

## First Chemical Characterization of the New Polish Meteorite "Baszkówka" by Neutron Activation Analysis<sup>†</sup>

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New Polish meteorite "Baszkówka" which fell in the vicinity of Warsaw on August 25 1994, has been studied by neutron activation analysis (NAA) 21 elements (As, Au, Co, Cr, Cu, Eu, Fe, Ga, Hf, Ir, K, La, Mn, Na, Ni, Os, Sc, Se, Sm, Yb and Zn) were determined by instrumental NAA. In addition Au and Pd as well as La, Ce, Nd, Sm, Eu, Tb, Dy, Tm, Yb and Lu were determined by radiochemical NAA and Al, Ca, Fe, Mg, P, Si and Ti by classical methods. Speciation study was also carried out by isolating magnetic fraction from the powdered meteoritic sample and subsequent fractionation of metallic phases by controlled dissolution in hydrofluoric acid. Preliminary analytical work on another meteorite "Mt. Tazerzait" which fell a few years earlier in Africa shows that both meteorites have very similar composition. The results of this study as well as other published petrographic, mass spectrometric *etc.* investigations suggest that "Baszkówka" (and probably also "Mt. Tazerzait") may originate from another parent body than all other known chondrites of L group.

Neutronową analizę aktywacyjną (NAA) zastosowano do badania nowego polskiego meteorytu "Baszkówka", który spadł w pobliżu Warszawy 25 sierpnia 1994 r. Za pomocą instrumentalnej NAA oznaczono 21 pierwiastków (As, Au, Co, Cr, Cu, Eu, Fe, Ga, Hf, Ir, K, La, Mn, Na, Ni, Os, Sc, Se, Sm, Yb i Zn). Ponadto za pomocą radiochemicznej NAA oznaczono Au i Pd, jak również La, Ce, Nd, Sm, Eu, Tb, Dy, Tm, Yb i Lu, a za pomocą metod klasycznych oznaczono także Al, Ca, Fe, Mg, P, Si i Ti. Przeprowadzono również badania specjacyjne wydzielając frakcję magnetyczną ze sproszkowanej próbki meteorytu i analizując poszczególne fazy metaliczne przez kontrolowane rozpuszczanie w kwasie fluorowodorowym. Wstępne badanie innego meteorytu "Mt. Tazerzait", który

<sup>†</sup> Dedicated to Professor Adam Hulanicki on the occasion of his 70th birthday.

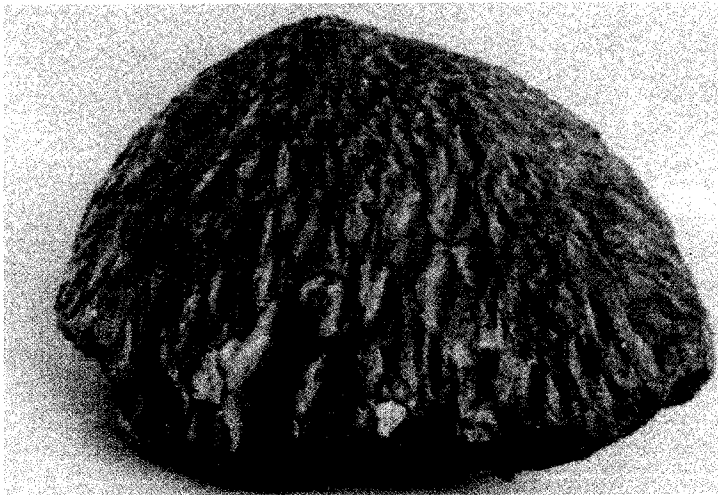
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spadł kilka lat wcześniej w Afryce wykazuje, że skład obu meteorytów jest bardzo podobny. Rezultaty tej pracy jak również opublikowane wyniki badań petrograficznych, badań za pomocą spektrometrii masowej itd. sugerują, że "Baszkówka" (a prawdopodobnie także "Mt. Tazerzait") może pochodzić od innego ciała macierzystego niż wszystkie znane do tej pory chondryty grupy L.

Meteorites, often called "Messengers from Space" [1], are unique extraterrestrial objects, the analysis of which can provide some information on the composition of the Earth's interior *i.e.* the region that is not and probably never will be accessible to our direct observation. While terrestrial rocks are predominantly composed of lithophile elements, chondrites – the most abundant class of stony meteorites contain also appreciable quantities of chalcophile and siderophile elements. It is generally assumed that chondrites are samples of the matter of the early solar nebula with only small degrees of fractionation of the chemical elements [2], and the Earth as a whole has a chondritic composition [1]. Meteorites are rare findings. Although it is estimated that over 4000 meteorites fall to the Earth each year, only a small percentage of them is recovered. The world collection by 1969 amounted roughly to 3000. Further 10000 were found since then in the cold and hot deserts of the Antarctic, Australia and Africa [2].

The full list of Polish meteorites does not exceed 20, and the one before last ("Łowicz") fell in 1935.

Baszkówka meteorite (Fig. 1) fell in the sunny afternoon August 25, 1994 on the freshly ploughed peasant's field in the vicinity of Warsaw. It was spotted by the woman working in the nearby garden and soon recovered while still warm. It was secured and a few months later it was acquired by the National Geological Institute, Warsaw.



**Figure 1.** Baszkówka meteorite has a shape of turtle's carapace *ca* 30 cm in diameter, and total weight of 15.5 kg. The meteorite when passing through the earth's atmosphere apparently did not somersault and thanks to that its surface is covered with a beautiful glassy crust of solidified rock's melt (regmaglypts) flowing from the top to the outer rim

Introductory investigation has shown that although it is an ordinary chondrite, classified as belonging to chemical class L and petrographic group 5 [3,4], it shows some peculiar features which indicate that it is in many respects a unique specimen.

The texture of this meteorite with numerous pores in which euhedral silicate crystals were observed, its unusually long cosmic age, no evidence of shocks as well as many etching patterns on mineral grains and results of analyses of mercury suggested its different origin and another cosmic history in comparison with other known and described chondrites of this group [5].

