

Na-metamorphic pyroxenes in low-grade metabasites from the External Zones of the Betic Cordilleras (southern Spain): influence of rock chemical composition on their formation

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ABSTRACT

Abundant metabasite blocks are present in the argillaceous sediments of the 'Trias de Antequera' unit, in the External Zones of the Betic Cordilleras (southern Spain). Two different geochemical affinities have been identified in these metabasites: one tholeiitic and the other transitional-alkaline. Na-rich metamorphic pyroxenes are present in both types of metabasites, although with different textural arrangement and chemical characteristics. In the tholeiitic metabasites Na-pyroxene is always present in veinlets, associated with albite and quartz. Compared to the fresh augite from which they derive, these pyroxenes are richer in Al_2O_3 , FeO_{tot} and Na_2O , and poorer in TiO_2 , MgO and CaO . In the transitional-alkaline metabasites, the metamorphic pyroxenes result from epitaxial replacement of primary Ti-rich augite. This replacement may be complete, but always preserving the original ophitic texture. These metamorphic pyroxenes are richer in SiO_2 , FeO_{tot} and Na_2O , and poorer in TiO_2 , Al_2O_3 , MgO and CaO than the primary ones. The jadeitic contents in both types of metamorphic pyroxenes are similar, with maximum values of ca. 15-19%. As the maximum P-T conditions of metamorphism estimated for the tholeiitic and transitional-alkaline metabasites are very close, the influence of primary rock composition is advocated to explain the chemical differences between the two types of metamorphic pyroxenes.

Key words: Na-pyroxene, Low-grade metamorphism, Metabasites, Betic Cordilleras, Spain.

RESUMEN

Piroxenos sódicos metamórficos en metabasitas de bajo grado de las Zonas Externas de las Cordilleras Béticas (sur de España): influencia de la composición química de la roca en su formación. Numerosos bloques de metabasitas aparecen entre los sedimentos arcillosos del 'Trias de Antequera', en las Zonas Externas de las Cordilleras Béticas (sur de España). En estas metabasitas se han evidenciado dos tipos de afinidades geoquímicas diferentes: una toleítica y otra transicional-alkalina. En ambos tipos aparecen piroxenos metamórficos ricos en sodio, pero con diferencias en cuanto a sus disposiciones texturales y a sus características químicas. En las metabasitas

toleíticas, los piroxenos sódicos aparecen siempre en venillas, asociados con cuarzo y albita. Con respecto a la augita fresca, los piroxenos metamórficos están enriquecidos en Al_2O_3 , FeO_{tot} y Na_2O , y empobrecidos en TiO_2 , MgO and CaO . En las metabasitas de afinidad transicional-alkalina, los piroxenos metamórficos son el resultado de un reemplazo epitaxial de las augitas titaníferas primarias. Este reemplazo puede llegar a ser completo, aunque conservándose siempre la textura óptica original. Estos piroxenos metamórficos están enriquecidos en SiO_2 , FeO_{tot} y Na_2O , y empobrecidos en TiO_2 , Al_2O_3 , MgO y CaO , comparado con los piroxenos primarios. El contenido en jadeíta de ambos tipos de piroxenos metamórficos es muy similar, con valores máximos próximos al 15-19%. Las condiciones máximas de P-T estimadas para ambos tipos de metabasitas son muy próximas, por lo que se invoca la influencia de la composición química de la roca original para explicar las diferencias observadas entre ambos tipos de piroxenos metamórficos.

Palabras claves: Piroxeno sódico, Metamorfismo de bajo grado, Metabasitas, Cordilleras Béticas, España.

INTRODUCTION

Na-clinopyroxenes are present as major phases in basic metamorphosed rocks, mainly in the blueschist facies and related eclogites, but rarely in low-grade metabasites. Maruyama and Liou (1985, 1987 and references therein) have described the presence of sodic metamorphic pyroxenes paragenetic with chlorite in metabasites from the pumpellyite-actinolite facies. On the other hand, the composition of metamorphic Na-rich pyroxenes is related to the extensive and intensive metamorphic parameters, *e.g.*, rock composition, pressure and temperature (Okay, 1978). The jadeitic content of Na-pyroxenes has been considered therefore as a good indicator of the P-T conditions of metamorphism (Essene and Fyfe, 1967).

With the exception of Lombardo *et al.* (1977), which have studied the formation of Na-metamorphic pyroxene in rocks with contrasted primary chemical compositions, few works have investigated the influence of bulk rock composition on the nature of these pyroxenes. This paper concentrates on the stability relations, nature and chemical composition of Na-pyroxene bearing metamorphic assemblages, developed in metabasite tectonic blocks with contrasted chemical composition, present in the External Zones of the Betic Cordilleras (southern Spain). The aim of this study is to show the influence of the primary whole-rock igneous composition on the generation of Na-pyroxenes in these low-grade metabasites.

GEOLOGICAL SETTING

The Betic Cordilleras, the Alpine mountain belt of southern Spain, comprise from south to north Internal and External Zones (Fig. 1a). The Internal Zone is considered as part of the 'Alboran Plate' (Andrieux *et al.*, 1971) and is characterized by the superposition of thrust sheets of Triassic and older metamorphic rocks. The External Zone represents the former continental margin of southern Iberia and consist of Mesozoic and Tertiary sediments with minor intercalations of basic rocks (García-Hernández *et al.*, 1980). The present thrust-contact between the Internal and External Zone originated during the Miocene orogeny.

Numerous outcrops of basic igneous rocks, corresponding to basalts and dolerites (hectometric

to kilometric in size), are found in the argillaceous materials of Triassic age (Keuper) in the External Zone of the Betic Cordilleras (Puga *et al.*, 1989; Morata 1993). These basic rocks, emplaced during the Triassic and Jurassic, correspond to volcanic and subvolcanic bodies which, due to the Alpine deformation, are now present as tectonic blocks whose original igneous contacts are not preserved. From their whole rock chemistry and primary clinopyroxene composition, Morata (1993) and Morata and Puga (1993) have found two different chemical affinities in these basic rocks: one tholeiitic (mostly represented by volcanic rocks) and the other of transitional-alkaline character (always as subvolcanic bodies).

