

Crystallization trends of pyroxenes from agpaite phonolites (Cantal, France)

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ABSTRACT. Ca- and Na-rich pyroxene compositions of four agpaite phonolites from the Cantal Volcano (France) have been studied. The pyroxenes from each sample show a range of compositions between X^{2+} pyroxenes (with $X = \text{Ca, Mg, Fe}^{2+}$) and aegirine. The main substitution, X^{2+} by $(\text{Fe}^{3+} + \text{Na}^+)$, occurs when $\text{Na} - \text{Mg} = 0.5$, by which time Si is already equal to 2.0. The crystallization of Fe-Na-rich pyroxenes seems to be related to the increasing peralkalinity of the environment, in which the initially high temperature was suddenly reduced. Other factors, such as the structure of the liquid, are also considered.

THIS study is based on a detailed investigation of four phonolite domes, Cournil, Repastils, Roche Pointue, and Autoeroche, in the north-western area of the Cantal Volcano (geological map: Riom-es-Montagnes 1/50 000, Brousse *et al.*, 1972). The domes range from 100 to 500 m in diameter and were intruded between 6.0 ± 0.4 mA (Repastils) and 5.8 ± 0.3 mA (Autoeroche) during the closing stages of a phase of phonolite and trachyte intrusion from 7.4 to 5.5 mA (Baubron *et al.*, 1977). Unlike many of the other phonolite intrusions in this area (Varet, 1967, 1968) which are miaskitic, these four phonolites are all agpaite ($\text{Na} + \text{K} > \text{Al}$), normative acmite 2.96-10.34, and normative sodium metasilicate 1.64-4.91, Table I. In addition, they contain higher contents of Zr, REE, Ti, Sr, Th, U, Cl, F, and H_2O than usual (Gerassimovsky, 1956, 1968; Edgar, 1974; Sorensen, 1974). The agpaite phonolites account for only 12% (by area) of the exposed phonolitic intrusives and are considered to represent the most differentiated phase of an under-saturated alkalic magma series. This series is thought to have evolved by crystal fractionation of an alkali basaltic parent magma in a high-level chamber (Brousse, 1971; Maury, 1976) during an early stage in the growth of the Cantal stratovolcano.

Cantal agpaite phonolites. The phonolites are massive and greenish grey in hand specimen with sparse phenocrysts of pyroxene, feldspathoid, and

Table I. Analyses of agpaite phonolites (Cl and F in ppm):
1 Cournil; 2 Roche Pointue; 3 Repastils; 4 Autoeroche

	1	2	3	4
SiO ₂	59.14	58.31	59.38	60.11
TiO ₂	0.33	0.17	0.14	0.12
Al ₂ O ₃	17.99	19.61	19.81	19.77
Fe ₂ O ₃	3.54	1.59	1.00	1.26
FeO	0.13	0.87	0.84	0.78
MnO	0.07	0.08	0.08	0.10
MgO	0.46	0.52	0.18	0.11
CaO	2.07	0.49	0.87	0.72
Na ₂ O	8.19	10.61	9.42	10.44
K ₂ O	6.25	5.61	5.91	5.71
P ₂ O ₅	0.12	0.02	0.04	0.04
H ₂ O ⁺	0.86	2.53	2.07	1.08
H ₂ O ⁻	0.22	0.27	0.31	0.18
Cl	2390	1560	1800	2300
F	1600	1300	1250	1300
Total	99.37	99.68	100.15	100.43
Q	0.00	0.00	0.00	0.00
or	37.57	40.28	35.71	34.02
ab	32.22	23.01	37.44	37.95
an	0.00	0.00	0.00	0.00
ne	14.91	23.33	18.23	17.83
le	0.00	0.00	0.00	0.00
co	0.00	0.00	0.00	0.00
ac	10.34	4.74	2.96	3.66
wo	2.52	0.00	0.00	0.00
wo	1.35	0.99	1.73	1.39
di	1.17	0.46	0.43	0.24
en	0.00	0.52	1.40	1.26
fs	0.00	0.00	0.00	0.00
en	0.00	0.00	0.00	0.00
fs	0.00	0.00	0.00	0.00
fo	0.00	0.61	0.02	0.02
fa	0.00	0.77	0.07	0.13
mt	0.00	0.00	0.00	0.00
he	0.03	0.00	0.00	0.00
il	0.43	0.33	0.27	0.23
pf	0.18	0.00	0.00	0.00
sm	0.00	4.91	1.64	3.35
ap	0.29	0.05	0.10	0.10
cc	0.00	0.00	0.00	0.00
AlP	1.20	1.40	1.15	1.26
[Na]/[Al-K]	1.12	1.25	1.10	1.18
PAI				
[(Na+K)/Al]				

Analysts: R. Duret, A. Pantaloni (Orsay); F. Cantagrel (Clermont Ferrand) for Cl and F (1979).

