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## ASSESSMENT OF REFRACTORY GOLD-BEARING ORES BASED OF INTERPRETATION OF THERMAL ANALYSIS DATA

Tatyana N. ALEKSANDROVA<sup>1</sup>, Gerhard HEIDE<sup>2</sup>, Anastasiya V. AFANASOVA<sup>1</sup>

<sup>1</sup> Saint-Petersburg Mining University, Saint-Petersburg, Russia

<sup>2</sup> Freiberg Mining Academy, Freiberg, Germany

The article presents the results of a study on the possibility to assess refractory gold-bearing ores using thermal analysis data. It studies the flotation concentrates obtained during the enrichment of double refractory sulfide gold-bearing ores. This type of ore is complicated by the fine impregnation of gold in sulphide minerals and the presence of sorption-active scattered carbonaceous matter, which is in close association with sulphides. The results of thermogravimetric and mass spectrometric studies of refractory gold-bearing ores are presented.

The obtained fragments for kerogen  $\text{CH}_3^+$  ( $m/z = 15$ ),  $\text{C}_2\text{H}_5^+$  ( $m/z = 29$ ) and  $\text{C}_3\text{H}_7^+$  ( $m/z = 43$ ) indicate the presence of various types of carbonaceous matter in the studied samples. It is justified that the degree of sorption activity of carbonaceous matter depends on the presence of kerogen and bitumen in the ore. High sorption activity of scattered carbonaceous material significantly affects the processing technology of ores and concentrates, both flotation and pyro- and hydrometallurgical methods.

Thermogravimetric and mass spectroscopic analyzes can be used to determine the degree of preg-robbing of refractory gold-bearing ores. The obtained results predetermine the direction of creating new methods and technologies in the field of decarburization of refractory gold-bearing ores in the integrated development of solid minerals in the mining regions of Russia.

**Key words:** black slates; pyrolysis; kerogen; bitumen; gold ore; sulphides; high sorption activity; carbon matter

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**Introduction.** Currently due to the depletion of the mineral and raw material base of gold ores, the share of «double refractory» ores is increasing in Russia and all around the world. Large gold deposits of black shale and Carlin types (Natalkinskoe, Olimpiadinskoe, Mayskoye, Bakyrchik, etc.) belong to the «double refractory» ores. The high prospectivity of carbonaceous rocks as a source of gold and platinoids is based on two factors: the high occurrence of black shale strata in many regions of the world and a large amount of analytical data on the high content of gold and platinoids in them [1]. The processing of this type of ore is complicated by the fine impregnation of noble metals into sulphide minerals and the presence of active dispersed carbonaceous matter. The main method of enrichment of this type of ore is flotation, thus the intensification of this process is currently extremely relevant [11, 16, 18].

High sorption activity of carbonaceous matter has a significant impact on the processing technology of ores and concentrates using both flotation and pyro- and hydrometallurgical methods [13]. During geological time, not all organic carbon of sedimentary rocks turned into hydrocarbons, which form the basis of oil and gas [6]. Organic carbon can be represented by kerogen – organic matter, insoluble in non-polar organic solvents and in non-oxidizing mineral acids, and by bitumen – soluble organic matter. Gold and gold-silver deposits, in which the organic component is mainly represented by carbonaceous matter, include black shales, ores and rocks of the Carlin type [2].

The degree of sorption activity depends on the type of carbonaceous matter. In [9], it was experimentally proved that humic acid, when interacting with the cyanide complex, reduces gold recovery from 95 to 21 %. The experiment was conducted on ore that does not contain carbonaceous matter. In [5, 20], on the contrary, it was shown that the carbonaceous component of the Witwatersrand deposit (South Africa) is long-chain hydrocarbons that do not interact with the cyanide complex, and organic acids like humic, which can form complexes with gold.

The aim of the study is to obtain new data on the composition of organic matter using thermogravimetric and mass spectrometric analyzes of samples of gold-bearing refractory ores to justify rational processing technologies.

**Materials and methods.** The Bakyrchik deposit is in northeastern Kazakhstan and ranks second in terms of gold reserves. The average gold grade in the ore is 7.7 g/t. The ores of this deposit are classified as double refractory carbon sulfide ores.