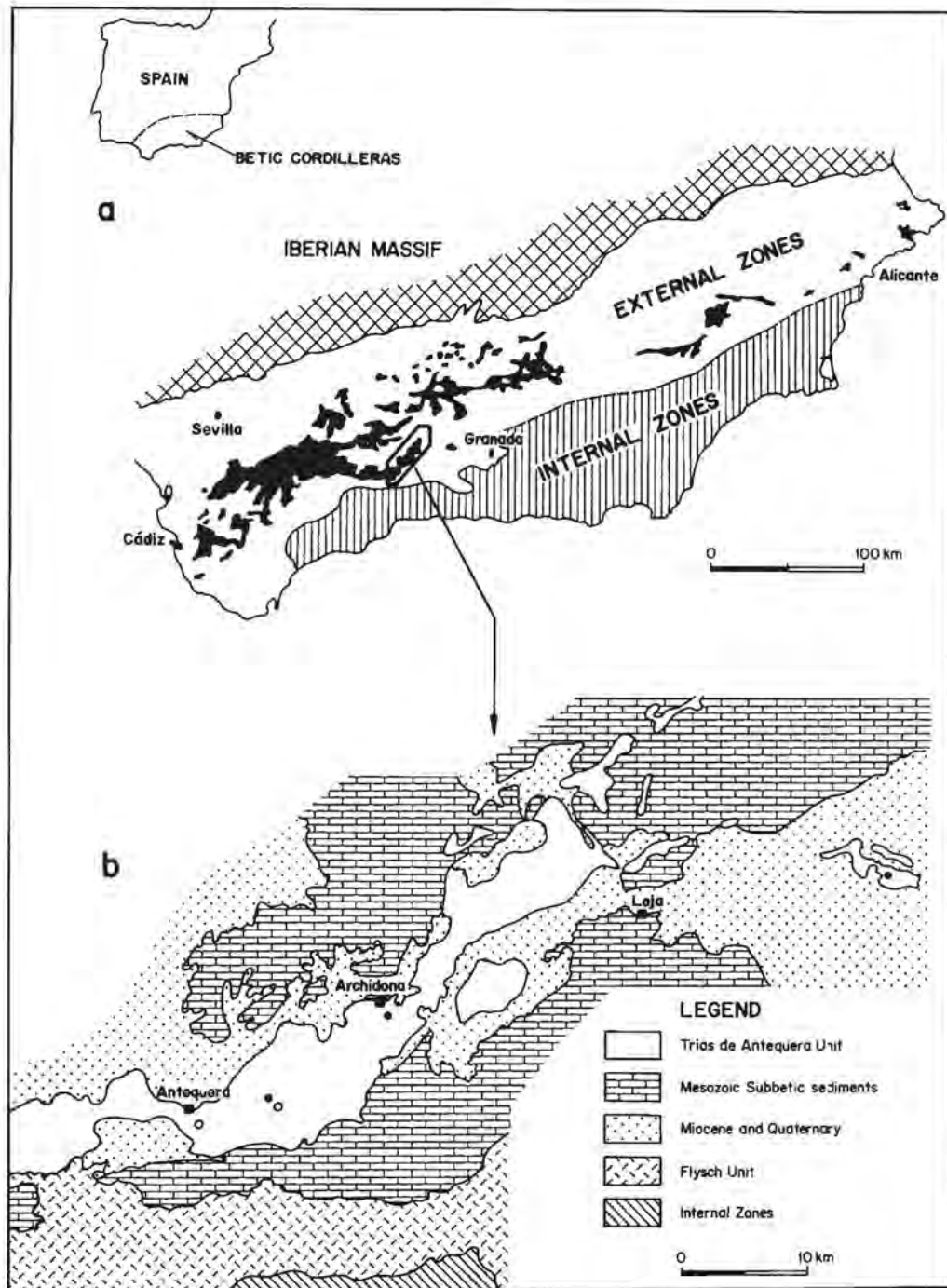


FIG. 1. a- geological simplified map of the Betic Cordilleras, showing the sedimentary Triassic outcrops in black (after Azema *et al.*, 1979, modified), inside which the basic rocks described are found. The marked area corresponds to the 'Trias de Antequera' unit; b-simplified geological map of the 'Trias de Antequera' unit, showing the location of the main metabasite blocks bearing Na-metamorphic pyroxenes. Open circles: metabasites with tholeiitic affinity. Black circles: metabasites with transitional-alkaline affinity. Geological map taken from Junta de Andalucía (1985), modified.

PRIMARY MINERALOGY

The primary mineralogy of the basic rocks is slightly different between the tholeiitic and the transitional-alkaline basaltic and doleritic types (Morata, 1993). In the **tholeiitic basalts and dolerites**, calcic plagioclase (An_{80-45}) and augite ($Wo_{36}En_{52}Fs_{12}$ to $Wo_{37}En_{39}Fs_{24}$) are the major components, with minor orthopyroxene ($Wo_{4.5}En_{75.5}Fs_{20}$ to $Wo_5En_{76}Fs_{19}$) in the less differentiated samples. Pigeonite ($Wo_8En_{68}Fs_{24}$ to $Wo_{10}En_{53}Fs_{37}$) appears also as a minor phase associated with augite. Amphibole, biotite and Fe-Ti ores are accessory minerals. These basic rocks are characterized by the presence of quartz as isolated crystals or intergrown with sodic plagioclase in the

more differentiated rocks. In the **transitional-alkaline basalts and dolerites**, the primary mineralogy consists of plagioclase (An_{70-50}) and Ti-rich clinopyroxene ($Wo_{46}En_{39}Fs_{15}$ to $Wo_{47}En_{31}Fs_{22}$). Minor olivine (Fo_{72-66}) appears in the more primitive basalts. Ti-rich amphibole, phlogopitic biotite and Fe-Ti ores are accessory minerals. Primary quartz is absent in this transitional-alkaline protolith.

Trace elements, REE patterns and discriminant trace element ratios are compatible with a continental extensional setting for this Mesozoic magmatism (Puga *et al.*, 1989; Morata, 1993).

GENERAL METAMORPHIC PATTERN

The rocks from the External Zone of the Betic Cordilleras have been classically considered as unmetamorphosed (*e.g.* De Smet, 1984). However, very low-grade metamorphic assemblages, corresponding mainly to the prehnite-actinolite, prehnite-pumpellyite and pumpellyite-actinolite facies, have been recently recognized in the basic rocks present into the Triassic sediments. This very low-grade metamorphism is nondeformational, and has preserved the original textures and igneous structures (Puga *et al.*, 1988; Morata *et al.*, 1992; Aguirre *et al.*, 1993; Morata, 1993). Moreover, in the unit known as 'Trias de Antequera', close to the boundary between the External and Internal Zones (Fig. 1a and 1b), the metamorphism of the basic rocks is in the pumpellyite-actinolite facies. This Triassic unit is characteristically chaotic, with numerous tectonic 'exotic

blocks' of different ages and lithologies, resembling a tectonic 'melange' (Morata *et al.*, 1992; Morata, 1993). Both tholeiitic and transitional-alkaline dolerites, with a random geographical distribution, are present as tectonic blocks in the 'Trias de Antequera' (Fig. 1b). Some of these basic rocks have Na-pyroxene and Na-amphibole in their metamorphic parageneses (Puga *et al.*, 1983; Morata *et al.*, 1992; Morata, 1993). Na-pyroxene is represented in both tholeiitic and transitional-alkaline types, although with different textural patterns. Relics of igneous pyroxene and, occasionally, amphibole are the only primary minerals preserved in these metabasites. Geothermobarometric studies carried out on some metabasic blocks from the 'Trias de Antequera' indicate maximum pressures in the interval 4-5 kb and temperatures close to 300°C (Morata *et al.*, 1992).

METAMORPHIC MINERALOGY

Primary igneous ophitic, subophitic and doleritic textures are always preserved in the metabasites contained in the Triassic sediments of the 'Trias de Antequera'. The metamorphic minerals most frequently represented are pumpellyite, actinolite, chlorite, epidote, titanite, white mica and scarce prehnite. Albite and quartz are ubiquitous and all the plagioclases

are albitized. These metamorphic minerals are found in different microdomains, *e.g.* replacing primary minerals, in the groundmass and filling veinlets. Pumpellyite is the most frequent metamorphic mineral in the tholeiitic metabasites but is rarely found in the transitional-alkaline metabasite blocks. In addition, Na-pyroxene, Na-amphibole and (Na-Ca) amphiboles

are also found. In the tholeiitic metabasites, Na-pyroxene is only present in veinlets, associated with chlorite+albite+quartz and, more rarely, (Ca-Na) amphiboles. In the transitional-alkaline metabasites light green Na-pyroxene grew as epitaxial replacement of primary pinkish, Ti-rich, clinopyroxene. The primary ophitic texture is preserved even when the replacement

is total. Chlorite and titanite are associated with the Na-pyroxene and, occasionally, a blue amphibole overgrows the Na-pyroxene (Puga *et al.*, 1983; Morata *et al.*, 1992). The metamorphic assemblages and the mineral compositions characterize the metamorphic conditions of the pumpellyite-actinolite facies.

PYROXENE CHEMISTRY

Chemical analyses of pyroxene were performed on a CAMEBAX microprobe, at the University of Montpellier (France), the analytical conditions being: 15 kV, 10 to 12 nA, 20s counting and beam width of 1 μ . Back-scattered images and mapping for Ca were obtained with a Zeiss DSM-950 scanning electron microscope equipped with a link analytical EDAX, at the Servicios Tecnicos of the Universidad of Granada

(Spain). Selected microprobe analyses and calculated structural formulae of both, igneous and metamorphic pyroxenes, are given in table 1. Fe^{3+}/Fe^{2+} partition was calculated following Droop (1987). The Wo, En, Fs, Jd and Ac components were calculated according to Morimoto *et al.* (1988).

