ISSN 1028-334X, Doklady Earth Sciences, 2007, Vol. 413, No. 2, pp. 308–314. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © A.A. Marakushev, V.S. Rimkevich, L.P. Dem'yanova, 2007, published in Doklady Akademii Nauk, 2007, Vol. 413, No. 2, pp. 237–243.

GEOCHEMISTRY

The Specific Character of Evolution of Fluid–Silicate–Metallic Immiscibility of Melts

Academician of the RAS A. A. Marakushev[a], V. S. Rimkevich[b], and L. P. Dem'yanova[b]

Received October 4, 2006

DOI: 10.1134/S1028334X07020407

Immiscibility in natural melts (magmas), which is expressed either in layering of intrusions or in formation of a droplike texture, develops under the influence of fluids that considerably decrease the crystallization temperature.

Rhythmic magmatic layering is provided by deviation from equilibrium during fast cooling, when the melt layers have no time to change their composition, enter to the field of immiscibility, and are subjected to further immiscibility.

Experiments for simulation of this phenomenon were carried out on aluminosilicate melts with addition of potassium silicofluoride (hieratite K_2SiF_6) [1]. The fluoride aluminosilicate melt underwent rhythmic layering in the course of fast cooling and standing at 1300 and 950°C. Doping with Nb and Ta revealed their contrasting distribution between the melt layers with concentration of both metals in the F-rich layers (Fig. 1). The addition of alkali fluoride (K_2SiF_6) mimics a fluid effect on magma that results in rhythmic layering typical of stratiform intrusions, while the contrasting distribution of Nb and Ta between the layers provides insight into the mechanism of formation of ore-bearing units (reefs). Rhythmic magmatic layering is characteristic of stratiform intrusions, whereas drop immiscibility is retained, only occasionally giving way to layering. Drop immiscibility is typical of volcanic rocks, in which this effect is retained owing to quenching and formation of variolites. The data concerning variolites are summarized in [2], where the variole and matrix compositions recalculated on a 100% volatile-free basis are given as the number of atoms per 50 oxygen atoms. The main types of these compositions are presented below (numerals in parentheses pertain to varioles): basalt–andesite K 0.998 (0.855), Na 1.331 (1.497), Ca 3.141 (2.860), Fe 3.746 (2.096), Mg 3.366

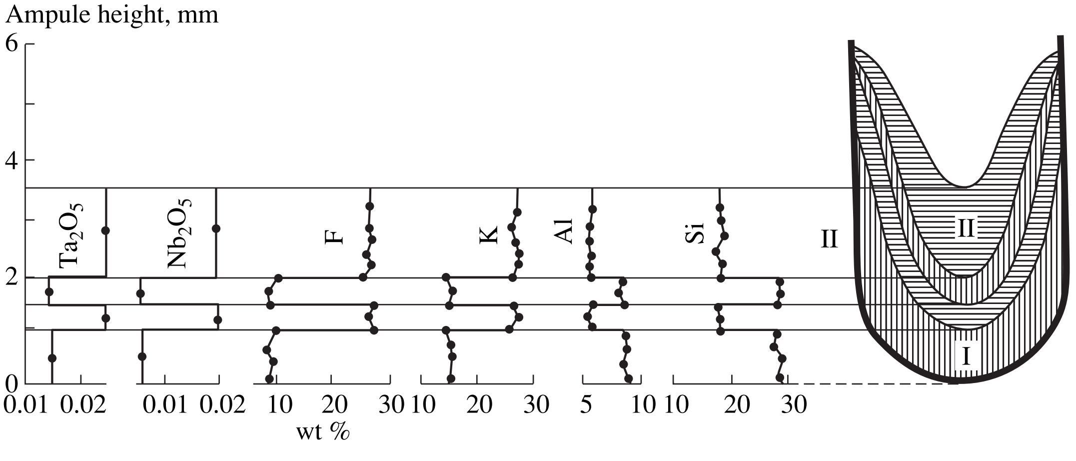

Fig. 1. Distribution of Ta, Nb, F, and rock-forming elements (Si, Al, K) in the aluminosilicate melt rhythmically layered into (I) silicic and (II) F-rich immiscible liquids (based on experimental data [1]).

