Mineralogical and geochemical features of human body ash residue of spatially-localized technogenic system (Norilsk city)

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Abstract. The paper presents the information on the element and mineral composition of the human body ash residue of Norilsk residents. The data are obtained by such methods as X-ray analysis, inductively coupled plasma mass spectrometry, and electron microscopy. This research has identified the content of 47 elements, 17 of which have their own mineral phases. Besides, the estimation of average content of chemical elements in terms of sex and correlation analysis of the data was conducted in this research. The final results indicate the influence of Norilsk industry on the element and mineral composition of ash residue. For example, the accumulation of such elements as Zr, Al, Ca, Y, some rare earth, and radioactive elements has been observed in the human body ash residue of Norilsk residents. The presence of Ag, Au, Pt microphases and numerous compounds of Cu, Ni etc. was detected among all mineral phases.

1. Introduction

Nowadays, study in element and mineral composition of human body is one of the priorities in modern geochemistry, medical geology and ecology. To develop these scientific areas, the Department of Geoecology and Geochemistry of Tomsk Polytechnic University is studying such material as human body ash residue (HBAR), which has been sampled in different Russian cities (Novosibirsk, Novokuznetsk, Yekaterinburg, St. Petersburg, and Rostov-on-Don). A long-term study of this material shows that the human body ash residue of every studied city has specific geochemical features reflected in high or low accumulation of certain chemical elements [1, 2].

In previous research of HBAR samples from the cities mentioned above it was required to take into account multifactorial industrial impact. In fact, there are several industrial engineering, chemical and metallurgical enterprises in large cities. Hence, it is interesting to study samples of human body ash residue of Norilsk residents.

Norilsk city is one of the Russian and world's most polluted cities. However, in contrast to other areas, the industry of Norilsk is presented not by the complex of different plants, but by the monoproduction, forming the technogenesis of the environment. Thus, this city represents spatially-localized technogenic system, as the local industrial enterprise uses ore, sand and coal, which are extracted in vicinity of Norilsk. Besides, the city is located in the north of the country, far from other industrial centres, which excludes the additional contribution of pollutants from other territories. One of the world's largest enterprises, which extracts, enriches and processes Cu-Ni ores, is the only industrial plant in Norilsk. The plant uses ores of Norilsk deposit, which are rich in such elements as Cu, Ni, Co, Se, Ag, Au, Cd, Te, Re, Bi, Zn, Pb, Cr, and Sn, as well as elements of the platinum group

(Ru, Rh, Pd, Ir, Pt etc). The main products of the local industry are Cu, Ni, Co, Se, S, and platinum concentrates.

Medical research of Norilsk and the surrounding area residents has shown that diseases of the respiratory and digestive systems prevail in the morbidity rate. It was also noted in the literature, that local residents have the elevated content of Cu and Ni in the blood plasma comparing with the control group [3].

2. Materials and methods

The material of the research is 22 samples of the human body ash residue, which were sampled in the Norilsk crematorium from the material unclaimed by the relatives with the official permission of administration. The ratio of men to women in the Norilsk samples is 13:9. The results of element composition of Norilsk residents' HBAR samples were compared with the previous results from the other cities (Novosibirsk, Novokuznetsk, Yekaterinburg, St. Petersburg, and Rostov-on-Don). Since ash residue of human body is a material burnt at high temperature (900-1100°C), it leads to the loss of some volatile elements. Therefore, only the comparative analysis of element content from different cities was performed.

Mass spectrometry with inductively coupled plasma was used to study the element content of HBAR. This method includes dissolution of sample at the preparatory stage. Thus, it is impossible to extract some elements thoroughly, that may lead to errors in determination of concentrations. Electron microscopy and X-ray analysis were used to study the mineralogical content of human body ash residue of Norilsk residents. Scanning electron microscope Hitachi S -3400N was applied to determine microphases, which content was studied by microanalysis (detection limit is 0.1-0.2%). The identification of mineral phases was conducted by Bruker D2 Phaser diffractometer (the detection limit is 0.1-0.5%).

