

Influence of magma composition and oxygen fugacity on the crystal structure of C2/c clinopyroxenes from a basalt-pantellerite suite

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Abstract. The crystallochemical variations of clinopyroxene in response to changes in f_{O_2} and melt composition have been determined for a basalt-pantellerite suite (Boseti Complex, Main Ethiopian Rift) by crystal structure refinement and microprobe analysis. The pyroxene evolutionary trend has both a “Ca-minimum” and late iron enrichment. During crystallization from basalts to trachytes, clinopyroxene geometry depends mainly on the relationships between T and M2 sites; for example, high SiO_2 activity in the magma causes high Si occupancy in T site, which in turn requires low Ca occupancy in M2 site in order to fulfill the local charge balance requirements. In contrast, clinopyroxene crystallized from acid melts is characterized by high Fe^{2+} (M1) content and therefore by a very large M1 site. Longer $\langle M1-O1 \rangle$ and $M1-O2$ bond lengths require shorter T–O1 and T–O2 bond lengths and high Si occupancy in T site. It is concluded that the “Ca-minimum” in the clinopyroxene structure is regarded as the lowest value at which the charge balance requirements are satisfied in a C2/c clinopyroxene structure.

al constraints, particularly those bearing on the “Ca-pyroxene minimum” typical of tholeiitic suites.

Petrological notes

The clinopyroxenes investigated in this study were from volcanic rocks of the Boseti Complex (Main Ethiopian Rift) whose compositions range from transitional basalts to pantellerites. The evolution from basalts to peralkaline rhyolites occurred through fractional crystallization under quartz – fayalite – magnetite (QFM) f_{O_2} buffer conditions, with the exception of the pantelleritic stage which was characterized by the absence of olivine and Fe–Ti oxides. Liquidus temperatures (Nathan and Van Kirk 1978) range from 1220° C (transitional basalt) to 1065° C (pantellerite) and are consistent with those calculated from mineral compositions (Brotzu et al. 1980; Ganeo 1982).

The selected rock types (cf. Appendix) are typical of basalt – trachyte – pantellerite suites. Whole rock and mineral compositions were presented by Brotzu et al. (1980), and mineral assemblages and some chemical and normative parameters are found in the Appendix.

Mineral separation and analytical methods

The analyzed clinopyroxenes were selected under a petrographic microscope from rock sections about 100 μm thick. Only optically homogeneous crystal fragments, usually from the cores of microphenocrysts, were chosen for X-ray diffraction and microanalysis. X-ray diffraction data were obtained with a computer-controlled SIEMENS AED II four-circle diffractometer with $MoK\alpha$ radiation monochromatized by a flat graphite crystal, using techniques and procedures given by Dal Negro et al. (1982). The crystal fragments used in the X-ray diffraction studies were subsequently mounted on glass slides and polished for electron microprobe analysis with an ETEC-AUTOSCAN-AUTOSPEC system operating at 15 KV. The ORTEC MAGIC IV version of the MAGIC program (Colby 1972) was used to convert X-ray counts into an oxide analysis. Results are considered to be accurate within 2–5% for major elements and about 9% for minor elements.

Chemical composition and crystal chemistry

The chemical compositions and crystal structural parameters of the clinopyroxene samples are presented in Tables 1 and 2, respectively.

Introduction

Clinopyroxene crystal structure is generally a sensitive indicator of the physico-chemical conditions of equilibration specific to the host rock suite (Dal Negro et al. 1989). A notable feature of clinopyroxene crystal chemistry is that intracrystalline variations depend on either the crystallization environment (e.g., pressure, temperature, oxygen fugacity) or the structural constraints that a specific site induces on the geometry of the other sites.

This paper discusses crystal chemical analyses of clinopyroxenes crystallized from magmas ranging in composition from basalt to pantellerite. The main objective here is to describe the relationships in clinopyroxene site geometry with melt composition variability and structur-

Table 1. Chemical composition and site occupancy of Boseti clinopyroxenes on the basis of six oxygens (see text): $R^{3+} = (Al^{VI} + Ti^{4+} + Cr^{3+} + Fe^{3+})$

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
SiO ₂	50.32	51.35	50.61	48.97	50.82	51.55	52.19	51.17	51.00	49.61	48.38	47.60	48.84	48.14	48.00	48.24	49.30	47.83
TiO ₂	1.24	1.36	1.61	1.66	0.67	0.63	0.37	0.41	0.28	0.34	0.37	0.48	0.44	0.64	0.07	0.58	0.19	0.39
Al ₂ O ₃	4.57	1.52	3.49	4.42	1.34	0.78	0.81	0.94	0.37	–	0.14	0.31	0.13	0.25	0.22	0.12	0.50	0.04
FeO _t	7.31	9.74	9.23	8.41	14.50	13.49	12.60	14.43	20.40	23.12	25.06	28.90	22.70	28.90	28.30	28.54	28.18	29.11
MnO	–	0.13	0.32	0.06	0.84	1.16	1.09	1.20	1.74	2.24	1.63	1.77	1.84	1.63	1.61	1.54	1.18	1.53
MgO	14.20	13.75	15.45	13.44	10.71	13.94	13.08	12.48	7.50	4.79	2.72	0.10	4.65	0.52	0.15	0.22	0.02	0.18
CaO	20.77	22.00	19.13	20.74	19.60	17.64	18.99	17.54	18.50	19.42	19.63	19.30	18.72	19.62	19.00	18.68	15.26	16.62
Na ₂ O	0.44	0.15	0.07	0.50	0.49	0.23	0.53	0.59	0.61	0.47	0.54	0.73	0.43	0.31	1.14	1.07	4.27	2.00
Cr ₂ O ₃	0.43	–	0.03	0.03	0.08	–	–	–	–	–	–	–	–	–	–	0.05	–	–
Sum	99.28	100.00	99.94	98.23	99.05	99.42	99.66	98.76	100.40	99.99	98.47	99.19	97.75	100.01	98.49	99.04	98.90	97.70
Si	1.875	1.933	1.881	1.852	1.960	1.962	1.975	1.964	1.993	2.000	1.993	1.985	1.996	1.988	1.989	2.000	1.998	1.998
Al ^{IV}	0.125	0.067	0.119	0.148	0.040	0.038	0.025	0.036	0.007	–	0.007	0.015	0.004	0.012	0.011	–	0.002	0.002
Sum	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Al ^{VI}	0.075	–	0.034	0.049	0.021	–	–	0.007	0.008	–	–	–	0.006	–	–	–	–	–
Fe ²⁺	0.157	0.167	0.129	0.143	0.342	0.190	0.241	0.262	0.546	0.680	0.828	0.966	0.695	0.948	0.909	0.950	0.690	0.837
Fe ³⁺	–	0.031	0.010	0.030	–	0.041	–	0.019	–	0.017	–	0.013	0.001	–	0.061	0.010	0.304	0.139
Mg	0.720	0.764	0.781	0.730	0.616	0.751	0.738	0.700	0.438	0.293	0.160	0.006	0.284	0.032	0.009	0.020	–	0.012
Ti ⁴⁺	0.035	0.038	0.045	0.047	0.019	0.018	0.011	0.012	0.008	0.010	0.012	0.015	0.014	0.020	0.021	0.018	0.006	0.012
Cr	0.013	–	0.001	0.001	0.002	–	–	–	–	–	–	–	–	–	–	0.002	–	–
Sum	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Ca	0.829	8.864	0.762	0.841	0.810	0.720	0.768	0.721	0.775	0.810	0.840	0.849	0.821	0.868	0.843	0.850	0.646	0.744
Na	0.032	0.011	0.005	0.037	0.037	0.017	0.039	0.044	0.046	0.035	0.038	0.042	0.034	0.025	0.037	0.048	0.300	0.162
Fe ²⁺	0.071	0.107	0.148	0.092	0.126	0.187	0.158	0.182	0.121	0.079	0.064	0.047	0.081	0.050	0.064	0.048	0.013	0.040
Mg	0.068	0.014	0.075	0.028	–	0.039	–	0.014	–	–	–	–	–	–	–	–	–	–
Mn ²⁺	–	0.004	0.010	0.002	0.027	0.037	0.035	0.039	0.058	0.076	0.058	0.062	0.064	0.057	0.056	0.054	0.041	0.054
Sum	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
R ³⁺	0.123	0.069	0.090	0.127	0.042	0.059	0.011	0.038	0.016	0.027	0.012	0.028	0.021	0.020	0.082	0.030	0.310	0.151

