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VARIATION IN MINERALOGY, TEMPERATURE, AND OXYGEN FUGACITY IN A SUITE OF STRONGLY PERALKALINE LAVAS AND TUFFS, PANTELLERIA, ITALY

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ABSTRACT

Eight samples of pantelleritic lava and tuff and a lithic inclusion of trachyte from Pantelleria, Italy, have been thoroughly analyzed with an electron microprobe. These samples reveal five different mineral assemblages if classified by the presence of fayalite, aenigmatite, ilmenite, and magnetite: (1) augite + fayalite + ilmenite + magnetite, (2) augite + fayalite + ilmenite, (3) hedenbergite or sodian hedenbergite + fayalite + ilmenite + aenigmatite + quartz, (4) sodian hedenbergite or aegirine-augite + ilmenite + aenigmatite + quartz \pm ferrichterite, and (5) aegirine-augite + aenigmatite + quartz. Alkali feldspar (Or_{35-37}) is present as the dominant phyrlic phase in each assemblage. Whole-rock silica and peralkalinity correlate strongly with the mineral assemblage: assemblage 1 is found in the sample with the lowest apaitic index [A.I. = molar (Na + K)/Al] and silica concentration (A.I. < 1.31, SiO₂ < 64.8 wt%) and equilibrated at 991–888°C at an oxygen fugacity between 0.7 and 1.1 log units below the FMQ buffer (FMQ – 0.7 to FMQ – 1.1). Assemblage 2 is associated with a higher apaitic index and silica concentration (A.I. = 1.42, SiO₂ = 67.1%) and equilibrated at ~794°C at FMQ – 0.5. Assemblage 3 is associated with a still higher apaitic index and silica concentration (A.I. in the range 1.55 – 1.63, 66.8 < SiO₂ < 67.8%) and equilibrated at 764–756°C at FMQ – 0.5 to FMQ – 0.2. Assemblage 4 is associated with a slightly higher apaitic index and yet higher silica concentration (1.61 < A.I. < 1.75, 67.6 < SiO₂ < 72.0%) and equilibrated between 740–700°C at oxygen fugacities at or just below the FMQ buffer. Assemblage 5 is associated with the highest apaitic index and highest concentration of silica (A.I. = 1.97, SiO₂ = 69.7%) and equilibrated at <700°C at an oxygen fugacity just above the FMQ buffer in a “no-oxide” field. Despite the paucity of two-oxide, two-pyroxene, or two-feldspar pairs, it may be possible to accurately constrain temperature and oxygen fugacity in peralkaline rocks with QUIIF equilibria given an equilibrium assemblage of fayalite, ilmenite, and clinopyroxene.

Keywords: QUIIF, geothermometry, oxygen barometry, pantellerite, aenigmatite, fayalite, Pantelleria, Italy.

SOMMAIRE

Nous avons analysé huit échantillons de lave et de tuff pantelléritiques et une inclusion lithique de trachyte provenant de Pantelleria, en Italie, au moyen d'une microsonde électronique. Ces échantillons révèlent cinq assemblages différents de minéraux selon la présence de fayalite, aenigmatite, ilménite, et magnétite: (1) augite + fayalite + ilménite + magnétite, (2) augite + fayalite + ilménite, (3) hédénbergite plus ou moins sodique + fayalite + ilménite + aenigmatite + quartz, (4) hédénbergite sodique ou aegirine-augite + ilménite + aenigmatite + quartz \pm ferrichterite, et (5) aegirine-augite + aenigmatite + quartz. Un feldspath alcalin (Or_{35-37}) constitue la phase phénocristique dominante avec chaque assemblage. La teneur de la roche en silice et le degré d'hyperalcalinité montrent une forte corrélation avec l'assemblage de ces minéraux. L'assemblage 1 caractérise l'échantillon le moins fortement hyperalcalin [indice d'appaïcité, I.A. = (Na + K)/Al, proportion molaire] et la plus faible teneur en silice (I.A. < 1.31, SiO₂ < 64.8%, poids), et s'est équilibré à 991–888°C à une fugacité d'oxygène entre 0.7 et 1.1 unités logarithmiques en dessous du tampon FMQ (FMQ – 0.7 to FMQ – 1.1). L'assemblage 2 est associé à un indice d'appaïcité et une teneur en silice plus élevés (I.A. = 1.42, SiO₂ = 67.1%) et aurait équilibré à environ 794°C et à FMQ – 0.5. L'assemblage 3 est associé à indice d'appaïcité et une teneur en silice encore plus élevés (I.A. dans l'intervalle 1.55 – 1.63, 66.8 < SiO₂ < 67.8%) et aurait équilibré à 764–756°C à entre FMQ – 0.5 et FMQ – 0.2. L'assemblage 4 est associé à un indice d'appaïcité légèrement plus élevé et une

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teneur en silice encore plus élevée ($1.61 < \text{I.A.} < 1.75$, $67.6 < \text{SiO}_2 < 72.0\%$) et marquerait un équilibre entre 740 et 700°C à une fugacité d'oxygène soit à ou légèrement sous le tampon FMQ. L'assemblage 5 est associé à l'indice d'appaïcité et la teneur en silice les plus élevés ($\text{I.A.} = 1.97$, $\text{SiO}_2 = 69.7\%$) et marquerait un équilibre à <700°C à une fugacité d'oxygène dépassant légèrement le tampon FMQ, dans un champ sans oxyde stable. Malgré la rareté d'assemblages à deux oxydes, deux pyroxènes ou deux feldspaths, il semble donc possible de délimiter les conditions de température et de fugacité d'oxygène dans les roches hyperalkalines au moyen des équilibres QUIIF impliquant un assemblage de fayalite, ilménite, et clinopyroxène à l'équilibre.

(Traduit par la Rédaction)

Mots-clés: QUIIF, géothermométrie, barométrie de l'oxygène, pantellerite, aenigmatite, fayalite, Pantelleria, Italie.

INTRODUCTION

Pantellerite is a strongly peralkaline, silica-oversaturated felsic rock that is relatively rich in FeO^T , TiO_2 , Na_2O , F, and Cl, and relatively poor in Al_2O_3 , CaO, and MgO (Macdonald 1974, Noble 1968). Mineral phases that crystallize in pantelleritic magmas reflect this unusual chemical composition, and include anorthoclase, aenigmatite, fayalite, sodic pyroxene, and sodic amphibole; many phases abundant in more common felsic rocks, such as plagioclase, biotite, hornblende, orthopyroxene, and titanian magnetite, are rare or absent in these rocks (Nicholls & Carmichael 1969). The lack of orthopyroxene, plagioclase, or titanian magnetite in most of these rocks makes determination of thermodynamic properties, such as temperature and oxygen fugacity, $f(\text{O}_2)$, impossible by methods utilizing pyroxene, feldspar, or oxide mineral pairs, and, as a result, very few quantitative data for these parameters are available (Scaillet & Macdonald 2001). Accurate knowledge of these parameters is necessary for many applications, including calculation of vapor fugacities and volatile solubilities in magmas (*e.g.*, Toulmin & Barton 1962, Newman & Lowenstern 2002), estimation of diffusion rates of elements and volatile species in minerals and melts (*e.g.*, Cherniak & Watson 1992, Zhang & Behrens 2000, Mungall 2002), estimation of trace-element partition coefficients (*e.g.*, Ren *et al.* 2003, Ren 2004), determination of melt viscosities (*e.g.*, Hess & Dingwell 1996, Dingwell *et al.* 1998, Hess *et al.* 2001, Giordano & Dingwell 2003), the development of thermodynamic models of igneous processes (*e.g.*, Ghiorso 1997, Ghiorso & Carmichael 1987), and the determination of the composition and relative stability of mineral and fluid phases associated with magmas (Frost 1991).

In this paper, we seek to better constrain the T - $f(\text{O}_2)$ evolution of a suite of pantelleritic lavas and tuffs from Pantelleria, Italy, through the use of a variety of techniques, including QUIIF equilibria (Lindsley & Frost 1992, Frost & Lindsley 1992, Andersen *et al.* 1993), clinopyroxene-liquid equilibria (Putirka *et al.* 2003), alkali feldspar-liquid equilibria (Carmichael & MacKenzie 1963), and by investigating the relationship between whole-rock composition (silica and peralkalinity) and mineral assemblage, mineral composition, temperature, and oxygen fugacity.

PREVIOUS WORK

Carmichael (1962) published the first detailed study of phyrlic phases in pantellerite and described anorthoclase, quartz, aenigmatite, sodic pyroxene, and fayalite as the common phenocrysts. He noted that ilmenite is the dominant Fe-Ti oxide in these rocks and that magnetite is extremely rare, which he interpreted as the result of crystallization in a highly reducing environment (*cf.* Carmichael 1991). Carmichael (1962) also suggested that aenigmatite is antipathetic with fayalite + ilmenite, and that these two minerals react with sodium-rich melt to form aenigmatite. The relationships among temperature, oxygen fugacity and melt peralkalinity, and their control on the minerals developed in peralkaline magmas, were also investigated in natural and experimental systems by Abbott (1967), Nicholls & Carmichael (1969), Lindsley (1971), Lindsley & Haggerty (1971), Marsh (1975), Ferguson (1978), Platt & Woolley (1986), Scaillet & Macdonald (2001), and many others. The T - $f(\text{O}_2)$ data for peralkaline and cogenetic high-alkali metaluminous rocks have been reported for natural systems by Carmichael (1967, 1991), Bizouard *et al.* (1980), Mahood (1981a), Wolff & Wright (1981), Conrad (1984), Novak & Mahood (1986), Vogel *et al.* (1989), and White *et al.* (2004), all of which have provided evidence for equilibration at oxygen fugacities near or below the fayalite - magnetite - quartz (FMQ) buffer over temperatures ranging from 1025° to 685°C (Table 1).

