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Two-stage model of carbonatite origin: evidence from metasomatised mantle xenoliths

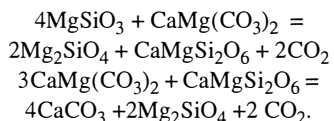
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ABSTRACT. — The geochemical study of mantle xenoliths from Montana Clara island (Canary archipelago), Fernando de Naronha island (Brazil) and East Antarctic revealed that mantle of these regions has been affected by intense carbonate metasomatism.

Primary generation olivine, orthopyroxene and clinopyroxene in mantle xenoliths of these regions are crossed by veinlets of fine-grained assemblage, which replaces minerals of the first generation, especially orthopyroxene. These finegrained zones contain second generation clinopyroxene, olivine, carbonate, glass, sulfides, sometimes apatite, Ba-rich mica, henrymeyerite, armalcolite, krishtonite, perovskite.

The carbonate metasomatism led to wehrlitization of the primary mineral assemblage according to the reactions:

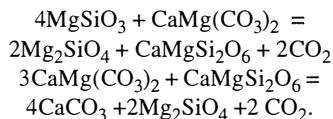


The interrelationships between the glass, sulfide and carbonate permit speculation that silicate, sulfide and Ca-rich carbonatite melts were in equilibrium with each other and originated from partial melting of metasomatized and wehrlitized peridotite.

On the basis of these data we developed the two-stage model of Ca-rich carbonatite formation: first stage-metasomatic wehrlitization and

carbonatization of mantle substrate; second stage-partial melting of the carbonatised wehrlite, resulting in the formation of calciocarbonatites.

RIASSUNTO. — Lo studio geochimico degli xenoliti mantellici provenienti dalle isole di Montana Clara (Arcipelago delle Canarie) e Fernando de Naronha (Brasile) e dalla regione Antartica orientale hanno rivelato che il mantello al di sotto di queste regioni è stato modificato da un intenso metasomatismo carbonatico. Olivina, ortopirosseno e clinopirosseno di prima generazione negli xenoliti mantellici di queste regioni sono tagliati da venuzze costituite da un insieme a grana fine che rimpiazza i minerali di prima generazione, in particolar modo ortopirosseno. Queste zone a grana fine contengono clinopirosseno, olivina, carbonato, vetro, solfati, a volte apatite, mica ricca in Ba, henrymeyerite, armalcolite, krishtonite, perovskite di seconda generazione. Il metasomatismo carbonatico ha portato alla wehrlitizzazione dell'insieme mineralogico primario seguendo la reazione:



Le relazioni interne tra vetro solfato e carbonato suggeriscono che fusi silicatici, carbonatici e solforici erano in equilibrio tra loro e si sono formati per fusione parziale di peridotite metasomatizzata e wehrlitizzata. Sulla base di questi dati abbiamo sviluppato un modello a due stadi per la formazione di carbonatite ricca di Ca: primo stadio -

wehrlitizzazione metasomatica e carbonatazione del substrato matellico; secondo stadio - fusione parziale della wehrlite carbonatata, e formazione di calciocarbonatiti.

KEY WORDS: - *Carbonate metasomatism, Ca-rich carbonatite formation, sulfide-carbonate-silicate immiscibility*

