Clinoenstatite-bearing lava from Népoui, New Caledonia

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Abstract

A vitrophyric clinoenstatite-bearing lava associated with tholeiitic basalts has been found lying immediately below an overthrust peridotite sheet near Népoui, on the west coast of New Caledonia. The lava consists mainly of clinoenstatite phenocrysts (29%), sometimes enclosing euhedral chromite, a lesser amount of microphenocryst bronzite (20%) and a glassy mesostasis. Clinoenstatite phenocrysts are compositionally homogeneous ($En_{89}Fs_{10.5}Wo_{0.5}$) with polysynthetic twins on (100), a feature which is believed to indicate inversion from protoenstatite. Bronzite is variable in composition with $En_{74-84}Fs_{14-22}$ Wo_{1.5-4}. Hypersthene ($En_{43-61}Fs_{36-52}Wo_{3-4}$), calcic and subcalcic augite and iron-rich hornblende occur as overgrowths on phenocrysts and as quench microlites.

The New Caledonian clinoenstatite boninite is similar chemically, mineralogically, texturally and in terms of age (Eocene–Oligocene) and tectonic setting (with ophiolite complexes) to the three other known clinoenstatite boninite localities (Cape Vogel, Papua New Guinea, Bonin Islands and Mariana Trench). Clinoenstatite boninite magmas are believed to result from extensive partial melting of depleted mantle peridotite under hydrous conditions and an abnormally high geothermal gradient.

Introduction

A vitrophyric clinoenstatite-bearing rock was found by one of the authors (J.-P. Paris) in a road cut a few tens of meters north of Riviere Blanche, on the main road (RT-1) north of Népoui on the west coast of New Caledonia and also *in situ* nearby in the bed of Riviere Blanche (Fig. 1).

The exposure in the road cut shows a mylonitic serpentinite sheet, an outlier of the ultramafic nappe overthrust on to the sialic basement of New Caledonia in the Upper Eocene (Paris *et al.*, 1979). The serpentinite overlies the "Formation des Basaltes" which is considered to be para-autochthonous and is composed mainly of basic submarine lavas (tholeiitic basalts and dolerites) with minor acid volcanics (andesite-rhyolite). The "Formation des Basaltes" was erupted during the Upper Cretaceous to Lower Eocene close to the site of the west Caledonian fault zone in a geotectonic setting believed by Paris (1981) to be an island arc environment. The clinoenstatite-bearing rock is possibly a flow and a member of the "Formation des Basaltes" but due to the poor exposure the precise relationship with other members of the formation is not clear.

The Népoui lava closely resembles the clinoenstatitebearing volcanics described from Cape Vogel, Papua New Guinea (Dallwitz *et al.*, 1966; Dallwitz, 1968), the Mariana Trench (Dietrich *et al.*, 1978; Sharaskin and Dobretsov, 1979), and Mukojima and Chichijima, Bonin Islands (Shiraki, *et al.*, 1979; Komatsu, 1980). All of these rocks have petrochemical similarities and are often closely geographically associated with the nonfeldspathic bronzite andesite named "boninite" by Petersen (1891a,b), which, however, lacks clinoenstatite. Sharaskin *et al.* (1979) have proposed the name "marianite" for clinoenstatite-bearing nonfeldspathic andesites; but, if a

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new name is to be applied to this whole group of clinoenstatite lavas, then it should be "vogelite" after the first discovery by Dallwitz *et al.* (1966). Other authors (*e.g.*, Jenner, 1981) prefer to use high magnesian andesites although this term could include feldspathic varieties. However, it seems desirable to use a name which will distinguish the feldspar-free lava types from the more common feldspathic igneous rocks so we have retained the term boninite because the clear mineralogical and chemical distinctions between boninites and the clinoenstatite (CE) rocks can be emphasized satisfactorily by the term "clinoenstatite boninite" (CE-boninite) which is adopted for this paper.