---

[a] *Institute of Experimental Mineralogy, Chernogolovka Scientific Center, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia; e-mail: belova@iem.ac.ru*

[b] *Institute of Geology and Nature Management, Amur Scientific Center, Far East Division, Russian Academy of Sciences, Relochnyi per. 1, Blagoveshchensk, 675000 Russia*

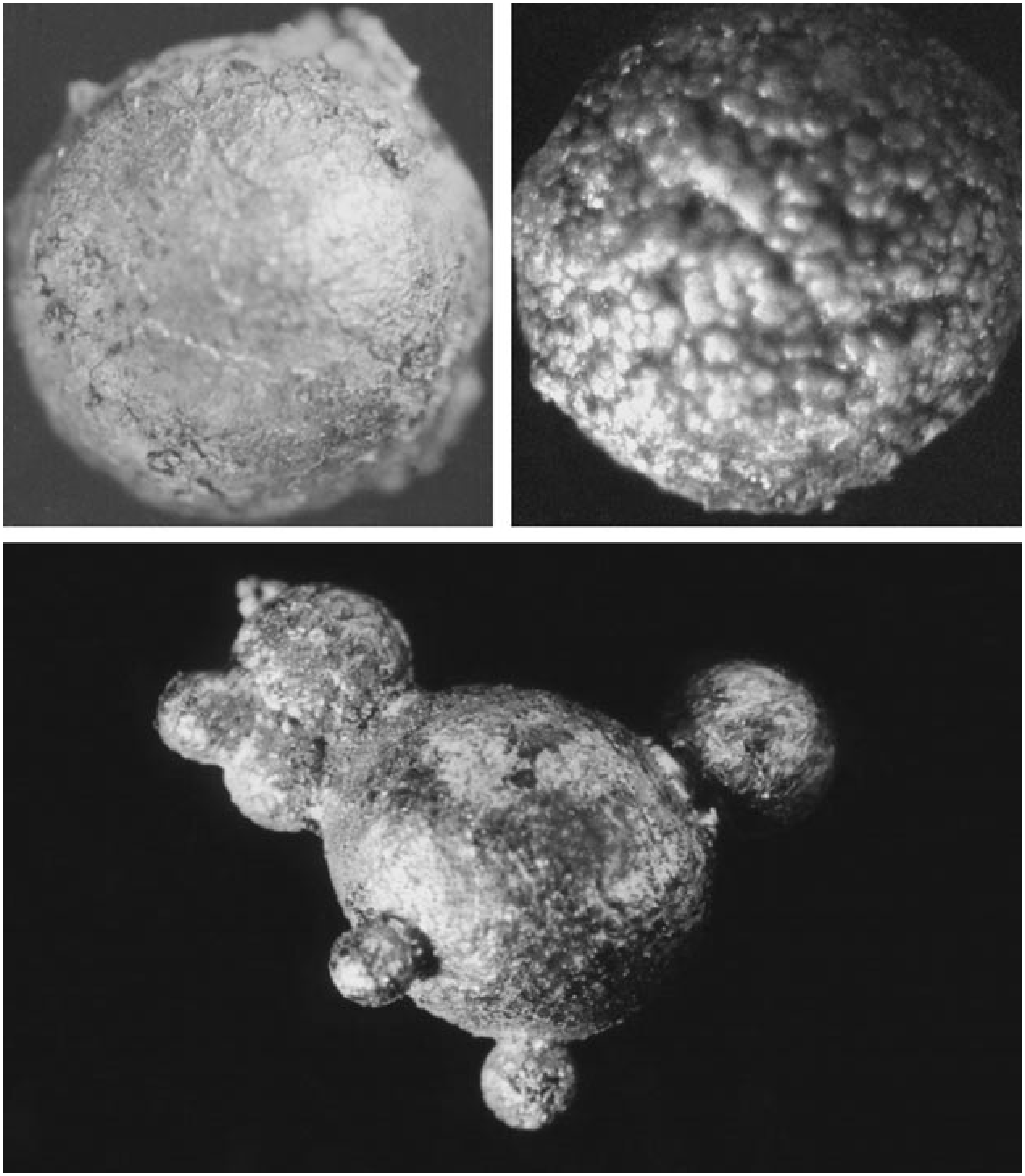

Fig. 2. Gold spheroids (upper images, magn. 40) and intergrowths of gold spheroids (lower image, magn. 10) recovered from alkaline melts after pyrohydrometallurgical melting of Au-bearing raw materials.

