Prospects of biogeochemical method implementation in identifying rhenium anomalies

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Abstract. This study was aimed at assessment of Re migration and its accumulation by organisms within the Zhireken ore field and neighboring territories (Eastern Transbaikalia). To measure the concentrations of Re in biogeochemical objects, the ISP-mass spectrometry method and solutions with known metal content were used. Other metal were determined by AAS. The hyperaccumulation of rhenium by plants growing around Zhireken quarry (up to 60 mg/kg) at a background level of 5-10 ng/g of dry matter was established. The Re content in the reservoir of the bottom part of the quarry (74 µg/l) and the duct (63 µg/l) exceeds the background concentrations by 1,000-5,000 times. The coefficient of water migration Re in the ore anomaly reaches 914 units, which indicates its high migration ability. Re concentrations in soils and ground correlate with Mo, Cu and Fe ones. In plants, this relationship is not established. The Re hyperaccumulation by plants is the basis for the development of technologies for extracting metal from ore materials and reconnaissance of rhenium anomalies.

1. Introduction
Rhenium is one of the rarest and most dispersed elements in the earth's crust. Its clarke is 7.10⁻⁸ % - 7 µg / kg, and the average content in the upper part of the continental crust is 2.7 µg / kg [1]. It is present in amounts higher than clarke in copper-molybdenum sulfide ores, uranium raw materials and bituminous rocks. Being one of the few elements of strategic importance, its production in the world lags behind the needs of industry. Taking into consideration the unique physical and chemical properties of rhenium, which determine its high need in modern technology, as well as lack of the own deposits and low content in the earth's crust, search and development of rhenium raw materials resources appears to be an important and timely task.

Rhenium hyperconcentration by plants was first established by L.V. Borisova and colleagues [2, 3]. When determining the rhenium content in waters, soils and plants of W-Mo and Mo-Cu ore occurrences in the North Caucasus and East Transbaikalia, selective accumulation of rhenium by plants was discovered, especially with its increased content in soil and sub-soil, as well as in high soil moisture. The most interesting results were obtained carrying out a selective analysis of plants examined at one of the sections of the Zhireken quarry. Rhenium maximum concentrations were found in a specie of astragalus (Astragalus adsurgens Pall.) with 1.41 mg/kg dry weight, while other plants contained rhenium in the amount ranging from 0.7 to 4 ng/kg with a background of 5-15 ng/g. At the same time, rhenium was found along with molybdenum and copper in cow milk, buttermilk, as well as in fractions of the xanthine oxidase enzyme [4].
This report is devoted to a further evaluation of the content of rhenium, ore and related chemical elements in the soil-vegetable complex within the Zhireken mining and concentrating plant (MCP).

It should be noted that the Zhireken molybdenum deposit was discovered in 1958 in the Chernyshevsky district of the Transbaikal Territory. Its ores contain (\%) - 0.1, Cu - 0.086 (0.004–0.51), Pb - 0.0174, Zn - 0.02, Sb - 0.002, Bi - 0.001; Re - 82 g/t, Se - 87 g/t, Te - 16 g/t. The main industrial ores are concentrated in kali shpatized granites [5].

2. Methods
Taking into consideration high degree of rhenium accumulation by plants, more detailed biogeochemical testing of the territory located near the edge of the Zhireken quarry was carried out in 2014. Test sites (in the northern, northeastern, western and southern parts) appeared to be the storage sites for waste or natural pebble material covered with a thin layer of soil overgrown with birch, larch, aspen, rhododendron and occasionally with cereals and different types of sagebrush. Macromycetes (mushrooms), lichens and epiphytic mosses were also found there. Samples were taken not only of soils and plants, stone material, but also of water that filled the bottom of the quarry.

Elemental analysis of soils, plants, and water samples was carried out using the inductively coupled plasma mass spectrometer (7500 CE model produced by Aglient Technologies, USA). Measurements were taken in a scanning mode and quantitatively using the standard rhenium solutions. Soil samples were mineralized with a mixture of perchloric, nitric, and hydrofluoric acids, and plants were mineralized with nitric and perchloric acids.

Copper, molybdenum, iron, lead and manganese content in most samples was determined by the atomic absorption technique according to the standard methods. Concentrations of Cu, Fe and Mn were measured in a flame version using the AAS-2A instrument, and molybdenum and lead concentrations were measured by electrothermal atomization technique on the AAS-Z ETA instrument with a Zeeman background corrector. Accuracy and reproducibility of the techniques were controlled using the analysis of standard samples of soils, plants and hair.

It was established that plants in the western part of the quarry contain practically background concentrations of Cu, Fe and Pb. The Mo content is almost 2 times higher than its background concentration and constitutes 0.63-2.20 mg/kg.

As far as Re is concerned, plants accumulate it up to 1.74-4.20 mg/kg of dry matter at a concentration of 0.098 mg/kg in soil. This is by 105 times higher than the background values (10-17 ng/kg), which indicates the presence of the Re mobile forms in soil and subsoil in appreciable amounts.

3. Results and discussion
Research results are presented in table 1.

Plants in the southern part of the quarry more intensively accumulate Re and Mo, but the level of other trace elements content (Cu, Fe, Pb) is not critical.

Mo and, in particular, Re accumulations are mostly expressed in the quarry northern and northeastern sections. Mo in plants there is found in up to 5.6-6.7 mg/kg amounts, Cu – in up to 150-200 mg/kg and Pb - in up to 66-160 mg/kg. It should be noted that Re concentrations in plants increase in up to 10-60 mg/kg of dry matter. Maximum concentrations of Re are characteristic for cowberry leaves (60 mg/kg), birch leaves (26 mg/kg) and larch needles (8.4 mg/kg).

