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GOLD ABUNDANCES IN WEST CARPATHIAN ULTRAMAFIC ROCKS

Abstract: Gold abundances in 25 samples of various ultramafic rock-types of the West Carpathians are $n \cdot 10^{-6}$. Only in 4 serpentinite samples ($n_{\text{total}} = 29$) the Au content lies below this concentration. Increase of Au abundance may be observed from Triassic over Carboniferous serpentinites to serpentinites in Pre-Carboniferous metamorphic complexes. Gold content in 11 analyzed samples of basic effusive rocks, lamprophyres, melanocratic syenodiorites and amphibolites are unsubstantially lower than in ultramafic rocks.

Au has been determined by atomic absorption spectrophotometry following previous extraction by organic agents.

Резюме: Концентрация Au в 25 образцах разных типов ультрамафических пород Западных Карпат находится в пределах $n \cdot 10^{-6}$. Только в четырех образцах серпентинитов ($n_{\text{общее}} = 29$) содержание Au находится под приводимой здесь концентрацией. Вообще повышенную концентрацию Au можно наблюдать в серпентинитах триаса, также в карбонских серпентинитах и даже в серпентинитах докарбонских метаморфических комплексов. Содержания Au в 11 проанализированных образцах основных эффузивов, лампрофиров, сиенодиоритов и амфиболитов является весьма невыразительно ниже нежели в ультрамафических породах. Золото было установлено методом атомной абсорбционной спектрофотометрии после предварительной экстракции реактивами.

Introduction

Geochemistry of gold in geological processes is one of the actual topics of theoretical and applied research. Analytical results from the last decade show that the highest clark contents belong to chondritic meteorites, where its concentration reaches $n \cdot 10^{-5}$ to $n \cdot 10^{-4}$. (W. D. Ehman — P. A. Baedeker 1968, A. A. Smales — D. Mapper — K. F. Fouché 1968, A. P. Vinogradov et al. 1972 etc). Among the terrestrial rocks, ultrabasic rocks have the highest gold contents; the contents are decreasing towards basic and acid plutonites (K. K. Turekian — K. H. Wedepohl 1961, P. A. Vinogradov 1962 etc). The dilemma of Au geochemistry arises from these notions: the highest abundances are in ultrabasic rocks, while concentrations of economical importance are allied either to acid plutonites, or to intermediate and basic volcanic rocks. The notion on gold contents in ultrabasic rocks may be therefore one of the assumptions for the solution of some theoretical and practical problems of the respective region. From the high Au clark content in ultrabasic rocks follows, that the region of the Upper Mantle is the Au source area. Differentiation processes, metamorphism and hydrothermal activity induce as a rule its migration in the Earth's crust under the formation of increased concentrations even to deposit extents.

So far quantitative data on Au distribution in West Carpathian rock complexes are not at disposal. The problem is topical, as knowledge of its primary and secondary occurrences is accumulating recently (J. Slávik 1967, P. Hvoždara 1967, M. Böhmer — M. Harman 1969, S. Polák 1971).

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Geology of ultramafic rocks

The West Carpathians alpine-type ultramafic rocks are represented by small bodies in several geological units. Their geological position and basic character may be summarized as follows:

1. Ultramafic bodies in metasediments of garnet amphibolite facies (Jarabá Group, Early Proterozoic?) are regarded as the gravity differentiation product of paleobasaltic magma (D. Hovorka 1967). Along with other rock types of this complex they were affected by Intraalgonkian (?), Variscan and Alpine metamorphic processes. They are of serpentinite, hornblende and chlorite serpentinite, hornblende peridotite and of rocks containing hornblende, chlorite, serpentine minerals or even talc nature. Primary silicate minerals are no more surviving.

2. For ultrabasic rocks occurring in metasediments of the greenschist to epidote amphibolite facies (Kokava Group, Late Proterozoic?) total serpentinization and presence of reaction rims on the contact of bodies with adjacent crystalline schists (blackwall) is typical. These are talc, actinolite and chlorite rocks. Peridotites of the Upper Mantle of harzburgite and lherzolite composition are considered to be the parent rocks of serpentinites of this geological unit (D. Hovorka 1965).

