

THE NEWEST TESTIMONY OF MAGMATIC ORIGIN OF SPILITE*

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The genesis of spilite-keratophyric volcanic rock assemblages being the important part of submarine volcanic rocks has long been in contention, the focus of which is the origin of sodium. Basing on the discoveries of albite with disorder-transition structure in spilite-keratophyre and the primary sodic magmatic inclusions in quartz phenocrysts of quartz-keratophyre, and the recent discovery of primary sodic magmatic inclusions in clinopyroxene phenocrysts of Ordovician pyroxene-spilite-porphyrite from Shihuigou area of Yongdeng County in Gansu Province, the authors have reasons to propose that spilite-keratophyric volcanic rocks possibly crystallized from magma being rich in sodium and water^[1,3].

I. PRIMARY MAGMATIC INCLUSIONS IN CLINOPYROXENE PHENOCRYSTS

The pyroxene-spilite-porphyrite occurs in the lower part of Ordovician submarine volcanic series, and is one of the major rock types of lower Palaeozoic submarine volcanic rocks in northern Qilian Mountains. The rocks have porphyritic texture. The phenocrysts consist of clinopyroxene (endiopside-augite) and albite (An 0.4 — 0.8, Ab 99.2 — 99.4, Or 0.0 — 0.9). The ground mass has interseptal and intergranular texture. The albite microlites (An 0.6 — 1.7, Ab 98.0 — 99.4, Or 0.0 — 0.1) form framework, in which clinopyroxene, chlorite, titanomagnetite, sphene, leucosene and chalcodite are filled (Fig. 1). The size of clinopyroxene phenocrysts, which have partly undergone chloritization and epidotization, is generally 0.5 — 1.5 mm × 0.1 — 0.4 mm. Most clinopyroxene phenocrysts have a positive zonal structure, characterized by decreasing magnesium content and increasing iron content from center to periphery while a few have a reversal zonal structure (Table 1). The clinopyroxene phenocrysts contain lots of evolved primary magmatic inclusions (Fig. 2) with dimensions from 7 to 30 μ , being negative crystals of host minerals. The filling material in the inclusions consists of daughter minerals (clinopyroxene

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+ titanomagnetite), residual glasses and shrinkage bubbles. The homogenization thermometric studies of magmatic inclusions have been conducted on Leitz-1350 micro-heating stage. During heating the first phenomenon observed at about 700°C was the initial fusion of glass filling. From 780° — 820°C, the daughter minerals began fusing. The homogenization temperature of magmatic inclusions ranged from 1185° to 1222°C. In clinopyroxene with positive zone, it decreases progressively (1218° → 1195° → 1185°C) from centre to periphery; in reversal zonal clinopyroxene, from center to transition zone, it also decreases; then up to the basic periphery of phenocryst, it increases again (Table 1). Based on the cryometric study of the above-mentioned inclusions on CHAIXMECA cooling-heating stage, it has been established that the shrinkage gas bubble of inclusions contains CO₂ (with density of about 0.04 g/cm³) homogenized in gas phase at -28.3°C. The fusing temperature of CO₂ is -54.5°C, which indicates that there are other gases in the shrinkage bubble besides CO₂. The above values of CO₂ density and complete homogenization temperature (1222°C) of magmatic inclusions are substituted into Bottinga-Richet's CO₂ state equation^[4]. The calculation result shows that the central phase of clinopyroxene phenocrysts crystallized under the condition of about 11.5 MPa and 1222°C.



Fig. 1. Pyroxene-spilite porphyrite. cpx, clinopyroxene phenocryst; ab, albite microlites.

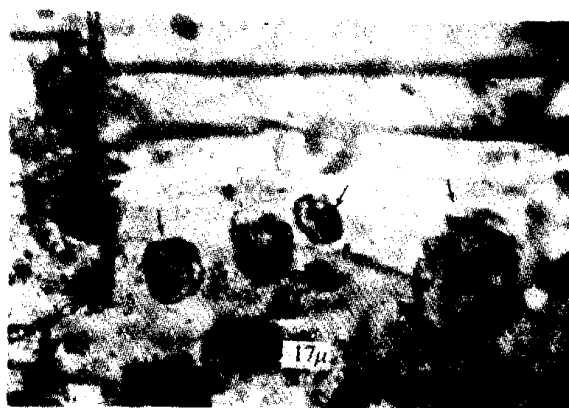


Fig. 2. Evolved magmatic inclusions in clinopyroxene phenocryst of pyroxene-spilite porphyrite (indicated by arrows).