Based on the analysis of the data presented in the works devoted to the study of the mineral composition of ores of the Bakyrchik deposit [4, 7, 10, 14], the following conclusions were made:

- distribution of carbonaceous matter in major ore minerals has the pattern of impregnation;
- main carriers and concentrators of gold are pyrite and arsenopyrite.

The mineral composition of the ores of the Bakyrchik deposit [8] is as follows:

Mineral	Content, %	Mineral	Content, %
Quartz.....	52.65	Pyrite.....	2.28
Mica.....	3.47	Arsenopyrite.....	1.81
Carbonates.....	3.45	Barite, chalcopyrite, sphalerite, fahl ore, antimonite, pyrrhotite, galena.....	0.11
Clay sericite material.....	23.03		
Carbonaceous matter.....	14.04		

The objects of research were concentrates obtained after flotation of ore from the Bakyrchik deposit. The results of chemical analysis of the samples are presented in the table.

Thermal analysis (TA) was used to study the organic component of the samples. TA is a complex of methods in which the physical and chemical properties of substance are investigated depending on temperature [12]. If the temperature effect on the sample is constant throughout the experiment, then it is an isothermal TA. The most widely used thermogravimetric analysis (TGA), in which there is a continuous recording of mass changes in the sample during heating. However, during decomposition there are such products that are difficult to interpret using TGA. Two main types of thermogravimetric analysis are distinguished: statistical – the change in sample mass is recorded at a constant temperature, and dynamic – the change in sample mass is recorded with a change in temperature according to a given law [22].

#### Results of chemical analysis of flotation concentrates

Concentrate	Au, g/t	S <sub>total</sub> , %	S <sub>sulph</sub> , %	Fe <sub>total</sub> , %	As, %	Sb, %	C <sub>total</sub> , %	C <sub>org</sub> , %
N 1	67.9	11.6	11.3	13.2	5.84	0.204	4.21	3.97
N 2	74.10	20.10	19.90	17.60	7.53	0.56	4.92	4.50

The analysis was performed using the SKIMMER system with a QMS403/5 quadrupole mass spectrograph, combined with the STA 409CD – DEGAS furnace (DEGAS) [21, 23]. Diagram of the device is shown in Fig. 1.

**Results and discussion.** *Thermogravimetric and mass spectrometric study of flotation concentrate N 1.*

Figure 2 presents the results of a thermogravimetric study of sample N 1 in an air atmosphere with a heating step of 5 °C/min. The mass of the original sample is 9.138 mg. Figures 3 and 4 show the results of mass spectrometry studies of the sample. The TGA curve (in percent) shows the change

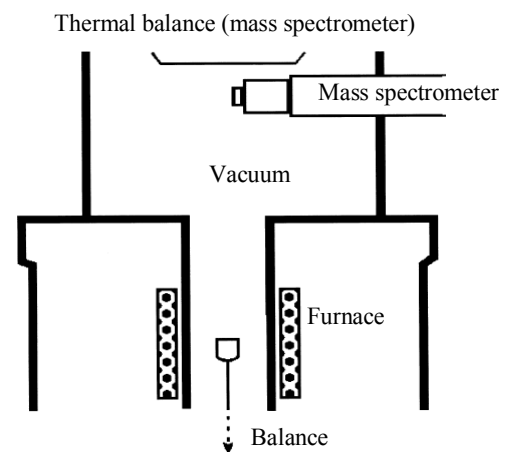


Fig. 1. Equipment for high vacuum degassing [25]