3. Minute ultrabasic bodies are known to occur also in Late Paleozoic complexes of Spišsko-gemerské rudohorie Mts. They are of serpentinite character with sporadic survived pyroxene relics. Vein-type chrysotile mineralization is developed in them in places. Their Upper Mantle origin is most likely.

4. Bodies occurring in the Low to Middle Triassic of Spišsko-gemerské rudohorie Mts. are most abundant. Harzburgites to lherzolites and some bodies with sporadic dunite and pyroxenite composition were the parent rocks. They are mostly intensively serpentinized; in places survived primary pyroxenes, scarcely even olivines may be found. Their tectonic (rootless) position and the presence of vein-type chrysotile is characteristic. It is a typical member of the Mesozoic ophiolite formation of Spišsko-gemerské rudohorie Mts.

5. The Low Triassic age of biotite pierite discovered by drilling near Banská Bystrica is probable. Limburgite forms an explosive breccia, in less amount also lava flows in the Neokomian beds of the Western Tatras. Augite porphyrite makes up minute bodies of likely Cretaceous age in the crest of Nízke Tatry Mts. The analyzed lamprophyres from the crystalline complexes show kersantite and spessartite character. Amphibolites form conform bodies in the complex of biotite plagioclase paragneisses to migmatites. They represent the product of metamorphism of basic eruptive rocks. Melanocratic syenodiorites form minute bodies in core mountains and in the Veporide crystalline complex. So far their origin has not been solved.

Analytical results

From data presented in following table (tab. I) follows that Au abundances in various ultramafic rock-types of the West Carpathians lie near the lower limit of the range $n \cdot 10^{-6}$. One rock analyses only from the blackwall of the serpentinite body in the crystalline complex showed a higher content ($1.1 \cdot n^{-5}$). In 4 analyzed specimens of Triassic serpentinites Au concentration under the sensitivity of used method were established, i. e. values lower than $1 \cdot 10^{-6}$.

Method of Au determination

Gold determination has been performed by the modified method described in the paper of the authors C. E. Thompson — H. N. Nakagawa — G. H. Van Sicle (1968). Sensitivity limit of the method is 0.01 ppm Au in sample.

Reagents: standard Au solution; concentrated HBr p. a.; HBr 0.1 N; HBr 1.5 N; Br₂; Methylisobutylketon (in the following MIBK).

Device: atomic absorption spectrophotometer (the Perkin-Elmer 303 type has been utilized).

Procedure: To 10 g of the fine pulverized sample (cca 150 mesh) 20 ml of Br₂ solution in concentrated HBr was added in a Erlenmayer flask and intensively mixed 15 minutes