Petrology

The New Caledonia CE-boninite is strongly porphyritic and contains 29% by volume of polysynthetically-twinned clinoenstatite phenocrysts, usually 1–2 mm in length; 20% of orthopyroxene microphenocrysts (0.1 mm diameter) and small amounts of calcic clinopyroxene and hornblende occurring either as slender acicular crystals sometimes forming overgrowths on clinoenstatite and orthopyroxene phenocrysts or as feather-form quench microlites scattered through the glass. Clinoenstatite phenocrysts are sometimes aggregated into stellate clusters and rare centimeter-sized megacrysts are also present. Euhedral chromite grains are enclosed in the clinoenstatite. Tiny magnetite grains in the glass have frequently acted as nucleii for hornblende dendrites.

The glass is usually clear and pale brown in color but occasional spherical brown patches, about a centimeter in diameter, are altered to smectite. Isolated clinoenstatite megacrysts and round altered patches are also common in the Mukojima (Bonin Islands) CE-boninite (Shiraki *et al.*, 1979).

Electron microprobe analyses of representative minerals from the Népoui CE-boninite are listed in Table 1 and the compositional range of the pyroxenes and chromites are shown in Figures 2 and 3, together with comparative mineral analyses from other localities.

The Népoui clinoenstatites are chemically homogeneous with compositions clustered within the very narrow range $En_{87.5-90}Fs_{11-9}Wo_{0.5}$. All the Népoui clinoenstatites are polysynthetically twinned on (100) with habits and textures like those in the Cape Vogel rocks described and figured by Dallwitz *et al.* (1966). For the Cape Vogel clinoenstatite, Sadanaga and Okamura (1969) found that the crystals had the morphology of orthorhombic protoenstatite; heating at 1100°C for 3 hours changed the clinoenstatite into the proto-form.

The Népoui bronzite microphenocrysts show a wider compositional range $(En_{78-83}Fs_{25-22}Wo_{2-4})$ than the clinoenstatites, but are similar to orthopyroxene microphenocrysts in other CE-boninites (Fig. 2) with the orthopyroxenes always having higher Al, Ca and Fe values than the clinoenstatites. The orthopyroxenes in small elongated prisms dispersed throughout the glassy groundmass are



Fig. 1. Map of New Caledonia showing the position of the clinoenstatite boninite locality and its relationship to the tholeiitic "Formation des Basaltes" and the obducted peridotite nappe.

hypersthenes. Calcic clinopyroxenes and amphiboles, whether rimming the clinoenstatite and bronzite or forming discrete prisms in the glass, are strongly zoned from Mg-rich cores (or from contacts with clinoenstatite) to Ca, Fe-enriched outer margins; undulose extinction suggests that they are quench crystals. Calcic clinopyroxene analyses plotted in Figure 2 have a large compositional scatter from calcic to subcalcic augite, reinforcing the suggestion that these are disequilibrium compositions formed during quenching.

The Népoui chromites are compositionally variable with crystals ranging from 49–59% Cr_2O_3 , 19–29% FeO*, 10–12% MgO and less than 10% Al_2O_3 . The high 100 Cr/ (Cr+Al) and low 100 Mg/(Mg+Fe) ratios are typical of all CE-boninite chromites in clear contrast to chromites from boninites and komatiites and from ultrabasic plutonic rocks and xenoliths (Crawford, 1980) as shown in Figure 3.

Geochemistry

Table 2 contains modal mineral, chemical and normative compositions of CE-boninites from New Caledonia, Cape Vogel (Dallwitz, 1968) and the Bonin Islands (Shiraki *et al.*, 1979) as well as the average of 21 CE-boninite chemical analyses from Cape Vogel (Jenner, 1981) and 5 from the Mariana Trench (Dietrich *et al.*, 1978). The chemical characteristics common to all these samples are high magnesia, and low values for alumina, lime, alkalies and titania relative to silica content. In comparison with other clinoenstatite rocks, the New Caledonian lavas are somewhat higher in silica and alkalies and slightly lower in iron oxides and lime (*cf.* Fig. 4).

