little is known of the operation of this process in magmatic systems. Information from field relations and possible pre-extrusive magmatic relationships are poorly constrained for the Nandewar rocks compared to zoned ash-flow tuff units for which this process has previously been invoked (e.g. Hildreth, 1979,1981; Mahood, 1981a). In the case of zoned ash-flow eruptives, the regions of the magma chamber sampled can be identified with some degree of confidence, whereas the possible order of extraction of a series of small intrusive plugs from a magma chamber (if indeed they were derived from a single chamber) is unknown. Even if the comenditic and trachytic magmas were derived from a single compositionally zoned magma chamber, the individual intrusive bodies are likely to have undergone further differentiation subsequent to their emplacement.

Recognition of geochemical trends which appear to be characteristic of this process is therefore very difficult, especially since these trends vary somewhat from subalkaline (Hildreth, 1979) to mildly peralkaline systems (Mahood, 1981a). These difficulties are enhanced in the Nandewar rhyolitic rocks where significant loss of alkalies and certain incompatible trace elements occurred during eruption.

Thermogravitational diffusion has only previously been proposed to explain marked variations in trace element and isotope chemistry over quite narrow ranges in major element composition. Hildreth (1979) suggested that compositional gradients develop by diffusion processes in the uppermost portions of silicic magma chambers where convection becomes inhibited by progressive development of a stable density gradient. Calculated viscosities (Table 7.6) and Rayleigh numbers indicate that active convection should occur in even relatively small chambers containing trachytic and comenditic magmas. This would possibly be expected to disrupt compositional and density gradients which develop in response to thermal gradients within a magma chamber. However, if a series of actively convecting cells of different composition can develop (see Chapter 6 for discussion of possible mechanisms), then convective-driven diffusive differentiation may be capable of operating over a broader compositional range appropriate to the Nandewar intermediate and silicic variants.

Some support for this suggestion is provided by the Thirsty Canyon Tuff in southern Nevada (Noble, 1965; Noble and Parker, 1974). It is a compound cooling unit composed of at least a dozen individual ash flows ranging from trachyte to comendite and pantellerite in composition. Trachyte, trachytic soda rhyolite and trachyandesite lavas were erupted synchronously from the Black Mountain Volcano and interfinger with the intermediate to silicic tuffs. It is clear from this example that melts ranging from trachyte to peralkaline rhyolite coexisted, probably within a single magma chamber, and were erupted within a short period of time. It is not clear by what process the trachytic and comendite members are related, although Noble (1965) and Noble and Parker (1974) suggest that they were not produced by fractional crystallization from a single parent magma. By analogy with mass-balance calculations for the Nandewar lavas, a relationship for the Black Mountain trachytes and comendites by fractional crystallization would appear to require excessively large degrees of crystallization (~50 weight percent). Even larger degrees of crystallization would be required to produce the extreme enrichments in incompatible trace elements which characterize the Black Mountain pantellerites (see Table 6.6, No.14). It has been argued previously that such large degrees of crystallization would necessarily prevent this range of liquids coexisting in a single magma chamber.

The suggestion that the more evolved members of the Nandewar suite (which display similar compositional trends to the Black Mountain eruptives) were produced by thermogravitational diffusion or a similar form of liquid-state differentiation is of course speculative. Further detailed studies of eruptives covering a similar compositional range, but with more closely constrained field relations enabling more precise determination of eruptive sources and compositional variation with time, are clearly required to ascertain the viability of this model in generating the relatively evolved members of transitional alkaline suites.

CONCLUSIONS

An important, albeit negative result of this study evident from the field, mineralogical and chemical data, is that while the transitional alkaline lavas (and intrusives) of the Nandewar suite comprise a cogenetic suite, *not all* are related by simple closed-system fractional crystallization.

The major and trace element variations amongst the mafic members (i.e. trachyandesites and hawaiites) cannot be adequately accounted for by removal of the observed phenocryst phases. It was therefore tentatively suggested that these lavas and perhaps also the tristanites may represent 'primary' partial melts of a relatively Fe-rich upper mantle source region. Production of the tristanites by fractional crystallization of the most evolved trachyandesites is not precluded by the major element mass-balance calculations. However, poor agreement for some calculated trace element abundances and the paucity of phenocrysts and cognate cumulate inclusions in the trachyandesites and tristanites does not support their relationships by this process.