Pyroxene compositions are represented in the jadeite-acmite-augite diagram (Fig. 2). The jadeite

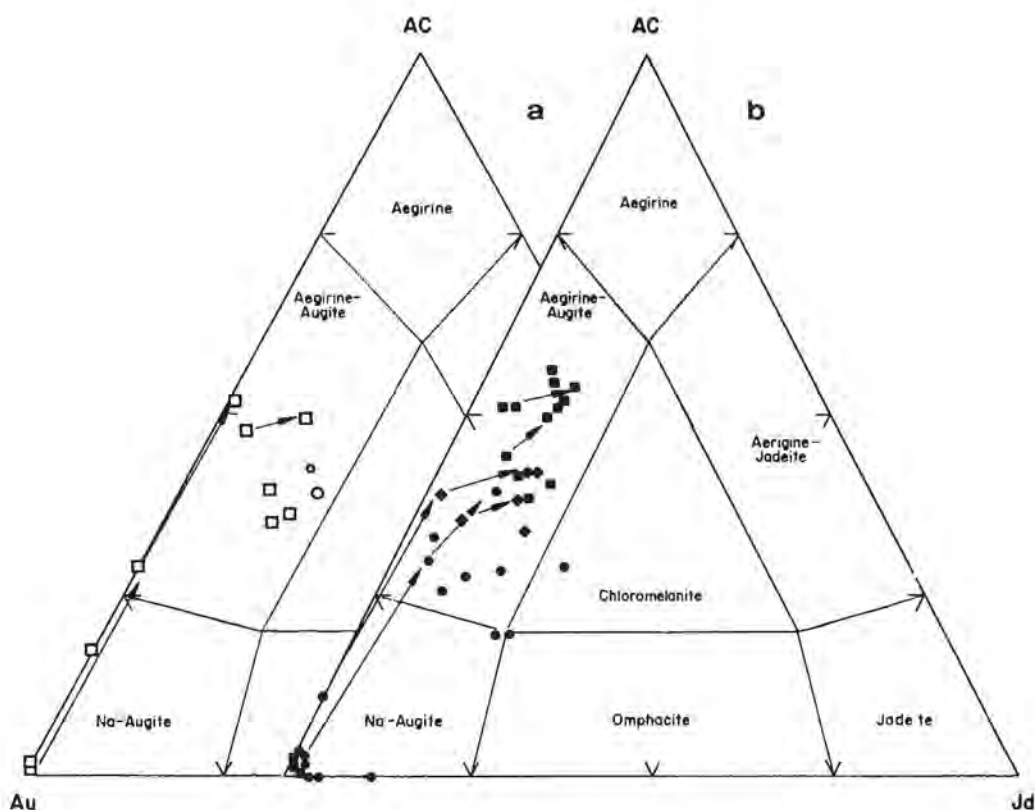


FIG. 2. Compositional variations of metamorphic pyroxenes from the 'Trias de Antequera' unit, expressed in terms of Ac, Au, Jd (Essene and Fyfe, 1967); a- pyroxenes from tholeiitic blocks, various open symbols; b- pyroxenes from transitional-alkaline blocks, various symbols in black. In both cases, the tie-line joins analytical points in the same crystal. Relic igneous pyroxenes are plotted in the Au (=QUAD) coin.

TABLE 1a. SELECTED MICROPROBE ANALYSES OF IGNEOUS (Cpx) AND METAMORPHIC (Na-Px) PYROXENE IN THE THOLEIITIC METABASITES.

POINT TYPE	162 Na-Px	163 Na-Px	58 Cpx	60 Na-Px	61 Na-Px	62 Cpx	63 Cpx	64 Cpx	65 Cpx	66 Na-Px	67 Cpx	82 Na-Px	83 Na-Px	84 Cpx	97 Cpx
SiO ₂	53.38	53.19	52.23	52.12	51.27	52.56	51.39	52.46	50.30	51.44	51.82	52.55	52.97	52.06	49.90
TiO ₂	0.06	0.19	0.32	0.00	0.00	0.27	0.00	0.27	0.00	0.00	0.38	0.00	0.01	0.29	0.61
Al ₂ O ₃	3.76	3.35	1.84	3.80	4.50	1.82	0.75	2.11	0.08	1.63	1.78	4.04	4.36	2.11	2.09
Cr ₂ O ₃	0.00	0.02	0.05	0.02	0.00	0.23	0.00	0.20	0.00	0.06	0.00	0.00	0.00	0.00	0.00
FeO	17.68	18.70	8.46	20.97	18.87	7.84	17.24	7.92	20.02	22.31	11.78	16.19	16.71	10.34	14.48
MnO	0.06	0.06	0.32	0.14	0.17	0.09	1.70	0.20	1.52	0.54	0.27	0.30	0.16	0.30	0.20
MgO	5.35	4.97	17.31	3.74	5.96	18.37	6.73	17.86	5.18	3.77	16.46	6.06	5.62	17.53	13.64
CaO	9.18	8.77	19.40	9.23	11.01	18.49	20.69	18.97	17.53	11.06	17.96	12.71	11.97	17.82	17.91
Na ₂ O	8.67	8.84	0.25	8.81	6.82	0.19	2.23	0.19	3.86	7.65	0.22	6.91	7.44	0.18	0.24
K ₂ O	0.00	0.00	0.02	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.01	0.01
SUM	98.13	98.08	100.19	98.83	98.60	99.86	100.73	100.17	98.49	98.47	100.67	98.76	99.27	100.62	99.08
Structural formulae calculated on the basis of 6 oxygens															
Si	1.954	1.952	1.915	1.928	1.927	1.924	1.964	1.918	1.952	1.933	1.911	1.947	1.947	1.906	1.899
Al ^{IV}	0.046	0.048	0.080	0.072	0.073	0.076	0.034	0.082	0.004	0.067	0.078	0.053	0.053	0.092	0.094
Ti	0.002	0.005	0.009	0.000	0.000	0.008	0.000	0.007	0.000	0.000	0.010	0.000	0.000	0.008	0.017
Al ^{VI}	0.122	0.102	0.000	0.097	0.126	0.002	0.000	0.009	0.000	0.008	0.000	0.126	0.139	0.000	0.000
Fe ³⁺	0.273	0.288	0.090	0.434	0.439	0.066	0.203	0.067	0.287	0.401	0.095	0.317	0.320	0.094	0.092
Cr	0.000	0.001	0.002	0.001	0.000	0.007	0.000	0.006	0.000	0.002	0.000	0.000	0.000	0.000	0.000
Fe ²⁺	0.301	0.323	0.171	0.255	0.177	0.176	0.357	0.177	0.387	0.346	0.271	0.206	0.217	0.226	0.372
Mn ²⁺	0.002	0.002	0.010	0.005	0.005	0.003	0.055	0.006	0.051	0.018	0.008	0.010	0.005	0.009	0.007
Mg	0.302	0.282	0.946	0.211	0.334	1.002	0.383	0.973	0.304	0.218	0.905	0.339	0.313	0.957	0.774
Ca	0.373	0.358	0.762	0.375	0.444	0.725	0.847	0.743	0.738	0.459	0.710	0.512	0.480	0.699	0.730
Na	0.637	0.653	0.018	0.647	0.497	0.014	0.165	0.014	0.294	0.574	0.015	0.504	0.539	0.012	0.018
K	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000
Σ	4.013	4.015	4.003	4.025	4.023	4.001	4.010	4.001	4.016	4.025	4.004	4.014	4.014	4.003	4.004
En	24.17	22.54	47.80	16.50	23.88	50.84	20.77	49.51	17.19	15.10	45.49	24.53	23.47	48.22	39.18
Fs	46.01	48.89	13.70	54.22	44.41	12.37	33.34	12.70	41.03	53.06	18.83	38.48	40.60	16.55	23.84
Wo	29.82	28.57	38.50	29.28	31.71	36.78	45.89	37.79	41.78	31.83	35.68	36.99	35.93	35.23	36.98
QUAD	43.37	42.44	98.17	39.39	48.99	98.60	82.75	98.57	70.82	47.10	98.40	51.20	48.35	98.69	98.12
Jd	17.52	15.11	0.00	11.10	11.40	0.05	0.00	0.17	0.00	0.98	0.00	13.89	15.64	0.00	0.00
Ae	39.12	42.45	1.83	49.51	39.61	1.36	17.25	1.27	29.18	51.92	1.60	34.91	36.02	1.31	1.88

TABLE 1b. SELECTED MICROPROBE ANALYSES OF IGNEOUS (Cpx) AND METAMORPHIC (Na-Px) PYROXENES IN THE ALKALINE-TRANSITIONAL METABASITES.

