

**Zeitschrift:** Schweizerische mineralogische und petrographische Mitteilungen = Bulletin suisse de minéralogie et pétrographie  
**Band:** 71 (1991)  
**Heft:** 2  
  
**Artikel:** Geochemistry of clinopyroxenes in plutonic and volcanic sequences from the Yanbian Proterozoic ophiolites (Sichuan Province, China) : petrogenetic and geotectonic implications  
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**DOI:** <https://doi.org/10.5169/seals-54360>

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## **Geochemistry of clinopyroxenes in plutonic and volcanic sequences from the Yanbian Proterozoic ophiolites (Sichuan Province, China): Petrogenetic and geotectonic implications\***

by Chuan Min Sun<sup>1</sup> and Jean Bertrand<sup>1</sup>

### **Abstract**

A geochemical study on clinopyroxenes in plutonic and volcanic sequences of the Middle Proterozoic ophiolites from Sichuan Province, China, has been undertaken by microprobe analysis. The sympathetic variations of Fe/Mg ratio between clinopyroxenes and their host rocks suggest that the clinopyroxene compositions can be used as a reliable indicator of the parent magma type. Al in clinopyroxenes correlates negatively with Si and positively with Ti.  $\Delta[\text{Ti}]/\Delta[\text{Al}]$  and  $\Delta[\text{Si}]/\Delta[\text{Al}]$  ratios (calculated from linear regression analysis on the cation numbers in structural formula) are very similar in plutonic (0.30 and -0.78, respectively) and volcanic (0.32 and -0.76, respectively) rocks, indicating a same mode of substitution ( $[0.6 \pm 0.04] \text{ Ti} + 2 \text{ Al} \rightleftharpoons \text{M}^{2+} + [1.6 \pm 0.04] \text{ Si}$ ) and a co-magmatic origin for the two sequences. In spite of an enrichment in Al and Ti, caused by the high cooling rate in some samples from the volcanic sequence, the overall chemical compositions of the analyzed clinopyroxenes display a tholeiitic affinity. These compositions are also comparable, in particular, to those of clinopyroxenes in plutonic and basaltic rocks of typical high-Ti Phanerozoic ophiolites, and even to those of clinopyroxenes from modern mid-ocean ridge rocks. This is in good agreement with the conclusions obtained from our petrographic and bulk geochemical studies on the elements resistant to alteration and metamorphism. The fact that the clinopyroxenes in the most Ti-enriched ferrogabbros are relatively poor in this element reveals that the high-Ti ophiolite magma would have reached, by differentiation, a stage of enrichment not only in Fe and Ti, but also in  $\text{SiO}_2$ ; thus, instead of entering the clinopyroxene structure, Ti would crystallize as titanomagnetite. This work provides some interesting geochemistry indications supporting the hypothesis that the petrogenetic and geodynamic processes accepted for the Phanerozoic ophiolites can also be applied to those of the Middle Proterozoic.

**Keywords:** Proterozoic ophiolites, high-Ti ophiolites, geochemistry, clinopyroxene, EMS analysis, Sichuan Province China.

### **Résumé**

Les clinopyroxènes des plutonites et volcanites des ophiolites du Protérozoïque moyen de Yanbian (Province du Sichuan, Chine), ont été analysés à la microsonde. La similitude des variations des rapports Fe/Mg entre clinopyroxènes et ceux de leurs roches hôtes autorise à considérer que la composition des clinopyroxènes peut être utilisée comme un bon indicateur de la nature originelle du magma. Les teneurs en Al des clinopyroxènes montrent une corrélation respectivement négative et positive avec celles en Si et Ti. Les rapports  $\Delta[\text{Ti}]/\Delta[\text{Al}]$  et  $\Delta[\text{Si}]/\Delta[\text{Al}]$  (calculés à partir de l'analyse de régression linéaire appliquée aux nombres de cations présents dans la formule structurale) sont très voisins entre plutonites (0,30 et -0,78, respectivement) et volcanites (0,32 et -0,76, respectivement). Cela indique un même mode de substitution ( $[0,6 \pm 0,04] \text{ Ti} + 2 \text{ Al} \rightleftharpoons \text{M}^{2+} + [1,6 \pm 0,04] \text{ Si}$ ) et une origine co-magmatique pour les deux séquences. Malgré l'enrichissement en Al et Ti de certains échantillons des volcanites, attribuable à une plus grande vitesse de refroidissement, les compositions des clinopyroxènes révèlent une affinité tholéiitique. Ces compositions sont, par ailleurs, en particulier comparables à celles des clinopyroxènes des ophiolites riches en Ti du Phanérozoïque, et même à celles des clinopyroxènes provenant de roches des dorsales médio-océaniques actuelles. Ces déductions sont en accord avec celles obtenues à partir de nos études pétrographiques et géochimiques des roches totales, en particulier sur les éléments réputés insensibles aux altérations et au métamorphisme. La relative pauvreté en Ti des clinopyroxènes dans les ferrogabbros, roches les plus riches en cet élément,

\* Contribution presented at the annual SSMP meeting, Geneva, October 4, 1990.

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révèle que le magma des ophiolites riches en Ti pourrait avoir atteint, par différenciation, un stade d'enrichissement non seulement en Fe et Ti, mais aussi en  $\text{SiO}_2$ ; de ce fait, le titane, au lieu d'entrer dans la structure du clinopyroxène, cristalliserait sous forme de titanomagnétite. Ce travail apporte plusieurs arguments en faveur de l'hypothèse selon laquelle les processus pétrogénétiques et géodynamiques envisagés pour les ophiolites phanérozoïques peuvent aussi s'appliquer à celles du Protérozoïque moyen.

## 1. Introduction

In the Phanerozoic, ophiolites are common. By contrast, Precambrian ophiolites are comparatively very restricted (DESMONS, 1985) and in most cases, the primary magmatic minerals have completely disappeared, particularly in the effusive rocks (cf. BODINIER et al., 1984; KONTINEN, 1987; HARPER, 1985; LEBLANC, 1976; DE WIT et al., 1987).

To our knowledge, no article dealing with these minerals in Precambrian ophiolites has been published until now.

It is known that the compositions of the magmatic minerals, even as relics, usually reflect the magma composition and crystallization conditions; therefore the post-magmatic overprint due to alteration and recrystallization can be neglected. Among these minerals, the clinopyroxenes are considered as good indicators not only for the magma type but also for the geotectonic environments of their host rocks (KUSHIRO, 1960; LEBAS, 1962; NISBET and PEARCE, 1977; LETERRIER et al., 1982; LOUCKS, 1990). This is due to their crystal chemistry and geochemical properties (compositional compatibility with magma, relatively wide range of crystallization temperature and stability, frequent occurrence in igneous rocks, etc.). For this reason, clinopyroxenes have been used in the investigations of both modern oceanic rocks (PRINZ et al., 1976; HODGES and PAPIKE, 1976; AYUSO et al., 1976; SCHWEITZER et al., 1979; HEBERT et al., 1983) and Phanerozoic ophiolites (CAPEDRI and VENTURELLI, 1979; BECCALUVA et al., 1980, 1989; ISHIWATARI, 1986; POGNANTE et al., 1982; HEBERT et al., 1989; HEBERT and LAURENT, 1989; LAURENT and HEBERT, 1989; COISH and CHURCH, 1979; SHERVAIS and KIMBROUGH, 1985).

The Yanbian Proterozoic ophiolites (YPO), which are exposed in Sichuan Province, still conserve relics of magmatic minerals, in particular of clinopyroxenes. In this paper, the compositions and the substitution formulas of the magmatic clinopyroxenes from the YPO plutonic and volcanic rocks have been investigated. In an attempt to discern the petrogenetic processes and geotectonic environments for the ophiolites, the compositions of the studied clinopyroxenes have been compared with those of clinopyroxenes in typical Phanerozoic ophiolites and modern oceanic rocks. This study should help to determine whether the magmatic processes and geodynamic models accepted for the

Phanerozoic ophiolites can also be applied to those of the Proterozoic.

## 2. Geological setting

A Late Proterozoic orogenic belt is exposed on the western rim of the Yangtse Craton (ZHANG et al., 1984; see Fig. 1). This belt, extending from north to south for about 700 km, comprises the following pseudo-stratigraphic units, from bottom to top:

(1) Archean crystalline basement, consisting of migmatites, granulites, amphibolites and gneiss.

(2) Middle Proterozoic folded metamorphic terrain, mainly composed of volcano-sedimentary rocks metamorphosed to the greenschist facies.

(3) Very-low-grade or non-metamorphic Sinian cover (Sinian: 570–850 Ma).

From the structural point of view, this belt can be simplified as being formed mainly by unit (2), which includes blocks of unit (1), covered discordantly by unit (3). The ophiolites in this belt are composed of tectonite peridotites, magmatic cumulates and volcanics (Fig. 2).

The YPO seem to occur as huge olistoliths within flysch formations in the western zone of unit (2), which are overlain discordantly by unit (3). These ophiolites consist of submarine volcanics including pillow lavas (1,006 ± 58.5 Ma, Rb–Sr, LI, 1984) and of plutonic cumulates (1,253 and 1,112 Ma for ultramafics and gabbros respectively, GEOLOGICAL TEAM 106, 1975) (Fig. 1). Only the crustal members in the ophiolite succession are present in the Yanbian area. The mantle section can be observed in Shimian area, about 300 km north to Yanbian, situated in the same orogenic belt (Fig. 2).

