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Compositions and miscibility gap in Na-Ca clinopyroxenes through high-pressure metamorphism

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ABSTRACT. — The Ligurian Alps expose several Alpine and pre-Variscan tectono-metamorphic units which record pressures in the range 0.9-1.7 GPa and temperatures of 300°- 750°C. Sodic and sodic-calcic clinopyroxenes were analysed in rocks of basic (basalt, gabbro and Fe-Ti oxide-gabbro), intermediate (Fe-Ti oxide-diorite, diorite) and acidic (rhyolite, rhyodacite) compositions and in metaarenite to quartzschist metasediments. The control of metamorphic parameters, protolith and site heritage on clinopyroxene composition was investigated evidencing i) strong dependence of clinopyroxene amphibole equilibria on Mg# and low Mg/Ca in the rock for different metamorphic conditions; ii) dehvdration reactions occurring during the development of eclogitic assemblages; iii) a largely incomplete re-equilibration under lower The metamorphic conditions. resulting compositional zoning depends on the site heritage, protolith textural features, deformation intensity and element diffusivity.

At the lowest temperatures, jadeites and aegirines or aegirine-augites commonly coexist. The presence of the compositional gap also between grains tightly in contact suggests the existence of a solvus. The miscibility gap extending from the Jd-Aeg to the Jd-Quad join below 400°C, is narrowed for increasing temperatures. Since about 400°C, omphacite compositions become stable, and the miscibility gap still exists between omphacite and omphacite-rich jadeite, and reduces for increasing aegirine contents.

For temperatures exceeding 450°C, compositional gaps between jadeite and omphacite are recorded. A compositional gap between omphacite and calcic pyroxene is likely, and tends to reduce for T > 700°C.

RIASSUNTO. — Nelle Alpi Liguri sono esposte numerose unità tettono-metamorfiche Alpine e pre-Varisiche i cui parametri di riequilibratura metamorfica variano tra 0,9 e 1,7 GPa e 300°-750°C. Pirosseni sodici e sodico - calcici sono stati analizzati in rocce di composizione basica (basalto, gabbro e gabbro ad ossidi di Fe-Ti), intermedia (diorite ad ossidi di Fe-Ti, diorite) e acida (riolite, riodacite) ed in metasedimenti (meta-areniti e quarzoscisti). È stato investigato il controllo di parametri metamorfici, chimismo del protolite ed eredità del sito strutturale sulla composizione del clinopirosseno, verificando i) la dipendenza degli equilibri clinopirosseno - anfibolo da Mg# e da un rapporto Mg/Ca relativamente basso ii) lo sviluppo di reazioni di deidratazione nello sviluppo delle paragenesi eclogitiche; iii) una riequilibratura largamente incompleta per condizioni metamorfiche di basso grado. La zonatura composizionale che ne risulta dipende da eredità composizionale del sito igneo, strutture tessiturali del protolite, intensità della deformazione e diffusività degli elementi. Alle

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più basse temperature, giadeiti ed egirine o egirinaugiti generalmente coesistono. La presenza del gap composizionale anche tra granuli direttamente a contatto suggerisce la presenza di un solvus. Il gap di miscibilità si estende tra il join giadeite - egirina e giadeite - ,quad al sotto dei 400°C, e si restringe all'aumentare dei contenuti in egirina. A partire da circa 400°C, composizioni onfacitiche aumentano di stabilità, il gap di miscibilità permane tra onfacite e giadeite ricca in onfacite, e si riduce con l'aumento del contenuto in egirina.

Per temperature al sopra dei 450°C si osservano gap composizionali tra giadeite ed onfacite. Tra onfacite e pirosseno calcico si registra un gap composizionale che tende a chiudersi per T > 700°C.

KEY WORDS: blueschist facies; eclogite facies; mineral chemistry; miscibility gap.

INTRODUCTION

Sodium- and Na-Ca clinopyroxenes are petrogenetic indicators of metamorphic processes; in particular, the jadeite content in clinopyroxene is a well-established geothermobarometric tool in high-P metamorphism (Coleman and Clark, 1968; Holland, 1980, 1983; Maruyama and Liou, 1987). Wide compositional overlaps for varying metamorphic conditions and large compositional ranges in clinopyroxene which equilibrated in similar *P-T* conditions largely depend on bulk rock composition.

Small-scale compositional differences are related to the effects of inheritance from pristine phases, mostly in the case of coarse grained igneous rocks, as a consequence of incomplete re-equilibration at the mesoscale (Bocchio, 1995). Compositional zoning is also correlated with P-T variations during crystallization (Cortesogno et al., 1977b, c, 1979; 1993). However, in the tectonic units examined here, recorded variations in metamorphic parameters during high-pressure events are moderate, and their bearing on the composition of clinopyroxenes may be disregarded within the frame of the present work. Lastly, the coexistence of Na-Ca clinopyroxenes of different composition is

ascribed to a miscibility gap (Dobretsov, 1964; Carpenter, 1980; Liou *et al.*, 1985; Maruyama and Liou, 1987).

Analysed samples are representative of several protoliths and cover a wide range of pressures and temperatures, from Pennidic units of the Ligurian Alps and from Northern Sardinia units; figure 1 shows sample localities. This provided the opportunity to compare the compositional variability of Na-Ca clinopyroxenes as a function of varying chemical and thermodynamic parameters.

ANALYTICAL METHODS

Mineral phases were analysed using a Philips SEM 515 scanning electron microscope (University of Genova) equipped with an EDAX PV9100 spectrometer in the energydispersive mode. Operating conditions were 15 kV accelerating voltage and 2.1 nA beam current. Reference standards for elements (in brackets) were: jadeite (Na), forsterite (Mg), albite (Al), augite (Si, Ca), microcline (K), ilmenite (Ti), chromite (Cr), rhodonite (Mn) and fayalite (Fe). Other elements are below detection limits. Na₂O and MgO contents analysed in silicates by an EDAX microprobe are generally underestimated if the analysis is processed with current automatic methods. To overcome this problem, the background for Na (1.040 keV) and Mg (1.252 keV) was manually corrected and considered to be between 0.9 and 4.2 keV. Accuracy of results was checked by the wavelength dispersive system microprobe installed at the University of Modena for a representative number of point analyses.

Pyroxene atomic proportions were calculated assuming stoichiometry and charge balance (Wood and Banno, 1973). Nomenclature follows the scheme of Morimoto *et al.* (1988), amplified by Rock (1990) for Na-Ca and Napyroxenes. Normalized end-member components were recast in the following order: i) aegirine ii) jadeite iii) Quad components iv) others. In the analysed Na-Ca and Na clinopyroxenes, diopside is the main Quad component; the amount of tschermakite is low.



Figure 1 – A) Tectonic sketch-map of Western Liguria, modified after Vanossi *et al.* (1984). B) Tectonic sketch-map of northern Sardinia, from Carmignani *et al.* (1994).

Representative clinopyroxene analyses, selected from over 1300, are reported in Tables 1-4. Data are plotted in the classification diagrams of Rock (1990) in figures 3-7. Zoned grains and coexisting pairs of Na-Ca clinopyroxene were analysed in detail; for graphical clarity, only selected point analyses representing compositional variation trends are plotted. Analysed rocks were selected from about 1000 samples. Abbreviations for minerals are according to Kretz (1983).