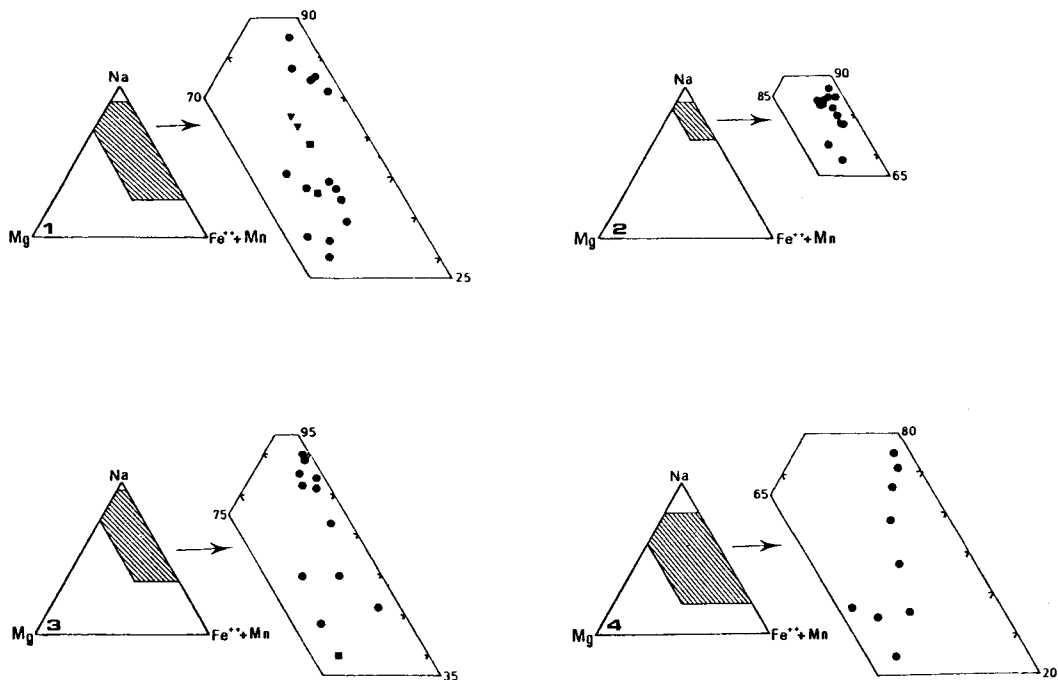


FIG. 1. Bulk analyses of pyroxenes from the agpaitic phonolites in terms of atom % Mg, ($\text{Fe}^{2+} + \text{Mn}$), and Na^+ . Solid circles represent microlites, squares microphenocrysts, and triangles phenocrysts. 1—Cournil, 2—Roche Pointue, 3—Repastils, 4—Auteroche.

alkali feldspar, the latter often showing well-developed zonation. Na-Zr-Ti-RE silicates, common in many agpaitic rocks, are rare (mosandrite and eudialyte). The phonolites have a pronounced trachytic texture formed by the preferred orientation of sanidine-anorthoclase microlites ($\text{Or}_{19}\text{Ab}_{74}\text{An}_7$ to $\text{Or}_{69}\text{Ab}_{30}\text{An}_1$). The feldspars crystallized prior to magnetite, clinopyroxene, nepheline, and sodalite, which is a characteristic of agpaitic rocks.

Description of the pyroxenes. Pyroxene phenocrysts (0.2 mm) and microphenocrysts (50 μm) are euhedral at Cournil and Repastils but anhedral elsewhere. The smallest grains are either elongated tabular crystals (20 μm), or dendritic microlites as in most agpaitic rocks (Azambre and Girod, 1966). Pyroxene commonly occurs in glomeroporphyritic aggregates with the other mafic minerals and accounts for between 6 and 15% of the mode. The rare phenocrysts are strongly zoned with pale-green or neutral cores and darker-green rims. This zoning is usually continuous but occasionally there is a sharp break between core and rim, probably representing a period of interrupted growth before the eruption. The microlites are unzoned and

strongly pleochroic (α apple green, β yellow green, γ yellow brown). There appears to be a complete range of optical characteristics between type-aegirine (biaxial negative) and type-augite (biaxial positive).

Chemistry of the pyroxenes. Fifty analyses were made using a Cameca automatic electron microprobe (CNRS-BRGM) and are presented in Tables II to V. Fe^{3+} contents were calculated by assuming four cations per formula unit (Cawthorn and Collerson, 1974). The range of pyroxene compositions in terms of atom % Mg, ($\text{Fe}^{2+} + \text{Mn}$), and Na^+ is shown in fig. 1 (Scott, 1976). Fig. 2 shows the variation in Ti with increasing aegirine content of the pyroxenes.

Some of the aegirines show enrichment in Ti simultaneously with Na increase and there is sometimes insufficient Al to account for all Ti as $\text{CaTiAl}_2\text{O}_6$ (Kushiro, 1962). Part of the Ti content can be attributed to titanite-aegirines, as is common in alkaline rocks (Pedersen *et al.*, 1975; Larsen, 1976; Ferguson, 1977a) although the place of Ti in $\text{NaTi}(\text{AlSiO}_6)$ or $\text{NaTi}(\text{Fe}^{3+}\text{SiO}_6)$ (Flower, 1974), as a neptunite component, $\text{Na}(\text{Fe}^{2+}, \text{Mg}_{0.5})\text{Ti}_{0.5}(\text{Si}_2\text{O}_6)$ (Ferguson, 1977a) or as octahedral Ti^{3+}

PYROXENES FROM AGPAITIC PHONOLITES

Tables II - V. Microprobe analyses of clinopyroxenes selected to indicate the main compositional variations present in each of the specimens studied.

