
GEOCHEMISTRY

Inclusions of Zircon-Based Solid Solutions in Diamonds

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Presented by Academician N.P. Yushkin, January 12, 2006

Received February 6, 2006

DOI: 10.1134/S1028334X06080344

Multicomponent solid solutions and their intermediate exsolutions hold a special place among syngenetic xenogenic mineral inclusions in diamonds. None of the presently known natural isomorphous mixtures reproduce their composition. Their main characteristic is crystallochemical incompatibility of mixed components under crustal conditions of mineral formation.

Data on such phases began to appear in the late 1980s, when melt inclusions in diamonds were studied for the first time. The most important results were obtained by Bulanova et al. [1], who found a hexagonal–tabular inclusion of the homogeneous crystallized melt in a diamond monocrystal. The electron microscopic study showed that this inclusion is heterogeneous and probably consists of rutile, clinopyroxene, Fe–Ti–Si, and K–Al–Si domains. However, the authors of [1] mistakenly attempted to correlate these domains with definite mineral species and the whole inclusion with a definite magmatic rock (high-Ti hypersthene andesite).

This attitude to unusual xenomineral phases could only be changed after the detection of a special (juvenile) type of syngenetic inclusions of homogenous Ti–Fe–Si–Zr–Al oxide solid solutions in the Uralian diamond monocrystals [2]. The existence of this natural phenomenon is supported by findings of homogeneous inclusions, which mainly consist of polycomponent zircon-based solid solutions, in Brazilian carbonado crystals [3–5].

We studied micropolycrystalline diamonds from modern and Neogene–Quaternary alluvial placers found in the main diamondiferous areas of Brazil

(Minas Gerais, Bahia, and Mato Grosso). The polycrystalline inclusions were found as droplike crystals up to $50 \times 70 \mu\text{m}$ in size (Figs. 1a, 1b), which are typical of zircon inclusions in mantle diamonds [6–8]. In addition, such inclusions are found in diamond phase interstices as irregular aggregates (from 1×2 to $5 \times 8 \mu\text{m}$ in size) and in micropores as specific subspherical aggregates consisting of numerous crystals no more than 100–200 nm in size (Figs. 1c–1f). According to Pb–Pb isotope geochronological data, the age of zircon-type inclusions in the Brazilian carbonado virtually correlates with that of the diamond phase (3599 ± 12 and 3811 ± 1800 Ma, respectively) [9].

The xenogenic mineral inclusions were studied on a JSM6400 (Jeol) scanning electron microscope equipped with an energy-dispersive analyzer (ISIS 300 software package) and a wavelength-dispersive spectrometer. The results showed that the zircon-type phase contains 18 components (Table 1) mainly represented by ZrO_2 , SiO_2 , TiO_2 , Al_2O_3 , and FeO providing from 78 to 100 wt %. The subordinate compounds are represented by HfO_2 , Sc_2O_3 , Y_2O_3 , and P_2O_5 , which are known as geochemical signatures of zircon from diamondiferous rocks [10], as well as ThO_2 and UO_2 , which are considered “forbidden” components for mantle zircons [6, 7, 11, 12]. In addition, the inclusions contain significant amounts of Ca, Mg, Zn, Cu, and S, which are atypical for zircon.

We revealed a complex system of strong positive and negative correlations between virtually all components of the phases studied (Table 2). Based on this property, the aforementioned components are subdivided into two contrasting (competitive) groups. The first group includes Zr, Si, and crystallochemically similar admixtures (Hf, Th, and Y). The second group includes such elements that are not quite compatible with zircon but are typical of zircon in the diamond association (Sc, Ti, Al, and Fe).