GEOLOGICAL BACKGROUND

The island of Pantelleria, Italy, the type locality for pantellerite, is located in the Strait of Sicily in the Mediterranean Sea between Sicily and Tunisia. It is situated in the Sicily Channel Rift Zone, a NW-SE-trending transtensional rift zone located on the northern margin of the African Plate (Dewey *et al.* 1989, Civetta *et al.* 1988). Most rocks exposed on the island are younger than the 45 ka Green Tuff (GT), the caldera-forming ignimbrite of the Cinque Denti caldera (Mahood & Hildreth 1983, 1986). The Green Tuff is a compositionally zoned, compound cooling unit that includes unwelded lapilli tuff, welded tuff, and rheomorphic tuff with an aggregate volume between 3.4 km³ (Mahood & Hildreth 1986) and 7 km³ (Wolff & Wright 1981).

The eruption of trachytic to pantelleritic lavas followed caldera collapse in several episodes of caldera-related silicic volcanism (Civetta *et al.* 1988, Mahood & Hildreth 1986). The Monte Gelkhamar (MG) lava cone consists of a series of pantelleritic trachyte to pantellerite lavas that erupted between 24 and 23 ka. Eruptions along the caldera rim shield at about 19 ka produced the Cuddie di Bellizzi (CB) lava flows in the southeastern end of the island. The youngest silicic lava on the island is represented by pantellerite erupted by the Cuddia Randazzo (CR) lava cone at about 5.5 ka (Mahood & Hildreth 1986).

TABLE 1. TEMPERATURE – OXYGEN FUGACITY DATA FOR PERALKALINE SUITES FROM THE LITERATURE

Sample	SiO ₂ wt%	Agpaitic index	T (°C)	log <i>f</i> (O ₂)	Method	T (°C)	QUILF95* log <i>f</i> (O ₂)	ΔFMQ
Carmichael (1967, 1991)								
3112			1025	-11.2	(1)	956	-13.0	-1.4
3112			848	-15.5	(6)			
Bizouard <i>et al.</i> (1980)								
D217	65.02	0.97	930	-12.6	(1)	810	-15.3	-1.0
TD7	64.00	0.94	960	-12.2	(1)	814	-15.8	-1.5
F53	71.20	0.95	840	-13.6	(1)	790	-14.5	0.3
Mahood (1981a, b): Rio Salado Dome								
193	74.34	1.09	850	-13.8	(1)	816	-14.9	-0.7
Wolff & Wright (1981)								
Green Tuff			960	-12.1	(1)	819	-15.6	-1.5
Green Tuff			933	-12.8	(3)			
Green Tuff			960		(2)			
Conrad (1984)								
CC-78-136	68.36	0.92	865	-14.7	(4)	914	-13.6	-1.3
JR-79-80(4)	64.30	0.73	865	-14.2	(4)	875	-14.0	-1.0
JR-79-80(5)	64.30	0.73	900	-13.3	(4)	901	-13.2	-0.7
CC-78-140	72.51	1.00	944		(3)			
Novak & Mahood (1986): Kane Wash Tuff								
V1-B 12			827	-14.9	(5)	785	-15.4	-0.5
V2-B 215			720	-17.6	(5)	732	-16.9	-0.8
V2-TF 379			835	-14.6	(5)	806	-15.0	-0.6
V3-B 390			685	-17.9	(5)	685	-17.3	0.0
Vogel <i>et al.</i> (1989): Rocket Wash (99) and Pahute Mesa (20, 22, 29)								
99	65.90	1.03	826	-14.7	(5)	833	-14.6	-0.7
20 basal	72.17	1.01	812	-15.4	(5)	819	-15.2	-1.0
29 basal	72.01	0.96	794	-15.6	(5)	805	-15.3	-0.9
22 P.M. 2	65.33	0.95	826	-15.1	(5)	832	-15.2	-1.3

Key to methods: (1) Fe–Ti oxides: Buddington & Lindsley (1964); (2) olivine – clinopyroxene: Powell & Powell (1974); (3) Fe–Ti oxides: Powell & Powell (1977); (4) Fe–Ti oxides: Spencer & Lindsley (1981); (5) Fe–Ti oxides: Andersen & Lindsley (1985); (6) Fe–Ti oxides: Ghiorso & Sack (1991).

* Fe–Ti oxides, recalculated using QUILF95, Andersen *et al.* (1993). Whole-rock data and mineral data for recalculation of Bizouard *et al.* (1980) values adopted from Barberi *et al.* (1975). ΔFMQ = log *f*(O₂) – FMQ (T).

WHOLE-ROCK GEOCHEMISTRY

Whole-rock compositions of most of the samples used in this study were presented by White *et al.* (2003a). The composition of an inclusion in sample 98521 (98521–Inc) is adapted from the composition of a similar inclusion (Opl361i) in the same unit (CR) reported by Civetta *et al.* (1998). New information include major-element data for 98529, which was obtained by the wavelength-dispersion X-ray-fluorescence method described by White *et al.* (2003a), and for 98527, which was obtained by inductively coupled plasma – optical emission spectroscopy at Activation Laboratories, Ancaster, Ontario. Results of whole-rock major-element analyses and the calculated CIPW normative mineralogy are presented in Table 2. CIPW norms were calculated using an FeO/FeO^T ratio of 0.830; this value represents the average of a set of values (over a total range of 0.821 to 0.844) calculated using the method of Sack *et al.* (1980) for each whole-rock composition at oxygen fugacities defined by the FMQ buffer (Myers & Eugster 1983) between 900 and 700°C.

TABLE 2. WHOLE-ROCK BULK COMPOSITIONS, PANTELLERIA SUITE, ITALY

Sample	98520	98521	98521–Inc	98522	98523	98526	98527	98529	98531
Unit	CR	CR	CR–Inc	CR	MG	MG	GT	CB	CR
Rock type	PT	P	CT	P	P	P	P	P	P
SiO ₂ wt%	64.80	67.83	63.95	67.64	67.84	67.12	72.04	69.73	66.79
TiO ₂	0.63	0.46	0.56	0.49	0.56	0.54	0.38	0.46	0.56
Al ₂ O ₃	12.56	9.15	14.30	9.13	10.13	11.54	8.68	7.72	10.06
FeO ^T	7.57	8.22	6.94	8.38	7.64	7.08	7.00	8.41	8.30
MnO	0.27	0.27	0.24	0.29	0.25	0.24	0.26	0.27	0.28
MgO	0.31	0.13	0.25	0.15	0.25	0.24	0.10	0.13	0.22
CaO	0.99	0.58	1.10	0.57	0.61	0.65	0.32	0.45	0.71
Na ₂ O	7.03	6.94	6.79	6.89	6.48	6.77	5.72	6.50	6.97
K ₂ O	4.81	4.27	5.08	4.29	4.65	4.83	4.23	4.20	4.51
P ₂ O ₅	0.08	0.04	0.08	0.05	0.04	0.03	0.03	0.02	0.05
Total	99.06	97.89	99.29	97.88	98.45	99.04	98.76	97.88	98.44
A.I.	1.34	1.75	1.17	1.75	1.55	1.42	1.61	1.97	1.63
Qtz wt%	9.82	23.73	4.38	23.48	21.26	16.34	31.80	30.39	19.37
Or	28.65	25.73	30.20	25.89	27.87	28.77	25.28	25.31	27.02
Ab	38.13	23.74	45.54	23.49	26.61	32.76	21.33	16.68	27.01
Ns	3.99	7.20	1.84	7.13	5.64	4.79	5.40	7.95	6.42
Ae	4.17	4.58	3.82	4.67	4.24	3.90	3.87	4.69	4.60
Di	4.37	2.59	4.85	2.55	2.73	2.86	1.43	2.03	3.16
Opx	9.58	11.48	8.23	11.80	10.54	9.52	10.12	12.06	11.29
Ilm	0.60	0.45	0.53	0.47	0.54	0.52	0.37	0.44	0.54
Ap	0.19	0.10	0.19	0.11	0.09	0.08	0.07	0.04	0.11

Key to unit: CR: Cuddia Randazzo, CR–Inc: Inclusion in CR lava, MG: Monte Gelkhamar, CB: Cuddie di Bellizzi, GT: Green Tuff.

Key to rock type: CT: comenditic trachyte, P: pantellerite, PT: pantelleritic trachyte (Macdonald 1974), A.I. (agpaitic index): molar (Na + K) / Al.

Analytical results for 98520, 98521, 98522, 98523, 98526, and 98531 were previously reported by White *et al.* (2003a). Composition of 98521–Inc is adopted from Opl361i of Civetta *et al.* (1998). The analytical data for 98527 and 98529 are new.