Production of the mafic trachytes by fractional crystallization of a tristanite magma involving separation of the major phenocryst types seems feasible. However, generation of the peralkaline trachytes and comendites from the mafic trachytes by this process requires inordinately large degrees of crystallization and in many cases satisfactory mass-balance is not achieved for either the major or the trace elements.

Instead it is tentatively suggested that the trachytes and comendites may be related by some form of liquid-state differentiation. Although the capacity of the thermogravitational diffusion process to generate this range of compositions is as yet unproven, it seems the most appropriate contender from the available range of genetic models.

Loss of a F- or H_2O-rich volatile phase appears to be an adequate mechanism by which peraluminous and metaluminous rhyolites[1] can be related to the comendites. Alkali loss and variable loss of Fe, Mn and certain incompatible trace elements is considered to have accompanied the loss of volatiles. The extent to which this occurs probably reflects the activity of the various volatile constituents in the melt and the degree of complex formation.

Acceptance of the conclusion that the closed-system fractional crystallization model (widely adopted as the principal mechanism for the genesis of these suites in the past) does not provide a satisfactory explanation for the genesis of all of the Nandewar lavas, leaves the vexing problem of a suitable alternative control(s). Whilst, the *ad hoc* genetic models tentatively proposed above have some relevance, it is acknowledged that they are far from compelling. Careful examination of

[1] It should be noted however, that these eruptives are essentially devoid of diagnostic peralkaline groundmass phases.

the literature on transitional suites similar to the Nandewar suite also showed that closed-system fractional crystallization models may not be generally applicable in their genesis. Further studies of these suites aimed at quantifying in more detail the relationships between alleged parent and daughter products are obviously required. Wider acceptance of the shortcomings of crystal fractionation models should lead to more detailed examination and evaluation of alternative genetic controls.

CHAPTER 8

SUMMARY OF CONCLUSIONS

The Nandewar Volcano, outcropping over an area of some 800 km², is a Miocene shield volcano located approximately 26 km east of Narrabri in north-eastern New South Wales. The major conclusions arising from the field, petrographic, mineralogical, chemical and genetic synthesis of the Volcano are listed below.

1) Petrographic and chemical data indicate that the Nandewar Volcano is dominated by a mildly potassic lineage extending from *hy*-normative trachyandesites to comendites via tristanites and mafic to peralkaline trachytes. Transitional hawaiites also occur, but more 'evolved' sodic eruptives have not been found.

2) Although the trachyandesites, hawaiites, tristanites and trachytes (the main shield-forming sequence) are collectively the most abundant volcanics, alkali rhyolites comprise the most voluminous eruptive type. Peralkaline trachytes and comendites represent only a relatively minor proportion of the extrusive/intrusive members of the suite. Field and geochronological data indicate that volcanism commenced with extrusion of the volumetrically important alkali rhyolites to form exogenous domes. Extrusion of the main shield-forming sequence began with hawaiites and trachyandesites. Later eruptives generally became more silicic with time, varying in composition from tristanites, mafic and peralkaline trachytes to occasional mafic comendites. The volcanic pile was subsequently intruded by peralkaline trachyte and comendite plugs and dykes.

3) The dominant mineral compositional trends throughout the volcanic series have been studied in some detail, employing microprobe analyses. Olivine (Fo_{88-50}) is a relatively prominent phenocryst phase in some trachyandesites and hawaiites. Olivine *mg*-values and modal olivine content decrease with increasing SiO_2 content and decreasing *M*-value of the hosts. The most Fe-rich olivine microphenocrysts (Fo_{10}) occur in peralkaline trachytes.

4) Ca-rich pyroxene is a common phenocryst and groundmass phase throughout the series, ranging in composition from augite ($Ca_{47}Mg_{44}Fe_9$)

in the hawaiites and trachyandesites to ferrohedenbergite ($Ca_{46}Mg_3Fe_{51}$) in the comendites. Tschermakitic Ca-rich pyroxenes and partially resorbed aluminian bronzites in several trachyandesites are considered to have crystallized from their host melts at approximately 6 to 8 kb. Groundmass pyroxenes in the peralkaline trachytes and comendites display significant $NaFe^{3+} \rightleftarrows Ca(Mg, Fe^{2+})$ substitution, and range in composition up to almost pure aegirine ($NaFe^{3+}Si_2O_6$).