Pressure and temperature conditions of the metamorphic Na-Ca clinopyroxenes were determined for each tectonic unit. Stable assemblages in various chemical systems (basic, pelitic, ultrabasic, etc.), continuous and discontinuous reactions, and exchange thermobarometry were considered in estimating P-T conditions; values are reliable within the limits of available methods; in any case, the relative positions of metamorphic units in the P-T field (fig. 2) are mutually consistent.

TABLE	1
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Symbols Unit	☆ BrI	☆ BrI	☆ BrI	+ BrI	CVM	CVM	• CVM	• CVM	• CVM
Oxides									
SiO ₂	52.77	53.34	53.59	51.21	53.41	53.03	53.16	52.92	52.71
TiO ₂	0.07	0.16	0.00	0.01	0.08	0.00	0.09	0.17	0.09
$Cr_2\tilde{O}_3$	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al_2O_3	5.07	3.90	6.26	3.18	3.10	2.30	3.87	3.85	3.85
FeO _{tot}	18.07	25.50	22.46	22.54	16.68	13.08	18.42	16.61	18.49
MnÖ	0.21	0.49	0.15	0.50	0.15	0.32	0.37	0.16	0.09
MgO	4.43	0.89	0.78	2.22	6.39	8.93	5.03	5.89	4.64
CaO	10.10	1.68	1.41	14.78	12.64	16.40	8.26	12.42	10.48
Na ₂ O	7.85	12.94	13.17	4.91	6.67	4.84	9.15	6.92	8.09
$K_2 \bar{O}$	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	98.66	98.90	97.82	99.35	99.12	98.90	98.35	98.94	98.44
Cations									
Si	1.976	1.980	1.983	1.990	1.993	1.978	1.976	1.976	1.977
Ti	0.002	0.004	0.000	0.000	0.002	0.000	0.002	0.005	0.003
Cr	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Al	0.224	0.171	0.273	0.146	0.136	0.101	0.170	0.169	0.170
Fe ³⁺	0.392	0.792	0.695	0.243	0.356	0.292	0.532	0.370	0.460
Fe ²⁺	0.174	0.000	0.000	0.489	0.165	0.116	0.041	0.149	0.120
Mn	0.007	0.028	0.005	0.017	0.005	0.010	0.012	0.005	0.003
Mg	0.247	0.027	0.043	0.129	0.356	0.497	0.279	0.328	0.259
Ca	0.405	0.067	0.056	0.616	0.506	0.656	0.329	0.497	0.421
Na	0.570	0.931	0.945	0.370	0.482	0.350	0.659	0.501	0.588
К	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Aegirine	39.2	79.2	69.5	24.3	35.6	29.2	53.2	37.0	46.0
Jadeite	17.8	13.9	25.0	12.7	12.6	5.8	12.7	13.1	12.8
Quad	40.5	5.5	4.6	62.1	51.3	62.8	31.9	48.0	39.1
CaAl ₂ SiO ₆	2.1	1.2	1.1	0.9	0.3	2.2	2.0	1.4	1.8
CaFeAlSiO ₆	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CaCrAlSiO ₆	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CaTiAl ₂ O ₆	0.2	0.4	0.0	0.0	0.2	0.0	0.2	0.5	0.3

Representative clinopyroxene analyses. Symbols in tables correspond to lithotypes as in figures. Abbreviations for tectonic units as in fig. 2.

PETROGRAPHIC OUTLINES AND MINERAL CHEMISTRY OF CLINOPYROXENES

Transition albite-lawsonite to blueschist facies

Internal Briançonnais Units

The Alpine metamorphic peak in the Ligurian Briançonnais Internal Zone was

estimated at 0.9 GPa pressure and $300^{\circ}C < T < 350^{\circ}C$ (fig. 2; Cabella *et al.*, 1991b, 1992). In spite of the polyphase foliation, igneous textures are generally preserved.

Aluminian aegirine augites (fig. 3B) developed in acid igneous rocks (dacite, rhyolite, granodiorite) as neoblastic grains (0.78-0.90 mm) or large (6-8 mm)



Figure 2 – *P-T* conditions of metamorphic peak for tectono-metamorphic units of present study. CVM: Cravasco-Voltaggio and Montenotte; G: Giglio Island; M: Montaldo; PC: Palmaro-Caffarella; CP: Cascine Parasi; BP: Beigua-Ponzema; ET: Erro-Tobbio; TV: Torrente Visone; BrI: Internal Briançonnais; B: Bagnaschino; pve: pre-Variscan eclogites: B=Ligurian Briançonnais, S1, S2=eclogites from Sardinian basement. **1**, **3**, **9**, **11**: Frey *et al.* (1991); **2**: Heinrich and Althaus (1980); **4**, **5**: Apted and Liou (1983); **6**: Holland and Powell (1990); **7**: Wyllie (1977); **8**: Liou *et al.* (1985); **10**, **12-16**: Jd isopleths from Essene and Fyfe (1967); **17**: Birch and Le Comte (1960); **18**: Chopin (1985). Abbreviations for tectonic units as in Fig. 1. Aeg: aegirine; Carph. carpholite; f: fluids.

Symbols	+	+	+	×	×	۲	۲	۲	۲	•
Unit	М	М	М	В	В	PC	PC	PC	PC	PC
Oxides										
SiO ₂	57.49	56.66	56.10	58.34	58.90	57.58	57.77	56.85	58.77	58.66
TiO ₂	0.00	0.00	0.00	0.11	0.00	0.00	0.00	0.00	0.10	0.00
$Cr_2 \tilde{O}_3$	0.00	0.00	0.10	0.00	0.00	0.08	0.00	0.04	0.00	0.00
Al ₂ O ₃	18.82	16.52	15.84	23.37	25.10	18.49	19.58	16.10	25.61	22.91
FeOtot	6.93	10.11	10.22	2.89	0.23	5.98	4.95	9.12	0.64	2.37
MnÖ	0.00	0.00	0.06	0.00	0.00	0.04	0.03	0.09	0.00	0.01
MgO	0.76	0.43	1.07	0.65	0.14	1.22	1.06	0.95	0.00	0.56
CaO	1.97	1.18	2.23	0.45	0.18	2.59	2.79	3.62	0.28	1.33
Na ₂ O	13.67	14.12	13.34	14.16	15.04	13.57	13.53	12.88	15.09	14.21
$K_2 \overline{O}$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	99.64	99.02	98.96	100.17	99.59	99.55	99.71	99.65	100.49	100.05
Cations										
Si	1.996	1.991	1.981	1.993	1.993	1.996	1.995	1.998	1.973	1.998
Ti	0.000	0.000	0.000	0.003	0.000	0.000	0.000	0.000	0.003	0.000
Cr	0.000	0.000	0.003	0.000	0.000	0.002	0.000	0.001	0.000	0.000
Al	0.770	0.684	0.659	0.938	1.001	0.756	0.797	0.667	1.014	0.920
Fe ³⁺	0.158	0.296	0.291	0.005	0.000	0.162	0.119	0.214	0.017	0.023
Fe ²⁺	0.043	0.001	0.011	0.077	0.006	0.012	0.024	0.055	0.001	0.044
Mn	0.000	0.000	0.002	0.000	0.000	0.001	0.001	0.003	0.000	0.000
Mg	0.039	0.022	0.056	0.033	0.007	0.063	0.055	0.050	0.000	0.028
Ca	0.073	0.045	0.084	0.016	0.007	0.096	0.103	0.136	0.010	0.049
Na	0.920	0.962	0.913	0.935	0.986	0.912	0.906	0.878	0.982	0.938
Κ	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Aegirine	15.8	29.6	29.1	0.5	0.0	16.2	11.9	21.4	1.7	2.3
Jadeite	76.2	66.6	62.2	93.0	98.6	75.0	78.7	66.4	96.5	91.5
Quad	7.6	2.9	6.7	6.1	0.7	8.4	8.9	12.1	0.1	5.9
CaAl ₂ SiO,	6 0.4	0.9	1.7	0.1	0.7	0.2	0.5	0.1	1.0	0.3
CaFeÃlSi	Ď ₆ 0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CaCrAlSi($D_{6}^{V} = 0.0$	0.0	0.3	. 0.0	0.0	0.2	0.0	0.1	0.0	0.0
CaTiAl ₂ O	₆ 0.0	0.0	0.0	0.3	0.0	0.0	0.0	0.0	0.3	0.0