Normative mineralogy was calculated using an FeO/FeO^T ratio of 0.830 (see text). Qtz: quartz, Or: orthoclase, Ab: albite, Ns: sodium metasilicate, Ae: aegirine, Di: diopside, Opx: orthopyroxene, Ilm: ilmenite, Ap: Apatite.

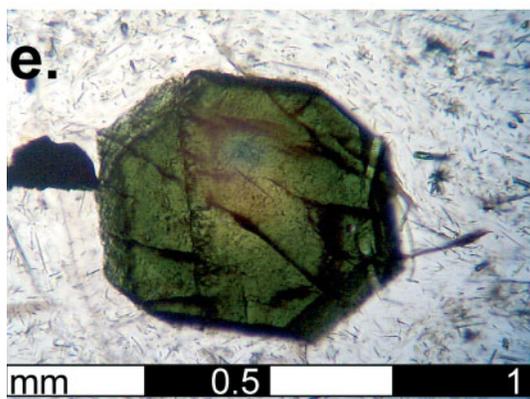
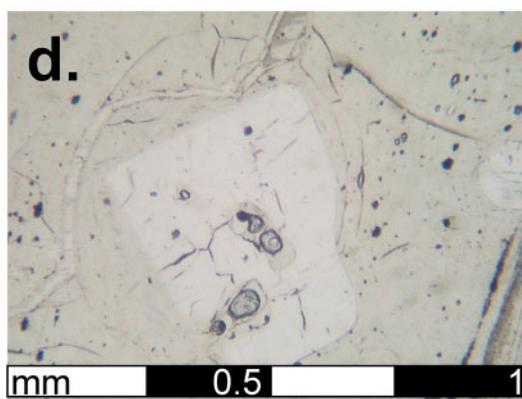
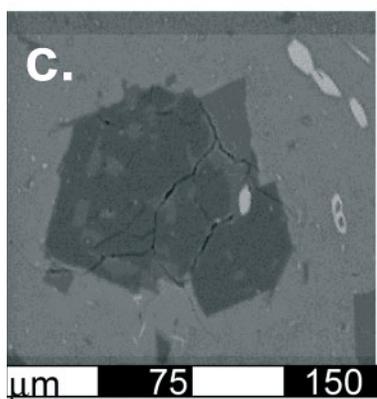
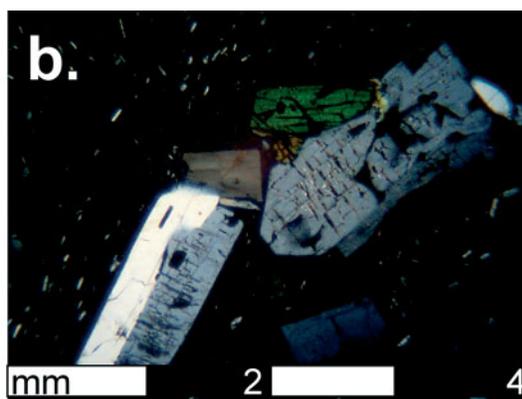
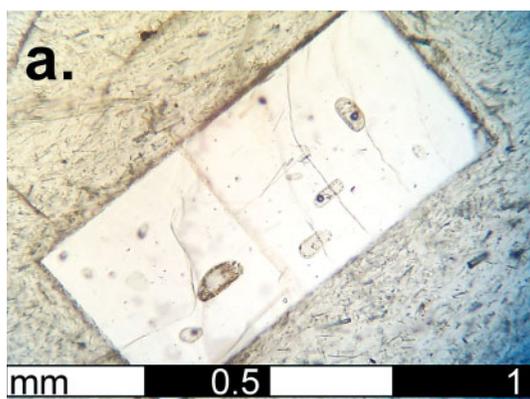
PETROGRAPHY AND MINERAL GEOCHEMISTRY

Each of the eight rock samples described in this study is a vitrophyre, and consists of between 6 and 23 vol.% total phenocrysts set in a glass matrix. Alkali feldspar is the dominant phenocryst in every sample, comprising >85% of each assemblage. Other phenocrysts may include fayalite, clinopyroxene, aenigmatite, ferrichterite, quartz, or iron–titanium oxides (see Table 3 in White *et al.* 2003a). Phenocrysts are unzoned

or negligibly zoned (*i.e.*, <2 mol.% variation), most are euhedral, and none show any texture that would suggest disequilibrium with the coexisting melt (glass) phase (Fig. 1).

Analytical methods

The composition of the ferromagnesian phases was obtained by electron-probe micro-analysis (EPMA) at the University of Texas at El Paso with a Cameca



SX50 instrument. The microprobe has four wavelength-dispersion detectors and a state-of-the-art Rontec solid state energy-dispersion detector. The operating software of the SX50 is SX RAY N50 on Solaris 2, which is the

revised SX100 software compatible with the SX50. Minerals were analyzed with a 15 keV accelerating voltage, a 20 nA beam current, a beam of 5 μm , and 20 seconds of peak-counting time. A block of standards

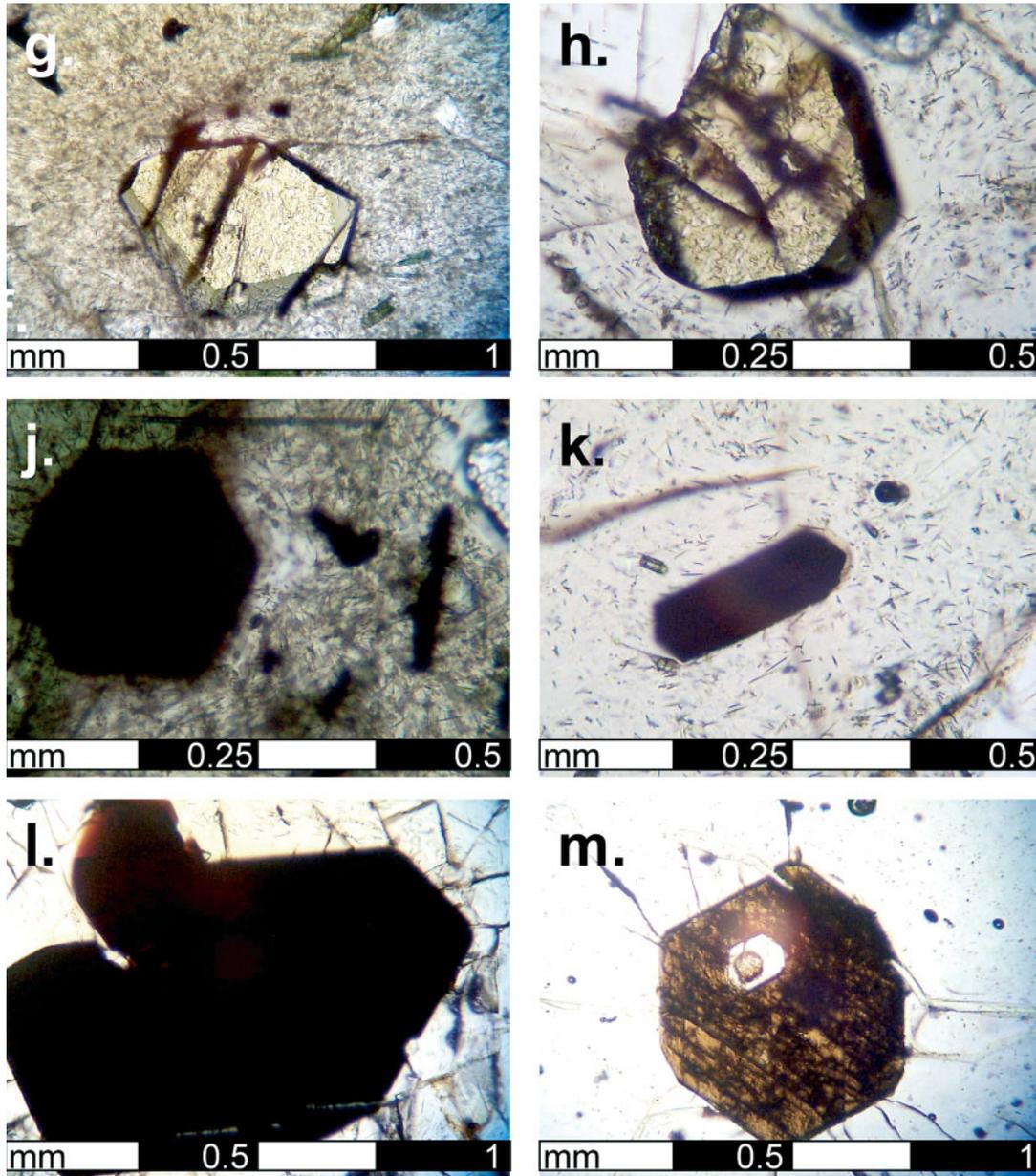


FIG. 1. Representative photomicrographs of mineral phases: a) anorthoclase, 98521, plane-polarized light (PPL); b) anorthoclase and augite, 98526, cross-polarized light (XPL); c) quartz, 98531, back-scattered electron (BSE) image (15 keV, 20 nA); d) quartz, 98527, PPL; e) aegirine-augite, 98521, PPL; f) sodic augite, 98523, PPL; g) fayalite, 98531, PPL; h) fayalite, 98523, PPL; j) ilmenite, 98531, PPL; k) aenigmatite, 98523, PPL; l) aenigmatite, 98529, PPL; m) ferrourichterite with alkali feldspar inclusion, 98527, PPL.

from the Smithsonian Institution was used for major elements. Calibration standards include Natural Bridge diopside (USNM 117733) for SiO₂, MgO, and CaO, Kakanui anorthoclase (USNM 133868) for Al₂O₃ and Na₂O, and Ilmen Mountains ilmenite (USNM 96189) for TiO₂ and FeO. For volatile components, the Astimex Scientific Ltd. MINM25–53 block of standards was used, with fluorite for F and tugtupite for Cl. A set of standards from both Smithsonian and Astimex were analyzed each day to monitor the accuracy and precision of the analytical results. We were particularly vigilant for precise measurements of the Na₂O, CaO, FeO and MgO contents. Through the results of our analyses of standards as unknowns, we have attained a good accuracy and precision for most of the elements reported. Alkali feldspar compositions were previously reported by White *et al.* (2003a) for all samples except for 98521–Inc and 98529, which were acquired using the method described above. All reported compositions of minerals represent average values.