5) Amphibole (edenite) is a rare groundmass phase in several trachyandesites. Amphibole is more common in the mafic trachytes (richterite to ferro-richterite with subordinate katophorite and arfvedsonite) and is relatively abundant in the groundmass of peralkaline trachytes and comendites (arfvedsonite).

6) Titanomagnetite is the dominant Fe-Ti oxide phase occurring both as a phenocryst and groundmass phase throughout the series. Only occasionally does it coexist with ilmenite. The ulvöspinel content of the titanomagnetites varies somewhat irregularly with host-rock composition, but tends to be highest in the most 'evolved' eruptives. Fe-Ti data indicate that magmas spanning the compositional range trachyandesite to comendite generally crystallized under conditions of decreasing T and fo_2 which were broadly parallel with the FMQ synthetic buffer curve. The older alkali rhyolites differ from the trachyandesite-comendite spectrum because they appear to have suffered pervasive oxidation during eruption, possibly as a result of selective loss of H_2 following dissociation of H_2O.

7) Aenigmatite of relatively restricted compositional range is a common groundmass constituent of peralkaline trachytes and comendites. The presence of aenigmatite rimming titanomagnetite and ilmenite microphenocrysts in several specimens provides some support for the existence of a 'no-oxide' field in T-fo_2 space.

8) The abundance of plagioclase phenocrysts varies considerably in the more mafic variants, and phenocrysts are less abundant in more 'evolved' types and absent from peralkaline eruptives. Comparatively rare, sieved, reverse-zoned plagioclase phenocrysts in some trachyandesites may represent relatively high-pressure precipitates. Phenocryst and groundmass alkali feldspar compositions in the trachytes and comendites display a relatively restricted compositional range (Or_{26-49}) with a

concentration in the range (Or_{34-42}) which corresponds to the experimentally-determined composition of the minimum in the Ab-Or series. Alkali feldspar phenocrysts in the mafic trachytes are zoned from relatively Ab-rich cores to more Or-rich rims, whereas those from peralkaline hosts display the reverse trend.

9) Major, trace element and isotopic data indicate that the Nandewar volcanics derived from a common upper mantle source with specific trace element and isotopic characteristics.

10) Major and trace element mass-balance calculations seeking to interelate the various members of the mildly potassic series do not favour a genetic model based on closed-system fractional crystallization. Mass-balance constraints are especially evident for the hawaiites and trachyandesites whose compositions cannot be bridged by reasonable crystal extracts based on observed phenocryst assemblages. An alternative interpretation of the genesis of these particular magmas has been suggested, and this is based on progressive partial melting of relatively Fe-rich amphibole-bearing upper mantle peridotites. A range of hypothetical upper mantle source compositions has been presented, and these have been modelled by adding to the composition of a relatively Fe-rich 'depleted' peridotitic residuum various proportions of potential derivative melt compositions.

11) Major and trace element mass-balance calculations do not preclude derivation of the tristanites and mafic trachytes by fractional crystallization of the most 'evolved' trachyandesites. However, this interpretation does not accord with the predominantly aphyric character of the most 'evolved' trachyandesites and the extreme rarity of cognate cumulates in all rock types. Generation of the tristanites by quite small degrees (~5 percent) of partial melting of a relatively Fe-rich upper mantle peridotite has been evaluated. Although this model is feasible in terms of major element mass-balance constraints, it is open to criticism because it requires unrealistically Fe-rich source peridotites (mg<70) as defined by Fe-Mg exchange partitioning data available at the present time.

12) Production of the older alkali rhyolites by extensive fractional crystallization of volumetrically subordinate mafic and peralkaline trachytic associates is considered unlikely and is not supported by mass-balance calculations.

13) Production of the comendites and peralkaline trachytes from less 'evolved' associates (mafic trachyte → peralkaline trachyte → comendite) requires inordinately large degrees of crystallization (30 to 60 percent) and crystal extracts, for which there is generally little evidence in the entire volcanic succession. Predicted and measured trace element contents of alleged derivatives for these transitions are strongly at variance. There is strong evidence that the trace element characteristics of *some* comendites have resulted from processes other than fractional crystallization. An alternative model based on some type of liquid-state differentiation process (e.g. thermogravitational diffusion) possibly aided by volatile transfer has been tentatively suggested to explain the compositional characteristics of the most 'evolved' variants.

