
SHORT
COMMUNICATIONS

Redistribution of Au in Volcanic Ashes in the Course of Their Postsedimentary Alterations

S. B. Felitsyn

*Institute of Precambrian Geology and Geochronology (IGGD), Russian Academy of Sciences,
nab. Makarova 2, St. Petersburg, 190034 Russia*

e-mail: felitsyn@peterlink.ru

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Abstract—The redistribution of Au in Late Precambrian volcanic ashes from the Vendian section of the East European Platform and the Sinian section of the South China Platform is characterized by high Au concentration (up to >20 ng/g) in Fe³⁺-rich samples. The Au content decreases to ~2 ng/g in Fe²⁺-rich volcanic ashes from the Vendian section of the East European Platform. This distribution pattern suggests the mobility of Au-bearing compounds in postsedimentary processes.

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The composition of water-soluble complex of volcanic ashes and the volume of the tephra of large explosions (10–100 km³) suggest that ore elements can enter sedimentary basins together with pyroclastic products. The available data on the composition of volcanic aerosols (Ivlev et al., 1986), exhalations (Menyailov et al., 1980), and volcanic ashes (Fruchter et al., 1980) testify to their considerable enrichment in Sb, Hg, As, Cd, Se, and other elements that are typical of the gaseous phase of volcanic eruptions. Concentrations of Ag and Au in the tephra of very large Holocene eruptions in Kamchatka are several times higher than average contents of these elements in the Earth's crust (Felitsyn et al., 1990). Eruption of the Opal Volcano (southern Kamchatka) in ~500 AD was characterized by a very large volume of eruption products (>17 km³). In their rhyolitic tephra, contents of Au and Sb show a direct correlation with the content of fine (<63 μm) ash particles. This is attributed to the sorption mechanism of Au concentration in the ash material (Melekestsev et al., 1991). In eruptions of the Plinian type, the volume of tephra can reach >1000 km³ (Huff et al., 1992) and the fine (<63 μm) ash particles can account for >60 wt % (Brazier et al., 1983). Given that volcanic ashes play a significant role as the source of Au for sedimentation basins and Au-bearing compounds occur in the tephra in the sorbed form, we can assume that Au can be redistributed in the course of secondary transformations of the ash material.

The present communication reports data on the Au distribution in volcanic ashes delivered to Late Precambrian epiplatformal basins of the East European and South China platforms.

The Au content in volcanic ashes was determined by the instrumental neutron activation analysis based on superheat neutrons (INAA), because this version of the

INAA method makes it possible to confidently determine low Au concentrations (1.0–10.0 ng/g).

MATERIALS AND METHODS

Our work is based on results of the sampling of distal tephra units in Upper Precambrian reference sections of the East European and South China platforms. Volcanic ashes of the Upper Vendian Redkino Group occur in terrigenous sections of the Moscow syncline, as well as the Mezen, Lvov–Kishinev, Verkhnyaya Kama, and Shkapovo–Shikhany depressions of the East European Platform (Aksenov, 1998). The volume of tephra in these sections exceeds 10000 km³ (Felitsyn and Sochava, 1996). Tuffogenic-sedimentary members of the Redkino Group (*n*–10 m thick) are composed of dense varieties with reddish brown, green, or chocolate color, obscure bedding, and vertical primary jointing. In the northeastern and central areas of the East European Platform, the tuffogenic unit includes light blue and lilac smectite layers (*n*–5 cm thick) related to vigorous eruptions of the acid pyroclastic material in the Redkino time. Ashes found in all areas of the platform can be divided into two types. The siliceous type is enriched in SiO₂ (up to 80 wt %), while the alumina-rich type is enriched in Al₂O₃ (up to 25 wt %). Compositional differences of Late Vendian volcanic ashes in the East European Platform are related to halmyrolysis followed by the pelitization and silicification of the rhyolitic material (Borkhvardt and Felitsyn, 1992).