POINT TYPE	68 Na-Px	162 Cpx	163 Na-Px	164 Cpx	166 Na-Px	167 Na-Px	168 Cpx	169 Cpx	170 Cpx	171 Na-Px	12 Na-Px	13 Na-Px	3 Cpx	51 Na-Px	53 Cpx	26 Cpx	27 Na-Px
SiO ₂	53.20	49.36	53.11	51.20	53.99	53.18	49.18	49.38	48.86	53.74	54.00	53.86	47.12	53.22	50.47	48.31	53.28
TiO ₂	0.05	1.77	0.06	1.08	0.00	0.07	1.63	14.3	1.57	0.00	0.00	0.00	2.53	0.01	0.63	1.41	0.06
Al ₂ O ₃	4.19	4.58	3.54	2.85	3.51	1.93	4.45	4.39	4.52	3.48	3.96	3.32	5.70	3.19	2.92	4.33	1.98
Cr ₂ O ₃	0.07	0.48	0.58	0.19	0.40	0.40	0.48	0.25	0.52	0.59	0.00	0.00	0.05	0.27	0.41	0.00	0.00
FeO	15.79	7.25	16.02	6.43	15.78	13.90	7.29	6.81	7.11	14.47	13.17	15.58	8.19	18.65	7.47	9.06	19.15
MnO	0.00	0.32	0.05	0.22	0.18	0.05	0.20	0.10	0.12	0.11	0.18	0.24	0.28	0.05	0.23	0.22	0.15
MgO	6.02	14.71	6.16	15.73	6.90	8.47	14.54	14.70	14.65	7.10	7.81	6.54	13.57	4.88	15.41	13.07	5.47
CaO	10.77	22.09	10.57	21.82	11.94	1.46	22.11	22.03	22.12	11.89	15.09	13.93	21.74	9.17	21.05	21.17	10.14
Na ₂ O	8.41	0.53	8.25	0.44	7.57	6.18	0.46	0.55	0.48	7.44	5.60	6.03	0.55	8.93	0.35	0.67	7.83
K ₂ O	0.01	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.11	0.01	0.00	0.00	0.01
SUM	98.21	101.09	98.34	99.94	100.27	98.34	100.34	99.65	99.93	98.82	99.81	99.50	99.82	98.38	98.95	98.23	98.06
Structural formulae calculated on the basis of 6 oxygens																	
Si	1.945	1.804	1.946	1.883	1.949	1.959	1.812	1.826	1.805	1.960	1.975	1.980	1.752	1.984	1.880	1.828	1.966
Al ^{IV}	0.055	0.196	0.054	0.117	0.051	0.041	0.188	0.174	0.195	0.040	0.025	0.020	0.248	0.016	0.120	0.172	0.034
Ti	0.001	0.049	0.002	0.030	0.000	0.002	0.045	0.040	0.044	0.000	0.000	0.000	0.071	0.000	0.018	0.040	0.002
Al ^{VI}	0.131	0.002	0.103	0.007	0.102	0.015	0.006	0.017	0.002	0.113	0.148	0.128	0.002	0.125	0.008	0.021	0.056
Fe ³⁺	0.327	0.120	0.326	0.076	0.304	0.244	0.111	0.110	0.125	0.243	0.152	0.120	0.147	0.529	0.090	0.120	0.202
Cr	0.002	0.014	0.017	0.006	0.012	0.012	0.014	0.007	0.015	0.017	0.000	0.000	0.001	0.008	0.012	0.000	0.000
Fe ²⁺	0.182	0.104	0.192	0.123	0.196	0.204	0.116	0.102	0.096	0.220	0.262	0.376	0.110	0.080	0.145	0.170	0.426
Mn ²⁺	0.000	0.010	0.002	0.007	0.006	0.002	0.006	0.003	0.004	0.003	0.006	0.008	0.009	0.002	0.007	0.007	0.005
Mg	0.337	0.802	0.345	0.862	0.379	0.476	0.799	0.810	0.807	0.396	0.433	0.368	0.752	0.272	0.856	0.738	0.314
Ca	0.421	0.865	0.426	0.860	0.472	0.572	0.873	0.873	0.875	0.477	0.601	0.563	0.866	0.366	0.840	0.858	0.419
Na	0.612	0.037	0.602	0.031	0.542	0.452	0.033	0.039	0.034	0.540	0.403	0.441	0.039	0.646	0.025	0.049	0.585
K	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.005	0.001	0.000	0.000	0.001
Σ	4.014	4.002	4.014	4.001	4.013	4.009	4.002	4.002	4.002	4.009	4.005	4.005	4.003	4.027	4.002	4.003	4.011
En	26.58	42.17	26.74	44.73	27.96	31.81	41.94	42.68	42.28	29.61	29.76	25.63	39.91	21.76	44.17	38.97	23.00
Fs	40.21	12.30	40.25	10.67	37.24	29.99	12.22	11.36	11.83	34.78	28.91	35.13	14.14	48.90	12.47	15.67	46.34
Wo	33.21	45.52	33.00	44.60	34.80	38.21	45.83	45.97	45.89	35.61	41.33	39.24	45.95	29.35	43.36	45.35	30.66
QUAD	43.43	95.95	44.48	96.75	49.13	58.10	96.48	95.81	96.28	50.29	61.62	59.70	95.64	35.72	97.31	94.72	49.76
Jd	16.14	0.06	13.31	0.27	12.76	6.56	0.17	0.56	0.05	15.82	18.92	20.73	0.06	12.27	0.23	0.79	10.91
Ae	40.43	3.99	42.21	2.98	38.10	35.34	3.36	3.64	3.67	33.88	19.46	19.57	4.30	52.01	2.46	4.49	39.33

content of the metamorphic pyroxenes from both, the tholeiitic and transitional-alkaline protoliths, increases up to a maximum of 19%, and the pyroxenes plot in the aegirine-augite field, close to the chloromelanite field. Both types of Na-pyroxene have high aegirine contents (a maximum of 50%), indicative of a relatively high fO_2 at the time of formation. However, some differences exist concerning the chemistry and textural nature of the Na-pyroxenes from the two primary protoliths.

SODIC PYROXENES IN THE THOLEIITIC METABASITES

Na-pyroxenes are present in two different textural arrangements, but always in relation to veinlets filled with albite and quartz (and less frequently pumpellyite). Na-pyroxene appears most commonly as a bright-green material adjacent to the vein wall where the vein is in contact with primary augite (Fig. 3). However, in some cases, small subidiomorphic green Na-pyroxene crystals (50-100 μm), form without direct contact with a primary augite.

Na-pyroxenes have higher Na_2O contents (up to 10% wt) and lower CaO contents than primary augite (Fig. 4a). As an increase of the Na_2O content of the pyroxene can be considered as a parameter indicative of a secondary event in the tholeiitic systems, those elements which have a high correlation index with

Na_2O would be also related to these secondary events. Table 2a gives the correlation index between the different oxides present in the pyroxenes. Together with Na_2O , the Al_2O_3 and the FeO_{tot} also increase (from 1.8% in the fresh augite to ca. 5% in the green pyroxene for the Al_2O_3 and from ca. 8% to 18-20%, for the FeO_{tot}). On the other hand, a decrease in TiO_2 (from 0.3% to nil), MgO (from 17-19% to 3%) and CaO (from 10% to 6%) occurs, as also shown in figure 4a, b and c. Only a slight increase in SiO_2 has been observed between fresh augite and Na-pyroxene in the tholeiitic metabasites, as shown by the change in Al^{IV} contents (Fig. 4d). Similar variations have been found by Badger and Sinha (1986) in clinopyroxenes from basalts metamorphosed in the greenschist facies containing relics of igneous pyroxene. In the latter case, the secondary pyroxenes are found in the margins and in cross-cutting fractures in the primary pyroxene, and they are richer in FeO and Al_2O_3 and poorer in MgO, CaO and SiO_2 as compared to fresh augite.