Due to the absence of a sheeted-dike complex between plutonic and volcanic sequences (Fig. 1), the problem arises whether the two sequences belong to the same magma type. Furthermore, the following questions should also arise: What are their magmatic affinities? What were their original geotectonic environments when compared to the Phanerozoic ophiolites and modern oceanic rocks? In general, the answers to these questions can be found by following two approaches: (1) petrographic considerations, with particular emphasis on the definition of the crystallization order of liquidus phases (CHURCH and RICCIO, 1977; SERRI, 1980, 1981; BECCALUVA et al., 1980), and (2) distribution and variation patterns for some alteration-resistant

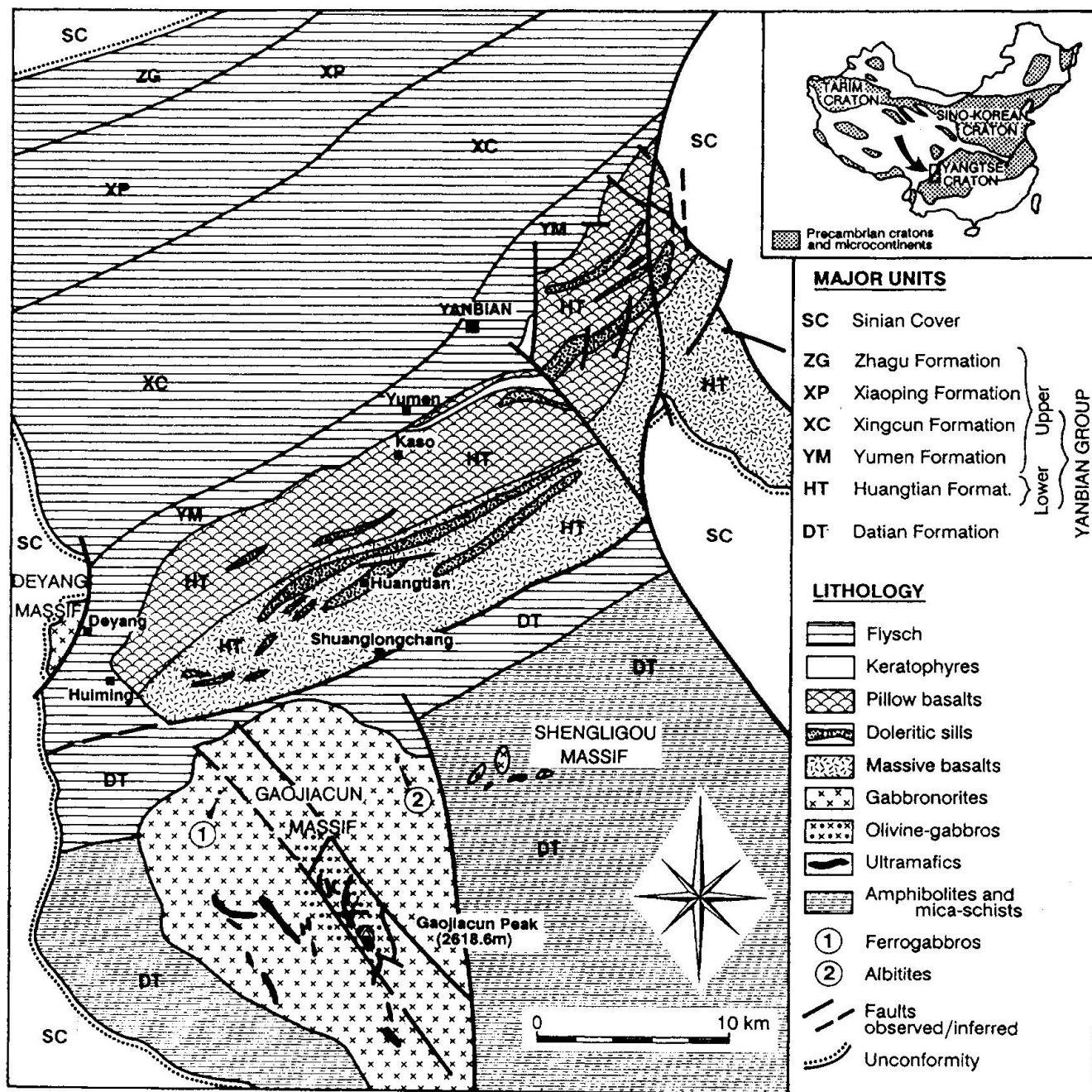


Fig. 1 Simplified geological map of the Yanbian area.

elements such as Ti, Zr, Y, V, Cr and Ni, as well as REE in the bulk compositions of rocks (PEARCE and CANN, 1973; PEARCE and NORRY, 1979; PEARCE, 1980; BECCALUVA et al., 1980; VENTURELLI et al., 1981; SHERVAIS, 1982).

However, as the YPO were mainly metamorphosed to the greenschist facies, the reliability of the interpretations based on these elements might be subject to debate if their immobility is not proved. Nevertheless, in spite of the alteration and metamorphism suffered by the ophiolites, relics of primary minerals, particularly clinopyroxenes, are observed in the plutonic rocks and in some samples

of the volcanic sequence. The study of these relics appears to be a more reliable approach to answer the questions raised above.

### 3. Sampling and analytical procedures

Representative rocks from both plutonic and volcanic sequences have been selected for the analytical work. The essential petrographic features of these samples are reported in table 1.

The microprobe analyses were performed with the ARL EMX-SM instrument of the University of



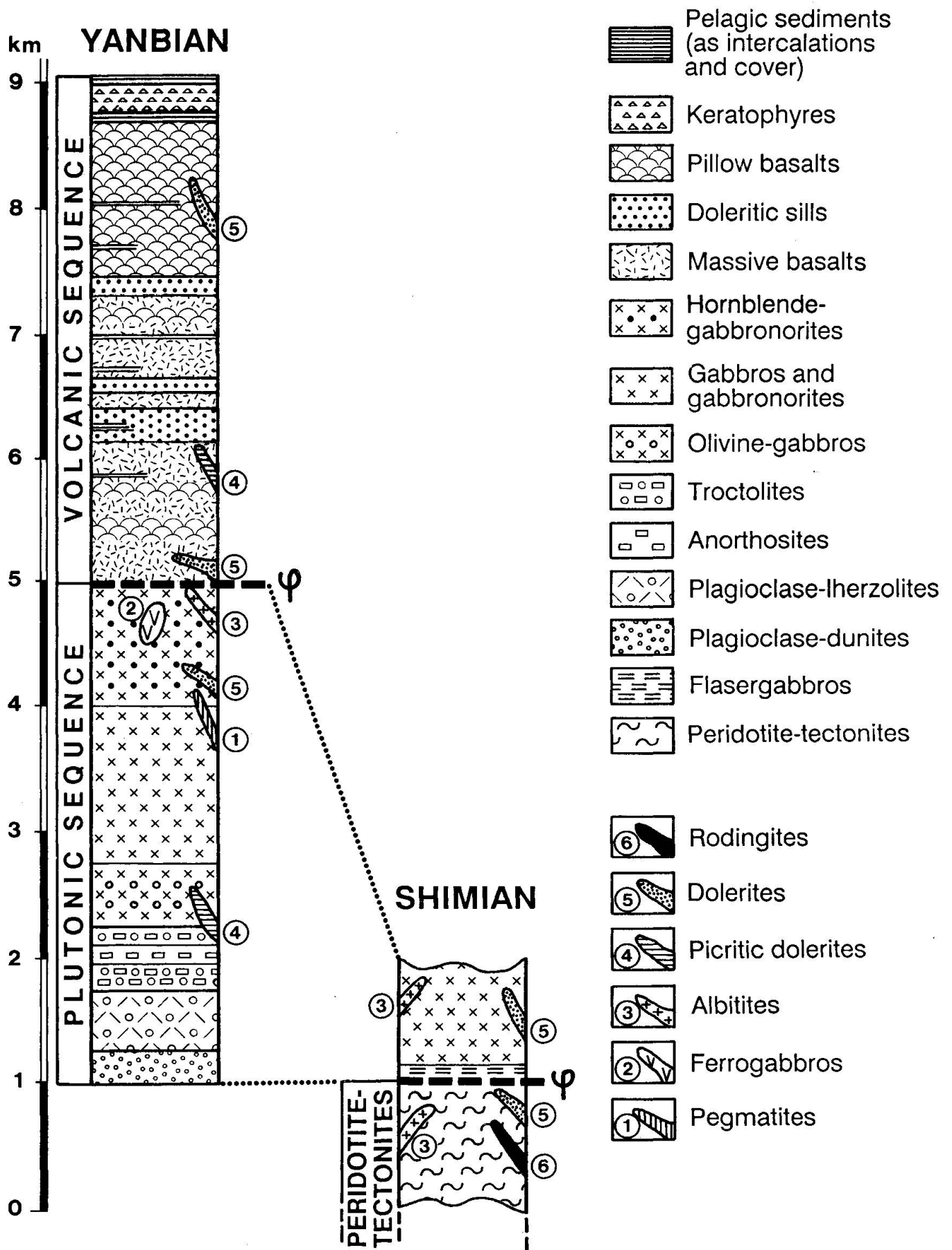


Fig. 2 Synthetic reconstruction of the ophiolite succession in the Yanbian-Shimian Late Proterozoic orogenic belt.

Tab. 1 Main petrographic characteristics of analyzed samples.

Sample No.	Rock type	Main magmatic minerals and textures	Characteristics of analyzed clinopyroxenes	Main secondary minerals
plutonic sequence	S-72 ultramafic cumulate	C: Ol (85%), Sp (2%) IC: Cpx (3%), Opx (5%), Pl (5%) mesocumulate	allotriomorphic (1-1.5 mm) alteration to green-Amph	Srp, Chl, Tlc, green-Amph, Act, Czo, Mag, Hem
	S-76 olivine gabbro (Mg-gabbroid)	C: Ol (15%), Pl (55%), Cpx(25%) IC: Opx (5%) adcumulate	allotriomorphic (1-2 mm) alteration to green-Amph	Srp, Chl, green-Amph, Act, Czo, Mag, Hem
	S-77 S-70 gabbro-norite	C: Ol (<1%), Pl (50%), Cpx(20%) IC: Opx (15%), Ti-Mag (5%), brown-Hbl (10%), Ap (<1%) heteradcumulate	corroded crystals (1-1.2 mm) included in large Opx and brown-Hbl crystals	Idd, Chl, green-Amph, Act, Czo, Hbl, Mag, Hem
	Y-35 ferrogabbro	C: Pl (40%), Cpx (30%), Opx(8%), Ap (1-2%) IC: brown-Hbl (8 %), Ti-Mag (13%) heteradcumulate	allotriomorphic (1-1.5 mm) relatively fresh	idem
	Y-15 coarse-grained massive basalt	Cpx (50%), Pl (40%), Ti-Mag (5%) + accessories (5%) ophitic or subophitic	dumpy prism (1-1.8 mm), broken ± corroded	Act, Ep, Chl, Spn, Ab, Cal
volcanic sequence	Y-11 fine-grained massive basalt	Cpx (50%), Pl (40%) + accessories (10%) intersertal	allotriomorphic (0.1-0.3 mm) in interstice of Pl microlites, with "comb structure"	idem
	S-90 type II dolerite dike (1 m thick)	Cpx (50%), Pl (30%) + others (20%) porphyritic and intersertal	small rounded phenocrysts (0.1-0.3 mm), with "hour-glass structure"	Act, Ep, Chl, Spn, Ab, Bt, Prh, Pum, Hem, Mag
	S-55 type II dolerite dike (2 m thick)	Cpx (50%), Pl (40%), Ti-Mag (5%) + accessories (5%) porphyritic and intersertal	idiomorphic phenocrysts (1-1.5 mm)	idem

C = cumulus; IC = intercumulus.