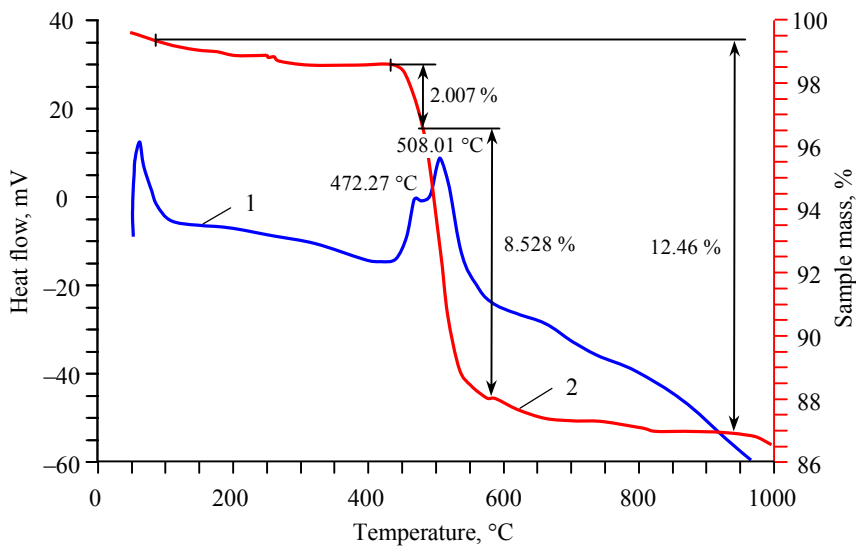


Fig.2. Thermogravimetric curves for sample N 1 at a heating rate of 5 °C/min  
1 – DSC; 2 – TGA

temperatures of 472.27 and 508.01 °C, respectively. This temperature range is accompanied by the release of significant amounts of thermal energy. The weight loss for the two intervals is 2.007 and 8.528 %, respectively. The total mass loss for sample N 1 is 12.46 %.

The record of  $C^+$  ( $m/z = 12$ ),  $O^+$  ( $m/z = 16$ ) and  $CO_2^+$  ( $m/z = 44$ ) fragments with three peaks within the temperature range of 400-650 °C may indicate the presence of carbonates in sample N 1. One peak was recorded at high temperatures (about 1100-1200 °C) for  $m/z = 12$ ; 28; 44 (Fig.3). This may be due to the oxidation of organic matter, which has not been subjected to pyrolysis at lower temperature ranges [23].

Figure 4 shows the registration of fragments typical for kerogen  $CH_3^+$  ( $m/z = 15$ ),  $C_2H_5^+$  ( $m/z = 29$ ) and  $C_3H_7^+$  ( $m/z = 43$ ). For sample N 1, two peaks were recorded for the fragments of methyl-, ethyl-, and propylions. One of the peaks is registered in the temperature range from 100 to 300 °C, which is typical for the pyrolysis of volatile free hydrocarbons (bitumen). The second peak is recorded in the temperature range between 300 and 600 °C, where pyrolysis of kerogen macromolecules takes place. Thus, it is possible to assume the presence in the sample N 1 of a soluble carbonaceous substance – bitumen, as well as a certain amount of an insoluble carbonaceous substance – kerogen [19].

*Thermogravimetric and mass spectrometric study of flotation concentrate N 2.* Figure 5 shows the results of thermogravimetric analysis of sample N 2 in air at a heating rate of 5 °C/min. The mass of the original sample is 13.448 mg. Figures 6 and 7 show the results of mass spectrometric study of sample N 2.

In the temperature range from 51 to 198 °C, the mass loss is due to the evaporation of external and hygroscopic moisture [15]. The maximum mass loss of the sample is observed at a temperature of 60.6 °C – the mass loss in this range is 1.9 %.

Similarly, like for sample N 1, at a temperature above 423 °C, intensive oxidation begins (see Fig.5). On the thermogravimetric curve, this process is characterized by three peaks at temperatures of 477.20; 504.31 and 525.26 °C, respectively. This temperature range is accompanied by the release of significant amounts of thermal energy. The energy release here is due to the oxidation reactions of a large amount of organic matter, presumably the carbon component. In the first interval, the weight loss is 5.159 %, which is 0.6938 mg. In the second interval, the mass loss is almost 2 times more: 8.812 % and 1.185 mg, respectively. In the temperature range of 515-595 °C, the mass loss is 3.935 %.

in sample mass; DSC curve (in millivolts) change in the enthalpy of the heat flow rate, the nature of the reaction – exo- or endothermic (see figure 2).

Mass loss in the temperature range of 51-451 °C is associated with evaporation of the internal and hygroscopic moisture. The maximum mass loss is observed at a temperature of 75.9 °C. The mass loss in this range is 1.1 %.