INTRODUCTION

Mantle metasomatism is a very powerful process of global geochemical differentiation. The large-scale mass transportation in the upper mantle is closely connected with the origin of carbonatitic magmatism. For example, isotopic data for Kola Peninsula alkaline rocks, carbonatites and related gigantic rare metal deposits suggest that they originated from a relatively depleted mantle source: ($\epsilon\text{Nd} = 4.5$; $\text{Sr}^{87}/\text{Sr}^{86} = 0,7035 - 0,7038$ (Kogarko *et al.*, 1983; Kogarko, 1996). So there is a paradox: on the one hand these rocks are extremely enriched in rare elements and on the other they have an isotopic signature corresponding to mantle rocks depleted in trace elements. The enormous concentration of rare elements in the alkaline rocks of this region is mostly related to large-scale processes of mantle metasomatism confined to a very narrow time span (371-361 Ma), so the primary isotopic signature of the depleted rocks stayed unchanged. Metasomatism, cryptic and patent, has been observed in upper mantle rocks world wide (Menzies and Hawkesworth, 1987). Various researchers have suggested that primary carbonate melts could be efficient metasomatizing agents, forming second generation clinopyroxene, olivine, spinel and minerals enriched in light rare earth elements (LREEs) such as apatite, kirshtonite kirschsteinite etc (Dautria *et al.*, 1992; Ionov *et al.*, 1993, 1994; Kogarko *et al.*, 1995; Rudnick *et al.*, 1993; Yaxley *et al.*, 1991, 1998). Experimental investigations demonstrated (Dalton, B.J. Wood, 1993) that at pressure about 15kb carbonatite melts reacting with mantle material are strongly

enriched in calcium and close to Ca-rich carbonatites.

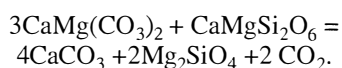
The experimental study conveyed by many authors suggest that the liquid immiscibility plays the leading role in the genesis of carbonatites (Freestone and Hamilton, 1980; Hamilton *et al.*, 1989; Kjarsgaard and Peterson, 1991). Experimental data demonstrated the presence of the extensive fields of two immiscible liquids in system $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2 - \text{MgO} + \text{FeO} - \text{CaO} - \text{Na}_2\text{O} + \text{K}_2\text{O} - \text{CO}_2$. Recently the detailed studies of the geochemistry of mantle nodules and primary mantle carbonates permitted to conclude that carbonatite magmas may be generated in the mantle (Amundsen, 1987; Pyle and Haggerty, 1994; Kogarko *et al.*, 1995a) as result of liquid immiscibility.

However, Lee and Wyllie (1994, 1996) have pointed out a number of limitations on this hypothesis. They presented evidence that crystalline calcite can grow in silicate-carbonate liquids with a remarkably rounded morphology simulating the characteristics of melts. On the basis of the available experimental evidence they concluded that the compositions of carbonate aggregates situated in the aluminosilicate glass in mantle xenoliths makes these aggregates unlikely candidates for Ca-rich carbonate liquids immiscible with silicate liquids.

Therefore the genesis of Ca-rich carbonatitic melts in the upper mantle still remains unsolved, so new mineralogical observations on the interrelationships between carbonate and silicate material in deep-seated xenoliths remain very important. Although mantle xenoliths provide convincing evidence for the presence of primary Ca-rich carbonates, comparable evidence has not yet been presented for the role of carbonate-silicate immiscibility phenomena in the upper mantle. In this paper we present such evidence based on data from a set of strongly metasomatized xenoliths in basaltic lava flow from Fernando de Noronha Island (South-West Atlantic), Montana Clara Island (Canary archipelago) and Est Antarctic.

METASOMATIZED MANTLE MATERIAL FROM
MONTANA CLARA ISLAND

During the investigation of a harzburgite nodules from the Montana Clara Volcano (Canary island archipelago) the evidence of the primary carbonate melt was discovered. This carbonate is enriched in calcium and it occurs together with glass (Fig. 1a) containing sulphide globules. In addition to primary olivine and orthopyroxene there are pockets of fine-grained minerals belonging to the metasomatic second generation (more magnesian olivine, sodium-bearing clinopyroxene, less aluminous spinels). The metasomatic assemblage was formed by reaction of sodium-bearing dolomitic melt with the harzburgite according to the reactions:



The calciocarbonatite and sulphide phase almost invariably form globules (Fig. 1b) in the silicate glass indicating the existence of three immiscible liquids under upper mantle conditions resulting from melting of the metasomatised mantle material during the uprising and adiabatic decompression. Therefore the investigated mineral assemblage including carbonate and glass can be considered as a micro model of the generation of the Ca-rich carbonatitic magmas during the processes of the partial melting of carbonatized metasomatized oceanic mantle.