Ab = albite; Act = actinolite; Amph = amphibole; Bt = biotite; Cal = calcite; Chl = chlorite; Cpx = clinopyroxene; Czo = clinozoisite; Ep = epidote; Hem = hematite; Hbl = hornblende; Idd = iddingsite; Mag = magnetite; Ol = olivine; Opx = orthopyroxene; Pl = plagioclase; Prh = prehnite; Pum = pumpellyite; Spn = sphene; Srp = serpentine; Tlc = talc; Ti-Mag = titanomagnetite.

Geneva using natural oxides and silicates as standards. Raw data have been corrected with a ZAF program (MAGIC).

Prior to quantitative analyses, two profiles across the selected crystals were recorded in order to detect possible zonation: one parallel and the other perpendicular to the {110} prism. No evident zonation has been observed, with the exception of sample S-90. In the latter, from core to rim, slight enrichment in Al and Ti has been observed, which

is in agreement with the hour-glass structure of the concerned clinopyroxene phenocrysts. Therefore, the analyzed points have been chosen in the inner part of the crystals; nevertheless, a relatively greater standard deviation is observed for this sample (Tab. 3).

For quantitative measurements, the instrument was operated at 20 kV and 40 nA (measured on benitoite), and counting was stopped by a constant digitized beam-current.

Tab. 2 Average chemical compositions of clinopyroxenes in the plutonic sequence from the Yanbian Proterozoic ophiolites.

Sample No.	S-72 (n=7)		S-76 (n=7)		S-77 (n=7)		S-70 (n=6)		Y-35 (n=7)	
	X	SD	X	SD	X	SD	X	SD	X	SD
SiO <sub>2</sub>	52.33	0.50	51.91	0.49	51.68	0.22	50.29	0.72	51.44	0.20
Al <sub>2</sub> O <sub>3</sub>	3.08	0.47	3.29	0.31	2.90	0.29	4.24	0.49	1.79	0.12
TiO <sub>2</sub>	0.43	0.24	0.72	0.25	0.73	0.12	1.12	0.15	0.48	0.10
MgO	15.39	0.26	14.98	0.35	14.36	0.60	13.45	0.34	13.97	0.30
FeO*	5.70	0.30	6.61	0.53	8.34	0.99	8.82	0.61	10.40	0.69
MnO	0.28	0.19	0.32	0.09	0.43	0.12	0.24	0.19	0.46	0.23
CaO	22.46	0.45	22.43	0.33	21.51	1.70	21.67	0.67	21.32	0.79
Na <sub>2</sub> O	0.34	0.03	0.27	0.12	0.33	0.06	0.46	0.03	0.37	0.02
Total	100.01		100.53		100.28		100.29		100.41	
Number of cations based on 6 oxygens										
Si	1.925	0.017	1.910	0.016	1.918	0.006	1.871	0.022	1.929	0.006
Al <sup>iv</sup>	0.075	0.018	0.090	0.016	0.082	0.005	0.129	0.022	0.071	0.006
Al <sup>vi</sup>	0.058	0.006	0.053	0.009	0.044	0.009	0.057	0.008	0.008	0.005
Ti	0.012	0.006	0.020	0.007	0.020	0.003	0.031	0.004	0.014	0.003
Mg	0.844	0.014	0.819	0.024	0.795	0.034	0.746	0.016	0.781	0.017
Fe*	0.175	0.009	0.204	0.017	0.259	0.031	0.274	0.018	0.326	0.021
Mn	0.009	0.006	0.008	0.004	0.013	0.004	0.008	0.006	0.015	0.007
Ca	0.885	0.019	0.881	0.014	0.855	0.067	0.864	0.029	0.857	0.033
Na	0.024	0.002	0.022	0.002	0.024	0.004	0.033	0.003	0.027	0.002
Total	4.007		4.007		4.010		4.013		4.028	
Wo	46.3	0.9	46.1	0.8	44.5	3.4	45.7	1.5	43.3	1.6
En	44.1	0.7	42.9	0.8	41.3	1.8	39.4	1.0	39.5	0.8
Fs	9.6	0.5	11.1	0.9	14.2	1.7	14.8	0.9	17.2	1.1
100 F/F+M	27.0	0.1	30.6	1.9	36.6	0.2	39.6	1.5	46.2	1.5
100 F/F+M of rocks	21.8		35.2		46.2		47.7		75.5	

FeO\*=total Fe expressed as FeO, F/F+M=FeO\*/FeO\*+MgO, X=average content, SD=standard deviation, n=numbers of measurement points; S-72: ultramafic cumulate; S-76: olivine gabbro; S-77 and S-70: gabbro-norites; Y-35: ferrogabbro. Designations of samples shown in Table 1.

About a hundred of measurement points were chosen in each sample. The following considerations were used to select the analyses: total oxides =  $100 \pm 0.7\%$ , sum Si + Al<sup>iv</sup> =  $2 \pm 0.05$  and sum of all cations =  $4 \pm 0.05$ .

#### 4. Clinopyroxenes in the plutonic sequence

The plutonic sequence consists of a complete and continuous differentiated suite, including the following rock types: ultramafic cumulates (plagio-

Tab. 3 Average chemical compositions of clinopyroxenes in the volcanic sequence from the Yanbian Proterozoic ophiolites.

Sample No.	Y-15 (n=10)		Y-11 (n=11)		S-90 (n=11)		S-55 (n=11)	
	X	SD	X	SD	X	SD	X	SD
SiO <sub>2</sub>	49.61	0.53	47.54	1.36	48.28	2.26	50.74	0.48
Al <sub>2</sub> O <sub>3</sub>	3.62	0.36	4.27	0.92	5.00	1.62	1.46	0.19
TiO <sub>2</sub>	1.29	0.22	2.17	0.55	1.78	0.68	0.75	0.18
MgO	14.47	0.36	11.18	0.58	15.32	2.00	11.43	0.48
FeO*	9.60	0.56	13.59	0.52	9.03	1.27	15.79	0.69
MnO	0.39	0.22	0.37	0.23	0.24	0.22	0.69	0.17
CaO	20.75	0.41	20.54	0.57	20.05	1.54	19.27	0.33
Na <sub>2</sub> O	0.33	0.03	0.48	0.04	0.40	0.07	0.30	0.03
Total	100.06		100.14		100.01		100.34	
Number of cations based on 6 oxygens								
Si	1.855	0.019	1.814	0.049	1.777	0.068	1.945	0.013
Al <sup>iv</sup>	0.145	0.021	0.185	0.047	0.214	0.070	0.053	0.011
Al <sup>vi</sup>	0.013	0.009	0.008	0.008	0.004	0.004	0.013	0.013
Ti	0.036	0.007	0.062	0.016	0.049	0.019	0.022	0.005
Mg	0.807	0.020	0.636	0.032	0.840	0.100	0.636	0.026
Fe	0.300	0.018	0.434	0.017	0.279	0.042	0.506	0.025
Mn	0.012	0.007	0.012	0.007	0.008	0.008	0.022	0.005
Ca	0.831	0.017	0.840	0.024	0.793	0.072	0.790	0.014
Na	0.024	0.002	0.036	0.003	0.029	0.006	0.022	0.004
Total	4.023		4.027		3.993		4.009	
Wo	42.4	1.1	43.7	1.5	41.3	3.7	40.5	0.7
En	41.2	0.8	33.1	1.4	43.8	5.0	32.6	1.2
Fs	16.6	1.3	23.2	1.0	14.8	2.3	26.9	1.3
100 F/F+M	40.1	1.5	54.9	1.5	37.3	6.0	58.6	1.9
100 F/F+M of rocks	65.1				58.5		86.4	

Y-15: coarse-grained massive basalt; Y-11: fine-grained massive basalt; S-90: small phenocrysts in a dike of type II; S-55: phenocrysts in another dike of type II. Same symbols and abbreviations as in Table 2. Designations of samples shown in Table 1.

clase dunites and plagioclase lherzolites), Mg-gabbroids (troctolites, anorthosites and olivine gabbros), gabbros and gabbro-norites, ferrogabbros, and albitites.

The petrographic observations show that all

these rock types belong to the same series. Throughout the sequence, the crystallization order is the following: olivine and Cr-spinel – plagioclase – clinopyroxene – orthopyroxene – apatite and titanomagnetite – brown hornblende – zircon –

quartz. This order corresponds to class D of ophiolite cumulates (olivine – plagioclase – clinopyroxene – orthopyroxene) (CHURCH and RICCIO, 1977). The bulk compositional evolution of these rocks clearly displays a Fe- and Ti-enrichment tendency, suggesting a tholeiitic affinity for this sequence. These characteristics are comparable to those of Phanerozoic high-Ti ophiolite plutonic rock suites (SERRI, 1981), and particularly to the North Apennine and the Western Alps ophiolites (SERRI, 1980; POGNANTE et al., 1982; BERTRAND et al., 1982, 1987), and even to those of modern oceanic plutonic rocks (ENGEL and FISHER, 1975; MIYASHIRO and SHIDO, 1980).

The analyzed samples comprise an ultramafic cumulate, an olivine gabbro, two gabbro-norites and a ferrogabbro (Tab. 1), representing the complete differentiated series of the plutonic sequence. This sampling allows us to investigate the clinopyroxene compositional variation through the sequence.