Similarity to Baszkówka shows only another new meteorite "Mt. Tazerzait" which fell a few years earlier (in 1991) but was first investigated in 1997. There is a substantial probability that these two meteorites come from another parent body than all other group L chondrites and that a collision that caused their fragmentation took place *ca.* 70 million years ago [6].

Some researchers believe that further studies on Baszkówka and Mt. Tazerzait should bring new interesting data which may even cause the necessity of revising some ideas on genesis of chondrites.

From analytical point of view meteorites are similar to geological samples, with some substantial differences, however. Each meteorite is a rare, unique and precious object, hence the masses that can be destined for analysis are as a rule small. Special procedures are sometimes needed for sampling and special care must be exercised during sampling and sample preparation to avoid contamination. Chondrites are highly heterogeneous materials; except of numerous minerals of widely different hardness they contain also *e.g.*, native copper and a lot of metallic Ni-iron that are malleable and difficult or impossible to pulverize. So, it is usually impossible to obtain analytical sample truly representative for the whole meteorite. This should be born in mind when looking at the results of analysis of any meteoritic matter.

Neutron activation analysis (NAA) is known as the reliable method capable of determining many trace elements from small sample with favourable detection limits [7-9]. What is equally important, NAA has the unique feature in comparison with other methods of inorganic trace analysis, being essentially free from blank. No wonder that it is very often a method of choice when analyzing such unique samples as meteorites [10-12].

In this paper the first results of chemical investigations of Baszkówka meteorite by NAA are presented.

## EXPERIMENTAL

### Sample preparation

After cutting a flat fragment from the bottom of the meteorite, a cylindrical sample from the interior of the specimen (*ca.* 5 cm depth) was taken using the milling cutter ( $N = 25$  mm). The sample was next

comminuted with agate mortar and pestle which were previously thoroughly washed and also cleaned with quartz. The powder was then kept in tightly closed glass bottle.

As follows from examination with the aid of optical microscope as well as with scanning electron microscope the range of particle size of the sample prepared in this way was quite broad. There was a considerable number of fine particles with diameter from 0.5 to 23  $\mu\text{m}$ , but at the same time there were numerous larger particles with diameters up to 400–500  $\mu\text{m}$ .

### Instrumental neutron activation analysis (INAA)

**Samples, certified reference materials.** 100–250 mg samples of meteorite as well as certified reference materials (CRMs): Fine Fly Ash (CTA–FFA–1) [13], Soil–5 [14], SARM–7 [15] and PTC–1 [16] were accurately weighed with the aid of analytical semi-micro balance (Precisa, Switzerland) into high purity polyethylene (PE) snap-cap capsules, 0.22  $\text{cm}^3$  (Faculteit der Biologie, Universiteit, Amsterdam). To avoid any contamination the distribution of the samples into capsules was carried out using laminar air flow cabinet with HEPA–filter, Holten (Denmark).

Water content of the CRMs was determined in separate subsamples by drying at 105° C to constant mass. Water contents determined this way amounted to 0.26, 1.43, 0.20 and 4.05%, for CTA–FFA–1, Soil–5 and SARM–7 and PTC–1, respectively.

**Standard preparation.** Stock solutions of As, Au, Ca, Ce, Co, Cr, Dy, Eu, Fe, Ga, Ge, Hf, Hg, Ir, K, La, Lu, Mn, Na, Nd, Ni, Os, Pd, Ru, Sc, Se, Sm, Tb, Tm, Yb and Zn were prepared from metals, oxides or salts of spectral purity by dissolving in high purity acids, and diluting with 18  $\text{M}\Omega\text{-cm}$  water obtained from Milli–Q RG ultra pure water system (Millipore Co.). Concentrations of stock solutions were usually close to 1 mg/g of solution, sometimes 10  $\text{mg g}^{-1}$  of solution.

Working standard solutions were made from stock solutions by diluting with 18  $\text{M}\Omega\text{-cm}$  water. Concentrations of the standard solutions were determined by weighing.

Multielement standards for INAA were prepared by transferring appropriate masses of standard solutions on filter paper discs ( $\phi = 7.7$  mm) placed in analogous PE capsules as those used for the samples. After drying at room temperature all capsules were closed and wrapped in Al foil similarly as the samples.

The approximate amounts of elements in the standards were as follows:

Standard 1: As (500  $\mu\text{g}$ ), Na (50  $\mu\text{g}$ ), Sc (2  $\mu\text{g}$ ), Co (55  $\mu\text{g}$ ), Cr (180  $\mu\text{g}$ ).

Standard 2: Cu (400  $\mu\text{g}$ ), Sm (10  $\mu\text{g}$ ), K (6000  $\mu\text{g}$ ), Ni (10000  $\mu\text{g}$ ), Os (100  $\mu\text{g}$ ), Yb (5  $\mu\text{g}$ ).

Standard 3: Mn (200  $\mu\text{g}$ ), La (200  $\mu\text{g}$ ), Pt (100  $\mu\text{g}$ ), Se (50  $\mu\text{g}$ ), Ga (30  $\mu\text{g}$ ).

Standard 4: Hg (100  $\mu\text{g}$ ), Eu (1  $\mu\text{g}$ ), Hf (10  $\mu\text{g}$ ), Ru (10  $\mu\text{g}$ ).

Standard 5: Fe (50000  $\mu\text{g}$ ), Au (10  $\mu\text{g}$ ), Ir (1  $\mu\text{g}$ ).

Standard 6: Ca (25000  $\mu\text{g}$ ), Ge (40  $\mu\text{g}$ ), Zn (500  $\mu\text{g}$ ).

