

rocks is oxidized to insoluble trivalent iron, which is marked by a change of rock color to brown, yellow, or red. For example, laterites in the tropics contain iron in amounts of up to 30% and more, but such ores are not yet utilized in metallurgy. *Sedimentary deposits of iron ore* formed from chemical sediments in marine basins contain by far the largest reserves and represent the basis of current iron production. Thus, the United States obtains a large part of its iron from hematite sedimentary ores in the region of the Great Lakes. Enormous reserves of iron are found in the Transvaal (Republic of South Africa), Ukraine, Australia (Homersly), Canada, and Brazil. If it is assumed that the world's annual needs are less than 10^9 t, we can safely say that reserves of iron are so great that there will be no serious supply problems for many centuries to come.

2. *Aluminum* is more widespread than iron in the Earth's crust and owing to its lightness has a better ratio of mass to hardness, which constitutes its advantage over iron. This element was first separated in pure form in 1827. The separation process, by the way, is very difficult. Only at the end of the 19th and beginning of the 20th Century were methods developed for industrial production of pure aluminum, after which the area of its application expanded considerably. World production of aluminum was already above 15 million tons in 1981.

Products of rock weathering under tropical conditions, bauxites are the main mineral raw material of aluminum. Bauxite - bearing laterite soils are very widely disseminated in tropical regions, but large deposits with high bauxite content occur somewhat more rarely there. The Caribbean island of Jamaica is the leading supplier of this raw material. Large deposits are found in Guyana, Surinam, and Brazil (South America); Guinea and Cameroon (Africa); countries of the former USSR; Southern France; the Middle East; and Taiwan, Indonesia, and Australia (Northern Queensland). In 1982, world reserves of bauxite were estimated at $25 \cdot 10^9$ tons. According to B. J. Skinner (1986), these reserves (like oil reserves) are sufficient for the near future. Mineral raw materials potentially capable of later replacing bauxite include kaolinite, nepheline, alunite, anorthosite, andalusite, etc. Today, aluminum is already obtained from nepheline (Russia) and alunite (Japan, Russia, Mexico, and the USA).

3. *Manganese* is an extremely important additive to steel, one that mitigates the negative action of small amounts of sulfur and oxygen. The largest deposits of manganese - in which pyrolucite (MnO_2) and other manganese minerals enter the composition of *chemogenic sedimentary rocks* are the Chiatureko (Georgia) and Nikopol'sko (Ukraine) deposits. The reserves of those two deposits amount to hundreds of millions of tons, which constitutes 75% of the world's reserves of manganese ore. Mainly represented by pyrolucite and psilomelane, significant *weathering crust* deposits in the tropics are found in the Republic of South Africa, India, Australia, Brazil, Gabon, and China. Available reserves of manganese comprise $25 \cdot 10^9$ t, which is not so much in comparison with the level of its consumption ($25 \cdot 10^6$ t in the year 1981). As in the case of aluminum, it will probably be necessary to exploit non - traditional sources in the near future. Ferro - manganese concretions of the ocean floor are one of the greatest potential sources of this metal. Useful admixtures (copper, nickel, cobalt, and other rare metals) can also be extracted from such concretions.

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4. Like aluminum, *titanium* has low specific gravity linked with great hardness and resistance to corrosion. It is difficult to separate this metal from ore, and its industrial production began only after the Second World War. Titanium reserves have not been precisely determined, but they are certainly considerable. Because the titanium minerals rutile and ilmenite are among the most resistant minerals of weathering crusts and at the same time are heavy minerals, they accumulate in debris. Large *disseminated deposits* were formed in this way in Australia, Sri Lanka, India, Sierra Leone, the Republic of South Africa, and the former Soviet Union. The reserves of marine debris on the Atlantic Coast of the United States attain 10^9 t, which in the opinion of experts is enough for the foreseeable future.

5. *Magnesium* is the lightest and most stable of widespread metals. Since it is hard, magnesium is needed in production of light alloys with high corrosion resistance, especially in alloys with aluminum. World production of metallic magnesium is relatively low, about 300,000 t (1981). However, magnesium is not generally used in the form of a metal, but rather in compounds, especially in oxide form (MgO), which is characterized by excellent thermo- and electro-insulatory properties. The main source of magnesium is the sea. It also enters the composition of very widespread minerals of the sedimentary rocks dolomite and magnesite. The reserves of this element are therefore practically unlimited, but the technological difficulty of extracting it is a limitation.

Rare Metals. These are metals whose distribution in the Earth's crust is under 0.1%. For this reason, together with gold, silver, and platinum, the category also includes copper, zinc, lead, and nickel, whose production is constantly increasing. All of them are vitally important elements, ones that accelerated the development of such technological wonders as production and transmission of electrical energy, the telegraph, radio, television, aviation, and rocket and nuclear energetics.

A large portion of rare metals in the Earth's crust (about 99.99%) forms part of the composition of rocks and minerals in the guise of admixtures, while only a tenth of a percent falls on ore minerals that can be enriched. For this reason, a portion of rare metals is obtained as a side product from ore minerals of copper, lead, and zinc. This is the case, for example, with silver.

Deposits of geochemically rare metals are formed under the influence of a number of factors. The following two classes of deposits containing concentrations of rare metals are especially important: 1. *deposits in which magma acts as the concentrating agent*; and 2. *hydrothermal deposits*, formed by the action of heated water rich in dissolved salts on sulfide and oxide ore minerals. Hydrothermal deposits are considered to be the most important class of deposits with concentration of rare metals.

Rare metals are mainly formed in sulfide deposits. In exceptional cases, chromium, antimony, tungsten, niobium, tantalum, and beryllium form oxide deposits, while rare native metals (platinoids and gold) can form disseminated deposits.

Copper has been used since ancient times and today represents the foundation of the electrical industry as the main material for energy transmission. Deposits of this element are very widespread, but (as hydrothermal deposits) are

most often with relatively low reserves. Since the beginning of the 20th Century, underground exploitation of deposits with a high percentage of copper (above 10%) has been abandoned in favor of surface processing of porphyry copper deposits (likewise hydrothermal) with low ore quality (less than 2% copper). Hundreds of *porphyry copper deposits* have been discovered to date, and they are especially numerous in both North and South America, the former USSR, Iran, Yugoslavia, the Philippines, New Guinea, and islands of the Pacific. Deposits of this type in North and South America constitute a distinct metallogenic province parallel with the western boundary of the continents. So - called *stratiform deposits* represent another important type of copper deposits. They were formed during the Permian in the former shallow Zechstein Sea in Central Europe (Germany, Poland), as well as in the Copper Belt of Zambia and Zaire. More than 50% of world production is linked with exploitation of *porphyry copper deposits*, and 20% with *stratiform deposits* (mainly the Zambian deposit). Available reserves of copper comprised 511 million tons in 1982, when production was 7.78 million tons.