3. Geochemical features of human body ash residue of Norilsk residents

The content of 47 chemical elements was detected in the human body ash residue of Norilsk residents using ICP-ms. Based on these results, the coefficients of concentration (relative to the average values of 6 cities) were calculated to determine the geochemical features of HBAR of this city (figure 1). The diagram shows that the ash residue of Norilsk residents is characterized by high accumulation of such elements as Al, Ca, Y, Zr, Ce, Pr, Nd, Cd, Tb, Dy, Ho, Yb, Lu, Th, and U in comparison with other cities.

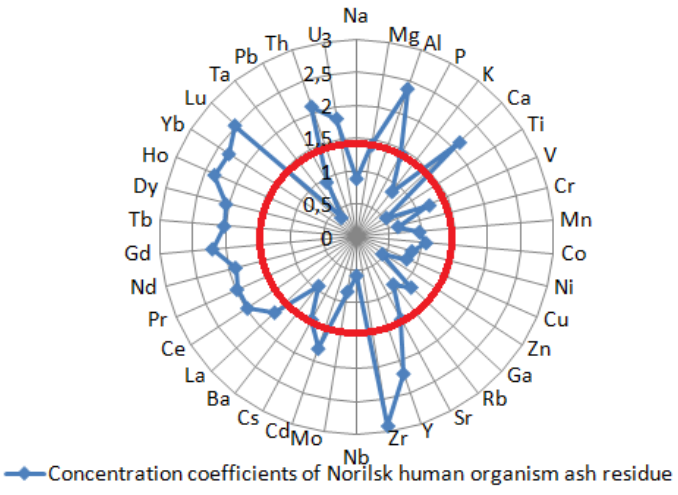

Figure 1. Concentration coefficients of human organism ash residue, Norilskcity.

The specificity of element accumulation is unlikely to reflect the content of Cu-Ni ores which are used in local industry, because the spectrum of concentrated elements in ash residue of Norilsk residents differs much from those concentrated in the ore.

The comparison of different cities accumulation specifics revealed the similarity in elements accumulation between ash residue of 2 Russian cities – Norilsk and Novokuznetsk. The simplest Jaccard similarity coefficient showed the 25% similarity in the accumulation of these cities that is likely to demonstrate the metallurgical features of the largest Russian industrial centres of ferrous and non-ferrous metallurgy.

The comparative analysis of element accumulation in terms of sex showed that most elements concentrate equally in the male and female organism of Norilsk residents (figure 2). However, such elements as Zr, Rb, Y, Sn, Dy, Ho, Tm, Yb, Lu, Hf, Th, U have a tendency to accumulate in male organism; but Mo, Gd, Pb, Bi tend to concentrate in female organism.