CARBONATE METASOMATISM OF THE OCEANIC
MANTLE BENEATH FERNANDO DE NORONHA
ISLAND, BRAZIL

Petrologic and geochemical study of lherzolitic and harzburgitic xenoliths from basanites of Fernando de Noronha island (San Joze formation) revealed that oceanic mantle of this region has been affected by very intense

carbonate metasomatism. Most of the spinel lherzolites and harzburgites have granoblastic and porphyroclastic texture. Xenoliths show clear evidence for patent metasomatism characterized by the presence of Ca-rich carbonate, apatite, kirschsteinite, Ba-Sr sulfate (barian strontianite) and second generation assemblages consisting of fine-grained olivine (5-40 μm , clinopyroxene (1-35 μm , spinel (1-15 μm , carbonate (10 up to 200 μm , glass (up to 1-2 μm) and sulfides (0.5-10 μm .) First mineral generation is crossed by numerous veinlets of a fine-grained assemblage which also often surrounds orthopyroxene as reaction zones (Figs. 1c, d, e). In these zones second generation clinopyroxene replaces primary orthopyroxene and occasionally second generation olivine.

The composition of first generation olivine, orthopyroxene, clinopyroxene and spinel (Table 2) is typical of upper mantle lherzolites. Second generation olivines are richer in calcium (up to 0.27 wt%) than the primary olivines (0.06-0.08 wt%). Second generation clinopyroxenes are more Ca- and Mg-rich and less aluminous and sodic compared with the original clinopyroxenes. However, in some second generation clinopyroxenes the sodium concentration reaches up to 2.55 wt%, which is higher than that of the primary clinopyroxenes. In some rocks networks of veinlets are present (up to 2 μm wide and up to 100 μm long) which are filled only with Ca-rich carbonate. The carbonate composition is Mg-bearing calcite with an atomic Ca/(Mg+Ca+Fe+Na) ratio in the range of 0.85-0.96 and which contains minor amounts of Si, Fe, Al and Na (Table 1).

Interstitial patches of brownish Na-Al glass incorporate second generation olivine, clinopyroxene, spinel and carbonate. Quench crystals of Cl-bearing apatite (Cl content is up to 0.65 wt%) and rutile are also present in the glass. The composition of the glass is variable (table 2) ranging from that of basaltic andesite to those of highly evolved melts: trachytic, phonolitic and dacitic. Glasses often include Fe-Ni sulfide globules with compositions typical for primary mantle sulfides (Table 2).