Trace element data for the Népoui CE-boninite are

10 11 8 9 5 6 7 3 4 2 1 0.91 1.48 40.72 39.97 49.62 50.84 51.47 56.04 57.07 54.59 Si0, 56.14 4.46 0.25 0.15 0.42 0.87 0.27 1.14 0.24 0.25 TiO₂ 0.04 0.13 6.23 5.53 5.56 13.24 3.45 1 4.18 0.97 1.01 5.01 2.35 A1203 0.14 0.04 59.14 0.28 nd 0.31 -Cr₂0₃ 0.12 79.25 19.72 23.27 21.73 12.75 15.56 Fe0* 7.60 9.38 11.96 23.81 16.36 0.32 0.21 0.22 0.16 0.30 0.31 0.44 0.25 FinO 0.16 0.25 0.26 ---NiO 0.07 2 1 -2 10.73 9.06 14.34 11.47 1.23 17.50 22.06 27.69 10.97 Mg0 35.72 31.02 0.35 13.68 0.02 18.14 7.31 1.51 8.28 12.18 0.25 1.30 0.83 Ca0 0.24 0.03 0.75 0.39 0.97 0.21 0.60 Na₂0 0.01 nd 0.07 0.03 0.74 80.0 0.47 0.02 0.13 0.01 nd K₂Û 92.58 95.74 97.75 97.36 99.74 98.90 100.11 97.57 100.53 Total 100.53 98.90

(8)

Table 1. Representative electron microprobe analyses of minerals in Népoui clinoenstatite boninite

a=9.61 (1) Å 1. clinoenstatite phenocryst $\propto = 1.667$ (1); $\chi = 1.676$ (1); $2V_{\chi} = 46.63^{\circ}$;

$$b = 8.87$$
 (1) Å; $c = 5.165(4)$ $\beta = 108.313$

small bronzite crystal attached to clinoenstatite;

3. bronzite microphenocryst

long prismatic hyperstheme 4.

5-7 calcic clinopyroxene 3.

acicular greenish hornblende brown feathery dendritic hornblende 9

10. chromite inclusion in clinoenstatite

magnetite, small groundmass crystal

listed in Table 3, showing the low Ti/Zr and high Cr/Ni and Zr/Y ratios typical of CE-boninite lavas. Compared with the Cape Vogel CE-boninites (Jenner, 1981) the Népoui rock has higher Y, Zr, Nb and La values and lower Ti/Zr and Zr/Y ratios.

Areas of clear glass in the New Caledonian CE-boninite were analyzed by electron probe microanalysis; to avoid surface damage and loss of alkalies the electron beam was defocussed to a diameter of about 10 µm and moved over the surface while counting. The analysis, which totalled 92.3%, was recalculated to 100% and is listed in Table 2 together with an analysis of a glass from a clinoenstatitefree boninite from Kuroda and Shiraki (1975).



Fig. 2. Compositions of pyroxenes from clinoenstatite boninites. Pyroxenes with symbols on legend from literature or from Table 1. Small closed circles and x's are additional clinopyroxene and orthopyroxene analyses from the New Caledonian lava.



Fig. 3. Compositions of chromites from clinoenstatite boninites from New Caledonia (closed circles) and Bonin Islands (open squares; Shiraki and Kuroda, 1977; Shiraki et al., 1979). Compositional fields for chromites in xenoliths in basic magmas, and from alpine and stratiform ultramafic complexes are indicated. B & B.K. is compositional fields of chromites from boninites and basaltic komatiites (Cameron et al., 1979). The chromite field for Howque clinoenstatite-bearing pyroxenite is from Crawford (1980).