Opal and chalcedony often replace ash particles in tuffogenic units with a high content of SiO₂. Dissolution of the ash material is also observed in some places (Kopeliovich, 1965). Based on the mineral composition of the pelite fraction of volcanic ashes from the Vendian section of the East European Platform, Aksenov and

Volkov (1969) concluded that the volcanic ash composition is altered at stages of diagenesis and initial epigenesis. The U–Pb zircon age of volcanic ashes of the Redkino Group in the Mezen depression (Zimniy coast, White Sea) is 553 ± 0.3 Ma (Martin et al., 2000). Therefore, we can assume that the majority of pyroclastic products in the Vendian section of the East European Platform have the same age (Felitsyn, 2004). Data on the composition of volcanic ash samples and their stratigraphic correlation are given in (Borkhvardt and Felitsyn, 1992; Felitsyn and Sochava, 1996; Felitsyn, 2004). In order to characterize Later Precambrian volcanic ashes of the South China Platform, we used results of the sampling of the lower part of the Sinian stratotype section in the Huangling anticline (30 km north of Ichang, Hubei province, China). In the Three Gorges area of the Yangtze River, the carbonate-dominated Sinian sequence (total thickness ~1100 m) overlies the Early Proterozoic Kuanling granites with the U–Pb zircon age of 819 ± 7 Ma (Ma et al., 1989). The Huangling granite is overlain by the Liantuo terrigenous formation (~100 m thick) containing rhyolitic vitroclastic tuffs (U–Pb zircon age 748 ± 12 Ma) at the top (Ma et al., 1989). The Sinian tuff of the Three Gorges area is identical in appearance with the Redkino tuff of the East European Platform. The Lower Sinian Liantuo and Nantuo formations are considered stratigraphic analogues of the Lower Vendian in the East European Platform (Sokolov, 1997).

We also determined the Au content in tholeiitic basalts of the trap formation of the Rataichitsa Formation (Lower Vendian Volyn Group) in the Belarus anticline (borehole Kobrin, western Brest district, Belarus), analogous basalts of the Berestovets Formation (Volyn Group) in the Volyn depression (borehole Ratno, northern Volyn district, Ukraine), and samples of Lower Vendian tuffogenic rocks from the same boreholes. The tuffogenic units are mainly represented by lithoclastic tuffs with basalt fragments in the chlorite-dominated matrix. We determined the Au content in volcanomictic sandstone samples of the Grushka Formation (Lower Vendian Volyn Group) related to the erosion of basalts of the Volyn Group (borehole 3628, interval 415–384 m, Settlement of Denisovka, northwestern Khmel'nitsa district, Ukraine).

Contents of minor, rare, and dispersed (hereafter, trace) elements in Late Precambrian volcanic ashes were determined with the INAA method. Air-dry weighed portions of the material (30–50 mg) were placed in specific purity quartz ampules and radiated for 48 h by superheat neutron fluxes (5×10^{13} neutron $\text{cm}^{-2} \text{s}^{-1}$) in research channels of a VVR-1 reactor of the Petersburg Institute of Nuclear Physics (Gatchina). The Au content was determined with a Ge–Li coaxial detector (volume 35 cm^3) after 36 h of radiation based on the Au γ spectrum (411.5 keV, radionuclide ^{198}Au). The content was calculated using standard samples AGV-1 (andesite, USGS, attested Au content

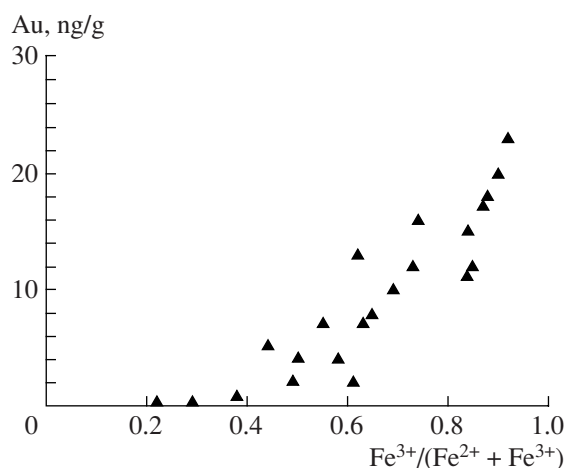


Fig. 1. Dependence of the Au content on the degree of Fe oxidation in Late Precambrian volcanic ashes of the East European and South China platforms.