As far as macromycetes are concerned, they, as a rule, concentrate Cu, and lichens and epiphytic moss concentrate Mo, Cu and Pb, which is consistent with the published data [Ermakov et al., 2018].

It should be mentioned that all quarry sections are characterized by a very high Mn content in plants. In general, Mo concentrations in plants are not high. They are noticeably lower than the levels thereof in plants at the Tyrmnauz and Bugdain ore occurrences’ landscapes [Danilova et al., 2015].
Table 1. Metal content in biogeochemical objects in the area of Zhireken quarry (data on dry weight).

| Sample                                      | Mo  | Cu  | Fe    | Mn   | Pb   | Re   |
|---------------------------------------------|-----|-----|-------|------|------|------|
| Grey forest soil, A0-10 (Haplic Greyzems)   | 0.24| 37.3| 13800 | 1152 | 64.8 | 0.098|
| Gray forest soil, A0-5 (Haplic Greyzems)   | 5.31| 556.3| 18800 | 1656 | 110.4| 0.174|
| Gray forest soil (Haplic Greyzems) low-power on the pebble bed rock, A0-8 | 1.09| 59.4| 13800 | 2876 | 324  | 0.234|
| Light-grey forest soil (Eutric Podzoluvisols) on the gravel | 5.93| 1513.8| 14600 | 408  | 403.2| 0.132|
| Xerocomus subtomentosus                     | 3.23| 34.7| 84    | 12   | 2.1  | 0.054|
| Betula middendorffii (leaves)              | 2.10| 10.3| 123   | 2880 | 5.7  | 9.00 |
| Vaccinium vitis-idaea (leaves)             | 1.69| 3.7 | 63    | 2787 | 2.7  | 60.00|
| Cladonia arbuscula                         | 5.20| 103.6| 1200  | 15   | 42.9 | 0.09 |
| Rhododendron dauricum                      | 2.70| 7.0 | 126   | 2666 | 4.5  | 0.09 |
| Pleurozium schreberi                       | 5.80| 150.0| 5010  | 1597 | 160.2| 10.90|
| Betula middendorffii (leaves)              | 0.80| 5.3 | 108   | 2620 | 1.5  | 26.10|
| Larix sibirica (needles of larch)           | 6.73| 42.7| 2088  | 2811 | 66.3 | 1.95 |
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Re concentration in the plant cuts is presented in the figure 1.
Figure 1. Rhenium concentration alteration in the plant cuts depending on its content in the soils of Zhireken mining and concentrating plant.

It is easy to notice that almost all samples are characterized by hyperaccumulation of Re. This indicates high mobility of Re compounds in the soil–vegetable complex, which is consistent with the Re high level in the waters of Zhireken MCP.

Thus, rhenium concentration was 74 μg/l in water of the reservoir formed at the bottom of the quarry, which is by 1,000-5,000 times higher than the background. For example, main water in Moscow contains Re in 3-5 ng/l.

If we take into account the Re content in soil (granite fragments, primarily) in the amount of 0.234 mg/kg, then the Re water migration coefficient calculated using the A.I. Perelman formula [1989] would be equal to 914. In samples of water taken from a channel flowing 100 m from the quarry in front of the tailing dump, rhenium concentration reaches 63 μg/l, and in the Alenur river near the village of Zhireken - 0.5 μg/l. Thus, Re is found in the 1st group of the most intensive migrants according to the A.I. Perelman classification.

Paired correlation coefficients between trace elements concentrations in soil-subsoils and in plant cuts are of interest. According to table 2, significant positive relationship in soils is observed in the Mo-Re pair (r = +0.598) and in the Mo-Cu pair (r = +0.908), i.e. in the main ore elements. It is expressed to a lesser extent in the Cu – Re, Cu – Pb and Pb – Re pairs. In this case, negative correlation is observed in the Fe – Re, Mn – Mo and Fe – Mo pairs.

Positive correlation was found in the analysis of plants in the Mo-Cu (r = +0.500), Mo-Pb (r = +0.502), Fe-Mo (r = +0.520) and Cu-Pb (r = +0.813) pairs. Weak negative relationship is manifested in the Mn-Mo pair (r = - 0.427). No significant relationship was found in the remaining pairs of trace elements.

It should be noted that any relationship between Mo and Re concentrations in plants is missing. Apparently, organisms sharply alter direction of the chemical elements’ flows, which is connected to the features of their root system, physiology of mineral substances absorption through the root membranes and metabolic role played by trace elements.

Table 2. Correlation coefficients between chemical elements concentration in soil-subsoils and in plants (Zhireken ore quarry).

| Pair of chemical elements | Correlation coefficient (r) | Soil-subsoils | Plants |
|--------------------------|-----------------------------|---------------|-------|
| Mo-Re                    | +0.598                      | -0.096        |       |
| Cu-Re                    | +0.400                      | -0.061        |       |
| Fe-Re                    | -0.575                      | -0.065        |       |
| Mn-Re                    | +0.274                      | -0.065        |       |
4. Conclusion

Thus, discrete distribution of rhenium is observed in the biosphere. The element tends to the Mo-Cu ore occurrences and intensively migrates with water and soil solutions in the oxidation zone being accumulated in plants. The latter significantly alters direction of the local biogeochemical cycles. The data obtained are the basis for developing rhenium phytoextraction from various materials (dumps, ores, etc.). Tyrnyauz and Zhireken ore fields are the most promising areas in this respect in Russia.

References

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