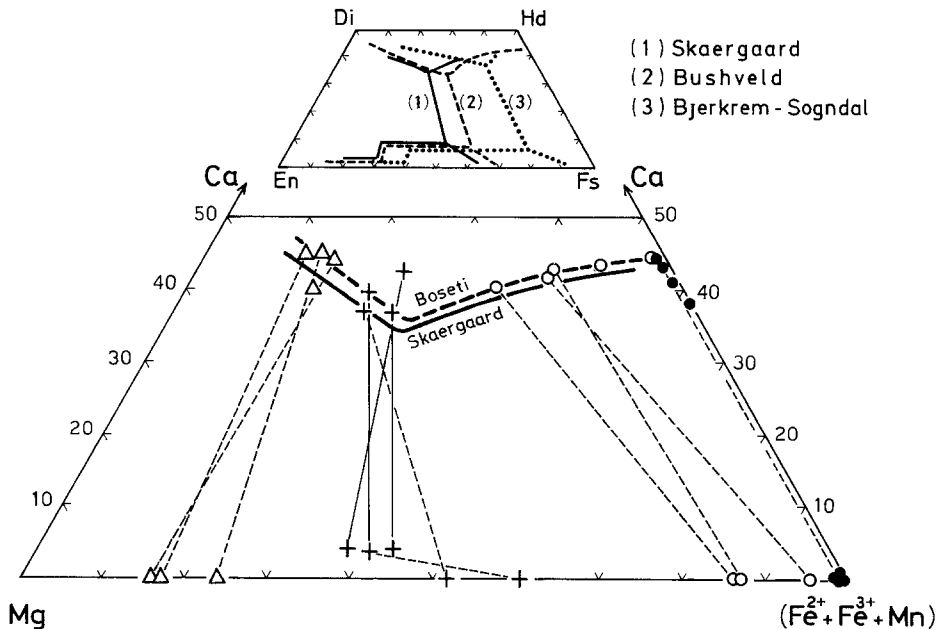
**Fig. 1.** Ca – Mg – (Fe²⁺ + Fe³⁺ + Mn) plot of the Boseti clinopyroxenes (Cpx) and coexisting orthopyroxene and olivine. Clinopyroxene evolutionary trends in subalkaline basic intrusions (Campbell and Nolan 1974) are shown for comparison. Triangles = basaltic rocks; crosses = intermediate rocks; circles = comendites; solid circles = pantellerites

Table 2. Polyhedral geometry of Boseti clinopyroxenes: ($\sigma^2(T)$: variance of the tetrahedral angles; Robinson et al. (1971); ($\lambda(T)$: mean tetrahedral quadratic elongation parameter; Robinson et al. 1971)

	1	2	3	4	5	6	7	8	9
a (Å)	9.743 (1)	9.754 (1)	9.742 (1)	9.749 (1)	9.765 (1)	9.745 (1)	9.753 (1)	9.752 (1)	9.782 (1)
b (Å)	8.900 (1)	8.924 (1)	8.906 (1)	8.901 (1)	8.948 (1)	8.934 (1)	8.941 (1)	8.944 (1)	8.976 (1)
c (Å)	5.269 (1)	5.262 (1)	5.267 (1)	5.273 (1)	5.259 (1)	5.256 (1)	5.256 (1)	5.254 (1)	5.255 (1)
β (°)	106.21 (1)	106.16 (1)	106.30 (1)	106.21 (1)	106.11 (1)	106.48 (1)	106.32 (1)	106.36 (1)	105.92 (1)
v (Å ³)	438.72	439.93	438.61	439.38	441.47	438.80	439.86	439.71	443.71
N _{obs.}	562	524	577	573	560	541	513	544	565
R _{obs}	2.0	2.4	2.7	1.8	2.4	2.5	2.9	2.9	2.3
<i>M1 site</i>									
M1–O2	2.034 (2)	2.048 (2)	2.041 (2)	2.035 (2)	2.057 (2)	2.049 (2)	2.055 (2)	2.054 (2)	2.068 (2)
M1–O1A2	2.056 (1)	2.063 (2)	2.056 (2)	2.057 (1)	2.077 (2)	2.064 (2)	2.069 (2)	2.069 (2)	2.093 (2)
M1–O1A1	2.129 (1)	2.138 (2)	2.134 (2)	2.131 (1)	2.143 (2)	2.146 (2)	2.143 (2)	2.148 (2)	2.154 (2)
mean	2.073	2.083	2.077	2.074	2.092	2.086	2.089	2.090	2.105
V (M1)	11.78	11.96	11.85	11.80	12.12	12.02	12.07	12.10	12.36
<i>M2 site</i>									
M2–O2	2.313 (2)	2.305 (2)	2.298 (2)	2.318 (1)	2.292 (2)	2.260 (2)	2.278 (2)	2.267 (2)	2.292 (2)
M2–O1	2.343 (1)	2.337 (2)	2.330 (2)	2.346 (1)	2.326 (2)	2.302 (2)	2.313 (2)	2.307 (2)	2.322 (2)
M2–O3C1	2.578 (2)	2.596 (2)	2.591 (2)	2.578 (1)	2.610 (2)	2.627 (2)	2.624 (2)	2.626 (2)	2.629 (2)
M2–O3C2	2.731 (2)	2.745 (2)	2.745 (2)	2.728 (1)	2.759 (2)	2.780 (2)	2.768 (2)	2.775 (2)	2.764 (2)
mean	2.491	2.496	2.491	2.493	2.497	2.492	2.496	2.494	2.502
V (M2)	25.51	25.60	25.43	25.56	25.57	25.32	25.48	25.40	25.70
<i>T site</i>									
T–O2	1.599 (2)	1.592 (2)	1.592 (2)	1.599 (1)	1.591 (2)	1.591 (2)	1.587 (2)	1.592 (2)	1.586 (2)
T–O1	1.617 (1)	1.610 (2)	1.616 (2)	1.617 (1)	1.607 (2)	1.610 (2)	1.607 (2)	1.606 (2)	1.605 (2)
T–O3A1	1.666 (2)	1.661 (2)	1.665 (2)	1.667 (1)	1.663 (2)	1.660 (2)	1.663 (2)	1.661 (2)	1.664 (2)
T–O3A2	1.683 (2)	1.685 (2)	1.680 (2)	1.686 (1)	1.684 (2)	1.675 (2)	1.678 (2)	1.675 (2)	1.677 (2)
T–O _{n,brg.}	1.608	1.601	1.604	1.608	1.599	1.601	1.597	1.599	1.596
T–O _{brg.}	1.675	1.673	1.673	1.677	1.674	1.668	1.671	1.668	1.671
V (T)	2.250	2.233	2.239	2.255	2.230	2.222	2.221	2.221	2.219
$\sigma^2(T)$	24.28	24.04	23.91	24.00	24.40	22.42	23.01	22.44	21.97
$\lambda(T)$	1.0057	1.0057	1.0057	1.0057	1.0058	1.0053	1.0054	1.0053	1.0052