**Irradiation and counting.** The irradiation package consisting of 6–8 samples, 2–3 flux monitors, 2–5 CRMs and 11–12 multielement standards, wrapped in Al foil was irradiated for 3 min. in the reactor MARIA in Świerk at a thermal neutron flux density of  $1.6 \cdot 10^{13}$   $\text{n cm}^{-2} \text{s}^{-1}$  ( $\Phi_{\text{fast}}/\Phi_{\text{th}} = 0.005$ ) and cooled for at least 4–6 h.

$\gamma$ -ray spectrometric measurements were done with the aid of well type HPGe detector (CANNBERA) 180  $\text{cm}^3$  nominal volume, 30% relative efficiency, well depth 40 mm, well diameter 16 mm, resolution 2.3 keV for 1332.5 keV  $^{60}\text{Co}$  line, coupled via ORTEC analog line to the multichannel analyzer TUKAN in the form of an ISA card inserted into a typical PC. Good and reproducible geometry of measurements was assured by placing the samples in the flat-bottomed test tube at the bottom of the well. The results were corrected for the background. Blank (from the irradiation capsule) was usually negligible for the elements studied in this work.

Several measurements were performed in a live time mode after decay time of approximately: 16 h, 2 d, 7 d and 1–2 months after irradiation and the time of measurement varied from 500 to 100000 s.

The concentration of an element  $x$  in a sample,  $C_x$  ( $\mu\text{g g}^{-1}$ ) was calculated from the formula:

$$C_x[\text{ppm}] = \frac{A_{0(s,\text{corr.})} \cdot m_{st}[\mu\text{g}]}{A_{0(st,\text{corr.})} \cdot m_s[\text{g}]} \quad (1)$$

$A_0$  – count rate of a radionuclide at the end of irradiation ( $t_0$ ),

$$A_0 = \frac{A_{n(\text{corr.})} \cdot \frac{\ln 2}{T} \cdot \Delta t \cdot \exp\left\{\frac{\ln 2}{T} \cdot (t_n - t_0)\right\}}{1 - \exp\left(-\frac{\ln 2}{T} \cdot \Delta t\right)} \quad (2)$$

where:  $A_{n(\text{corr.})(x,s./st.)}$  – count rate of a radionuclide in a sample (s) or standard (st) measured in a live-time mode and corrected (if needed) for spectral interferences,

$t_n$  – time of start of the measurement,

$t_0$  – time at the end of irradiation,

$\Delta t$  – time of duration of a measurement (clock time);

$$A_{n(\text{corr.})(x,s.)} = [N_{(x,s.)} - w_k \cdot N_{(y,\text{main}1)}] / t(s) \quad (3)$$

Where:  $w_k$  – correction factor used when spectral interference occur, calculated from the  $\gamma$ -ray spectrum of an interfering element (y):

$$w_k = A_{(y,\text{interf.}1)} / A_{(y,\text{main}1)} = N_{(y,\text{interf.}1)} / N_{(y,\text{main}1)} \quad (4)$$

$N_{(x,s.)}$  – number of counts in the photopeak of an element x, recorded during measurement of a sample,

$N_{(y,\text{main}1)}$  – number of counts recorded in the same measurement in the undisturbed photopeak of an interfering element (y),

$N_{(y,\text{interf.}1)}$  – number of counts for the line of an element (y) interfering with the analytical line of an element x,

$t_1(s)$  – live time of measurement of the sample.

Usually two different standards were employed to calculate element content according to eq. (1) and the average was taken as a final value of  $C_x$ .

Another series of determinations was done with the aid of 213 cm<sup>3</sup> coaxial HPGe detector (ORTEC), 40% efficiency, peak to Compton ratio 54:1, resolution 1.9 keV for 1332.5 keV <sup>60</sup>Co. The detector was coupled via ORTEC analog line, which included also precision pulse generator (ORTEC) to the multi-channel analyzer TUKAN in the form of an ISA card inserted into a typical PC. The distance of the sample from the detector was adjusted so as to keep the total count rate below 15000 cps for the very first measurements (*i.e.* shortly after irradiation) and below 7000 cps later on.

In this case the content of an element in the sample was calculated from the formula:

$$C_x[\text{ppm}] = \frac{A_{0,s} \cdot k_{st} \cdot m_{st}[\mu\text{g}]}{A_{0,st} \cdot k_s \cdot m_s[\text{g}]} \quad (5)$$

where:

$$A_{0,s/st} = \frac{N_{\text{corr.}} \cdot \frac{\ln 2}{T} \cdot \exp\left\{\frac{\ln 2}{T} \cdot (t_n - t_0)\right\} \cdot A_{\text{puls},0}}{\left\{1 - \exp\left(-\frac{\ln 2 \Delta t}{T}\right)\right\} \cdot A_{\text{puls},s/st.}} \quad (6)$$

$N_{\text{corr}}$  – number of counts in the photopeak of an element  $x$  (corrected if needed for the contribution of interfering element  $y$ ),

$k_{s./st}$  – normalized activity of a neutron flux monitor for a given position of the sample or standard in the irradiation package,

$A_{\text{puls},0}$  – count rate of a pulser in the absence of a sample,

$A_{\text{puls},s/st}$  – count rate of a pulser recorded during the measurement of a given sample or standard.

Other symbols are the same as defined in earlier formulae.

The summary of measurement conditions for individual elements is given in Table 1.