When samples are heated in air, intense oxidation begins at temperatures above 451 °C. On the thermogravimetric curve, this process is characterized by two peaks at tem-

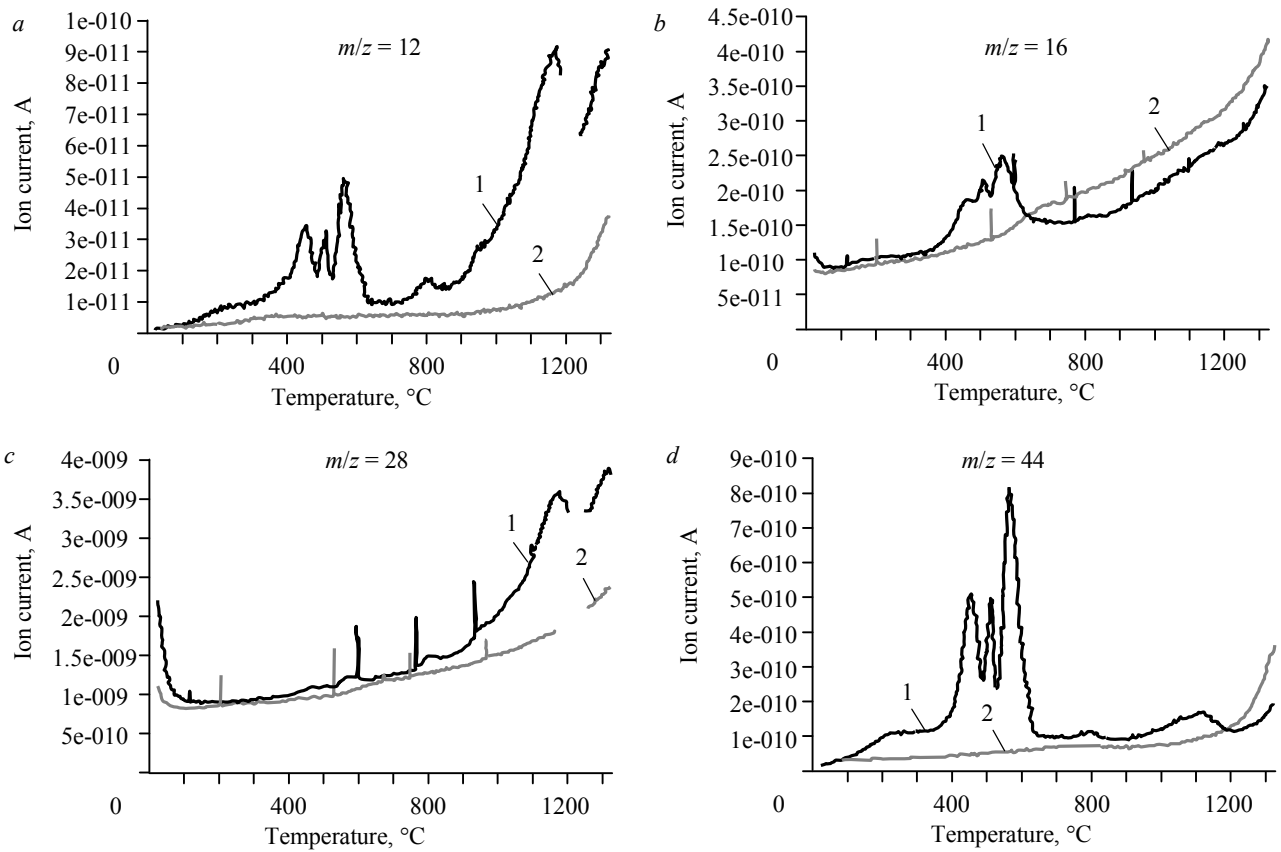


Fig.3. Records of  $C^+$  (a),  $O^+$  (b),  $CO^+$  (c),  $CO_2^+$  (d) of fragments for sample N 1  
1 – sample; 2 – empty measurement