14) The development of the metaluminous or peraluminous younger alkali rhyolites which are common field associates of the intrusive comendites is attributed to volatile-loss during extrusion of partially crystallized comenditic magma. Similarly, the voluminous older alkali rhyolites are regarded as the products of degassing of slightly more mafic comenditic magmas which have their counterparts in the main shield-forming sequence.

15) In a detailed review, the volumetric, chemical and other characteristics of transitional alkaline suites (for oceanic and continental regimes) have been discussed. Closed-system fractional crystallization is the control most often invoked in the genesis of the 'evolved' members (M<66) of these suites, but the evidence necessary to enhance the internal consistency of fractionation models is often lacking. This evidence should include:

a) successively smaller volumes of successively more 'evolved' differentiates;

b) convincing major and trace element mass-balance between the alleged parent, derivative and the observed phenocryst compositions which are representative of the crystal extract; and

c) reasonable evidence of cognate cumulates (the complementary crystal extracts) as inclusions within the eruptive sequence.

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APPENDIX I

ANALYTICAL TECHNIQUES

SAMPLE PREPARATION

Approximately 300 g of each sample was sawn into thin slabs, broken into chips and crushed to -150# in a tungsten-carbide vessel of a Siebtechnik disc-mill. Contamination was assessed as negligible for all analyzed elements.

MAJOR ELEMENT ANALYSES

The major elements SiO_2, TiO_2, Al_2O_3, total Fe as Fe_2O_3, MnO, MgO, CaO, K_2O and P_2O_5 were determined by X-ray fluorescence spectrometry (XRF) on a Philips PW1540 spectrometer at the U.N.E. Geology Department. The method employed was that of Norrish and Hutton (1969) involving linear calibration after sample dilution in a lanthanum oxide-lithium tetraborate glass. MgO was also determined by atomic absorption spectrometric (AAS) techniques for samples in which it was found to be at low concentrations. The AAS results are presented in this thesis.

A Corning EEL flame photometer was used for the determination of Na_2O on solutions diluted with appropriate quantities of an internal standard (Li_2SO_4).

Ferrous iron was determined titrametrically against a standardized ammonium cerric sulphate solution following dissolution of 0.5 g of sample in a mixture of hydrofluoric and sulphuric acids. N-phenyl anthranilic acid was used as an indicator.

Total H_2O was determined by weighing the cooled condensate after heating the powdered sample at 1050°C for 40 minutes. H_2O^- was determined by measuring the loss in weight after heating the sample at 100°C for 1 hour. H_2O^+ is reported as the difference between total H_2O and H_2O^-.

TRACE ELEMENT ANALYSES

Li, Cu and Zn were determined by AAS on solutions containing 1.0 g sample/100 ml.

V, Cr, Ni, Rb, Sr, Y, Zr, Nb, Ba, La, Ce, Nd, Pb and Th were analyzed by XRF on pelletized powder samples following the general procedures outlined by Norrish and Chappell (1977). Linear calibrations were obtained for each element using the USGS and NIM international rock standards. Mass absorption coefficients were calculated from major element analyses and corrections were applied to remove effects of interfering peaks where appropriate. Sc was also determined by XRF on several phenocryst and groundmass separates.

Trace element analyses of rock samples which include data for Sc, Cs, La, Ce, Nd, Sm, Eu, Tb, Dy, Yb, Lu, Hf, Ta, Th and U, were determined by instrumental neutron activation analysis (INAA) in the Geochemistry laboratory of the Atomic Energy Commission at Lucas Heights, N.S.W. REE analyses of phenocryst and groundmass separates used for the calculation of mineral/liquid partition coefficients were also determined by neutron activation analysis following a radiochemical group separation.

The analytical procedures followed at the Lucas Heights facility were detailed by Porrit and Porrit (1977). They involve 2 radiation periods and 4 separate counting intervals. Short irradiations (1 minute) and long irradiations (9 hours) are performed at thermal neutron fluxes of 5×10^{13} and 5×10^{12} n. cm^{-2} s^{-1} respectively.