(1.802), Al 6.409 (4.988), Si 14.48 (17.36); ferrobasalt–icelandite K 0.048 (0.283), Na 1.009 (1.179), Ca 3.720 (1. 223), Fe 5.584 (1.691), Mn 0.243 (0.035), Mg 0.928 (0.339), Al 2.781 (3.466), Ti 1.840 (0.574), Si 14.58 (19.66), P 0.786 (0.122); basalt–rhyolite K 0.003 (0.132), Na 0.203 (2.602), Ca 4.077 (0.530), Fe 3.170 (0.265), Mg 1.788 (0.003), Al 5.774 (3.894), Ti 0.254 (0.210), Si 15.84 (20.78); and ferrobasalt–rhyolite K 0.184 (2.335), Na 0.110 (0.070), Ca 4.030 (0.470), Fe 9.67 (0.690), Mn 0.095 (0.012), Mg 0.410 (0.030), Al 2.240 (3.700), Ti 1.110 (0.140), Si 14. 82 (20.84), P 0.170 (0.035).

Varioles are more leucocratic (feldspathic, feldspathoid) than a matrix that largely consists of dark-colored minerals. The glass-forming chemical elements

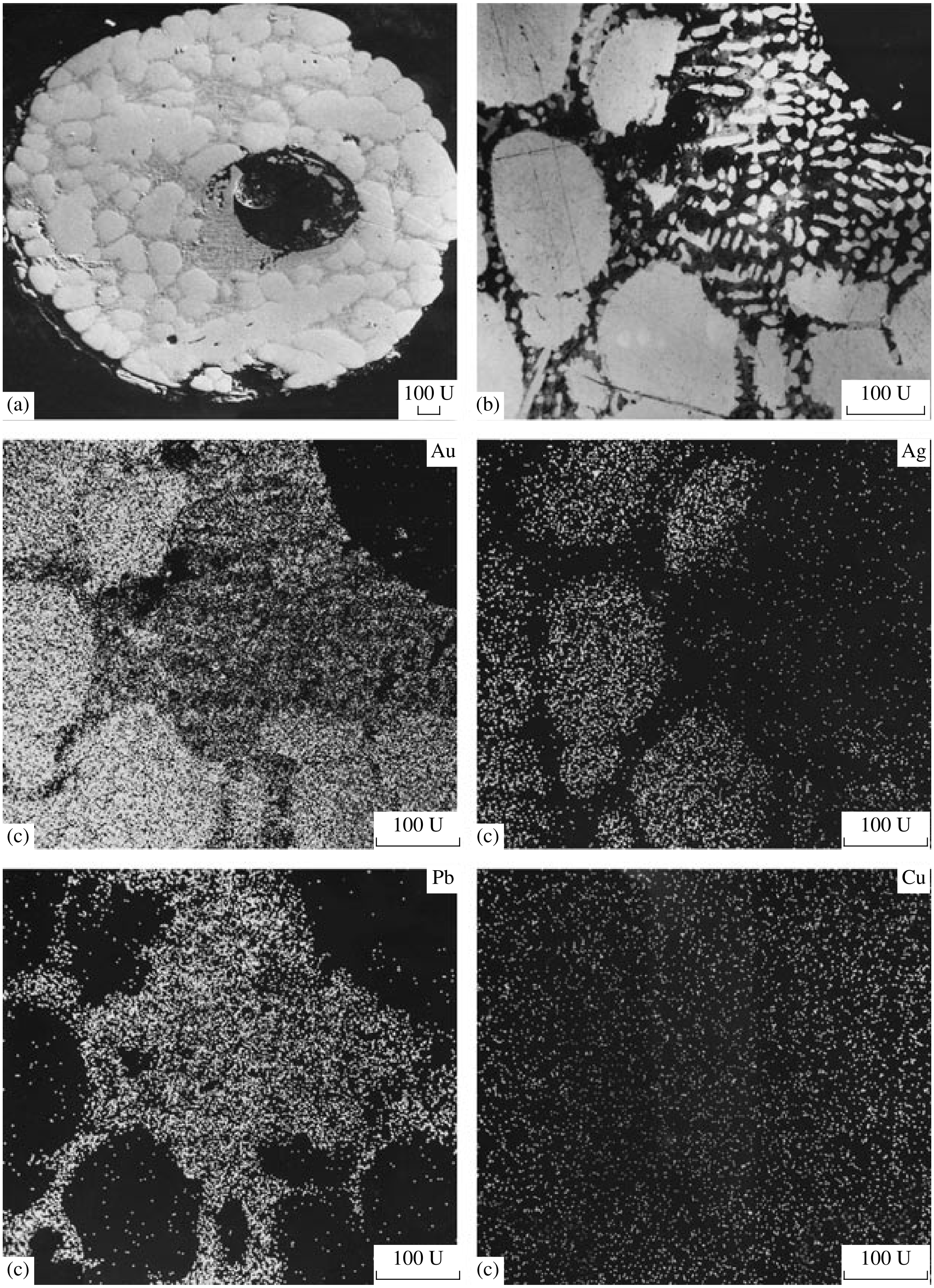

Fig. 3. Structure of a gold spheroid consisting of small spherules: (a) general view (BSE image); (b) closeup of image (a); (c) distribution of Au, Ag, Pb, and Cu at the surface of the analyzed site (characteristic X-ray irradiation).

(Si, Al), which increase viscosity, are commonly predominant in varioles, whereas modifier-elements (Fe, Mg, Ca) with contrasting properties concentrate in the matrix. These elements decrease viscosity and inhibit glass formation. These relationships are complicated by the effect of volatile components (H_2O and others), which serve as modifiers that dilute melts and decrease their crystallization temperature. Iron is incorporated into rocks in the oxidized state (FeO, Fe_2O_3). Native iron sporadically occurs in basalts of some traps, but it is common in lunar rocks and meteorites where Fe makes up solid solutions with Ni (kamacite, taenite). The structure resulting from iron–silicate liquid immiscibility is clearly seen in chondrites, the most abundant type of meteorites (95% of total falls). Chondrites consist of tiny silicate droplets (olivine, pyroxene, pyroxene–plagioclase, plagioclase chondrules) incorporated into the Ni–Fe (kamacite) matrix. Chondrules consolidated before the matrix and were later replaced with a Ni–Fe melt retained in the matrix as numerous shapeless (amoebalike) silicate inclusions. Sporadic or abundant kamacite droplets are found in both these inclusions and completely retained chondrules. A silicate melt serves as a matrix with respect to these droplets. Thus, the metallic Ni–Fe phase in chondrites has a dual structural position. This phase makes up a matrix of silicate chondrules, on the one hand, and occurs as droplike segregations within the chondrules, on the other hand. At the same time, both structural positions of the metallic phase bear a systematic character in chondrites [3].