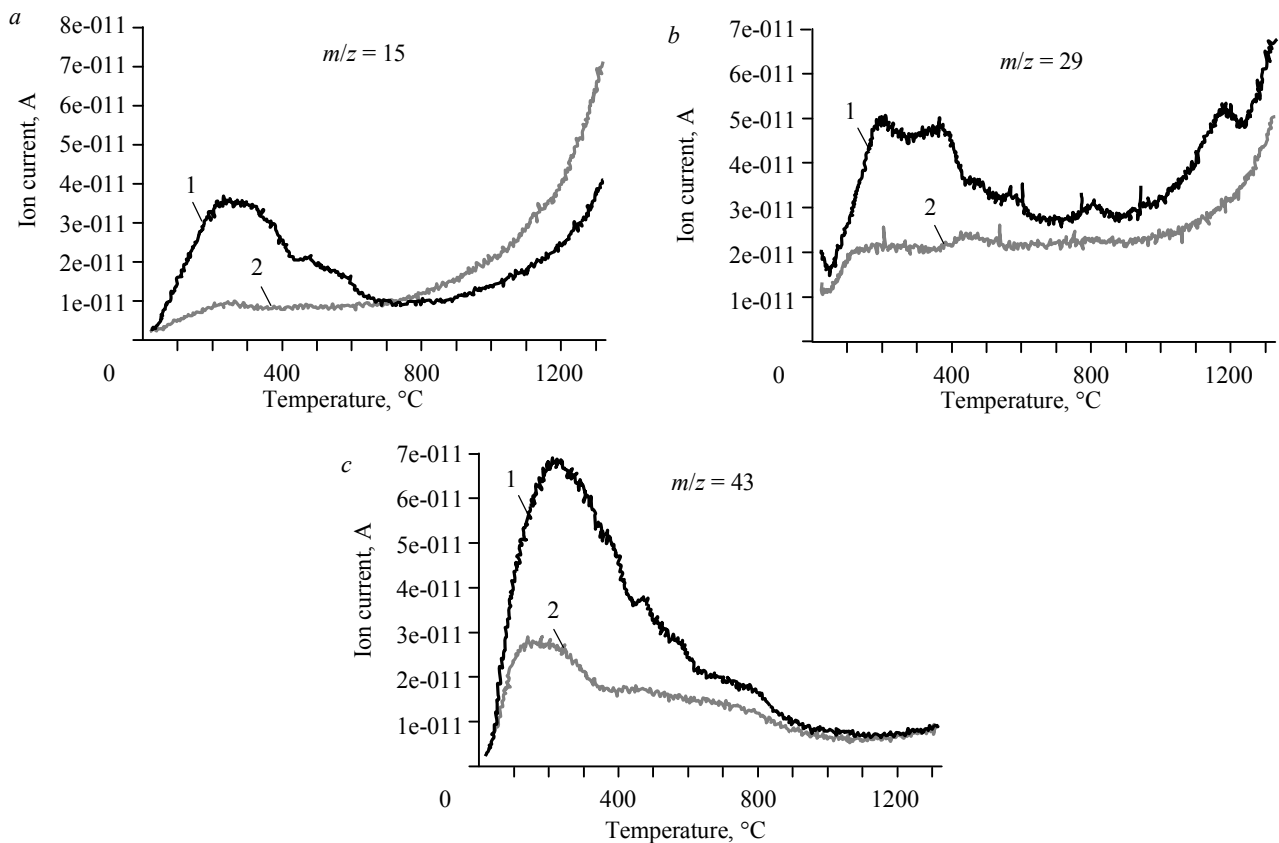


Fig.4. Records of  $CH_3^+$  (a),  $C_2H_5^+$  (b) and  $C_3H_7^+$  (c) of fragments for sample N 1  
1 – sample; 2 – empty measurement

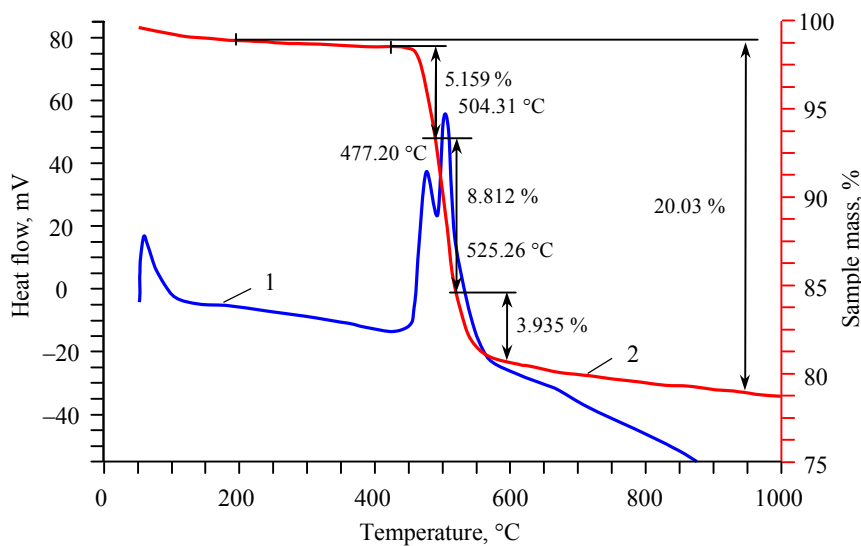


Fig.5. Thermogravimetric curves for sample N 2 at a heating rate of 5 °C/min  
1 – DSC; 2 – TGA

Comparison of figures 2 and 5 showed that the amount of the organic component in sample N 2 is about 2 times greater than in sample N 1.

