

The First Finding of Carbonatite Tuffs in Cenozoic Basaltic Volcano of Southeastern Primorye

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Presented by Academician A.A. Marakushev September 7, 2005

Received September 8, 2005

DOI: 10.1134/S1028334X06040246

The origin of carbonatites and carbonatite-type rocks remains a debatable petrologic problem. Therefore, any information on findings of these rocks is valuable for the better understanding of key mechanisms of their formation.

We found carbonatite tuffs among eruption products of the early Neogene Amba Volcano in southwestern Primorye (Fig. 1). The volcanic edifice occupies an area of ~20 km² in the middle reaches of the Amba River at a distance of 28 km from Amur Bay. The basalts of the stratovolcano base overlie the Permian carbonate and volcanosedimentary rocks and the Triassic arkose sandstones. The basalts are, in turn, overlapped by the upper Miocene volcanosedimentary rocks of the Ust-Suifun Formation and basalts of the Shufan Plateau. The central vent of the Amba Volcano is filled with explosion breccia and basaltic lavas. Pyroclastic rocks, including layers of carbonatite tuffs, compose the peripheral facies of the volcano.

The eruption is characterized by a sequential transition from olivine–clinopyroxene to spinel–Ti–augite–plagioclase varieties. Spinel and clinopyroxene megacrysts (3–8 mm across) in basalts contain rounded carbonate inclusions. In addition, the basalt groundmass contains numerous late carbonate segregations in gas cavities. The segregations are especially abundant in the vent facies, indicating predominance of carbon dioxide among volcanic gases.

The basalts are characterized by subalkali, high-Ti, high-Mg, and high-Ca composition with low content of silica, high contents of Sr, Ba, Nb, and Zr, and less common Ce, Nd, Sm, and Th (Table 1). According to their HFSE and REE contents, they correspond to within-plate alkali basalts with negative slope of PM-normalized REE pattern.

The carbonatite tuff layers were found in the southwestern part of the volcanic edifice on the right wall of the Vtoroi Creek, the right tributary of the Amba River. The welded carbonatite tuffs occur as two layers (2.0–2.5 m thick) at the base and top of the visible section. They are separated by interlayers of tuffaceous basaltic sandstones and gravelstones with a variable carbonate admixture. The tuffs are dark gray massive, severely welded rocks with psammitic and psephitic dimensions of crystal fragments and lithic clasts. The high degree of tuff welding is related to enrichment of the natural carbonate–silicate cement in calcareous component. Tuffs contain fragments of tree trunks and xenoliths of intrusive and sedimentary rocks from the basement. The geological observations indicate that the bedded volcanoclastic member of carbonatite tuffs was formed as a result of multiple directed volcanic explosions with formation of gas-saturated pyroclastic flows deposited in depressions (often waterlogged) around the volcano.

The welded tuffs in the section are supplemented with tufflavas represented by more compact carbonate–silicate aggregates (20–25 cm in size) with large spinel and clinopyroxene phenocrysts. Walls of numerous gas cavities and pores in this rock are coated with pale crystalline carbonate.

The carbonatite tuffs are composed of crystal and lithic clasts. The white or light gray lithic clasts (0.2–0.5 cm in diameter) have irregular or rounded (ocellar) shape. They are largely composed of carbonate material with spinel and pyroxene phenocrysts and plagioclase laths (Figs. 2, 3). The lithic clasts have an unusually high content (up to 3–5 vol %) of rather large (up to 5–12 mm) crystals of aluminous spinel and their fragments. The fassaite clinopyroxene is less abundant (Table 2). They also contain relatively large (up to 0.5 cm) orange (less frequently, transparent white or cherry-colored) euhedral and rhombohedral Fe–Mg–calcite crystals incorporated into the cement (Fig. 3, Table 2). Crystals of spinel (with faces of dissolution), clinopyroxene, and calcite occur in both the carbonatite clasts



Fig. 1. Location of carbonatite tuffs in the Amba River basin and carbonate-bearing rocks on the Shufan basaltic plateau. (1) Base-ment rocks; (2) outcrops of limestone of the Permian Barabash Formation; (3) basalts of the Shufan Plateau; (4) basalts and tuffs of the Amba Volcano; (5) occurrences of (a) carbonatite tuff of the Amba Volcano and (b) carbonate-bearing basalts. (1) Shufan Plateau, (2) Baranovsky Volcano.