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1	U	1	2

	New Cal	edonia	Papua-Ne	w Guinea		Bonin Is	i.	Mariana	CE Boninite	Av Bonin	ite Boninite
	Nép 1	oui 2	Cape 3	Vogel 4	5 Muc	hojima Chi	ichijima 7	Trench	Groundmass	10	Glass
Si0,	57.41	66.93	53.97	54.09	57.48	55.73	53.05	55.58	3 54.81	54.47	62.91
Ti0,	0.22	0.29	0.23	0.30	0.25	0.19	0.19	0.19	0.26	0.24	0.08
A1203	8.80	18.87	7.97	9.55	8.38	10.83	10.81	10.31	10.58	12.31	17.63
Fe ₂ 0 ₃	1.28		2.57	2.49		1.56	2.21	3.12	2.80	1.30	17700
Fe0	5.79	2.90*	6.95	6.54	9.58	6.81	6.15	5.56	6.22	6.42	6.56
NinO	0.15	0.05	0.21	0.15	0.20	0.28	0.21	0.17	0.21	0.17	0.10
MgO	15.92	0.50	16.03	13.03	17.82	10.55	13.42	13.54	10.38	11.59	1.59
CaO	3.38	4.02	4.79	5.46	4.92	6.60	6.55	5.52	6.06	6.77	6.72
Na ₂ 0	1,89	4.55	0.60	0.75	0.84	1.30	0.80	1.77	1.28	1.63	3.82
K20	0.62	1.89	0.35	0.41	0.33	0.53	0.25	0.75	0.51	0.51	0.56
P205	0.06		0.06	0.07		0.01	0.01	0.03	0.05	0.04	
H ₂ O±	4.88		6.07	7.36		5.22	6.55		7.32	4.66	
Total	100.40	100.00	99.80	100.20		99.61	100.20		100.48	100.11	100.00
Q	9.52	21.64	11.48	13.93	7 62	13 39	10 67	9.02	14 70	9 20	17 04
Or	3.66	11.17	2.07	2.42	1.95	3 13	1 48	4 43	3.01	3 01	3 /0
Ab	15.99	38.49	5.08	6.34	7 11	11 00	6 77	1/1 07	10.83	13 70	3.49
An	13.70	19.94	18.02	21 48	18 12	22 15	25 17	17.07	21.62	24 77	32.32
En	39.63	1.24	39.91	32.44	44 36	26.27	33 41	33 71	25.84	29.95	29.22
Fs	9.49	4.94	10.65	9.73	17.55	11.42	9.54	7 63	9 15	10.63	12 10
Wo	1.12		2.23	2.15	2.62	4.39	3.03	3.85	3 39	3 57	1 72
Mt	1.86	2	3.73	3.61		2.26	3,20	4.52	4.06	1.88	0.15
11	0.42	0.55	0.44	0.57		0.36	0.36	0.36	0.46	0.45	-
Ap	0.14		0.14	0.17		0.02	0.02	0.07	0.12	0.09	-
C	-	2.03	120	-			-			-	-
01ivine			540 ·	3 - -1		-	4.0				
Clinoenstatite	29.2		19	5		1.2	6.8				
Bronzite (Phene)	-		2	1		-	-				
Orthopyroxene	20.8		177.0			16.1	20.7				
Ca-Pyroxene	5.8		14	12		35.3	25.7				
Hicrolites	-		22	30		-	1.000				
Hornblende	5.9		<u>i</u>	121		25	-				
Chromite	0.1		0.3	0.3		-	0.4				
Zeolite	-		8	12		÷	1.6				
Glass includin altered glass	g 38.0		35	40		47.4	40.1				

Table 2. Chemical, normative and modal analyses of clinoenstatite boninites

whole rock (1) and groundmass glass (2) whole rock analyses LB107 (3) and LB 105 (4) from Dallwitz (1968) Average of 21 whole rock analyses listed by Jenner (1981) Whole rock analyses from Shiraki et al. (1979) 3,4 5

6,7

8

Average of 5 clinoenstatite boninites listed by Dietrick et al. (1978) Average CE boninite groundmass calculated by subtracting modal clinoenstatite from rock analyses 1,3,4,6 and 7. Average boninite analyses from Bonin Islands (listed by Shiraki (1977)