Average compositions and cation proportions in analyzed clinopyroxenes from the plutonic rocks are listed in table 2. In the En–Wo–Fs classification diagram (MORIMOTO, 1988) (Fig. 3), these clinopyroxenes overlap the fields of diopside and augite. Their major component proportions (quadrilateral)

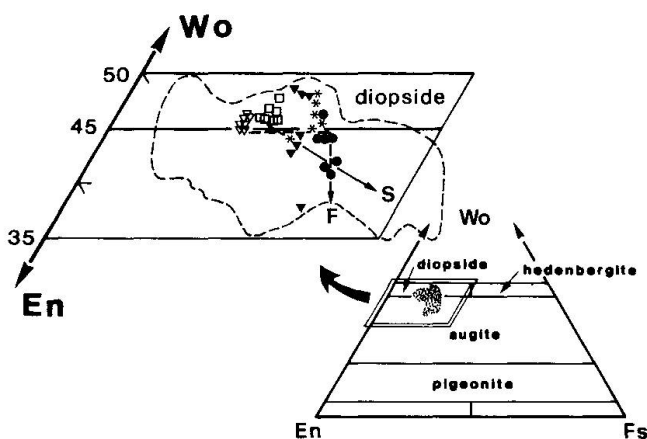


Fig. 3 Quadrilateral compositional diagram for clinopyroxenes of the Yanbian ophiolite plutonic rocks. Open triangles: ultramafic cumulates (S-72); open squares: Oligabbros (S-76); asterisks and solid triangles: gabbro-norites (S-77 and S-70, respectively); solid circles: ferrogabbros (Y-35).

Dark field: compositional range of clinopyroxenes of the Yanbian ophiolite plutonic rocks. Field enclosed by dashed line: compositional range of clinopyroxenes from oceanic plutonic rocks (after HEBERT et al., 1989). S: clinopyroxene evolutionary trend of the Skærgaard complex. F: clinopyroxene evolutionary trend of cumulates from the Romanche fracture zone and the Garret transform fault zone (after HEBERT et al., 1983).

roxenes from the North Apennine and Western Alps ophiolites (SERRI, 1980; BECCALUVA et al., 1980; POGNANTE et al., 1982; HEBERT et al., 1989), and even to those of modern oceanic plutonic clinopyroxenes (PRINZ et al., 1976; HODGES and PAPIKE, 1976; HEBERT et al., 1983, 1989). The mean clinopyroxene compositional variations clearly show an enrichment tendency for the ferrosilite molecule from ultramafic cumulate ( $\text{Fs}_{9.6}$ ) to ferrogabbro ( $\text{Fs}_{17.2}$ ) (Tab. 2), accompanied by a deviation towards the augite domain in the ferrogabbros (Fig. 3). The evolutionary trend of the studied clinopyroxenes seems to be comparable to that of the clinopyroxenes in the plutonic rocks from the Garret and Romanche transform fault zones, but different from that of the clinopyroxenes in the Skærgaard intrusion complex (HEBERT et al., 1983).

Among the minor components of the clinopyroxenes,  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  are the most significant. The relationship diagrams (Fig. 4) clearly show that Al correlates negatively with Si and positively with Ti. These correlations can also be expressed by the following linear regression equations:

$$[\text{Al}] = 2.5686 - 1.2746 [\text{Si}], \quad r = -0.8382, \quad ([ ] = \text{numbers of cation})$$

$$[\text{Al}] = 0.0678 + 3.3169 [\text{Ti}], \quad r = 0.8924$$

According to CAPEDE and VENTURELLI (1979) and BECCALUVA et al. (1989), the most important substitution types concerning Si, Al and Ti in the clinopyroxenes of ophiolite rocks are the following:

- (1)  $\text{Al}^{\text{vi}} + \text{Al}^{\text{iv}} \rightleftharpoons \text{M}^{\text{vi}} + \text{Si}^{\text{iv}}$   
(M = bivalent cation)
- (2)  $\text{Ti}^{\text{vi}} + 2 \text{Al}^{\text{iv}} \rightleftharpoons \text{M}^{\text{vi}} + 2 \text{Si}^{\text{iv}}$
- (3)  $\text{Na} + \text{Ti}^{\text{vi}} + \text{Al}^{\text{iv}} \rightleftharpoons 2 \text{M}^{\text{vi}} + \text{Si}^{\text{iv}}$

From the linear regression equations, we can determine the values of  $\Delta[\text{Si}]/\Delta[\text{Al}]$ ,  $\Delta[\text{Ti}]/\Delta[\text{Al}]$  and  $\Delta[\text{Ti}]/\Delta[\text{Si}]$  ratios, which represent the slope of correlation lines for the analyzed clinopyroxenes; these values are equal to  $-0.7846$ ,  $0.3014$  and  $-0.3843$ , respectively.

It is evident that the substitution type (3) cannot explain the substitution for these clinopyroxenes, since in that case,  $\Delta[\text{Si}]/\Delta[\text{Al}] = -1$ ,  $\Delta[\text{Ti}]/\Delta[\text{Al}] = 1$  and  $\Delta[\text{Ti}]/\Delta[\text{Si}] = -1$ ; moreover the results of the analyses in table 2 do not display an obvious correlation of Al, Ti and Si with Na. Even with each of the substitution types (1) and (2), it is also difficult to explain the cation replacement in the analyzed clinopyroxenes, because in the case of type (1), the  $\Delta[\text{Si}]/\Delta[\text{Al}]$  ratio is equal to  $-0.5$ , and in the case of type (2), the  $\Delta[\text{Si}]/\Delta[\text{Al}]$ ,  $\Delta[\text{Ti}]/\Delta[\text{Al}]$  and  $\Delta[\text{Ti}]/\Delta[\text{Si}]$  ratios are equal to  $-1$ ,  $0.5$  and  $-0.5$ , respectively.

Apparently, none of these ratios given by the substitution types (1) and (2) is in agreement with those of the studied clinopyroxenes. However, if the two types are considered together, the mode of



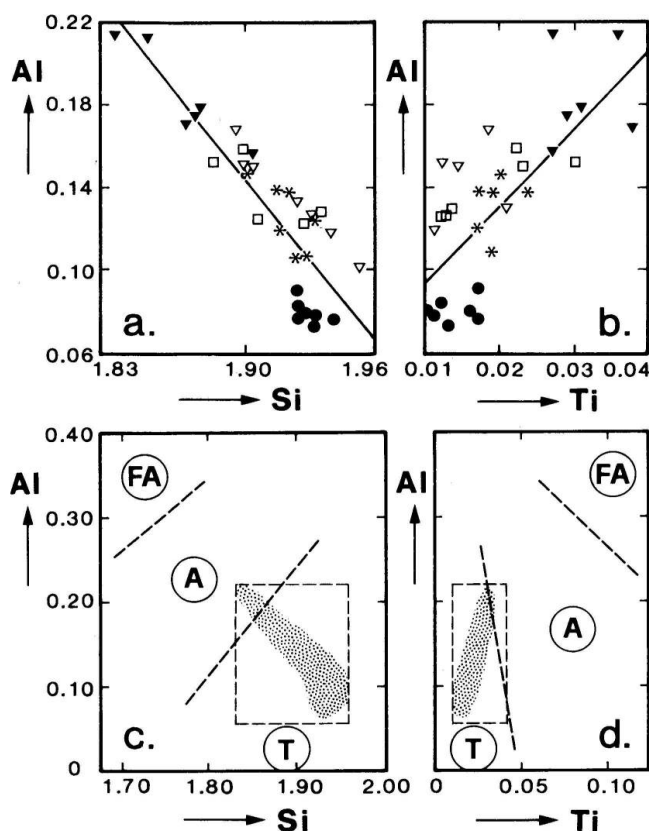
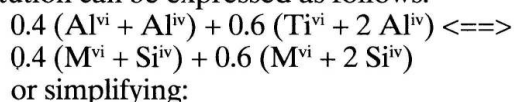


Fig. 4 Clinopyroxene compositional variations (structural formula based on 6 oxygens) of the Yanbian ophiolite plutonic rocks. (a.) and (c.): Al vs Si; (b.) and (d.): Al vs Ti.

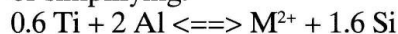
Delimitation lines in (c.) and (d.) according to KUSHIRO (1960). T: tholeiitic rocks. A: feldspathoid-free alkaline rocks. FA: feldspathoid-bearing alkaline rocks. Same symbols as in figure 3.

the clinopyroxene substitutions can be well explained.

In fact, the  $\Delta[\text{Ti}]/\Delta[\text{Al}]$  ratio equal to 0.3014 in the clinopyroxenes suggests a contribution of about 60% from the type (2) ( $\Delta[\text{Ti}]/\Delta[\text{Al}] = 0.5$ ) and a contribution of about 40% from the type (1) in the whole substitution. So the formula for such a substitution can be expressed as follows:



or simplifying:



If this combination is valid, then the  $\Delta[\text{Si}]/\Delta[\text{Al}]$  ratio calculated from the substitution formula must be comparable to that obtained from the linear regression equation.

That is:

$$\begin{aligned} & \Delta[\text{Si}]/\Delta[\text{Al}]_{\text{cpx calc.}} = \text{contribution \% of type (2)} \\ & \times \Delta[\text{Si}]/\Delta[\text{Al}]_{\text{type (2)}} + \text{contribution \% of type (1)} \\ & \times \Delta[\text{Si}]/\Delta[\text{Al}]_{\text{type (1)}} = 60\% \times (-1) + 40\% \times (-0.5) \\ & = -0.80. \end{aligned}$$

This ratio is very similar to that obtained from

the linear regression equation ( $-0.7846$ ); thus the proposed contribution percentages of the types (1) and (2) are confirmed to be correct.

KUSHIRO (1960) and LEBAS (1962) have pointed out that the compositions of clinopyroxenes depend upon the physical and chemical conditions of the magma from which they crystallized. Consequently, Si-, Al- and Ti contents can be used to characterize the magma types if physical conditions are comparable. However, it is important to note that care must be taken when applying these diagrams. For instance, direct comparison of these elements in clinopyroxenes from some volcanic rocks may lead to erroneous interpretations in distinguishing magma types, due to the effects of fast cooling rates (see afterwards the case of the volcanics). Our petrographic observations demonstrate that the plutonic rocks display cumulate features (Tab. 1). This implies that the crystallization of the clinopyroxenes is sufficiently slow, allowing to neglect all the influences of fast cooling. In figures 4 c and d, almost all the data points of the studied clinopyroxenes fall in the tholeiitic field.