TABLE 2Representative clinopyroxene analyses. Symbols in tables correspond to lithotypesas in figures. Abbreviations for tectonic units as in fig. 2.

pseudomorphs replacing biotite. Crossite, albite, pumpellyite, epidote, phengite and grandite (but not chlorite) are coexisting phases.

In metaquartz-arenite, pyroxene coexisting with albite, phengite ± magnetite shows a wide compositional range between aluminian aegirine augite to the ferrian omphacite boundary, except for two compositions within the aluminian aegirine field. In metachert, nearly pure aegirine coexists with hematite and hollandite.

In intermediate and basic volcanites, Naamphibole, actinolite, albite, chlorite, lawsonite, pumpellyite, titanite and epidote $(0.22 < X_{Fe3+} < 0.30)$ represent the stable assemblage; Na-Ca clinopyroxene was never found.

Symbols						۲	۲	۲	۲	۲	۲	•
Unit	CP	СР	СР	СР	CP	СР	СР	СР	СР	СР	СР	CP
Oxides												
SiO ₂	53.65	53.34	54.71	54.03	54.69	55.65	53.16	57.33	52.45	57.85	56.71	57.09
TiO_2	0.00	0.00	0.06	0.01	0.00	0.11	0.16	0.00	0.52	0.00	0.04	0.00
$Cr_2 \tilde{O}_3$	0.00	0.00	0.00	0.00	0.00	0.13	0.00	0.00	0.00	0.00	0.00	0.00
Al_2O_3	6.30	5.45	8.07	5.40	7.79	9.50	5.66	17.79	3.78	22.17	11.53	19.89
FeO _{tot}	14.51	14.78	8.27	11.82	8.00	7.40	22.49	6.89	23.79	4.36	2.88	5.91
MnÖ	0.41	0.35	0.31	0.24	0.38	0.25	0.00	0.00	0.00	0.00	0.25	0.00
MgO	5.40	5.92	8.09	7.74	8.33	7.73	1.02	1.51	1.51	0.00	8.35	0.81
CaO	11.39	11.72	13.12	13.54	13.21	12.40	2.72	2.61	3.72	0.75	12.93	1.86
Na ₂ O	7.38	7.23	6.89	6.61	6.92	7.02	12.48	13.24	11.75	14.37	7.30	13.87
K ₂ Ō	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	99.04	98.79	99.52	99.39	99.32	100.19	97.69	99.37	97.52	99.50	99.99	99.43
Cations												
Si	1.985	1.979	1.973	1.976	1.973	1.990	1.980	1.998	1.975	1.990	2.000	1.976
Ti	0.000	0.000	0.002	0.000	0.000	0.003	0.004	0.000	0.015	0.000	0.001	0.000
Cr	0.000	0.000	0.000	0.000	0.000	0.004	0.000	0.000	0.000	0.000	0.000	0.000
Al	0.275	0.238	0.343	0.233	0.331	0.401	0.249	0.731	0.168	0.899	0.479	0.812
Fe ³⁺	0.284	0.325	0.190	0.283	0.206	0.096	0.684	0.168	0.711	0.081	0.018	0.167
Fe ²⁺	0.164	0.134	0.060	0.079	0.036	0.125	0.017	0.033	0.039	0.045	0.067	0.004
Mn	0.013	0.011	0.010	0.008	0.012	0.008	0.000	0.000	0.000	0.000	0.007	0.000
Mg	0.298	0.328	0.435	0.422	0.448	0.412	0.056	0.079	0.085	0.000	0.439	0.042
Ca	0.452	0.466	0.507	0.531	0.511	0.475	0.109	0.098	0.150	0.028	0.489	0.069
Na	0.529	0.520	0.482	0.469	0.484	0.487	0.901	0.895	0.858	0.959	0.499	0.931
К	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Aegirine	28.4	32.5	19.0	28.3	20.6	9.6	68.4	16.8	71.1	8.1	1.8	16.7
Jadeite	24.5	19.5	29.2	18.6	27.8	39.1	21.7	72.7	14.7	87.8	47.9	76.4
Quad	45.6	45.9	49.3	50.7	49.0	50.6	8.3	10.3	13.0	3.1	49.9	4.5
CaAl ₂ SiO ₆	1.5	2.1	2.4	2.4	2.6	0.0	1.2	0.2	0.0	1.0	0.0	2.4
CaFeAlSiO ₆	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CaCrAlSiO ₆	0.0	0.0	0.0	0.0	0.0	0.3	0.0	0.0	0.0	0.0	0.0	0.0
CaTiAl ₂ O ₆	0.0	0.0	0.2	0.0	0.0	0.4	0.4	0.0	1.1	0.0	0.1	0.0

TABLE 3Representative clinopyroxene analyses. Symbols in tables correspond to lithotypesas in figures. Abbreviations for tectonic units as in fig. 2.

Cravasco-Voltaggio and Montenotte Units

In the Cravasco-Voltaggio and Montenotte Units, ophiolitic sequences include serpentinite, gabbro and Fe-Ti oxide-gabbro, basaltic dykes, quartz-diorite, effusive basalt and chert which equilibrated under lawsonitealbite-bearing blueschist facies metamorphism (Beccaluva *et al.*, 1979; Chiesa *et al.*, 1975; 1976; 1977; Cortesogno *et al.*, 1979; Cortesogno and Haccard, 1984; Lucchetti *et al.*, 1990; Desmons *et al.*, 1999a, b, c). Estimated P-T conditions are: ~ 0.8 GPa, and 300° - 350° C (fig. 2). An early foliation develops in effusive and sedimentary protoliths, associated with high-pressure conditions, but is scarcely evident in the massive igneous rocks.

