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Application of neutron activation analysis in geochemistry and cosmochemistry

G. M. Kolesov

Vernadsky Institute of Geochem. & Anal. Chem., Russian Academy of Sciences, Kosygin St. 19, 117975, Moscow, V-334, Russian

Abstract— Generalized the use of neutron activation analysis (NAA) in the investigations of unique processes occurring in early stages of formations and evolution of bodies in solar system. Out of them the formation of chondrules, emergence of ultra refractory inclusions in carbonaceous chondrites, formation of metallic and silicate phases of iron and stone meteorites, and formation of iron meteorites of different chemical groups. Changes in regolite and lunar rock contents, differentiation in the upper mantle matter, identification of earthly meteoritic craters, transportation of cosmic (meteoritic) materials on to the Earth, investigations of unique events like Tunguska fall of the year 1908 and also ore formation studies and processes taking place on geochemical barrier type river-sea, ocean-atmosphere and so on. Prospectives of NAA are pointed out.
Keywords: neutron activation analysis; geochemistry; cosmochemistry; solar system.

1 Introduction

Geochemistry and cosmochemistry linked to other sciences (astrophysics, geophysics, nuclear physics, crystallography, mineralogy, biology, geology and technology) and based on the data of contents and distribution of elements, obtained by different methods including NAA (Elving, 1986).

Investigations of primary processes related to origin and evolution of bodies in solar system in early stages and their development and secondary processes related mostly to delay periods (Anikiev, 1987) are said to be important and actual problems. Among them the following are most important: (1) Determination of elemental (isotonic) contents of primary matter of the solar system; (2) Investigating the roles played by chemical and physico-chemical processes in early periods in the formation of atoms and particle association and then in the formation of solar system bodies, (3) Determination of chemical contents of cosmic dust, lunar rocks, meteorites, comets, asteroids and other planets: (4) Explaining the differentiation conditions of the matter in hard parent bodies like asteroids, meteorites and so on; (5) Studying the contents and evolution of the earthly matter; (6) Investigating the processes occurring on the surface of the planet (fall of gigantic meteorites, comets of the past); (7) Explaining the formation conditions for ore associations, search for place of deposits and new minerals. (8) Study long and short period natural processes occuring at the boundaries of river-sea, ocean-atmosphere, i.e. geochemical barriers and also volcanic eruptions and so on.

In order to solve these problems, exclusively the spread and distribution of different elements, such as REE, U, Th, Ir, Hf, Ta, W, Ga, Ge, Ni, Rb, Cs and platinum group elements (PGE) having different physico-chemical properties (high volatility, oxidizability, refractoriness) or crustallo-chemical peculiarities. Most of them present in low level ($10^{-4}\% - 10^{-9}\%$) in geochemical and cosmochemical objects, masses and their sizes also much small consists of 10^{-6} g and 10^{-6} mol/L, respectively. That is why most appropriate methods are needed for the determination of chemical contents in such samples, chosen NAA which allows multielement determination with low detection limits, low analysis error and without destroying the sample.

Uniqueness and high metrological characteristics of the method have been established (even in our investigations) regarding the processing and application of some examples and possibilities. Among them are: (1) Scheme modification for sample dissolution, group separation of elements based on methods such as co-precipitation, solvent-extraction, ion-exchange, micro-fire assay concentration and so on (Saposhznikov, 1988); (2) Use of combination of thermal and resonance neutrons of reactors; (3) Application of latest spectrometric instruments and semiconductor detectors; (4) Automatization of measurements and information processing (Shubina, 1991), and (5) Application of latest standards.

The aim of present work is to give detailed investigation and demonstrate the role of neutron activation method in solving some of the above mentioned problems, particularly origin of meteorites, investigation of upper mantle content and study of secondary processes on the Earth and the Moon.

2 Results and discussion

2.1 Solar system

Important studies about the formation of the solar system is reminded and schematically represented in Fig. 1. Most difficult and not widely studies is second stage. Important information about this obtained during the study of meteorites. Besides that also from the processes originating from early studies of gas-dust nebula, from chondrite investigations and iron meteorite delay studies. Important information about third stage is obtained while studying mantle material.