Na-pyroxenes from the metabasites studied are texturally very similar to those found in the altered oceanic basalt of hole 504B (Laverne, 1987), although some important chemical differences exist. Thus, in the green Na-rich pyroxene from southern Spain, Ca strongly decreases, Ti does not increase, and the Al content is higher with respect to fresh augite. On the contrary, in the pyroxenes from hole 504B (Laverne 1987), Ca is rather constant, but the secondary

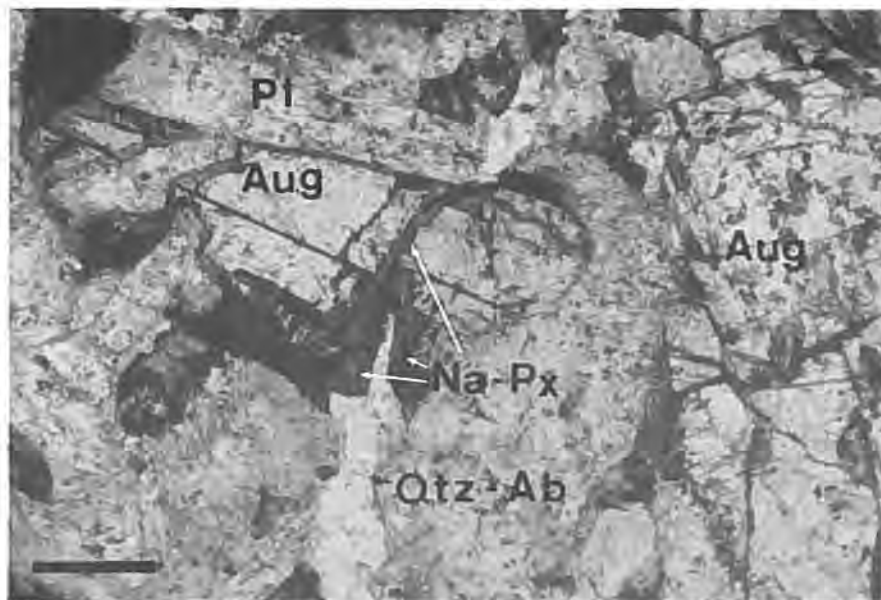


FIG. 3. Microphotography of Na-pyroxene developed in a veinlet in tholeiitic metabasite. Scale: 200 μm ; Ab: albite; Aug: primary augite; Na-Px: sodium-rich metamorphic pyroxene; PI: primary plagioclase; Qtz: quartz.

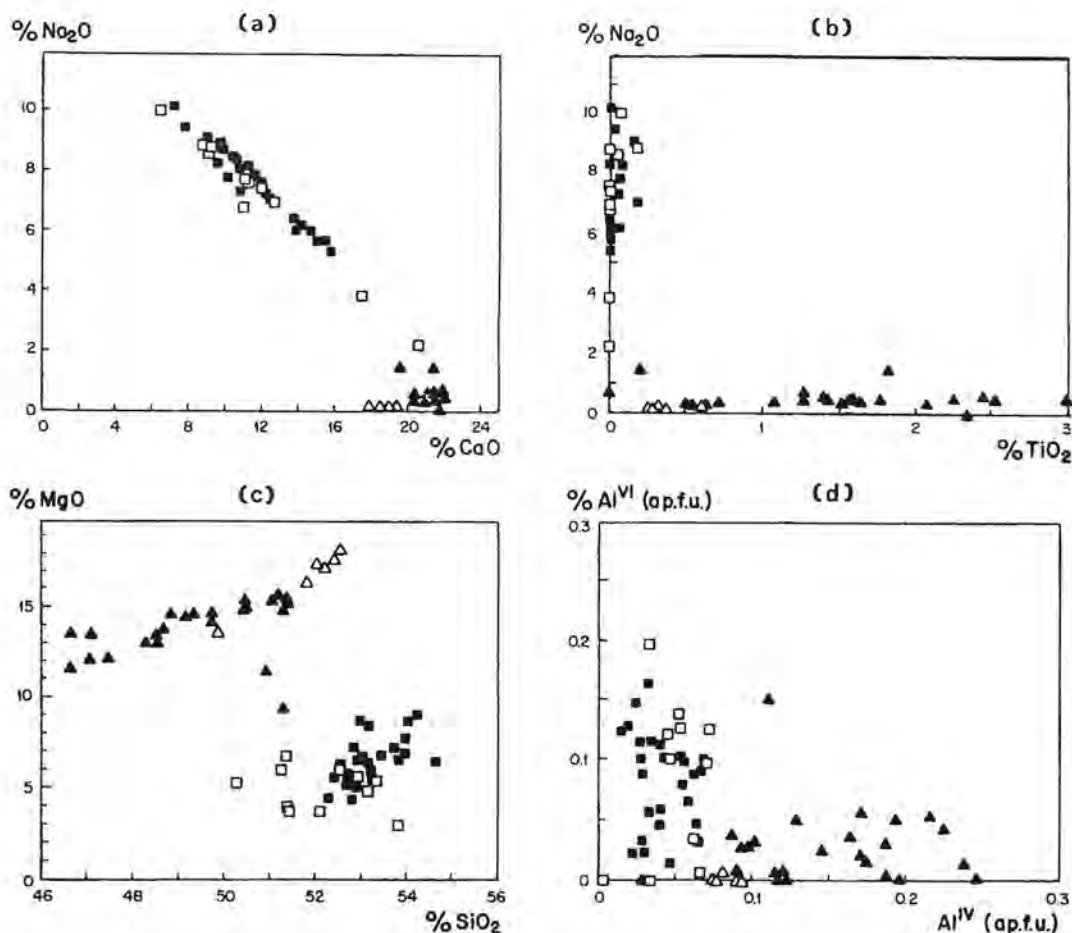


FIG. 4. Chemical variation between igneous pyroxenes (triangles) and metamorphic pyroxenes (squares). Pyroxene from tholeiitic metabasites in white and those from transitional-alkaline metabasites in black.

pyroxene is richer in Ti and poorer in Al than the fresh augite. The aegirine content of the secondary pyroxene is similar in both cases, but the jadeitic content is negligible in the altered oceanic basalt.

SODIC PYROXENES IN THE TRANSITIONAL-ALKALINE METABASITES

In the transitional-alkaline metabasites, Na-pyroxene always occurs as replacement of primary Ti-rich augite (Fig. 5a). This replacement can be complete, preserving the original ophitic texture, but in some cases relics of igneous pyroxene are still present (Fig. 5a, 5b). Previous studies by Morten and Puga (1983) concern the chemistry and the

crystallography of this Na-pyroxene. These authors have evidenced the cationic exchange of Ca by Na, the metamorphic origin of the Na-rich pyroxenes and have related their formation to a possible Late Cretaceous subduction stage during the geodynamic evolution of the Betic Cordilleras.

As in the case of the Na-pyroxene developed in the tholeiitic metabasites, FeO_{tot} increases, whereas, TiO₂, MgO and CaO decrease when Na₂O increases. On the contrary, Al₂O₃ decreases and SiO₂ increases strongly when Na₂O increases (Table 2b and Fig. 4a, b, c). This contrasting behaviour of the SiO₂ is easily explained by the silica oversaturation of the tholeiitic metabasites (presence of quartz in the CIPW norm). In this case, the SiO₂ content of the primary pyroxenes

TABLE 2. CORRELATION COEFFICIENT MATRIX FOR THE OXIDE COMPONENTS OF CLINOPYROXENES FROM:
a- the tholeiitic metabasites; b- the transitional-alkaline metabasites.