II. CHEMICAL COMPOSITION OF MAGMATIC INCLUSIONS AND THEIR SIGNIFICANCE

The present glass existing in evolved magmatic inclusions is only the residual melt after the crystallization and separation of daughter minerals. We have analysed the quenched inclusions by microprobe after homogenization in order to obtain the initial chemical composition of evolved magmatic inclusions in clinopyroxene phenocrysts. The analytical results are listed in Table 1. We can see that the magmatic inclusions situated in the central phase of phenocrystal are most basic, their composition is quite similar to that of the whole rock and

Table 1

Chemical Compositions of Magmatic Inclusions in Clinopyroxene Penocrysts of Pyroxene-spilitic Porphyrite From Shihuigou, Yongdeng, in Gansu Province (wt.%)

Type Chemical Composition	Total rock ^{a)}	Magmatic Inclusions in Clinopyroxene (With Reversal Zonal Structure)						Magmatic Inclusions in Clinopyroxene (With Positive Zonal Structure)													
		Central zone			Transition zone			Structure		Central zone		Transition zone		Periphery							
		host mineral	inclusion (after homogenization)	host mineral	inclusion (after homogenization)	host mineral	inclusion (after homogenization)	host mineral	inclusion (after homogenization)	host mineral	inclusion (after homogenization)	host mineral	inclusion (after homogenization)	host mineral	inclusion (after homogenization)						
SiO ₂	53.87	53.43	53.47	53.46	54.61	54.16	54.40	51.14	56.34	52.70	54.53	52.47	54.35	52.24	56.26	57.53	56.78	57.04	56.54	51.91	59.71
TiO ₂	0.30	0.09	0.24	0.00	0.20	0.22	0.22	0.16	0.18	0.14	0.18	0.06	0.23	0.05	0.18	0.19	0.14	0.15	0.13	0.00	0.13
Al ₂ O ₃	16.34	1.55	15.45	1.78	16.07	16.03	16.59	2.14	14.68	1.58	15.60	1.75	14.95	2.07	17.96	17.83	17.74	17.91	18.40	1.71	15.48
Fe ₂ O ₃	7.24	6.66	8.15	6.23	6.43	6.90	6.18	7.40	6.58	6.01	5.93	6.85	6.54	6.88	4.17	4.01	4.44	4.63	4.90	8.59	5.83
FeO	4.78																				
MgO	4.54	18.20	5.27	17.96	4.56	4.72	4.42	17.84	5.62	18.84	4.84	18.65	6.77	17.38	3.00	2.99	3.10	3.26	3.00	16.78	4.67
CaO	2.29	19.93	9.38	20.69	9.89	10.21	9.90	20.06	9.82	21.20	9.84	20.34	9.18	20.48	7.92	7.77	8.67	7.39	8.69	19.80	7.35
Na ₂ O	6.86	0.10	3.85	0.13	3.90	3.67	4.44	0.10	4.00	0.10	4.41	0.13	3.69	0.15	4.91	3.82	4.48	4.63	4.67	0.19	4.14
K ₂ O	0.21	0.00	0.30	0.00	0.49	0.42	0.39	0.00	0.10	0.00	0.43	0.00	0.00	0.00	0.76	0.66	0.73	0.62	0.60	0.00	0.40
MnO	0.12	0.06	0.00	0.17	0.10	0.21	0.13	0.29	0.15	0.17	0.09	0.19	0.10	0.21	0.17	0.12	0.13	0.08	0.00	0.19	0.00
Cr ₂ O ₃	0.002	0.07	0.01	0.20	0.00	0.00	0.00	0.00	0.05	0.13	0.09	0.29	0.05	0.49	0.07	0.00	0.13	0.09	0.00	0.20	0.00
NiO	0.003	0.12	0.13	0.04	0.03	0.00	0.13	0.00	0.05	0.10	0.08	0.00	0.08	0.05	0.12	0.08	0.03	0.01	0.00	0.00	0.03
H ₂ O ⁺	3.04																				
Total	99.595	100.21	96.25	100.67	96.27	96.54	96.79	99.14	97.57	100.97	96.03	100.73	95.94	100.00	95.51	95.00	96.35	95.81	96.93	99.37	97.73
En		50.2		49.4				49.0		50.3		50.3		48.3						46.8	
Wo		39.5		50.0				39.6		40.7		39.4		50.0						39.7	
Fs		10.3		9.6				11.4		9.0		10.3		10.7						13.5	
Homogenization temperature, °C			1222			1218			1204		1218		1218			1195					1185

a) Wet analysis. Analysts: SHI Bao-gui, GONG Xin-cai. The rest were analysed by microprobe;

analysts: XIA Lin-qi, LIU Wen-feng; microprobe: JXA-733; conditions: 15 kV, 10 nA, 2 — 5 μ .