Weight loss in the range of 595-998 °C is 1.7 %. The increase in energy is associated with the oxidation of sulfides and release of sulfur dioxide. Note that the amount of sulfur in sample N 2 is slightly higher than in sample N 1. This is also confirmed by chemical analysis data (see table).

The total mass loss for sample N 2 at a heating rate of 5 °C/min is 20.03 %.

From Fig.6 it can be seen that for sample N 2 a signal was registered – an ionic carbon (mass number  $m/z = 12$ ), which has two peaks at temperatures of 450 and 600 °C. Similar peaks were recorded for mass numbers  $m/z = 16$ ; 28 and 44. On the basis of the obtained data on the registered signals, it can be concluded that carbonates are present in sample N 2.

Figure 7 shows typical fragments for kerogen  $\text{CH}_3^+$  ( $m/z = 15$ ),  $\text{C}_2\text{H}_5^+$  ( $m/z = 29$ ) and  $\text{C}_3\text{H}_7^+$  ( $m/z = 43$ ). For sample N 2, three peaks were recorded at a temperature between 300 and 600 °C. Pyrolysis of kerogen macromolecules occurs in this range [24].

Sedimentary rocks usually contain organic matter in two different forms – finely dispersed macromolecular matter (kerogen, insoluble in common organic solvents) and free hydrocarbons (bitumen, soluble in common organic solvents) (Fig.8) [24]. Under temperature exposure, bitumen can become insoluble (asphaltene) [23].

The recovery of gold in sample N 1 was 46.4 % (high degree of preg-robbing), and for sample N 2 – 88.90 % (low degree of preg-robbing). The amount of organic carbon in both samples is almost the same (for sample N 1 – 4.21 %, for sample N 2 – 4.92 %), however, the difference in the extraction of gold is quite large. In both samples, the presence of an insoluble carbonaceous substance, kerogen, was recorded, whereas for sample N 1, the presence of a soluble carbon-containing substance, bitumen.

Refractory sulfide gold-bearing ores, for which, based on the interpretation of thermal analysis data, the presence of kerogen and bitumen were found, have low rates of gold recovery, while hard-ores, which contain only kerogen, have high rates. Consequently, thermogravimetric and mass spectroscopic analyzes can be effectively used to determine the refractory degree of gold-bearing ores.

**Conclusion.** The article presents the results of thermogravimetric and mass spectrometric studies of samples of flotation concentrates of «resistant» gold-bearing ores. In samples N 1 (a high degree of preg-robbing, gold extraction ratio – 46.4 %) and N 2 (a low degree of preg-robbing, gold extraction ratio – 88.9 %) the presence of insoluble carbonaceous substance – kerogen was registered, but also for sample N 1 the presence of a soluble carbon-containing substance, bitumen, was also recorded.