Ore minerals of *lead* and *zinc* make up a close association in nature. For practical purposes, only two mineral forms are represented: galenite (PbS) and sphalerite (ZnS), on which the world's production of lead and zinc is based. As in the case of copper, hydrothermal and stratiform deposits are industrially important. *Hydrothermal deposits* constitute an expansive metallogenic province from the states of Ohio and Missouri to Wisconsin (USA), and they also occur in Northwest Canada, a number of countries of Europe and North Africa, Northern Australia, and the former USSR. Production of these two metals from *stratiform deposits* is gradually increasing, and among the largest deposits of this type are the Sullivan and Kimberley deposits in British Columbia and three deposits in Australia. Total world reserves of lead comprised 146 million tons in 1981 (when production was 3.46 million tons). For zinc, these figures were 243 and 6.16 million tons, respectively.

Nickel is obtained from two classes of deposits: *magmatic deposits* (Canada, the former USSR, Australia); and *deposits of weathering crusts of certain volcanic rocks* (New Caledonia, the state of Oregon in the USA, Cuba, the Philippines, Greece). Available reserves of this metal comprised 56.1 million tons in 1981, when production was 784 thousand tons. It is considered that human needs for this element will be satisfied well into the distant future.

Molybdenum is present in the mineral molybdenite (MoS_2), which is very unevenly distributed. Molybdenum deposits are concentrated in a metallogenic province from Mexico to Alaska extending parallel to the porphyry copper province mentioned earlier. World production of this metal was 90 thousand tons of this metal in 1982 (when reserves comprised 6 million tons).

Silver usually occurs in *hydrothermal vein deposits* with copper, lead, and zinc. Large deposits are found in the Cordilleras from Alaska to Tierra del Fuego. These deposits account for more than 55% of the world's production of silver. The remainder falls on Australia and territories of the former USSR.

Platinoids are associated with rocks formed from magma of the Earth's inner shell. Their content is extremely low. Platinoid reserves are in large part concentrated in the Bushveld Complex (Republic of South Africa) and in the former USSR.

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In contrast to platinoids, *gold* is associated with magmatic rocks formed in the Earth's crust. Among the best - known deposits of gold are those in the region of Witwatersrand (Republic of South Africa), where gold ore is concentrated in layers of conglomerates. Although many disseminated deposits of gold occur throughout the globe, the indicated deposit (also a disseminated deposit) has since 1984 represented the world's leading gold producer (with 52% of world production in 1982).

The only industrially important mineral of *chromium* is chromite, which has limited reserves. This to some extent does not apply to the stratified intrusive massifs characteristic of the African continent (the Bushveld Complex in the Republic of South Africa and the Big Dike of Zimbabwe). If chromium ores with low content of this metal were to be exploited, there would be no problem about securing the amounts of chromium needed in the future.

Antimony and *tungsten* often occur together in minerals. Their content in the Earth's crust is low and the number of deposits small. Two metallogenic provinces embrace a significant part of the world's antimony reserves. One of the provinces extends from Java through Malaysia, Eastern China, and Korea to Eastern Siberia. The other is located in the high Andes of Bolivia and Peru. Approximately half of the world's production of tungsten is realized in the East Asian metallogenic belt.

Non - Metallic Mineral Raw Materials

In prehistoric times, man incorporated selected stones into his dwellings and fashioned monuments of culture and works of art from attractively shaped stones and costly materials. Approximately 30 thousand years ago, the Krapina Prehistoric Man made tools out of several kinds of silicate rocks and tuffs, and he subsequently used coarse - grained aggregates of quartz, opal, and dense chert for this purpose. Later on, the prehistoric inhabitant of Lepenski Vir knew enough to select rounded pieces of solid rock and the hardest minerals for his building needs, tools, jewelry, and weapons. Not only that, he used attractive red and reddish - brown porphyrite, marble, crystalline limestone, and sandstone for fences, plates, tables, shrines, and tombs. We also mention the magnificent Pyramids of Egypt, about 3,500 years old, which were built of compact limestones and Nubian sandstones, with obelisks and columns carved in granular and porphyroid granites, sphinxes of basalt and gabbros, etc.

Non - metallic mineral raw materials, above all geological building materials, today represent the product we extract in greatest volume from the bosom of the Earth. After energy raw materials, they are the second most significant form of mineral wealth. The majority of non - metallic mineral raw materials have enormous reserves, and for some (building stone, for example) there is no need to estimate them quantitatively, since they are very plentiful in the Earth's crust. This means that the future looks optimistic where the majority of non - metallic raw materials are concerned, and the tendency to use them as replacements for rare metals is increasingly pronounced.

Non - metallic mineral raw materials are characterized by the enormous diversity of rocks and minerals. The group of main raw materials includes the following: *limestone, crushed rock, rock for block making, sand, gravel, phosphate rocks, clays, sulfur, potassium salts, and gypsum*. However, there is a whole series of economically valuable non - metallic materials apart from the most important ones mentioned. The group of second - rank raw materials is made up of: *abrasives, asbestos, asphalt, barite, bentonite, borates, bromine, diamonds, diatomite, feldspar, fluorite, garnets, graphite, magnesite, mica, olivine, perlite, pumice, quartz, sodium, talc, vermiculite, and zeolites*.

The application of all the listed raw materials is quite varied. Two groups can be distinguished on the basis of the area of their application: 1. agrochemical and chemical raw materials (fertilizers and raw materials for the chemical industry); and 2. geological building materials.

Agrochemical and Chemical Raw Materials. *Deposits of raw materials for production of fertilizers* are unquestionably among the most necessary of resources. As the source of the world's food reserves, plants require nitrogen, phosphorus, potassium, calcium, and sulfur, which they extract from the soil. The role of fertilizers is to correct the content of those very often deficient elements. This need is especially pronounced in the poor soils of Brazil, Australia, and an increasing number of other countries throughout the world. The need for fertilizers worldwide is increasing at an accelerating rate. To be more precise, it doubles every ten years.