Alkali feldspar and quartz

Alkali feldspar is by far the most abundant mineral phase in all of the rocks included in this study, comprising >85% of the total phenocryst assemblage in each sample. Feldspar crystals are typically 1 to 4 mm in length, euhedral, and unzoned (Figs. 1a, b). Compositions span a remarkably small range despite whole-rock compositions that vary from ~64 to 72 wt% SiO₂ (Table 3; *cf.* Avanzinelli *et al.* 2004). The feldspar is very An-poor (<0.9 mol.%), except for the feldspar from the trachyte inclusion (98521–Inc), which has 2.2 mol.% An. Modal quartz is present in all samples with >67 wt% SiO₂, except 98526. In most samples, quartz is a minor phase (<1 vol.%) and occurs as ~100 μm

microphenocrysts (Fig. 1c); quartz is only relatively abundant (~5 vol.%) and macroscopic (~0.50 to 0.75 mm) in 98527 and 98529, the two samples richest in silica (>69 wt% SiO₂) (Fig. 1d).

Clinopyroxene and olivine

Clinopyroxene is the only ferromagnesian phase present in each assemblage, typically as small (0.5 to 1.0 mm), euhedral crystals (Table 4, Figs. 1e, f). The clinopyroxene becomes increasingly Na- and Fe-rich with increasing aegirite index (A.I.), rising from 0.70 to 2.69 wt% Na₂O before dropping slightly down to 2.53 wt% (Fig. 2a). Over the same interval, the ferrosilite component (Fs) increases from ~41 to ~52 mol.% (Fig. 2b). Microphenocrysts of pyrrhotite commonly occur as inclusions in clinopyroxene in all samples but the two richest in silica (98527 and 98529).

Fayalite (Table 5, Figs. 1g, h) is present only in samples with lower SiO₂ (<67.8 wt%) and A.I. (<1.63) in assemblages with augite + ilmenite + titanian magnetite, augite + ilmenite, or hedenbergite or sodian hedenbergite + ilmenite + aenigmatite. Fayalite compositions become more Fe-rich with increasing A.I., rising from Fa_{90.5} to Fa_{96.4} (Fig. 2c). Fayalite phenocrysts are not significantly zoned (*i.e.*, <2 mol.% Fa).

Iron–titanium oxides

Compositions of Fe–Ti oxides are presented in Table 6. Ilmenite (Fig. 1j) is present in all but the most strongly peralkaline sample (98529, A.I. = 1.97), and coexists with titanian magnetite only in the two least peralkaline samples (98520, A.I. = 1.34; 98521–Inc, A.I. = 1.17). Hematite content in all ilmenite crystals

TABLE 3. COMPOSITION OF ALKALI FELDSPAR, PANTELLERIA SUITE

Sample	98520	98521	98521 -Inc	98522	98523	98526	98527	98529	98531
Type	Anr	Anr	Anr	Anr	Anr	Anr	San	Anr	Anr
SiO ₂	66.52	66.93	67.98	66.58	66.62	66.41	67.90	67.80	66.44
Al ₂ O ₃	18.86	18.33	19.46	18.72	18.83	19.06	18.37	18.70	19.17
Fe ₂ O ₃	0.61	0.99	0.25	0.96	0.76	0.81	0.80	0.54	0.65
CaO	0.07	0.00	0.23	0.01	0.01	0.02	0.00	0.03	0.09
Na ₂ O	7.62	7.38	7.24	7.44	7.52	7.46	6.99	7.14	8.04
K ₂ O	6.22	6.29	6.31	6.27	6.24	6.23	6.47	6.28	5.55
Total	99.91	99.93	101.47	99.96	99.98	99.98	100.53	100.49	99.95
An	0.0035	0.0001	0.0110	0.0003	0.0007	0.0010	0.0000	0.0015	0.0044
Ab	0.65	0.64	0.63	0.64	0.65	0.64	0.62	0.63	0.68
Or	0.35	0.36	0.36	0.36	0.35	0.35	0.38	0.37	0.31

Key to type (Deer *et al.* 1966): Anr: anorthoclase (Or <37, triclinic); San: sanidine (Or >37, monoclinic). Bulk compositions in wt%.

Key to end members (proportions in mol.%): An: anorthite, Ab: albite, Or: orthoclase.

Compositions of 98520, 98521, 98522, 98523, 98526, 98531 were previously reported by White *et al.* (2003a).

TABLE 4. COMPOSITION OF CLINOPYROXENE, PANTELLERIA SUITE

Sample	98520	98521	98521 -Inc	98522	98523	98526	98527	98529	98531
Type	Aug	Ae-Aug	Augite	Ae-Aug	Na-Hd	Aug	Na-Hd	Ae-Aug	Hd
SiO ₂ wt%	48.35	48.59	48.89	48.62	48.71	48.53	49.24	48.25	47.06
TiO ₂	0.57	0.43	0.44	0.27	0.40	0.41	0.29	0.55	0.55
Al ₂ O ₃	0.29	0.14	0.41	0.13	0.15	0.21	0.15	0.15	0.20
FeO ^T	25.83	28.88	23.54	29.00	27.59	25.63	27.12	29.14	27.68
MnO	1.47	1.46	1.38	1.30	1.52	1.49	1.64	1.46	1.57
MgO	2.88	0.93	4.35	0.93	2.40	3.57	2.41	1.30	1.67
CaO	19.39	16.76	20.32	16.75	17.02	18.15	16.59	16.13	18.66
Na ₂ O	0.70	2.69	0.62	2.57	1.76	1.15	2.35	2.53	1.06
K ₂ O	0.02	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
Total	99.51	99.87	99.95	99.56	99.55	99.13	99.79	99.50	98.43
Wo mol.%	0.44	0.45	0.44	0.45	0.43	0.42	0.44	0.43	0.42
En	0.10	0.04	0.15	0.04	0.09	0.13	0.10	0.05	0.07
Fs	0.46	0.51	0.41	0.51	0.48	0.45	0.47	0.52	0.51

Clinopyroxene types classified following Morimoto *et al.* (1988): Aug: augite, Hd: hedenbergite, Na-Hd: sodian hedenbergite, Ae-Aug: aegirine-augite. Key to end-member components: Wo: wollastonite, En: enstatite, Fs: ferrosilite. End-members compositions calculated with QUILF95, v. 6.42 (Andersen *et al.* 1993).

analyzed is very low (<7 mol.%), which is typical of ilmenite compositions in fayalite-bearing rhyolite (Frost *et al.* 1988). The two-oxide pairs in samples 98520 and 98521-Inc are in equilibrium according to the criteria of Bacon & Hirschmann (1988). Temperatures and log oxygen fugacities for these samples are 1005°C, -11.54 (98521-Inc) and 903°C, -13.55 (98520), determined with the approach of Andersen & Lindsley (1988).

Aenigmatite and amphibole

Aenigmatite (Table 7, Figs. 1k, l) phenocrysts are present only in samples with an agpaite index above 1.50. At A.I. <~1.61, it coexists with fayalite + ilmenite + sodic augite, at higher A.I. (from ~1.61 to <1.97), it is found with ilmenite + aegirine-augite or sodic augite ± ferrichterite, and with only sodic augite in the most strongly peralkaline sample (A.I. = 1.97) (*cf.* Nicholls & Carmichael 1969). Experimental data have shown that aenigmatite has a maximum thermal stability of 900°C (dry) at oxygen fugacities controlled by the FMQ buffer (Lindsley 1971, Lindsley & Haggerty 1971, Kunzmann

1999), which places an upper constraint on equilibration temperature in the aenigmatite-bearing samples.