In the conventional Ca–Mg–Fe diagram (Fig. 1), the Boseti clinopyroxene shows a trend which parallels that of the Skaergaard suite. In general, most Boseti rock types are characterized by clinopyroxene and olivine (Fa_{16–96}), except for trachytes 5, 7, and 8, in which clinopyroxene is associated with orthopyroxene and aenigmatite-bearing pantellerites (17, 18) where olivine and magnetite are absent. The clinopyroxene of these rock types has high Fe³⁺ content (0.139–0.304 atoms formula unit) and Na (0.162–0.300 a.f.u.). The Boseti clinopyroxene trend (Fig. 1) has a Ca-minimum, like those shown by clinopyroxene suites of several tholeiitic intrusions (e.g., inset of Fig. 1). The latter intrusions show clinopyroxene trends with Ca-minima with quite different Mg/Fe ratios (0.5–1.6), but similar Ca content (0.65–0.75 a.f.u.).

M1 polyhedron

The geometry of the M1 site of the Boseti clinopyroxene appears to be particularly influenced by Fe²⁺ (M1), which ranges from 0.13 to 0.97 a.f.u. A minor role is played by R³⁺ cations (Fe³⁺, Cr³⁺, Al³⁺, Ti⁴⁺) because of their low concentration (average 0.07 a.f.u.).

As documented by Dal Negro et al. (1982), the shortening of the M1–O2 bond length is well correlated with increasing R³⁺ content, implying positive correlations between Fe²⁺ and Mg content and longer M1–O1, A1 and M1–O1, A2 bond distances. The best linear correlation ($r=0.998$) is found between Fe²⁺ and M1–O1, A2 (Fig. 2), while that of M1–O1, A1 shows significant deviations from linearity (inset in Fig. 2). These deviations are observed in the clinopyroxenes of basalts 1, 3, and 4 and pantellerites 15, 17 and 18 all of which are characterized by high R³⁺ content (0.08–0.31 a.f.u.). The substitution of R³⁺ on M1 causes an important volume reduction, for similar Fe²⁺ (M1) content (Fig. 3).

The linear relationships between Fe²⁺ (M1) content and <M1–O> bond distances, particularly for clinopyroxene with R³⁺ lower than 0.06 a.f.u., permit the calculation of <M1–O> bond lengths for M1 site fully occupied by Fe²⁺. Such calculations give the following values (Å):

M1–O2=2.080 ($r=0.982$), M1–O1, A2=2.131 ($r=0.998$) and M1–O1, A1=2.166 ($r=0.952$), giving a mean <M1–O> = 2.126. The <M1–O> mean value of 2.126 Å for clinopyroxene corresponds exactly to that (2.126 Å) reported by Ungaretti (1981) for metamorphic

Table 2 (continued)

	10	11	12	13	14	15	16	17	18
a (Å)	9.796 (1)	9.814 (1)	9.827 (1)	9.800 (1)	9.828 (1)	9.819 (1)	9.822 (1)	9.778 (1)	9.800 (1)
b (Å)	8.989 (1)	9.002 (1)	9.015 (1)	8.988 (1)	9.012 (1)	9.004 (1)	9.008 (1)	8.955 (1)	8.981 (1)
c (Å)	5.256 (1)	5.256 (1)	5.256 (1)	5.256 (1)	5.256 (1)	5.258 (1)	5.257 (1)	5.267 (1)	5.264 (1)
β (°)	105.75 (1)	105.44 (1)	105.30 (1)	105.67 (1)	105.30 (1)	105.40 (1)	105.31 (1)	105.83 (1)	105.67 (1)
V (Å ³)	445.45	447.59	449.13	445.75	449.02	448.17	448.61	443.70	446.09
N _{obs.}	521	528	532	539	542	540	523	537	537
R _{obs.}	2.1	1.7	2.4	2.4	2.0	3.7	1.6	1.7	3.0
<i>M1 site</i>									
M1–O2	2.071 (2)	2.076 (2)	2.077 (2)	2.071 (2)	2.079 (2)	2.070 (3)	2.076 (1)	2.042 (1)	2.057 (3)
M1–O1A2	2.103 (2)	2.117 (2)	2.126 (2)	2.105 (2)	2.125 (2)	2.123 (3)	2.126 (1)	2.101 (1)	2.118 (2)
M1–O1A1	2.157 (2)	2.161 (2)	2.162 (2)	2.153 (2)	2.165 (2)	2.159 (3)	2.161 (1)	2.144 (1)	2.155 (2)
mean	2.110	2.118	2.122	2.110	2.123	2.117	2.121	2.096	2.110
V (M1)	12.45	12.59	12.66	12.44	12.68	12.58	12.64	12.18	12.44
<i>M2 site</i>									
M2–O2	2.295 (2)	2.311 (2)	2.319 (2)	2.303 (2)	2.318 (2)	2.324 (3)	2.327 (1)	2.348 (1)	2.329 (3)
M2–O1	2.326 (2)	2.336 (2)	2.342 (2)	2.335 (2)	2.340 (2)	2.345 (3)	2.348 (1)	2.364 (2)	2.350 (3)
M2–O3C1	2.629 (2)	2.629 (2)	2.635 (2)	2.627 (2)	2.632 (2)	2.623 (2)	2.624 (1)	2.567 (2)	2.604 (3)
M2–O3C2	2.764 (2)	2.750 (2)	2.752 (2)	2.755 (2)	2.752 (2)	2.757 (3)	2.749 (1)	2.770 (2)	2.768 (2)
mean	2.504	2.507	2.512	2.505	2.511	2.512	2.512	2.512	2.513
V (M2)	25.77	25.90	26.07	25.83	26.04	26.09	26.10	26.15	26.13
<i>T site</i>									
T–O2	1.590 (2)	1.586 (2)	1.587 (2)	1.589 (2)	1.588 (2)	1.588 (3)	1.588 (2)	1.589 (2)	1.589 (3)
T–O1	1.605 (2)	1.604 (2)	1.605 (2)	1.605 (2)	1.605 (2)	1.605 (3)	1.603 (2)	1.609 (1)	1.602 (2)
T–O3A1	1.660 (2)	1.664 (2)	1.661 (2)	1.665 (2)	1.660 (2)	1.659 (3)	1.664 (2)	1.654 (1)	1.656 (2)
T–O3A2	1.680 (2)	1.681 (2)	1.682 (2)	1.678 (2)	1.683 (2)	1.683 (3)	1.678 (2)	1.677 (1)	1.680 (2)
T–O _{n.brg.}	1.598	1.595	1.596	1.597	1.597	1.597	1.596	1.599	1.596
T–O _{brg.}	1.670	1.673	1.672	1.672	1.672	1.671	1.671	1.666	1.668
V (T)	2.222	2.222	2.223	2.223	2.224	2.222	2.221	2.217	2.215
σ^2 (T)	22.14	22.72	22.20	23.12	21.84	21.71	21.18	20.02	20.52
λ (T)	1.0053	1.0054	1.0053	1.0055	1.0052	1.0052	1.0051	1.0048	1.0049