Such duality distinctly reflects the two-stage evolution of chondrites [4]. The chondritic melts made up high-density cores of the parental giant planets. They split into chondrules and the matrix under the great pressure of their fluid shells at the protoplanetary evolutionary stage that predated the planetary evolutionary stage, when the parent planets lost their giant fluid shells and the cores consisting of melts underwent explosive breakdown into asteroids. The enormous fluid pressure that dominated at the protoplanetary stage of chondrite evolution was the main factor of immiscibility development in chondritic melts, which split into silicate droplets and the melted Fe–Ni matrix. After occlusion, the Fe–Ni melt interacted with hydrogen that lowered the viscosity of the metallic melt, which cemented the tiny droplike chondrules of the more viscous silicate melt. However, the chondrules already consolidated at the planetary evolutionary stage characterized by moderate and low fluid pressures. Such conditions fostered the development of principally distinct structural relationships between iron and silicate phases in the course of their liquid immiscibility: Ni–Fe, iron–sulfide, and sulfide drops systematically appeared within silicate chondrules [3]. These conditions predetermined the structural relationships, which, in fact, were opposite to those in chondrites under a great fluid pressure created by outer shells of their parental giant planets. This conclusion is supported by the occurrence of all groups of chemical elements (H, L, LL, E, C) in the matrix of chondrites, as well as numerous diamond nuclei overfilled with fluid inclusions to such an extent that their volumetric density decreases down to 2.2 g/cm^3, whereas a natural diamond has a density of 3.5 g/cm^3.

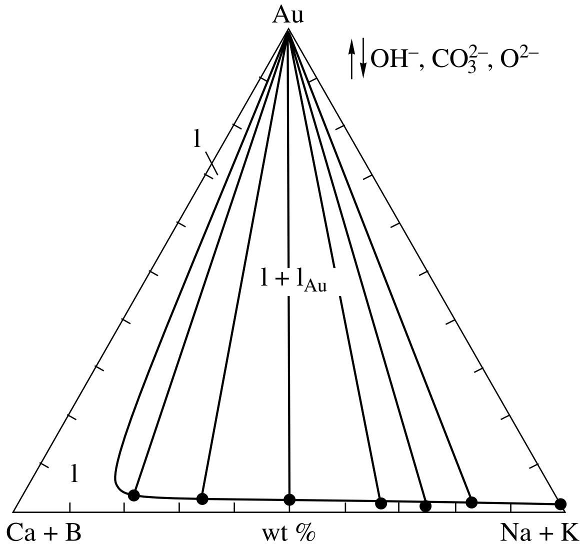

Fig. 4. Field of immiscibility in the ternary system that corresponds to the products of high-temperature fire assay (Ca + B) and low- and medium-temperature pyrohydrometallurgical (Na + K) melting of Au-bearing raw materials.

Hence, the combination of the natural chondritic and the opposite structures of liquid immiscibility reflects the polyfacies nature of chondrites characterized by very high gradients of fluid pressure during their formation.

Metallic drops (spheroids) in a silicate matrix of rocks and sulfide ores are largely composed of noble metals that are retained in the native state even at the oxidizing state of petrogenetic systems. Gold spheroids were described at the Tokur deposit in the Amur region [5]. When the rocks are destroyed, the gold spheroids are retained in placers [6]. The magmatic origin of some noble metal spheroids was substantiated in [7].

We synthesized gold spheroids from Au-bearing raw materials (Table 1) using the pyrohydrometallurgical technique at a temperature of 350–800°C under atmospheric pressure. The melting with admixtures of Na and K compounds (NaOH, KOH, $NaNO_3$, KNO_3) was carried out in crucibles made of stainless steel, nickel, or glass carbon on electric hot plates or in muffle electric furnaces.

The groundmass of the starting material (barren rock) was dissolved in salts of alkali metals or transformed into hydrosilicates, hydroaluminosilicates, and other compounds that are soluble in diluted hydrochloric acid. Virtually all the gold entered the insoluble residue. Then it was removed by the gravity separation method or hand-picked under a binocular microscope.

Table 1. Chemical composition of Au-bearing raw materials used in pyrohydrometallurgical melting

No	Raw material	Content, wt %														
		SiO_2	Al_2O_3	TiO_2	Fe_2O_3	FeO	MgO	MnO	CaO	Na_2O	K_2O	SnO_2	P_2O_5	SO_3	L.O.I.	Total
1	Quartz–gold ore	65.04	12.24	0.46	3.10	1.23	1.51	0.09	1.96	1.83	4.66	n.a.	n.a.	2.62	4.63	99.37
2	Gold concentrate from placer deposit	31.08	12.74	13.05	15.45	8.83	0.95	0.70	15.18	0.56	0.36	″	0.68	n.a.	0.03	99.61
3	Sulfide concentrate	33.70	8.38	3.65	14.60	4.17	0.72	1.80	3.76	0.74	0.37	1.55	1.78	15.39	8.43	99.04
4	Cassiterite concentrate	2.70	0.23	1.98	5.74	4.04	0.12	0.50	1.87	0.08	0.08	77.93	0.24	n.a.	0.51	96.02
5	Technological wastes	7.20	0.80	0.54	11.87	8.72	0.21	1.43	0.50	0.66	0.04	59.60	1.42	″	1.17	94.16