Fluorine-rich (0.97% F) ferrichterite (Table 7, Fig. 1m; Leake *et al.* 1997) phenocrysts are found only in 98527 (Green Tuff). Ferrichterite in F-free systems is stable with clinopyroxene only at low temperatures and very reducing conditions (<750°C at oxygen fugacities on the magnetite-wüstite buffer, and <525°C on the FMQ buffer at P = 1000 bars); at higher temperature and

TABLE 5. COMPOSITION OF OLIVINE, PANTELLERIA SUITE

Sample	98520	98521-Inc	98523	98526	98531
SiO ₂ wt%	29.63	30.17	29.64	29.40	28.37
TiO ₂	0.06	0.04	0.06	0.03	0.12
Al ₂ O ₃	0.01	0.03	0.00	0.00	0.00
FeO ^T	63.16	63.64	63.47	64.81	65.09
MnO	4.14	4.15	3.97	4.02	3.95
MgO	2.50	3.25	2.24	2.43	1.05
CaO	0.64	0.69	0.36	0.44	0.43
Na ₂ O	0.03	0.03	0.03	0.02	0.01
K ₂ O	0.01	0.01	0.01	0.00	0.01
Total	100.17	102.00	99.77	101.14	99.02
Fa mol.%	0.92	0.91	0.93	0.93	0.96
Fo	0.07	0.08	0.06	0.06	0.03
La	0.01	0.01	0.01	0.01	0.01

Key to end-member components: Fa: fayalite, Fo: forsterite, La: lamite. End-member compositions calculated using QUILF95, v 6.42 (Andersen *et al.* 1993).

TABLE 6. COMPOSITION OF IRON-TITANIUM OXIDES, PANTELLERIA SUITE

Sample	98520	98521	98521-Inc	98522	98523	98526	98527	98529	98531
Type	Ilm	Mgt	Ilm	Ilm	Mgt	Ilm	Ilm	Ilm	Ilm
SiO ₂	0.03	0.08	0.00	0.02	0.07	0.04	0.01	0.03	0.04
TiO ₂	48.46	23.68	48.87	48.68	24.89	48.90	47.71	49.02	41.60
Al ₂ O ₃	0.00	0.00	0.00	0.00	0.19	0.00	0.00	0.00	0.03
FeO ^T	45.62	69.36	46.82	46.77	69.64	46.83	46.32	47.16	53.05
MnO	2.24	1.73	2.27	2.26	1.81	2.11	2.05	2.02	2.07
MgO	0.18	0.15	0.37	0.38	0.28	0.12	0.24	0.25	0.25
CaO	0.01	0.09	0.02	0.02	0.03	0.02	0.01	0.10	0.03
Na ₂ O	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.01	0.02
K ₂ O	0.03	0.02	0.01	0.01	0.01	0.02	0.00	0.01	0.01
Total	96.58	95.13	98.37	98.16	96.94	98.05	96.37	98.60	97.09
Ilm	0.89		0.90	0.87		0.89	0.88	0.89	0.88
Hem	0.05		0.06	0.06		0.06	0.06	0.06	0.06
Gkl	0.01		0.01	0.01		0.00	0.01	0.01	0.01
Pyf	0.05		0.05	0.05		0.05	0.04	0.04	0.05
N-Ti		0.69			0.71				
N-Mg		0.09			0.02				
N-Mn		0.06			0.06				
T (°C)		903			1005				
log f(O ₂)		-13.5			-11.5				

Key to end-member components of ilmenite (Ilm): ilm: ilmenite, hem: hematite, gkl: geikielite, pyf: pyrophanite. End-member compositions of ilmenite and magnetite (Mgt) were calculated with QUILF95 v. 6.42 (Andersen *et al.* 1993) and reported in mol.%. T-f(O₂) values calculated following Andersen & Lindsley (1988). Chemical compositions reported in wt%.

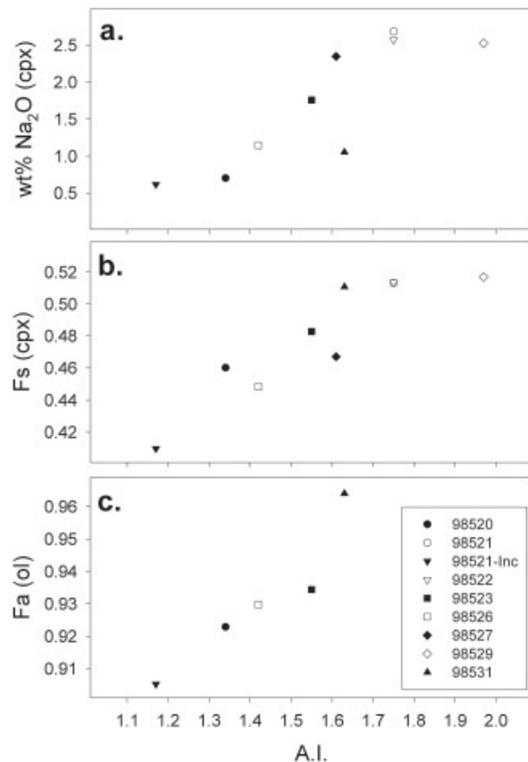


FIG. 2. Variation with whole-rock agpaite index [A.I. = mol. (Na + K)/Al] of: a) Na₂O in clinopyroxene, b) ferrosilite (Fs) component in clinopyroxene, and c) fayalite (Fa) component in olivine.

more oxidizing conditions, amphibole + clinopyroxene decomposes to aegirine-augite + fayalite + magnetite + quartz + vapor (Charles 1975). The presence of F may expand this stability field considerably (Carmichael *et al.* 1974, p. 287, Conrad 1984); nonetheless, the presence of ferrichterite suggests crystallization at low temperature and oxygen fugacity.

VARIABILITY IN MINERAL ASSEMBLAGE

This suite can be divided into five different assemblages, classified by the presence of oxides, fayalite, and aenigmatite (Table 8). Assemblage 1 (two oxides) is associated with the lowest silica and aegirite indices (A.I. < 1.31, SiO₂ < 64.8 wt%) and consists of anorthoclase + augite + fayalite + ilmenite + magnetite + pyrrhotite. Assemblage 2 (fayalite-ilmenite) is associated with slightly higher concentrations of silica and aegirite index (A.I. = 1.42, SiO₂ = 67.1 wt%) and consists of anorthoclase + augite + fayalite + ilmenite + pyrrhotite. Assemblage 3 (fayalite – ilmenite – aenigmatite) is associated with higher concentrations of silica and aegirite indices (1.55 < A.I. < 1.63, 66.8 < SiO₂ < 67.8 wt%) and consists of hedenbergite or sodian hedenbergite + fayalite + ilmenite + aenigmatite + quartz + pyrrhotite. Assemblage 4 (ilmenite-aenigmatite) is associated with even higher concentrations of silica and aegirite indices (1.61 < A.I. < 1.75, 67.6 < SiO₂ < 72.0 wt%) and consists of anorthoclase or sanidine + sodian hedenbergite or aegirine-augite + ilmenite + aenigmatite + quartz; pyrrhotite or ferrichterite also is present. Assemblage 5 (aenigmatite only) is associated with higher concentrations of silica (69.7 wt%) and the highest aegirite index (1.97), and consists of anorthoclase + aegirine-augite + aenigmatite + quartz.

GEOOTHERMOMETRY AND OXYGEN BAROMETRY

QUIF equilibria

The presence of fayalite with ilmenite and titanian magnetite in assemblage 1 allows us to apply QUIF equilibrium to refine the results of the two-oxide geothermometer presented in the previous section; this may reduce the uncertainty in the T–*f*(O₂) values determined by an order of magnitude or more (Frost *et al.* 1988). Likewise, T and *f*(O₂) can be constrained from one-oxide systems with fayalite (with or without augite or quartz) using QUIF equilibria (Frost *et al.* 1988, Lindsley & Frost 1992, Frost & Lindsley 1992). The program QUILF95, version 6.42 (Andersen *et al.* 1993) for Microsoft Windows 95 was used to evaluate equilibrium and calculate T and *f*(O₂); the results are presented in Table 9. Calculated fayalite + two-oxide T – log *f*(O₂) values are 14° to 15°C and 0.2 to 0.3 log units lower than the two-oxide values: 991°C and –11.8 (98521–Inc), and 888°C and –13.8 (98520). Calculated fayalite + ilmenite T – log *f*(O₂) values are

794°C and –15.2 (98526); fayalite + ilmenite + quartz T – log *f*(O₂) values are 764°C and –15.9 (98531), and 756°C and –15.8 (98523). A log *f*(O₂) of –16.9 was calculated by QUILF95 based on a temperature of 703°C (estimated from feldspar and clinopyroxene equilibria, see discussion below) for an assemblage of ilmenite + clinopyroxene + quartz (sample 98527). In all cases, calculated equilibrium values for the trial end-member compositions were close to the observed values; this provides strong evidence that these phases form equilibrium assemblages. However, it was necessary to exclude

TABLE 7. COMPOSITION OF AENIGMATITE AND AMPHIBOLE, PANTELLERIA SUITE

Sample Type	98521 Aen	98522 Aen	98523 Aen	98527 Aen	98529 Aen	98531 Aen	98527 Frt
SiO ₂ wt%	40.34	40.84	41.04	40.00	40.15	40.04	47.64
TiO ₂	8.76	8.00	8.06	8.46	9.04	8.63	2.27
Al ₂ O ₃	0.71	0.35	0.43	0.50	0.44	0.39	1.17
FeO ^T	41.31	42.02	40.94	40.30	40.98	40.76	29.19
MnO	1.23	1.30	1.23	1.38	1.30	1.19	1.14
MgO	0.46	0.41	0.49	0.98	0.64	0.60	4.25
CaO	0.77	0.43	0.43	0.50	0.48	0.40	5.55
Na ₂ O	6.94	7.02	6.92	6.90	6.74	6.87	5.03
K ₂ O	0.00	0.02	0.07	0.00	0.00	0.01	1.20
F							0.97
Cl							0.05
Total	100.49	100.38	99.61	99.02	99.77	98.88	98.45

Key to type: Aen: aenigmatite, Frt: ferrichterite. The amphibole is classified following Leake *et al.* (1997).