amphiboles with M1 and M3 sites fully occupied by Fe²⁺. For natural clinopyroxene, the <M1–O> mean bond distance of 2.126 Å is close to that (2.130 Å) obtained by Cameron et al. (1973) for a synthetic hedenbergite.

M2 polyhedron

M2 is the most irregular site since it coordinates eight oxygens at very variable bond lengths. The shortest bond distances (M2–O2 = 2.26–2.35 Å and M2–O1 = 2.30–2.37 Å) of the Boseti clinopyroxene correlate linearly with (Ca + Na) increase (Fig. 4A). The average decrease of M2–O2 and M2–O1 bond distances with the entry of Fe²⁺, Mg and Mn substituting for (Ca + Na) is 3.4%. In contrast, the longest bond lengths (M2–O3, C1 = 2.57–2.63 Å and M2–O3, C2 = 2.73–2.78 Å) generally correlate negatively with (Ca + Na) increase; the best linear correlation is observed for the M2–O3, C2 bond distance.

The clinopyroxene of the aenigmatite-bearing pantellerites (17, 18) is distinct from that of the other acid rock-types due to its high Na content which causes a significant shortening of M2–O3, C1 and concurrent lengthening of M2–O3, C2 distances in order to provide the charge balance of oxygen O3. In general, the longest

<M2–O3> bond distances of clinopyroxenes from acid volcanics are longer than those of clinopyroxenes from basalts (Dal Negro et al. 1982; present study), while the contrary tends to occur for the shortest M2–O2 and M2–O1 bond lengths (Fig. 4). These differences in geometrical variations are due to the comparatively high Al^{IV} and low Fe²⁺ (M1) content in clinopyroxenes from basalts with respect to that from acid volcanics. Note that the latter clinopyroxene has the T site virtually filled by Si⁴⁺ (higher than 1.96 a.f.u.), which greatly contributes to the charge balance of the oxygen O3 and allows lengthening of <M2–O3> bond distances (see below).

T polyhedron

Typically, the Boseti clinopyroxenes from acid rock types show a near-full occupancy of T site by Si⁴⁺. As documented by Carbonin et al. (1984), high Si⁴⁺ content in clinopyroxene from acid volcanics is essentially related to high Fe²⁺ content in the M1 site rather than to the alkaline or subalkaline nature of the magmas (e.g., phonolite or rhyolite). The increase of Fe²⁺ in the M1 site causes lengthening of M1–O bond distances and this requires shortening of T–O1 and T–O2 bond lengths and Si enrichment. The trachytic-rhyolitic clinopyroxene from Boseti, which is characterized by high

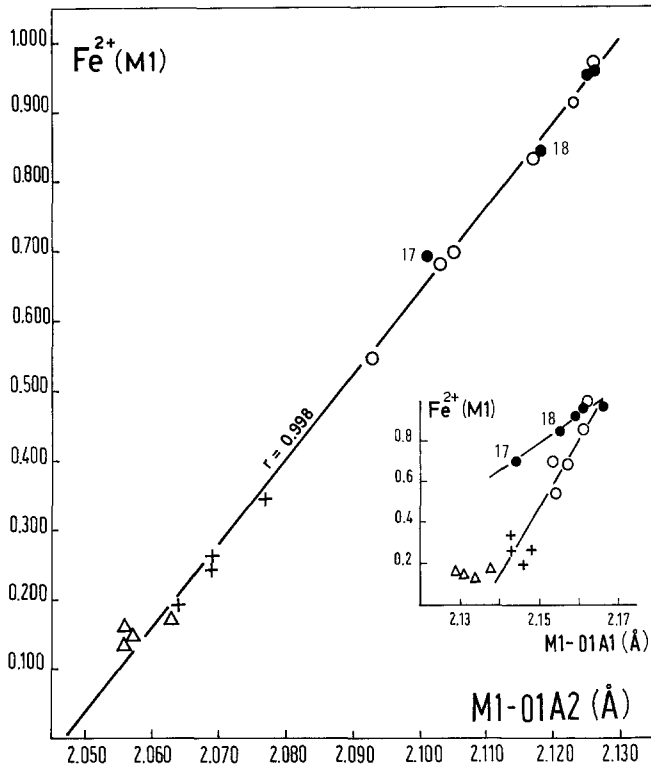


Fig. 2. Fe^{2+} (M1) (a.f.u.) vs M1-O1A2 bond length plot. The positive correlation in the Boseti clinopyroxenes has a linear coefficient of 0.998, whereas the plot of Fe^{2+} (M1) vs M1-O1A1 bond length (*inset*) shows a deviation from linearity in pantellerite clinopyroxenes. Symbols as in Fig. 1