Na-Ca clinopyroxene commonly coexists

				-						
Symbols Unit	• BP) BP	▲ TV	TV	TV	L ET	D ET	D ET	▲ pVE	pVE
Oxides										
SiO ₂	54.42	54.68	53.94	55.54	54.55	56.27	56.32	56.00	55.79	54.37
TiO ₂	0.11	0.00	0.10	0.00	0.00	0.02	0.35	0.08	0.09	0.00
$Cr_2\bar{O}_3$	0.00	0.00	0.00	0.06	0.00	0.32	0.25	0.73	0.04	0.22
Al_2O_3	8.02	8.43	8.30	10.91	7.93	7.36	11.56	9.90	12.16	9.09
FeO _{tot}	13.15	11.92	9.49	7.66	8.88	1.37	1.81	1.36	4.31	6.78
MnO	0.00	0.00	0.10	0.07	0.00	0.07	0.00	0.03	0.00	0.00
MgO	4.78	5.92	7.42	6.31	7.88	12.65	9.24	10.88	8.27	8.82
CaO	11.55	12.54	13.49	11.12	13.22	18.35	14.22	15.47	12.89	14.53
Na ₂ O	7.34	6.49	6.66	8.07	6.91	4.27	6.59	5.70	7.07	6.02
K ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	99.37	99.98	99.50	99.74	99.37	100.68	100.34	100.15	100.62	99.83
Cations										
Si	2.009	1.999	1.957	1.986	1.973	1.988	1.982	1.977	1.964	1.954
Ti	0.003	0.000	0.003	0.000	0.000	0.001	0.009	0.002	0.002	0.000
Cr	0.000	0.000	0.000	0.002	0.000	0.009	0.007	0.020	0.001	0.006
Al	0.349	0.363	0.355	0.460	0.338	0.307	0.480	0.412	0.504	0.385
Fe ³⁺	0.176	0.099	0.193	0.126	0.202	0.000	0.000	0.000	0.046	0.121
Fe ²⁺	0.230	0.265	0.095	0.103	0.067	0.041	0.053	0.040	0.081	0.083
Mn	0.000	0.000	0.003	0.002	0.000	0.002	0.000	0.001	0.000	0.000
Mg	0.263	0.323	0.401	0.336	0.425	0.666	0.484	0.572	0.434	0.473
Ca	0.457	0.491	0.524	0.426	0.512	0.695	0.536	0.585	0.486	0.559
Na	0.525	0.460	0.468	0.559	0.485	0.292	0.449	0.390	0.483	0.420
К	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Aegirine	17.6	9.9	19.3	12.6	20.2	0.0	0.0	0.0	4.6	12.1
Jadeite	34.9	36.1	27.5	43.3	28.3	29.2	44.9	39.0	43.7	29.9
Quad	47.3	53.9	49.2	42.7	48.8	69.6	52.7	58.8	48.3	53.4
CaAl ₂ SiO ₆	0.0	0.1	3.7	1.2	2.7	0.2	0.3	0.00	3.1	4.0
CaFeAlSiO ₆	0.0	0.0	0.0	0.0	0.0	0.00	0.0	0.00	0.0	0.0
CaCrAlSiO ₆	0.0	0.0	0.0	0.2	0.0	0.9	0.7	0.20	0.1	0.6
CaTiAl ₂ O ₆	0.3	0.0	0.3	0.0	0.0	0.1	0.9	0.20	0.2	0.0

TABLE 4Representative clinopyroxene analyses. Symbols in tables correspond to lithotypesas in figures. Abbreviations for tectonic units as in fig. 2.

with Na-amphibole and albite in rocks of Fe-Ti oxide-gabbro and quartz-diorite composition. Lawsonite, pumpellyite, epidote $(0.15 < X_{Fe3+} < 0.24)$ in gabbro and $0.32 < X_{Fe3+} < 0.37$ in Fe-Ti oxide-diorite) and titanite are common, depending on bulk rock or site composition. Pyroxene rarely occurs in high Mg# bulk rock compositions, such as basalt and olivine-gabbro, where Na-

amphibole, chlorite and albite are prevailing phases.

In gabbroic protoliths, large (5-10 mm) primary augite commonly preserves a relic core; progressive alteration to aluminian aegirine augite (fig. 3C) is evidenced by exsolutions of very fine-grained Ti- and/or Feoxides along cleavages. Near the rim (0.5-3 mm inwards), replacement by aegirine augite is



Figure 3 – A: Nomenclature of Na-Ca clinopyroxenes according to classification diagram of Rock (1990). B: Na-Ca clinopyroxenes from Internal Briançonnais Units. Clinopyroxenes from 2 intermediate to acid metavolcanics (cross), 3 quartz-schists (open star) and 1 manganiferous chert (full star). C: Representative compositions of clinopyroxenes from Cravasco-Voltaggio and Montenotte Units (3 metagabbros, 4 meta- Fe-Ti oxide-gabbros and -diorites) and from Giglio Island (one metadiorite, shaded field). Symbols: squares: metagabbro;, circles: meta- Fe-Ti oxide-gabbros and -diorites. Arrows a, b, and c: rim-core zoning patterns in pyroxene pseudomorphic after augite. Tie-line connects compositions of grains in contact.

complete, and the augite boundaries are epitaxially overgrown by neoblastic, sometimes acicular, aluminian aegirine augite, enriched in jadeite. As a consequence, evident zoning results.

Core-rim compositional profiles are shown in fig. 3C for clinopyroxene of gabbro (a, b), Fe-Ti oxide-gabbro (c) and oxide-diorite. From the core, the patterns show an increase in aegirine at nearly constant jadeite; jadeite increases towards the rim and attains the highest values in the epitaxial rim.

Jadeite contents up to 0.22 and 0.69 mole and aegirine up to 0.45 and 0.84 mole are found in gabbro and Fe-Ti oxide-gabbro protoliths, respectively. Ferrian jadeite developed in the plagioclase site, and is found to coexist in contact with the aluminian aegirine augite overgrowing augite. The sharp boundary between grains and the lack of intermediate compositions over a large number of point analyses defines a compositional gap (fig. 3C).

Sodic clinopyroxene overgrowing ilmenite is on average higher in aegirine contents than clinopyroxene replacing primary augite.

Neoblastic aluminian- and calcian aluminian aegirine overgrowing augite and opaques in Fe-Ti oxide gabbro within the Giglio Island metaophiolite, considered isometamorphic with Cravasco-Voltaggio and Montenotte Units (Capponi *et al.*, 1994; 1997), are also shown in fig. 3C.

Blueschist facies

Montaldo Unit

Metamorphic rocks from basic to intermediate igneous protoliths occur in the flysch-type metasedimentary sequence of the Montaldo Unit (Dallagiovanna, 1993, 1995; Dallagiovanna and Vanossi, 1987). Alpine polyphase foliations are the dominant textural feature, and high pressure assemblages rarely survived the retrograde greenschist overprint. Ferrian jadeite (0.26-0.52 mm) aggregates replace plagioclase (fig. 4A), in equilibrium with quartz, Na-amphibole, lawsonite, phengite, and titanite. Clinopyroxene from quartz-rich metasediments is aluminian aegirine.

The mineral assemblage is consistent with temperatures not exceeding 400°C and minimum pressures of about 1.2 GPa (fig. 2).

Bagnaschino Unit

High pressure (at least 1.3 GPa) and very low temperature (300°C) (fig. 2; Cabella *et al.*, 1991a) were estimated for the Bagnaschino basement unit. In paragneisses and quartzmicaschists, nearly pure jadeite (0.70-2.20 mm; fig. 4B) showing submicroscopic vermicular inclusions of quartz and minor lawsonite replaces plagioclase. Mg-glaucophane, phengite, titanite and minor clinozoisite and pumpellyite, replace biotite and muscovite. Naclinopyroxene never occurs in Na-amphibole, lawsonite and pumpellyite assemblages from the associated amphibolite.

Palmaro-Caffarella Unit

In the Palmaro-Caffarella Unit (Chiesa *et al.*, 1975, 1976, 1977) gabbro cut by basalt and diorite dykes underwent blueschist facies reequilibration together with its associated covers (metabasalt, metachert, impure marble and metapelite; Chiesa *et al.*, 1975; Cortesogno *et al.*, 1979). The composite Alpine foliation is rarely penetrative in the plutonic rocks and dykes, but is pervasive in metabasalts and metasediments.