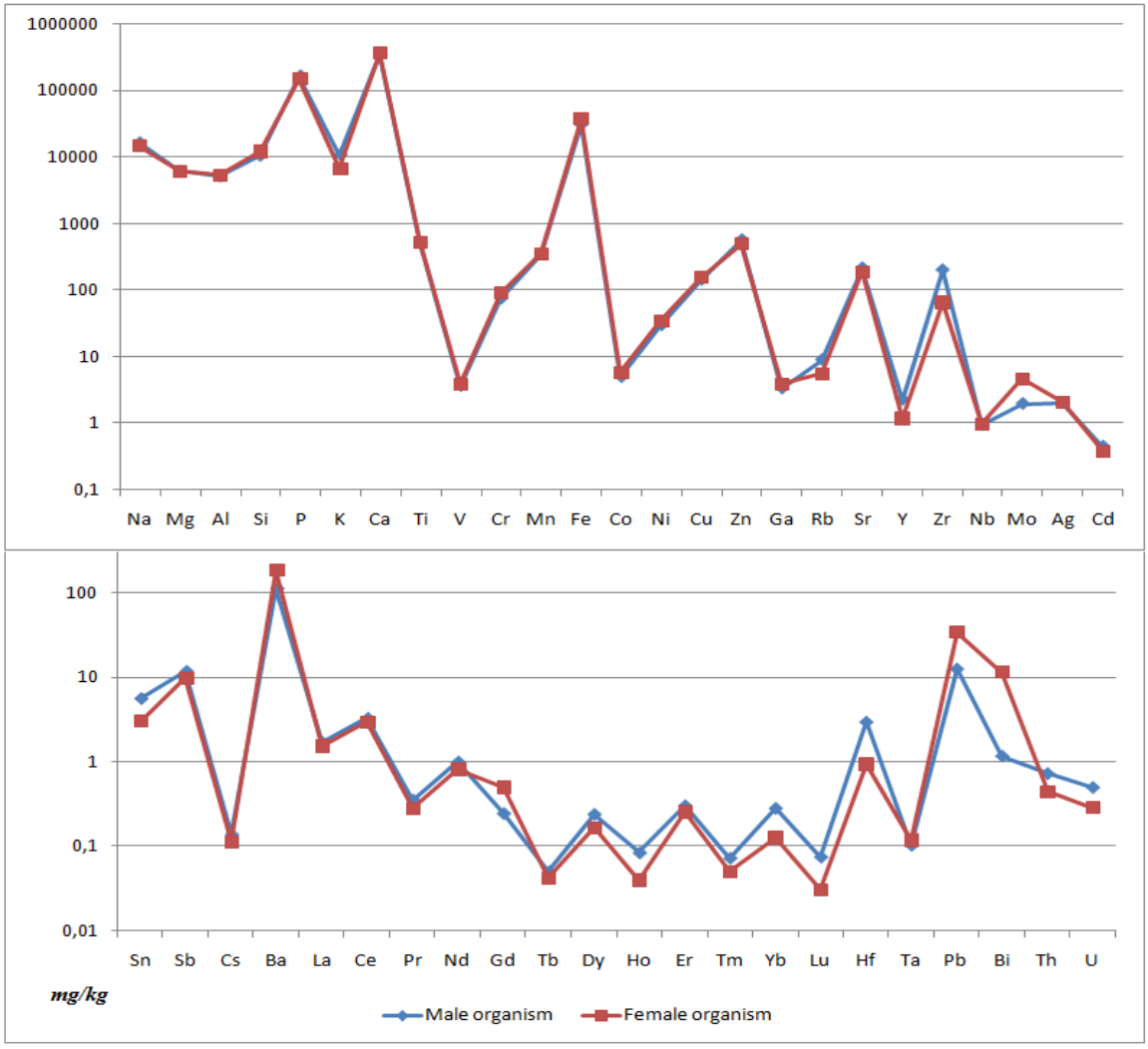

Figure 2. Estimation of the average content of elements in the human body ash residue of Norilsk residents in terms of sex.

Correlation analysis showed close relations of many elements. The highest positive pair correlation coefficient (r = 0.99) belongs to the pair of Zr-Hf (critical coefficient r = 0.404, p = 0.05). Besides, 19 pairs are characterised by significant relations with correlation coefficient from 0.90 to 0.98; these include: Y-Tb, Y-Dy, Zr- Tm, Zr-Yb, Zr-Lu, Y-U, Zr-Th, U-Th, Nd-Pr, Dy-Yb, Dy-U, Tm-Yb, Tm-Lu, Tm-Hf, Yb-Lu, Yb-Hf, Yb-Th, Hf-Lu and Hf-Th. The strongest negative correlation coefficient ($\bar{r}$ = 0.95) belongs to the pair Ca-Nd. Wherein, such element as Ca is associated with almost all elements with negative relations except P.

Results of cluster analysis (Figure 3) allowed determining several groups of elements, which are likely to have different source and mechanism of accumulation. The pair Ca-P was chosen as significant relation, because this is one of the strongest relations in a human body, which constitutes the main mineral of human bones –hydroxyapatite. Thus, the following groups of tightly related elements in the human body ash residue of Norilsk residents may be distinguished:

- Ho, Yb, U, Hf, Zr;
- Nd, Pr, La, Ce, Dy, Th, Y;
- Ta, Ga, Fe;
- Sn, Cr, Mn, Ti;
- Cu, V, Nb, Si, Al;
- Rb, K, Sb, Co, Mg;
- Zn, Ba, Na;
- Pb, Mo.