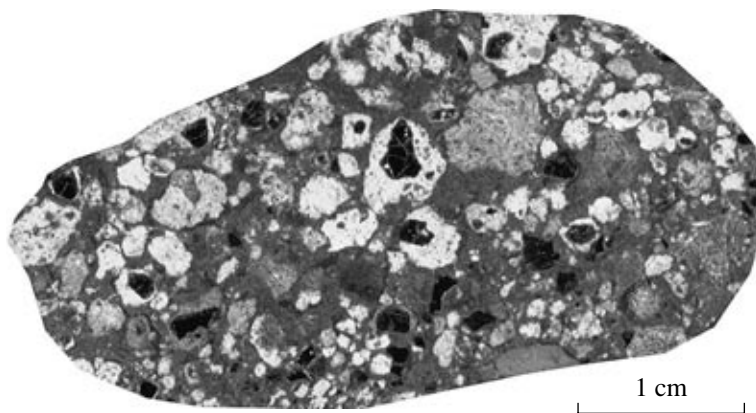


Fig. 2. Spinel-fassaite carbonatite tuff from the Amba Volcano (polished sample). Spinel (black) and clinopyroxene grains in carbonatite clasts (light) and groundmass (dark gray). Sample P-496/2.

and carbonate-silicate matrix. Calcite, often intergrown with spinel and clinopyroxene, contains microinclusions of these minerals (Fig. 3). Clinopyroxene and spinel, in turn, contain two-phase melt inclusions

and droplets of solidified carbonate melt. Spinel droplets in fassaite are also noteworthy. In general, spinel and clinopyroxene in carbonatitic clastic rocks are variable in composition (Fig. 2).

Table 1. Chemical composition of major oxides (wt %) and minor elements (ppm) in basalts and carbonatite tuffs from the Amba Volcano

Component	Sample P-490/1	Sample P-491/1	Sample P-492/3	Sample P-494/6	Sample P-492/5	Sample M-5407/1	Sample M-5539/2	Sample P-496/2	Sample M-5537
	1	2	3	4	5	6	7	8	9
SiO ₂	44.56	44.18	43.39	43.94	44.77	46.63	30.93	33.36	23.31
TiO ₂	2.20	2.31	2.27	1.97	2.17	2.25	1.13	1.30	1.88
Al ₂ O ₃	15.81	15.37	15.34	14.70	15.79	17.89	12.62	11.53	11.70
Fe ₂ O ₃	2.50	8.59	6.70	5.51	3.48	4.69	3.04	4.17	2.64
FeO	7.40	2.52	3.71	4.55	6.30	5.08	2.34	1.85	1.52
MnO	0.18	0.19	0.18	0.14	0.16	0.16	0.46	0.17	0.33
MgO	9.00	6.43	9.36	7.34	9.91	5.61	4.60	6.81	2.76
CaO	9.50	9.57	9.74	10.15	9.76	8.34	22.72	16.29	27.72
Na ₂ O	3.03	2.85	2.36	3.28	2.62	3.36	0.90	1.03	0.88
K ₂ O	0.68	0.66	0.69	1.26	1.05	1.43	0.56	0.64	0.15
P ₂ O ₅	0.42	0.40	0.41	0.39	0.39	0.44	0.23	0.25	–
CO ₂	–	–	–	–	–	–	13.95	14.07	20.93
H ₂ O [–]	0.51	1.99	0.85	1.39	0.34	0.70	1.79	2.60	1.03
L.O.I.	3.83	4.51	4.57	4.88	3.11	3.12	4.91	6.46	4.78
Total	99.62	99.93	99.57	99.50	99.85	99.70	100.18	100.53	99.63
Ni	160	160	120	120	167	65	–	100	–
Co	46	44	36	28	49	23	–	28	–
Cr	210	190	170	170	217	66	–	69	–
V	140	150	150	120	236	130	–	110	–
Rb	15	23	15	12	27	58	23	–	–
Cs	–	–	–	–	–	18.4	5.31	–	–
Sr	766	724	821	782	1085	1303	518	–	–
Ba	706	657	781	771	528	1084	527	–	–
Y	16	23	29	24	25	34	18	–	–
Zr	158	168	165	194	180	225	90	–	–
Nb	31	31	36	32	39	38	13	–	–
Ta	6	5	6	6	2	2.7	5.31	–	–
Hf	–	–	7.0	7.0	4.1	5.6	2.7	–	–
La	–	–	–	–	25	68	19	–	–
Ce	–	–	–	–	53	118	30	–	–
Pr	–	–	–	–	6.7	16	39	–	–
Nd	–	–	–	–	25	70	18	–	–
Sm	–	–	–	–	4.9	12	3.3	–	–
Eu	–	–	–	–	1.92	3.4	1.13	–	–
Gd	–	–	–	–	5.2	10	3.7	–	–
Tb	–	–	–	–	0.7	1.3	0.56	–	–
Dy	–	–	–	–	4.4	6.8	3.23	–	–
Ho	–	–	–	–	0.9	1.3	0.60	–	–
Er	–	–	–	–	2.1	3.65	2.12	–	–
Tm	–	–	–	–	0.33	0.48	0.26	–	–
Yb	–	–	–	–	1.80	2.47	1.42	–	–
Lu	–	–	–	–	0.26	0.41	0.21	–	–
Pb	–	–	–	–	2.2	4.2	4.5	–	–
Th	–	–	–	–	2.83	5.52	2.18	–	–
U	–	–	–	–	0.80	0.85	0.69	–	–