LOUCKS (1990) has pointed out that the variation tendency of  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  contents in clinopyroxenes may be used to discriminate ophiolitic from non-ophiolitic ultramafic-mafic plutonic rocks. In plotting the compositions of clinopyroxenes from these two types of rock associations in the  $\text{TiO}_2$  vs  $\text{Al}_2\text{O}_3$  ( $= \text{Al}^{\text{iv}} \times 100/2$ ) diagram originally established by LEBAS (1962) (Fig. 5), LOUCKS demonstrated that the slope of variation trends of clinopyroxenes from arc plutonic cumulates (non-ophiolitic) ( $\text{Al}_2\text{O}_3/\text{TiO}_2 = 13$ ) is twice as steep as those of oceanic and ophiolitic plutonic cumulates ( $\text{Al}_2\text{O}_3/\text{TiO}_2 < 6$ ) from Bay of Island, Canyon Mountain and Semail. Petrographic and geochemical studies have demonstrated that the Bay of Island ophiolites show typical high-Ti features (SERRI, 1981), with a crystallization order as follows: olivine – plagioclase – clinopyroxene – orthopyroxene (CHURCH and RICCIO, 1977). However, the Canyon Mountain and Semail ophiolites are more complex. The Canyon Mountain ophiolites exhibit two types of crystallization order, on the one hand: olivine – plagioclase – clinopyroxene (high-Ti feature), and on the other hand, olivine – clinopyroxene – plagioclase – orthopyroxene (OHNENSTETTER, 1985). The Semail ophiolite plutonic rocks include two magmatic suites, of which the most developed can reach the ferrogabbro stage by differentiation (JUTEAU et al., 1988), with olivine – plagioclase – clinopyroxene – orthopyroxene crystallization order (high-Ti feature) (OHNENSTETTER, 1985). It can be seen that the clinopyroxene data of the Canyon Mountain and the Semail ophiolites, plotted in figure 5, like those of the Bay of Island ophiolites, should correspond

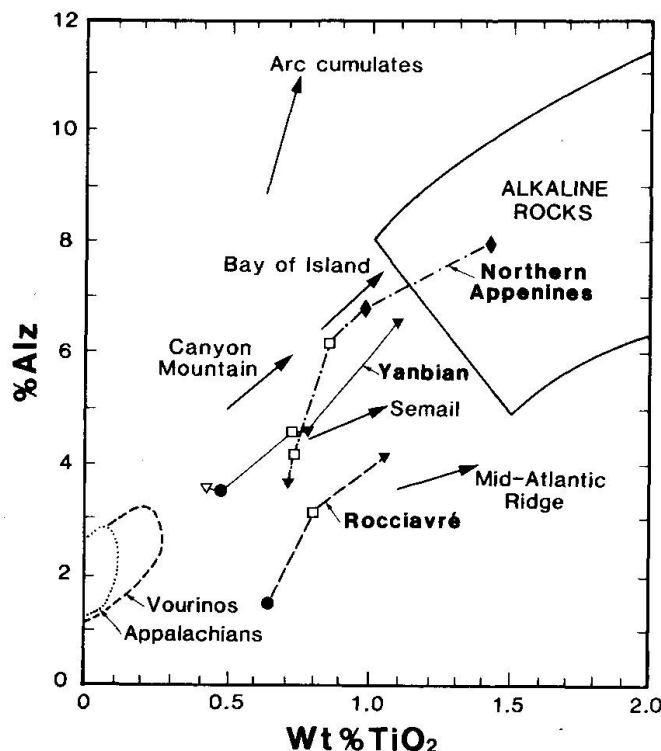


Fig. 5  $Alz (= Al^{iv} \times 100/2)$  vs  $TiO_2$  variations in clinopyroxenes of the Yanbian ophiolite plutonic rocks (data from Tab. 2) and comparison with the clinopyroxene variations of Phanerozoic ophiolite and non-ophiolite (arc-related) rocks (modified after LOUCKS, 1990). Open triangles: ultramafic cumulates; solid diamonds: troctolites; open squares: Ol-gabbros; solid triangles: gabbronorites; solid circles: ferrogabbros. Trends of Rocciavré (Western Alps) and Northern Apennine ophiolite plutonic rocks according to the data of POGNANTE et al. (1982) and HEBERT et al. (1989), respectively. Fields of Appalachian and Vourinos ophiolites according to the data of HEBERT and LAURENT (1989) and BECCALUVA et al. (1984), respectively.

to the high-Ti ophiolite types. This can also be confirmed by the trends of clinopyroxene variation similar to those of the typical high-Ti ophiolites such as the North Apennine ophiolites (HEBERT et al., 1989) and the Rocciavré ophiolites (POGNANTE et al., 1982) (Fig. 5). By contrast, the clinopyroxenes of plutonic rocks from typical low-Ti ophiolites, such as those of Vourinos and Appalachians, are strongly depleted in  $TiO_2$  (< 0.5% and 0.2%, respectively) (BECCALUVA et al., 1984; HEBERT and LAURENT, 1989). For this reason, these clinopyroxenes do not show any obvious tendency in figure 5. Based on linear regression analysis, the YPO plutonic clinopyroxenes have an  $Alz/TiO_2$  ratio equal to 4.0646 ( $Alz = 1.6710 + 4.0646 TiO_2$ ,  $r = 0.9510$ ). Moreover, in figure 5, their variation tendency is very comparable to those of the North Apennine and the Rocciavré ophiolite plutonic clinopyroxenes.

It is interesting to compare the composition variations of the studied clinopyroxenes with those of their host rocks. For the bulk compositions of the plutonic rocks (Fig. 6b), the  $SiO_2$ ,  $CaO$  and  $Al_2O_3$  contents increase simultaneously from ultramafics to olivine gabbros (Mg-gabbroids), in agreement with important concentration of calcic plagioclase and decrease of olivine. From Mg-gabbroids to gabbronorites, the  $CaO$  and  $Al_2O_3$  contents decrease and those of  $SiO_2$  increase. This can be explained by a significant crystallization of pyroxenes. Finally, from gabbronorites to ferrogabbros, the  $CaO$ ,  $Al_2O_3$  and  $SiO_2$  contents decrease while the  $TiO_2$  content and the  $Fe/Mg$  ratio increase considerably, which is in agreement with high proportion of titanomagnetite. In addition, through the whole sequence,  $TiO_2$  contents and  $Fe/Mg$  ratios increase systematically, clearly demonstrating a tholeiitic affiliation for this sequence.

As far as the compositional variations of the studied clinopyroxenes are concerned (Fig. 6a), from ultramafics to gabbronorites,  $Fe/Mg$  ratios and  $Ti$  contents increase continuously; from gabbronorites to ferrogabbros, the continuous increase of the  $Fe/Mg$  ratios is still observed but, surprisingly, in ferrogabbros, which are the most  $Ti$ -enriched rocks of the plutonic sequence, the  $Ti$  content de-

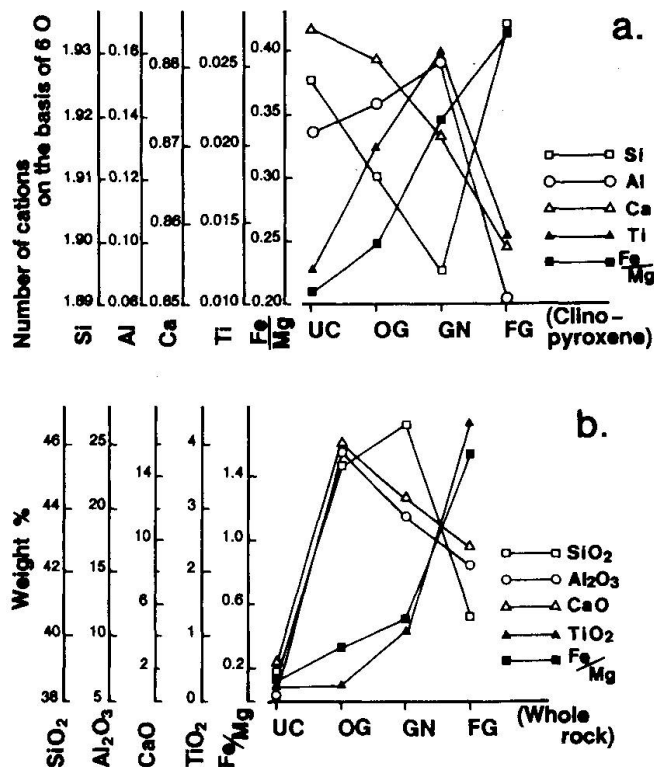


Fig. 6 Comparison of chemical compositional variations between the Yanbian ophiolite plutonic clinopyroxenes (a.) and their host rocks (b.). UC: ultramafic cumulates. OG: Ol-gabbros. GN: gabbronorites. FG: ferrogabbros.

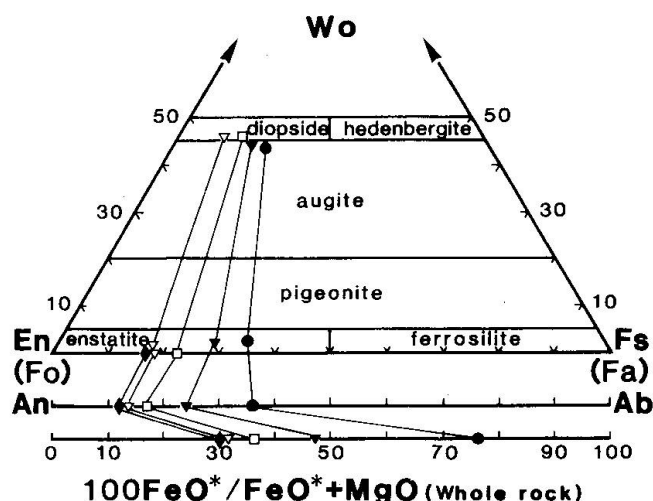


Fig. 7 Chemical compositional variations of clinopyroxenes, orthopyroxenes and olivines coexisting in the Yanbian ophiolite plutonic rocks, and comparison with those of normative plagioclase and of whole rocks. Open triangles: ultramafic cumulates; solid diamonds: troctolites; open squares: Ol-gabbros; solid triangles: gabbro-norites; solid circles: ferrogabbros.

creases abruptly. As demonstrated by the correlations between Al, Si and Ti discussed before, Al behaves in the same way as Ti, but Si inversely. The continuous decrease of Ca contents and increase of Fe/Mg ratios through the whole sequence can be explained by the decreasing temperature during fractionation (GAMBLE and TAYLOR, 1980).