Short irradiation samples (20 to 80 mg) are irradiated individually and allowed to decay for 20 minutes before counting at an appropriate geometry to limit dead time to less than 20 percent. The Ge(Li) detector is coupled to a 4096 channel analyzer, has a resolution of 2.1 keV for the 1332 keV peak of ^{60}Co, and a relative efficiency of 15 percent. Each sample is counted for 10 minutes and gamma ray analysis is repeated after 24 hours.

Long irradiations are performed simultaneously for samples and standards (100 to 200 mg). High resolution gamma ray spectrometry measurements are made after 5 to 7 and 28 to 40 days cooling interval on a detector having a resolution of 1.8 keV for the 1332 keV peak and a relative efficiency of 20 percent.

The gamma ray spectra are stored on floppy disk and processed by computer programs devised at the Lucas Heights laboratory. The USGS standard rock BCR-1 is used as a rare-earth standard. The rare-earth concentrations adopted for this standard (J. Fardy, personal communication) are as follows:-

	μg/g		μg/g
La	25.5	Dy	6.40
Ce	54.4	Tb	0.96
Na	28.8	Yb	3.37
Sm	6.64	Lu	0.504
Eu	1.98		

ISOTOPE ANALYSES

Isotope analyses were performed by Dr. H.D. Hensel at the Research School of Earth Sciences (RSES), A.N.U., Canberra following the isotope dilution techniques outlined by Compston *et al.* (1965), Arriens and Compston (1969), Page *et al.* (1976), McCulloch and Perfit (1981) and McCulloch and Chappell (1982).

Strontium Isotopes

Rock samples (0.06 to 0.3 g, depending on Rb and Sr concentration) were dissolved and converted to chlorides using HF, $HClO_4$ and HCl. Rb and Sr were concentrated using large and small anion exchange columns containing Dowex AG 50W resin. Rb and Sr blanks were approximately 0.02 μg, which would result in errors an order of magnitude less than instrumental errors for $^{87}Sr/^{86}Sr$.

Most Sr isotope measurements were made by magnetic-field switching on a Nuclide Analysis Associates instrument (30.5 cm radius of curvature, 60° sector). Most Rb isotope measurements were determined on a MSX mass spectrometer (15.25 cm radius of curvature, 90° sector). Both instruments employed 6 kV accelerating voltage, Faraday cup collector and Cary electrometer. They were operated on-line to a HP-1000E computer which also controlled magnetic-field peak-switching.

The remaining Rb and Sr isotopic measurements were performed on a MSZ mass spectrometer (23 cm radius of curvature, 60° sector) which was described by Clement and Compston (1972). Rhenium triple-filament sources were used for all determinations.

Analysis of NBS 987 strontium carbonate on the Nuclide and MSZ instruments gave $^{87}Sr/^{86}Sr = 0.71022 \pm 4$ and 0.71027 ± 5 respectively.

Results derived from the Nuclide mass spectrometer were normalized to the MSZ value. All strontium isotopic ratios were corrected for variable mass discrimination by normalizing $^{88}Sr/^{86}Sr$ to 8.3752.

Experimental uncertainties for $^{87}Rb/^{86}Sr$ and $^{87}Sr/^{86}Sr$ are estimated to be less than 0.5 and 0.2 percent respectively.

The Rb decay constant used in age calculations is $1.42 \times 10^{-11}\ y^{-1}$ and regression analysis of the data is based on the technique of McIntyre *et al.* (1966).

Neodymium Isotopes

Samples were dissolved in open beakers using a $HF\text{-}HClO_4$ mixture and then converted to chlorides by addition of HCl. The REE were separated from the major elements in cation exchange columns using HCl as an elutriant. Nd was subsequently separated from the other REE in a second column using 0.2M 2-methyllactic acid with a pH of 4.6. Total chemical blank for Nd was ~0.001 μg and hence no corrections to measured ratios were necessary. Nd was measured as Nd^+ on the MSZ mass spectrometer (described above) using rhenium triple filament sources. Effects of mass fractionation were eliminated by normalizing Nd isotopic ratios to $^{146}Nd/^{142}Nd = 0.636151$. The $^{143}Nd/^{144}Nd$ ratio for BCR-1 determined in the RSES laboratory is 0.511843 ± 20.