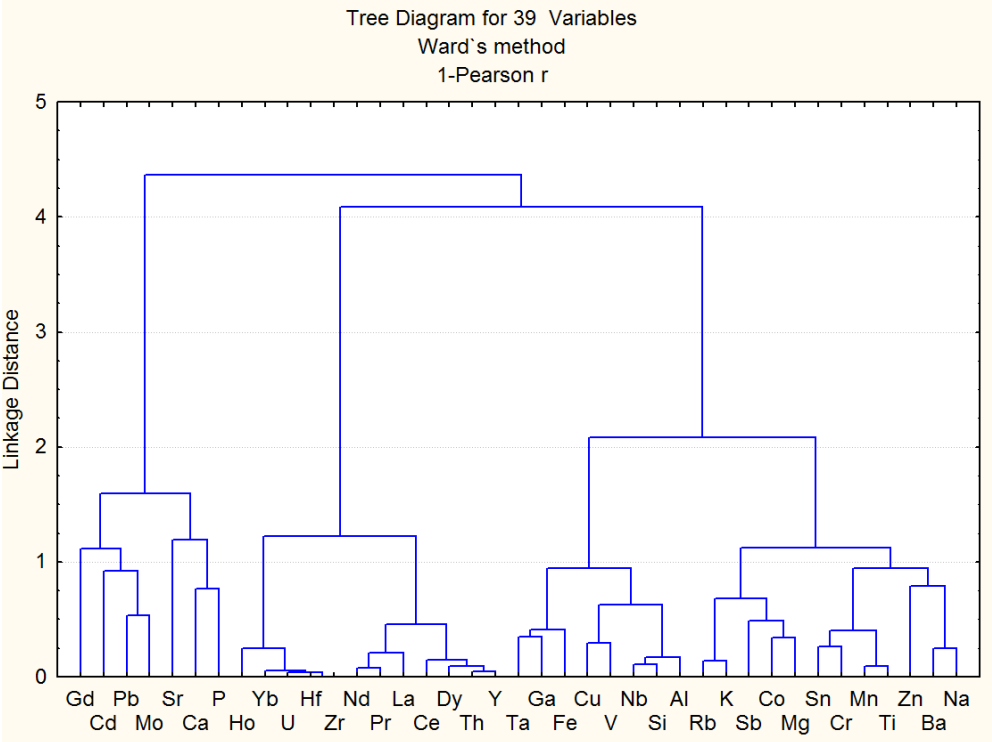

Figure 3. The diagram of cluster analysis.

4. Mineralogical features of the human organism ash residue of Norilsk residents

The previous mineralogical research of the ash residue samples from different Russian cities has shown that material consists of more than 99.5% of hydroxyapatite ($Ca_5(PO_4)_3(OH)$), that is the main mineral of bone tissue. The X-ray analysis of HBAR samples from Norilsk identified not only hydroxyapatite in the mineral content, but also hydroxyapatite with the significant impurity of the silicate ($Ca_5(PO_4)_3(SiO_4)(OH)$). Electron microscopy analysis of the Norilsk samples also showed the impurities of Na, K, Mg, Al, S, Si, and Cl in the content of hydroxyapatite. Besides, the aggregates of hydroxyapatite were found in the samples, in which Na, K and Mg replace Ca more than 70-90%.

Microphases of different composition with less than 0.5% of the sample volume were also found in the studied material. In general, 27 mineral phases of different composition were found in the human

body ash residue of Norilsk residents including mineral phases of Cu, Ni, and Pt, that are likely to reflect the impact of local industry. Thus, the specificity of mineralogical content of Norilsk material is a large number of mineral phases characterized by a complex composition which is not typical for the samples from other cities. Some micromineral phases of Zn, Cu, Zr, and Pt are shown in figures 4, 5, 6, and 7.

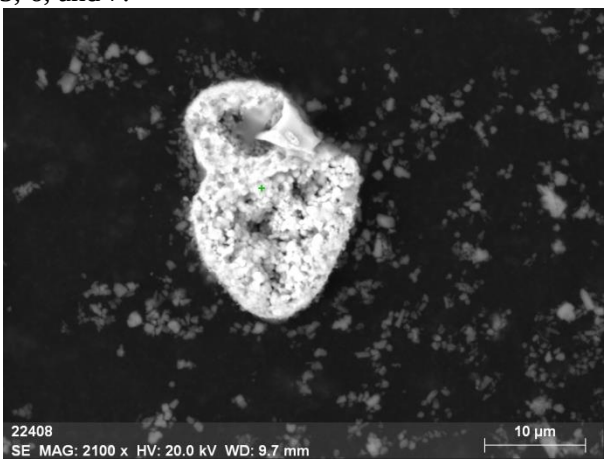

Figure 4. Micromineral phase of Zn in the HOAR of Norilsk residents.