Note: (1–6) Basalts, (7, 8) carbonatite tuffs, (9) carbonatite ocellus from tuff. Major oxides were determined by chemical analysis at the Analytical Center, Far East Geological Institute (L.I. Alekseeva, analyst). In samples P-492/5, M-5407/1 and M-5539/2, minor elements were determined by ICP-MS at the Institute of Geochemistry, Irkutsk (G.P. Sandomirova, analyst); in other samples, by emission spectroscopy (Ni, Co, Cr, and V) and XRF analysis at the Analytical Center, Far East Geological Institute (L.I. Azarova and E.A. Nozdrachev, analysts). (–) Not analyzed.

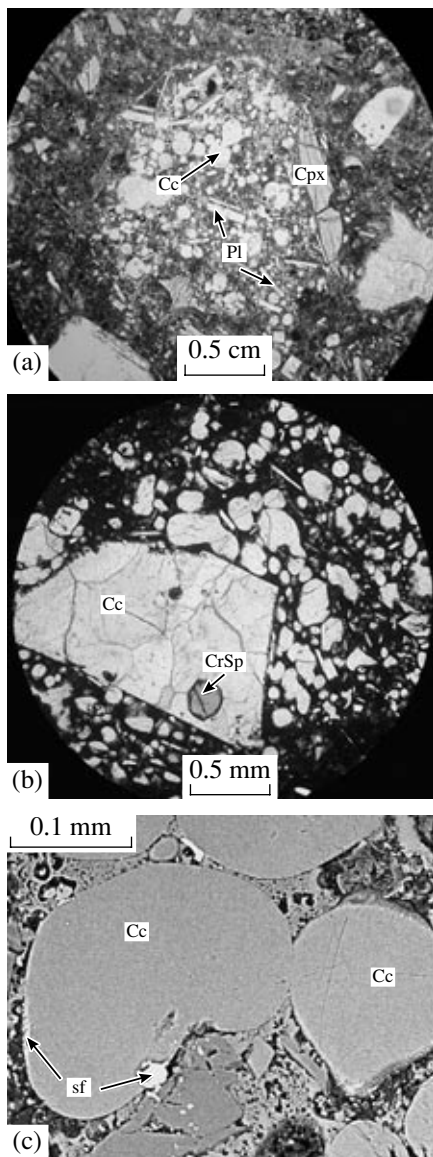


Fig. 3. Microphotographs of thin sections. (a) Carbonatite ocelli with calcite globules (Cc) containing crystals of plagioclase (Pl) and fassaite (Cpx); (b) crystal of Fe-Mg calcite (Cc) with inclusions of Cr spinel (CrSp); (c) globules of Fe-Mg calcite (Cc); white patches are sulfide segregations (sf). Sample M-5539/2.