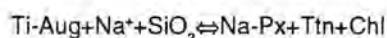
a	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O
SiO ₂	1.000									
TiO ₂	-0.179	1.000								
Al ₂ O ₃	0.139	-0.229	1.000							
Cr ₂ O ₃	0.064	0.247	-0.157	1.000						
FeO	-0.292	-0.641	0.345	-0.535	1.000					
MnO	-0.356	-0.313	-0.655	-0.217	0.204	1.000				
MgO	0.236	0.690	-0.511	0.437	-0.946	-0.132	1.000			
CaO	-0.528	0.496	-0.536	0.367	-0.551	0.405	0.505	1.000		
Na ₂ O	0.119	-0.688	0.689	-0.367	0.837	-0.211	-0.903	-0.785	1.000	
K ₂ O	0.591	0.005	-0.379	-0.135	-0.280	0.062	0.454	-0.315	-0.266	1.000

b	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O
SiO ₂	1.000									
TiO ₂	-0.882	1.000								
Al ₂ O ₃	-0.668	0.701	1.000							
Cr ₂ O ₃	-0.192	0.194	0.148	1.000						
FeO	0.735	-0.745	-0.458	-0.412	1.000					
MnO	-0.225	0.116	0.008	-0.146	-0.295	1.000				
MgO	-0.720	0.695	0.313	0.397	-0.977	0.337	1.000			
CaO	-0.786	0.758	0.372	0.271	-0.956	0.353	0.955	1.000		
Na ₂ O	0.805	-0.768	-0.386	-0.309	0.960	-0.331	-0.967	-0.992	1.000	
K ₂ O	-0.398	0.302	0.314	-0.127	-0.146	0.242	0.150	0.181	-0.181	1.000

is close to the maximum accepted by the pyroxene structure, with Si > 1.9 atoms p.f.u. (see Table 1a and Fig. 4d). In the transitional-alkaline metabasites (undersaturated in SiO₂ and with normative olivine), the SiO₂ content of the primary pyroxene is lower than in the tholeiitic metabasites, so it can increase through secondary processes (see Table 1b and Fig. 4d).

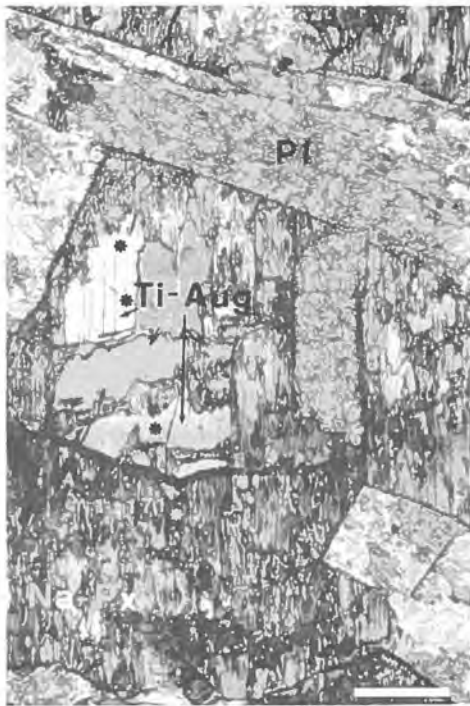
During metamorphism the TiO₂ content of the igneous Ti-clinopyroxene (up to 2% wt) is consumed (together with the CaO released from the same pyroxene) in the formation of titanite which appears as small crystals in the exfoliation surfaces of the Na-pyroxene (Fig. 5a, 5b). The Na content increases from the igneous pyroxene (0.03 atoms p.f.u.) to the metamorphic one (up to 0.53 atoms p.f.u.), as can be seen in figure 6. In figure 5c, mapping of the Ca content illustrates a relatively homogeneous distribution of this element throughout the Na-pyroxene. Figure 4a shows a progressive general increase in Na with decreasing Ca towards the rim in a same crystal (Fig. 6). This Na ↔ Ca exchange is accompanied by an increase in Si and a decrease in Al in the tetrahedral position, a typical feature of high pressure metamorphic pyroxenes (see Table 1 and Fig. 6). Na-pyroxenes have higher Al^{IV} content than

the igneous ones because, despite the general decrease in Al₂O₃ in the secondary pyroxene, the increase in Si enables most of the aluminium to enter the octahedral position. An 'ideal' ionic reaction to form this metamorphic pyroxene can be expressed as follows:



According to the results of Otten and Buseck (1987), the formation of Na-pyroxene should be characterized by cationic exchange of Mg²⁺ by (Al^{IV}+Fe³⁺) in the M1 position, and of Ca by Na in the M2 position. Carpenter and Okay (1978) have shown a similar ionic exchange between the igneous Ti-rich clinopyroxene and the Na-rich metamorphic pyroxene, with exchange of (Na+Al+Fe³⁺) by (Ca+Mg+Fe²⁺), and Si increase with Al^{IV} decrease in Turkish metadolerites. Aguirre (1977) and Shibakusa and Hirajima (1988) have found a similar transformation from primary alkaline-type pyroxene (Ti-rich augite) to Na-rich metamorphic pyroxene in the moderate to high pressure zone of the Kamuikotan metamorphic belt (Hokkaido, Japan).

a



b



c



FIG. 5. a- microphotography of Na-pyroxene overgrowing primary Ti-rich augite in a transitional-alkaline metabasite. Dots show the position of microprobe spot analyses. Igneous plagioclase is mainly pseudomorphosed by white mica; b- back-scattered electron image of the same pyroxene than in a clean zone corresponds to primary Ti-augite. White spots are titanite crystals developed by metamorphic reactions; c- X-Ray image for Ca content. Lighter zone is the igneous pyroxene relic. In the three cases, scale: 200 μm ; Na-Px: sodium-rich metamorphic pyroxene; PI: primary plagioclase; Qtz: quartz; Ti-Aug: titanium rich igneous augite; Ttn: titanite.

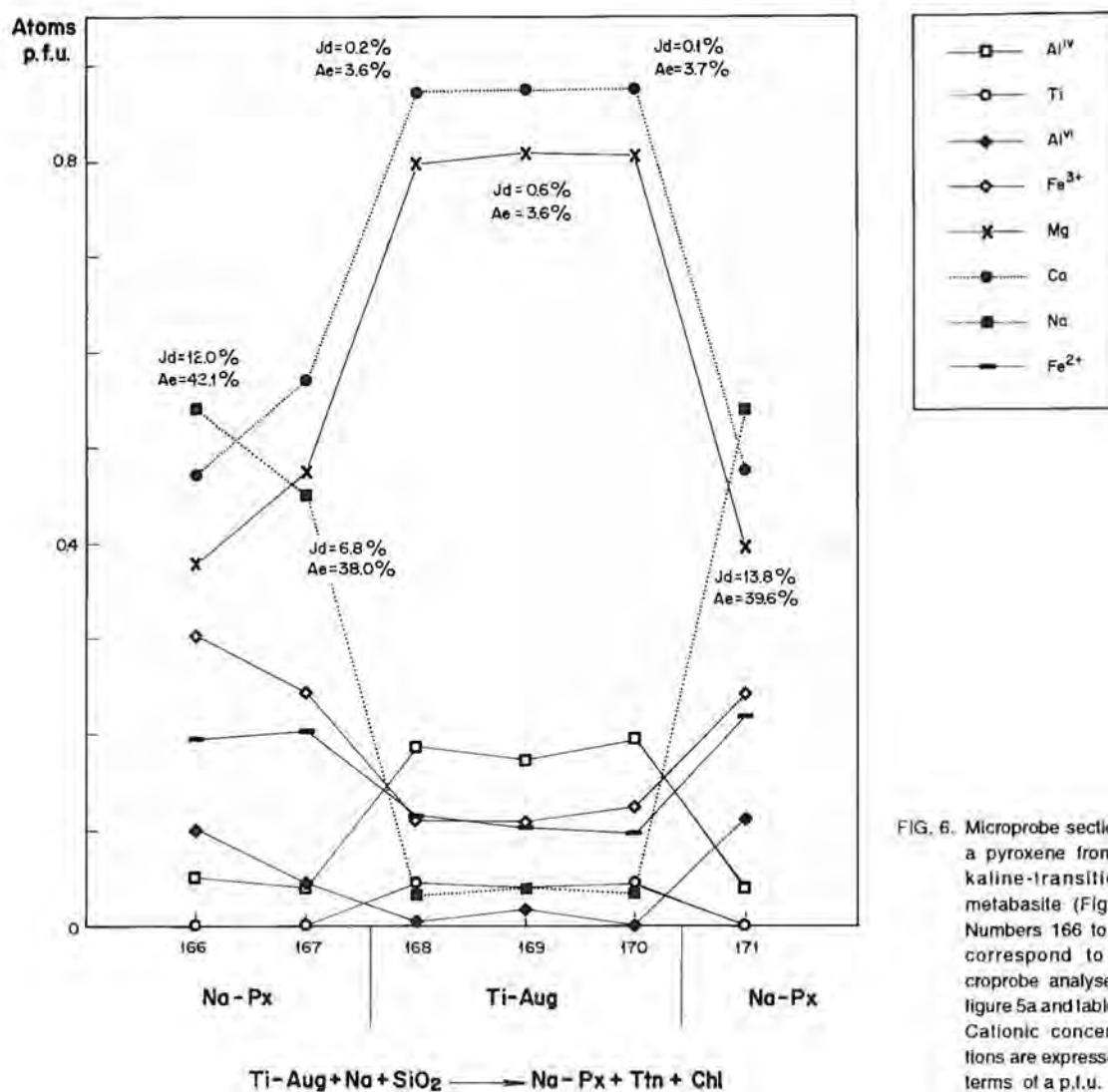


FIG. 6. Microprobe section in a pyroxene from alkaline-transitional metabasite (Fig. 5). Numbers 166 to 171 correspond to microprobe analyses in figure 5a and table 1b. Cationic concentrations are expressed in terms of a p.f.u.