No	Content, wt %															
	Au	Ag	Co	Ni	Cr	W	Mo	Pb	Cu	Zn	Bi	Sb	Cd	As	Se	Total of admixtures
1	0.0011	0.008	<0.002	0.002	0.01	0.03	n.d.	0.02	0.002	0.01	çÂ Ó·Ì.	0.001	<0.001	0.47	<0.002	0.5519
2	0.0033	0.0005	0.019	0.002	0.016	0.125	″	0.051	0.025	0.048	0.03	0.0067	<0.001	0.008	0.0062	0.3417
3	0.1563	0.0331	0.007	0.02	0.15	0.1	0.002	0.03	0.05	0.3	0.03	0.03	<0.001	0.38	0.007	1.2964
4	0.5185	0.0635	<0.002	0.007	0.586	1.05	0.005	0.564	0.024	0.092	0.06	0.018	0.0001	0.1	<0.0002	3.0903
5	0.9610	0.150	0.0027	0.083	0.342	0.51	0.005	1.16	1.05	0.035	0.31	0.684	<0.001	0.03	<0.0002	5.3239

Note: The compositions of raw materials given in Tables 1 and 2 were determined at the Laboratory of Chemical Analytical Methods, Institute of Geology and Nature Management, Far East Division, Russian Academy of Sciences. (<) Below the detection limit; (n.a.) not analyzed; (n.d.) not detected.

Table 2. Chemical composition of spherules obtained by pyrohydrometallurgical processing of various Au-bearing raw materials

No.	Composition	Content, wt %										
		Au	Ag	Ti	Fe	Mg	Mn	Ca	Na	K	Co	Ni
1	Spheroids from quartz–gold ore	86.04	10.78	0.017	0.07	n.d.	0.085	0.012	0.012	0.026	<0.001	0.031
2	Spheroids from concentrates of placer deposits	87.41	10.53	0.015	0.04	"	0.03	0.001	0.026	0.021	<0.001	0.040
3	Spheroids from sulfide concentrates	81.42	13.93	0.018	0.074	0.017	0.12	0.007	n.d.	0.036	<0.001	0.022
4	Spheroids from cassiterite concentrates	88.76	9.18	0.019	0.011	0.015	0.008	0.018	"	0.032	<0.001	0.084
5	Spheroids from technological wastes	83.90	8.75	0.010	0.041	0.026	0.024	0.024	"	0.027	<0.001	1.50

No.	Content, wt %										
	Cr	Pb	Cu	Sn	Zn	Bi	Sb	Cd	As	Total	Total of admixtures
1	0.025	0.43	0.42	<0.1	0.026	n.d.	<0.01	<0.001	0.039	98.125	1.305
2	0.005	0.025	0.004	0.2	0.02	0.007	<0.01	<0.001	n.d.	98.386	0.446
3	n.d.	2.72	0.85	<0.1	0.13	0.15	<0.01	<0.001	0.12	99.726	4.376
4	0.13	1.07	0.39	<0.1	0.03	0.18	<0.01	<0.001	n.d.	100.039	2.099
5	0.010	2.63	0.258	0.1	0.252	0.10	<0.01	<0.001	0.067	97.731	5.081

The removed barren rock amounted to 60–99.9 wt % of the starting material, and 0.5–3.0 wt % of extracted Au was removed with technological solutions (gold recovery was 90–95%).

The gold grains left in the sediment after melting made up crystalline intergrowths (*n* mm to 15 cm in size), and the Au grade in concentrate increased 10 times or more [8]. According to [9], a similar processing of Pt-bearing concentrates also results in the coarsening of metallic grains.