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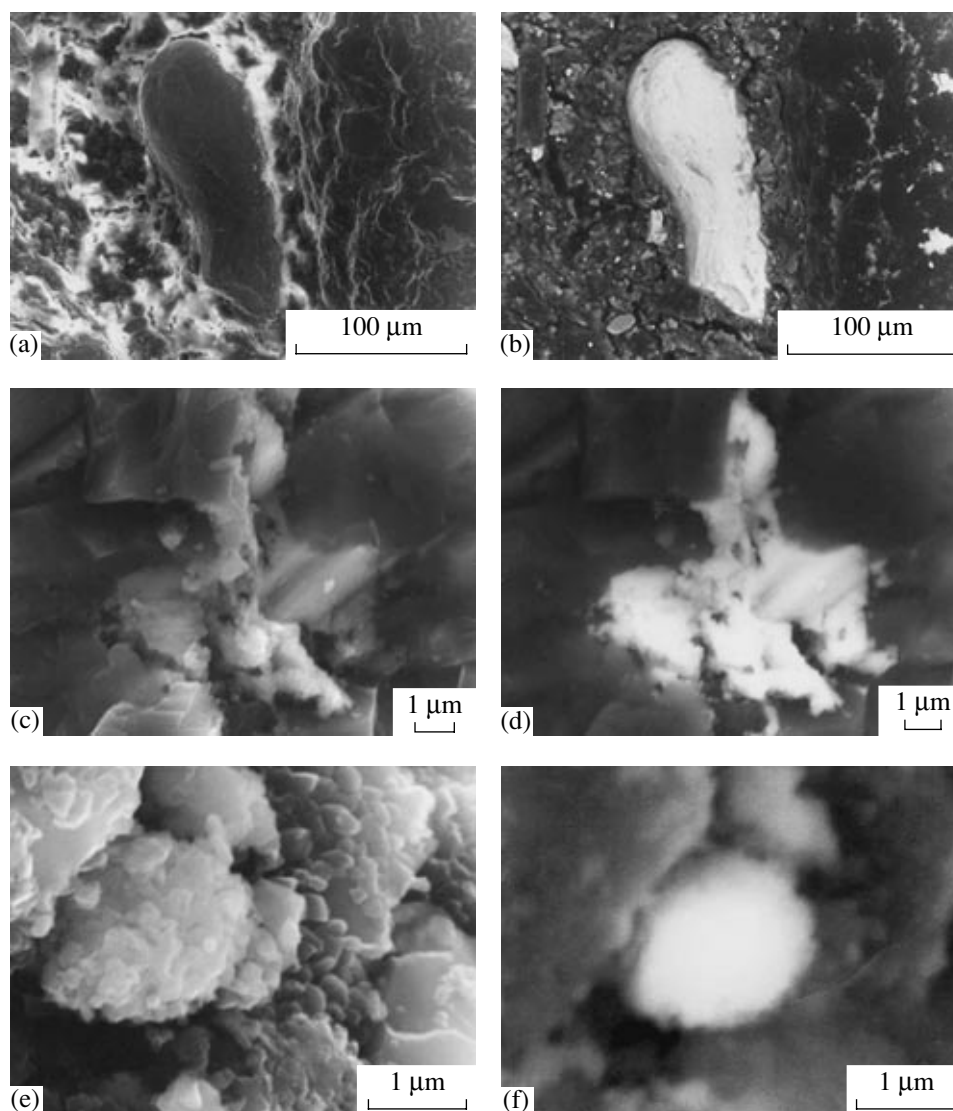


Fig. 1. (a, b) Droplike, (c, d) interstitial, and (e, f) druse-spherical inclusions of zircon-based solid solutions in carbonado. SEM-image in secondary (a, c, e) and elastically scattered electrons.

Scanning electron microscope and X-ray microprobe data showed that the inclusions in carbonado can be considered solid solutions of baddeleyite (ZrO_2), rutile (TiO_2), corundum (Al_2O_3), iozite (FeO), and many other solid phase components. Occasionally, the inclusions contain zircon + iozite and iozite + rutile solutions (Table 3). Correlation analysis shows that normative end members of the phases are divided into two contrasting groups: (1) zircon + baddeleyite and (2) corundum + rutile + iozite and other trace components (Table 4). This is quite consistent with the concept of zircon-type phases as multicomponent solid solutions (Table 4).

Evidently, inclusions found in carbonado have unusual composition. They are similar only to Ti-Fe-

Si-Zr-Al oxide solid solutions detected in monocrystal diamonds from the Middle Urals. Although, data points from the Uralian diamonds and Brazilian carbonado are plotted separately in the tetrahedral diagram, they have many similar geochemical features (Fig. 2), e.g., a strong tendency for fractionation of TiO_2 , FeO , and ZrO ; maximum concentration of the third component in the intermediate composition area, and so on.