The tufflavas contain numerous white and subordinate lilac oval carbonate-silicate segregations (ocelli), 10–12 mm in diameter, characterized by sharp boundaries with groundmass. The carbonate globules (droplets) are uniformly dispersed therein (Fig. 3). The flattened carbonate drops and silicate laths are conformably oriented within ocelli. The carbonate drops contain iron sulfide microglobules and rims (Fig. 3). The orange carbonate drops correspond to Fe-Mg-calcite in composition (Table 2).

As compared to typical carbonatites, the carbonatite tuffs and immiscible ocelli are enriched in silicate com-

ponent and characterized by low REE, Nb, and Zr contents even relative to the basalts of the Amba Volcano (Table 1). This is consistent with the conclusion [1] on the partition of REE into silicate melt (relative to immiscible carbonate liquid) in low-alkaline calcic systems.

The isotopic compositions of carbon and oxygen in calcite from carbonatite tuffs (samples M-5533 and M-5534) are as follows: $\delta^{13}\text{C}_{\text{PDB}} = -5.9$ and -6.0‰ , respectively; $\delta^{18}\text{O}_{\text{smow}} = +16.2$ and $+14.9\text{‰}$, respectively. These values differ markedly from carbon and oxygen isotopic compositions in calcite from the Permian limestone of the basement: $\delta^{13}\text{C}_{\text{PDB}} = +2.0\text{‰}$ and $\delta^{18}\text{O}_{\text{smow}} = +23.2\text{‰}$. The range of $\delta^{13}\text{C}$ values is typical of carbonatites.

We also found magmatic carbonate segregations in subalkali olivine and hypersthene basalts at the Shufan volcanic plateau, trachyandesites and basalts from vents of the Baranovsky Volcano (Fig. 1) that complete the Cenozoic plateau-basaltic volcanism in southern Primorye [2], and plagioclase-free potassic microbasalts from the Badzhal and Kuidusun volcanic zones in Khabarovsk krai (Fig. 4) [3]. These rocks commonly occur as dikes, sills, necks, and extrusions.

In carbonate-bearing basalts, the intergrowths of crystals and isometric segregations of fine-crystalline carbonate aggregate fill intergranular interstices, occur at grain boundaries of silicate minerals, make up regular intergrowths with silicate microlites, or are surrounded by the microlites. The content of carbonate material occasionally reaches a few volumetric percent. The carbonate-bearing basalts are also depleted in silica and enriched in TiO_2 , P_2O_5 , REE, and LILE [12].

Following [4, 5], we regard globular carbonate droplets in silicate rocks as evidence for coexistence of two immiscible liquids. Interstitial segregations of carbonate melt in microlitic silicate aggregate are similar in their mechanism of formation to globular segregations. The interstitial segregations merely reflect conditions of segregation and consolidation of the carbonate liquid in a lower-temperature region (in comparison with silicate matrix).

The carbonate-silicate immiscibility in mafic magmas may be caused by a high affinity of CO_2 to Ca, which may be extracted from silicate melts in the process of their interaction with carbon dioxide [6], or the assimilation of carbonate rocks and their recycling accompanied by variations in isotopic geochemical characteristics of the magmatic melt. Absorption of carbonate material by silicate melts is accompanied by its depletion in silica and enrichment in alkali metals with precipitation of silica-undersaturated mineral phases [7]. This is evidenced by the mineral and chemical compositions of basalts from the Amba Volcano.

The formation of carbonatite melt is accompanied by desilication, mass crystallization of spinel and fassaite, and oversaturation of the melt with Ca. These processes indicate that the genesis of carbonatites of

Table 2. Chemical composition of minerals from carbonatite tuffs (microprobe results, wt %)