the content of Na_2O (3.69 – 4.44 wt. %) and K_2O (0.00 – 0.49 wt. %) is just the characteristic of the chemical composition of spilite. This indicates that the ambient magma has already been rich in sodium during the crystallization of clinopyroxene which is the early mineral phase of pyroxene-spilitic porphyrite. From center to periphery in the positive zonal clinopyroxene phenocrysts, with the progressive decrease of crystallization temperature, the chemical composition of magmatic inclusions progressively tends to be more acid (Table 1); from central to transition zone in reversal zonal clinopyroxene phenocrysts, with the decrease of crystallization temperature, it becomes more acid. Up to the basic periphery of clinopyroxene being rich in magnesium and poor in iron, with the reversal increase of crystallization temperature, the chemical composition of magmatic inclusions, which is similar to that of magmatic inclusions in central zone, becomes again more basic (Table 1). The above facts signify that there has occurred magma mixing in the course of the formation of pyroxene-spilitic porphyrite: the phase of endiopside-augite crystallized first from the early spilitic magma and with temperature decrease, the evolution degree of magma increased; the clinopyroxene separated from magma became augite; then, a new and primitive spilitic magma with low evolution degree was injected and mixed with the magma of intermediate basicity which was early injected into the upper volcanic magma reservoir and had evolved in some degree. An endiopsidic zone with higher crystallization temperature grew around the margin of early clinopyroxene crystals.

The total content of volatile components dissolved in the filling material of magmatic inclusions can be estimated to be 2.5 – 5.0 wt. % according to the deficit non-analysed quantitatively by electronic microprobe^[2,5]. Among them the proportion of volatile elements F, Cl, S (S, 0.87 wt. %, F, 0.14 wt. %, Cl, 0.08 wt. % were analysed by microprobe) is less than 25%. It is considered that CO_2 solubility in basic magma near the surface is generally less than 1 wt. %^[6], so we can estimate that the quantity of H_2O dissolved in spilitic volcanic magma in this area is about 1.5 – 3 wt. %. For the evolved magmatic inclusions, because of the separation of daughter minerals, most of the other volatile components have transferred into the shrinkage gas bubble, except a considerable part of H_2O which has still dissolved in residual glass phase. In the shrinkage gas bubble, the gas components, analysed by laser Raman microprobe, are mainly CO_2 , besides, there are N_2 , CH_4 , H_2O , H_2 , H_2S , SO_2 (Table 2). Based on the composition of gas phases in the shrinkage gas bubble of magmatic inclusions, the complete homogenization temperature and pressure at homogenization, the fugacities of gas components (Table 2) and the condition of oxygen fugacity ($f_{\text{O}_2} = 10^{-11.02}$ bars) at crystallization of clinopyroxene have been calculated by a thermodynamic method^[7].

To sum up, the results of this study have provided the newest conclusive evidence of magmatic origin of spilites. It proves at least that the clinopyroxenes in Ordovician pyroxene-spilitic porphyrite from Shihuigou area of Yongdeng County in Gansu Province have

crystallized from basic magma which is rich in sodium and water.

Table 2
Chemical Compositions and Fugacities of Gas Phases in the Shrinkage Bubble of Magmatic Inclusions

T_h (°C)	P_{total} (MPa)	Composition of Gas Phase (Mol. %)							Fugacity of Gas Components (bar)							
		CO ₂	N ₂	CH ₄	H ₂ O	H ₂	H ₂ S	SO ₂	f_{O_2}	f_{CO_2}	f_{N_2}	f_{CH_4}	f_{H_2O}	f_{H_2}	f_{H_2S}	f_{SO_2}
1222	11.5	60.4	4.8	6.4	8.4	3.4	7.9	8.7	$10^{-11.02}$	$10^{1.86}$	$10^{0.76}$	$10^{0.88}$	$10^{0.99}$	$10^{0.60}$	$10^{0.97}$	$10^{1.01}$

Notes: The compositions of gas phases have been analysed by laser Raman microprobe. Analyst: XU Peicang. Instrument: RAMANOR U-1000; ionized argon laser: 514.5 nm; power: 400 mW; width of slit: 400 μ ; rate of scanning: 6 cm⁻¹/min. T_h : homogenization temperature of magmatic inclusions; P_{total} : the pressure at homogenization of magmatic inclusions (calculated by the density of CO₂ contained in shrinkage bubbles and the homogenization temperature of inclusions).