However, the studied phases also show some differences from their counterparts in the Uralian diamonds. The most important difference is the following: the phases are enriched in chemical admixtures of orthosilicates and orthophosphates of Hf and Th, Sc and Y (their total content is as high as 10 mol %). In addition, the studied carbonados contain rare interstitial solid inclusions of homoge-

Table 1. Chemical composition of inclusions of zircon-based solid solutions in carbonado, wt %

Ord. no.	ZrO ₂	HfO ₂	ThO ₂	Y ₂ O ₃	Sc ₂ O ₃	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	ZnO	CuO	MgO	CaO	K ₂ O	P ₂ O ₅	SO ₃	UO ₃	Cl
1	63.05	2.14	1.03	–	1.61	23.74	1.20	4.18	1.43	–	–	–	0.86	0.40	–	–	–	0.36
2	52.15	–	–	5.23	2.01	22.78	4.11	2.29	1.23	–	–	–	0.89	0.35	8.54	–	–	0.42
3	56.41	–	1.30	11.53	1.50	22.49	0.42	2.27	1.01	–	–	–	0.68	0.43	–	–	1.65	0.31
4	53.86	–	1.31	4.7	1.66	23.10	0.47	2.17	1.13	–	–	–	0.75	0.46	8.20	–	1.82	0.37
5	53.04	–	–	14.01	1.52	22.0	1.20	–	1.52	–	–	2.69	0.73	0.30	–	2.99	–	–
6	51.55	–	–	9.19	1.66	21.75	1.30	3.19	1.67	–	–	1.26	0.80	0.33	5.93	0.77	–	–
7	55.17	–	1.59	4.82	1.86	20.62	–	1.92	1.97	1.98	2.51	–	0.81	0.66	7.29	–	–	–
8	24.22	–	–	–	0.77	19.93	0.54	14.30	28.47	1.31	2.08	–	0.44	0.37	7.57	–	–	–
9	47.95	–	–	5.31	1.55	21.37	3.41	4.19	1.21	2.94	2.78	–	–	–	7.98	–	–	1.31
10	48.05	–	–	–	–	38.52	1.09	10.65	1.69	–	–	–	–	–	–	–	–	–
11	29.10	–	–	–	–	13.90	50.31	2.30	1.74	–	–	–	–	–	2.65	–	–	–
12	42.85	–	–	–	–	21.65	–	6.03	22.38	–	–	–	0.48	–	6.61	–	–	–
13	11.44	–	–	–	–	12.70	1.08	10.24	59.04	–	–	–	–	2.34	3.16	–	–	–
14	54.73	–	–	3.91	–	24.62	2.46	4.68	2.54	–	–	–	0.86	–	6.20	–	–	–
15	25.94	–	–	–	–	33.41	23.25	10.14	7.04	–	–	–	–	0.22	–	–	–	–
16	56.41	–	1.30	11.53	1.50	22.49	0.43	2.27	1.01	–	–	–	0.68	0.43	–	–	1.65	0.30
17	53.86	–	1.31	4.7	1.66	23.10	0.47	2.17	1.13	–	–	–	0.75	0.46	8.20	–	1.82	0.37
18	55.17	–	1.59	4.82	1.86	20.62	–	1.92	1.36	1.98	2.51	–	0.81	0.66	6.7	–	–	–
19	53.03	–	–	14.01	1.52	22.00	1.20	–	1.52	–	–	2.69	0.73	0.30	–	3.00	–	–
20	51.55	–	–	9.20	1.66	21.74	1.30	3.19	1.67	–	–	1.26	0.80	0.33	5.93	1.37	–	–
21	24.46	–	–	–	0.78	19.12	0.54	14.44	28.75	1.32	2.10	–	0.44	0.38	7.67	–	–	–
22	47.96	–	–	5.31	1.55	21.37	3.41	4.19	1.21	2.94	2.78	–	–	–	7.98	–	–	1.30
23	53.62	–	–	–	1.66	24.61	1.24	3.38	1.51	–	–	–	0.87	0.39	12.34	–	–	0.38
24	63.05	2.14	1.03	–	1.61	23.74	1.2	4.18	1.43	–	–	–	0.86	0.40	–	–	–	0.36
25	52.15	–	–	5.23	2.01	22.78	4.11	2.29	1.23	–	–	–	0.89	0.35	8.54	–	–	0.42
26	69.18	–	–	–	–	30.82	–	–	–	–	–	–	–	–	–	–	–	–
27	63.11	–	–	–	–	32.15	4.74	–	–	–	–	–	–	–	–	–	–	–