GENETIC CONDITIONS

It is commonly accepted that the jadeite content of metamorphic pyroxenes increases with pressure (Liou *et al.*, 1987 and references therein). In fact, the Jd content can be considered as a good geobarometer, based on the transformation $Ab \leftrightarrow Jd + Qtz$ calibrated by Essene and Fyfe (1967) and Popp and Gilbert (1972). Assuming that in the Antequera zone Na-clinopyroxenes were in equilibrium with albite, the variations of their jadeite component could have been related to the P-T gradient. However, the metamorphic

pyroxenes studied here are not the result of the albite reaction above and so, the variations in their jadeite component could indicate only an approximate value of the pressure during their formation. For a temperature of 300°C obtained from chlorites (Morata *et al.*, 1992; Morata, 1993) the range of pressures considering the maximum Jd content (19%) is 4-5 kbar. Similar pressures were obtained (Morata *et al.*, 1992; Morata, 1993) with other geobarometers applied to metamorphic parageneses of these metabasites;

in particular, the crossite content of the calcic amphibole (Brown, 1977) and the experimental geobarometer for sodic amphiboles (Maruyama *et al.*, 1986).

These pressures are in good agreement with those estimated by other authors in areas where Na-rich metamorphic pyroxenes have been found. In fact, Na-rich metamorphic pyroxenes with a jadeitic content of about 15 to 20%, in metastable coexistence with igneous relic clinopyroxene, is a common feature in low-grade metabasites found in moderate to high pressure metamorphic terranes (Brown and Ghent, 1983; Brown, 1986; Sakakibara, 1986; Maruyama and Liou, 1987, 1988; among others). Na-pyroxene plus chlorite is a stable metamorphic association in metabasites formed under pumpellyite-actinolite and prehnite-pumpellyite facies conditions (Maruyama and Liou, 1985).

Based upon the previous assumptions and on the approximate P-T values obtained, it can be concluded that the physical conditions during the formation of the metamorphic pyroxenes were similar in both, the tholeiitic and transitional-alkaline metabasites. Due to the fact that these intensive physical parameters do not appear as a major factor controlling the different textural arrangements and chemical composition of the Na-metamorphic pyroxenes, it is necessary to imply another control. The different textural patterns of these pyroxenes would be a consequence of the contrasting chemical composition of the primary rocks and, notably, of the primary igneous pyroxene. In the very low-grade metamorphic processes, dominated by low temperature and low diffusion rates, the epitaxial overgrowth of a primary mineral phase will be easier than the nucleation of a new metamorphic mineral. Maruyama and Liou (1987) have shown how metamorphic clinopyroxene may appear in very low-grade blueschists only if the rock contains igneous pyroxenes. In such a low-T environment, igneous clinopyroxene apparently provided nuclei for the metamorphic clinopyroxene to grow and therefore the latter reflects

the composition of the original pyroxenes.

The igneous Ti-rich pyroxenes in the transitional-alkaline rocks have higher structural and chemical affinities with the sodic metamorphic pyroxenes than the igneous pyroxenes from the tholeiitic rocks. This explains the widespread replacement observed in the transitional-alkaline metabasites. In the tholeiitic rocks, on the contrary, Na-rich pyroxene, associated with Ab+Qtz, is restricted to fissures and veinlets, but never overgrows igneous pyroxene outside the veinlets. In these rocks, the formation of Na-pyroxene seems to be favoured by the presence of a Na-rich fluid phase during the metamorphic event. However, these Na-pyroxenes have a similar Na₂O content, with Jd close to 19% (Fig. 2), than those in the transitional-alkaline metabasites.

The Jd content and the chemical differences observed between Na-pyroxene in the tholeiitic metabasites and in oceanic basalts from hole 504B (Laverne, 1987) are a clear consequence of different conditions of formation. In the metabasites from the Betic Cordilleras a pressure component is involved in the formation of the secondary pyroxene, whereas the estimated temperature is lower than that in hole 504B. A high-T deuteritic origin is invoked for the Ti-rich augite-aegirine found in the altered oceanic basalts (Laverne, 1987). Meanwhile, a moderate pressure metamorphic event would explain the generation of Na-pyroxene in the metabasites from the 'Trias de Antequera'.

The behaviour of TiO₂ is also interesting to comment. Although Ti is classically considered as 'immobile' we have shown evidence of its intracrystal mobility; this mobility is higher in the transitional-alkaline metabasites. Nevertheless, the TiO₂ content is similar between metamorphosed and non-metamorphosed basic rocks of both chemical groups (Morata, 1993). Therefore, whole rock can be taken as a 'closed system' for TiO₂, and this element is considered as a discriminant for the magmatic affinity.

CONCLUSIONS

The presence of Na-pyroxene is interpreted as indicative of a moderately high pressure metamorphism in some areas of the External Zone of the Betic Cordilleras, in particular in the 'Trias de Antequera' unit. The metabasites from this unit are metamor-

phosed in the pumpellyite-actinolite facies. The chemical composition of the igneous protoliths determines the nature and textural arrangement of the metamorphic pyroxenes. In the tholeiitic metabasites, Na-pyroxenes are found in veinlets with albite and

quartz, mostly where these veins cut primary augite crystals. Na-pyroxene has developed at the contact with augite. Compared to the fresh augite, Na-pyroxenes are richer in Al_2O_3 , FeO_{tot} and Na_2O , and poorer in MgO , CaO and TiO_2 , whereas SiO_2 decreases only slightly. In the transitional-alkaline metabasites Na-pyroxenes are found as epitaxial replacement (topotactic?) of primary Ti-rich augite. This replacement may be total, although the original igneous ophitic texture is always preserved. The formation of epitaxial Na-pyroxenes through the $Na \rightleftharpoons Ca$ replacement is accompanied by a release of Ti. Na-pyroxenes are richer in SiO_2 and FeO_{tot} and poorer in MgO , Al_2O_3 , TiO_2

and CaO compared to fresh augite. The jadeitic content in both types of metamorphic pyroxenes is similar with maximum values between 15% and 19%.

The P-T conditions established from the Jd content in the Na-pyroxenes, or based on amphibole barometry and chlorite thermometry, are similar for both types of metabasites present in the 'Trias de Antequera' unit (P~4-5 kb and T~300°C). Therefore, the primary chemical composition of the protolith is considered to be the main cause of the contrasting chemical composition and textural arrangement of the Na-pyroxenes found in the tholeiitic and transitional-alkaline metabasites.