Table II. Courmil

	A 1	B 1	C 1	D 1	E 1	F 1	G 1	H 1	I 1	J 1	K 1	L 1	M 1
OXIDE WEIGHT PERCENTAGE													
SiO ₂	51,55	47,11	50,80	52,15	48,76	49,74	50,11	48,21	51,05	49,79	49,24	51,32	52,41
TiO ₂	0,55	1,30	0,60	0,79	1,41	0,65	0,78	1,15	2,38	1,39	0,83	1,65	0,76
Al ₂ O ₃	3,77	2,45	3,87	1,29	2,16	0,97	0,96	2,19	0,88	1,60	1,25	0,87	0,77
Fe ₂ O ₃	15,11	12,79	25,35	21,64	16,98	14,97	12,30	10,71	21,54	14,89	11,50	20,19	20,54
Cr ₂ O ₃	0,00	0,00	0,00	0,15	0,00	0,01	0,03	0,00	0,00	0,00	0,00	0,05	0,00
FeO	4,87	7,25	1,30	4,02	4,08	9,21	9,67	10,16	6,27	7,01	9,33	5,33	6,12
MnO	2,94	3,25	1,76	2,44	3,22	3,37	4,35	3,36	2,13	2,93	3,60	1,18	1,56
MgO	2,05	3,97	0,80	0,65	3,42	2,33	2,56	3,85	0,53	3,40	3,48	2,67	2,60
CaO	11,13	16,41	6,09	5,89	14,60	12,60	14,07	15,95	4,54	12,97	15,97	7,02	7,72
Na ₂ O	6,89	4,04	11,09	10,18	5,87	5,80	5,10	3,81	10,35	6,06	4,25	9,18	8,87
K ₂ O	1,45	0,04	0,05	0,22	0,07	0,08	0,10	0,05	0,00	0,01	0,09	0,00	0,00
TOTAL	100,31	98,61	99,11	99,27	100,57	99,54	100,00	99,44	99,67	100,05	99,54	99,41	101,35
ATOMIC PROPORTIONS ON THE BASIS OF 6 OXYGENS													
Si	1,973	1,869	1,943	2,020	1,885	1,962	1,970	1,903	1,985	1,934	1,940	1,983	1,994
Ti	0,016	0,039	0,017	0,023	0,041	0,019	0,023	0,034	0,070	0,041	0,025	0,048	0,022
Al ₃₊	0,170	0,115	0,176	0,056	0,098	0,045	0,044	0,102	0,040	0,073	0,058	0,040	0,034
Fe ₂₊	0,435	0,382	0,730	0,631	0,494	0,439	0,364	0,318	0,620	0,435	0,341	0,587	0,588
Fe ³⁺	0,156	0,241	0,062	0,130	0,132	0,304	0,318	0,335	0,204	0,228	0,307	0,172	0,195
Mn	0,095	0,109	0,057	0,080	0,105	0,113	0,145	0,112	0,070	0,096	0,120	0,039	0,050
Mg	0,117	0,235	0,046	0,037	0,197	0,137	0,150	0,226	0,031	0,197	0,204	0,154	0,147
Ca	0,456	0,698	0,250	0,244	0,605	0,533	0,593	0,675	0,189	0,540	0,674	0,291	0,315
Na	0,511	0,311	0,823	0,764	0,440	0,444	0,389	0,292	0,780	0,456	0,325	0,688	0,654
K	0,071	0,002	0,002	0,011	0,003	0,004	0,002	0,000	0,001	0,001	0,005	0,000	0,000
Na-Mg	0,394	0,076	0,777	0,727	0,243	0,307	0,239	0,066	0,749	0,259	0,121	0,534	0,507
END MEMBER COMPOSITIONS													
En	9,30	14,11	4,40	3,32	12,85	8,97	9,56	13,60	2,73	13,17	12,39	12,37	11,38
Fs	54,48	43,98	71,61	74,91	47,71	56,11	52,67	45,95	80,44	50,76	46,67	64,25	64,32
Wo	36,22	41,91	23,99	21,77	39,44	34,92	37,77	40,45	16,83	36,08	40,93	23,38	24,30
D1	13,29	26,22	4,72	3,70	22,54	13,74	14,98	23,45	2,83	20,14	21,36	14,60	14,08
Hd	28,57	39,07	10,21	20,76	27,14	41,77	46,20	46,35	25,26	33,16	44,70	20,04	23,40
Ac	58,13	34,71	85,07	75,54	50,33	44,49	38,82	30,19	71,90	46,69	33,94	65,35	62,51