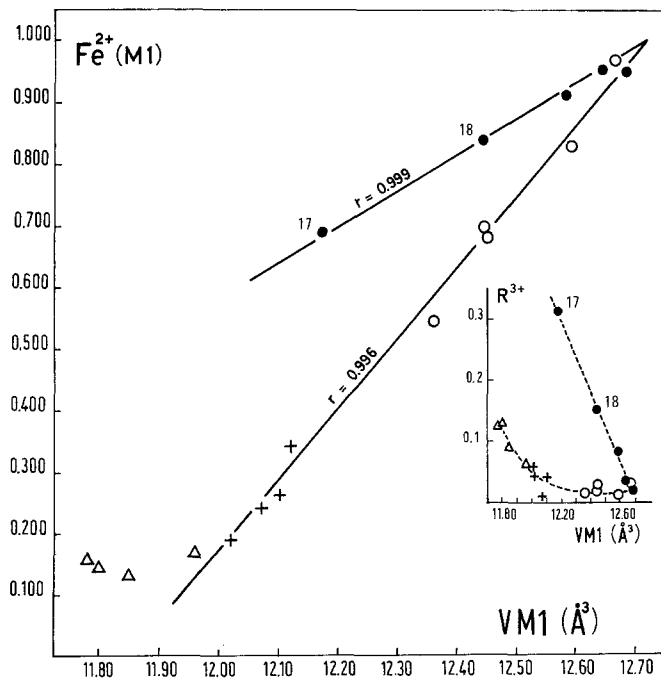


Fig. 3. Relationships between V M1 and Fe^{2+} (M1) content (atoms per formula unit) in Boseti clinopyroxenes. Pantellerite clinopyroxenes show relevant volume reduction relative to others with same Fe^{2+} (M1) because of significant R^{3+} (M1) (*see inset*). Symbols as in Fig. 1

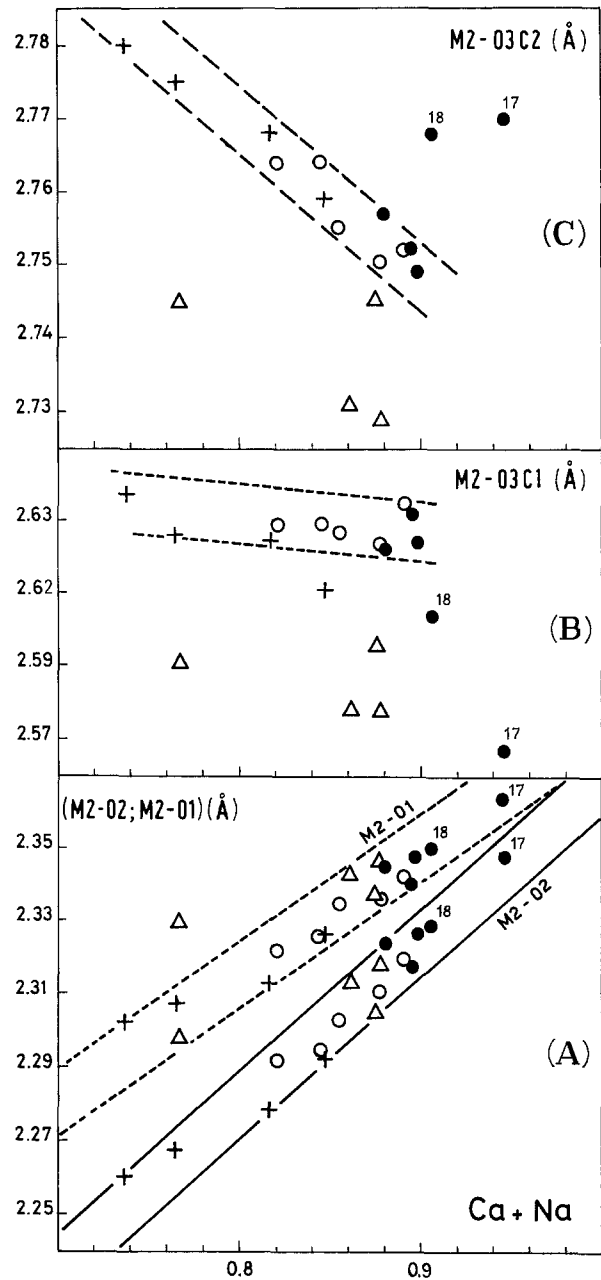


Fig. 4A-C. Plot of Ca+Na (a.f.u.) vs $\langle \text{M2-O} \rangle$ bond lengths in Boseti clinopyroxenes: positive correlations for M2-O2 and M2-O1 (A), negative for M2-O3C1 and M2-O3C2 bond lengths (B) and (C). Note shortening and lengthening of M2-O3C1 and M2-O3C2 respectively, in pantellerite clinopyroxenes 17, 18 caused by high Na content. Symbols as in Fig. 1

Fe^{2+} in the M1 site (ca. 0.20–0.95 a.f.u., Table 1) and large VM1 ($> 12.0 \text{ \AA}^3$), conforms to this picture.

A striking feature of the Boseti clinopyroxene with Si contents higher than 1.960 a.f.u., is the large variation of λ (T) and σ^2 (T) distortion parameters (Robinson et al. 1971). Note that in Fig. 5 the smallest degrees of distortion with very short $\langle \text{T-O} \rangle_{\text{brg}}$ bond lengths (1.665 and 1.668 Å, respectively) occur for clinopyroxene with the highest Na content (n. 17, 18) which gives a lower charge contribution to oxygen O3 than that of a corresponding amount of Ca.

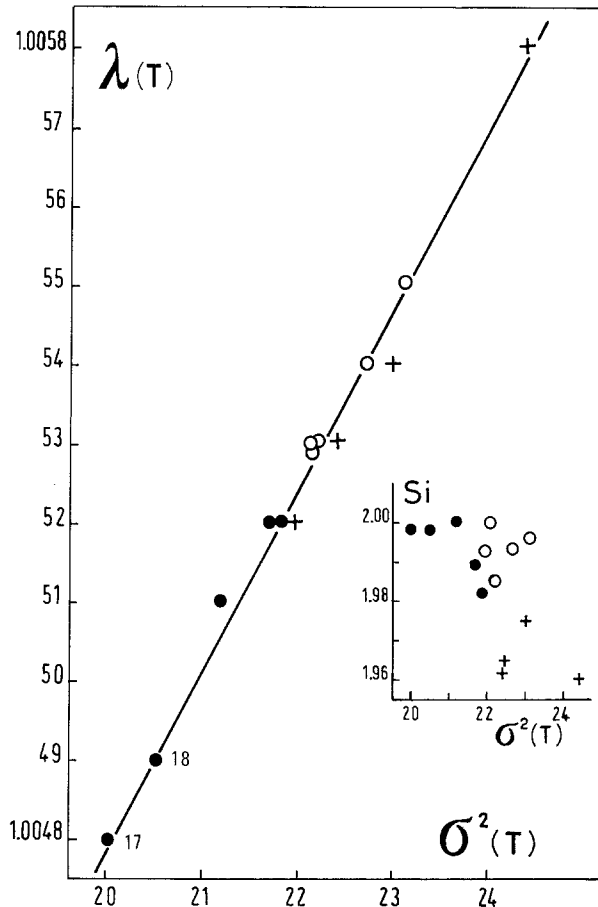


Fig. 5. Plot of σ^2 (T) vs λ (T) (Robinson et al. 1971) in Boseti clinopyroxenes with Si > 1.96 a.f.u. Smallest distortion parameters refer to pantellerite clinopyroxenes 17, 18 with very short $\langle T-O \rangle_{\text{brg}}$ bond lengths and high Na content