Table 1. Gold abundances in West Carpathian ultramafic rocks

	locality	rock-type	Au (n, 10 ⁻⁶)	
1. Ultramafites in Jarabá Group				
1	MF-138	Veľká Lúka	hornblende peridotite	2
2	vcp 263	Filipovo	hornblende peridotite	3
3	vcp 351	Hudák	chlorite-hornblende serpentinite	1
4	vcp 261	Filipovo	chlorite-actinolite schist	3
5	vcp 270	Beňuš	hbl-chlorite-serp. schist	3
6	vcp 260	Filipovo	chlorite schist	1
2. Ultramafites in Kokava Group				
7	S-80	Čierna Lehota	serpentinite	7
8	S-81	Čierna Lehota	serpentinite	4
9	vcp 352	Krokava	steatite serpentinite	1
10	S-82	Mur. Dl. Lúka	serpentinite	4
11	V-24	Mur. Dl. Lúka	serpentinite	2
12	S-7	Uhorské	serpentinite	2
13	vcp 403	Málinec	actinolite-chlorite schist	7
14	XXX	Mur. Dl. Lúka	chlorite-steatite schist	4
15	vcp 272	Málinec	chlorite-hbl-serp. schist	11
3. Ultramafites in Carboniferous				
16	SGR 48	Breznička	serpentinite	4
17	SGR 20	Banská valley	serpentinite	2
18	SGR 66	Slovenská skala	serpentinite	3
19	SGR 39	Ploské	serpentinite	2
20	SGR 68	Tri peniašky	serpentinite	2
4. Ultramafites in Triassic				
21	Ko-1	Komárovec	serpentinite	4
22	SGR 552	Dobšiná	serpentinite (with secondary garnet)	2
23	SGR 98	Svablica	serpentinite	4
24	SGR 18	Kobeliarovo	serpentinite	2
25	SGR 45	Sedlice	serpentinite	1
26	SGR 31	Danková	serpentinite	< 1
27	SGR 30	Rudník	serpentinite	< 1
28	SGR 56	Jasov	serpentinite	< 1
29	SGR 32	Danková	serpentinite	< 1
30	SGR 49	Danková	rodingite	< 1
5. Basites, metabasites				
31	VP 24	Poniky	biotite picrite (Triassic)	2
32	75/65	Nízke Tatry Mts.	augite porphyrite (Cretaceous?)	5
33	limb 1	Oravice	limburgite (Cretaceous)	< 1
34	MF m	Malá Fatra Mts.	diorite porphyrite	2
35	MF 200	Malá Fatra Mts.	kersantite	4
36	NT 62	Nízke Tatry Mts.	kersantite	2
37	4/60	Rochovce	spessartite	1
38	vcp 237	Petovcovo	syenodiorite	1
39	vcp 304	Dlhá valley	syenodiorite	2
40	1968 9	Čierna Lehota	amphibolite	< 1
41	V 21	Zelený potok	amphibolite	1

at a temperature of cca 20° C. If sulphides (and organic matter) are present the sample ought to be annealed before this operation. After finished Au extraction 20–30 ml of distilled water and 10 ml of methylisobutylketon is added to the sample; intensive mixing for 2 minutes follows. The gained solution is centrifugated (1 min.), the upper MIBK layer with the extracted Au is transferred to a flask containing 25 ml 0.1 N HBr and both solutions are intensely shaken for 15 seconds. The clarified MIBK is atomized. Owing to its high volatility it is necessary to keep on the time limits of the individual operations.

Working parameters of the device Perkin-Elmer 303; wave length 2428 Å; slit — 4, gain — 4, damping (MR) — 2, scale — 5, intensity of the lamp — 15 mA.

From the comparison of Au contents in serpentinites from various geological-stratigraphical units it follows that Au contents rise from Triassic serpentinites over serpentinites in Carboniferous metasediments to serpentinites in metamorphic rocks of the Kokava Group. Generally with increasing metamorphism of complexes containing ultramafic rocks, elevated gold contents may be observed (tab. 2).

Table 2. Average Au contents in different ultramafic rock-types

serpentinites in Triassic (n = 9; No 21–29)	$1.6 \cdot 10^{-6}$ /*
serpentinites in Carboniferous (n = 5; No 16–20)	$2.6 \cdot 10^{-6}$
serpentinites in Kokava Group (n = 6; No 7–12)	$3.3 \cdot 10^{-6}$
rocks of the reaction rim (blackwall) of ultrabasite	
bodies in metamorphic complexes (n = 6; No 4–6, 13–15)	$4.8 \cdot 10^{-6}$
hornblende peridotites (n = 2; No 1–2)	$2.5 \cdot 10^{-6}$

/* For the $\bar{x}$ calculation instead of the value $< 1 \cdot 10^{-6}$ the values $5 \cdot 10^{-7}$ were substituted.

The content increase is more outstanding considering also Au contents in rocks from the reaction zone of ultrabasic bodies in metamorphic complexes ($\bar{x} = 4.6 \cdot 10^{-6}$). If the extremely low value of the sample No 6 (table 1) has not been applied for $\bar{x}$ calculation of these rock groups, $\bar{x}$ abundance of gold in blackwall is $5.6 \cdot 10^{-6}$.

Owing to the low number of analyzed basite and metabasite samples (table 1, No 31–41) these will not be discussed in the following.