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REFERENCES

- Aguirre, L. 1977. Petrology of the Kamuikotan metamorphic belt at the Kamietanbetsu-Numaushi cross-section, Central Hokkaido, Japan: *In Comparative studies on the Geology of the Circum-Pacific orogenic belt in Japan and Chile. Japanese Society for Promotion of Science, First Report*, p. 125-149.
- Aguirre, L.; Morata, D.; Puga, E.; Baronnet, A.; Beiersdorfer, R. 1995 (In press). Chemistry and crystal characteristics of pumpellyite in a metadolomite from the Archidona region, Subbetic Cordillera, Spain. *Geological Society of America, Special Paper*.
- Andrieux, J.; Fortboté, J.M.; Mattauer, M. 1971. Sur un modèle explicatif de l'arc de Gibraltar. *Earth and Planetary Science Letters*, Vol. 12, p. 191-198.
- Azema, J.; Foucault, A.; Fourcade, E.; García-Hernández, M.; González-Donoso, J.M.; Linares, A.; Linares, D.; López-Garrido, A.C.; Rivas, P.; Vera, J.A. 1979. Las microfacies del Jurásico y Cretácico de las Zonas Externas de las Cordilleras Béticas. *Universidad de Granada, Servicio de Publicaciones de la Universidad de Granada*, 83 p.
- Badger, R.L.; Sirha, A.K. 1986. Low-grade metamorphism of basaltic rocks: chemical variations within clinopyroxene. *Geological Society of America, Abstracts with Programs*, Vol. 18, p. 531.
- Brown, E.H. 1977. The crossite content of Ca-amphiboles as a guide to pressure of metamorphism. *Journal of Petrology*, Vol. 18, p. 53-72.
- Brown, E.H. 1986. Geology of the Shusksan Suite, North Cascades, Washington, U.S.A. *Geological Society of America, Memoir*, Vol. 164, p. 143-154.
- Brown, E.H.; Ghent, E.D. 1983. Mineralogy and phase relations in the blueschist facies of the Black Butte and Ball Rock areas, northern California Coast Ranges. *American Mineralogist*, Vol. 68, p. 365-372.
- Carpenter, M.A.; Okay, A. 1978. Topotactic replacement of augite by omphacite in blueschist rocks from north-west Turkey. *Mineralogical Magazine*, Vol. 42, p. 435-438.
- De Smet, M.E.M. 1984. Wrenching in the External Zone of the Betic Cordilleras, southern Spain. *Tectonophysics*, Vol. 107, p. 57-79.
- Droop, G.T.R. 1987. A general equation for estimating Fe^{3+} concentrations in ferromagnesian silicates and oxides from microprobe analyses, using stoichiometric criteria. *Mineralogical Magazine*, Vol. 55, p. 431-435.
- Essene, E.J.; Fyfe, W.S. 1967. Omphacite in Californian

- metamorphic rocks. *Contributions to Mineralogy and Petrology*, Vol. 15, p. 1-23.
- García-Hernández, M.; López-Garrido, A.C.; Rivas, P.; Sanz de Galdeano, C.; Vera, J.A. 1980. Mesozoic paleogeographic evolution of the external zones of the Betic Cordillera. *Geologie en Mijnbouw*, Vol. 59, No. 2, p. 155-168.
- Junta de Andalucía. 1985. Mapa Geológico-Minero de Andalucía. *Consejería de Economía e Industria, Dirección General de Industria, Energía y Minas*. Escala 1:500.000.
- Lavigne, C. 1987. Unusual occurrences of aegirine-augite, fassaite and melanite in oceanic basalts (DSDP Hole 504B). *Lithos*, Vol. 20, No. 2, p. 135-151.
- Liou, J.G.; Maruyama, S.; Cho, M. 1987. Very low-grade metamorphism of volcanic and volcanoclastic rock-mineral assemblages and mineral facies. In: *Low Temperature Metamorphism*, (Frey, M.; editor). *Chapman and Hall*, p. 59-113. New York.
- Lombardo, B.; Compagnoni, R.; Fiora, L.; Faccinelli, A. 1977. Composition of some sodic pyroxenes from the eclogitic micaschists of Lower Val d'Aosta (Sesia-Lanzo zone, Western Alps): In High pressure-low temperature metamorphism of the oceanic and continental crust in the Western Alps. *Rendiconti della Società Italiana di Mineralogia e Petrologia*, Vol. 33, No. 2, p. 375-388.
- Maruyama, S.; Cho, M.; Liou, J.G. 1986. Experimental investigations of blueschist-greenschist transition equilibria; pressure dependence of Al_2O_3 contents in sodic amphiboles; a new geobarometer. *Geological Society of America, Memoir*, Vol. 164, p. 1-16.
- Maruyama, S.; Liou, J.G. 1985. The stability of Ca-Na pyroxene in low-grade metabasites of high-pressure intermediate facies series. *American Mineralogist*, Vol. 70, p. 16-29.
- Maruyama, S.; Liou, J.G. 1987. Clinopyroxene; a mineral telescoped through the processes of blueschist facies metamorphism. *Journal of Metamorphic Geology*, Vol. 5, No. 4, p. 529-552.
- Maruyama, S.; Liou, J.G. 1988. Petrology of Franciscan metabasites along the jadeite-glaucophane type facies series, Cazadero, California. *Journal of Petrology*, Vol. 29, p. 1-37.
- Morata, D. 1993. Petrología y geoquímica de las ofitas de las Zonas Externas de las Cordilleras Béticas. Ph.D. Thesis, *Universidad de Granada*, 342 p.
- Morata, D.; Puga, E. 1993. Los piroxenos de las doleritas triásicas de las Zonas Externas de las Cordilleras Béticas como indicadores petrogenéticos. *Sociedad Española de Mineralogía, Boletín*, Vol. 15, p. 175-187.
- Morata, D.; Puga, E.; Aguirre, L. 1992. Very low-grade metamorphism of triassic dolerites from the Archidona region, Subbetic Cordillera, Spain. In *The transition from Basalt to Metabasalt: Environments, Processes and Petrogenesis*. IGCP 294, *Abstracts*. California
- Morimoto, N.; Fabries, J.; Ferguson, A.K.; Ginzburg, I.V.; Ross, M.; Seifert, F.A.; Zussman, J.; Aoki, K.; Gottardi, G. 1988. Nomenclature of pyroxenes. *American Mineralogist*, Vol. 73, p. 1123-1133.
- Morten, L.; Puga, E. 1983. Augite to chloromelanite transformation in ophites from the Subbetic Zone, Betic Cordilleras, Spain. *Periódico de Mineralogía*, Vol. 52, No. 3, p. 355-367. Tivoli, Italy.
- Okay, A.I. 1978. Sodic pyroxenes from metabasites in the eastern Mediterranean. *Contributions to Mineralogy and Petrology*, Vol. 68, No. 1, p. 7-11.
- Otten, M.T.; Buseck, P.R. 1987. TEM study of the transformation of augite to sodic pyroxene in eclogitized ferrogabbro. *Contributions to Mineralogy and Petrology*, Vol. 96, p. 529-538.
- Popp, R.K.; Gilbert, M.C. 1972. Stability of acmite-jadeite pyroxenes at low pressure. *American Mineralogist*, Vol. 57, p. 1210-1231.
- Puga, E.; Morten, L.; Bondí, M.; Bargossi, J.M.; Ruiz-Cruz, M.D.; Díaz de Federico, A. 1983. Metamorphosed 'ophites' from the Archidona region, Subbetic Zone (Spain). *Estudios Geológicos*, Vol. 39, Nos. 5-6, p. 307-317.
- Puga, E.; Van de Fliert, J.R.; Torres-Roldán, R.L.; Sanz de Galdeano, C. 1988. Attempts of whole-rock K/Ar dating of Mesozoic volcanic and hypabissal igneous rocks from the Central Subbetic (southern Spain): a case of differential argon loss related to very low-grade metamorphism. *Estudios Geológicos*, Vol. 44, p. 47-59.
- Puga, E.; Portugal, M.; Díaz de Federico, A.; Bargossi, G.; Morten, L. 1989. The evolution of the magmatism in the external zones of the Betic Cordilleras during the Mesozoic. *Geodinámica, Acta*, Vol. 3, p. 253-266.
- Sakakibara, M. 1986. A newly discovered high-pressure terrane in eastern Hokkaido, Japan. *Journal of Metamorphic Geology*, Vol. 4, No. 4, p. 401-408.
- Shibakusa, H.; Hirajima, T. 1988. Jadeite from the Horokanai-Kamietanbetsu area in the Kamuikotan zone, Hokkaido. *Journal of Mineralogical and Petrological Economic Geology*, Vol. 83, p. 507-513.