**Table 1.** Irradiation and measurement conditions INAA  $t_{\text{ir}} = 3$  min.  $\Phi_{\text{th}} = 1.6 \cdot 10^{13}$  n cm<sup>-2</sup> s<sup>-1</sup>,  $\Phi_{\text{fast}} \sim 8 \cdot 10^{10}$  n cm<sup>-2</sup> s<sup>-1</sup>

Element determined	Indicator Radionuclide	Half-life $T_{1/2}$	Analytical $\gamma$ -ray energies employed, keV	Cooling time days	Measurement time, days	Remarks
As	<sup>76</sup> As	1.097 d	559; 657	1.4–6	0.02–0.5	
Au	<sup>198</sup> Au	2.6935 d	411.8	1.4–12	0.01–1.2	
Co	<sup>60</sup> Co	5.271 y	1173.2; 1332.5	3–60	0.02–1.2	
Cr	<sup>51</sup> Cr	27.7 d	320	3–60	0.02–1.2	Corrected for contribution from <sup>192</sup> Ir 316.5 keV line
Cu	<sup>64</sup> Cu	12.7 d	1345.8; 1022 <sup>*)</sup>	1.4–2.7	0.02–1.2	<sup>*)</sup> For well-type detector
Eu	<sup>152</sup> Eu	13.33 y	121.78 <sup>+) </sup>	25–60	0.5–1.2	<sup>+) </sup> Corrected for contribution from <sup>75</sup> Se 121.12 keV line
Fe	<sup>59</sup> Fe	44.496 d	1099.3; 1291.6	6–60	0.02–1.2	
Ga	<sup>72</sup> Ga	14.1 h	834.09 <sup>*)</sup> , 630	1.4–2.5	0.02–0.5	<sup>*)</sup> Corrected for contribution from <sup>54</sup> Mn, 834.8 keV line
Hf	<sup>175</sup> Hf	70 d	343.4 <sup>@</sup>	25–60	0.5–1.2	<sup>@</sup> Corrected for contribution from <sup>152</sup> Eu, 344.29 keV line
	<sup>181</sup> Hf	42.39 d	482.0	7–50	0.5–1.2	
Ir	<sup>192</sup> Ir	73.831 d	468; 296; 784.6	5–60	0.1–1.2	
	<sup>194</sup> Ir	19.15 h	328.46 <sup>&amp;)</sup>	1.4–2.5	0.02–0.5	<sup>&amp;)</sup> Corrected for contribution from <sup>140</sup> La, 328.76 keV line
K	<sup>42</sup> K	12.36 h	1524.6	1.4–2.5	0.02–0.5	
La	<sup>140</sup> La	1.678 h	1596.5	1.4–8	0.1–0.5	
Mn	<sup>56</sup> Mn	2.5785 h	846.8	0.3–1.4	0.06–0.1	
Na	<sup>24</sup> Na	14.9 h	1368.6	1.4–8	0.07–0.5	
Ni	<sup>58</sup> Co	70.916 d	810.8	7–60	0.1–1.2	
Os	<sup>191</sup> Os	15.4 d	129.4	1.5–30	0.03–0.5	
Sc	<sup>46</sup> Sc	83.83 d	889.25; 1120.5	5–60	0.02–1.2	
Se	<sup>75</sup> Se	119.77 d	400	5–60	0.1–1.2	
Sm	<sup>153</sup> Sm	1.946 d	103.2	1.4–2.5	0.02–0.5	
Yb	<sup>175</sup> Yb	4.19 d	396.3	2.5–8	0.07–0.5	
Zn	<sup>65</sup> Zn	244.1 d	1115.5	25–60	0.5–1.2	
	<sup>69m</sup> Zn	13.76 h	438.6	1.4–3	0.02–0.5	

### Radiochemical neutron activation analysis

**Determination of rare earth elements after preirradiation preconcentration.** 500 mg sample of a meteorite was dissolved with the use of microwave digestion unit (Plazmatronika BM-18) employing *aqua regia* + HF digestion mixture, the solution was next transferred to PTFE vessel and evaporated. After treating with HCl, H<sub>3</sub>BO<sub>3</sub> and HNO<sub>3</sub> to remove fluorides followed by evaporation with HCl, the residue was dissolved in 1 mol l<sup>-1</sup> HCl and transferred on Dowex 50W-X8[H<sup>+</sup>] column. Separation of the group of rare earth elements (REE) from other elements based on sequential elution from cation exchange column as described earlier [17] was used, supplemented by additional steps: elution of iron with 1.5 mol l<sup>-1</sup> HCl in 80% C<sub>2</sub>H<sub>5</sub>OH [18] and after elution of REE fraction with 5 mol l<sup>-1</sup> HCl removal of sodium on the column with composite ion exchanger selective for sodium from 8 mol l<sup>-1</sup> HCl [19]. The effluent containing REE group was evaporated with HNO<sub>3</sub> transferred quantitatively into PE capsule evaporated to dryness and irradiated together with several mixed standards of REE for 2 h at a thermal neutron flux of  $1.6 \cdot 10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$ . Samples and standards were measured several times by  $\gamma$ -ray spectrometry after cooling times varying from a few hours to two months.

**Determination of palladium and gold after preirradiation preconcentration.** Newly developed procedure employing amphoteric (chelating) resin Chelex 100 for selective separation of Pd and Au was used. 500 mg sample was digested in a microwave oven with *aqua regia* + HF and silica was removed by evaporation, the solution was evaporated twice with concd. HCl to wet salts. The residue was dissolved in 0.5 mol l<sup>-1</sup> HCl and passed through the column with Dowex 50X8[H<sup>+</sup>] to remove most of cations. The effluent was evaporated, treated with *aqua regia* followed by evaporation with concd. HCl (twice). The residue was dissolved in *ca* 15 ml of 0.5 mol l<sup>-1</sup> HCl + 0.01 mol l<sup>-1</sup> Ce(IV) and transferred quantitatively on the top of Chelex 100 [H<sup>+</sup>] column (5 cm  $\times$  0.071 cm<sup>2</sup>, 200–400 mesh). After washing with 0.5 mol l<sup>-1</sup> HCl the resin bed was dried, transferred into Al foil bag and irradiated together with Au and Pd standards and a blank at a thermal neutron flux density of  $1.6 \cdot 10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$  for 3 h and cooled for 12–18 h. The sample was wet ashed with concd. HNO<sub>3</sub> + HClO<sub>4</sub> (1+1), evaporated twice with concd. HCl, dissolved in 15 ml of 0.5 mol l<sup>-1</sup> HCl + 0.01 mol l<sup>-1</sup> Ce(IV) and introduced quantitatively onto 5 cm  $\times$  0.071 cm<sup>2</sup>, 200–400 mesh Chelex 100 [H<sup>+</sup>] column. Palladium was eluted with 15 ml of 8 mol l<sup>-1</sup> HCl, followed by elution of gold with 15 ml of thiourea in 2 mol l<sup>-1</sup> HCl. Pd and Au fractions were measured as liquids by  $\gamma$ -ray spectrometry and compared with standards measured in the same geometrical conditions.