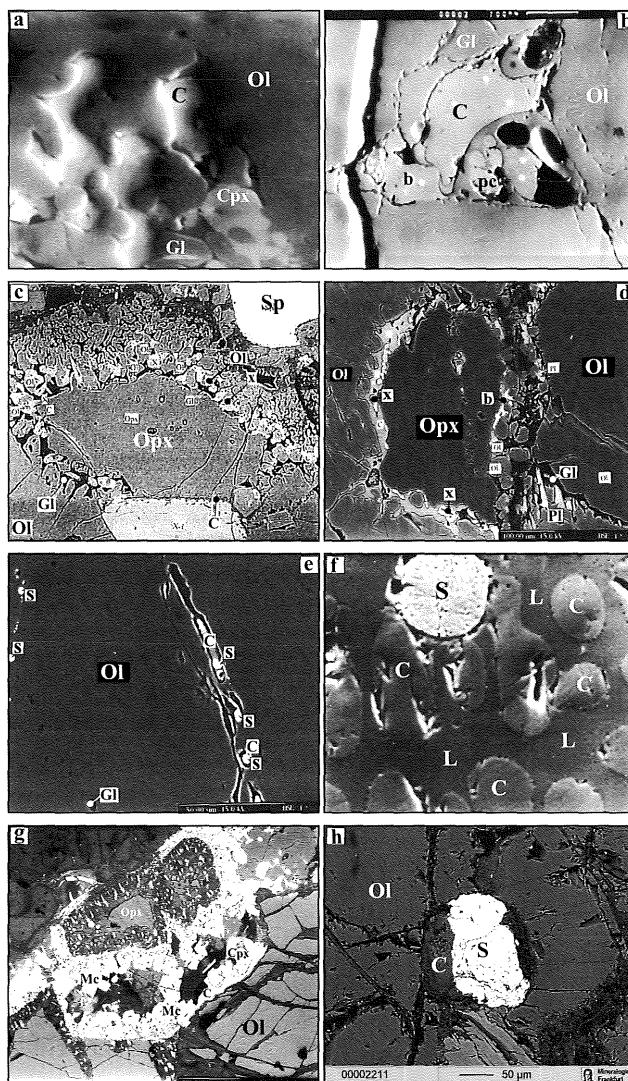


Fig. 1 – Examples of reactions. **a)** Back-scattered electron image of carbonate-containing reaction zone, xenolith from Montana Clara island. C-carbonate, cpx-clinopyroxene, Ol-olivine, Gl-glass. **b)** Montana Clara Island (Canary Archipelago) Back-scattered electron image of carbonate – silicate segregation in nodule. Interstitial patch between first generation olivine crystals (abbreviations: C-carbonate, pc-«plucked-out» carbonate, Gl-silicate glass, S-sulphide globule, as-altered sulphide bleb, Ol-olivine. Round marks – in carbonate and glass (labelled b) mark positions of EMP spots. **c)** Fernando de Noronha Island. Back-scattered electron image of orthopyroxene being replaced by fine-grained mineral assemblage. Opx-orthopyroxene, Ol-olivine, X-clinopyroxene, Gl-glass, C-carbonate. **d)** Fernando de Noronha Island. Back-scattered electron image of orthopyroxene being replaced by fine-grained mineral assemblage. Opx-orthopyroxene, Ol-olivine, X-clinopyroxene, Gl-glass, C-carbonate, Ba-strontianite. **e)** Fernando de Noronha Island. Back-scattered electron image of inclusions in carbonate inclusion containing a sulfide globule (C), inclusion is partly leached; grey: inclusions of trachytic phonolitic glass (Ge). **f)** Back-scattered electron image of the melt experiment product, T=1220°C, p=8 kbar. Sulfide-silicate-carbonate immiscibility, bright-sulfide liquid, dark-glass silicate liquid (L). **g)** Antarctic. Back-scattered electron image of reaction zone. Orthopyroxene is substituted by clinopyroxene, Ba-rich mica, carbonates. **h)** Antarctic. Back-scattered electron image of inclusion in olivine containing carbonate (grey) and sulfide (white).

TABLE 1

Compositions of nodules and minerals and carbonates from nodule MC-1 Nodule analyzed by XRF at Institute of Geochemistry, Moscow; Minerals by electron microprobe at Manchester University, and Moscow With beam current 15 nA and spot size 2 μm except for glass and carbonate where beam was 10 μm .