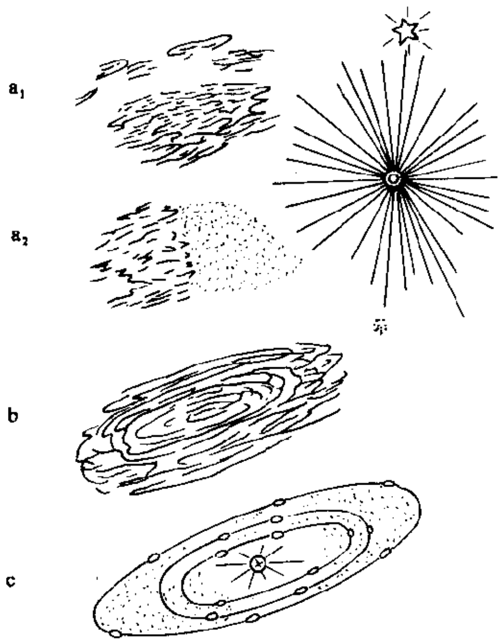

Fig.1 Schematic representation of basic steps involved in the evolution of primary gas-dust nebula a1: Primary gas-dust nebula; a2: Nebula in the Sun's reactive sphere; b: Ordered processes of condensation, compression protoplanet formation of gas-dust nebula; c: Formation of the solar system bodies

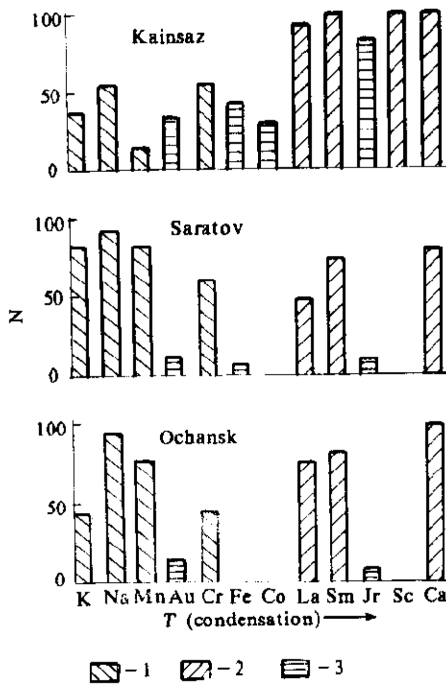

Fig. 2 Relative contents of (1) average volatile; (2) weak volatile; (3) lithophilic and sidrophilic elements in chondrules of meteorites, Kainsaz, Saratov and Ochansk

2.2 Meteorites

It is known that chondrules are the main characteristics of the chondrites. To explain the conditions of their formation, particularly, the primary (formed from gas-dust nebula) or secondary objects (arised from matter fusion) are the key problems in cosmochemistry (Lavrukhina, 1987).

Presented as an examples investigation results of the contents of some chondrites analysed by us. Out of them, normal chondrites satarov and ochansk (Fig.2) formed during secondary process, carbonaceous meteorite kainsaz formed during the process related to condensation of matter. Interesting to note that even among the chondrules which are similar according to their structures, but ordinary and carbonaceous chondrites different by their chemical contents and elemental composition. For example, redially radiating chondrus of carbonaceous chondrites enriched with r are earth elements (REE) compared to chondrules of typical chondrites (Lavrukhina, 1987). ,

2.3 Refractory inclusions

Carbonaceous chondrites of type CU, CO, CR are found enriched with Ca, Al and sometimes Ti-inclusions contains high temperature minerals. Characterized their chemical content, particularly distribution of REE. For example, separated a group, in which observed the increase (related to Cl chondrites) in REE contents; they reflects early condensation period of matter in the nebula. Sometimes we come across inclusions deficit with REE, particularly deficit of most volatile Eu, Yb elements; they formed from condensation with early loss of refractory REE. It may be noted similar group of inclusions distributed with REE in which contents of Eu and Yb (volatile elements of all REE) observed as symmetric minimum; this allow to suppose that REE were separated from gas at the time of complete condensation of Eu and Yb(Fig. 3, Lavruknina, 1987).

In Efremovka meteorites we detected other inclusions which are not found earlier, differs by REE spectra and REE contents witnesses about nonuniformity of early trace element contents of gas-dust nebula (Nazarov, 1987).

Interesting to note that one more type of formation found firstly in Ornans Chondrite in 1982, after we found Kainsaz chondrite (LJUL. 1990). They were detected and separated with the help of INAA method on the variations in the radionuclide activities of Ir/Ni and Sc/Cr elements of different volatility. Using same methods determined contents of these inclusions are found to be ultra-refractories with unusual high contents of Ir (400 μg/g). Sc (2000 μg/g) and also REE (Fig. 3, curve 4). Mass of the inclusions consisted of some microgram amounts and their size is about some tens of microns.