ANALYTICAL PRECISION AND ACCURACY

Precision of the major element analyses is generally considered to be better than ± 1 percent relative. Precision for the trace elements determined by XRF is better than 5 percent for most elements, whereas uncertainties for the INAA analyses are, Sc (2 percent), La, Eu (3 percent), Ce, Sm, Tb, Yb, Lu, Th (5 percent), Hf (7 percent) and Cs, Ba, Nd, Ta, U (10 to 20 percent).

The accuracy of the major and trace element analyses determined at U.N.E. was monitored by concurrent analysis of several international rock standards. Analyzed and recommended values (Flanagan, 1973) are listed in Table I for comparison.

The accuracy of the trace element analyses determined at Lucas Heights was checked by inclusion of two unidentified standard rocks in

TABLE I

Comparison of analyzed major and trace element values with recommended values (from Flanagan, 1973) of several U.S.G.S. rocks

	G-2		AGV-1		BCR-1	
Wt.Percent	Analyzed	Recommended	Analyzed	Recommended	Analyzed	Recommended
SiO_2	69.34	69.11	59.58	59.00	54.70	54.50
TiO_2	0.49	0.50	1.05	1.04	2.25	2.20
Al_2O_3	15.29	15.40	17.24	17.25	13.63	13.61
Fe_2O_3	1.08	1.08	4.40	4.51	3.58	3.68
FeO	1.45	1.45	2.08	2.05	9.00	8.80
MnO	0.03	0.03	0.10	0.10	0.19	0.18
MgO	0.76	0.76	1.56	1.53	3.50	3.46
CaO	1.95	1.94	4.91	4.90	6.95	6.92
Na_2O	4.07	4.07	4.32	4.26	3.32	3.27
K_2O	4.49	4.51	2.90	2.89	1.71	1.70
P_2O_5	0.14	0.14	0.49	0.49	0.37	0.36
H_2O^+	-	0.55	-	0.81	0.50	0.77
H_2O^-	-	0.11	-	0.16	0.83	0.80
μg/g						
Li	-	35	-	12	12	13
V	37	35	122	125	416	399
Cr	7	7	12	12	12	18
Ni	6	5	18	19	17	16
Cu	-	12	-	60	18	18
Zn	-	85	-	84	125	120
Rb	169	168	67	67	48	47
Sr	476	479	659	657	337	330
Y	11	12	16	21	28	37
Zr	301	300	219	225	184	190
Nb	13	14	14	15	14	14
Ba	1922	1870	1209	1208	662	675
La	103	96	43	35	28	26
Ce	154	150	62	63	54	54
Nd	61	60	35	39	29	29
Pb	31	31	36	35	20	18
Th	25	24	7	6	7	6

the sample set. The analyses of these standards are presented in Table II with the recommended values from Flanagan (1973) for comparison.

MINERAL ANALYSES

The majority of electron probe microanalyses were performed at the Research School of Earth Sciences, A.N.U. using a T.P.D. probe fitted with a Si(Li) detector. Instrumental conditions and data reduction techniques were outlined by Ware (1981).

The remaining probe analyses were performed at the University of New England on a JSM-35 SEM with Tracor-Northern TN2000 EDS system. Analytical conditions were as follows:-

accelerating voltage 15 kV
beam current 10 nA (measured with a Faraday cup)
take-off angle 35°.

The calibration standards were simple silicates such as $CaSiO_3$ for SiO_2, $NaAlSi_2O_6$ for Na_2O, $KAlSi_3O_8$ for K_2O; simple oxides for MgO and TiO_2; pure metals for Zr, V, Cr, Mn, Ni and Zn; pyrite for FeO and halite for Cl. A series of well-analyzed secondary mineral standards were checked on both instruments and compared satisfactorily. Data reduction techniques were the same as those described by Ware (1981).

Detection limits for both instruments are as follows:-

SiO_2, Al_2O_3, MgO, Na_2O, NiO - 0.1 wt. percent
FeO, MnO, SO_3 - 0.09 " "
TiO_2, Cr_2O_3, V_2O_3 - 0.08 " "
CaO - 0.07 " "
K_2O, Cl - 0.05 " "

MINERAL SEPARATIONS

The groundmass and phenocrysts of several strongly porphyritic lavas were separated to determine crystal/liquid trace element partition coefficients. Rock powders (-120#) were cleansed of fine dust by washing and decanting. Initial separation involved repeated runs through a Franz Isodynamic separator. Further concentration of phases was achieved by centrifuging in diodomethane-acetone mixtures or Clerici's solution, and finally hand-picking until >98 percent purity was obtained.