Discussion

Gold abundances in ultrabasic rocks from various sites of the Earth's surface varies in the range of $n \cdot 10^{-5}$ to $n \cdot 10^{-7}$; most authors mention contents of $n \cdot 10^{-7}$ order. Differences in contents may be due to diverse Au contents in different parts of the Upper Mantle, or to content changes in various ultrabasic rock types owing to metamorphic processes. Based on present accessible analytical data, it is not possible to solve univocally the problem of Au connection with primary or redeposited occurrences. From this aspect also Au contents in ultramafic rocks of different geological formations of the West Carpathians should be envisaged.

Within the analyzed ultramafic rock types of the West Carpathians, the rocks of the blackwall zone from metamorphic complexes have the highest gold content. It is thus probable that these contents are conditioned by regional metamorphic processes of complexes containing these bodies, or by processes of hydrothermal activity, which

participated in the formation of these rocks types. The role of hydrotherms in the origin of elevated Au concentrations in ultrabasic rocks has been emphasized in past by A. F. Mac Gregor (1951 — in S. A. Šček a et al. 1971), according to which author Au accumulations of deposit character originate only by hydrothermal "re-working" of parent rocks of this element. In addition to the role of acid intrusions for Au migration, S. A. Šček a et al. (1971) emphasized also regional dynamometamorphism under greenschist facies conditions, where by migration of Au is allied particularly to Na-metasomatism.

Few analytical data are to disposal according to which Au behaviour during serpentinization processes could be followed (tab. 3). Opinions are valid according to which serpentinization takes place (L. V. Li — T. Ja. Kornev 1972, S. P. Sobolev et al. 1973), as well as data proving for the increase of Au content in this process (J. H. Crockett — L. L. Chyi 1972).

For the solution of Au behaviour in the serpentinization process of the West Car-

Table 3. A review of gold abundances in various ultramafic rock-types

K. K. Turekian — K. H. Wedepohl (1961)	$\bar{x}$, ultrabasic rocks	$6 \cdot 10^{-7}$
P. A. Vinogradov (1962)	$\bar{x}$, ultrabasic rocks	$5 \cdot 10^{-7}$
G. G. Goles (1967, in P. J. Wyllie 1967)	$\bar{x}$, ultrabasic rocks	$9 \cdot 10^{-7}$
Ju. G. Ščerbakov (1967)	$\bar{x}$, ultrabasic rocks	$1 \cdot 10^{-6}$
W. D. Ehman — P. A. Baedeker (1968)	$\bar{x}$, carbonaceous chondrites	$2.3 \cdot 10^{-5}$
	achondrites	$1.9 \cdot 10^{-7}$
		$- 3 \cdot 10^{-6}$
A. A. Smales — D. Mapper — K. F. Fouché (1968)	iron meteorites	$4.3 \cdot 10^{-5}$
	metal phase	$- 2.2 \cdot 10^{-4}$
	of chondrites	$1.1 \cdot 10^{-4}$
		$- 2.9 \cdot 10^{-4}$
N. T. Voskresenskaja — N. F. Zvereva (1968)	$\bar{x}$, ultrabasic rocks	$4.4 \cdot 10^{-7}$
G. N. Anošin — E. M. Jemeljanov (1969)	$\bar{x}$, ultrabasic rocks of the ocean floor	$1.3 \cdot 10^{-7}$
F. J. Flanagan (1969)	$\bar{x}$, PCC-1 (peridotite)	$6.8 \cdot 10^{-7}$
	DTS-1 (dunite)	$8.5 \cdot 10^{-7}$
L. F. Borisenko — E. D. Uskov (1971)	$\bar{x}$, ultrabasic rocks of D-P-H assemblage / ⁺	$1 \cdot 10^{-5}$
S. A. Šček a et al. (1971)	$\bar{x}$, ultrabasites of D-H assemblage / ⁺	$21.3 \cdot 10^{-7}$
J. H. Crockett — L. L. Chyi (1972)	$\bar{x}$, peridotites	
	dunites, Mt. Albert	$1.1 \cdot 10^{-7}$
	$\bar{x}$, serpentinites, Mt. Albert	$2.4 \cdot 10^{-7}$
	$\bar{x}$, chromspinelides, Mt. Albert	$3.4 \cdot 10^{-7}$
	$\bar{x}$, chromite veinlets, Mt. Albert	$8.3 \cdot 10^{-8}$
L. F. Borisenko et al. (1972)	Ural Mts. ultrabasic rocks	$1.1 \cdot 10^{-5}$
		$- 5 \cdot 10^{-6}$