10 Boninite glass from Kuroda and Shiraki (1975).

The water contents of the CE-boninite and boninite glasses have not been measured directly but can be estimated either from the electron probe analysis (the difference between the total and 100%) as 7.5 and 5.7% respectively for the CE-boninite and boninite glasses, or from the modal analysis and H₂O values of the bulk rock chemical analyses which gives values of 8.5% and 8.7%. The estimated H₂O contents of the glasses (6-9%) are compatible with the low refractive indices of the glasses:

1.520 for the New Caledonian CE-boninite and a range of 1.535-1.550 for a boninite from the Bonin Islands (Kuroda and Shiraki, 1975).

The composition of the CE-boninite glass is dacitic and extremely low in MgO; virtually all the Mg in the rock must be held in the chain silicates (as is also suggested by mineral analyses in Table 1). Compared with the boninite glass, the CE-boninite glass contains less iron and lime and more silica. Calculated groundmass compositions



Fig. 4. Plot of weight percent Al_2O_3 versus MgO and total iron as FeO+MgO for all available analyses of clinoenstatite boninites and boninites from the Bonin Islands. Data for the New Caledonian clinoenstatite boninite are indicated by N. En = the average composition of clinoenstatite phenocrysts occurring in boninites.

obtained by subtracting the modal percentage of clinoenstatite from the bulk rock composition are similar to that of average boninites (Table 2).

Plots of wt.% Al₂O₃ versus MgO and (MgO+FeO*) (Fig. 4) for all available CE-boninite whole rock analyses and groundmass and glass compositions for CE-boninites and some data for boninites (Table 2) show strong linearity suggesting simple crystal fractionation and depletion of the liquid of an Fe-Mg phase (clinoenstatite) is the major factor controlling the chemical variation observed in the CE-boninites. The position of the average boninite composition and glass at the high Al₂O₃, low FeO and MgO section of the plot suggests that addition of clinoenstatite to boninite liquids would change them towards CEboninite compositions. The data seem to support the idea of Bloomer et al. (1979), and Howard and Stolper (1981) that there is a boninite series (including CE-boninite) which is controlled by Fe-Mg pyroxene and/or olivine and spinel fractionation.

Origin of the CE-boninites

Experimental work on the stability of MgSiO₃ includes the enstatite–protenstatite transition which has been determined at 985°C by Atlas (1952) and redetermined at 1042 ± 3 °C by Sarver and Hummel (1962). The presence of the FeSiO₃ molecule apparently raises the inversion temperature (Boyd and Schairer, 1964; Kuno, 1966; Nakamura, 1971). Pressure also raises the inversion temperature and Boyd and England (1965) showed that the protoenstatite field disappears above 8 kbar. More recently, Chen and Presnall (1975) have extended the stability field to 15 kbar at temperatures approaching 1800°C. Sadanaga and Okamura (1969) inverted natural Cape Vogel clinoenstatite into protoenstatite by heating at 1100°C for 3 hours.

The experimental results indicate that the conditions for crystallization of protoenstatite in a boninite magma would be at least 1100°C at a low pressure, perhaps less than a few kilobars. Dallwitz *et al.* (1966) suggested it was the high MgO content of the CE-boninite that was responsible for the crystallization of protoenstatite in the magma.

The geochemistry of boninites and CE-boninites indicates an origin depleted in incompatible elements and rich in refractory constituents. Melting of refractory mantle is facilitated by the presence of water, and the high water contents of CE-boninites plus the modal amphibole are evidence for hydrous conditions at the source.

Experimental work by Green (1973) has shown that high degrees of melting of pyrolite under water-saturated conditions and relatively low pressures (10 kbar) can yield magnesian, quartz normative basaltic andesites but the melt produced in his experiment had "normal" CaO and Al_2O_3 contents such that plagioclase should be a modal constituent. More recently, Kushiro and Takahashi (1981) have produced a liquid chemically similar to a boninite with about 13% MgO and 59% SiO₂ by partial melting of Iherzolite under hydrous conditions at relatively low pressures (12–15 kbar) and high temperatures (1130°C).