### Speciation analysis

Studies on metal phases of Baszkówka meteorite were done by slightly modified method of Kong *et al.* [20]. The magnetic fraction was separated from the Baszkówka chondrite with a hand magnet and was then boiled with concd. HF for 2 min, washed with distilled water, ultrasonified, dried and again separated with a hand magnet. After weighing, the magnetic fraction was transferred into PE capsule and sent for irradiation together with samples of bulk meteorite and standards as described above.

Irradiated magnetic fraction after  $\gamma$ -ray measurements was boiled for 20 min with concd. HF, immediately decanted afterwards, washed 3 times with distilled water, then with ethanol, placed in a PE capsule, dried, weighed and measured by  $\gamma$ -ray spectrometry.

### Determination of some elements by classical methods

Some macro- and minor constituents were also determined by classical methods using 1 g sample: Si gravimetrically as SiO<sub>2</sub> [21], Fe by redox titration with a potentiometric end point [21], Mg and Ca by complexometric titration [22], Al spectrophotometrically with chromazurol S [23], Ti spectrophotometrically as peroxide complex [23] and P spectrophotometrically as a phosphomolybdate complex [23].

## RESULTS AND DISCUSSION

## INAA results for the bulk composition of Baszkówka meteorite

The present work is the first attempt of determining chemical composition of Baszkówka meteorite. Therefore every effort was made to assure the reliability of analytical results. As each sample was measured several times, the results for a given element were averaged (whenever possible) and this average was used as a single entry for the calculation of the overall mean and standard deviation in case when several individual samples of meteorite were analyzed. The INAA measurements were performed using two independent  $\gamma$ -ray spectrometers operated by different analysts. For many of the elements being determined the data from both spectrometers were available and in general there was a good agreement between the two series of measurements. In this case the overall mean was taken as the average of the means from two series of measurements and uncertainty as the square root of the pooled variance. The results are shown in Table 2. Twenty one elements could be determined in this way. The analytical signals for hafnium were very weak, near the detection limit, so the result for this element should be treated as semiquantitative one. The results for copper may be slightly overestimated as this element was determined from 1022 keV photopeak measured with well-type detector. On the other hand when measuring samples with higher Cu content (*e.g.* magnetic fraction of a meteorite), where the use of 1345.8 keV line of  $^{64}\text{Cu}$  was also possible, there was very good agreement between the two approaches. As can be seen from Table 2, the uncertainties associated with the determined concentrations of individual elements are quite moderate, considering obvious inhomogeneity of the material and relatively small masses of the analyzed samples.

Table 2. Element content as determined by INAA in "Baszkówka" meteorite

Element	Concentration unit	Baszkówka $\bar{x} \pm s$
As	$\mu\text{g g}^{-1}$ (ppm)	$1.79 \pm 0.48$
Au	$\text{ng g}^{-1}$ (ppb)	$171 \pm 31$
Co	$\mu\text{g g}^{-1}$ (ppm)	$601 \pm 201$
Cr	$\mu\text{g g}^{-1}$ (ppm)	$3531 \pm 54$
Cu	$\mu\text{g g}^{-1}$ (ppm)	$130 \pm 8$
Eu	$\text{ng g}^{-1}$ (ppb)	$96 \pm 71$
Fe	wt. %	$21.91 \pm 1.71$
Ga	$\mu\text{g g}^{-1}$ (ppm)	$5.79 \pm 0.44$
Hf	$\text{ng g}^{-1}$ (ppb)	$290 \pm 111$
Ir	$\text{ng g}^{-1}$ (ppb)	$514 \pm 37$
K	$\mu\text{g g}^{-1}$ (ppm)	$680 \pm 71$
La	$\text{ng g}^{-1}$ (ppb)	$520 \pm 119$
Mn	$\mu\text{g g}^{-1}$ (ppm)	$2392 \pm 402$



Na	wt. %	0.635 ± 0.163
Ni	wt. %	1.14 ± 0.14
Os	µg g <sup>-1</sup> (ppm)	1.67 ± 0.15
Sc	µg g <sup>-1</sup> (ppm)	8.67 ± 0.61
Se	µg g <sup>-1</sup> (ppm)	10.7 ± 1.1
Sm	ng g <sup>-1</sup> (ppb)	235 ± 54
Yb	ng g <sup>-1</sup> (ppb)	179 ± 22
Zn	µg g <sup>-1</sup> (ppm)	67.7 ± 22.9

$\bar{x}$  – Arithmetic mean.

s – Standard deviation of single determination.

It is always desirable to demonstrate the reliability of analytical results by the analysis of certified reference materials. In Table 3 the results for CTA-FFA-1 and Soil-5 analyzed together with meteorite samples are presented. One can easily note that in all cases, with the possible exception of hafnium, there is good or very good agreement between our results and the certified values.