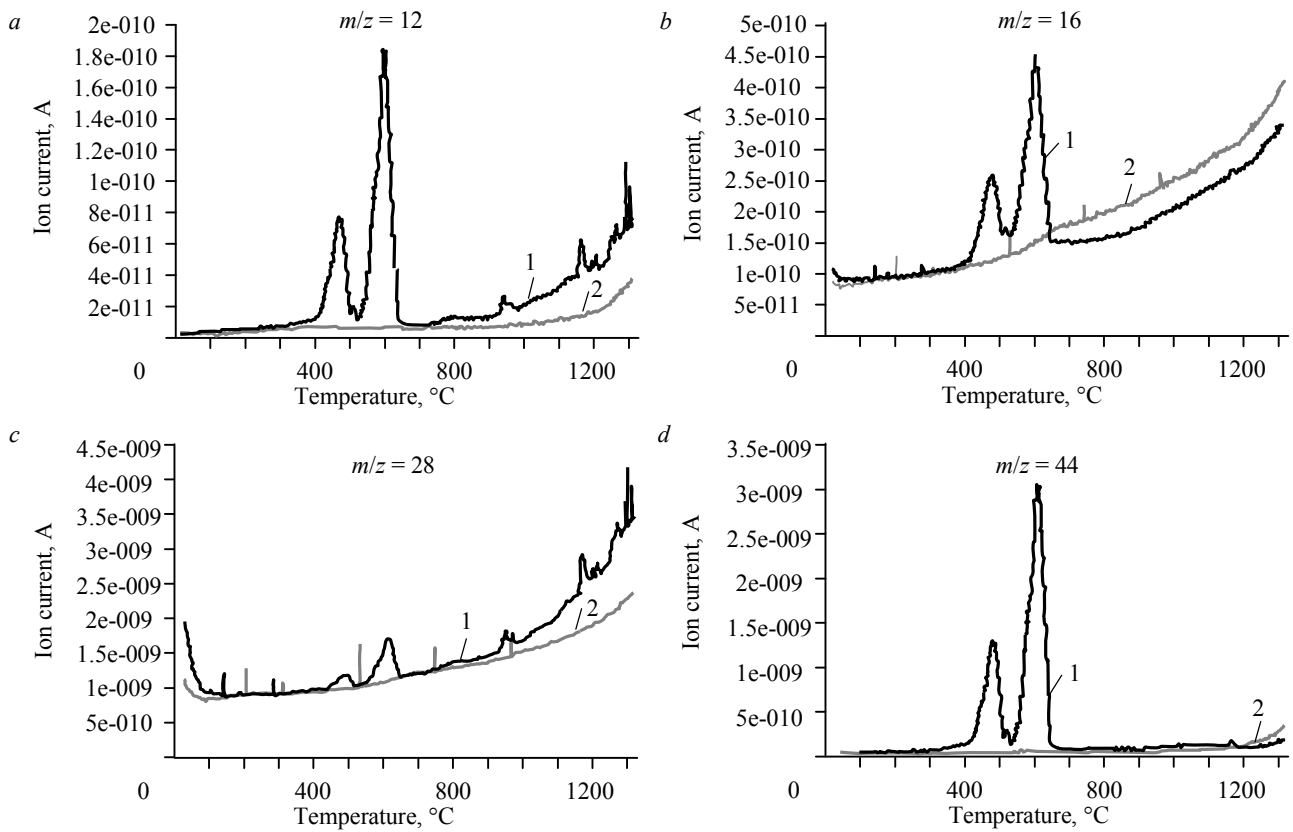


Fig. 6. Records for  $C^+$  (a),  $O^+$  (b),  $CO^+$  (c) and  $CO_2^+$  (d) of fragments for sample N 2  
1 – sample; 2 – empty measurement