Considering the one more group of meteorites called iron meteorites, their classification by their chemical contents.

This was carried out firstly by the data obtained by NAA method of the contents of Ni, Ga and Ge followed by Ir. Os and Pt and other elements, sixteen chemical groups were separated. Ten iron meteorites fallen in the former USSR territory were analyzed by us.

2.4 Mantle rocks

In present times much attention is paid for the study of mantle rocks, astro-blems and rare events of geology, based on the main data on the distribution of REE and platinum group elements (PGE, mainly iridium). Briefly we discussed about these investigations.

Besides meteorites, as noted there are other reliable sources which tells about contents of primary matter of the Earth and the Moon with the help of deep nodules content, which are brought to upper level by alkaline melts and kimberlites.

Excluding the siderophilic and volatile elements the upper mantle is similar to chondrite in relation to the contents of all elements. Volatile elements F, Cl, Br and so on were lost during high temperature accretion process, part of sidrophilic elements go to metallic nucleus due to high distribution coefficients in metal-silicate systems. In that case, primary material in mantle nodules may be not subjected to partial melting, metasomatic or metamorphic processes. Based on the distribution of petrogenic elements model of the nondifferentiated upper mantle was designed. We tried (Kagarko, 1986) to calculate its contents with respect minor elements and particularly, with respect to REE in spinel iherzolites volcano of Shavarin-Tsaram and nodule samples from other regions. As an example some results are given in Table 1 and Fig.4.

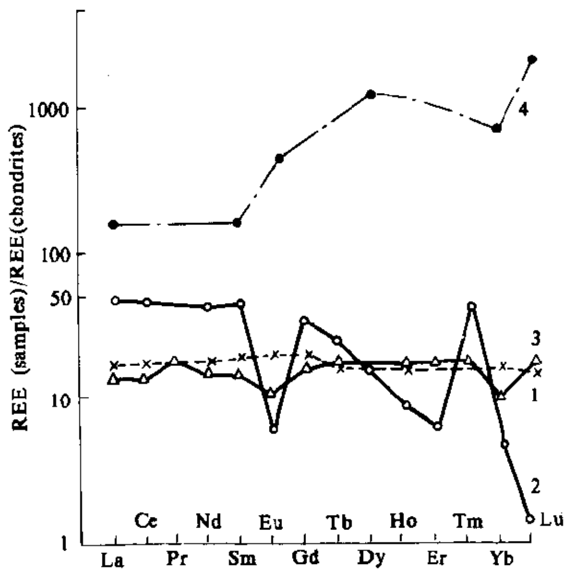

Fig. 3 Relative distribution of REE in refractory inclusions, chondrite Allends (curves 1–3) and Kainsaz (4)

From the data of Fig 4 (a), it follows that it has correlation dependance in the contents of Al, Ca, Si, and Mg witnesses about the partial fusion of resultant material. Agreeing to this (Hutchinson, 1974), it characterizes minimum magnesium and maximum concentration of "basaltic" components CaO, Al_2O_3 and Na_2O. Such contents mostly characterized for one of the investigated sample KO-1 by us. It is differentiated from others based on the distribution of REE. They are closely related to chondrites, but the contents are higher by two times (Fig. 4b), this answers the calculated contents of non-differentiated primary material of the Earth, after loosing volatile and siderophile elements during accretion process. According to this model contents of U, Th, Hf, Sc and Co were obtained by neutron activation method. In that case, sample KO-1 represents as primary, non-differentiated material of the upper mantle.