Table III. Roche Pointue

	A2	B2	C2	D2	E2	F2	G2	H2
OXIDE WEIGHT PERCENTAGE								
SiO ₂	53,23	53,10	53,26	52,59	52,72	53,17	52,53	52,83
TiO ₂	0,26	2,16	0,01	0,01	2,42	1,56	1,10	2,79
Al ₂ O ₃	1,42	1,09	0,87	0,73	1,06	1,34	2,15	1,62
Fe ₂ O ₃	22,26	22,65	23,32	24,23	23,21	24,26	19,66	16,74
Cr ₂ O ₃	0,09	0,04	0,00	0,00	0,00	0,02	0,00	0,02
FeO	3,67	3,44	3,30	2,39	2,90	2,37	3,74	6,36
MnO	2,46	1,34	0,85	2,71	1,21	1,33	1,90	1,64
MgO	0,63	0,80	0,54	0,61	0,81	0,39	1,73	1,60
CaO	3,43	2,79	2,11	4,51	2,34	1,67	6,68	5,08
Na ₂ O	11,16	12,00	12,50	10,95	12,19	12,58	10,02	10,12
K ₂ O	0,15	0,00	0,00	0,04	0,04	0,03	0,01	0,45
TOTAL	98,67	99,37	99,09	98,77	98,91	98,70	99,52	99,23
ATOMIC PROPORTIONS ON THE BASIS OF 6 OXYGENS								
Si	2,058	2,032	2,041	2,042	2,025	2,043	2,009	2,029
Ti	0,008	0,062	0,067	0,000	0,069	0,045	0,032	0,081
Al ₃₊	0,065	0,049	0,039	0,033	0,048	0,061	0,097	0,073
Fe ₂₊	0,648	0,652	0,672	0,708	0,671	0,701	0,566	0,484
Fe ³⁺	0,119	0,110	0,106	0,077	0,093	0,076	0,120	0,204
Mn	0,081	0,043	0,027	0,089	0,039	0,043	0,061	0,053
Mg	0,036	0,046	0,031	0,035	0,046	0,022	0,099	0,092
Ca	0,142	0,114	0,087	0,188	0,096	0,069	0,274	0,209
Na	0,838	0,890	0,929	0,824	0,908	0,937	0,743	0,754
K	0,007	0,000	0,000	0,002	0,002	0,001	0,001	0,022
Na-Mg	0,802	0,844	0,898	0,789	0,862	0,915	0,644	0,662
END MEMBER COMPOSITIONS								
En	3,53	4,72	3,32	3,20	4,90	2,44	8,82	6,95
Fs	82,62	83,44	87,29	78,70	84,91	90,01	66,74	80,53
Wo	13,86	11,84	9,40	17,10	10,19	7,55	24,44	12,52
D1	3,39	4,19	2,82	3,44	4,27	2,06	9,64	8,30
Hd	18,58	14,07	12,20	12,63	12,19	11,08	17,72	23,35
Ac	78,03	81,74	84,98	80,33	83,53	86,85	72,64	68,34

Table IV. Repastils

	A3	B3	C3	D3
OXIDE WEIGHT PERCENTAGE				
SiO ₂	48,90	52,09	51,95	50,87
TiO ₂	0,63	0,58	0,22	2,41
Al ₂ O ₃	5,22	1,82	1,39	0,99
Fe ₂ O ₃	12,12	29,19	30,17	26,08
Cr ₂ O ₃	0,00	0,11	0,00	0,00
FeO	6,32	2,34	1,23	0,74
MnO	2,90	2,88	1,54	2,34
MgO	3,09	0,48	0,22	0,74
CaO	13,60	3,31	1,68	4,11
Na ₂ O	5,79	12,19	12,76	11,78
K ₂ O	0,00	0,20	0,09	0,05
TOTAL	98,57	100,40	98,79	98,63
ATOMIC PROPORTIONS ON THE BASIS OF 6 OXYGENS				
Si	1,903	1,979	2,003	1,971
Ti	0,018	0,016	0,006	0,070
Al ₃₊	0,239	0,081	0,063	0,045
Fe ₂₊	0,555	0,535	0,535	0,476
Fe ³⁺	0,206	0,074	0,039	0,024
Mn	0,096	0,093	0,050	0,077
Mg	0,179	0,027	0,013	0,043
Ca	0,567	0,135	0,069	0,171
Na	0,437	0,898	0,954	0,885
K	0,000	0,009	0,004	0,002
Na-Mg	0,258	0,871	0,941	0,842
END MEMBER COMPOSITIONS				
En	12,77	2,70	1,31	4,14
Fs	46,81	84,01	91,54	79,23
Wo	40,42	13,29	7,15	16,63
D1	19,54	2,49	1,19	4,15
Hd	32,85	15,30	8,52	9,78
Ac	47,62	82,21	90,29	86,06

Table IV (cont.)