TABLE II

Comparison of INAA analyses of U.S.G.S. standard rocks
with recommended values from Flanagan (1973)

Trace Elements	AGV-1		BCR-1	
µg/g	Analyzed	Recommended	Analyzed	Recommended
Sc	12	13	32	33
Cs	1.2	1.4	0.89	0.95
La	39	35	24	26
Ce	71	63	54	54
Nd	31	39	30	29
Sm	5.5	5.9	3.5	6.6
Eu	1.7	1.7	1.8	1.9
Tb	0.68	0.70	1.1	1.0
Yb	1.5	1.7	3.5	3.4
Lu	0.26	0.28	0.58	0.55
Hf	4.9	5.2	4.9	4.7
Ta	1.1	0.9	0.92	0.91
Th	6.1	6.4	6.2	6.0
U	2.4	1.9	1.3	1.7

APPENDIX II

SPECIMEN NUMBERS, ROCK TYPES AND GRID REFERENCES

The following specimen numbers refer to samples housed in the University of New England Geology Department collection and grid references based on the 1000 metre universal transverse mercator grid, zone 56J, Australian National Spheroid, refer to the Horton 1:100 000 topographic sheet. This sheet was used as a base map to prepare the accompanying geological map.

U.N.E. Specimen No.	Rock Type	Grid Reference
49000	Hawaiite	375393
49001	Hawaiite	475389
49002	Hawaiite	483398
49003	Hawaiite	398387
49004	Hawaiite	247459
49005	Trachyandesite	500363
49006	Trachyandesite	263426
49007	Trachyandesite	362397
49008	Trachyandesite	501415
49009	Trachyandesite	500415
49010	Trachyandesite	270426
49011	Trachyandesite	274469
49012	Trachyandesite	178466
49013	Trachyandesite	202469
49014	Trachyandesite	497412
49015	Trachyandesite	491408
49016	Trachyandesite	425368
49017	Trachyandesite	404367
49018	Trachyandesite	216468
49019	Trachyandesite	325428
49020	Trachyandesite	317433
49021	Trachyandesite	288467
49022	Trachyandesite	285468
49023	Trachyandesite	272469
49024	Trachyandesite	263467
49025	Trachyandesite	257456
49026	Trachyandesite	258454
49027	Trachyandesite	258452
49028	Trachyandesite	258450
49029	Trachyandesite	257452
49030	Trachyandesite	238467
49031	Trachyandesite	218471
49032	Trachyandesite	213473
49033	Trachyandesite	204469
49034	Trachyandesite	185464
49035	Trachyandesite	206473

U.N.E. Specimen No.	Rock Type	Grid Reference
49036	Trachyandesite	277470
49037	Trachyandesite	268468
49038	Trachyandesite	205470
49039	Trachyandesite	198468
49040	Trachyandesite	171472
49041	Trachyandesite	192461
49042	Trachyandesite	181657
49043	Trachyandesite	182648
49044	Trachyandesite	500364
49045	Trachyandesite	173669
49046	Trachyandesite	255535
49047	Trachyandesite	215532
49048	Trachyandesite	239748
49049	Trachyandesite	179378
49050	Trachyandesite	251465
49051	Trachyandesite	220536
49052	Trachyandesite	374458
49053	Trachyandesite	168670
49054	Porphyritic Trachyandesite	265440
49055	Porphyritic Trachyandesite	271422
49056	Porphyritic Trachyandesite	287411
49057	Porphyritic Trachyandesite	289467
49058	Porphyritic Trachyandesite	259463
49059	Porphyritic Trachyandesite	257453
49060	Porphyritic Trachyandesite	225469
49061	Porphyritic Trachyandesite	213473
49062	Porphyritic Trachyandesite	174468
49063	Porphyritic Trachyandesite	286412
49064	Porphyritic Trachyandesite	177375
49065	Porphyritic Trachyandesite	371470
49066	Vesicular Trachyandesite	198461
49067	Tuffaceous Trachyandesite	197463
49068	Tuffaceous Trachyandesite	418270
49069	Tuffaceous Trachyandesite	286413
49070	Monzonite	218535
49071	Monzonite	216533
49072	Monzonite	216533
49073	Micromonzonite	220530
49074	Monzonitic inclusion in Alkali Rhyolite[1]	170525
49075	Tristanite	267471
49076	Tristanite	258451
49077	Tristanite	272420
49078	Tristanite	253457
49079	Tristanite	207458
49080	Tristanite	271460
49081	Tristanite	183647
49082	Trachyte	286410
49083	Trachyte	175468
49084	Trachyte	187640
49085	Trachyte	263448