Phosphorus, potassium, and nitrogen fertilizers are the most important.

The most widespread mineral of phosphorus - apatite - is poorly soluble, and very complex chemical reactions are employed to obtain *superphosphate*. Syenites of the Kola Peninsula (Russia) and carbonatites of Brazil and the Republic of South Africa are rich in apatite. About 82% of the world's needs are satisfied by apatite of *marine sedimentary deposits*, 16% by apatite of *volcanic magmatic rocks*, and 2% by apatite of guano. In the USA, for example, phosphate - enriched deposits were formed in a shallow marine basin encompassing parts of the present - day states of Idaho, Nevada, Utah, Colorado, Wyoming, and Montana with an area of more than 160,000 km².

Soluble minerals of *potassium* are also used as fertilizers. They occur exclusively in marine evaporites formed by accumulation of salt during evaporation of seawater. Evaporites are in fact the main source of *halite* (kitchen salt), gypsum, and potassium salts. In the USA alone, evaporitic salts are distributed over an area of more than 160,000 km² (in the states of New Mexico, Texas, Oklahoma, and Kansas), not counting the much larger potassium salt deposits. Basins in the Canadian province of Saskatchewan represent enormous reserves elsewhere in the world, together with deposits on territory of the former Soviet Union, South America, and Southeast Asia.

Nitrogen is extracted from the atmosphere and introduced into the soil in the form of various soluble nitrates, although the natural nitrates of Chilean deposits are also used in smaller amounts.

Sulfur is predominantly obtained from evaporites following secondary enrichment (USA, Mexico) or from sulfuric volcanic gases (Japan). Sulfur production attained a level of 52 million tons in 1982. In relation to needs, sulfur reserves are limited, but alternative sources of sulfur are being discovered in the meantime.

Halite (NaCl) stands out among the diverse non - metallic materials used as *raw materials for the chemical industry*. Enormous reserves of that salt are found in seawater, as well as in marine evaporites. Salt domes are known in many regions of the world (in Europe, South America, the former Soviet Union, and the Middle East), but are especially concentrated in the coastal zone of the Gulf of Mexico.

Geological Building Materials. *The more important natural stone materials* include the following: 1. *building stone*, above all limestones and granites, which in the USA account for 70% of total production (1,2 million tons in 1982); 2. *crushed rock*, primarily of limestone and dolomitic composition, whose production in the USA alone comprised 800 million tons in 1982 (when worldwide production was 2.5 billion tons); and 3. *sand and gravel*, used especially in roadwork and mixing with cement (consumption in the USA was 835 million tons in 1982).

The following products of rock processing stand out among others:

1. *Cement*, made from suitable mixtures of dolomites or sandstones with marls and clay, with a worldwide production of the order of 889 million tons in 1982;
2. *Alabaster*, obtained by heating gypsum (just in the USA, gypsum - bearing rocks cover 10% of the country's territory);
3. *Clays* for various uses in ceramics, obtained predominantly from large surface digs;
4. *Glass*, a product with fast - growing needs obtained by melting of rocks or minerals, especially quartz;
5. *Asbestos*, the fibrous variety of serpentine minerals (former USSR, Canada), used widely up until the 80's of the last century, but noticeably less so after that on account of its carcinogenic properties.

Energy and Mineral Raw Materials of Yugoslavia

On the territory of Yugoslavia, magmatic, metamorphic, and sedimentary processes over the course of geological time were especially favorable for formation of different kinds and types of rocks and deposits of mineral raw materials, resources needed to improve the economic and the cultural life of the population. This natural wealth has been exploited for a relatively long period of time: for about 5000 years in the cases of copper, gold, and silver. The period of Roman rule was characterized by significant intensification of exploration and exploitation of iron, silver, lead, and copper ores, as well as mercury⁴⁸. The Kopaonik region and the mountains

⁴⁸ The Suplja Stena mercury mine in the vicinity of Mt. Avala is one of the oldest mines in the world, as is indicated by archaeological evidence found in the remains of a prehistoric settlement from the Younger Iron Age in the village of Vinca and pieces of ceramics from this settlement found in the mine.

Rudnik, Kosmaj, Avala, and Brskovo were well - known for mining activity, and traces of old mines have also been preserved to the present day in the vicinity of Krupanj, Majdanpek, Rudna Glava, and other places. In those days, the wealth of people and states was valued from the amount of precious metals, gold, and silver in their possession. At the time of the great migration of people with the decline of Byzantium, mining production - which up to then had been highly developed - declined noticeably until establishment of the Serbian Medieval State. Thus, after a long period of stagnation, mining attained a high level of development during the 13th and 14th Centuries, with ores of silver, lead, copper, and iron being extracted in the greatest amounts. The advance of the Turks and gradual establishment of their rule at the end of the 14th and beginning of the 15th Century marked the beginning of a new stage in organization of economic activity and thereby in mining as well, albeit on a minor scale. Such a state of affairs was maintained practically until the first decades of the 20th Century, when Serbia gained limited independence. Mining activity then flourished again: already in 1837 the first coal mine in Serbia was opened in Miliva, and it was followed by many other mines. Mines of ferrous and non - ferrous metals were opened somewhat later, and their exploitation increased at a rapid pace.

Energy Raw Materials. Energy raw materials are present in all of their main forms, but with distinct dominance of coal.

1. *Coal* is represented mainly by lignite (95% of all available reserves). The great lignite deposits of Yugoslavia are characterized by favorable tectonic structure, considerable depth of the beds, and the possibility of surface exploitation. Among such deposits is the Kosovo Basin, with an area of about 10.5 km² and estimated reserves of 11.7 billion tons, one of the largest deposits in Europe. The Kostolac, Kolubara, Metohija, Mazgoski, and Kovin Basins can also be singled out;
2. *Oil* and *gas* are predominantly concentrated in Vojvodina (in The Banat region above all), where oil has been produced since 1956 and gas since 1952. Total reserves of oil in Serbia are estimated at 9.5 million tons, while gas reserves are estimated at 20 billion m³.
3. *Oil shales* extend from Bolevac to Pirot, and also occur in the Babusnica, Vranje, Aleksinac, Krusevac - Cacak, and Valjevo - Mionica Basins. With the highest percentage of kerogen (18 - 24%), the Aleksinac deposit is the most significant from the economic standpoint;
4. *Uranium* deposits and occurrences have been discovered in several places. Uranium was found first in 1947 at the confluence of the streams Dobroticka Reka and Vojnicka Voda south of Prokuplje and later in a granite massif in the vicinity of Kalna (in the Stara Planina Mountains of Eastern Serbia). Explorations have shown that uranium - bearing granites, volcanites, Paleozoic schists, and some Tertiary sediments occur in Sumadija. Elsewhere, uranium - bearing trachytes have been found south

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of Gnjlane, uranium - bearing granites on Mt. Cer, etc. Uranium content in ore (pitchblende) ranges from 50 to more than 2,500 ppm. It is characteristic that the Janja and Bukulja granites have a greater clark of uranium (with reserves of the order of 3,000 t of U₃O₈) than in other granites in Yugoslavia.