Com- ponent	Clinopyroxene					Spinel					Plagioclase		Carbonate			
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
SiO ₂	46.67	46.79	45.56	48.24	44.70	0.00	0.00	0.00	0.00	0.00	48.03	49.08	–	–	–	–
TiO ₂	2.20	2.32	8.95	0.70	2.05	0.56	0.73	16.12	0.43	0.73	0.00	0.06	–	–	–	–
Al ₂ O ₃	10.38	10.80	6.60	7.86	9.14	62.41	58.83	14.87	54.23	46.85	32.63	31.07	–	–	–	–
FeO*	6.82	8.64	12.13	5.73	7.91	18.69	24.91	60.43	18.41	20.32	0.39	0.53	2.20	5.22	1.40	2.31
Cr ₂ O ₃	0.00	0.30	0.00	0.61	0.00	0.00	0.02	0.00	8.85	15.32	0.00	0.00	–	–	–	–
MnO	0.00	0.28	0.04	0.20	0.10	0.05	0.06	0.24	0.06	0.15	0.00	0.00	2.30	1.09	1.00	1.07
MgO	12.74	11.81	16.97	15.53	13.81	19.02	16.23	6.98	18.25	16.54	0.07	0.21	2.23	2.50	1.80	2.09
CaO	20.64	19.71	9.60	19.10	20.35	0.20	0.00	0.00	0.00	0.01	16.00	14.92	55.82	47.24	52.90	47.98
Na ₂ O	1.15	1.15	0.06	0.53	0.94	0.00	0.00	0.00	0.00	0.00	3.05	3.34	–	–	–	–
K ₂ O	0.01	0.01	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.22	–	–	–	–
Total	100.61	101.54	100.27	98.48	99.03	101.54	100.77	98.65	100.30	99.93	100.17	99.43	–	–	–	–
<i>f</i>	23	29	28	17	24											
Wo	47	46	22	42	44											
En	41	39	55	48	42											
Fs	12	15	22	9	14											
An											74	70				

Note: (10) Inclusion in clinopyroxene; (13–15) crystals; (16) carbonate globule from an ocellus. (–) Not analyzed.

Amba Volcano is related to assimilation. This inference is consistent with the location of the volcanic edifice in the field of carbonate rocks and enrichment of oxygen in heavy isotopes. The extreme gain of Ca in silicate melt makes it unstable [1] and promotes separation of immiscible carbonate liquid [8–10].

The thermal breakdown of carbonates with dissolution of CaO in basaltic magma and accumulation of CO₂ in the closed magma chamber resulted in an auto-clave gas effect, which provoked a vigorous explosion that is atypical of subalkali basalts, and immiscibility of carbonate and silicate melts.

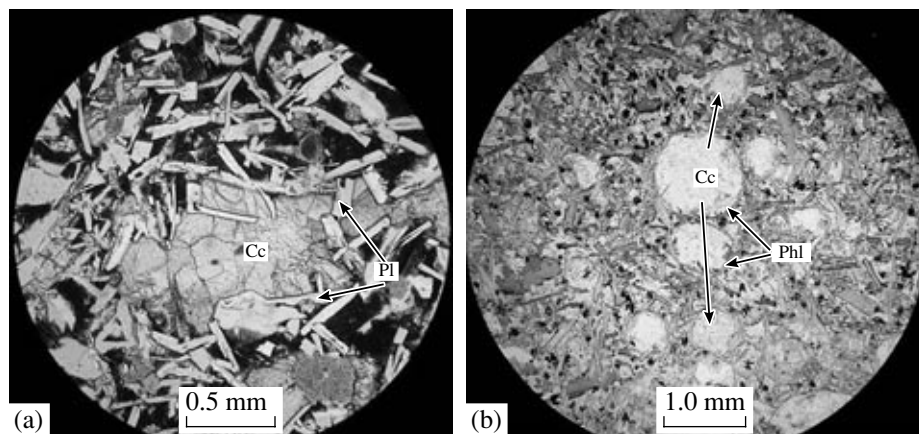


Fig. 4. Microphotographs of thin sections. (a) Interstitial magmatic calcite (Cc) in hypersthene basalt (Shufan Plateau, sample M-5214); (b) immiscible carbonate globules (Cc) in alkali picobasalt are rimmed by phlogopite (Phl) and sanidine (Kuidusun Basin, Okhotsk Massif; sample M-4821).

ACKNOWLEDGMENTS

This work was supported by the Far East Division, Russian Academy of Sciences (project no. 06-III-A-08-319), and Program no. 13 of the Presidium of the Russian Academy of Sciences.

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