	E3	F3	G3	H3	I3
OXIDE WEIGHT PERCENTAGE					
SiO ₂	50,84	50,73	49,35	52,89	52,92
TiO ₂	0,54	0,60	0,64	0,37	0,81
Al ₂ O ₃	1,00	3,35	1,05	1,10	1,55
Fe ₂ O ₃	19,51	16,67	13,15	29,05	25,19
Cr ₂ O ₃	0,06	0,00	0,04	0,00	0,00
FeO ³	4,31	5,94	8,32	1,40	3,22
MnO	2,82	2,96	3,58	1,49	1,34
MgO	2,86	1,68	3,14	0,28	0,28
CaO	9,74	9,60	14,56	2,23	2,05
Na ₂ O	7,88	7,65	5,03	12,36	12,13
K ₂ O	0,00	0,49	0,02	0,00	0,02
TOTAL	99,49	99,67	98,85	101,17	99,50
ATOMIC PROPORTIONS ON THE BASIS OF 6 OXYGENS					
Si	1,973	1,962	1,954	2,005	2,029
Ti	0,016	0,017	0,019	0,010	0,023
Al ₃₊	0,046	0,153	0,049	0,049	0,070
Fe ₂₊	0,570	0,485	0,392	0,828	0,727
Fe	0,140	0,192	0,276	0,044	0,103
Mn	0,093	0,097	0,120	0,048	0,043
Mg	0,165	0,097	0,183	0,016	0,016
Ca	0,405	0,398	0,618	0,091	0,084
Na	0,593	0,574	0,386	0,908	0,902
K	0,000	0,024	0,001	0,000	0,001
Na-Mg	0,428	0,477	0,201	0,892	0,886
END MEMBER COMPOSITIONS					
En	12,06	7,64	11,64	1,52	1,62
Fs	58,44	61,00	49,51	89,66	89,74
Wo	29,51	31,35	38,84	8,82	8,64
Dl	16,69	10,09	19,16	1,55	1,50
Ed	23,46	30,13	40,91	9,06	13,78
Ac	59,85	59,78	39,92	89,38	84,72

Table V. Auteroche

	A4	B4	C4	D4	E4	F4	G4	H4
OXIDE WEIGHT PERCENTAGE								
SiO ₂	48,81	49,96	45,56	53,11	50,40	50,31	52,25	47,20
TiO ₂	0,81	1,04	1,90	1,67	0,77	0,82	0,95	2,14
Al ₂ O ₃	1,38	1,49	1,49	2,40	1,13	0,82	4,54	5,34
Fe ₂ O ₃	12,06	12,25	9,41	19,16	14,17	20,57	16,96	18,55
Cr ₂ O ₃	0,00	0,02	0,00	0,00	0,00	0,00	0,00	0,00
FeO ³	8,54	6,59	8,46	5,43	8,18	5,06	5,57	2,01
MnO	3,85	2,89	2,23	1,62	2,79	2,52	2,15	0,90
MgO	3,43	5,42	5,00	0,93	2,91	1,48	1,03	1,57
CaO	13,90	15,20	18,84	4,10	12,88	8,84	6,33	11,66
Na ₂ O	4,29	4,73	2,60	10,63	6,05	8,48	9,77	7,86
K ₂ O	0,09	0,03	0,12	0,57	0,07	0,00	0,11	1,16
TOTAL	99,16	99,60	98,66	99,62	99,35	98,90	99,64	99,26
ATOMIC PROPORTIONS ON THE BASIS OF 6 OXYGENS								
Si	1,931	1,935	1,800	2,03	1,974	1,976	1,991	1,852
Ti	0,024	0,030	0,056	0,048	0,023	0,024	0,027	0,063
Al ₃₊	0,064	0,068	0,212	0,108	0,052	0,038	0,204	0,245
Fe ₂₊	0,359	0,357	0,279	0,551	0,418	0,608	0,486	0,544
Fe	0,283	0,213	0,279	0,173	0,268	0,166	0,177	0,066
Mn	0,129	0,095	0,075	0,052	0,093	0,084	0,070	0,030
Mg	0,202	0,313	0,294	0,053	0,170	0,087	0,058	0,092
Ca	0,674	0,631	0,798	0,168	0,540	0,372	0,258	0,481
Na	0,329	0,355	0,199	0,788	0,459	0,646	0,722	0,579
K	0,004	0,001	0,006	0,028	0,003	0,000	0,005	0,058
Na-Mg	0,127	0,042	-0,095	0,735	0,289	0,559	0,664	0,487
END MEMBER COMPOSITIONS								
En	12,27	19,45	17,06	5,30	11,40	6,56	3,22	4,53
Fs	46,80	41,35	36,72	77,88	52,29	65,19	77,14	61,83
Wo	40,93	39,20	46,22	16,82	36,31	28,24	19,78	33,61
Dl	21,44	32,04	34,74	4,97	17,17	8,82	5,69	11,99
Ed	43,65	31,57	41,77	21,18	36,42	25,44	24,03	12,52
Ac	34,90	36,38	23,49	73,85	46,42	65,74	70,27	75,49