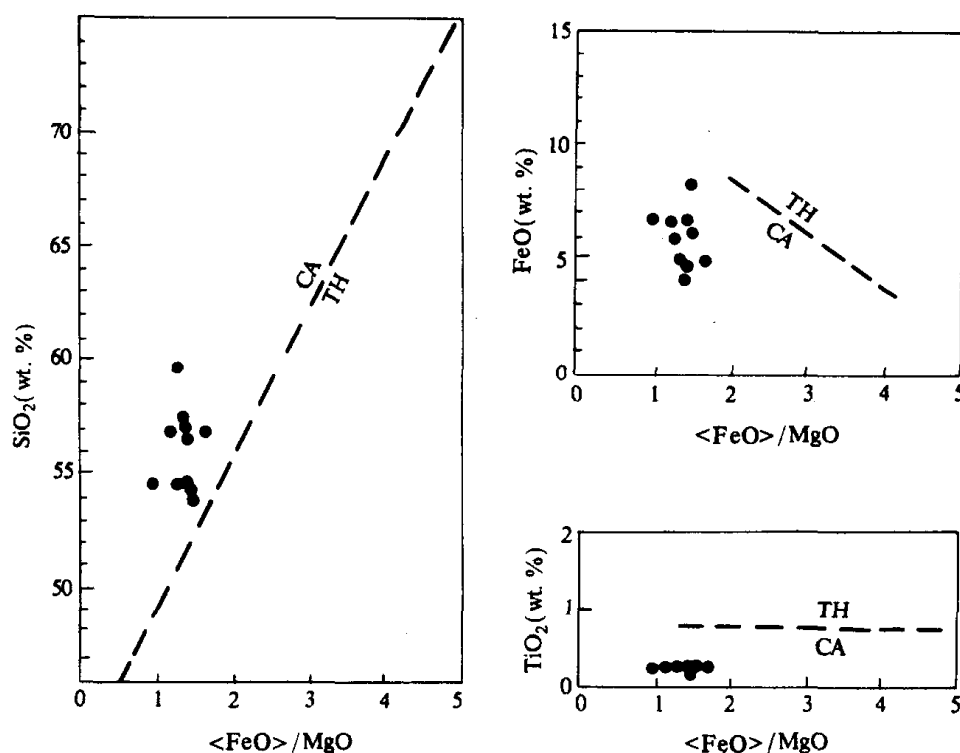


Fig. 3. Classification diagrams of volcanic rock series (after Miyashiro, 1975).

●, Magmatic inclusions in clinopyroxene; TH, tholeiite series; CA, calc-alkaline series.

After having projected the chemical compositions of magmatic inclusions in clinopyroxenes into the classification diagrams (Fig. 3) of volcanic rock series of Miyashiro^[8], we may discriminate that the "source" magma type of spilites in this area must belong to calc-alkaline volcanic suite of island arc type. We need further study whether the sodic spilitic magma in this area is the product derived from differentiation of normal calc-alkaline magma or that of hot brine-magma contamination occurring in seafloor sediments

during the ascension of calc-alkaline volcanic magma^[9]. The authors think that the genetic model of "hot brine on seafloor-magma contamination" referring to the formation of spilite-keratophyre, proposed by Soler^[10] and based on the data of the study on hydrogen and oxygen isotope of spilites from Huelva area in Spain, is more convincing.

REFERENCES

- [1] 夏林圻、黄月华, 地球化学, 1979, 1: 13 — 27.
- [2] Xia Linqi (夏林圻), *Contribution à l'étude des inclusions vitreuses dans différents minéraux des laves: thermométrie, barométrie, compositions chimiques*, Thèse de Doctorat, Université de Paris sud, 1984, 316.
- [3] 夏林圻, 岩石学报, 1987, 2: 51 — 63.
- [4] Bottinga, Y. & Richet, P., *Amer. J. Sci.*, **281**(1981), 615 — 660.
- [5] 夏林圻, 岩石矿物学杂志, 7(1988), 1: 1 — 11.
- [6] Mysen, B. O. et al., *Amer. J. Sci.*, **276**(1976), 455 — 479.
- [7] Булах, А.Г. И Кривовичев, В.Г., *Расчет минеральных равновесий*, 1985, Л. Недра, 183.
- [8] Miyashiro, A., *J. Geol.*, **83**(1975), 249 — 281.
- [9] 夏林圻、夏祖春, 中国地质科学院西安地质矿产研究所所刊, 1987, 19: 1 — 30.
- [10] Soler, E., *Spilites et métallogénie: La province pyrito-cuprifère de Huelva (SW Espagne)*, C.N.R.S., Nancy, 1980, 461.