Discussion

The compositional variations of the Boseti clinopyroxenes are shown in Fig. 6 in which cation abundances (a.f.u.) are plotted against the Mg/Mg + Fe²⁺ ratio (mg) of the clinopyroxene. In general, the progressive Cpx-mg decrease is associated with clear trends in the different cations concentrations, indicating continuous crystal-chemical response of the clinopyroxene to compositional variations in the source melt. This is illustrated, for example, by the regular Mg (M1) decrease, and Fe²⁺ (M1) and Mn increases for clinopyroxene crystallized from basalt to peralkaline acid magmas. Thus, Fe²⁺ (M1) can be taken as a monitor of the evolutionary degree from basalt to pantellerite, for the studied suite. It is important to note that the sharp decrease in Fe²⁺ (M1) and the concurrent sharp increase in Fe³⁺ and Na in the aenigmatite-bearing pantellerites reflect changed f_{O_2} conditions. In the latter rock-types, clinopyroxene crystallized under unbuffered conditions (the “no-oxide” field of Carmichael et al. 1974) in contrast to the clinopyroxene which crystallized from the other peralkaline rocks that are characterized by olivine and magnetite (i.e., QFM buffer).

The transition from basalt to trachyte Cpx is characterized by a Ca decrease (0.86 to 0.72 a.f.u.) associated

with concurrent Mg (M2) exhaustion, while Fe²⁺ (M1), Fe²⁺ (M2) and Mn (M2) increase. Ca decrease is probably related to high activity of low-Ca pyroxene component in Cpx, and the sharp Si increase (over 1.955 a.f.u.) reflects the higher SiO₂ activity in the trachytic melt. High Si content causes a reduction in $\langle T-O \rangle_{\text{non-brg}}$ and a concurrent Fe²⁺ (M1) increase (i.e., lengthening of M1–O1 and M1–O2 bond distances).

The transition from trachyte to pantellerite Cpx (Fig. 6) is characterized by a distinct Ca increase (up to 0.87 a.f.u.), associated with significant Fe²⁺ (M2) depletion, with simultaneous Fe²⁺ (M1) increase. The Boseti-Cpx suite thus shows a Ca-minimum, similar to those of Cpx suites crystallized from basalt intrusions that have evolved under reducing conditions (cf. Campbell and Nolan 1974; Fig. 1).

In general, the existence of Ca-pyroxene minima indicates that the stability of clinopyroxene is influenced by the relationships between Ca and $\langle M2-O \rangle$ bond length variations, as shown in Fig. 7. The lowest Ca content (0.607 a.f.u.) occurs in a lunar augite 12052 (Takeda 1972a, b), which is characterized by lamellar exsolutions (c. 2.5% vol.) of pigeonite. It appears that, with decreasing Ca content, there is shortening of the shortest distances (M2–O1, M2–O2) and the lengthening of the longest ones (M2–O3, C1, M2–O3, C2). These variations are important, particularly for M2–O2 and M2–O3, C2 distances which, for Ca = 0.5 a.f.u., would become 2.190 and 2.820 Å, respectively. These bond distances appear, respectively, too short and too long for Ca (M2) coordination in a diopside-like structure. It follows that clinopyroxene with Ca content as low as or lower than 0.5 a.f.u. is unstable; this may explain the “pyroxene miscibility gap” in terms of crystal structure (cf. Takeda 1972a, b; Mellini et al. 1988). Note that M2 site of pigeonite is sevenfold coordinated lacking, relative to Ca-rich clinopyroxene, the bond length corresponding to M2–O3, C2 in the diopside-like structure.

In summary, crystal structure parameters indicate that the minimum Ca content in natural clinopyroxenes, which are a single phase in terms of crystal structure, is about 0.6 a.f.u. (cf. Mellini et al. 1988). This may explain why the “Ca-pyroxene minima” of equilibrium crystallization trend (cf. Muir and Matthey 1982) between 0.6–0.7 a.f.u. Ca, although the Cpx Mg/Fe ratio may show large variations (cf. Fig. 1). It should be stressed that clinopyroxene with microprobe compositions equal to, or lower than, 0.5 a.f.u. Ca (the “Ca-pyroxene minimum” of the metastable trends of Muir and Matthey 1982) does not represent a single phase, as documented by Mellini et al. (1988) with TEM analysis, but is rather composed of fine-scale spinodal-lamellar exsolutions of augite and pigeonite.

The abundant crystal structural data now available on low- and high-pressure clinopyroxenes (Dal Negro et al. 1982, 1984, 1985, 1986, 1989a, b; Carbonin et al. 1984, 1989; present study; Cundari et al. 1986; Cundari and Salviulo 1987; Faraone et al. 1988; Manoli and Molin 1988; Mellini et al. 1988; Secco 1988; Princivalle et al. 1989; Secco et al. 1989) indicate that the chemistry