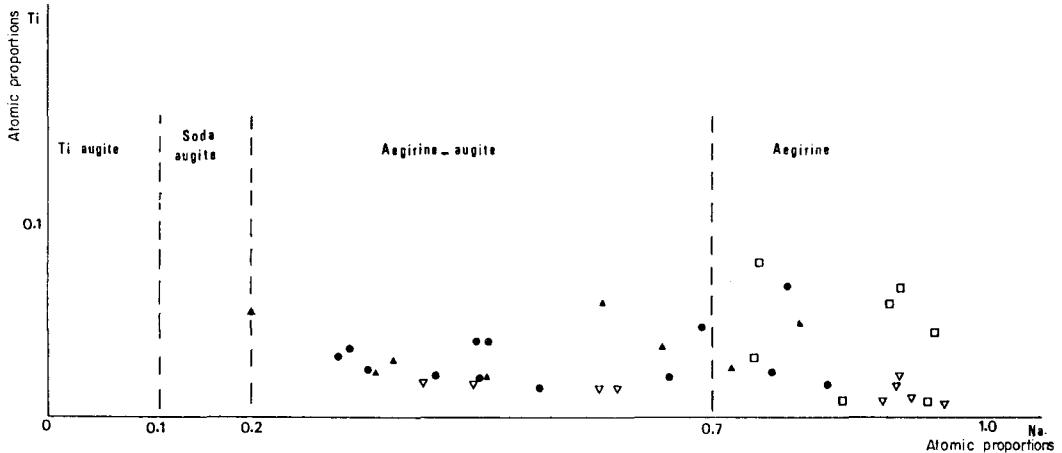


FIG. 2. Plot of Ti/Na (atomic proportions on the basis of 6 oxygens) for the pyroxenes. Symbols: circles, Cournil; squares, Roche Pointue; open triangles, Repastils; solid triangles, Auteroche.

(Scott, 1976) has been discussed (Scott, 1976; Ferguson, 1977b, 1978; Rossi, 1978) and refuted in this last case (Ronsbo *et al.*, 1977).

Fig. 3 shows the variation of certain major elements plotted against an appropriate fractionation index (Na-Mg in atomic proportions; Stephenson, 1972).

Si increases up to a maximum of 2.0 in aegirines

when the fractionation index reaches a value of 0.5. Conversely, Al decreases to values as low as 0.5, although with some erratic digressions. Clearly, the main substitution is Ca(Fe²⁺, Mn, Mg) instead of Na Fe³⁺; but while Ca, Mn, and Mg decrease progressively through the series, the depletion in Fe²⁺ occurs in two stages: rapidly up to Na-Mg = 0.5 and then more slowly. In other

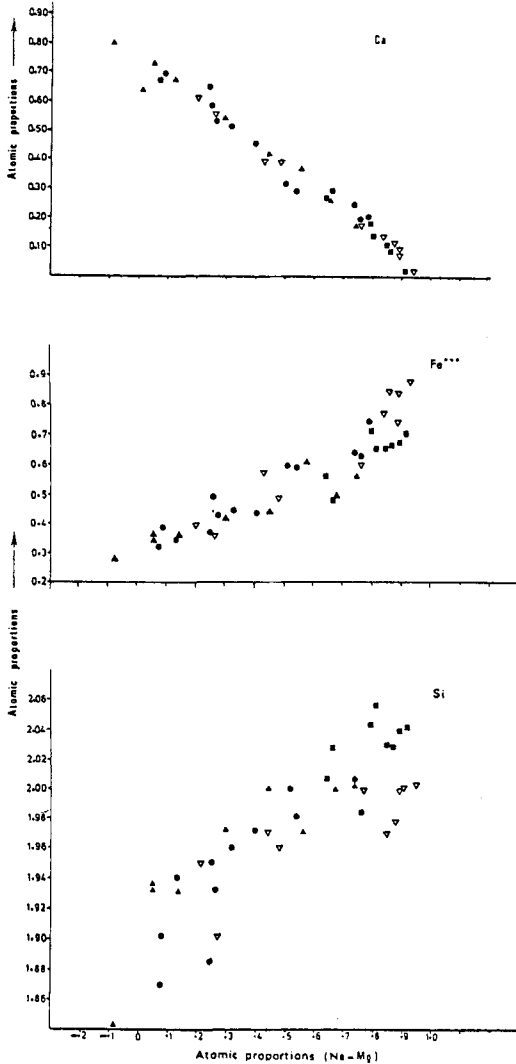


FIG. 3. Variations of certain major elements in the pyroxenes relative to the fractionation index (Na-Mg). Symbols as fig. 2.

words, when aegirines reach formulae containing $[\text{Si}_2\text{O}_6]$ units, the amount of $(\text{Al}, \text{Fe}^{2+})$ is maintained, while $(\text{Ca}, \text{Mg}, \text{Mn})$ continues to decrease as a result of increasing $(\text{Fe}^{3+}, \text{Na})$ and, to some extent, Ti.