[1] Chemically a tristanite (see Tables 5.1 and 5.2, p 97 and 112).

U.N.E. Specimen No.	Rock Type	Grid Reference
49086	Trachyte	260455
49087	Trachyte	264603
49088	Trachyte	263450
49089	Trachyte	297458
49090	Trachyte	175402
49091	Trachyte	172474
49092	Trachyte	190472
49093	Trachyte	171481
49094	Trachyte	223536
49095	Trachyte	272423
49096	Trachyte	275458
49097	Porphyritic Trachyte	206408
49098	Peralkaline Trachyte	164481
49099	Peralkaline Trachyte	265436
49100	Peralkaline Trachyte	265433
49101	Peralkaline Trachyte	185380
49102	Peralkaline Trachyte	301459
49103	Peralkaline Trachyte	263471
49104	Peralkaline Trachyte	192455
49105	Peralkaline Trachyte	194468
49106	Peralkaline Trachyte	173469
49107	Peralkaline Trachyte	277463
49108	Peralkaline Trachyte	214680
49109	Peralkaline Trachyte	280464
49110	Peralkaline Trachyte	310446
49111	Peralkaline Trachyte	277463
49112	Peralkaline Trachyte	276461
49113	Peralkaline Trachyte	274459
49114	Peralkaline Trachyte	277465
49115	Peralkaline Trachyte	250462
49116	Peralkaline Trachyte	180465
49117	Peralkaline Trachyte	194469
49118	Peralkaline Trachyte	295470
49119	Alkali Rhyolite	180579
49120	Alkali Rhyolite	181532
49121	Alkali Rhyolite	244511
49122	Alkali Rhyolite	208630
49123	Alkali Rhyolite	196588
49124	Alkali Rhyolite	274603
49125	Alkali Rhyolite	181604
49126	Alkali Rhyolite	175659
49127	Alkali Rhyolite	140465
49128	Alkali Rhyolite	234637
49129	Alkali Rhyolite	179660
49130	Alkali Rhyolite	138681
49131	Alkali Rhyolite	209618
49132	Alkali Rhyolite	142511
49133	Alkali Rhyolite	132564
49134	Alkali Rhyolite	231615
49135	Alkali Rhyolite	230561

U.N.E. Specimen No.	Rock Type	Grid Reference
49136	Alkali Rhyolite	266537
49137	Alkali Rhyolite	267538
49138	Alkali Rhyolite	268538
49139	Alkali Rhyolite	270538
49140	Alkali Rhyolite	270540
49141	Alkali Rhyolite	271541
49142	Alkali Rhyolite	272543
49143	Alkali Rhyolite	159628
49144	Alkali Rhyolite	151581
49145	Alkali Rhyolite	232539
49146	Alkali Rhyolite	250551
49147	Alkali Rhyolite	230546
49148	Alkali Rhyolite	232544
49149	Alkali Rhyolite	276558
49150	Alkali Rhyolite	211493
49151	Alkali Rhyolite	283534
49152	Alkali Rhyolite	204572
49153	Alkali Rhyolite	258642
49154	Alkali Rhyolite	151517
49155	Alkali Rhyolite	172660
49156	Alkali Rhyolite	174647
49157	Alkali Rhyolite	208712
49158	Alkali Rhyolite Breccia	266549
49159	Alkali Rhyolite Breccia	183570
49160	Comendite	252454
49161	Comendite	258464
49162	Comendite	200600
49163	Comendite	287588
49164	Comendite	223660
49165	Comendite	179660
49166	Comendite	225523
49167	Comendite	289597