	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	Cr ₂ O ₃	NiO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	S	Sum	Mg#
Nodule MC-11	44.50	0.03	0.88	7.70	0.13	0.30	NA	45.60	0.75	0.11	0.04	0.05	NA	100.1	0.91
Nodule MC-12	44.10	0.05	1.40	7.90	0.15	0.57	NA	44.40	0.73	0.10	0.09	0.05	NA	99.5	0.91
Olivine (I) ^{ab}	41.60	-	-	8.60	-	-	0.31	50.10	0.07	-	-	-	-	100.7	0.91
Spinal (I) ^d	-	0.03	30.30	15.40	-	39.50	0.10	15.40	-	-	-	-	-	100.7	0.67
Spinal (I) ^d	-	-	25.70	13.90	-	44.70	0.10	15.00	-	-	-	-	-	99.4	0.66
Spinal (I) ^d	-	0.10	19.30	11.40	-	53.80	-	15.70	-	-	-	-	-	100.3	0.71
Glass ^c	63.80	0.70	16.00	2.00	-	0.06	-	2.50	3.80	6.40	3.80	-	-	99.1	0.69
Carbonate ^c	4.10	-	1.20	0.59	0.09	0.14	-	6.80	54.30	0.20	0.13	1.90	0.24	69.7	0.95
Carbonate ^c	1.10	-	0.27	0.28	-	0.18	-	3.10	50.80	0.31	-	-	-	56.0	0.93
Carbonate ^c	-	-	-	0.10	-	-	-	3.10	47.00	0.13	-	0.15	0.14	50.6	0.98
Cpx (host lava) ^b	49.50	1.60	5.70	5.80	-	0.57	-	14.30	22.80	0.67	-	-	-	100.9	0.82
Ortho-piroxene (I) ^d	57.40	-	1.00	5.20	0.11	0.50	0.11	34.60	0.21	-	-	-	-	99.1	0.92
Olivine (II) ^f	39.30	-	-	7.30	0.14	-	0.37	51.10	0.20	-	-	-	-	98.4	0.93
Clino-piroxene (II) ^b	54.30	-	3.00	2.60	0.12	0.97	-	17.90	19.80	1.10	-	-	-	99.8	0.93
Clino-piroxene (II) ^b	53.50	0.05	2.60	2.30	0.10	0.34	0.11	18.30	21.50	0.19	-	-	-	99.0	0.94

(- not detected, NA not analyzed).

TABLE 2
Chemical compositions of bulk rocks, minerals and melt inclusions

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	Fe	MnO	Cr ₂ O ₃	NiO	Ni	MgO	CaO	Na ₂ O	K ₂ O	Zn	Cu	S	Sum
Xenoliths																	
FN-20	44.3	0.2	2.7	8.6	-	0.1	0.2	-	-	40	2.2	0.3	0.1	-	-	-	98.7
Olivine (I)	40.9	-	-	9.9	-	0.1	-	0.3	-	48.5	0.1	-	-	-	-	-	99.8
Olivine (II)	40.6	0.1	-	10.1	-	0.2	0.1	0.2	-	47.5	0.2	-	-	-	-	-	99
Orthopyroxene (I)	54.1	0.1	4.7	6.3	-	0.1	0.5	0.1	-	32.1	0.8	0.1	-	-	-	-	98.9
Clinopyroxene (I)	51.1	0.2	5.7	3.04	-	0.1	0.9	-	-	15.8	18.7	1.2	-	-	-	-	97.1
Clinopyroxene (II)	53.1	1	1.2	2.9	-	-	1.2	0.1	-	18.1	22.7	0.6	-	-	-	-	100.9
Spinel (I)	0.1	0.1	45.5	17.8	-	0.1	16.2	0.3	-	17.8	-	-	-	-	-	-	97.9
Spinel(II)	0.1	68.5	1.3	11.7	-	0.1	1.6	-	-	11.3	0.1	-	-	-	-	-	94.7
Carbonate																	
inclusion	2.9	0.7	1	1.3	-	-	-	-	-	4.3	45.5	0.5	0.4	-	-	-	56.6
Carbonate	0.3	-	-	0.3	-	-	-	-	-	1	52.4	0.1	-	-	-	-	54.1
Glass inclusion	57.5	1	25.4	1.6	-	-	-	-	-	-	1	9	3.9	-	-	-	99.4
Sulphide inclusion	-	-	-	-	32.7	-	-	-	32.5	-	-	0.1	-	-	-	34	99.3
Sulphide in carbonate																	
microinclusion	-	-	-	-	33.3	-	-	-	31.8	-	-	-	-	2.6	0.8	31.4	99.9
Kirschsteinite	30.9	0.1	0.3	19.7	-	0.4	-	0.1	-	15.8	31.4	-	-	-	-	-	98.78
Cpx (host lava)	47.4	2.5	4.5	6.8	-	0.4	-	0.2	-	12.3	25.2	0.7	-	-	-	-	100