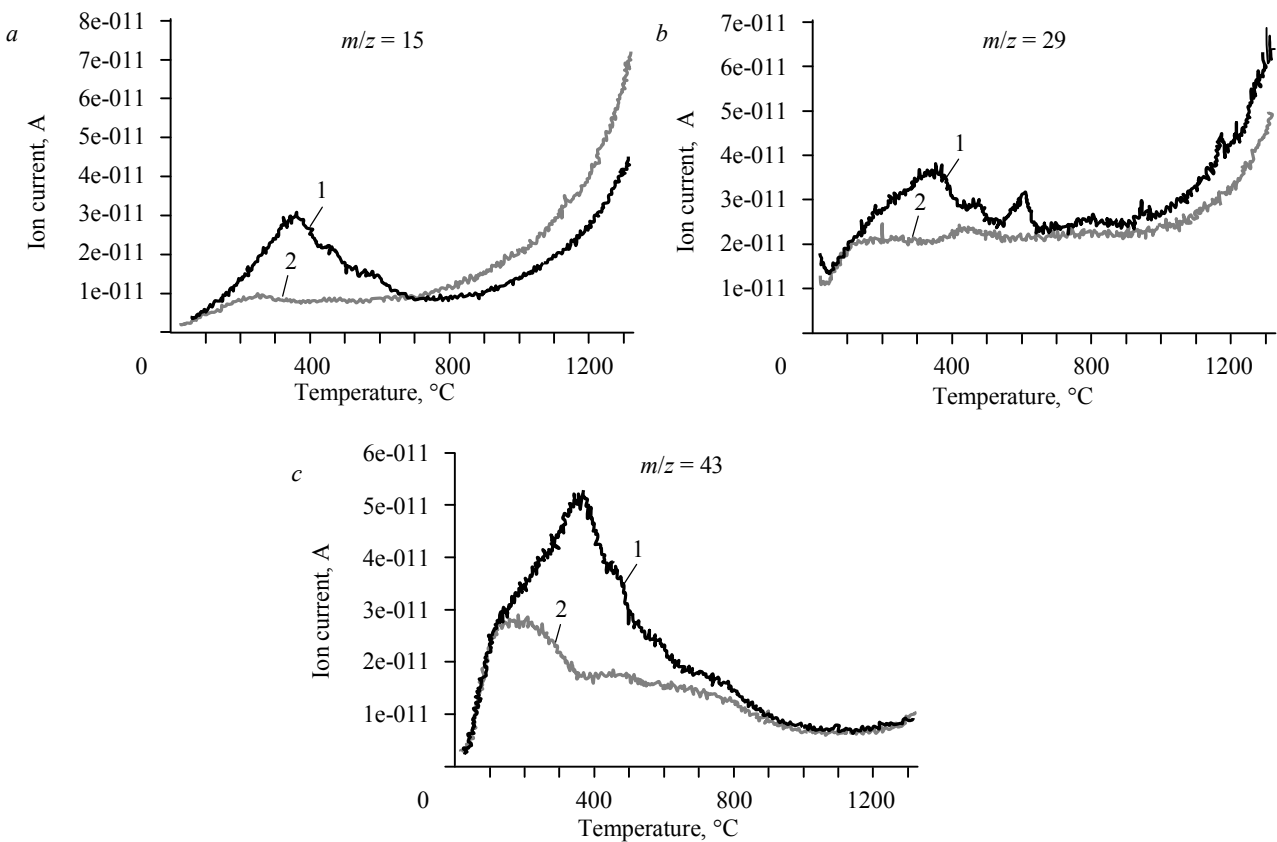


Fig. 7. Records of  $CH_3^+$  (a),  $C_2H_5^+$  (b) and  $C_3H_7^+$  (c) of fragments for sample N 2  
1 – sample; 2 – empty measurement



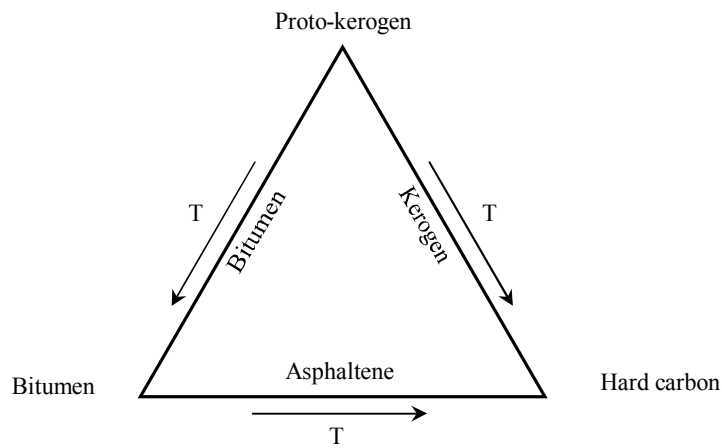


Fig.8. Connection between proto-kerogen, kerogen, and bitumen [17]

Based on the systematization of the results obtained after interpreting the data of thermal analysis of flotation concentrates with different degrees of gold recovery, it was established that the presence of bitumen in the ore is an additional refractory factor. Thermogravimetric and mass spectroscopic analyzes can be effectively used to clarify the refractory degree of gold-bearing ores. For gold-bearing resistant ores, in which not only kerogen is present, but also bitumen, it is necessary to

apply additional processing methods to increase the recoverability of gold, aimed at the destruction of organometallic compounds of noble metals and decrease in the sorption activity of organic carbon.

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**Authors:** **Tatyana N. Aleksandrova**, Doctor of Engineering Sciences, Professor, [aleksandrovat10@gmail.com](mailto:aleksandrovat10@gmail.com) (Saint-Petersburg Mining University, Saint-Petersburg, Russia), **Gerhard Heide**, Doctor, Professor, [gerhard.heide@tu-freiberg.de](mailto:gerhard.heide@tu-freiberg.de) (Freiberg Mining Academy, Freiberg, Germany), **Anastasiya V. Afanasova**, Postgraduate Student, [afanasovaop-10@yandex.ru](mailto:afanasovaop-10@yandex.ru) (Saint-Petersburg Mining University, Saint-Petersburg, Russia).

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