In summary the evolution of aegirine goes from $[\text{Si}_2\text{O}_6]\text{Al}_{0.08}\text{Fe}_{0.52}^{3+}(\text{X}^{2+})_{0.78}\text{Na}_{0.64}$ (where $\text{X}^{2+} = \text{Fe}^{2+} + \text{Ca} + \text{Mg} + \text{Mn}$; $\text{Na} - \text{Mg} = 0.52$; $\text{Xac} = \text{Fe}^{3+}/(\text{Al} + \text{Fe}^{3+}) = 0.866$ and $\text{Fe}^{3+}/\Sigma\text{Fe} = 0.703$) to $[\text{Si}_2\text{O}_6]\text{Al}_{0.08}\text{Fe}_{0.83}^{3+}(\text{X}^{2+})_{0.15}\text{Na}_{0.97}$ (where $\text{X}^{2+} = \text{Fe}^{2+} + \text{Ca} + \text{Mg} + \text{Mn}$;

$\text{Na} - \text{Mg} = 0.94$; $\text{Xac} = 0.912$; and $\text{Fe}^{3+}/\Sigma\text{Fe} = 0.965$).

In other words, for a constant amount of Si, Al, and Ti, the bivalent ions $\text{X}^{2+} = (\text{Fe}^{2+} + \text{Ca} + \text{Mg} + \text{Mn})$ are progressively replaced by $(\text{Fe}^{3+} + \text{Na})$ in the proportion $0.64 \text{X}^{2+} = 0.31 \text{Fe}^{3+} + 0.33 \text{Na}^+$. Therefore, although the acmicity index (Xac) is slightly modified (0.87–0.91), the ratio $\text{Fe}^{3+}/\Sigma\text{Fe}$ is greatly increased (0.70–0.97).

A parallel may be drawn between this observation and the work of Mysen and Virgo (1978) who showed that at constant temperature and pressure (1 atm.) this iron ratio for a pyroxenic liquid increases greatly and suddenly as Xac changes from 0.10 to 0.15, with interaction between Fe^{3+} and Fe^{2+} and the silicate framework. Ferrous ion in 6-coordination must be associated with at least one non-bridging oxygen from a tetrahedral unit. In such a model, increasing Xac results in an increase of the activity of oxygen ions in the melt, thus resulting in increasing $\text{Fe}^{3+}/\Sigma\text{Fe}$.

The nature of Na and Fe^{3+} enrichment in clinopyroxenes has been the subject of debate since Aoki (1964) proposed a miscibility gap between Ca- and Na-rich pyroxenes. The data presented here support studies by Ernst (1962, 1968), Yagi (1966), Nolan (1969), Bailey (1969), and Gilbert (1969) who demonstrate that aegirine may be stable over a range of oxygen fugacities, in some as low as the FMQ buffer. Numerous data on natural assemblages have also shown complete compositional variation between Ca- and Na-rich pyroxenes in alkaline rocks (Le Maitre, 1962; Baker, 1969; Sutherland, 1974).

Substitution controlling factors. The increasing solution of Fe^{3+} and Na^+ in the pyroxenes must be controlled by the chemical composition and the temperature of the magma from which they crystallized. The effects of pressure can be discounted here as most of the Na-rich pyroxenes occur in the groundmass and must therefore have crystallized at pressures close to 1 atm.

The structure of the melt may also be important in determining the partitioning of elements between crystals and melt (Kushiro, 1976). For example, Fe^{3+} , like Al, can be considered as both a network former (6-coordination) and as a network modifier (4-coordination) in a silicate melt. Iron, like Ca^{2+} and Mg^{2+} , behaves as a network modifier.

Variations in chemical composition. In studying the groundmass pyroxenes of these rocks it is difficult to distinguish between crystals generated simultaneously in different chemical environments and grains formed consecutively from a progressively evolving melt. In the second case, zoned pyroxenes like the clinopyroxenes occur in peralkaline

syenites of the Gardiner complex (Nielsen, 1979), but this cannot be the general rule since grains in the rocks under consideration are chemically different.

During groundmass crystallization chilling is rapid, which results in the formation of numerous small nuclei which never grow very large. It is suggested that the range of groundmass pyroxene compositions observed in these rocks represents a group of crystals growing in a short period of time, although not simultaneously, from a melt which is changing rapidly in composition. This continuous chemical variation would seem to argue against disequilibrium effects. In this case, the range of chemical variation within a single rock is almost as wide as that in magmatic series from several other alkaline provinces (fig. 4).

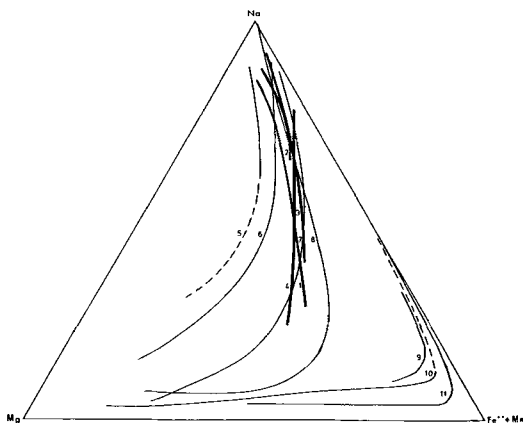


FIG. 4. A comparison of published alkali pyroxene trends (atomic %). *Undersaturated*: (1, 2, 3, 4): this work; (5) Lovozero, USSR (Bussen and Sakharov, 1972); (6) Itapirapua, Brazil (Gomes *et al.*, 1970); (7) Morotu, Sakhalin (Yagi, 1966); (8) South Qôroq centre, South Greenland (Stephenson, 1972). *Oversaturated*: (9) Pantellerite trend (Nicholls and Carmichael, 1969); (10) Nandewar volcano, Australia (Abbott, 1969); (11) Ilimaussaq intrusion (Larsen, 1976).