It is clear from both the known stability relations of protoenstatite and the partial melting experiments producing a boninite-like liquid, that generation of a clinoen-

Table 3. Trace element compositions of clinoenstatite boninites

		,C	ape Vogel,	Papua	New Guinea		
New Caledonia		НМА Туре С		НМА Туре Е			
		1*	6	7	9	16	18
Rb	13	8	9	6	4	1	11
Sr	180	274	96	69	63	59	110
Zr	90	30	62	32	28	42	24
Nb	8	0.88	3.2	1.7	1.3	2.2	1.3
Cr	1390	715	735	2225	2191	2178	1831
v	130	187	211	158	149	163	164
Ni	265	154	212	415	574	415	288
La	7	1.47	4.06	2.88	2.03	3.25	2.10
Ce	<5	3.51	9.74	5,35	4,35	6.45	4.30
Y	9	7	9	3	4	4	3
Rb/Sr	0.07	0.03	0.09	0.09	0.06	0.02	0.1
Cr/Ni	5.1	3.8	3.5	5.4	3.8	5.2	6.3
Ti/Zr	15	60			39		
Ti/Y	144	257			316		
Zr/Y	10	4.3			8.9		
Zr/Nb	11	34			19.4		
La/Nb	0.9	1.7			1.5		
La/Zr	0.09	0.05			0.078		

*Numbers refer to Analyses listed in Tables 2 and 3 of Jenner (1981)

statite boninite requires a hydrated, high temperature environment at shallow depths (less than 15 kbar). How water is introduced into refractory mantle at depths shallow enough to stabilize clinoenstatite, without introducing incompatible elements is an enigma, especially since hydrous metasomatic fluids are widely advocated by petrologists as a method of producing, for example nephelinite enriched in incompatible elements (*e.g.* Menzies and Murthy, 1980; Wass, 1980). Perhaps extensive mantle melting, causing extreme dilution of incompatible elements, would have the same effect (Shiraki *et al.*, 1980) but this requires an abnormally high heat input.

Anomalous heating of the upper mantle should be reflected by some corresponding unusual geological event. Cameron *et al.* (1979) have pointed out that boninites are almost exclusively associated with ophiolites. The CE-boninite occurrences are restricted to Eocene-Oligocene ophiolite associations along the western Pacific margin but in no locality is the relationship between the CE-boninites and associated ophiolites sufficiently clear to point to some common genetic event.

Ideas on the type of geological environment in which CE-boninites were erupted are various and contradictory. Shiraki et al. (1980) hypothesized that a possible site for generating clinoenstatite-bearing rocks may be at shallow depths below a spreading ridge or island arc after the main magmatic episode in an environment with an exceptionally steep geothermal gradient where water liberated from the underlying subducted oceanic crust could be introduced into the melting zone. Crawford et al. (1981) however, considered that the boninites (some clinoenstatite-bearing) associated with ophiolites and MORB tholeiites of the West Philippine-Mariana region and elsewhere were erupted in a fore-arc position after arc magmatism and before eruption of voluminous MORB tholeiites. In contrast to the above, Paris (1981) concludes that the "Formation des Basaltes" with which the New Caledonian CE-boninites are associated, were erupted in a backarc expansion zone.

In conclusion, it can be said that CE-boninites are confined to the same tectonic environments as ophiolites and that CE-boninite magmas appear to result from extensive partial melting of depleted mantle peridotite under hydrous conditions and an abnormally high geothermal gradient. CE-boninites are not related, at least in any simple way, to geologic and petrographic processes that give rise to an island arc volcanic suite.

Acknowledgments

We are indebted to Professor R. N. Brothers and Dr. I. E. M. Smith for critical reading of the draft manuscript and their many helpful comments.

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Manuscript received, May 24, 1982; accepted for publication, April 18, 1983.