Metallic Raw Materials. The territory of Yugoslavia is characterized by many deposits and occurrences of ferrous and non - ferrous metals. The following four metallogenic provinces can be singled out (Fig. 2.31.): 1. The *Dacian Province*, of limited area, with sedimentary deposits of gold and clay; 2. the *Carpatho - Balkan Province*, with several lithogenic zones and characteristic presence of deposits of copper ore, uranium, gold, and iron; 3. the *Serbo - Macedonian Province*, with many endogenous deposits of lead, zinc, and antimony, as well as exogenous deposits of iron, nickel, magnesium, bauxite, and boron; and 4. the *Dinaric Province*, with deposits of chromium, iron, bauxite, lead, and zinc.

About 30 deposits and occurrences of *iron* have been registered on the territory of Serbia. Because they have small reserves and ore of low quality, there is not a single active mine of iron ore today. The situation is similar with *manganese*. *Chromium* reserves are exclusively associated with peridotite massifs, among which the richest in this metal is the Djakovo Massif (with more than 25 smaller deposits), whose reserves have been for the most part exhausted. Among deposits of *molybdenum*, Mackatica represents the largest deposit of this metal in Southeastern Europe. *Copper* is one of the most economically important mineral raw materials on the territory of Yugoslavia, and it occurs in 25 deposits concentrated in the Bor - Majdanpek and Ridanj - Krepoljina zones. Of similar economic importance are *lead* and *zinc*, deposits of which are likewise significantly represented. There are today 13 active mines of lead - zinc (polymetallic) ore. These mines are concentrated in the Serbo - Macedonian Metallogenic Province. Ore of *aluminum* (bauxite) is present in limited reserves associated with limestone terrains in the Dinaric Province. *Antimony* reserves are numerous in Southwest Serbia, i.e., part of the Dinaric Province. The distribution of occurrences and deposits of *gold* is limited to the eastern half of Serbia. *Mercury* ore (cinnebarite) occurs in several places.

Non - Metallic Raw Materials. Deposits of non - metals are many and diverse. Among 50 kinds represented, the following raw materials are undoubtedly the most important economically: 1. *Magnesites*, formed in peridotites of the Serbo - Macedonian Province, with production of 253,000 t (in 1990); 2. *dolomite*, with many deposits; 3. *phosphorite*, whose main deposit is the Lisina deposit near the town of Bosiljgrad; 4. *cement marl*, a component of several geological formations, with significant reserves; 5. deposits and occurrences of *asbestos*, associated with ultrabasites of the Vardar Geotectonic Zone (Strugari, Korlace, Borance, and Stave); 6. *limestones*, among the best represented of non - metallic raw materials, with wide distribution in the Dinarides and Carpatho - Balkanides; 7. *quartzites* and *quartz sand*; 8. *clay* deposits, which are numerous in Serbia (especially widespread are ceramic and brick clays); and 9. Occurrences and deposits of *fluorite*, with significant reserves in the vicinity of Krupanj.

Of special interest to us are various ecological non - metals to be discussed later. Here we single out *medicinal non - metals (peloids)*, fine - grained unbound

sediments or broken - up and pulverized solid rocks that in combination with water form a "batter" used in balneotherapy. Rocks with granulation of under 2 mm (clays, carbonaceous clays, oil shale, chalk, tuffites, etc.) are used, or solid rocks that are broken up to achieve the appropriate granulation (bentonite clays, limestones, volcanites and tuffs, crystalline schists). Like various other ecological non - metals, the given raw materials are very well represented on the territory of Serbia (Tomanec et al., 2001).

Mineral Raw Materials - Risks and Positive Effects

In many areas of exploitation and processing of mineral raw materials (including energy sources), the environment is disturbed to a greater or lesser extent, often with serious consequences to public health. However, it is unrealistic to expect significant reduction in the scale of such activity. Except for products of agriculture, fisheries, and forestry, practically everything that humans use in the modern world - oil, gas, coal, metals, non - metals, mineral fertilizers - comes from the Earth.

In contrast to agricultural, forest, and water resources, the majority of mineral resources are unrenovable, and they are exhausted in the process of exploitation. On the other hand, the expenditures involved in building constantly growing cities rise considerably due to long - distance transport of geological building materials. The global problem of permanent or sustainable development of mankind will unquestionably depend largely on the management of mineral resources, i.e., protection of raw materials from exhaustion and irrational exploitation.

At the present time, the shortage of energy throughout the world as a whole is not acute, even in the case of oil, not counting political aspects of the problem and international disputes, which especially in the last decades have led to devastation of territories, injury and death of people, and pollution of the environment. Without doubt, we need to begin using ecologically more suitable new sources as soon as possible, so as to avoid restrictions in energy use that would entail an appreciable decline in the standard of living.

Environmental problems remain to be resolved. Use of some new forms of energy resources prompts debates as to adverse consequences, above all to human health. For example, public protests occasioned by the serious consequences of possible breakdowns in nuclear power plants have halted the construction of new units in certain places in the USA and other countries. In utilization of coal, on the other hand, many difficulties arise due to release into the atmosphere of oxidized sulfur during coal burning, with unfavorable consequences such as smog and acid rain⁴⁹.

⁴⁹ Another problem very present in the world is that of underground combustion of coal, with numerous consequences to the environment. The given phenomenon is especially present in China, USA, Australia, and India. In Northern China, for example, under-

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Underground combustion of coal, a natural phenomenon is especially common in northern China, for example, under-

For this reason, gasification of coal and production of gasoline from coal increasingly suggest themselves as possible solutions to the problem of effective utilization of the world's enormous coal reserves with minimal damage to the environment. Waste disposal represents another big problem throughout the world. All of this will be more closely considered at a later time in the text on anthropogenic factors. Risks and positive effects in areas of mineral deposits under natural conditions are treated below.

