Indications of an Ensimatic Island Arc of the Silurian-Early Devonian Paleo-Ocean in the Polar Urals

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Summary: A large fragment of a paleovolcano of Silurian to Early Devonian age was discovered in the Voikar volcanic belt suggesting an ensimatic island arc as its geodynamic environment. Formationally, the rocks under study are comparable to Pleistocene island arc volcanites and their paleo-analogues. The volcanites of the Toupugol complex underwent strong hydrothermal-metasomatic alteration: propylites, acid metasomatic rocks and quartz-carbonate veins, which must have resulted from hydrothermal-metasomatic alteration of andesitoids. Both volcanites and apovolcanic hydrothermal rocks in Toupugol were found to host noble metal mineralisation. It is found in close association with sulphides, particularly pyrite. Free gold was discovered in all investigated volcanites and hydrothermal rocks and is characterised by low mercury content and an unusual set of microimpurities (Pt, Pd, Cu, Fe, S) suggesting its links to the mantle substrate.

GEOLOGY

The Toupugol volcanogenic complex is found as a single, rather typical paragenesis of lava, pyroclastic and volcanogenic-sedimentary facies indicating a moderately eroded volcanic paleoconstruction of the central type (Fig. 1). The pillow shape of the lavas, their spilitization, the same degree of iron oxidation in the extrusive and pyroclastic rocks, radiolarians found in tuffites, all suggest an under-water environment of the volcanicity.

Rocks of the vent and extrusive facies, crystal tuffs of andesite-basaltic composition and the intervening dacites, are observed in the northeastern wall of the quarry and may constitute the marginal parts of the southern sector of the root zone of the volcano. In the south, they are semi-circled by agglomeratic tuffs with clasts of basic effusites, dacites, tuffites and light-grey limestones in approximately equal proportions.

Next to the group of the root zone rocks is a field of rudaceous and macroclastic tuffs of the andesite-basalt composition. In the southern and eastern directions, they are replaced by pillow-shaped andesite-basaltic lavas, occupying the entire eastern part of the quarry. In the western direction, the size of the clasts in the lithoclastic tuffs decreases with the share of tuffites and limestones increasing. Tuffite and tuffosilicite interlayers are occasionally observed.

The centre of the quarry is occupied by a flat interbedding

member of lithoclastic tuffs, tuffites and tuffosilicites. Found in the latter are numerous radiolarian remains. Farther to the west, the member is gradually replaced by horizontal massive and massive-platy tuffites with indistinct banding. In the facies



Fig. 1: Geological position of the Toupugol paleovolcano (A) and scheme of a fragment of the Toupugol paleovolcano exposed in the quarry (B). Numbered dots on B denotee chemical analyses in Tab. 1.

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of the western wall of the quarry, tuffites are laterally replaced by light-grey mid-Devonian limestones.

PETROCHEMISTRY OF THE VOLCANITES

The volcanites of the Toupugol complex are essentially represented by subalkaline, potassium-sodium, high-aluminum andesite-basalts. The proportion of more acidic varieties is insignificant. The effusive and pyroclastic facies show no substantial differences (Tab. 1). The Rittmann index describes the rocks as alkaline and subalkaline, while by the type of alkalinity they can be determined as potassium-sodium andesitoids. Among the associations earlier recognised in the Voikar volcanic belt (YAZEVA & BOCHKAREV 1984), the Toupugol volcanites are most similar to the andesite-basalts and andesites of the Elkashor and Yurtymsoim complexes (Fig. 2). Formationally, the rocks under investigation are comparable to Pleistocene island arc volcanites and their paleo-analogues. Compared to typical ophiolitic and abyssal-oceanic basaltoids of today, the Toupugol effusives are distinguished by lower magnesium, titanium and iron contents and higher concentrations of alkali, especially potassium. In a Pearce plot (Fig. 3A), almost all points of the composition of the rocks fall on the area of island-arc and continental-margin basaltoids; in Dobretsov diagram, the area of island-arc high-alumina andesite-basalts.

According to petrochemical trends, the Toupugol volcanites occupy an intermediate position between island-arc tholeiites and calc-alkali andesites. The latter is well illustrated by an AFM diagram in which the composition points lie in the interval between the corresponding curves and the trajectory of iron content rises which is typical of calc-alkali series (Fig. 3B).