The similarity of the variation of the Fe/Mg ratios in the studied clinopyroxenes and in their host rocks has two implications: (1) There is a potential equilibrium of these two elements among various coexisting ferromagnesian phases (olivine, clinopyroxene and orthopyroxene; Fig. 7); this is suggested by simultaneously increasing proportions of Fe-rich end-members in these minerals. At the same time, the proportions of the albite end-member in plagioclase and the  $\text{FeO}^*/\text{FeO}^* + \text{MgO}$  ratios in their host rocks also increase. (2) Since these ferromagnesian minerals are magmatic phases, the composition of the studied clinopyroxenes is a good indicator of magma types.

A peculiar characteristic consists in the fact that the clinopyroxenes in the most Ti-enriched ferrogabbros are depleted in titanium. This depletion may be explained by high  $\text{SiO}_2$  enrichment in the evolved magma from which the clinopyroxenes crystallized. At this differentiation stage, the magma would have high concentrations of  $\text{SiO}_2$  to form the clinopyroxene lattice, and the tetrahedral position available for  $\text{Al}^{IV}$  would be very low.

Thus, the concentrations of Ti in the octahedral site, which compensates the negative charge caused

by the  $\text{Al}^{3+} \rightarrow \text{Si}^{4+}$  substitution, would also decrease. In that case, Ti would remain in the magma, contributing to the crystallization of Fe-Ti oxides. Such a silica enrichment is confirmed by the absence of olivine and by the presence of hypersthene and normative quartz in the ferrogabbros.

Fe-enrichment and Ti-depletion in clinopyroxenes of ferrogabbros have been found in Phanerozoic high-Ti ophiolites and in modern oceanic plutonic rocks. In the Rocciavré ophiolite (POGNANTE et al., 1982), the clinopyroxenes occurring in olivine gabbros have  $\text{TiO}_2 = 0.76\%$  and  $\text{FeO} = 6.23\%$ ; in gabbro-norites,  $\text{TiO}_2 = 1.04\%$  and  $\text{FeO} = 9.52\%$ ; finally, in ferrogabbros (ilmenite and magnetite gabbros), these contents are  $0.56\%$  and  $10.81\%$ , respectively. In modern oceanic plutonic rocks, the clinopyroxenes in ilmenite norites (comparable to our ferrogabbros) have lower  $\text{TiO}_2$  contents ( $0.84\%$ ) and higher FeO contents ( $9.60\%$ ) than the other rocks (PRINZ et al., 1976).

### 5. Clinopyroxenes in the volcanic sequence

The volcanic sequence consists of: (1) massive basalts with some pillow lavas in the lower part of the section; (2) variolitic pillows with hyaloclastites, breccias and massive basalts in the upper part of the sequence; and (3) some keratophyres and minor ferrobasalts at the top. Pelagic sediments appear as intercalations or as cover of the volcanic pile. Sills and two types of dikes (dikes I, without chilled margins and strongly altered; dikes II, with chilled margins and relatively fresh) are also present (Figs 1 and 2).

Based on petrographic observations and bulk-rock geochemical characteristics, the volcanic rocks can be subdivided into two distinct lava groups. The volumetrically most important group includes massive and pillowed basalts, sills and dikes I; these rocks are characterized by the presence of plagioclase and sometimes olivine phenocrysts, and display a tholeiitic affinity. These rocks are comparable to the N-type mid-ocean ridge basalts (N-MORB). The other group is represented only by the dikes II, which are characterized by the appearance of clinopyroxene phenocrysts, sometimes accompanied by olivine and plagioclase phenocrysts, and exhibit the same affinity as the first rock group. However, according to the bulk composition in discrimination diagrams, these dikes are scattered in various geotectonic fields, mostly in the within-plate basalts (WPB) and in the plume-type mid-ocean ridge basalts (P-MORB) fields (SUN, 1990).

The clinopyroxenes of both groups (the main characteristics are listed in table 1), were analyzed;

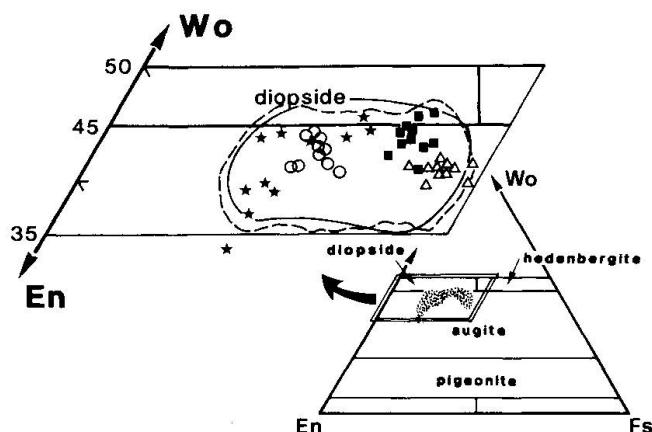


Fig. 8 Quadrilateral compositional diagram for clinopyroxenes of the Yanbian ophiolite basaltic volcanics. Open circles: coarse-grained massive basalt (Y-15); solid squares: fine-grained massive basalt (Y-11); open triangles: small phenocrysts in type II dolerite dike (S-90); solid stars: phenocrysts in another type II dolerite dike (S-55). Dark field: compositional range of clinopyroxenes of the Yanbian ophiolite basaltic volcanics. Field enclosed by solid line: compositional range of clinopyroxenes from high-Ti ophiolite basaltic volcanics (after Beccaluva et al., 1989). Field enclosed by dashed line: compositional range of clinopyroxenes from oceanic basalts (after PRINZ et al., 1976).

the textures and their crystal size indicate two rates of cooling: one is relatively slow (samples Y-15 and S-55), the other is very fast (samples Y-11 and S-90)

Average compositions of the clinopyroxenes and standard deviations are shown in table 3.

In contrast to the distinction based on the alteration- and metamorphism-resistant trace elements and REE of whole rocks, the chemical compositions of the studied clinopyroxenes do not show a significant difference between the basalts of the first group (Y-11 and Y-15) and the dikes II (S-55 and S-90). In the classification diagram of figure 8 (MORIMOTO, 1988), the Yanbian volcanic clinopyroxenes plot in the augite field and in the fields of the clinopyroxenes from Phanerozoic high-Ti ophiolite basalts (BECCALUVA et al., 1989) and from modern oceanic tholeiites (PRINZ et al., 1976).

As is the case for the clinopyroxenes in the plutonic sequence, the FeO and MgO contents (expressed by the  $\text{FeO}^*/\text{FeO}^* + \text{MgO}$  ratio) also show a positive correlation with those of their host rocks (Fig. 9), suggesting some equilibrium between the clinopyroxenes and the magma during their crystallization.

It is important to note that even in the same rock type, the clinopyroxene composition may show significant variation. For instance, samples Y-15 and Y-11 belong to the massive basalts with a similar bulk composition, but their clinopyroxenes

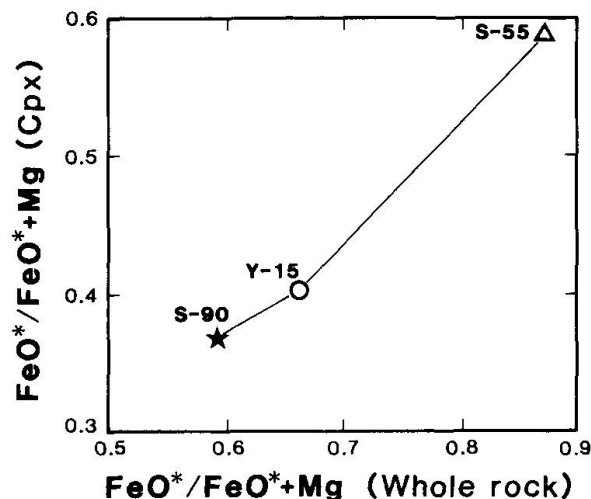


Fig. 9 Comparison of  $\text{FeO}^*/\text{FeO}^* + \text{MgO}$  ratios of the Yanbian volcanic clinopyroxenes and their host rocks. Same symbols as in figure 8.

exhibit a great difference in  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  contents. It seems that the finer the grain size of the rocks is, the higher are the  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  contents as well as the standard deviations of the clinopyroxenes (Tab. 3).

As underlined by several authors (e.g. LETERIER et al., 1982; BECCALUVA et al., 1989), the chemical variations of clinopyroxenes in magmatic rocks, particularly in volcanic rocks, are very complex. The factors controlling the clinopyroxene compositional variations can briefly be summarized as follows:

- (a) composition of magma at the time of clinopyroxene crystallization;
- (b) mineral crystallization order, related mainly to the pressure, including total pressure, water pressure and oxygen fugacity, etc., during fractionation;
- (c) magma temperature at effusion;
- (d) cooling rate of the magma during clinopyroxene crystallization.

The factor (a) is the most important among them. Since there is a distribution equilibrium for some elements between the clinopyroxene and the liquid, the composition of this mineral can reflect that of the latter. In fact, the discrimination methods of magma types and geotectonic environments based on the clinopyroxene compositions are established on such distribution equilibrium. Factors (b) and (c) are not entirely independent variants and have some complex liaison with factor (a). For instance, in the great majority of the cases, the mid-ocean ridge magmas differentiate under low pressure. This explains the crystallization of plagioclase prior to clinopyroxene; the inverse is very rare (BRYAN et al., 1976; BRYAN, 1983; SCHILLING et al., 1982). Usually, the effusion temperature of subma-



rine basalts varies only within a limited range (1150–1200°C). Factor (d) is completely independent from the other factors and it may be responsible for the great variations of Si, Al and Ti contents in the clinopyroxenes. Experimental studies on lunar basalts have revealed that the clinopyroxenes contain more Al and Ti when they crystallized from a quickly cooled liquid than those formed at a slow cooling rate from a liquid of the same composition (GROVE and BENCE, 1977; GAMBLE and TAYLOR, 1980). This phenomenon is in agreement with the compositional variations of clinopyroxenes from Alpine Mesozoic ophiolitic pillow lavas, where the clinopyroxenes from the quickly cooled pillow rim are richer in Ti and Al than those from the slowly cooled core (MEVEL and VELDE, 1976). This is the same case for the compositional changes of clinopyroxenes in modern oceanic basalts where the clinopyroxenes from the margins contain more Al and Ti than those from the inner part of a cooling unit flow characterized by a uniform bulk rock composition (COISH and TAYLOR, 1979).