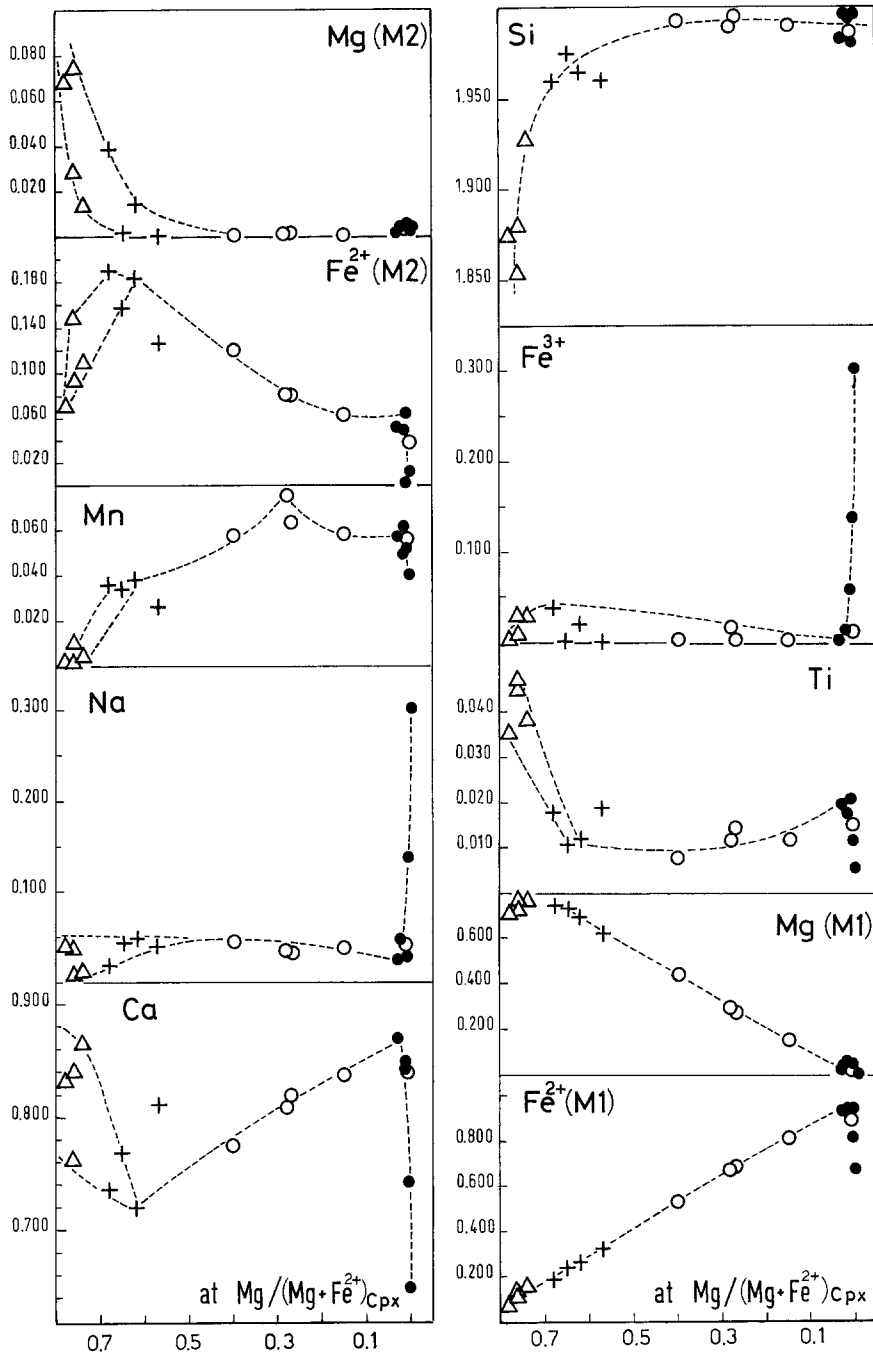


Fig. 6. M2, T, and M1 site occupancy (atoms per formula unit) of Bosseti clinopyroxenes relative to $Mg/(Mg+Fe^{2+})_{Cpx}$ ratio of clinopyroxene. Symbols as in Fig. 1

of clinopyroxene crystallizing from basalt magmas is strongly dependent on the structural relationships between T and M2 sites. This means, for example, that if a basalt melt is characterized by high silica activity, the crystallizing clinopyroxene will be characterized by a T site with high Si content (e.g., 1.90 a.f.u.), which in turn requires relatively low Ca content (e.g. 0.60 a.f.u.) in M2 site in order to obtain the charge balance of the O3 oxygens. In contrast, crystallization of clinopyroxene from intermediate and acid melts is strongly dependent on the geometric variations in the M1 site. For example, large amounts of Fe^{2+} (M1) require large amounts of Si in T site, independently of whether the melt is oversaturated or undersaturated relative to silica. As shown

by Carbonin et al. (1984), this is due to crystal structural constraints, since Fe^{2+} (M1) causes lengthening of M1—O1 and M1—O2 distances and therefore T—O1 and T—O2 bond lengths must become shorter. Note that clinopyroxene from acid volcanics is characterized by high amounts of Si and Ca, which would provide a balance overcharge for the O3 oxygens. Actually, the charge balance is ensured by lengthening of M2—O3, C1 and M2—O3, C2 bond distances relative to those of basalt clinopyroxene (Fig. 7).

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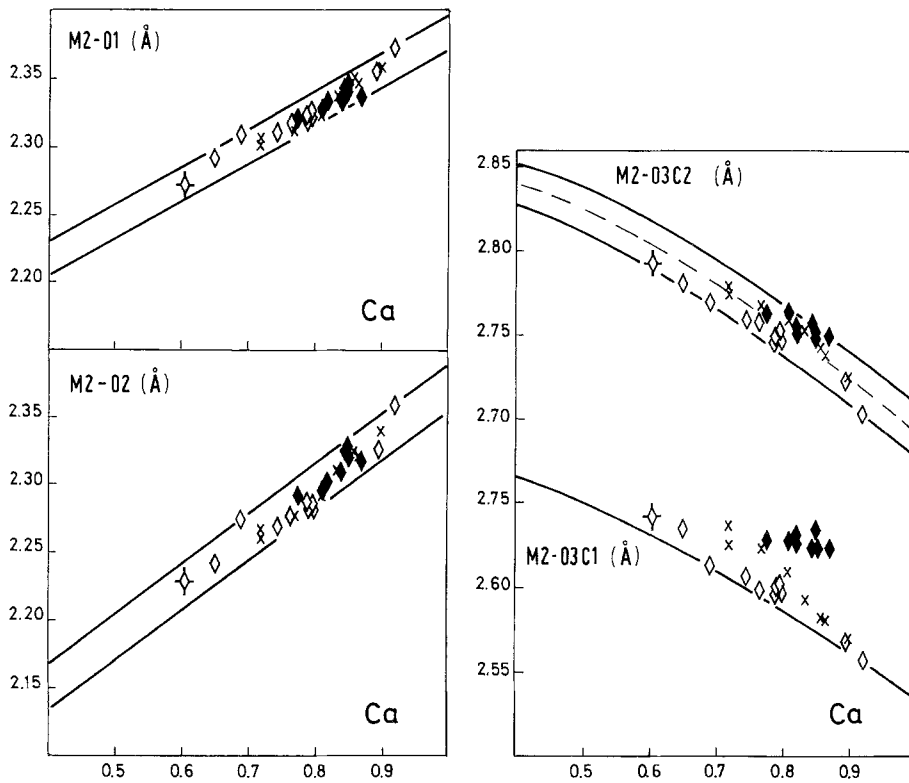


Fig. 7. Plot of Ca content (atoms per formula unit) vs <M2-O> bond lengths in clinopyroxenes with Si > 1.90 and Na < 0.05 a.f.u. relative to basic (diamonds), intermediate (x) and acid (solid diamonds) rock-types. Source data: Takeda (1972a; crossed diamond=lunar sample), Dal Negro et al. (1982), Ganeo (1987) and present study

Appendix

Abbreviations: olivine (ol), plagioclase (pl), Ca-rich pyroxene (cpx), orthopyroxene (opx), opaques (op), alkali feldspar (af), aenigmatite (aeg), magnetite (mt), amphibole (amph). mol. (Na₂O+K₂O)/Al₂O₃=A.I.; at Mg/Mg+Fe²⁺=M(Fe₂O₃/FeO=0.15). Normative (CIPW) minerals: quartz (Q) hyperstene (Hy), olivine (Ol), acmite (Ac), Na-silicate (Ns).