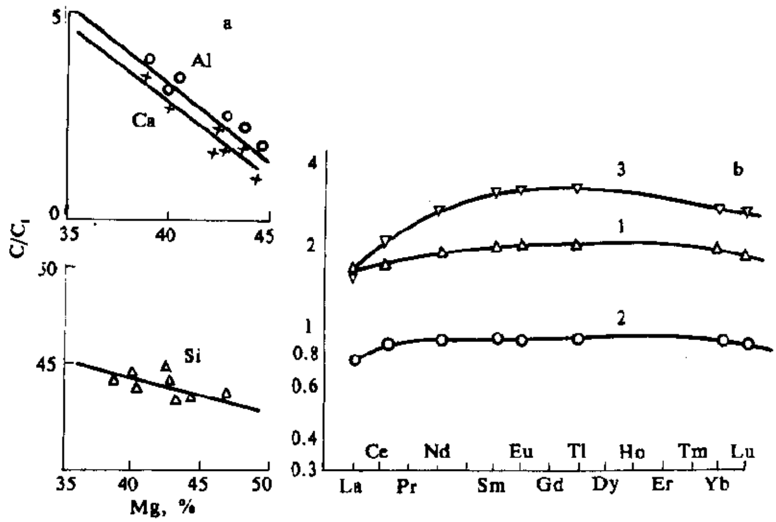

Fig. 4 Correlation dependance between contents of aluminium, calcium, silicon and magnesium (a); relative distribution of REE in Shavarin-Tsaram nodules, Mongolia, central massif France (b)

2.5 Astro-bleme

In recent times, the important role of meteoritic bombardiers on early development studies of core of the planet bodies of the Earth type. Impacts of meteorites detected by the account of changes in rock target materials and contamination of formed products with meteoritic materials (Bazilevsky, 1984). Carried out investigations based on the contents of trace elements and iridium in young and well preserved earth craters. Some of the results are given in Fig. 5. From this it can be seen that the iridium contents of rock targets corresponding to the iridium content of rocks of the earth core, is not present in crushed breccia, and accumulates in fusion products. In this event its distribution is answered by two peaks. First peak is due to rock fusions from crater groups, enriched with iridium and second one is due to fusion from crater with low contents. These relations suggest that this is due to impact or low contents of iridium or separation of material during fusion process. For complete explanation if this question needed data about the distribution of other elements with different physio-chemical properties.

Carried similar investigations with Elgigitgin Crater (Kapustkina, 1985). Established that contamination of glass fission by meteoritic material and it is not based on the comparison of obtained level of relation to elements Ni/Cr, Ni/Co, Ni/Ir, Cr/Co, Cr/Ir and Co/Ir with meteorites, suppose that astro-blem of Eligitgin formed by falling of Govargite, i.e. chondrite enriched with calcium.

Analogical investigations were done with the samples of Popigai crater, Balthishkoi and other astro-blems. Stressed the idea that many astro-blems are linked with the falling of huge meteorites, which are more intensive during the early periods of formation of the Earth as a geological body. So after million years, it is possible to establish impact body type.

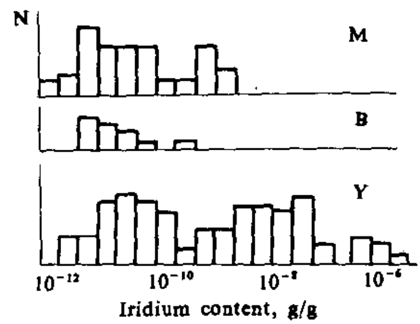

Fig. 5 Relative distribution of iridium in rocks of meteorite craters
M: target; B: breccia; Y: impact melt

We performed model experiments (Yakovlev, 1990) for studying the behavior of elements in fast vaporizing processes occurs during high speed impact of bodies of copper or iron meteorites on the targets of basalts, granite and serpentite. The vapor formed during the impact is condensed on Al-foil, after that is analyzed by neutron activation method for the contents of lithophilic and siderophilic elements and according to obtained data the interpretation of the character of running processes is done.

2.6 Rare events

Geochemical properties of iridium has been investigated (Nazarov, 1983) and also to evaluate the possibility of collisions of huge cosmic objects with the Earth at the boundary K-F_9 and Paleogon (65 million years ago), which can be served as the reason for the mass killing of bio-system. This was done on the basis to establish unique iridium high contents (up to 70 ng/g) at boundary layers and correlations with concentrations in them and impact in metamorphic quartz, which observed to be only in the impacts of the Earth meteoritic craters. Calculated possible masses of impacts: for chondrites in the order of 10^{12} T (diameter 9 km) of iron meteorites is 2×10^{11} T(diameter 3 km) and crater dismeter is 75−300km (Alekseev, 1988).

The data of iridium content obtained by neutron activation method showed that the value is vital for the identification of nature of the Tunguska event of the year 1908. It is also established by us (Karina, 1987) that peat layers of catastrophical region of same year is more enriched with iridium compared to mentioned above peak layers. This indicates that the Tunguska body has the contents of comet. It is the cosmic character of Tunguska phenomenon (Fig. 6).