The service to civilization that certain microbes performed by causing coal to be formed from plant remains was enormous, but they also created the source of great disasters, namely *marsh gas* or *methane*. That gas killed thousands of miners in Couriere (France), and in many other coal mines throughout the world. On the other hand, enormous potential resources of methane - interesting from the industrial and balneological standpoints - are dissolved in many water - bearing horizons of the Earth's crust. The best - known zone of anomalous pressures is found in the United States, along the coastline of Texas and Louisiana. In this zone (which is 100 km wide and several hundreds of kilometers long), sedimentary rocks contain layers with dissolved methane in hot brines at very high pressures.

Pollution of the environment by *ecologically toxic chemical elements* (primarily mercury, cadmium, lead, arsenic, chromium, copper, nickel, fluorine, and sulfur) represents an even more important problem in evaluating the influence of mining production and planning protective measures. In addition to this, there are also problems linked with dispersion aureoles as natural sources of pollution in regions of mineral deposits. There is no need to emphasize particularly the fact that occurrences and deposits (and thereby dispersion aureoles) are associated with certain geological (metallogenic) formations, as is the case, for example, with the extensive diabase - chert formation in Serbia or the sedimento - volcanogenic formation in the wider vicinity of Konjic in Bosnia - Herzegovina.

In contrast to many other pollutants, chemical elements do not get involved in processes of self - purification: their concentration in the course of migration is only diluted. Moreover, chemical elements (and above all the most toxic heavy metals) take part in all types of migration and biological circulation, which inevitably leads to pollution of vitally important media, namely water, air, and food. Numerous studies have shown the ability of elements to accumulate in living organisms, with toxic influence on many of their systems, such influence resulting in the

ground coal fires are present over an area about 5,000 km long and 750 km wide (Fig. 2.34.) (X. M. Yhang, C. J. S. Cassells, and J. L. van Genderen, 1999).

incidence of specific diseases, weakening of immunobiological reactions, and aggravation of overall nonspecific ailments (especially of the allergic type). Typical further consequences of the negative action of toxic chemical elements on living organisms include, above all, disturbance of the reproductive function, decline of bioproductivity, and mutagenic and carcinogenic effects. For all these reasons, we shall dwell on natural geochemical anomalies and components of the environment linked with natural processes of migration and dispersion of substances from deposits. This is especially important because in regions of mining activity, plans are usually made for the creation of a developed economic infrastructure, including settlements, agricultural concerns, water - engineering projects, and recreation zones.

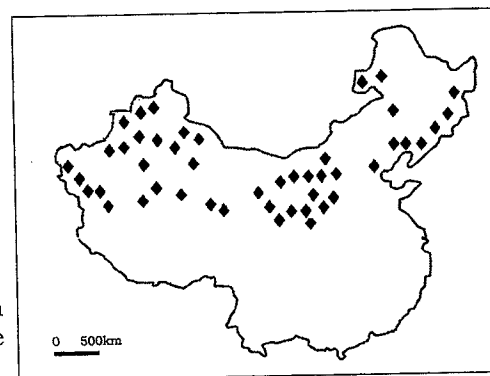


Fig. 2.34. Map of locations with distribution of fires in subsurface deposits in Northern China.

A field with increased content of ore elements and elements accompanying them is formed in rocks, water, plants, and the atmosphere around every ore body. This is the so - called *dispersion aureole* of the deposit. The rocks surrounding ore bodies contain a fairly high concentration of the chemical elements that mark the *primary aureole*, which is formed at the same time as the deposit. The dimensions of primary aureoles and quantity of their chemical elements usually exceed parameters of the ore bodies themselves (Fig. 2.35.). Their composition includes both the main elements of the deposit and a whole series of accessory elements - mercury, lead, zinc, copper, cadmium, arsenic, silver, fluorine, bismuth, cobalt, indium, selenium, tellurium, iron, and sulfur - currently held to be ecologically toxic and hygienically dangerous.

Disturbance of the deposit sends elements into biogenic, physico - chemical, and mechanical migration. For this reason, the soil in valleys and on slopes or in streams near the deposit contains greater quantities of indicator elements than in the more distant surroundings (Fig. 2.35.). The

unobiological reactions, especially of the allergic action of toxic chemical pollutants, disturbance of the natural environment, and mutagenic and carcinogenic effects shall dwell on natural environment linked with substances from deposits. In the case of mining activity, plans for economic infrastructure, engineering projects,



elements and elements in plants, and the atmosphere contain a fairly high concentration of indicator elements mark the *primary aureole* of the deposit. The dimensions of the primary aureole usually exceed hundreds of meters (Fig. 2.35.). Their composition includes a whole series of elements: uranium, cadmium, arsenic, silver, mercury, iron, and sulfur - chemically dangerous.

Due to biogenic, physico-chemical reasons, the soil in valleys contains greater quantities of indicator elements in the surroundings (Fig. 2.35.). The

extent of such *secondary dispersion aureoles* in loose rocks and soil is measured in hundreds and thousands of meters.

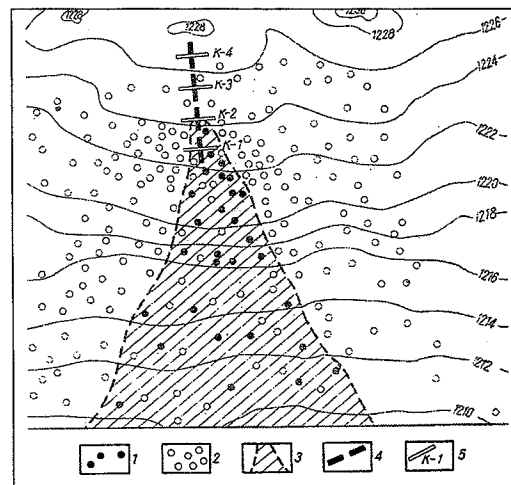


Fig. 2.35. One of typical examples of secondary dispersion aureoles in the area of wolframite deposit. 1 - quartzite particles with wolframite; 2 - granite particles with quartzite; 3 - aureoles of scattering of mining particles; 4 - position of ore vein; 5 - exploratory trenches.