Na-Ca clinopyroxene commonly coexists with Na-amphibole and sometimes chlorite, associated with lawsonite, clinozoisite $(X_{Fe3+}=0.05-0.07)$ and titanite. Pumpellyite is restricted to pseudomorphs with chlorite and Na-amphibole after olivine. Mn-rich almandine is rare and coexists with Na-Ca clinopyroxene, Na-amphibole and epidote in a Fe-Ti oxidegabbro metabreccia; spessartine associated with crossite, phengite and stilpnomelane is common in metachert. The estimated temperature of equilibration is about 400°C, for minimal pressures of 1.3 GPa (fig. 2; Desmons *et al.*, 1999a, b, c).



Figure 4 – A: Na-Ca clinopyroxenes from the Montaldo Unit. Clinopyroxenes from 1 metasediment (star) and 1 metavolcanite (cross). B: Na-Ca clinopyroxenes from the Bagnaschino Unit. Pyroxenes from 4 paragneisses (oblique cross) and 1 quartzschist (star) affected by Alpine high pressure overprint. C: Na-Ca clinopyroxenes from the Palmaro-Caffarella Unit. a: Clinopyroxenes from 1 metagabbro (square) and 1 metabasalt (triangle); b: Clinopyroxenes from 21 meta-Fe-Ti oxide-gabbros and metadiorites (circle). Arrows represent rim-core zoning patterns in pyroxenes pseudomorphic after augite. Tie lines connect compositions of pairs in contact.

Sodium- and Na-Ca clinopyroxenes are common in Fe-Ti oxide gabbro and quartzdiorite protoliths, restricted to the plagioclase site in metagabbro and metabasalt (fig. 4C, a) and never found in metatroctolite. In gabbroic protoliths, augite survived metamorphic reequilibration, but shows some alteration to Naamphibole. In Fe-Ti oxide gabbro and diorite, augite is commonly replaced by zoned Na-Ca clinopyroxene. From core to rim, the increase in aegirine content is followed by enrichment in jadeite towards ferrian omphacite or aluminian aegirine augite compositions (fig. 4C, b).

Ti-magnetite and ilmenite aggregates are partially altered to titanite and overgrown by pyroxene with the highest aegirine contents. Compositions within the aegirine field are frequent also in pyroxene overgrowing femic phases in Fe-Ti oxide gabbro. Pyroxene replacing plagioclase ranges from pure jadeite to ferrian omphacite (fig. 4C, a, b). Calcian aluminian aegirine compositions appear in contact with calcian ferrian jadeite and show sharp boundaries and sometimes lamellar intergrowths (Plate 1, # 2, 4, 6; Plate 2, #5; Photo 1). Jadeite-poor ferrian omphacite replacing augite and jadeite-rich ferrian omphacite (on plagioclase sites) were found in the same sample, but never in contact.

Lawsonite-glaucophane-bearing eclogites

Cascine Parasi Unit

Small ophiolite slices, some tens to about one hundred metres thick, are ascribed to the same dismembered tectono-metamorphic unit because of a similar metamorphic overprint (Cascine Parasi Unit; Cortesogno *et al.*, 1977b; Desmons *et al.*, 1999a, b, c). The protoliths are gabbro, Fe-Ti oxide-gabbro, quartz-diorite, rarer basalt, and siliceous sediments. Highpressure assemblages developed in banded augen textures, defining a composite foliation.

Polyphase recrystallization of omphacite, Na-amphibole \pm almandine-rich garnet + lawsonite \pm clinozoisite (0.11<X_{Fe3+}<0.13), \pm white mica \pm rutile \pm titanite is a typical feature. Pumpellyite is rare, associated with Na-amphibole in pseudomorphic aggregates on olivine. Pressures in excess of 1.3 GPa and temperatures in the range 400°-450°C are inferred for this unit (fig. 2; Cortesogno *et al.*, 1977a; Cortesogno *et al.*, 1979; Desmons *et al.*, 1999c).

Large zoned Na-Ca clinopyroxene replaces augite topotactically and shows concentrations of submicroscopic rutile, titanite and opaque oxides along cleavages or cracks. In metagabbro, plagioclase alters to aggregates of lawsonite, Na-amphibole, and Na-Ca clinopyroxene, whereas in Fe-Ti oxide gabbro and diorite it alters to Na-Ca clinopyroxene \pm clinozoisite aggregates. Jadeitic clinopyroxene after plagioclase, and aegirine-rich Na-Ca clinopyroxene after hornblende, develop in diorite and quartz-diorite protoliths (Plate 1, # 1, 3, 5; Plate 2, # 1- 4; Photo 2).

Na-Ca clinopyroxenes after augite sites are rich in aegirine and Quad component (fig. 5); Na-Ca clinopyroxenes from the plagioclase site, in contrast, vary along the Jd-Quad join, from omphacite in more primitive protoliths, to jadeite in more evolved compositions. Na-Ca clinopyroxenes overgrowing Fe-Ti oxides have the highest aegirine contents. Zoning towards intermediate compositions occurs at the boundaries of the precursor phase. However, a compositional gap exists between grains in contact or in lamellar intergrowths (fig. 5A). In fine-grained samples (metabasalt, strongly foliated metaplutonics), the compositions of Na-Ca clinopyroxenes tend to be more homogeneous, but never fall within the compositional gap defined by grains in contact (fig. 5B).

In quartz-schist (metachert), Na-Ca clinopyroxenes in equilibrium with phengite, glaucophane and quartz, are aluminian aegirine augite close to the calcian-aluminian aegirine field.

Na-Ca clinopyroxenes analysed in the lawsonite-bearing eclogite of Monte Petrone (Corsica) are reported for comparison. Based on garnet-omphacite geothermometry and coexistence with lawsonite, metamorphic



PLATE 1 – Thin-section photomicrographs of metamorphic assemblages. Symbols are located on analysed areas. Dotted lines: boundaries between different Na-Ca pyroxenes. Dashed-dotted lines: boundaries between minerals other than two pyroxenes. Photo 1. Cascine Parasi Unit. Protolith: Fe-Ti oxide gabbro. Pseudomorphic jadeite (J) and chlorite (C) replacing plagioclase (left) and strongly zoned aegirine augite (A) replacing (top right, very dark) or overgrowing (centre, dark) primary augite and Fe-Ti oxides (T, bottom). Sparse apatite (a); Photo 2. Palmaro-Caffarella Unit. Protolith: gabbro. Jadeite (J) and Na-amphibole (N) replacing plagioclase. Zoned aegirine augite pseudomorphic on augite. Nearly pure aegirine (Aeg) overgrows partially altered ilmenite (T); Photo 3. Cascine Parasi Unit. Protolith: gabbro. Jadeite (J) - clinozoisite (Cz) replacing plagioclase; aegirine augite (A) replacing augite. Darker areas: fine-grained clinozoisite; Photo 4. Palmaro-Caffarella Unit. Protolith: gabbro. Jadeite (J), garnet (G) and Na-amphibole (N) from plagioclase site. Aegirine augite (A) replacing (dark) and overgrowing (light) augite; Photo 5. Cascine Parasi Unit. Protolith: Fe-Ti oxide diorite. Jadeite (J) and epidote (Ep) replacing plagioclase; dark spots in jadeite are very fine-grained clinozoisite. Aegirine augite (A) replacing and overgrowing hornblende; Photo 6. Palmaro-Caffarella Unit. Protolith: gabbro. Jadeite (J) replacing plagioclase. Aegirine-rich clinopyroxene (A) replacing and overgrowing augite. Apatite (a). Grey areas in jadeite: incipient breakdown to albite + quartz.