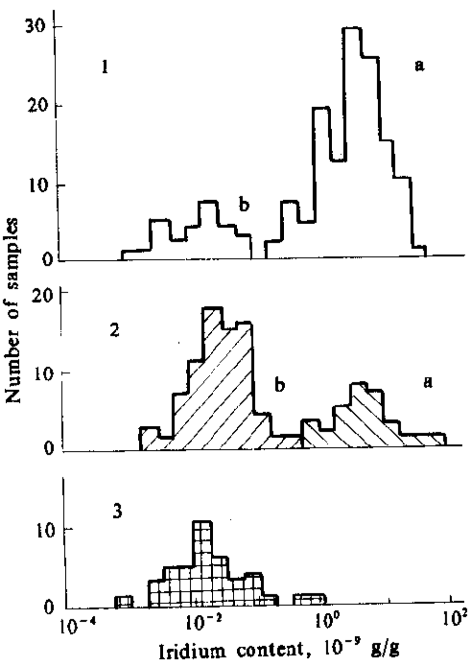

Fig. 6 Iridium content in lunar rocks from mainland, breccia, main rocks, K/T-sediments, plutonic rocks and AR-rocks

2.7 Early history of the Earth, lunar regolite

Much attention paid for the contents of iridium in important types of the earth's core material (AR-18 pg/g, FA-32pg/g) in comparison to magmatic rocks of lunar mainlands are 53 pg/g and K/T-sediments 50 pg/g (contaminated with meteoritic material 65 million years ago). As it can be seen from Fig. 6 that iridium content in AR-rocks is somewhat lower compared to lunar intrinsic rocks and much more lower than the impact of lunar meteorite core (Nazarov, 1984). This indicates that iridium distribution in AR-rocks was being controlled by magmatic fractionation processes, the Earth's core does not consists of cosmic components which confirmed during meteoritic bombardment studies. In such case, the age of the Earth core should not be more than 4 milliard years or it might have formed still later.

Interesting results about the chemical contents of regulate, lunar rock fragments which were widely used for studying the evolution and formation processes of the Moon (Fig.7).

2.8 Geochemical barriers

Neutron activation method is of great use in studying composition and distribution and transportation of elements by river loads and volcanic eruptions (Kolesov, 1988; Anikiev, 1991). Complete detailed examples can be taken, but even obtained and describes the vital, unique role of neutron activation method in solving actual problems of geochemistry and cosmochemistry.

3 Conclusions

It can be noted that very interesting information about above mentioned

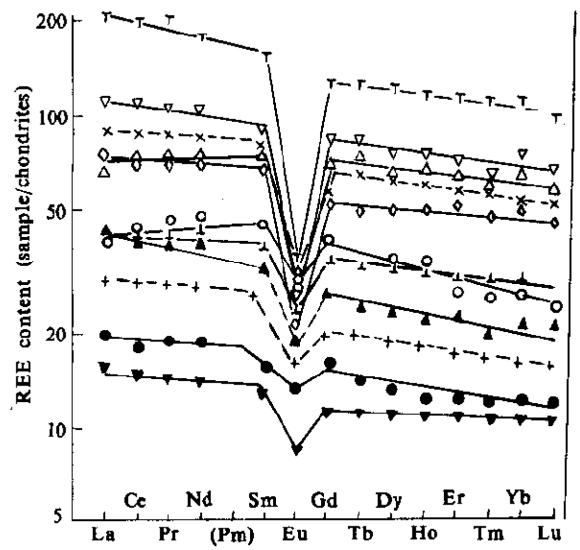

Fig. 7 Relative distribution of REE in regolites (average values for continental and for marine regions of the Moon)

questions, mainly about the contents of REE, Ir, Hf, Ta, U, Th, Ge, Ga, Ni and Pt group metals, for which used a good processed neutron activation determination. Exclusively important information (about accretion, aglomeration, transportation of matter) is contained from chalcophite and siderophile elements, for example, Ti, Bi, Hg, Cd, Sc, Te and others, but there is no concrete method for their determination. Besides that for unique geochemical and cosmochemical investigations present times needed high sensitivity and low detection limits of elements. This stands on front of experimentalist the task of improving the neutron activation analysis. Thus it represents the following: (1) Increase in rapidness; (2) lowering the detection limits, and (3) increase in accuracy and reproducibility of results.

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