Note: /⁺ D-P-H = dunite — peridotite — harzburgite assemblage; D-H = dunite — harzburgite assemblage; $\bar{x}$ = arithmetic mean.

pathian area only serpentinites in the Triassic of Spišsko-gemerské rudohorie Mts. may be considered. This group only fulfils the presumption, according to which serpentinitization was the sole metamorphic process creating the present-day mineral and chemical composition of these rocks.

In some serpentinites of the Spišsko-gemerské rudohorie Mts. Triassic an gold content lower than $1 \cdot 10^{-6}$ has been determined. These were types, where intensity of serpentinitization compared with the other analyzed samples of this group is the most intensive (without relics of primary minerals, without bastite pseudomorphs after pyroxenes, predominantly light-coloured serpentinites).

Also the mode of Au occurrence in ultrabasic massifs is a not less interesting and not uniformly answered problem. Considerable differences in Au distribution in ultrabasic rocks deriving from various regions some authors ascribe to primary differing Au contents in Upper Mantle rocks. Recently most authors simultaneously drew to the conclusion, that Au does not enter into silicates or ore minerals of ultrabasic rocks substituting other cations (I. S. Rožkov et al. 1971), but forms a separate micro-disperse phase, or is present in atomic state. This presumption was confirmed by the finding of native gold in ultramafic rocks (L. F. Borisenko et al. 1969).

Disperse Au, or Au in atomic state occurs prevalently in sulphide minerals (S. A. Ščekka et al. 1971, V. G. Moiseenko — I. I. Fatyánov 1972). The views on the Au bond to chromspinellides are at variance. A part of the authors (S. A. Ščekka et al. 1971) suggests that the presence of chromspinellides reduces the Au amount in ultrabasic rocks: in turn studies of J. H. Crockett — L. L. Chyi (1972) from the Mt. Albert pluton (Canada) brought evidence of increased Au concentration in rock-forming chromspinellides.

In applying these results to West Carpathian ultramafites, the problem of Au distribution may be summarized as follows:

The highest Au contents are in ultramafic rocks from crystalline complexes. Intensive regional metamorphism with the formation of chlorite, hornblende and talc is typical for these rocks. At the same time also the presence of an increased amount of sulphides (pyrite, chalcopyrite, pyrrhotite — tab. 1, No 2—6), or the occurrence of hydrothermal pyrite in the reaction zone of bodies in crystalline complexes of the Kokava Group is characteristic (table 1 — No 13—15). The elevated Au contents in these rock types ought to be thus related to hydrothermal activity, or to the presence of primary sulphides (bodies in the Jarabá Group crystalline complex).

Conclusion

Among 29, for Au analyzed samples of various West Carpathian ultramafic rock types, 25 samples have Au contents $n \cdot 10^{-6}$. Simultaneously 4 serpentinites from the Triassic have Au concentrations below $1 \cdot 10^{-6}$. Also the analyzed rodingite from the contact of the ultrabasic body shows a lower concentration. From 11 basite and metabasite samples 9 have Au concentration $n \cdot 10^{-6}$, the remaining 2 samples have lower concentration.

Comparison of Au contents of ultramafite rocks deriving from various geological units of the West Carpathians showed that the content raises beginning by Triassic serpentinites over Carboniferous ones, up to ultramafic rocks in crystalline complexes. The highest concentrations were found in rocks from the blackwall zone of ultrabasic bodies with the adjacent metamorphites. Increase of Au contents is proportional to the

intensity of postserpentinization metamorphism of ultrabasic massifs and the allied hydrothermal alteration.

Translated by L. MINÁRIKOVÁ.

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