Indeed, from one rock to the next, the alkaline series of Lovozero, USSR (Bussen and Sakharov, 1972), Itapirapua, Brazil (Gomes *et al.*, 1970), Morotu, Japan (Yagi, 1966), and South Qôroq Centre, Greenland (Stephenson, 1972), increasingly sodic pyroxenes appear, following trends that are not much different (Lovozero, Itapirapua) or even identical (Morotu, South Qôroq Centre) to those of the agpatic phonolites of Cantal.

The change of pyroxene chemistry with progressive evolution of the magma can be related to the degree of silica undersaturation. In a saturated or

oversaturated environment the pyroxenes become progressively enriched in the hedenbergite end member prior to any (NaFe^{3+}) enrichment (Carmichael, 1962; Larsen, 1976; Abbott, 1969). However, in an undersaturated environment, enrichment in (NaFe^{3+}) occurs at an early stage relative to (CaMg-CaFe^{2+}) substitution (Yagi, 1953, 1958; Gomes *et al.*, 1970; Bussen and Sakharov, 1972; Ferguson, 1978) as exemplified by the data presented in fig. 4, and in the present case of the Cantal rocks.

Since the pyroxene trend of agpatic phonolites ends more or less within the acmite field, an attempt was made to correlate this specifically with the degree of agpaticity reached by the lava. In fig. 5 it can be seen that, as a general rule, the trends begin and end with more-evolved pyroxenes as the agpaticity of the rock is more pronounced.

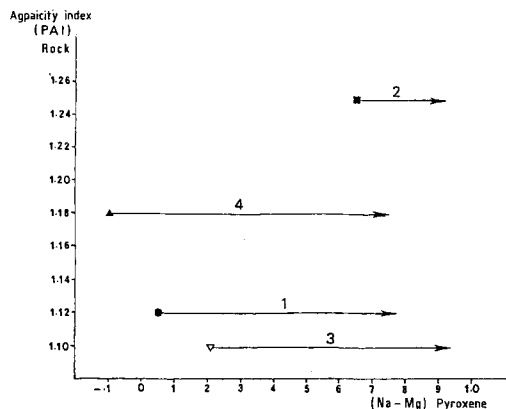


FIG. 5. Plot of PAI $[(\text{Na} + \text{K})/\text{Al}]$ of the rock versus $(\text{Na} - \text{Mg})$ of the pyroxenes in the Cantal agpatic phonolites. Symbols as fig. 2.

The case of Roche Pointue, with its less-evolved starting-point reflecting the composition of phenocrysts, may represent a greater depth of origin in the underlying magma reservoir, similar to the successive intrusions of nepheline syenites in Qôroq, Greenland (Stephenson, 1972), which show a regression in starting-points due to tapping from deeper levels.

Changes in thermodynamic conditions. The restricted mineralogy of agpatic phonolites (i.e. lacking plagioclase, the magnetite-ilmenite pair, and any ferromagnesian minerals other than pyroxenes) makes estimation of temperature and oxygen fugacity at the time of crystallization difficult. Particularly, the absence of amphiboles is presumably a result of the loss of most of the H_2O vapour during eruption and crystallization (Noble *et al.*, 1967; Noble, 1970; Larsen and Steenfelt, 1974; Ferguson,

1978). However, nepheline phenocrysts indicate near-liquidus temperatures of 1050–1100 °C (Hamilton, 1961; Roux, 1979), close to the approximating nepheline–feldspar geothermometer (Powell and Powell, 1977).

The oxygen fugacity must have been sufficiently high for crystallization of aegirine, which is more stable at higher oxygen fugacities (Mn_2O_3 – Mn_3O_4 buffer or Mt–Hm buffer), but with a range descending as low as the FMQ buffer (Gilbert, 1969; Bailey, 1969).

The oxidation state of the magma (but not necessarily the activity of oxygen) may have varied widely during groundmass crystallization, becoming progressively more oxidizing with falling temperature (Powell, 1978). This could account for the wide variation in acmite content of the groundmass pyroxenes.

In order to explain the evolution of the Cantal agpaitic phonolites, the crystallization of which ended under 1 atm. pressure, only a hypothesis which implies no major changes in the physical conditions, temperature, and oxygen fugacity, can be retained. When the composition of the magmatic melt evolves, even at constant temperature, it was shown by Mysen and Virgo (1978) that, at 1 atm., the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio shows an abrupt change from 0 to 0.65 when the acmicity index (X_{ac}) increases slightly (0.10 to 0.15). They suggested that such a modification results from changes in the melt structure with interaction between Fe^{3+} and Fe^{2+} and the silicate framework. A ferrous ion in 6-coordination must be associated with at least one non-bridging oxygen from a tetrahedral unit. In such a model increasing X_{ac} results in an increase of the activity of oxygen ions in the melt thus resulting in increasing $\text{Fe}^{3+}/\Sigma\text{Fe}$.

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