PLATE 2. Thin-section photomicrographs of metamorphic assemblages. Symbols are located on analysed areas. Dotted lines: boundaries between different Na-Ca pyroxenes. Dashed-dotted lines: boundaries between minerals other than two pyroxenes. Photo 1. Cascine Parasi Unit. Protolith: diorite. Jadeite (J) replacing plagioclase and aegirine-rich pyroxene (A) replacing hornblende. Primary zoning in plagioclase is preserved as extremely fine-grained (dark) Ca-Al silicate inclusions in jadeite; Photo 2. Cascine Parasi Unit. Protolith: diorite. Sodic pyroxene vein (centimetre thick). Neoblastic wedge-shaped jadeite (J) and fine-grained to wedge-shaped aegirine-augite (A). At boundaries, lamellae of jadeite and aegirine-augite are intergrown (see SEM detail in Photo 2); Photo 3. Diorite from Cascine Parasi Unit. Protolith: Giorite. Jadeite (J), aegirine-augite (A) and Na-amphibole (N); in most cases, Na-amphibole is located on boundaries of two pyroxenes. Top left: retrograde alteration of jadeite to albite (ab) and minor chlorite; Photo 4. Cascine Parasi Unit. Protolith: Fe-Ti oxide-gabbro. Prismatic jadeite (J) and aegirine augite (A) overgrown at boundaries of plagioclase and augite respectively; Photo 5. Palmaro-Caffarella Unit. Protolith: diorite. Jadeite (J) replacing plagioclase and jadeite pseudomorphs after hornblende. At contact, fine lamellar intergrowth of two pyroxenes; Photo 6. Beigua Ponzema Unit. Protolith: Fe-Ti oxide-diorite. Post-kinematic assemblage of garnet, omphacite, Na-amphibole and quartz. Note equilibrium boundaries between phases. Retrograde fine-grained barroisite at dark rims and fractures, mostly within garnet.



Photo 1: Scanning electron microphotograph, back-scattered image. Scale bar: 0.1 mm. Palmaro Caffarella Unit. Protolith: gabbro. Jadeitic clinopyroxene (J) replacing euhedral plagioclase and zoned aegirine augite (A) from augite.



Photo 2: Scanning electron microphotograph, back-scattered image. Scale bar: 0.1 mm. Palmaro Caffarella Unit. Protolith: diorite. Detail of plate 2, #2. Fine-grained aggregate of jadeitic clinopyroxene (J) at bottom grades to parallel wedge-shaped grains in contact with fine-grained aggregates of patchy, zoned aegirine augite (A).



Figure 5 – Na-Ca clinopyroxenes from Cascine Parasi Unit. A: Clinopyroxenes from 18 metaox-gabbros and metadiorites (circle). Tie-lines connect compositions of grains in contact. B: Clinopyroxenes from 4 metagabbros (square) and 1 metaradiolarite (star). Full triangles: composition of a metabasalt from Monte Petrone ophiolite (Corsica).

parameters are P>1.3 GPa and T = 420° C, in accordance with the data of Péquignot *et al.* (1984) and Caron and Péquignot (1986).

Na-amphibole-bearing eclogites

Beigua-Ponzema Unit

The Beigua-Ponzema Unit (Chiesa et al., 1975) is represented by antigoritic serpentineschists including large lenses of gabbroic or Fe-Ti oxide gabbroic protolith compositions, and more or less rodingitized gabbro and basalt dykes (Cimmino et al., 1980; Cortesogno et al., 1977a; Morten and Bondi, 1984; Messiga and Scambelluri, 1991; Bocchio, 1995; Bocchio and 1996). Sedimentary Liborio, covers (ophicalcites, quartz-schists, mica-chlorite schists) occur locally. The development of eclogitic assemblages is associated with a main schistosity followed by folding and retrograde recrystallization to greenschist facies conditions. In eclogites from Fe-Ti oxide gabbro and rarer basalt protoliths, Na-Ca clinopyroxene, garnet and rutile coexist with Na-amphibole and clinozoisite (0.15<X_{Fe3+}<0.17). In gabbro zoisite or clinozoisite protoliths, $(0.05 < X_{Fe3+} < 0.10)$ and Na-amphibole coexist with Na-Ca clinopyroxene, garnet and white micas. In ophicarbonate rocks, diopside with variable amounts of sodic components up to aegirine augite coexists with calcite and garnet, having grandite to almandine, or uvarovite-rich compositions (Cortesogno et al., 1981). Tremolite and olivine coexist with diopside.

The estimated metamorphic peak for this unit (fig. 2) is $T=475^{\circ}\pm 25^{\circ}C$ and pressures in excess of 1.3 GPa (Cimmino *et al.*, 1980; Cortesogno *et al.*, 1981; Messiga and Scambelluri, 1991; Desmons *et al.*, 1999b, c).

Igneous textures are largely preserved,

except for localized blastomylonitic domains. In eclogite, augite is topotactically replaced by ferrian omphacite, with higher Quad component than the fine-grained ferrian omphacite (and rare omphacite) replacing plagioclase (fig. 6A). However, a relatively large compositional overlap becomes evident. Aluminian aegirine augite and rutile replace pristine ilmenite-Ti-magnetite exsolutions; natalyite (NaVSi₂O₆) up to 11 mole% (Borsi *et al.*, 1994) is present in the pyroxene, replacing the Ti-magnetite site.

In high-strain eclogite, omphacite porphyroclasts (Cortesogno *et al.*, 1977a) have compositions similar to pseudomorphic omphacite, whereas fine-grained granoblastic to subidioblastic (0.04-0.16 mm) Na-Ca clinopyroxenes intergrown with Na-amphibole (Plate 2, #6) are ferrian omphacite to aluminian-aegirine augite, with relatively constant Quad component (about 50%), and the compositional variation correlates with the bulk rock (fig. 6A).

In metagabbro, coarse-grained pseudomorphs after augite are ferrian omphacite and fine-grained clinopyroxene rimming pseudomorphic aggregates (Naamphibole or sodic tremolite, talc and/or chlorite) after olivine, or replacing the plagioclase with (clino)zoisite and Naamphibole are mostly omphacite; no compositional gap occurs.

Torrente Visone Unit

Continental crust of inferred Apulian provenance (Torrente Visone Unit, formerly Valosio Massif, Cabella *et al.*, 1990; Cortesogno *et al.*, 1993) underlies the metaophiolite of the Voltri Group.

Granoblastic eclogitic assemblages (Na-Ca clinopyroxene, garnet, rutile, Na-amphibole, clinozoisite ($X_{Fc3+} \simeq 0.04$)) developed from metabasalt at an estimated pressure of 1.5 GPa and temperatures of 550°C ± 30°C (fig. 2; Cabella *et al.*, 1990; Messiga *et al.*, 1992; Desmons *et al.*, 1999b, c).

Clinopyroxenes are omphacite and ferrian omphacite showing a near constant Quad component (~ 50%) and relatively low jadeite/aegirine variability (fig. 6B), in agreement with wide textural re-equilibration and whole rock homogeneity.