The most interesting result of the performed experiments consists in the formation of gold spheroids of variable dimension and structure (Fig. 2). They were formed as a result of the liquid immiscibility of gold (spheroids) and the alkali melt. The studied gold spheroid consisted of numerous small spherules (Fig. 2, upper right image). The spheroid was examined at the Laboratory of Electron Microprobe Spectroscopy (Institute of Geology and Nature Management, Blagoveshchensk) on a JSM-35C analytical SEM equipped with a wave-dispersive spectrometer that detects chemical elements from Si to U. After pressing into an epoxy pellet with graphite (15 wt %), the sample was studied in the BSE regime.

The distribution of chemical elements at the sample surface was revealed from characteristic X-ray radiation with quantitative determination of elements (accelerating voltage 10–20 keV, current 20–40 mA).

A cavity was found within the sawed spheroid (Figs. 3a, 3b). Small gold spherules are cemented by a groundmass mainly consisting of Pb (Fig. 3c). Silver is concentrated in gold spherules with 88.94 wt % Au, 9.06 wt % Ag, and 1.18 wt % Pb. The average composition of the cement is as follows (wt %): Pb 52.09, Au 41.07, and Ag 5.4. Copper is distributed uniformly over the sample surface. Bi, Sn, Ni, and Co contents are at the background level. Fe and Zn were not detected.

Thus, gold spherules were refined from admixtures in the process of immiscible liquid separation and the fineness of gold and silver was upgraded.

The gold spheroids were formed by melting of a B-rich slag left after fire assay fusion with addition of NaOH, KOH, and their mixtures at a minimal temperature of 350°C. Figure 4 shows the compositions of the starting material, doped components, and final products.

The field of immiscibility occupies a rather wide area in the diagram and exists at a temperature above 350°C. The Au–(Ca + B) side of the triangle is devoid of immiscibility and characterizes the high-temperature fire assay fusion at >1200°C, when the gold melt and a complex melt (soda, borax, lime, and others) are formed. The increase in Na and K contents leads to the development of immiscibility.

As can be seen from Fig. 4, the Au solubility in the melted additional components is insignificant and, conversely, the additional components are poorly soluble in the gold melt. At a temperature below the immiscibility level, a complex (largely alkaline) melt coexists with gold crystals [8].

The experimental results testify to the importance of liquid immiscibility, which is not only an efficient mechanism of spherule formation in magmatic melts but also is a factor that has technological implications for recovery of noble metals from raw materials.

REFERENCES

1. A. A. Marakushev, I. P. Ivanov, and V. S. Rimkevich, Dokl Akad. Nauk SSSR **258**, 183 (1981).
2. A. A. Marakushev, *Petrogenesis* (Nedra, Moscow, 1988) [in Russian].
3. A. A. Marakushev, L. B. Granovsky, N. G. Zinov'eva, et al., *Cosmic Petrology* (Nauka, Moscow, 2003) [in Russian].
4. A. A. Marakushev, *Origin of the Earth and Nature of Its Endogenic Activity* (Nauka, Moscow, 1999) [in Russian].
5. V. G. Moiseenko, *Metamorphism of Gold at Ore Deposits in the Amur Region* (Khabarov. Knizhn. Izd, Khabarovsk, 1965) [in Russian].
6. R. N. W. Dilabio, J. W. Newsame, D. F. McIvor, et al., Econ. Geol. **83**, 153 (1988).
7. G. N. Gamyanin and Yu. Ya. Zhdanov, Dokl. Earth Sci. **377A**, 298 (2001) [Dokl. Akad. Nauk **377**, 663 (2001)].
8. V. G. Moiseenko and V. S. Rimkevich, RF Patent No. 2140460, Moscow, 1999.
9. V. G. Moiseenko, V. I. Palazhchenko, T. B. Makeeva, et al., Rus. J. Inorg. Chem. **48**, 647 (2003) [Zh. Neorg. Khim. **48**, 735 (2003)].