TABLE 8. MINERAL ASSEMBLAGES IN THE PANTELLERIA SUITE

Assemblage ¹	Whole Rock wt% SiO ₂	A.I.	Feldspar mol.% Or	Clinopyroxene Type	wt% Na ₂ O
(1) Fa + Ilm + Mgt + Po					
98521–Inc (CR)	63.95	1.17	35.55	Aug	0.62
98520 (CR)	64.80	1.34	34.59	Aug	0.70
(2) Fa + Ilm + Po					
98526 (MG)	67.12	1.42	35.31	Aug	1.15
(3) Fa + Ilm + Aen + Qtz + Po					
98531 (CR)	66.79	1.63	30.88	Hd	1.06
98523 (MG)	67.84	1.55	35.14	Na-Hd	1.76
(4a) Ilm + Aen + Qtz + Po					
98522 (CR)	67.64	1.75	35.55	Ae-Aug	2.57
98521 (CR)	67.83	1.75	35.81	Ae-Aug	2.69
(4b) Ilm + Aen + Qtz + Frt					
98527 (GT)	72.04	1.61	37.75	Na-Hd	2.35
(5) Aen + Qtz					
98529 (CB)	69.73	1.97	36.45	Ae-Aug	2.53

¹ Alkali feldspar and clinopyroxene are present in each assemblage.

Key to assemblage: Fa: fayalite, Ilm: ilmenite, Mgt: magnetite, Aen: aenigmatite, Qtz: quartz, Frt: ferrichterite, Po: pyrrhotite. Italics indicate minerals that occur as microphenocrysts (<100 μm).

Key to clinopyroxene: Aug: augite, Hd: hedenbergite, Na-Hd: sodian hedenbergite, Ae-Aug: aegirine-augite.

clinopyroxene from the QUIF calculations for sample 98521–Inc in order to find an optimized solution. The clinopyroxene in that sample thus does not seem to be in equilibrium with fayalite + ilmenite + magnetite.

Alkali feldspar – melt equilibria

An approximation of temperature of crystallization was made by comparing the whole-rock and feldspar compositions of the samples in this study with the experimental data of Carmichael & MacKenzie (1963), who determined the alkali feldspar liquidus surface in the system Qtz–Ab–Or in pantelleritic liquids (*i.e.*, with 8.3% Ae + Ns added) at H₂O saturation ($P_{\text{Total}} = P_{\text{H}_2\text{O}} \approx 1000$ bars), and under strongly oxidizing conditions (Scaillet & Macdonald 2001). If the whole-rock data from this study are plotted on the Qtz–Ab–Or triangular diagram, they show a trend best explained by crystal fractionation of an assemblage dominated by feldspar with 35–36 mol.% Or (Fig. 3); this is consistent with crystal-fractionation models based on trace elements for this suite reported in previous studies (Civetta *et al.* 1998, White & Parker 2000, White *et al.* 2003b, Avanzinelli *et al.* 2004). This trend follows the “thermal valley” of Carmichael & MacK-

enzie (1963), and the most evolved samples in this study have compositions (98527, Qtz_{40.6}Or_{32.2}Ab_{27.2}; 98529, Qtz₄₂Or₃₅Ab₂₃) very similar to the experimental minimum (Qtz_{40.5}Or_{34.5}Ab₂₅). Samples 98527 and 98529 each have relatively abundant (~5 vol.%) phyr quartz, and both plot on the alkali feldspar – quartz cotectic for this system. These results strongly suggest that the system described by Carmichael & MacKenzie can be considered a reasonable experimental analogue for this suite, and that intersections of these data with the liquidus surface in this system may provide an accurate estimate of temperature. However, because oxidizing conditions tend to raise the liquidus temperature by up to ~40°C (Scaillet & Macdonald 2001), and also because these rocks are porphyritic, these values should be considered maximum temperatures for these reduced magmas. These estimated values are: >825°C (98521–Inc), 820°C (98520), 780°C (98526), 760°C (98523, 98531), 740°C (98521, 98522), 705°C (98527), and 700°C (98529).

Clinopyroxene–melt equilibria

To estimate temperature (T) from clinopyroxene–melt equilibria, a modified version of the algorithm

TABLE 9. QUIF95 RESULTS, PANTELLERIA SUITE

Sample	98520		98521–Inc		98523		98526		98527		98531	
	Input	Calc										
Spinel												
N-Ti	0.689		0.710									
N-Mg	<i>0.009</i>	0.013	<i>0.016</i>	0.019								
N-Mn	0.057		0.581									
Ilmenite												
Hem	0.051		0.064		0.065		0.059		0.063		0.054	
Gkl	<i>0.007</i>	0.011	<i>0.015</i>	0.016	<i>0.009</i>	0.008	<i>0.010</i>	0.009	<i>0.010</i>	0.006	0.004	
Pyf	<i>0.049</i>	0.040	<i>0.049</i>	0.047	0.075		0.044		0.048		0.045	
Olivine												
Fo	0.064		0.083		0.059		0.062				0.028	
La	<i>0.013</i>	0.012	0.012		0.009		0.008				0.008	
Augite												
En	<i>0.100</i>	0.094			<i>0.091</i>	0.103	<i>0.130</i>	0.103	0.095		<i>0.066</i>	0.052
Wo	<i>0.440</i>	0.399			<i>0.427</i>	0.430	0.422		0.438		<i>0.421</i>	0.436
Activity SiO ₂ (Qtz)					1.000				1.000		1.000	
T (°C)	888		991		756		794		703		764	
log <i>f</i> (O ₂)	-13.83		-11.77		-15.76		-15.15		-16.91		-15.88	
ΔFMQ	-1.06		-0.74		-0.24		-0.51		-0.09		-0.55	

All results are calculated at P = 1000 bars. Entries in italics in the "Input" column signify values that were set as trial values; the values calculated by QUIF95 are in normal font in the adjacent "Calc" column. ΔFMQ: log *f*(O₂) – FMQ (T).

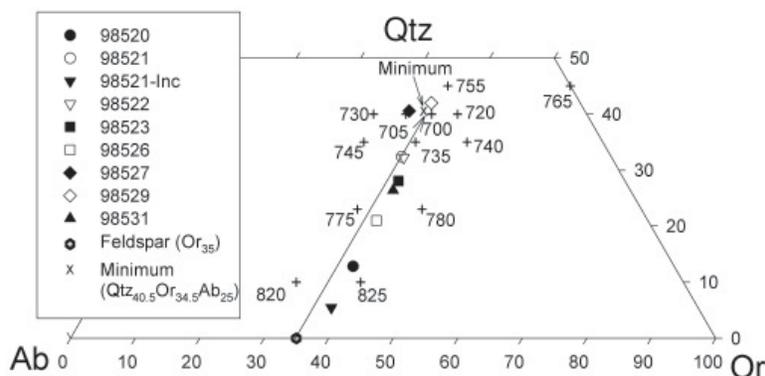


FIG. 3. Whole-rock normative mineralogy plotted in the system Qtz–Ab–An–H₂O with 8.3% Ae + 8.3% Ns added (Carmichael & MacKenzie 1963) for the alkali feldspar liquidus surface (projected from H₂O + Ae + Ns) plotted as crosses (+). Each cross is labeled with the experimentally determined alkali feldspar liquidus temperature (°C) for that composition. Also shown is the minimum for this system, and the differentiation path for a system undergoing crystal fractionation of feldspar with a composition Or₃₅, which corresponds to the “thermal valley” of Carmichael & MacKenzie (1963).

devised by Putirka *et al.* (2003) was used. In the original formulation, pressure (P) and T are determined by a set of iterative calculations; for this study, P was fixed at 1 kbar (based on the experimental work of Mahood & Baker 1986) and T was calculated based on that value. The lack of a jadeite (Jd) component in clinopyroxene for samples 98520, 98521–Inc, 98526, and 98531 prevented an estimate of T for these samples. For the other samples, calculated temperatures were 745°C (98523), 711°C (98522), 700°C (98521), 701°C (98527), and 678°C (98529).

Comparison of techniques

The temperatures and oxygen fugacities determined using the techniques described above are listed in Table 10 and plotted in Figure 4. In general, there is good agreement among the three techniques utilized. However, a notable discrepancy does exist between the QUIIF and the alkali feldspar values in the less evolved and less peralkaline samples. This discrepancy exists because the strongly peralkaline (8.3% Ae and Ns added) system studied by Carmichael & MacKenzie (1963) may not be a good analogue for the less strongly peralkaline melts (98521–Inc and 98520) in this suite. If, however, these samples are plotted in the “pure” Qtz–Ab–An system of Tuttle & Bowen (1958), estimated temperatures rise to >860°C for 98521–Inc and 840–860°C for 98520 at ~1000 bar, which are much closer to the QUIIF-calculated values. Calculated T–f(O₂) values for this suite are also within the range of other values reported for peralkaline rocks (Fig. 5). We therefore suggest that QUIIF equilibria

TABLE 10. COMPARISON OF TECHNIQUES, RESULTS ON GEOTHERMOMETRY AND OXYGEN BAROMETRY

Technique Sample	Ksp T (°C)	Cpx T (°C)	Fe–Ti oxides T (°C) log f(O ₂)		QUIIF95 T (°C) log f(O ₂)	
98521–Inc	>825	n.d.	1005	-11.54	991	-11.77
98520	820	n.d.	903	-13.55	888	-13.83
98526	780	n.d.	n.d.	n.d.	794	-15.15
98531	760	n.d.	n.d.	n.d.	764	-15.88
98523	760	745	n.d.	n.d.	756	-15.76
98522	740	711	n.d.	n.d.	n.d.	n.d.
98521	740	700	n.d.	n.d.	n.d.	n.d.
98527	705	701	n.d.	n.d.	n.d.	-16.91
98529	700	678	n.d.	n.d.	n.d.	n.d.