neous xenotime–zircon phases, which were previously reported by Gorshkov et al. as xenotime–zircon phases in the micropolycrystalline diamonds from the Yakutian kimberlite pipes [13, 14]. In our case, inclusions of this composition are represented by sufficiently developed prismatic crystals $5 \times 7 \mu\text{m}$ in size (Fig. 3). One of these inclusions has the following empirical formula: $(\text{Zr}_{0.39}\text{Y}_{0.42}\text{Gd}_{0.01}\text{Dy}_{0.03}\text{Er}_{0.01}\text{Yb}_{0.01}\text{Ti}_{0.09})_{0.96} \times [\text{Si}_{1.049}\text{P}_{0.51}\text{O}_4]$. This formula indicates virtually equimolecular proportions of zircon and xenotime end members in the solid solution. Based on this hypothesis, the compositions of normative end members can

be presented as follows: (1) $(\text{Zr}_{0.81}\text{Ti}_{0.19})[\text{SiO}_4]$; (2) $(\text{Y}_{0.88}\text{Gd}_{0.02}\text{Dy}_{0.06}\text{Er}_{0.02}\text{Yb}_{0.02})[\text{PO}_4]$.

The finding of equimolecular xenotime–zircon mixtures is obviously inconsistent with known experimental data on the solubility of yttrium orthophosphate in zirconium orthosilicate [15]. These data indicate that the limit of YPO_4 solubility in ZrSiO_4 even at 1630°C is no more than 15 mol%, which is three times lower than the content found at the maximum content of the xenotime end member in natural xenotime–zircon solid solutions.

Table 2. Pair correlation coefficients for elements in zircon-based solid solutions

ZrO ₂	1																		
HfO ₂	0.30	1																	
ThO ₂	0.38	0.3	1																
Y ₂ O ₃	0.31	0	0	1															
Sc ₂ O ₃	0	0	0	0	1														
SiO ₂	0.33	0	0	0	-0.62	1													
TiO ₂	-0.38	0	0	-0.24	0	0	1												
Al ₂ O ₃	-0.75	0	-0.27	-0.51	0	0	0	1											
FeO	-0.79	0	0	-0.36	0	-0.33	0	0.69	1										
ZnO	0	0	0	0	0.53	-0.46	0	0	0	1									
MgO	0	0	0	0.7	0	0	0	-0.31	0	0	1								
CaO	0.43	0.26	0.44	0.43	0	0	-0.41	-0.28	-0.3	0	0.25	1							
K ₂ O	0	0	0	0	0.94	-0.68	0	0	0	0.49	0	-0.27	1						
P ₂ O ₅	0	0	0	0	0	0	0	0	0	0	0	0.4	0	1					
SO ₃	0	0	0	0.69	0	0	0	-0.31	0	0	0.99	0	0	0	1				

ZrO₂ + HfO₂ + ThO₂ + Y₂O₃ + SiO₂ + MgO + CaO + P₂O₅ + SO₃
 Sc₂O₃ + TiO₂ + Al₂O₃ + FeO + ZnO + K₂O

Thus, we discovered that the Brazilian carbonado contains previously unknown syngenetic inclusions of zircon-based solid solutions. This discovery suggests a rather wide range of metastability of not only diamond but also syngenetic associated minerals under mantle conditions. Since attainment of a general minimum of internal energy is not required for the phase instability state, the corresponding crystallization products can be realized as solid phase solutions of diverse molecular configuration. The solid phase mixtures of peculiar components, which are crystallochemically incoherent

under conditions of the Earth's crust, in monocrystal and micropolycrystal diamonds, probably represent a unique state of natural crystalline matter typical of only high-pressure mineral formation in the mantle.

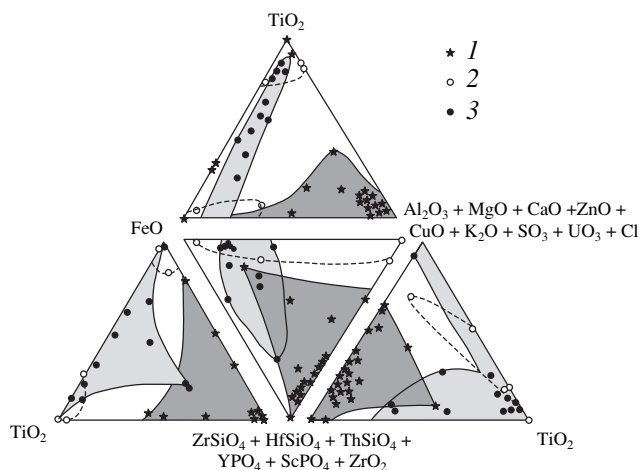


Fig. 2. (1) Correlation between chemical composition of studied inclusions of zircon-based solid solutions and (2, 3) Ti-Fe-Si-Zr-Al oxides in the monocrystal diamonds from the Middle Urals.