Erro-Tobbio Unit

The Erro Tobbio (Chiesa *et al.*, 1975), is a lherzolitic unit with minor gabbro lenses and basalt dykes, which underwent a high-pressure (> 1.3-1.6 GPa), intermediate-temperature (450°-550°C) Alpine overprint (Scambelluri *et al.*, 1991; Desmons *et al.*, 1999b, c).

Na-Ca clinopyroxenes were analysed from garnet, zoisite, chloritoid, talc and chlorite assemblage in a metagabbro. The clinopyroxenes are omphacite, with Quad decreasing and jadeite increasing from augite to plagioclase sites. Calcian jadeite (fig. 6C) associated with zoisite occurs within the plagioclase site. As omphacite and calcian jadeite grains are not in contact, the lack of intermediate compositions may depend on analytical bias.

Hornblende-bearing eclogites

Pre-Variscan basement from Sardinia and Ligurian Briançonnais

In the Sardinia basement along the Posada-Asinara Line (fig. 1), granoblastic, mediumgrained eclogite lenses, of homogeneous basalt tholeiitic composition, occur in the staurolite + garnet + kyanite - bearing micaschists and paragneisses. Eclogite is characterized by almandine-rich garnet, Na-Ca clinopyroxene, hornblende + rutile + clinozoisite + quartz assemblages, partially re-equilibrated to diopside + hornblende + plagioclase + titanite assemblages. The inferred metamorphic peak is $T = 630^{\circ} \pm 25^{\circ}C$ and P in excess of 1.2-1.3 GPa (Cortesogno et al., 2000). Clinopyroxenes are omphacite to ferrian omphacite with homogeneous composition and jadeite content between 37-43 mole % (fig. 7B).

In the Ligurian Briançonnais basement (fig. 1), eclogite associated with migmatite records polyphase pre-Variscan metamorphic evolution. They are characterized by decimetric



Figure 6 – A: Na-Ca clinopyroxenes from Beigua-Ponzema Unit. Clinopyroxenes from low to high strain domains in 1 metagabbro (square) and 4 meta- Fe-Ti oxide-gabbros and -diorites (low-strain domains: filled circles; high-strain domains: open circles). In area a): pyroxene replacing augite, in b): replacing plagioclase, in c): replacing Fe-Ti oxide. Area d): clinopyroxene from 3 ophicarbonate rocks (Cortesogno *et al.*, 1981). B: Na-Ca clinopyroxenes from Torrente Visone Unit. Clinopyroxenes from 4 metabasalts (triangle). C: Na-Ca clinopyroxenes from Erro-Tobbio Unit. Clinopyroxenes from 4 metabasalts (triangle). C: Na-Ca clinopyroxenes from Erro-Tobbio Unit. Clinopyroxenes from 4 metagabbros: open and filled squares: pyroxene from augite and plagioclase sites, respectively.

metamorphic banding and medium to coarsegrained granoblastic textures, which developed at an estimated temperature of $750^{\circ}\pm20^{\circ}$ C and a pressure in excess of 1.7 GPa (fig. 2). A granulite facies overprint, developing during the decompressive retrogression to amphibolite facies conditions, is locally preserved (Capelli *et al.*, 1994; Cortesogno *et al.*, 1993; 1997; Desmons *et al.*, 1999a). The bulk rock composition is tholeiitic basalt. Na-Ca clinopyroxene coexists with garnet, rutile, Na-Ca amphibole, zoisite, less common biotite and

white mica, and rare kyanite. Clinopyroxene composition varies, depending on bulk rock composition, but pre-kinematic omphacite included in garnet has Jd 26-36 mole%, whereas syn-kinematic omphacite has Jd 30-47 mole%, depending on bulk rock composition (Cortesogno *et al.*, 1997; fig. 7A).

In the polymetamorphic high-grade complex of the Sardinia basement (migmatite complex; Ghezzo et al., 1982; Di Pisa et al., 1993), eclogitic assemblages are preserved in metabasite of tholeiitic MORB-type chemical character and relatively evolved composition. Complex polyphase evolution includes: i) textural relics of an older schistosity preserved at garnet cores; ii) development of an eclogitic assemblage (almandine-rich garnet + pargasite amphibole) associated with decimeter-thick compositional banding. Biotite, ilmenite, rutile, quartz, apatite, zircon and allanite occur in variable amounts; iii) breakdown of the eclogite assemblage to diopside + plagioclase symplectite and to orthopyroxene + hornblende + plagioclase-bearing assemblages; iv) retrograde evolution to amphibolite facies



Figure 7 – Na-Ca clinopyroxenes from pre-Variscan eclogites. A: Clinopyroxene from 5 metabasites from Ligurian Briançonnais basement (triangle). B: Circles: clinopyroxene from eclogite interbedded with Ky-gneisses (Sardinia); squares: clinopyroxene from eclogite associated with migmatite (Sardinia).

conditions. Thermobarometric calibrations provide a wide span of results; temperatures > 700°C and pressures exceeding 1.3 GPa (Franceschelli *et al.*, 1998; Cortesogno *et al.*, 2000) may be regarded as minimal values for the metamorphic peak. Na-Ca clinopyroxenes are omphacite and ferrian omphacite to aluminian aegirine augite, with a relatively constant Jd/Quad ratio and Jd in the range 21-28 mole%. Compositional variability correlates well with that of the bulk rock.

DISCUSSION

Control of metamorphic parameters, protolith and site heritage on clinopyroxene composition

Sodic pyroxene is stable in assemblages including hydrous phases such as amphibole, micas, epidote, lawsonite, chlorite, chloritoid, and talc. Clinopyroxene replacing hornblende or biotite evidences its origin by dehydration reactions; however, in the lowest metamorphic conditions, the stability of sodic clinopyroxene is restricted to compositions with low Mg# and relatively low Mg/Ca with respect to amphibole stability. At increasing metamorphic P and T, the compositional field of stable Na-Ca clinopyroxene widens.

In accordance with experimental and calculated data on the stability of Naclinopyroxene (Dobretsov, 1964; Dobretsov et al., 1971; Liu and Bohlen, 1995; Holland, 1980; 1983; Holland and Powell, 1990; Guiraud et al., 1990), for relatively low pressures within the blueschist facies, the composition of pyroxene is restricted to the aegirine-rich field, and the maximum jadeite al., 19/1; Liu and Bohlen, 1995; Holland, 1980; 1983; Holland and Powell, 1990; Guiraud et al., 1990), for relatively low pressures within the blueschist facies, the composition of pyroxene is restricted to the aegirine-rich field, and the maximum jadeite content increases with pressure. At low temperature, all compositions between Quad and aegirine are stable, whereas the Quad content in jadeite-rich compositions is low (figs. 3, 4). Omphacite compositions become stable only above 400°C (figs. 5, 6). At higher temperatures, omphacitic pyroxene is in equilibrium with hornblende or pargasite (fig. 7) and the Quad/Jd probably increases with

temperature. On the grounds of the stable mineral assemblages, the formation of omphacite may be envisaged through the reaction Lws + Pmp + Na-Am + Ab $\langle = \rangle$ omphacite + H₂O, proceeding to the right with increasing temperature.

In low-grade conditions, progressive replacement of igneous augite, characterized by aegirine molecule increases at the core and jadeite increase towards the rim, mirrors differential increase in Na and Al contents and Fe³⁺/Fe²⁺, depending on the higher diffusivity of oxygen and sodium compared with alumina. The compositional zoning patterns (figs. 3, 4) are related with augite composition, with possible contribution from oxides, which in turn depend on protolith composition.