Underground and surface water in the near or distant surroundings of ore bodies also contains greater amounts of indicator elements than at more remote locations. The dimensions of *hydrogeochemical (water) aureoles* likewise attain hundreds and thousands of meters. When plants take root in an ore body or a dispersion aureole and absorb indicator elements from them, a *biogeochemical aureole* is formed in the plants. With elevated content of methane, carbon dioxide, radon, mercury vapor, and other indicator gases in air of the soil, *gas aureoles* are recorded around oil and gas deposits, deposits of radioactive ores, coal-bearing and mercury deposits, and deposits of other kinds.

By determining the content of indicator and accessory elements in rocks, soil, water, plants, and the atmosphere, it is possible to establish the extent and chemical composition of dispersion aureoles. It is much easier to find ores when an aureole is discovered. It is also easier to establish the risk to public health in given regions, which is of greater interest to us.

Water aureoles of ore deposits as a rule are of a multi-component nature. In complex study of the Chu - II' ore zone - one of the important metal-bearing regions of Kazakhstan - investigators isolated and described more than 130 hydrogeochemical anomalies with high content

(150 - 170 mg/l) of mercury, copper, zinc, lead, molybdenum, aluminum, titanium, cobalt, vanadium, niobium, fluorine, etc. Another characteristic of water aureoles is that their content of macro - and microelements often is not constant in time, but instead depends on the level of precipitation.

In a zone of sulfide deposits with oxidative conditions, oxidation of sulfide occurs in addition to other reactions of biochemical transformation (oxidation). Thus, in groundwater near sulfide ore bodies, acidic sulfate water with high content of heavy metals and formation of secondary minerals can occupy large areas. According to S. L. Shvertsev (1973), maximal metal concentrations in such water can attain the following values (g/l): Cu, 45.6; Zn, 12.0; Co, 3.6; As, 0.4; and Ni, 30. Due to combined action with the surrounding natural environment, water dispersion aureoles undergo differentiation, with the result that it is possible to speak of zonality of their composition. In arid regions, the chemical composition of water aureoles depends to a significant extent on the influence of processes of continental salinization, with formation of soda, sulfate, and chloride water of high mineralization and elevated content of arsenic, iodine, molybdenum, selenium, uranium, etc.

One of the most important problems linked with mine water of sulfide deposits is the problem of protecting the environment from pollution, above all pollution of water resources. In the Borska and Kriveljska Rivers and lower course of the Timok, for example, the flora and fauna have been completely destroyed under the influence of "blue" copper - bearing water. The content of sulfate in such water varies from 1.24 to 2.78 g/l, copper content from 0.5 to 1.7 g/l, and iron content from 2.5 to 3.0 g/l.

In any event, such regions must be the subject of careful geochemical and hydrogeological investigation, since they carry potential risks to human health, whether through water or through soil (food). The negative and positive influence of macro - and microelements on human health will be discussed in greater detail in a special section of the book.

In neutral and weakly alkaline environments in the vicinity of sulfide deposits, conditions of formation of the chemical composition of groundwater are sharply altered, and its enrichment with heavy metals occurs for the most part at the expense of electrochemical dissolution.

Water in **zones of silicate, carbonate, and oxide mineralization** with its dispersion aureole differs significantly from that of sulfide deposits. Enrichment of such water with heavy metals in zones with oxidative conditions essentially occurs through the action of physical and chemical weathering and radioactive processes. With respect to the solubility of ore minerals and degree of groundwater enrichment with the corresponding metals, non - sulfide deposits can be arbitrarily divided into three groups: 1. *boron deposits*; 2. *deposits of silicates, carbonates, and oxides of various metals*; and 3. *deposits of radioactive elements*. The content of boron in

molybdenum, aluminum, etc. Another characteristic and microelements often the level of precipitation.

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and **oxide mineralization** om that of sulfide deposits. s in zones with oxidative a of physical and chemical pect to the solubility of ore nt with the corresponding divided into three groups: *ates, and oxides of various* s. The content of boron in

water of its deposits can very often attain 100 mg/l, and water aureoles are also characterized by high content of accessory elements, namely fluorine, copper, arsenic, mercury, etc. Increased concentrations of *aluminum*, especially in compounds with organic components, are peculiar to regions of bauxite deposits under conditions of a humid climate. *Deposits of the second group* are characterized by lower concentrations of elements in water of ore bodies and dispersion aureoles, while water of *uranium* deposits under oxidative geochemical conditions has a very unique composition. The highest concentrations of uranium, radium, radon, and accessory elements (arsenic, fluorine, lead, copper, etc.) are linked with water of metallo - riftogenic and hydrothermal uranium deposits. Moving toward the peripheral zone of a water aureole, only the content of uranium and sometimes that of radon and highly migrative accessory salts are above background levels.

A very rich spectrum of components is formed in water aureoles of **petroleum deposits**. Together with increase in total gas saturation of water following contours of the deposit and the degree of its enrichment with methane homologs, biogenic nitrogen, organic acids, benzene, toluene, phenol, and other organic components, anomalies are also recorded here with respect to sulfur, heavy metals, pure phosphorus, radio - and carbon isotopes, and nitrogen.

Significant enrichment of groundwater in the vicinity of **salt deposits** is primarily dictated by the high solubility of salts, especially chloride salts. Thus, mineralization of water as a rule comprises about 300 g/l near halite deposits, which are very widespread. When magnesium salts occur in salt deposits, magnesium ions can prevail over sodium ions. Water of this type has high mineralization (above 200 g/l) and a significant quantity of microcomponents. Groundwaters of potassium deposits are in fact brines with high concentrations of chlorine, bromine, calcium, sodium, magnesium, potassium and various microcomponents. Apart from very significant application in industrial production of salt and soda and use in spa and recreational tourism, highly mineralized saline waters represent a threat to the environment: saline springs and watercourses destroy the surrounding plant and animal life and indirectly act adversely on human health. Moreover, due to melting of salt deposits, empty spaces are created and terrain subsidence with consequent material damage occurs in zones of direct exploitation (for example, near Tuzla in Bosnia - Herzegovina). For all that, we must not forget the great importance of salt in human life, especially since it is possible through preventive exploration and regionalization to isolate zones of occurrence of unfavorable elements linked with mineral raw materials in general.