N	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P_2O_5	TTE	Totals
1	50.18	0.84	16.56	5.39	4.60	0.09	4.51	8.12	3.35	1.29	0.30	4.66	99.89
2	49.40	0.72	16.05	3.57	3.13	0.09	4.12	11.53	3.03	1.05	0.22	7.01	99.92
3	43.92	0.50	14.48	2.28	5.07	0.11	7.42	11.88	4.88	0.21	2.42	6.73	99.90
4	47.10	1.00	17.36	7.01	2.82	0.12	2.84	8.79	4.89	1.54	0.26	6.13	99.86
5	41.74	0.80	15.40	1.48	6.23	0.21	5.46	11.76	4.89	0.26	0.14	11.15	99.62
6	46.99	0.78	23.65	4.42	2.54	0.04	1.99	5.80	3.75	3.19	0.29	6.46	99.90
7	48.22	0.78	16.41	2.00	6.21	0.10	7.58	6.56	0.64	2.53	0.23	8.59	99.85
8	51.59	0.84	19.50	2.99	4.40	0.13	4.95	4.80	3.85	3.27	0.38	3.64	100.34
9	50.22	1.41	21.41	7.68	1.30	0.02	1.81	0.69	3.40	5.47	0.19	6.39	100.01
10	48.45	0.85	16.62	4.54	6.50	0.21	9.40	6.40	0.69	0.17	0.22	5.84	99.89
11	47.10	1.00	17.36	7.01	2.82	0.12	2.84	8.79	4.89	1.54	0.26	6.13	99.86
12	35.26	0.13	12.10	2.39	4.19	0.12	3.05	20.06	0.44	3.05	0.19	18.11	99.96
13	59.30	0.21	8.68	4.15	1.54	0.23	2.98	14.38	0.11	1.11	0.07	7.17	99.93
14	56.37	0.51	14.59	5.04	1.87	0.09	3.16	11.38	1.28	0.94	0.08	4.60	99.91
15	30.76	0.22	10.60	2.90	4.24	0.18	6.55	22.74	3.59	0.28	0.09	17.76	99.91
16	74.10	1.00	17.36	7.01	2.82	0.12	2.84	8.79	4.89	1.54	0.26	6.13	99.86
17	35.26	0.13	12.10	2.39	4.19	0.12	3.05	20.06	0.44	3.05	0.19	18.11	99.96
18	71.25	0.49	11.07	7.81	0.63	0.01	1.17	0.21	0.61	1.94	0.21	4.44	99.84
19	84.29	0.24	6.90	3.52	0.39	0.01	0.29	0.12	0.56	1.07	0.12	2.40	99.91
20	72.84	0.37	10.35	4.57	1.78	0.03	1.46	2.17	0.61	1.81	0.07	3.85	99.88
21	85.42	0.29	5.16	3.29	0.34	0.01	0.74	0.29	0.06	1.99	0.02	2.36	99.98
22	76.30	0.18	3.64	11.30	0.48	0.01	0.41	0.34	0.43	0.94	0.07	5.79	99.90
23	85.60	0.13	1.76	4.27	0.75	0.01	0.59	2.99	0.20	0.22	0.05	3.00	99.57
24	57.18	0.14	1.56	23.81	0.48	0.02	0.50	2.57	0.07	0.46	0.03	12.59	99.43
25	8.30	0.07	0.71	3.76	1.16	0.33	1.86	46.25	0.21	0.04	0.01	36.58	99.61

Tab. 1: Chemical composition of the Toupugol paleovolcano rocks (mass %)1-5 = and esite-basalt lavas; 6-12 = agglomeratic tuffs; 13-17 = propulites; 18-23 = quartzites beresite-like; 24-25 = veins quartz-carbonate.



Fig. 2: Volcanic associations of the Voikar belt in the SiO2-(Na2O+K2O) diagram: 1 = andesite-basalts of the Toupogol paleovolcano; 2 = Yurtym-Soim (Kharmatalou); 3 = Yurtym-Soim andesitic complex (Yanas-Tere ridge); 4 = Teren andesite-dacite; 5 = Elkoshor basalt-andesite; 6 = Kevsoim trachyandesite.