1 – *M335 (Strongly porphyritic basalt)* Phenocrysts: ol (Fo=83; 2.0%vol), pl (An=63-48; 22.7% vol), cpx (Wo=45; 4.0%vol) and mt (2.4%vol). Groundmass: ol, cpx, pl, op. Q=0.11, Hy=8.5, M=0.442.

2 – *M321 (Transitional basalt)* Phenocrysts and microphenocrysts: ol (Fo=84; 3.2%vol), pl (An=77-55; 9.5%vol), cpx (Wo=44; 0.5%vol) and mt (0.2%vol). Groundmass: ol, cpx, pl, op. Ol=13.3, Hy=0.2, M=0.572.

3 – *M329 (Low-Al hawaiite)* Phenocrysts and microphenocrysts: ol (0.7%vol), pl (An=60-52; 0.6%vol), cpx (Wo=40; 0.2%vol) and mt (1.5%vol). Groundmass: ol, cpx, pl, op. Ol=3.7, Hy=4.8, M=0.372.

4 – *M172 (Low-Al mugearite)* Phenocrysts and microphenocrysts: Ol (Fo=76; 0.6%vol), cpx (Wo=45; 0.5%vol), pl (An=65-50; 3.2%vol), mt (0.1%vol). Groundmass: pl, cpx, op. Q=0.01, Hy=9.4, M=0.360.

5 – *M450 (Mafic trachyte)* Phenocrysts and microphenocrysts: pl (An=36-33; 1.8%vol), cpx (Wo=42; 0.3%vol), opx (En=54; 0.2%vol), mt (2.0%vol). Groundmass: pl, cpx, op, af. Q=0.8, Hy=9.5, M=0.216.

6 – *M421 (Trachyte)* Phenocrysts and microphenocrysts: cpx (Wo=37; 1.7%vol); pl (An=37-17; 0.7%vol), af (Or=13-11; 4.5%vol), ol (Fo=48; 0.7%vol), mt (0.7%vol). Groundmass: pl, cpx, ol, af, op. Q=4.5, Hy=4.3, A.I.=0.96.

7 – *M438 (Trachyte)* Phenocrysts and microphenocrysts: cpx (Wo=40; 1.1%vol), pl (An=25-16; 0.1%vol), af (Or=15-11;

7.6%vol), ol (Fa=57; 0.1%vol), opx (En=56; 0.1%vol) and op (1.9%vol). Groundmass: pl, af, op. Q=8.0, Hy=4.0, A.I.=0.98.

8 – *M526 (Trachyte)* Phenocrysts and microphenocrysts: af (Or=23-15; 7.5%vol), cpx (Wo=37; 1.1%vol), opx (En=48; 0.2%vol), pl (An=18; 0.1%vol) and mt (1.3%vol). Groundmass: af, cpx. Q=7.9, Hy=4.1, A.I.=0.99.

9 – *M531 (Comenditic trachyte)* Phenocrysts and microphenocrysts: ol (Fa=81; 0.7%vol), af (Or=23-16; 8.4%vol), cpx (Wo=40; 0.7%vol), mt (0.5%vol). Groundmass: af, cpx. Q=8.8, Ac=1.8, A.I.=1.02.

10 – *M534 (Comendite)* Phenocrysts and microphenocrysts: ol (0.2%vol) af (Or=24-19; 1.9%vol), cpx (Wo=41; 0.4%vol), mt (0.1%vol). Groundmass: af and cpx. Q=15.8, Ac=2.7, Ns=0.9, A.I.=1.10.

11 – *M535 (Comendite)* Phenocrysts and microphenocrysts: ol (Fa=89; 0.4% vol), af (Or=25-20; 0.8%vol), cpx (Wo=43; 0.4%vol), mt (0.2%vol). Groundmass: af, cpx, op. Q=16.5, Ac=4.5, Ns=1.1, A.I.=1.14.

12 – *M154 (Comendite)* Phenocrysts and microphenocrysts: ol (Fa=92; 0.2%vol), af (Or=20-17; 7.2%vol), cpx (Wo=44; 0.8%vol), mt (0.9%vol), amph (0.1%vol). Groundmass: af, cpx, op. Q=21.0, Ac=2.8. A.I.=1.05.

13 – *M353 (Comendite)* Phenocrysts and microphenocrysts: ol (Fa=88; 0.4%vol), af (Or=20-17; 3.1%vol), cpx (Wo=42; 0.9%vol), mt (0.6%vol). Groundmass: af, cpx, op. Q=12.5, Ac=6.6, Ns=0.03, A.I.=1.11.

14 – *M397 (Pantelleritic trachyte)* Phenocrysts and microphenocrysts: ol (Fa=96; 0.6%vol), af (Or=29-24; 8.7%vol), cpx (Wo=45; 1.2%vol), mt (0.6%vol). Groundmass: af, cpx, op. Q=7.0, Ac=10.7, Ns=0.5, A.I.=1.21.

15 – *M168 (Pantellerite)* Phenocrysts and microphenocrysts: af (Or=30-26; 9.4%vol), ol (Fa=93; 0.8%vol), cpx (Wo=43; 0.8%vol), mt (1.9%vol), aeg(trace). Groundmass: af, cpx. Q=13.3, Ac=8.6, Ns=1.3, A.I.=1.24.

16 - M384 (*Pantellerite*) Phenocrysts and microphenocrysts: af (Or=32; 11.2%vol), ol (Fa=96; 0.4%vol), cpx (Wo=44; 0.9%vol), mt (0.4%vol). Groundmass: af, cpx, op. Q=13.7, Ac=16.9, A.I.=1.31.

17 - M395 (*Pantellerite*) Phenocrysts and microphenocrysts: af (Or=36; 0.8%vol), cpx (Wo=38; 0.4%vol), aeg (0.5%vol). Groundmass: af, cpx, aeg. Q=25.1, Ac=7.3, Ns=6.3, A.I.=1.72.

18 - M360 (*Pantellerite*) Phenocrysts and microphenocrysts: af (Or=35; 1.8%vol), cpx (Wo=41; 0.9%vol), aeg (0.2%vol). Groundmass: af. Q=24.1, Ac=5.6, Ns=8.8, A.I.=2.01.

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