Radioactive Elements in Rocks, Soil, and Groundwater

Pitchblende was probably known already in the Bronze Age as a mineral of unknown composition to miners of cassiterite in Cornwall (Southwest England), where these two metals occur together. It is quite certain that this black ore came to man's attention already in 1512, when exploitation of silver began in the now famous mine of St. Joachimsthal (currently Jahimova in the Czech Republic). Finally, the German apothecary Martin Heinrich Klaproth established 210 years ago that the black resinous ore in question is a mineral of a new element, which he named after the planet Uranus (discovered in 1781). With the discovery of radioactivity 104 years ago, the new element of unusual behavior entered the annals of the so-called *atomic era*, marking it above all as material for a heretofore unseen super weapon and an excellent source of energy.

Since the beginning of the 50's of the last century, we have been witness to the greatest search for some ore in the history of mankind. Thus, apart from Jahimova and Cornwall, the Urgeirica Mine of uranium (radium) was opened around 1912 in Portugal. The following year, the Shinkolobwe deposit was discovered in what was then the Belgian Congo (Zaire), while the Eldorado deposit was discovered in 1931 on the shores of Great Bear Lake in Northern Canada. Mass construction of nuclear power plants starting in the 1960's led to spectacular discoveries of major uranium deposits, and already at the outset of the next decade the Cigar Lake deposit was discovered in Canada. This deposit is the unsurpassed world record holder with more than 10% average uranium content and more than 10,000 t of reserves of this metal^{50,51}. Deposits and reserves of uranium were discussed in greater detail in the chapter on energy raw materials.

Characteristics of Natural Radionuclides

Radioactive elements and ionizing radiation are present everywhere in space and on our planet as well. Very high - energy particles reach the Earth's surface from the depths of space in the form of *cosmic radiation* and *electromagnetic radiation* of varying energy from the stars. There is also the *radioactive radiation* of radionuclides dispersed in the Earth's

⁵⁰ Already in 1980 there were 186 nuclear power plants using U_{235} in the world, and these plants satisfied 7.6% of all energy needs (as much as 45.5% in the USA and 28% in Europe).

⁵¹ It is interesting that a phenomenon observed at the Oklo deposit in Gabon suggested the possibility of nuclear reactors. To be specific, it was found that losses of U_{235} in ore are a consequence of consumption in the process of fission, which here took place in a natural nuclear reactor. It is believed that the circumstances that made a chain process of fission possible in Oklo do not represent an exceptional case in the Earth's past.

Underground water

Bronze Age as a mineral in Cornwall (Southwest). It is quite certain that in 1512, when exploitation of Joachimsthal (currently German apothecary Martin) the black resinous ore in the planet named after the planet of radioactivity 104 years ago and the annals of the soil for a heretofore unseen

In the last century, we have been through the history of mankind. The Jagersfontein Mine of uranium in the following year, the Belgian Congo in 1931 on the shores of the construction of nuclear reactors. The discovery of major deposits in the next decade the Cigar Lake deposit is the unsurpassed uranium content and deposits and reserves of uranium in the chapter on energy raw

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crust. Radioactive elements from rocks enter water and the atmosphere as a result of migration and through them gain admission to the biosphere and the forms of life in it. Contributions to radioactivity of the atmosphere are also made by radionuclides that are formed as a result of human activity (whether in processes of fission or by irradiation of stable isotopes in nuclear reactors or irradiation of high - energy particles) and which today unquestionably represent the most numerous and diversified sources of radiation in the world.

The abundance of radiation in the Earth's remote past was considerably greater than today. To put it more precisely, amounts of U_{238} in the Earth's crust have due to decay been reduced since its formation by exactly half, while amounts of U_{235} have shrunk approximately fivefold. Thus, the natural radioactive elements that we encounter today represent only a part of the abundant radionuclides that once existed, but which have disappeared due to radioactive decay. Their half - lives were short in relation to the Earth's lifetime.

By *radioactivity* we mean instability of the nucleus, while *radioactive decay* refers to the transformations undergone by radioactive isotopes. The main types of radioactive decay are *alpha (α) decay*, *beta (β) decay*, and *gamma (γ) decay*. *Alpha rays* are positively charged helium ions, and this radiation occurs mainly in the heaviest radionuclides. It has the greatest strength of ionization, but passes poorly through different materials. Although the range of action of alpha radiation is limited, radioisotopes that emit alpha particles penetrate the organism and cause serious damage to it. *Beta particles* represent elementary particles carrying a negative (more rarely positive) charge, i.e., electrons. They are more penetrative than alpha particles. Because they have lower ionizing ability, these particles are not as dangerous as alpha particles to living cells. *Gamma radiation* is photonic energy emission, and gamma rays are identical in nature to X - rays, but of different origin. In contrast to α - particles, gamma rays can penetrate soil and rocks to a depth of the order of a meter, as well as the whole human body. The biological damage caused by gamma radiation is very similar to that caused by X - rays.

There are three main series of radioactive decay: *the uranium - radium* (U_{238} - Ra_{226}) series; *the uranium - actinium* (U_{235} - Ac_{227}) series; and *the thorium* (Th_{232}) series. The final (stable) members of the series are lead 206, 207, and 208. Apart from the indicated series, there exist in nature many other radionuclides that exert very little influence on the overall background of radiation. The most significant among them is *potassium - 40* because it makes large contribution to total gamma ionizing radiation on the surface of the Earth due to its relatively high content (2%) in the Earth's crust.

About 63 radionuclides occur in nature. On the basis of their half - lives, they can be divided into two groups: *long - lived* (U, Th, Re, Rb, V, K, etc.); and *short - lived*. The long - lived category includes radionuclides whose half - life exceeds a hundred million years and which remain present in nature for billions of years (the so - called *primary radionuclides*: U_{235} , U_{238} , Th_{232} , Rb_{87} , K_{40} , etc.). The half - life of

short - lived radionuclides amounts to only several days, minutes, or seconds (Ra_{223} , Rn, Po, Bi, Ti, etc.), or several years in exceptional cases. Let us dwell on the more important radionuclides (radioisotopes).