Conclusions about the island arc nature of the Toupugol volcanites are confirmed by geochemical data: the original ⁸⁷Sr/⁸⁶Sr ratio (0.706), a low Rb/Sr value (0.02-0.25), and enriched Cr, Ni, Co contents and the pattern of their differentiation in deep generations (Fig. 4).

APOVOLCANIC HYDROTHERMALITES

The volcanites of the Toupugol complex underwent strong hydrothermal-metasomatic alteration. The most widespread among the hydrothermal rocks are propylites, which were subsequently overlain by acid metasomatic rocks and quartzcarbonate veins, which must have resulted from hydrothermalmetasomatic alteration of andesitoids (Fig. 5).

The most abundant among the metasomatic rocks are pyritised propylites found in three facies (from earlier to more recent): carbonate-prehnite-zeolite, epidote-amphibole-chlorite, and quartz-epidote. Pyrite content in the propylites ranges 1-12 %. The propylites, however, are overlain by the crossing zones of beresites, still more enriched in pyrite and chalcopyrite (to 40 %). Chlorite-carbonate-sericite-quartz, carbonate-quartz and carbonate mineralisations filling veins and streaks are the most recent in Toupugol. The veins are normally pyritised, pyrite accounting for 10-12 % in their composition.

Carbon and oxygen isotope composition of the carbonates also suggests geochemical links between the volcanites and metasomatites. The Toupugol volcanites show the following average values for the isotope compositions: $\delta^{13}C = -3.2$; $\delta^{18}O = 13.7$ %. Observed in transition to hydrothermal-metasomatic rocks is only a slight lightening of carbon to -5.7 % against the background of a stable isotopic oxygen composi-





Fig. 3: Pearce diagram (A) and AFM (B) for andesite-basalts of the Toupugol paleovolcano. Fields of the chemical composition: 1 = oceanic abyssal basalts; 2 = oceanic island basalts; 3 = continental basalts; 4 = island-arc and continental-margin basalts; 5 = spreading zone basalts.

Differentiation trends of: 1 =oceanic tholeiites; 2 =island-arc tholeiites; 3 =island-arc calc-alkali volcanic series.

Fig. 4: The geochemical characteristics of volcanic and hydrothermal rocks from the Toupugol paleovolcano. Composition fields of the rocks under investigation: AB = lavas and tuffs; T = tuffites; P = propylites; V = quartzites and veins.

Compositions of the model and compared volcanic complexes: OP = ophiolitic; MOR = middle-oceanic ridges; YIA, MIA, PIA = young, mature and paleo island-arcs, respectively; PC = paleocontinental (Polar Urals).

1-3 = active continental margin of the Polar Urals (elkashor, yurtymsoim, kevsoim, respectively).



Fig. 5: Chemical differentiation of hydrothermal-metasomatic rocks overlying the andesite-basalts of the Toupugol paleovolcano: 1 = volcanites; 2 = propylites; 3 = acid metasomatics; 4 = carbonate veins.

tion (12.4 ‰). Note that it is similar to carbon and oxygen isotope composition in carbonate-bearing metasomatites from volcanogenic and epithermal gold ore deposits.

Chromium and cobalt turned out to be the most metasomatically stable indicator elements. Nickel was obviously redistributed to propylites, which is assumed by a shift of the area representing the rocks in Figure 4. Zinc content in the volcanites was decreasing during the hydrothermal alteration, while lead content was increasing. Copper accumulation occurred only during propylitisation (Tab. 2).

GOLD SULPHIDE MINERALISATION

Both volcanites and apovolcanic hydrothermal rocks in Toupugol host noble metal mineralisation. It is found in close association with sulphides, particularly pyrite.

Neutron activation analysis (Tab. 2) disclosed that even in relatively recent andesite-basalts of the Toupugol paleovolcano,

Rocks			ppb				ppm			
		Au	Ag	Au/Ag	Cr	Ni	Co	Cu	Zn	Pb
Andesite-basalts (22)	1	92	1020	0,31	60	28	49	102	82	99
	2	252	693	0,55	19	13	14	40	19	33
Tuffites (6)	1	*	*	**	52	22	45	95	80	107
	2				5	13	17	25	22	55
Propylites (14)	1	407	1050	0,02	55	35	30	475	35	95
	2	615	673	0,02	7	7	14	643	7	6
Propylites	1	3030	2801	1,18	53	20	40	38800	63	80
with sulphides (4)	2	4180	3111	1,14	6	19	30	29419	40	12
Quarztites	1	13520	2550	2,87						
beresite-like (10)	2	10241	354	2,59	49	20	40	38	22	170
Quartz-carbonate	1	5146	1280	9,89	2	11	21	25	15	225
veins and streaks (12)	2	9627	972	14,93						