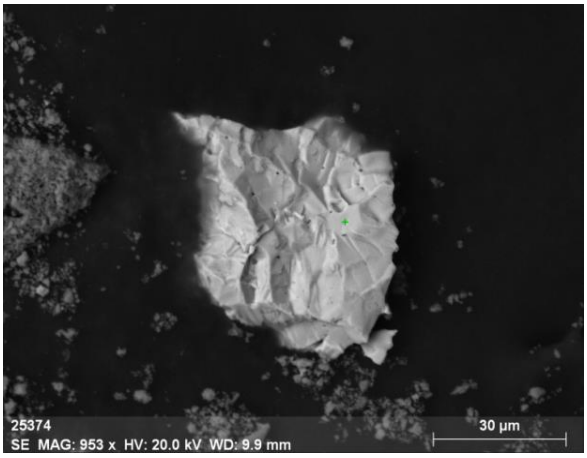

Figure 5. Micromineral phase of Cu in the HOAR of Norilsk residents.

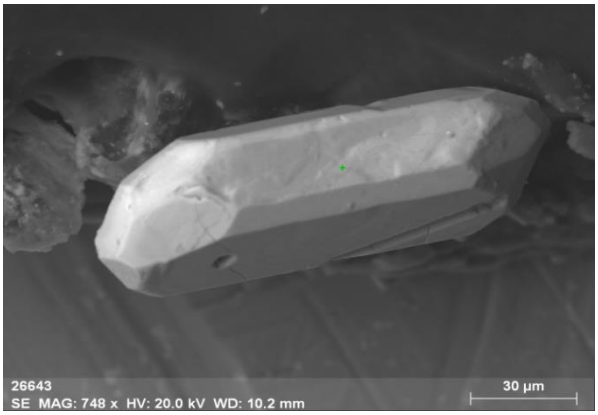

Figure 6. Micromineral phase of zircon in the HOAR of Norilsk residents.

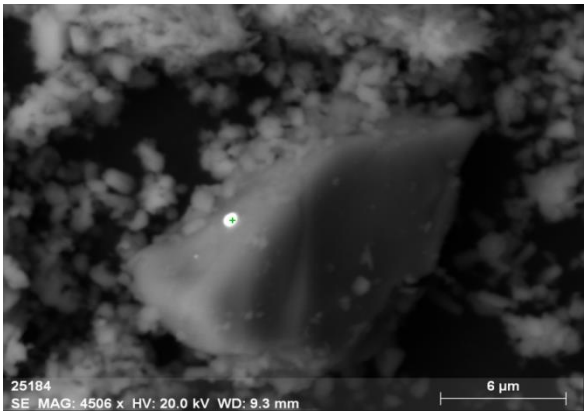

Figure 7. Micromineral phase of Pt in the hydroxyapatite aggregate in the HOAR of Norilsk residents.

5. Conclusion

The content of 47 chemical elements was studied in the human body ash residue of Norilsk residents, as well as modes of occurrence were determined for some of them. Based on the results of the research, some conclusions about the specificity of the element accumulation and distribution in the HBAR of Norilsk residents can be made. Probably, the spectrum of accumulated elements (Al, Ca, Y, Zr, Ce, Pr, Nd, Cd, Tb, Dy, Ho, Yb, Lu, Th and U) and mineral phases (Cu, Pt, Ceetc) indicate two main sources of elements: ore used in the local industry and emissions of the industrial plant. Besides, the accumulation of radioactive and rare-earth elements and the presence of such minerals as zircon and monazite indicate the possible use of zircon-ilmenite sands or zirconium crucibles in the production. Nevertheless, the source of the studied elements in the organisms of Norilsk residents has not been determined yet and requires additional study of the local water and industrial materials.

References

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