In relatively higher metamorphic conditions (figs. 6A and C), sodic pyroxene compositions from coarse-grained protoliths still reflect the site heritage, but zoning is restricted to site boundaries; homogeneous compositions observed in fine-grained protoliths (fig. 6B) or pervasively deformed metabasite suggest complete re-equilibration.

The minor compositional differences between pre-kinematic and syn- to postkinematic Na-Ca clinopyroxenes have been interpreted as due to moderate pressure and temperature changes during the deformative event (Morten and Bondi, 1984; Cabella *et al.*, 1994; Bocchio, 1995; Bocchio and Liborio, 1996). These effects may be disregarded within the frame of the present work.

Compositional gap

In the lowest metamorphic conditions, compositional gaps are observed between jadeite-rich and aegirine-rich compositions and, in increasing conditions, they are also observed between jadeite-rich omphacite and omphacite (figs. 3C, 4A and C, 5). The bulk rock (e.g., Montaldo Unit) or site composition can control compositional gaps. In the Palmaro-Caffarella and Cascine Parasi Units, and more rarely in the Cravasco-Voltaggio and Montenotte Units, the compositional gap between pyroxene developing on augite/oxides and plagioclase respectively, is restricted to rims, but is still present in neoblastic grains in contact at the site boundaries (Plate 1). Also, in high-strain domains, a compositional gap is found between intergrown grains. The sharp boundaries between coexisting pyroxenes of different composition and the lack of intermediate compositions indicate that compositional gaps may correspond to miscibility gaps.

The existence of miscibility gaps on the jadeite-Quad join was proposed and discussed by Dobretsov (1964), and Dobretsov et al. (1971). Carpenter (1980) described the secondorder transformation from P2/n to C2/c space groups in omphacite and suggested a phase diagram for the solvus omphacite (P2/n) and jadeite (C2/c) and the solvus omphacite (P2/n) and augite (C2/c). Subsequently, Holland (1983) suggested the presence of a jadeiteomphacite gap for temperatures lower than 450°C. Then, based on Landau theory, Carpenter et al. (1990),provided thermodynamic models for the order/disorder transition in omphacite. In addition, from the observed coexistence of C2/c omphacite and P2/n omphacite, Enami and Tokonami (1984) proposed a model of a first-order transformation in the epidote amphibolite facies. In accordance with the suggestion that the aegirine component enlarges the field of ordered P2/n clinopyroxene (Carpenter, 1980), the observed compositional gap is narrower at higher aegirine contents, and is restricted to compositions with aegirine < 30 mole %.

The extension of the compositional gap from Jd-Omp towards the Jd-Aeg join was observed in metabasite of the Maritime Alps (Cortesogno *et al.*, 1979). The gap was further confirmed by Maruyama and Liou (1987) on the evidence that, in clinopyroxene from Ward Creek metabasite, the miscibility gap extends at a lower temperature to the $Jd_{26}Aug_8Aeg_{66}$ point (fig. 8 B) and is progressively reduced with increasing temperatures at a higher metamorphic grade. The existence of a gap between jadeite and aegirine, which have the same space group C2/c, can only be explained



Figure 8 – Compositional gaps inferred for increasing metamorphic conditions in metabasite from Ligurian Alps; estimated temperatures and pressures are: I) 300° <T<350°C, P=0.8 GPa (CVM); II) T≈400°C, P≥1.3 GPa (PC); III) 400° <T<450°C, P>1.3 GPa (CP); IV) 450° <T<600°C; P>1.3 GPa (BP, ET, TV). A) space groups and miscibility gaps in the jadeite-aegirine-Quad system proposed by Carpenter (1980). B) Compositional gap between coexisting clinopyroxenes observed by Maruyama and Liou (1987) in middle lawsonite zone of Ward Creek metabasite. C-E) Compositional gaps deduced by Maruyama and Liou (1987) on basis of analysed compositions of clinopyroxene from the Ward Creek metabasite according to Carpenter's model. C: Epidote zone (250°<T<350°C, 0.7<P<0.8 GPa); D', D': upper and lower pumpellyite zones (200°<T<250°C; 0.6<P<0.7 GPa); E', E'': upper and lower and middle lawsonite zones (T≈ 150°C, P ≈ 0.4 GPa).

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by the large disparity in ion radii between Al and Fe³⁺. Our compositional gap extends in lower metamorphic conditions from omphacite-jadeite to jadeite-aegirine joins, and becomes smaller with increasing pressure and temperature (fig. 8 I-IV). This may be explained by the interference of a jadeiteomphacite miscibility gap according to the model of Carpenter, which was expanded by Maruyama and Liou (1987; fig. 8 C-E) with a jadeite-aegirine solvus.

The data of the present study suggest a compositional gap extending from the Omp-Jd join to the Jd-Aeg join (fig. 8 I-III) and confirm that this gap closes with increasing pressure and temperature. At temperatures exceeding 450°C, pyroxene is mostly omphacite and the gap between omphacite and jadeite closes. Fig. 6 shows the resulting compositional gap between omphacite and calcic pyroxene. In medium-grade units (T $\approx 500^{\circ}$ C; Beigua Ponzema, Erro Tobbio and Torrente Visone Units) between omphacite and the Quad ($Q \ge$ 80) field a relatively wide compositional gap occurs, even when Na-Ca pyroxenes occur with metamorphic diopside as a consequence of bulk rock control. However, this gap tends to disappear with increasing aegirine. In highergrade eclogites (T \geq 700°C; pre-Variscan eclogite), depending on bulk rock composition, omphacite attains compositions close to the Q=80 boundary. The existence of a gap in the proximity of the Jd-Quad join (low aegirine) for temperatures lower than $\approx 700^{\circ}$ C may fit the omphacite-Quad solvus of Carpenter (1980) and Enami and Tokonami (1984).

CONCLUDING REMARKS

The mineral chemistry of Na-Ca clinopyroxenes from the Ligurian Alps gives insights on the control of metamorphic parameters, bulk rock compositions, and chemical sites. Compositional gaps restricted to lower metamorphic grades may also be deduced.

In lower metamorphic conditions, largely incomplete re-equilibration arises from the site heritage and evident compositional zoning. More homogeneous compositions result from increased equilibration, ruled by deformation intensity and increase in metamorphic grade. At relatively low temperatures, compositions fall within the jadeite field, or within the aegirine and aegirine augite fields which commonly occur in the same rock. In the case of contact between pyroxenes of different composition, convergence is observed towards the boundaries (increase of aegirine in jadeite and of jadeite in aegirine). The persistence of a compositional gap between grains in contact suggests the existence of a solvus. For relatively higher temperatures, the zoning tends to disappear, and sodic pyroxene with omphacite compositions become stable. The miscibility gap between jadeite-rich and aegirine-rich terms is reduced and tends to disappear, and a gap along the jadeite-Quad join is evidenced between omphacite and omphacite-rich jadeite. The width of the gap appears to be restricted as aegirine contents increase.

In accordance with predictions based on crystallographic data (Carpenter, 1980; Enami and Tokonami, 1984), the miscibility gap between jadeite and omphacite disappears at temperatures exceeding 450°C.

A compositional gap between omphacite and calcic pyroxene, predicted on a crystallographic basis (Carpenter 1980; Enami and Tokonami, 1984) corresponds to the compositional gap which tends to be reduced only in eclogite equilibrating at $T > 700^{\circ}C$.

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