Tab. 2: Gold, Silver and accompanying impure elements contents in the Toupugol paleovolcano rocks. Data by neutron-activation (Au, Ag, ppb) and atomic absorption (other elements, ppm) analyses. 1 = average; 2 = std. deviation. * = the element was not detected; ** = sample was not analysed for the element; bracketed = number of analyses.

Rocks		Au	Ag	Hg	Pt	Pd	Cu	Fe	Pb	Bi	S
Andesite-basalts (16)	1	89,12	9,42	0,31	0,13	0,02	0,03	0,01	*	*	0,08
	2	1,77	1,38	0,25	0,12	0,03	0,02	0,01	*	*	0,02
	3	100	100	100	75	50	75	38	*	*	100
Quarztites	1	90,02	8,99	0,09	0,04	0,02	0,01	0,02	< 0,01	0,04	0,08
beresite-like (22)	2	2,27	1,99	0,12	0,07	0,03	0,01	0,02	*	0,04	0,02
	3	100	100	64	43	57	36	45	25	75	73
Veins	1	91,09	7,69	0,13	0,06	0,01	0,11	*	0,05	0,13	0,06
quartz-carbonate (50)	2	2,48	2,68	0,15	0,07	0,02	0,2	*	0,05	0,2	0,03
	3	100	100	76	67	35	72	*	71	57	88

Tab. 3: Chemical composition of gold from the Toupugol paleovolcano rocks (mass %). Data by microprobe analysis. Bracketed = number of analyses; 1 = average; 2 = std. Deviation; 3 = frequency of occurrence (%); * = element not detected.

gold and silver concentrations are one order of magnitude higher than those in ancient and contemporary basaltoids, including volcanic complexes in the Urals. Besides, the gold to silver ratio is five times greater in the effusives than in the earth's crust, and eight times greater compared to basalts of the average composition, which is untypical for most of the known volcanogenic gold-silver occurrences (OLSHEVSKY 1975, STEPANOV 1994, SHERBINA 1956). The apovolcanic hydrothermal rocks in Toupogol contain commercial gold and silver concentrations with a still larger gold to silver ratio.

The calculations suggested that up to 80 % of gold in the propylites are in the form of dispersed impurities (inclusions in sulphides and rock-forming minerals), in quartzites and veins, up to 60 %. Pyrite is the major gold concentrator. In the relatively fresh Toupugol volcanites, gold content in pyrite reaches the level of gold deposits. It sharply increases in hydrothermal rocks proportional to the total gold content, 2.5-7 times exceeding the minimal gold content in recognised gold deposits. Carbonates, chlorites, epidote and amphiboles to contain the highest gold concentrations among the rock-forming minerals.

GOLD COMPOSITION

Free gold was found in all investigated volcanites and hydrothermal rocks and is characterised by low mercury content and an unusual set of microimpurities (Pt, Pd, Cu, Fe, S) suggesting its links to the mantle substrate (Tab. 3). The sequence of gold enrichment in platinum group elements is the following: $Rh \rightarrow Pd \rightarrow Pt$. The Pd/Pt value (0.2-1), describing platinoid disproportioning in the mineralogical-geochemical system, is in agreement with the given sequence of concentrations. The presence of rhodium and a sharp predominance of platinum over palladium account for the fundamental difference between the Toupugol gold and its other varieties with platinum group elements reported from the paleocontinental sector of the Urals (MALUGIN et al. 1986, TARBAYEV et al. 1996).

The pattern of platinum and palladium disproportioning in the gold of the Toupugol paleovolcano is similar to that in ophiolitic dunite-harzburgites, apoharzburgite metasomatites and native gold directly linked to the latter (VOLCHENKO et al. 1989).

Thus, our investigations have first disclosed in the Polar Urals a Paleozoic volcanic-hydrothermal system, including a moderately mature island arc, formed on a femic basement, and a productive gold-sulphide mineralisation of the front-arc type.

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