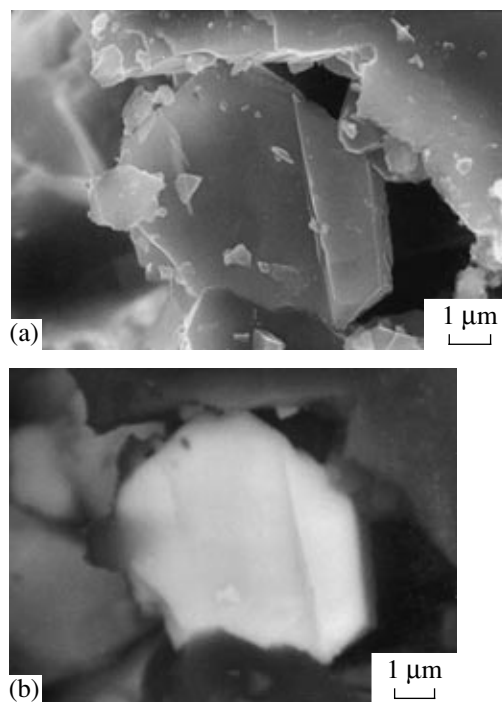


Fig. 3. Solid-phase inclusions of equimolecular xenotime-zircon mixtures in the carbonado. (a) SEM in scattered and (b) elastically scattered electrons.

Table 3. End member composition of zircon-based solid solutions, mol %

Ord. no.	ZrSiO ₄	ZrO ₂	Al ₂ O ₃	TiO ₂	FeO	Admixture: SiO ₂ + Y ₂ O ₃ + Sc ₂ O ₃ + ZnO + CuO + MgO + CaO + K ₂ O + P ₂ O ₅ + SO ₃ + UO ₂ + Cl
1	76.1	12.6	3.94	1.44	1.92	4
2	78.29	4.57	2.32	5.3	1.76	7.76
3	77.01	9.11	2.29	0.54	1.44	9.61
4	77.22	5.81	2.14	0.59	1.59	12.65
5	71.36	6.27	0	1.46	2.05	18.86
6	72.3	5.64	3.12	1.63	2.31	15
7	68.4	11.02	1.87	0	2.73	15.98
9	68.1	3.21	3.93	4.07	1.61	19.08
10	66.55	0	8.89	1.16	2	21.4
12	61.44	0	5.21	0	27.4	5.95
14	78.62	3.32	4.4	2.95	3.38	7.33
15	33.53	0	7.9	23.1	7.78	50.79
16	77.02	9.11	2.29	0.55	1.44	9.59
17	77.24	5.81	2.14	0.59	1.57	12.65
18	69.06	11.13	1.89	0	1.9	16.02
19	71.35	6.26	0	1.46	2.05	18.88
20	71.52	5.61	3.9	1.61	2.29	15.07
21	37.45	0	13.33	0.64	26.54	22.04
22	67.73	3.2	3.91	4.05	1.6	19.51
23	78.5	2.46	3.16	1.48	2.01	12.39
24	75.38	12.48	3.91	2.38	1.9	3.95
25	74.16	4.32	2.2	5.02	1.67	12.63
26	95.47	4.53	0	0	0	0
27	94.55	0	0	5.45	0	0
\bar{X}	71.6	5.27	3.45	2.73	4.12	13.8
\bar{S}_x	13.5	3.99	3.05	4.67	7.18	10.16
8*	33.24	0	11.84	0.57	33.38	20.97
11**	39.86	0.42	1.94	54.09	2.08	1.61
13***	14.46	0	7.81	1.05	63.77	12.91

Note: Ordinal numbers are as in Table 1. Statistical parameters were calculated only for zircon-based solid solutions. Other variants of solid solutions: (*) based on zircon + iozite, (**) based on rutile, (***) based on iozite.

Table 4. Correlation matrix of pair correlation coefficients for end members in zircon-based solid solutions

ZrSiO ₄	1						
ZrO ₂	0.3	1					
Al ₂ O ₃	-0.78	-0.44	1				
TiO ₂	-0.49	-0.37	0	1			
FeO	-0.63	-0.43	0.65	0	1		
Admixture	-0.82	-0.32	0.47	0.69	0	1	

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 05-05-64615) and the Federal Program for the Support of Leading Scientific Schools (project no. NSh-2250-2003-5).

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