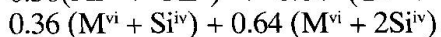
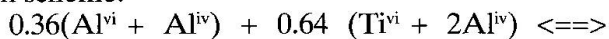
In the Yanbian volcanic clinopyroxenes, the  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  contents of sample Y-11 (2.17 and 4.27%, respectively) are higher than those of sample Y-15 (1.29 and 3.62%, respectively), although the bulk composition of the two samples is similar. This apparent contradiction can be explained by the difference in cooling rate of the host magma, as shown by the textures of the samples in table 1.

As is the case for the plutonic sequence, Al in clinopyroxenes of the volcanic sequence correlates negatively with Si and positively with Ti (Figs 10 a and b). These correlations can be expressed by the following linear regression equations:

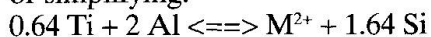
$$[\text{Al}] = 2.0119 - 1.3091 [\text{Si}], r = -0.9821$$

$$[\text{Al}] = 0.0276 + 3.0797 [\text{Ti}], r = 0.8550$$

It can be seen that the  $\Delta[\text{Si}]/\Delta[\text{Al}]$  and  $\Delta[\text{Ti}]/\Delta[\text{Al}]$  ratios are very similar to those of the plutonic clinopyroxenes. The value of the  $\Delta[\text{Ti}]/\Delta[\text{Al}]$  ratio (0.32) allows us to propose the following substitution scheme:

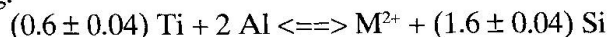


or simplifying:



In this case, the  $\Delta[\text{Si}]/\Delta[\text{Al}]$  ratio should be equal to -0.82. Compared with the value obtained from the linear regression equation (-0.76), this ratio appears to be slightly different but acceptable. It is possible that the small differences in  $\Delta[\text{Ti}]/\Delta[\text{Al}]$  and  $\Delta[\text{Si}]/\Delta[\text{Al}]$  ratios between the plutonic clinopyroxenes (0.3014 and -0.7846) and the volcanic clinopyroxenes (0.3247 and -0.7639) may result mainly from statistical deviation. Therefore, the  $\Delta[\text{Ti}]/\Delta[\text{Al}]$  and  $\Delta[\text{Si}]/\Delta[\text{Al}]$  ratios of the clinopyroxenes for the two sequences should be

equal to  $0.3 \pm 0.02$  and  $-0.78 \pm 0.02$ , respectively, and the substitution formula, should be the following:



The experiments of GAMBLE and TAYLOR (1980) have revealed an important fact: despite the changes in temperature and in cooling rate of the liquid, the  $\Delta[\text{Ti}]/\Delta[\text{Al}]$  ratio of clinopyroxenes in the rock resulting from this magma remains constant. Thus, the similarity of this ratio between the plutonic and volcanic rocks can be considered as an indication of a co-magmatic origin for the two sequences.

Statistical studies on the chemical composition of clinopyroxenes from oceanic basalts show that Al and Ti correlate positively, and that the  $\Delta[\text{Ti}]/\Delta[\text{Al}]$  ratios vary in the range between 0.14 and 0.5. Moreover, the majority of the clinopyroxene analyses are grouped around the line  $\Delta[\text{Ti}]/\Delta[\text{Al}] = 0.33$  (SCHWEITZER et al., 1979). As far as the ophiolites are concerned, the clinopyroxenes from the basalts of the Pindos ophiolites (low-Ti type) have a very low  $\Delta[\text{Ti}]/\Delta[\text{Al}]$  ratio (0.16), whereas those of the Corsican and North Apennine ophiolites (high-Ti type) have very high  $\Delta[\text{Ti}]/\Delta[\text{Al}]$  ratios, ranging between 0.24 and 0.45 (CAPEDRI and VENTURELLI, 1979). It is evident that the YPO volcanic clinopyroxenes, with a high  $\Delta[\text{Ti}]/\Delta[\text{Al}]$  ratio (0.32), are comparable to those of the latter type of ophiolites.

The clinopyroxene compositions, in particular the minor-element contents, such as Ti, Al, Mn, Na, as well as Si, have been widely used to identify the magmatic affinities and geotectonic environments of the volcanic rocks (KUSHIRO, 1960; LEBAS, 1962; NISBET and PEARCE, 1977; LETERRIER et al., 1982; BECCALUVA et al., 1989).

In order to avoid the effect of Ti and Al enrichment in clinopyroxenes caused by a high cooling rate of magma, LETERRIER et al. (1982) proposed to use the composition of the phenocrysts in place of the microlites. In the diagrams established by these authors (Fig. 11), the coarse-grained clinopyroxenes (Y-15 and S-55, slow cooling) from Yanbian area plot in the tholeiitic field, whereas the fine-grained clinopyroxenes (Y-11 and S-90, fast cooling) fall in the alkaline basalt field (Fig. 11a). Nevertheless, all the points are grouped in the domain of "non-orogenic" or "distension" areas (ocean ridges, back-arc basins, continental rifts and oceanic islands) (Fig. 11b). In figures 10 a and b, the distribution of the representative points is the same as in figure 11: the clinopyroxenes of the slowly cooled rocks fall in the tholeiitic field, whereas the clinopyroxenes of the quickly cooled rocks plot in the alkaline basalt field. This particularity have been observed in clinopyroxenes from ocean floor tholeiitic basalts: the clinopyroxenes sampled from



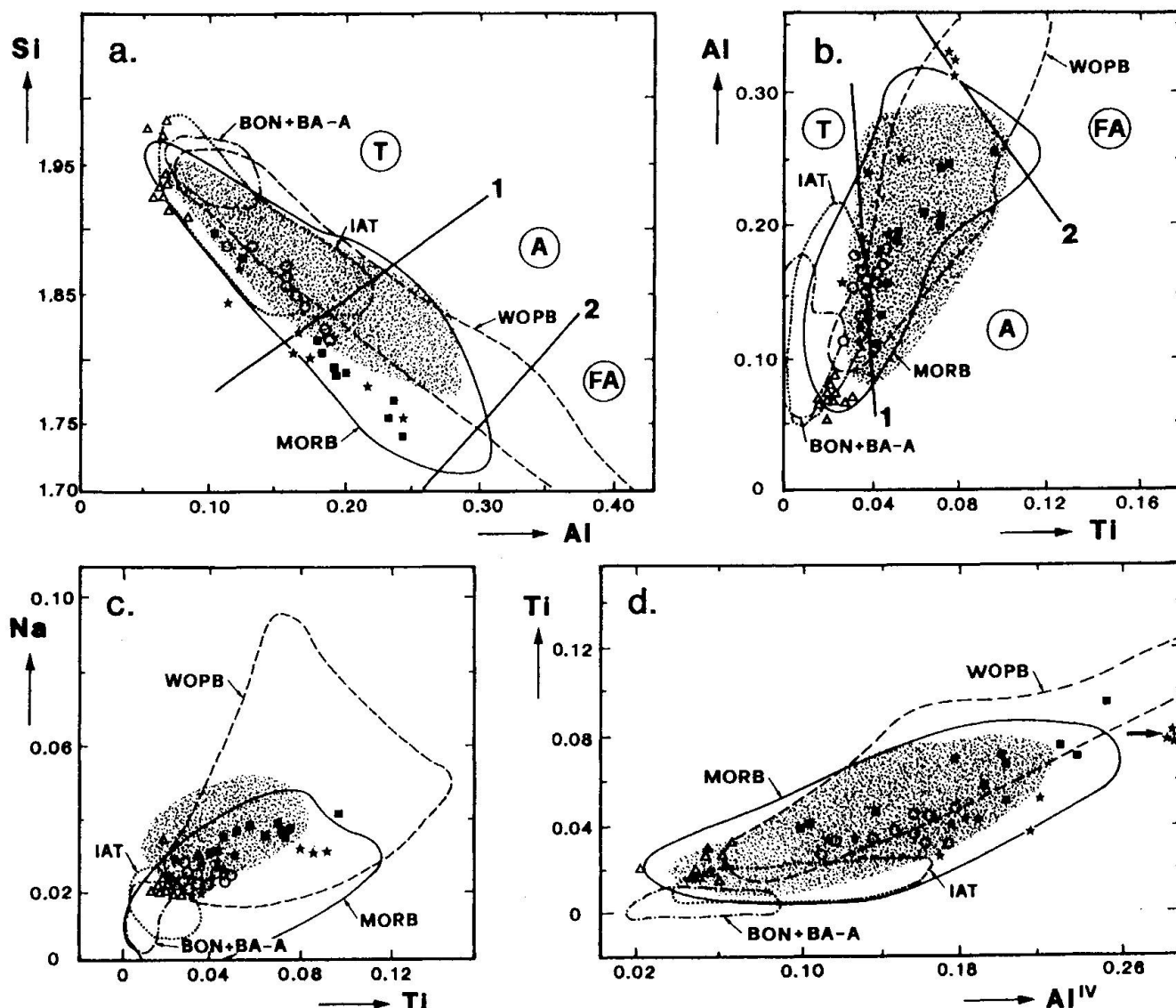


Fig. 10 Clinopyroxene compositions (structural formula based on 6 oxygens) of the Yanbian ophiolite basaltic volcanics plotted in Si vs Al (a.), Al vs Ti (b.), Na vs Ti (c.) and Ti vs Al<sup>IV</sup> (d.) diagrams (simplified after BECCALUVA et al., 1989). MORB: mid-ocean ridge basalts; WOPB: within oceanic plate basalts; IAT: island-arc tholeiites; BON + BA-A: boninites, quartz tholeiites, basaltic andesites and andesites from intraoceanic fore-arc regions. Dark fields: compositional range of clinopyroxenes of Internal Liguride high-Ti ophiolite basalts. Lines 1 and 2: delimitation of tholeiitic rocks (T), feldspathoid-free alkaline basalts (A) and feldspathoid-bearing alkaline basalts (FA) after KUSHIRO (1960). Same symbols as in figure 8.

the margins of the flow plot in the alkaline field, and those from the centre, in the tholeiite field (COISH and TAYLOR, 1979). Leaving aside the effect of fast cooling, the compositions of the studied clinopyroxenes agree well with a tholeiitic affiliation for the volcanic rocks.