0.6 ng/g) and RZS-3 (Au- and Ag-bearing quartz ore, TsNIGRI, attested Au content 940 ng/g). The lower detection limit was 0.4 ng/g; average relative error, <16% at Au concentration of <5 ng/g and <12% at Au concentration of >5 ng/g. Contents of FeO and Fe_2O_3 were determined by the bulk dichromate and photometric methods, respectively, in the Experimental Methodical Laboratory of the Sevtzapgeologiya Industrial-Geological Association (average relative error <5%).

RESULTS

The average Au content in volcanic ashes from Upper Vendian sections of the East European Platform is 7 ng/g. In host mudstones of the Redkino Group, the Au content increases to 10 ng/g (Felitsyn and Pshenichnova, 1992). In Late Precambrian volcanic ashes, the Au content correlates with the $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ ratio (table, Fig. 1). The Au content is maximum in Fe^{3+} -rich samples and minimum in Fe^{2+} -rich samples.

In basalts of the Volyn Group, the Au content varies from 7 to 10 ng/g (average 8 ng/g, $n = 6$). In lithoclastic tuffs of the basic composition, the average Au content is 8 ng/g ($n = 5$) and the Fe content varies from 8.0 to 8.5 wt %. In volcanomictic sandstones of the Grushka Formation, the Au content varies from 4 to 11 ng/g (average 7 ng/g, $n = 6$) and the Fe content is slightly higher (8.8 wt %) than in the basalts and basic tuffs.

DISCUSSION

Estimates of the amount of elements leached from basaltic ashes of the Great Tolbachik Fissure Eruption in 1975–1976 showed that the ash material governs the elemental composition of synchronous sediments and/or bottom waters (Yudovich and Ketris, 1988). Data on the Au distribution in tephra of different com-

Contents of Au and Fe in Late Precambrian volcanic ashes of the East European and South China platforms

Sample no.	Au, ng/g	Fe ₂ O ₃ , wt %	FeO, wt %	Fe ³⁺ /(Fe ²⁺ + Fe ³⁺)
East European Platform				
Lvov–Kishinev depression				
735-58	2	1.48	1.64	0.49
735-60	10	3.44	1.37	0.69
735-63	8	3.13	1.51	0.65
735-66	13	2.33	1.28	0.62
735-67	7	4.72	2.49	0.63
710-17A	1	2.17	3.14	0.38
710-17B	2	2.53	1.45	0.61
Moscow syncline				
939-56A	12	1.03	0.34	0.73
939-56B	16	1.55	0.49	0.74
Mezen depression				
1000-119	0.5	3.53	7.72	0.29
1000-194	4	2.81	1.83	0.58
1000-240	0.5	1.26	4.00	0.22
1000-200	5	5.27	6.03	0.44
1000-233	7	2.98	2.19	0.55
1000-201	4	6.64	5.96	0.50
South China Platform				
Three Gorges area of the Yangtze River				
YG-2	11	2.07	0.36	0.84
YG-5	17	2.70	0.36	0.87
YG-7	18	2.48	0.30	0.88
YG-9	23	2.40	0.18	0.92
YG-10	20	1.24	0.13	0.90
YG-8	12	1.51	0.25	0.85

positions (Felitsyn et al., 1990; Melekestsev et al., 1991) and the volume of the pyroclastic rhyolite–dacite material accumulated during large explosive eruptions indicate that the amount of Au delivered with the water-soluble acid tephra to sedimentation basins is considerably higher than the amount delivered by the basaltic volcanic ash.