Key to techniques: Ksp: Carmichael & Mackenzie (1963), Cpx: Putirka *et al.* (2003), Fe–Ti oxides: Andersen & Lindsley (1988), QUIIF95: Andersen *et al.* (1993). n.d.: not determinable.

may be used to determine accurate T–f(O₂) estimates for peralkaline rocks with fayalite, one-oxide, one-pyroxene assemblages.

Aenigmatite–ilmenite equilibrium

On the basis of an apparent antipathetic relationship between Fe–Ti oxides and aenigmatite, Nicholls & Carmichael (1969) proposed the existence of a “no-oxide” field in T–f(O₂) space in which aenigmatite is stable but the oxides are not. However, it is clear from the strongly peralkaline suite under investigation that although there may be an antipathetic relationship between aenigmatite and magnetite in these silica-over-saturated rocks, such a relationship between aenigmatite

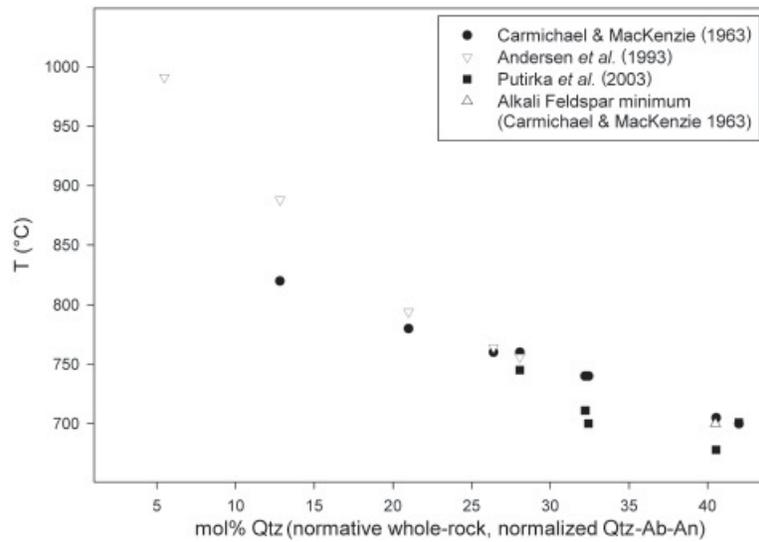


FIG. 4. Comparison between the geothermometry techniques used in this study. Temperatures are plotted *versus* normative Qtz, normalized to Qtz–Ab–An in order to also be able to show the minimum for the strongly peralkaline Qtz–Ab–An system (Carmichael & MacKenzie 1963). Note the strong agreement among the various techniques, especially at Qtz > 20%.

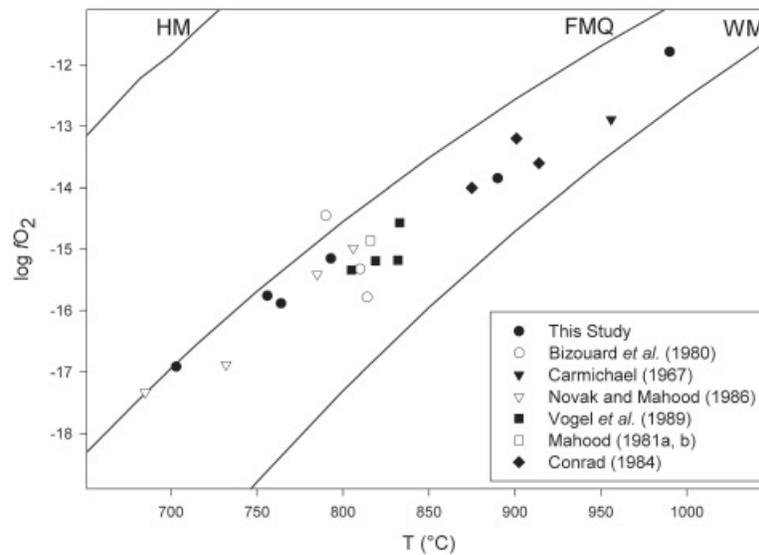
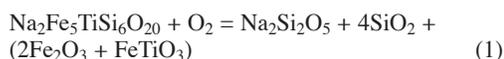


FIG. 5. Temperature and $\log f(\text{O}_2)$ data from this study plotted with T – $f(\text{O}_2)$ data for peralkaline rocks from literature. The location of the hematite–magnetite (HM), fayalite–magnetite–quartz (FMQ), and wüstite–magnetite (WM) buffers are calculated from the data presented by Frost *et al.* (1988).

and ilmenite is observed only in the most strongly peralkaline sample studied. Equilibrium between ilmenite and aenigmatite can be expressed by the following equation:



aenigmatite + gas = Nds + silica
+ ilmenite solid-solution

At equilibrium, the variation of oxygen fugacity $f(\text{O}_2)$ with temperature (T, in Kelvin) for equation (1) is given by:

$$\log f(\text{O}_2) = \frac{\Delta G^\circ}{2.303 RT} + \log a_{\text{Nds}} + 4 \log a_{\text{SiO}_2} + 2 \log a_{\text{hem}}^{\text{ilm}} + \log a_{\text{ilm}}^{\text{ilm}} - \log a_{\text{Aen}} \quad (2)$$

where a_{Nds} is the activity of sodium disilicate (Nds) in the melt, a_{SiO_2} is the activity of silica in the melt, $a_{\text{hem}}^{\text{ilm}}$ is the activity of the hematite component in the phase ilmenite, $a_{\text{ilm}}^{\text{ilm}}$ is the activity of the ilmenite component in the phase ilmenite, a_{Aen} is the activity of aenigmatite, R is the ideal gas constant ($8.31451 \text{ J K}^{-1} \text{ mol}^{-1}$), and ΔG° is the standard-state free energy of the reaction (Table 11). Sources of the free energy data are Robie & Hemingway (1995) for Fe_2O_3 , FeTiO_3 , and SiO_2 (glass), Chase *et al.* (1985) for $\text{Na}_2\text{Si}_2\text{O}_5$ (liquid), and Marsh (1975) for $\text{Na}_2\text{Fe}_5\text{TiSi}_6\text{O}_{20}$.

Equilibrium curves for this reaction are plotted relative to the FMQ buffer in Figure 6, along with the data reported in this study and from the literature. Activities for the ilmenite and hematite components were calculated from the solution model of Andersen & Lindsley (1988), as calculated by QUILF95, for ilmenite in sample 98531 for temperatures between 800 and 1200 K. Modal quartz in aenigmatite-bearing samples indicates that these magmas were at or very near quartz saturation; therefore, activities of silica in the melt were calculated following Nicholls *et al.* (1971) for glass–quartz equilibria. These should be considered minimum values for

quartz-bearing rocks and maximum values for rocks that lack phryic quartz (see also Carmichael *et al.* 1970). Unit activity was selected for aenigmatite. The curves plotted represent a_{Nds} values of 1.0, 0.5, and 0.1, as labeled. At $a_{\text{Nds}} = 1.0$, the curve follows the trend of the suite very closely, especially through the more silicic and strongly peralkaline samples that have coexisting aenigmatite and ilmenite, and where Nds activity may truly be close to unity. It is clear that in less peralkaline suites with lower a_{Nds} (which “can be taken as a measure of the peralkalinity”, Carmichael *et al.* 1974, p. 288), aenigmatite may not be a stable crystallizing phase although it has $T-f(\text{O}_2)$ values similar to or even more reducing than this suite. Lower activities of silica (*i.e.*, below quartz saturation) will also displace this

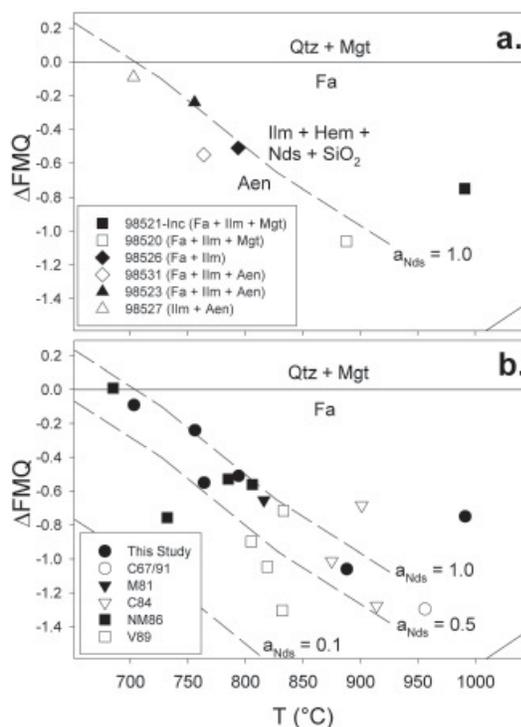


FIG. 6. (a) Temperature and $\log f(\text{O}_2)$ data from this study and the calculated aenigmatite–ilmenite stability curve for $a_{\text{Nds}} = 1.0$ at quartz saturation, plotted relative to the FMQ buffer (Frost *et al.* 1988), where $\Delta\text{FMQ} = \log f(\text{O}_2) - \text{FMQ}(T)$. (b) Data from this study and literature (recalculated; see Table 1) and the calculated aenigmatite–ilmenite stability curves for $a_{\text{Nds}} = 1.0, 0.5,$ and 0.1 at quartz saturation. Symbols used are: Aen, aenigmatite; Ilm, ilmenite; Hem, hematite; SiO_2 , silica liquid; Nds, sodium disilicate ($\text{Na}_2\text{Si}_2\text{O}_5$) liquid; Fa, fayalite; Mgt, magnetite; Qtz, quartz. Key to literature data: C67/91: Carmichael (1967, 1991), C84: Conrad (1984), NM86: Novak & Mahood (1986), and V89: Vogel *et al.* (1989).