In the diagrams established by NISBET and PEARCE (1977) and BECCALUVA et al. (1989) (Figs 10, 12, 13), nearly all the data points of the Yanbian volcanic clinopyroxenes are grouped in the domain of ocean floor basalts (OFB) or of mid-ocean ridge basalts (MORB). Their locations are clearly different from those of typical low-Ti ophiolitic basalts, such as those of Troodos, Pindos and Vourinos,

whose clinopyroxenes plot in the fields of island-arc tholeiites (IAT), fore-arc boninites, quartz tholeiites, basaltic andesites (BON + BA-A), but very similar to those of typical high-Ti ophiolite basalts, such as those of North Apennines, particularly of Internal Ligurides.

## 6. Conclusions

From the geochemical study of the plutonic and volcanic clinopyroxenes of the YPO, the following points can be emphasized:

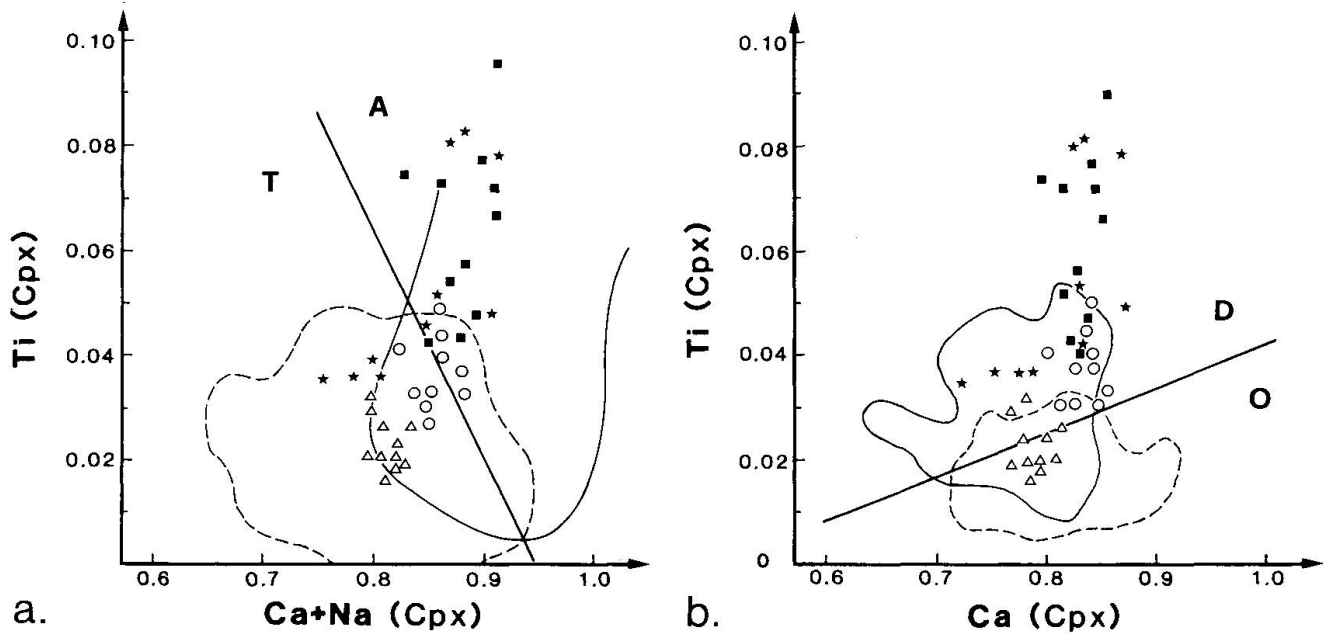


Fig. 11 Clinopyroxene compositions (structural formula based on 6 oxygens) of the Yanbian ophiolite basaltic volcanics plotted in Ti vs Ca + Na (a.) and Ti vs Ca (b.) diagrams (modified after LETERRIER et al., 1982). T: tholeiite field. A: alkaline basalt field. D: non-orogenic tholeiite field. O: orogenic tholeiite field.

(1) The similarity of the Fe/Mg ratio variations between the clinopyroxenes and their host rocks suggests equilibrium between the clinopyroxenes and the host magma. Therefore, the compositions and compositional variations of the clinopyroxenes can be considered as indicators of the magmatic affinity and magmatic evolution.

(2) The clinopyroxenes in the slowly cooled plutonic rocks clearly show a tholeiitic affinity. Their compositions, particularly the low  $Al_2/TiO_2$  ratios (4.0646) preclude their formation from an arc-related geotectonic setting. In addition, these clinopyroxenes are well comparable to those of modern oceanic plutonic rocks and to those of typical Phanerozoic high-Ti ophiolites, in particular to those of the North Apennines and the Western Alps.

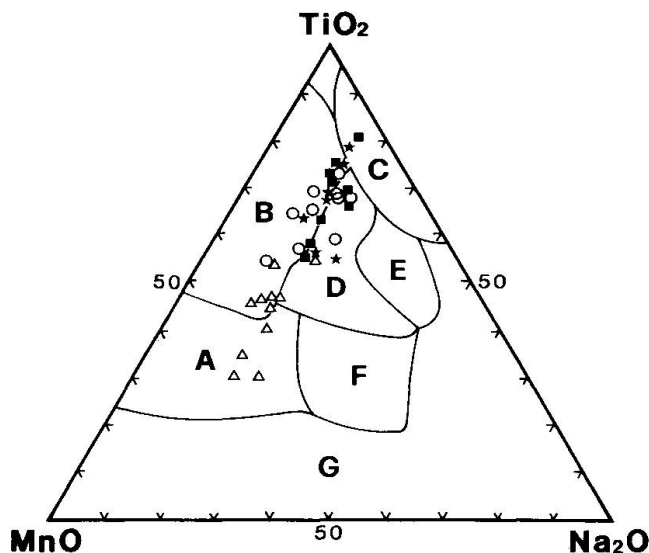


Fig. 12  $TiO_2$  -  $MnO$  -  $Na_2O$  (wt%) diagram for clinopyroxenes of the Yanbian ophiolite basaltic volcanics (after NISBET and PEARCE, 1977). A: VAB (volcanic arc basalts). B: OFB (ocean-floor basalts). C and G: WPA: (within-plate alkaline basalts). D: all environments. E: VAB + WPA + WPT (WPT: within-plate tholeiites). F: VAB + WPA. Same symbols as in figure 8.

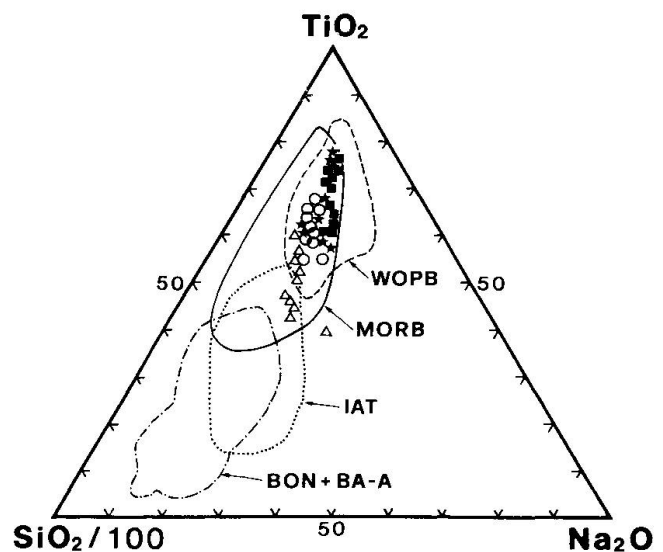


Fig. 13  $TiO_2$  -  $Na_2O$  -  $SiO_2/100$  (wt%) diagram for clinopyroxenes of the Yanbian ophiolite basaltic volcanics (simplified after BECCALUVA et al., 1989). Same symbols and abbreviations as in figure 8.

(3) In spite of the enrichment in Ti and Al due to fast cooling in some samples, the clinopyroxenes in the volcanic rocks also exhibit a tholeiitic affinity. Their compositions correspond to those of typical Phanerozoic high-Ti ophiolite basalts (e.g. the North Apennine ophiolites), and to those of mid-ocean ridge basalts (MORB).

(4) The similarity of the clinopyroxene  $\Delta[\text{Ti}]/\Delta[\text{Al}]$  and  $\Delta[\text{Si}]/\Delta[\text{Al}]$  ratios between the plutonic rocks (0.30 and -0.78) and the volcanic rocks (0.32 and -0.76) indicate a same type of substitution  $[(0.6 \pm 0.04) \text{ Ti} + 2 \text{ Al} \rightleftharpoons \text{M}^{2+} + [1.6 \pm 0.04] \text{ Si}]$  and a co-magmatic origin for the two sequences.

(5) The comparison between the Ti content of clinopyroxenes and that of their host plutonic rocks reveals an important fact: the high-Ti ophiolite magma would have reached a stage of enrichment not only in Fe and Ti, but also in Si. At this stage, Ti could not enter the clinopyroxene structure, but remained in the liquid to crystallize as titanomagnetite or ilmenite.

These points are in agreement with the conclusions obtained from the petrographic and bulk-rock geochemical studies on the "immobile" elements (SUN, 1990). The similarities in bulk compositions and in clinopyroxene compositions of the YPO, to those of typical Phanerozoic high-Ti ophiolites, can be considered as an argument in favour of the hypothesis that the petrogenetic and geodynamic models accepted for the Phanerozoic ophiolites can also be applied to those of the Middle Proterozoic.

### Acknowledgements

We are greatly indebted to Prof. M. Vuagnat for his advice on petrographic and mineralogical matters. We wish to thank F. Capponi for his assistance in microprobe analysis and J. Metzger for his drawing work. Thanks are also due to Drs J. Martini and A.F. Waibel for improving the English manuscript, and to Dr. G. Venturelli who provided critical and constructive comments on the manuscript.

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Manuscript received December 3, 1990; revised manuscript accepted April 3, 1991.