Dependence of the Au content on the degree of Fe oxidation suggests the possibility of Au migration at postsedimentary stages of the volcanic ash transformation. According to petrographic observations, the major part of iron oxides and hydroxides is probably formed at early stages of postsedimentary transformation of volcanic ashes from Vendian sections of the southwestern East European Platform. They occur not only as fine-dispersed inclusions, but also as a coating of ash particles. If biotite is present in the ash units, iron oxides replace this mineral in the course of its decom-

position and intralayer dissolution (Kopeliovich, 1965). A similar process is developed in the biotite-bearing volcanic ashes of the Liantuo Formation (Sinian section, the Three Gorges area), which contains biotite crystals (up to 300 µm in size) partly replaced by iron hydroxides. In tephra of recent eruptions of the rhyolitic composition, the biotite content can be as much as 5 vol % (Melekestsev et al., 1991). Therefore, this mineral can be considered a source of Fe during the oxidation of the acid ash. Tephra with dacitic and rhyolitic pyroclastic materials deposited during Holocene and Recent eruptions in Kamchatka is dominated by Fe²⁺ (Kir'yanov et al., 1987). Correlation between the Au content and the degree of oxidation is absent in these materials. However, Fe²⁺ prevails ($\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}_2\text{O}_3) < 0.18$) in the 1500- to 7000-yr-old tephra from soils and glacial sediments. Therefore, we can suggest that high $\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}_2\text{O}_3)$ values in the Late Precambrian volcanic ashes (table) are related to the oxidation of Fe during postsedimentary transformations of the ash material.

Among supergene minerals, iron hydroxides are marked by the maximal Au content of 25 µg/g (Boyle, 1979). In iron hydroxides from sedimentary rocks of the central East European Platform, the maximal Au content is 240 ng/g. The Au content is appreciably lower in aluminosilicate clay minerals (Nikitin and Yasyrev, 1974). Gold is likely to occur in the native form in iron oxides and hydroxides of the supergene zone. Concentration of Au in these minerals can be related to the reduction of this element by salts of Fe and Mn and/or its sorption by gels of these elements, the subsequent breakdown of the complex anion of gold chloride, and the formation of native gold (Boyle, 1979).

Dependence of the Au content on the $\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}_2\text{O}_3)$ value testifies to the of Au mobility during the ash material alteration. Under oxidizing conditions, the ash material is enriched in Au together with iron oxides. If the amount of reducers is insufficient in the sedimentary sequence, ash units can be enriched in Au (10–20 ng/g) and the $\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}_2\text{O}_3)$ ratio can reach >0.70. In a reducing environment, Au is not accumulated in the volcanic ash. In Vendian volcanic ashes of the East European Platform, the smectite content in ashes varies from 10–20 to >40 vol %; the kaolinite content, from 0 to >25 vol % (Aksenov and Volkova, 1969). In clay minerals of the sedimentary cover of the East European Platform, the average Au content is 0.8–1.1 ng/g in smectite and chlorite, 2.5 ng/g in muscovite and sericite, 5.0 ng/g in glauconite, and 8.2 ng/g in halloysite and kaolinite (Nikitin and Yasyrev, 1974). However, Vendian bentonites with the maximal kaolinite content (samples 1000–119, 1000–200, and 1000–240) from the Mezen depression are not enriched in Au (table). The Au content shows a certain correlation with the input/output of Si during the pelitization of volcanic ashes (Fig.2): high-aluminous and silicified tuffs have

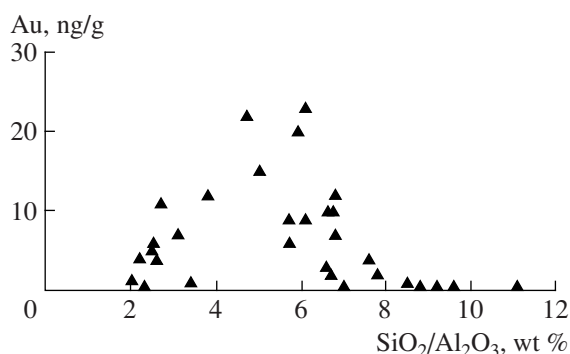


Fig. 2. Dependence of the Au content on the $\text{SiO}_2/\text{Al}_2\text{O}_3$ value in Late Precambrian volcanic ashes of the East European and South China platforms.