TABLE 11. FREE-ENERGY AND ACTIVITIES USED TO CALCULATE AENIGMATITE–ILMENITE EQUILIBRIUM

T (K)	ΔG° (kJ mol ⁻¹ K ⁻¹)	[SiO ₂]	[Ilm]	[Hem]
800	-294.770	0.5847	0.8602	0.3429
900	-280.090	0.6503	0.8614	0.1542
1000	-258.754	0.7081	0.8624	0.0814
1100	-241.374	0.7593	0.8633	0.0483
1200	-223.059	0.8046	0.8640	0.0312

ΔG° : free energy for equation (2) at temperature T (see text). [SiO₂]: silica activity of the melt, following Nicholls *et al.* (1971); [Ilm]: activity of ilmenite, and [Hem]: activity of hematite in ilmenite for sample 98531, calculated with QUILF95 (Andersen *et al.* 1993).

curve to lower oxygen fugacities. Conversely, in silica-undersaturated peralkaline magmas that crystallize Ti-poor aenigmatite or wilkinsonite ($\text{Na}_2\text{Fe}^{2+}_4\text{Fe}^{3+}_2\text{Si}_6\text{O}_{20}$) (Dungan 1990), a_{Aen} will be less than unity and displace the curve toward higher fugacities of oxygen.

The close correlation between the calculated $T-f(\text{O}_2)$ data and the thermodynamic model for aenigmatite-ilmenite equilibrium is further evidence that these data determined by QUILF95 for fayalite – ilmenite – clinopyroxene, fayalite – ilmenite – clinopyroxene – quartz, and clinopyroxene – ilmenite – quartz (given T) are accurate. This curve can also be used to constrain the position in $T-f(\text{O}_2)$ space of samples 98521, 98522, and 98529, for which QUIIF modeling was not possible: 98520 and 98521 lie along the curve between samples 98523 and 98527, and 98529 must lie below this line but above the FMQ buffer in a “no-oxide” field.

DISCUSSION: IMPLICATIONS FOR PETROGENESIS

The continuous change in T from ~1000 to 700°C at low $f(\text{O}_2)$ with increasing SiO_2 is consistent with an origin of pantellerite from a trachytic parent *via* fractional crystallization of an assemblage dominated by alkali feldspar with subordinate clinopyroxene, fayalite, oxides, aenigmatite, and apatite, as previous investigators have proposed for Pantelleria (Civetta *et al.* 1998, Avanzinelli *et al.*, 2004) and other peralkaline trachyte–rhyolite magma systems (*e.g.*, Paisano volcano, Texas: Parker 1983; Leyva Canyon volcano, Texas: White & Urbanczyk 2001; Ascension Island: Kar *et al.* 1998; Terceira, Azores: Mungall & Martin 1995; Boina volcanic center, Ethiopia: Barberi *et al.* 1975). Fractionation of any feldspar from a peralkaline magma will result in a more strongly peralkaline residual liquid; this is the “orthoclase effect” described by Bailey & Schairer (1964). Alkali feldspar crystallizing from a peralkaline melt will also be more potassic than the melt, depleting the residual liquid with respect to Al_2O_3 and K_2O ; any CaO or BaO in the feldspar further enhances this effect. An increase in peralkalinity will be accompanied by an increase in Nds activity in the melt (Carmichael *et al.* 1974, p. 288), which in turn expands the stability field of aenigmatite to higher oxygen fugacities. Low $f(\text{O}_2)$ has the effect of inhibiting the fractionation of magnetite and consequent Fe depletion in residual liquids; thus, these liquids are progressively enriched in Fe with respect to Al toward increasingly pantelleritic compositions.

Although $\log f(\text{O}_2)$ in this suite decreases from –11.8 to –16.9 with decreasing T and increasing SiO_2 , the suite becomes more oxidized with respect to the FMQ buffer, rising from FMQ – 1.1 to at least FMQ – 0.1. This change in the oxidation state could be due to reaction between the Fe-rich silicate liquid and H_2O in the magma *via* thermal dissociation of H_2O and subsequent degassing of H_2 (Mungall & Martin 1995,

Carmichael 1991), although clearly the magma would need to be vesiculating for this hypothesis to be tenable. Bailey & Macdonald (1987) reasoned that peralkaline magmas in general are very H_2O -poor because: (1) of the virtually anhydrous analyses of almost all peralkaline glasses in the compilation of Macdonald & Bailey (1973) and others, (2) the simultaneously high halogen content of these glasses, considered to be inconsistent with exsolution of a vapor phase, and (3) the agreement of phase-equilibrium experiments conducted under anhydrous conditions with crystallization histories observed in nature (*e.g.*, Bailey & Cooper 1978). However, pre-eruptive concentrations of H_2O in pantelleritic lavas from Pantelleria have been determined from melt-inclusions studies, and shown to range from 1.4 wt% (Lowenstern & Mahood 1991) to 4.3 wt% (Kovalenko *et al.* 1988). Melt-inclusion investigations in other pantelleritic magmas have yielded similar results (*e.g.*, 4.6 to 4.9 wt% H_2O in Fantale pantelleritic magma; Webster *et al.* 1993). Likewise, in a recent experimental phase-equilibrium investigation of peralkaline magmas, Scaillet & Macdonald (2001) have shown that pre-eruptive concentrations of H_2O in peralkaline magmas may be significant (4–6 wt% H_2O) despite the fact that EPMA and Fourier-transform infrared spectroscopy analyses of the same rocks that imply contents <1 wt% H_2O . Therefore, on the basis of the insights from both this experimental study and melt-inclusion studies from previous investigators of Pantelleria and other pantelleritic systems, the observed oxidation with respect to the FMQ buffer with increasing differentiation of the suite discussed in this study, and the favorable comparison of the results of QUILF95 and clinopyroxene–melt geothermobarometry for this suite with the H_2O -saturated synthetic peralkaline system of Carmichael & MacKenzie (1963), we suggest that these pantelleritic magmas may have had high initial pre-eruptive concentrations of H_2O , that must have increased with differentiation.

SUMMARY

Despite the paucity of two-oxide, two-pyroxene, or two-feldspar mineral pairs, it may be possible to accurately constrain temperature and oxygen fugacity in peralkaline rocks with QUIIF equilibria given an equilibrium assemblage of fayalite, ilmenite, and clinopyroxene. If an independent estimate of temperature or oxygen fugacity is available, it may also be possible to apply QUIIF equilibria to an equilibrium assemblage of ilmenite, clinopyroxene, and quartz to recover the other. Similarly, if an assemblage includes both aenigmatite and ilmenite in equilibrium, it may now be possible to determine oxygen fugacity if an estimate of temperature is available from either alkali feldspar – melt or clinopyroxene–melt equilibria.

These techniques were used to determine these intensive parameters from a suite of strongly peralkaline rocks from Pantelleria, Italy. Differentiation of this suite by fractional crystallization of an assemblage dominated by alkali feldspar is marked by an increase in silica from ~64 and 72 wt% SiO₂ and agpaitic index from 1.17 to 1.97, accompanied by a decrease in temperature from 991°C to ~700°C and in log oxygen fugacity from -11.8 to -16.9. Alkali feldspar and clinopyroxene crystallized throughout differentiation; although alkali feldspar compositions remained fairly constant (Or₃₅₋₃₇), the clinopyroxene became gradually more Na- and Fe-rich. Fayalite also became more Fe-rich with differentiation, but ceased to crystallize as temperatures dropped and oxygen fugacities moved closer to the FMQ buffer. Magnetite crystallized only at the highest temperatures and at relatively higher oxygen fugacities, whereas ilmenite crystallized at all but the lowest temperatures in the most evolved sample studied. Ilmenite was in equilibrium with aenigmatite over a large interval of differentiation (~67 to 72 wt% SiO₂, 1.61 < A.I. < 1.75), suggesting a “no-oxide” field for the suite only at extremely low (<703°C) temperatures.

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