**Table 3.** INAAA results for certified reference materials as obtained in this study. Results for all elements are presented as: mean ± st. dev. in µg g<sup>-1</sup> (ppm), except of these marked: \*) which are in m%. Certified values are given with their confidence intervals

Element	Fin Fly Ash CTA-FFA-1		IAEA Soil-5	
	Our results	Certified value or (information value)	Our results	Certified value or (information value)
As	47.9 ± 7.5	53.6 ± 2.7	96.4 ± 18.3	93.9 ± 7.5
Co	37.9 ± 2.2	39.8 ± 1.7	14.0 ± 1.2	14.8 ± 0.8
Cr	160 ± 11	156 ± 8	30.6 ± 6.1	28.9 ± 2.8
Cu	178 ± 34	158 ± 9	–	–
Eu	2.32 ± 0.14	2.39 ± 0.08	1.28 ± 0.07	1.18 ± 0.08
Fe	4.64 ± 0.22 <sup>*)</sup>	4.89 ± 0.14 <sup>*)</sup>	4.45 ± 0.19 <sup>*)</sup>	4.45 ± 0.19 <sup>*)</sup>
Ga	43.5 ± 8.4	(49)	–	–
Hf	5.2 ± 0.1	6.09 ± 0.45	5.41 ± 1.32	6.30 ± 0.30
K	2.10 ± 0.23 <sup>*)</sup>	(2.2) <sup>*)</sup>	1.81 ± 0.37 <sup>*)</sup>	1.86 ± 0.15 <sup>*)</sup>
La	62.9 ± 9.3	60.7 ± 4	28.5 ± 5.1	28.1 ± 1.5
Mn	1009 ± 184	1066 ± 41	829 ± 197	852 ± 37
Na	1.84 ± 0.34 <sup>*)</sup>	2.19 ± 0.08 <sup>*)</sup>	1.61 ± 0.30 <sup>*)</sup>	1.92 ± 0.11 <sup>*)</sup>
Sc	24.0 ± 1.3	24.2 ± 1.1	14.8 ± 0.8	14.8 ± 0.7
Sm	9.3 ± 2.2	10.9 ± 0.6	4.51 ± 0.72	5.42 ± 0.39
Yb	4.10 ± 0.9	4.24 ± 0.19	2.07 ± 0.21	2.24 ± 0.20
Zn	633 ± 122	569 ± 58	–	–

### Determination of some noble metals and rare earth elements by RNAA

The new method for the determination of Pd and Au using Chelex 100, assured practically 100% yield and good decontamination factors with respect to most of elements. The reliability of the method was confirmed by analysis of the reference materials.

The results for gold in SARM-7:  $0.296 \pm 0.044 \mu\text{g g}^{-1}$  and in PTC-1:  $0.647 \pm 0.202 \mu\text{g g}^{-1}$  are in a good agreement with the certified values ( $0.310 \pm 0.015 \mu\text{g g}^{-1}$  [15] and  $0.65 \pm 0.10 \mu\text{g g}^{-1}$  [16], respectively). Two samples of Baszkówka meteorite were analyzed giving the results: 0.192 and  $0.134 \mu\text{g g}^{-1}$  ( $\bar{x} \pm s = 0.163 \pm 0.041 \mu\text{g g}^{-1}$ ) being in a good agreement with the mean result by INAA (Table 2).

Palladium for which the best  $\gamma$ -ray line (88 keV) lies in the low energy region cannot be determined in low concentrations by INAA. The new radiochemical method was shown to be very reliable. The results for palladium in the two CRMs (SARM-7:  $1.49 \pm 0.09 \mu\text{g g}^{-1}$  and PTC-1:  $11.9 \pm 0.6 \mu\text{g g}^{-1}$ ) are in a good agreement with the certified values:  $1.530 \pm 0.032 \mu\text{g g}^{-1}$  [15] and 12.0–13.0 (median  $12.7 \mu\text{g g}^{-1}$ ) [16], respectively.

The results for palladium in two samples of Baszkówka were: 6.33 and  $4.35 \mu\text{g g}^{-1}$  ( $\bar{x} \pm s = 5.34 \pm 1.40 \mu\text{g g}^{-1}$ ), almost an order of magnitude higher than the mean concentration in chondrites of the L group [24].

Only one sample was run for the determination of REE by RNAA. In preliminary experiments with several radioactive tracers of the lanthanides and mineral sample simulating meteorite composition it was found that the average chemical yield of the preconcentration step was  $90 \pm 4\%$ , and so the results were corrected accordingly. The radiochemical purity of the final REE fraction was not quite satisfactory as trace amounts of antimony were leaking from the composite ion exchanger used in the preconcentration step. Nevertheless it was possible to obtain the results for several elements and these are (in  $\text{ng g}^{-1}$ ) as follows: La (1167), Ce (900), Nd (919), Sm (238), Eu (67), Tb (61), Dy (176), Tm (57), Yb (182), Lu (12). In Figure 2 the results for REE normalized with respect to mean concentration of REE in L chondrites [24] are plotted as a function of atomic number. There is good agreement between RNAA results and mean INAA values for Sm and Yb. The agreement is poorer for La and Eu, but one has to remember that RNAA results are from single experiment only.

As a general conclusion one can note that light lanthanides are slightly enriched and heavy ones slightly depleted in Baszkówka with respect to mean composition of chondrites of the L group.

### Additional data on some macro- and minor constituents

Results for Al, Ca, Fe, Mg, P, Si and Ti determined by classical methods are shown in Table 4. If these concentrations were recalculated into oxides and added as is customarily done in the case of geochemical analyses the sum would already ex-

ceed 100%. It is known, however that part of iron together with nickel, cobalt *etc.* exist in meteorites as metal and Baszkówka is not an exception as will be shown below.

**Table 4.** Content of major and minor constituents in Baszkówka (in m%) as determined by classical methods

Element	Content wt. %		
	Sample 1	Sample 2	$\bar{x} \pm s$
Al	1.53	1.56	1.545 $\pm$ 0.021
Ca	1.02	1.08	1.05 $\pm$ 0.04
Fe	21.89	23.43	22.66 $\pm$ 1.09
Mg	15.02	16.10	15.56 $\pm$ 0.76
P	0.100	0.100	0.100
Si	18.42	17.43	17.93 $\pm$ 0.70
Ti	0.16	0.17	0.165 $\pm$ 0.007

$\bar{x}$  – Arithmetic mean.

s – Standard deviation of single determination.