the minimal Au content. In silicified tephra from Vendian sections of the East European Platform with $\text{SiO}_2/\text{Al}_2\text{O}_3 > 7.0$, the Au content is 0.5–2 ng/g, which is comparable with the Au content (0.5–4 ng/g) in high-aluminous tuffs and bentonites with $\text{SiO}_2/\text{Al}_2\text{O}_3 < 3.0$. In the rhyolitic tephra from Sinian sections of the South China Platform, the $\text{SiO}_2/\text{Al}_2\text{O}_3$ value is 5.7–7.0. Together with petrographic data, this value suggests the initial stage of pelitization of the ash material. In the rhyolitic tephra of Recent and Holocene volcanic eruptions in Kamchatka, the $\text{SiO}_2/\text{Al}_2\text{O}_3$ value varies from 4.5 to 6.0 (Kir'yanov et al., 1987; Melekestsev et al., 1991) and the average Au content is 12 ng/g (Felitsyn et al., 1990). These data suggest the possibility of Au removal at the reducing stage of early diagenesis and during epigenetic transformations. According to (Kopeliovich, 1965), the latter processes were characterized by the pelitization of volcanic ashes from Vendian sections of the East European Platform.

Gold concentrated in the sedimentary sequence migrates as AuCl_4^{-1} in the reducing environment (Yasyrev, 1971). The presence of Cl in mud waters can be related not only to the salinity of paleobasins, but also to the high content of Cl in the acid pyroclastic material. The Cl content in rhyolitic pyroclastic products is 0.1–0.6 wt % (Coradossi and Martini, 1983; Hall et al., 1984). Chlorine is a major acid-forming agent in the gaseous component of explosive volcanic eruptions with the acid pyroclastic material (Menyailov et al., 1980).

Concentrations of Au in basalts of the Volyn Group, basic tuffs, and erosion products of volcanic rocks are virtually similar and close to the average Au content in igneous basic rocks. Lower Vendian volcanic rocks and Upper Vendian volcanic ashes underwent similar post-sedimentary transformations. However, the volcanic rocks lack any significant correlation between $\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+})$, $\text{SiO}_2/\text{Al}_2\text{O}_3$, and Au. This can be related to different modes of Au occurrence in effusive and pyroclastic rocks. In igneous rocks, Au can occur as

compounds with other noble metals and as native form. Gold can also replace other elements in the crystal lattice of the rock-forming and/or accessory minerals (Boyle, 1979). In the tephra, primary gold can most probably occur as Au-rich halogenides in the volcanic ash. Maximal Au concentrations are recorded in the dacitic and rhyolitic tephra, in which the morphology of ash particles suggests their high sorption capacity (Melekestsev et al., 1991). Sorbed elements in the volcanic ashes can probably be redistributed in the sedimentary sequence at early stages of the postsedimentary transformation of the pyroclastic material.

CONCLUSIONS

Gold was redistributed during postsedimentary transformations of the rhyolitic tephra delivered to Late Precambrian sedimentation basins of the East European Platform and South China Platform. At the oxidizing stage of diagenesis, Au was accumulated together with iron oxides and hydroxides produced by the dissolution of volcanic glass and Fe-bearing minerals. At the subsequent stages of the transformation of pyroclastic material and the formation of clay minerals, Au was probably removed from the volcanic ash units. Comparison of the Au content in the present-day dacitic and rhyolitic tephra, on the one hand, and Late Precambrian volcanic ashes, on the other hand, makes it possible to estimate the amount of Au removed from ashes together with the water-soluble compounds. Let us consider 1 km³ of the acid tephra material with the Au content of 10 ng/g. If pelitization of this material produces tuffs with smectite (30 wt %), kaolinite (15 wt %), and Au (average content 2 ng/g), the amount of Au transported to the sedimentary sequence will be ~20 t. Taking the volume of tephra in the Vendian sedimentary cover of the East European Platform into consideration, the minimal amount of Au delivered to the sedimentary sequence together with the ash material is estimated at ~10⁵ t. Volcanic ashes occupy a sufficiently narrow stratigraphic interval in the Vendian section and they are used as the regional lithological marker. Hence, the amount of Au indicated above was delivered to the sedimentary sequence in a relatively short period (probably, 100n ka). Organic matter (Varshal et al., 2000) and/or sedimentary phosphates (Yasyrev, 1971; Turlychkin and Gorenkov, 1999) could serve as collectors of the mobilized Au. These materials play a crucial role as geochemical barriers for the precipitation of Au.

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