TABLE 3
Composition of minerals in Antarctic nodules

	SiO ₂	Al ₂ O ₃	TiO ₂	FeO	MgO	MnO	CaO	NiO	SrO	BaO	Na ₂ O	K ₂ O	La ₂ O ₃	Nb ₂ O ₅	Ce ₂ O ₃	P ₂ O ₅	F	Cl	Total	F=O	Cl=O	Total
Apatite	0.3				0.09		45.89		9.77				0.5		0.71	39.07	1.62	0.11	98.06	0.68	0.03	97.35
Perovskite			51.8	1.09	0.02	0.04	32.44		4.14		1.9		1.28	2.46	2.09				97.26			97.26
Mical	33.32	14.4	11.97	7.9	14.62	n.d.	0.11	0.13		7.75	0.53	6.48					1.07		97.25	0.45		96.8
Mica2	33.78	15.48	4.61	3.48	21.74	n.d.	0.07	0.06		9.12	0.16	6.86					0.77		95.87	0.32		95.55
Henrymairite	1.84	0.14	65.13	8.06	0.86	n.d.	0.19	n.d.		18.16	0.4	0.2					n.d.		94.98			94.98

The metasomatism led to a wehrlitization of the primary harzburgitic minerals assemblage (Ol, OPx, Sp) (figs 1c,d,e) and to an increase of the Mg/Fe ratios of the minerals. The wehrlitization was the result of interaction between an ephemeral sodic dolomitic melt or fluid with the harzburgitic rock according to the reactions 1 and 2. This model is in agreement with the experimental results of Dalton and Wood (1994). Olivine have abundant polyphase, glass-rich inclusions consisting of trachytic glass, monosulphide of Fe, Ni, and Cu, Ca-rich carbonate and dense CO₂ (Fig. 1e). All major silicate phases of the rocks are rich in CO₂ inclusions. The interrelationships between glass, sulphide and carbonate inclusions permit to speculate, that silicate and sulphide in the Ca-rich carbonatite melts were in equilibrium with each other and originated from partial melting of metasomatized and wehrlitized mantle of Fernando de Noronha island. We have experimentally investigated, with a piston-cylinder apparatus, the immiscibility relationships in the system Ca-rich carbonate - Fe, Ni sulphide - silicate melt of phonolitic composition, containing F. Experiments were made at 1250°C and 4-15 kbar. The double-Pt-capsule method has been employed in order to control the oxygen fugacity. Immiscibility has been observed in the investigated system as a complete separation of the carbonate and silicate liquids, with sulphide melt present in the form of small globules in both liquids. The sulphur solubility in the silicate melt varies from 0.15 to 0.35% and in carbonate liquid from 0.02 to 3.7% depending on the alkali content.

INTENSE CARBONATE METASOMATISM OF THE EAST ANTARCTIC MANTLE

Petrological and geochemical evidence suggests that lithospheric mantle of Eastern Antarctic has been affected by very intense carbonate metasomatism resulting in the development of such minerals as Sr-rich apatite, Nb and REE-rich perovskite, Ba and

Ti-rich mica, sulphides, carbonates and clinopyroxenes of second generation.

For the first time henrymeyerite was found in mantle material.

Many inclusions mostly in olivine contain simultaneously sulphides and carbonate with obvious meniscus. Which is the evidence of liquid immiscibility between sulphide and carbonate liquid (Fig. 1h).

CONCLUSION

The results obtained allow the development of the two-stage model of Ca-rich carbonatite formation: 1-st stage-metasomatic wehrlitization and carbonatization of mantle substrate; 2-nd stage - partial melting of the wehrlitic peridotites containing carbonates, and resulting in the formation of immiscible silicate and sodic carbonate liquid, and ultimately generation of calciocarbonatites.

If the sulphur concentration was high in the metasomatised mantle three immiscible liquids could be produced.

We suggest a close connection between carbonatite metasomatic processes in the oceanic and continental lithosphere and the origin of very Ca-rich, silica-undersaturated and carbonatitic magmas in some of the Canary, Cape Verde, Fernando de Noronha islands and East Antarctica.

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