### Composition of Baszkówka's magnetic fraction

The results of analysis of the magnetic fraction ( $m = 20.93$  mg) isolated, as described in experimental part, from 329.49 mg sample of the meteorite are shown in Table 5. In addition the concentration of elements, that form long-lived radio-nuclides, in kamacite *i.e.* in this metal phase that is dissolved during 20 min boiling with conc. HF [20], are also given in Table 5.

**Table 5.** Element content of magnetic fraction of "Baszkówka" meteorite as determined by NAA

Element	Concentration unit	Baszkówka <sup>#)</sup>	
		Bulk magnetic fraction	kamacite
As	$\mu\text{g g}^{-1}$ (ppm)	19.8	
Au	$\text{ng g}^{-1}$ (ppb)	1335	
Co	$\mu\text{g g}^{-1}$ (ppm)	6686	7561
Cr	$\mu\text{g g}^{-1}$ (ppm)	1113	1910
Cu	$\mu\text{g g}^{-1}$ (ppm)	376	
Eu	$\text{ng g}^{-1}$ (ppb)	N.D. <sup>*)</sup>	
Fe	w.t. %	75.77	90.9
Ga	$\mu\text{g g}^{-1}$ (ppm)	18.2	
Hf	$\text{ng g}^{-1}$ (ppb)	N.D.	
Ir	$\text{ng g}^{-1}$ (ppb)	2921	903
K	$\mu\text{g g}^{-1}$ (ppm)	N.D.	
La	$\text{ng g}^{-1}$ (ppb)	N.D.	
Mn	$\mu\text{g g}^{-1}$ (ppm)	637	

Na	$\mu\text{g g}^{-1}$ (ppm)	567	
Ni	wt. %	8.54	7.80
Os	$\mu\text{g g}^{-1}$ (ppm)	9.2	
Sc	$\mu\text{g g}^{-1}$ (ppm)	0.83	N.D.
Se	$\mu\text{g g}^{-1}$ (ppm)	N.D.	
Sm	$\text{ng g}^{-1}$ (ppb)	N.D.	
Yb	$\text{ng g}^{-1}$ (ppb)	N.D.	
Zn	$\mu\text{g g}^{-1}$ (ppm)	N.D.	

<sup>a</sup>N.D. – Not Detected.

<sup>b</sup>Results from single experiment.

Siderophile elements like As, Au, Co, Cu, Ga, Ir, Ni and Os are substantially enriched, as expected, in the magnetic fraction, which contained, also measurable quantities of some lithophile elements (Cr, Mn and Na). However, most of lithophile trace elements (Eu, Hf, K, La, Sm, Yb and Zn, as well as chalcophile element Se, were not detected in the magnetic fraction of Baszkówka meteorite.

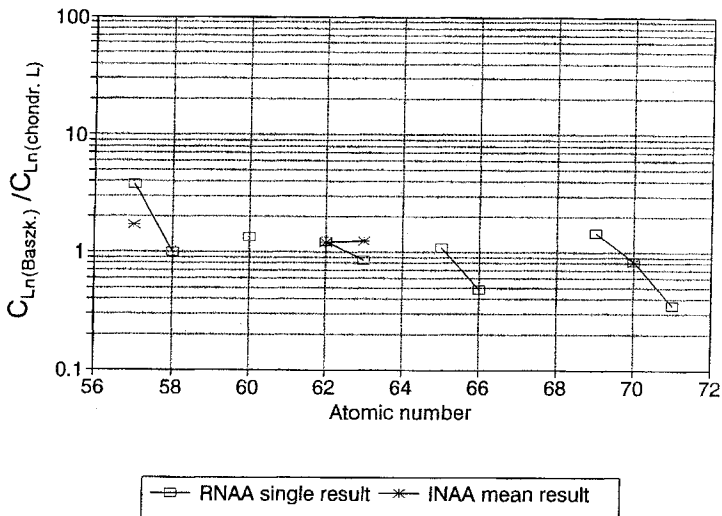


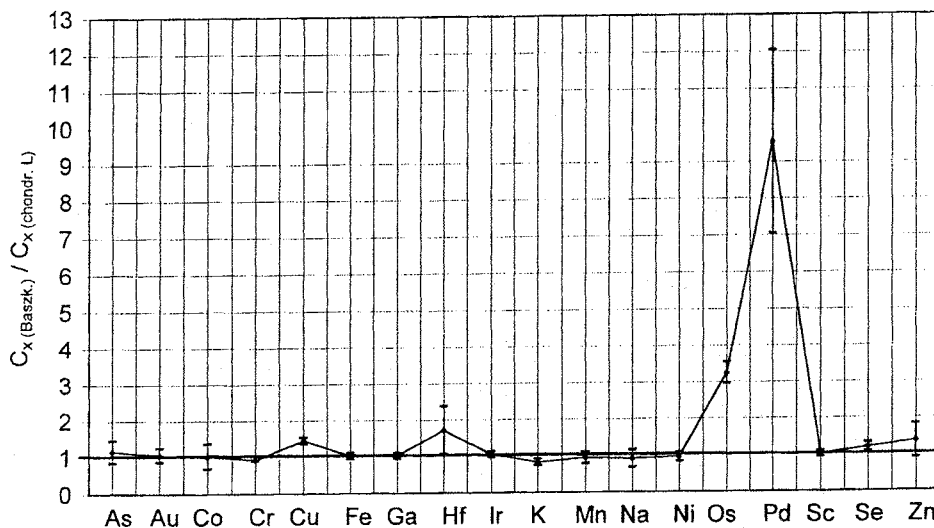
Figure 2. Rare earth element concentrations in Baszkówka normalized to mean content in L chondrites [24], as a function of atomic number

### Cosmochemical implications

Chemical and petrologic criteria are the basis for classification of meteorites into groups. Baszkówka was tentatively classified as an L group chondrite on the basis of study on olivine and pyroxene phases by electron microprobe analysis and by oxygen isotope analysis [5]. However, some other data, among others low Hg content

[5] and sulfur isotope analysis [25] suggested that this meteorite may have some peculiar features.

In Figure 3 concentrations of elements as determined by NAA in this study (except of lanthanides which are shown in Fig.2), normalized with respect to mean composition of L chondrites, are presented. One can easily note that while for many elements this ratio is close to unity, there are some notable exceptions. In particular they encompass some noble metals (Os, Pd) as well as some rare earths (cf. Fig. 2).



**Figure 3.** Content of individual elements in Baszkówka meteorite normalized with respect to mean composition of L chondrites [24]

One of criteria used in chondrite classification is the ratio of total iron to nickel. The ratio  $Fe(t)/Ni$  calculated from the data shown in Table 2 amounts to 19.22 and is considerably higher than the corresponding ratio for L chondrites ( $17.73 \pm 1.37$ ) and closer rather to that characteristic for LL chondrites ( $18.64 \pm 2.18$ ) [26]. On the other hand the  $Fe(t)/Si$  ratio for Baszkówka (1.26 from classical methods, or 1.22 when INAA value for Fe is used) is closer to mean value for L chondrites ( $1.18 \pm 0.06$ ) than to corresponding values for H chondrites ( $1.60 \pm 0.06$ ) or LL chondrites ( $1.03 \pm 0.04$ ) [26]. Similarly, cobalt content in kamacite (cf. Table 5) is characteristic for L chondrites rather than for H or LL group [20]. But on the other hand the  $MgO/SiO_2$  ratio in the case of Baszkówka is rather far away from the approximately linear relationship observed by Jarosevich [26] for most of H, L, and LL chondrites.

Our preliminary results on chemical composition of Mt. Tazerzait meteorite show its striking similarity to Baszkówka.

All these facts seem to support the view that these two meteorites may have a common parent body different from most of other L chondrites. Further work on the analysis of Baszkówka and Mt. Tazerzait meteorites is in progress.

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#### REFERENCES

1. Heide F. and Wlotzka F., *Meteorites, Messengers from Space*, Springer, Berlin 1995.
2. Ulyanov A.A., in: *Advanced Mineralogy, Vol. 3, Mineral Matter in Space, Mantle, Ocean Floor, Biosphere*, Environmental Management, and Jewelry, (Marfunin A.S., Ed.), Springer, Berlin 1998.
3. Stępniewski M., Radlicz K., Siemiątkowski J. and Borucki J., *Meteoritics & Planetary Science*, **31**, Suppl., p.A134 (1996).
4. Wlotzka F., *Meteoritical Bull.*, **78**, 792 (1995).
5. Stępniewski M., Borucki J. and Siemiątkowski J., *Meteoritics & Planetary Science*, **33**, No. 4, Suppl., pp. A150–A151 (1998).
6. Wlotzka F., Scherer P., Otto J. and Stępniewski M., *Meteoritics & Planetary Science*, **32**, No. 4, Suppl., pp. A140–A141 (1997).
7. Dybczyński R., *Chem. Anal. (Warsaw)*, **30**, 749 (1985).
8. Parry S.J., *Activation Spectrometry in Chemical Analysis*, Wiley, New York 1991.
9. Goeij de J.J.M. and Woittiez J.R.W., *J. Radioanal. Nucl. Chem., (Articles)*, **168**, 429 (1993).
10. Lipschutz M.E., Wolf S.F., Vogt S., Michlovich E., Lindstrom M.M., Zolensky M.M., Mittlefehldt D.W., Satterwhite C., Schultz L., Loeken T., Scherer P., Dodd R.T., Sears D.G.W., Benoit P.H., Wacker J.F., Burns R.G. and Fisser D.S., *Meteoritics*, **28**, 528 (1993).
11. Zipfel J., Palme H., Kennedy A.K. and Hutcheon I.D., *Geochim. Cosmochim. Acta*, **59**, 3607 (1995).
12. Xiao X. and Lipschutz M.E., *Geochim. Cosmochim. Acta*, **55**, 3407 (1991).
13. Dybczyński R., Polkowska-Motrenko H., Sameczyński Z. and Szopa Z., *Geostandards Newsletter*, **15**, No. 2, 163–185 (1991).
14. Dybczyński R., Tugsavul A. and Suschny O., *Geostandards Newsletter*, **3**, No. 1, 61–87 (1979).
15. Steele T.W., Levin J. and Copelowitz I., The preparation and certification of a reference sample of a precious-metal ore, National Institute for Metallurgy Report No.1696, Randburg, South Africa, 10th March 1975.
16. McAdam R.C., Sutarno and Moloughney P.E., *Noble-metals-bearing sulphide concentrate PTC: its characterization and preparation for use as a standard reference material*, Department of Energy, Mines and Resources, Mines Branch technical Bulletin TB 176, July 1973, Ottawa, Canada.
17. Wasek M., Kulisa K. and Dybczyński, *Chem. Anal. (Warsaw)*, **41**, 647 (1996).
18. Wódkiewicz L. and Dybczyński R., *Chem. Anal. (Warsaw)*, **19**, 175 (1974).
19. Bilewicz A., Bartoś B., Narbutt J. and Polkowska-Motrenko H., *Anal. Chem.*, **59**, 1737 (1987).
20. Kong P., Ebihara M., Nakahara H. and Endo K., *Earth and Planetary Science Letters*, **136**, 407 (1995).
21. Minczewski J. and Marczenko Z., *Analytical Chemistry*, Vol. 2, PWN, Warszawa, 1976 (in Polish).
22. Welcher F.J., *The analytical Uses of Ethylenediaminetetraacetic Acid*, WNT, Warszawa 1963, (in Polish).
23. Marczenko Z., *Spectrophotometric Determination of Elements*, PWN, Warszawa 1979, (in Polish).
24. Wasson J.T. and Kallemeyn G.W., *Phil. Trans. R. Soc. Lond. A*, **325**, 535 (1988).
25. Hałas S., (private communication).
26. Jarosewich E., *Meteoritics*, **25**, 323 (1990).

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