Natural uranium consists of three isotopes (U_{238} , U_{234} , U_{235}). It exists exclusively in the four - valent state in the UO_2 and UO_3 oxide (uranate) form (uraninite and pitchblende being mixtures of these two oxides) or as the uranyl complex UO_2^{2+} , of which a large number of minerals are built. Apart from uraninite, minerals of the best - represented isotope of uranium (U_{238}) are also known, namely torbernite and carnotite. It is held today that uranium in soil is found in two main forms, inert and mobile. The *inert form* of uranium has no significance whatever for radioecology and biotechnology, even though more than 97% of total uranium in the environment belongs to this form. The *mobile form* of uranium - although it represents only 0.1 to 3% - is of great biological and ecological significance, since through the process of ionic alteration it can pass from the soil into plants or penetrate plants in the form of complex compounds with organic acids secreted by the root system. The solubility of many uranium compounds in water is fairly high, with the result that almost all groundwater is to a certain extent radioactive. Uranium in solution circulates only in the form of uranyl complex and can be adsorbed by different materials (zeolites, clays, natural colloids).

The most widespread isotope of *radium* Ra_{226} is a product of decay of U_{238} (half - life: 1622 years). Another isotope of this element is Ra_{228} , a product of decay of thorium Th_{232} (half - life: 67 years). Radium 226 in nature is found in varying concentrations in virtually all kinds of rocks and soils that contain natural uranium, occurring in the greatest amounts in the mineral uraninite. Radium Ra_{228} is the only isotope of this element that is a beta - emitter. In nature it is found in soil and water in a ratio of 1:1 with Ra_{226} . However, because of the different half - lives of these two radionuclides, Ra_{228} disappears faster from organisms, so that in older persons this ratio is displaced in favor of Ra_{226} .

Radon is a radioactive inert gas formed by emanation of Ra_{226} . It is an invisible gas without taste and odor that is seven and a half times heavier than air. It has 12 short - lived isotopes. The most widespread of these isotopes is Rn_{222} with a half - life of 3.8 days. The remaining isotopes of radon have a very short half - life (several seconds) and are of no radioecological significance. Rn_{222} is found in rocks, soil, and groundwater and air. It migrates readily along fissures and faults in the Earth's crust, often over great distances from the place of its formation. Elevated concentrations of this gas are associated with deposits of uranium and phosphorus that have high radium content, areas with greatly cracked granitoids, and certain thermal springs. Radon is considered to be a very important source of natural radiation.

Among **cosmogenic radionuclides**, the best - known are *radioactive carbon* C_{14} and *tritium* H_3 , while the other radionuclides of this group are without radioecological significance. In the phase of life of organisms, carbon and organic substances are found in virtual equilibrium with carbon from the atmosphere, i.e., the ratio between radioactive carbon C_{14} and stable carbon is the same as in the atmosphere. After the death of organisms, the equilibrium of C_{14} is no longer maintained and its concentration decreases at a rate of 50% every 5,700 years.

This regularity makes it possible to ascertain the age of organic matter by determining the presence of C^{14} . With a half-life of 12.26 years, the radioactive isotope of hydrogen tritium H_3 is continuously formed in the atmosphere by the interaction of cosmic radiation with nuclei of nitrogen and hydrogen atoms. Up until the period of more intensive nuclear tests in the 50's of the 20th Century, the content of H_3 in water ranged from 222 to 888 mBq/l, only to increase five- to tenfold and more in the course of nuclear testing (for example, a level of as much as 2,937 tritium units was measured in Ottawa in 1954).

Among *radionuclides of artificial origin* (formed during nuclear reactions in production of atomic energy, during tests of nuclear weapons, etc.), the most interesting are *strontium* Sr_{90} and *cesium* Cs_{137} . With about a thousand other known artificial radioisotopes, they represent sources of radioactive pollution that are dangerous to human health. On the other hand, owing to the possibility of reliably monitoring them by measuring radiation, they have found very diverse applications in many branches of medicine, industry, science, and other domains of human endeavor.

Concentration of Natural Radionuclides in Rocks and Soil

Table 2.12. presents the content of uranium and thorium in different rocks and some magmatic rocks of former Yugoslavia. Perceptible variations in the content of those two radionuclides are also present in acidic or intermediate alkaline rocks, but uranium and thorium are in the same constant ratio of 1:3.5.

Table 2.13. gives average content of uranium and thorium in magmatic and sedimentary rocks. It follows from the table that granites and granitoid rocks are richest in these elements, but their share is also appreciable in sedimentary rocks. Minerals of the feldspar and mica group are of greatest significance for the concentration of these elements in granitoids. Since these are very widespread minerals, considerable concentrations of uranium can be released from them in spite of relatively low uranium content. Considerable concentrations of uranium in granitoids are linked with zircon and monazite. Monazite is regularly found in the alluvial sediment of rivers passing through regions built of rocks containing it (sediment of the Pek River, for instance)⁵².

The concentration of uranium in soil is very different in different parts of the world (Table 2.14.), ranging somewhat more often in the interval of from 7.4 to 37.7 mBq/g, although there are regions in the world (Peru, for example) where it attains 76.2 mBq/km².

Thorium is found in soil in concentrations ranging from 8.1 to 33 ppm. Its main minerals - thorianite and thorite - readily pass from granites and pegmatites into debris. As the main economically significant

⁵² As for uranium, it is interesting to note that the bulk of ore is obtained from deposits in sandstones and conglomerates, the rest from uranium-bearing phosphates, schists, granites, and granodiorites.

carrier of thorium, monazite is an accessory mineral considerably more frequent than the two minerals mentioned, and much more of it is present in debris, especially in sediments of marine beaches. The insolubility of thorium and its very low specific activity cause thorium to be found in quite small amounts in the biological world, i.e., they account for the relatively slight radioecological significance of this radionuclide.

TABLE 2.12.

Contents of U and Th in some magmatic rocks of former Yugoslavia. 1- Marlovo; 2 - Kratovo; 3 - Timok - Pek; 4 - Gnjilane; 5 - Cer; 6 - Bukulja; 7 - Janja; 8 - Bujanovac.

Ppm	1	2	3	4	5	6	7	8
U	9.7	5.7	1.3	11.7	4.5	4.3	6.4	1.9
Th	33	25	4.6	49	13	15	29	4.5
Th/U	3.4	4.4	3.5	4.2	2.9	3.2	4.5	2.4

TABLE 2.13.

Average concentrations in U, Th, Pb in magmatic and sedimentary rocks (ppm).

Type of rock	U	Th	Pb	Th/U
Granite with low Ca	3.0	17.0	19.0	5.7
Granite with high Ca	3.0	8.5	15.0	2.8
Syenite	3.0	13.0	12.0	4.3
Basalt	1.0	4.0	6.0	4.0
Ultramafic rocks	0.001	0.004	1.0	4.0
Clay schists	3.7	12.0	20.0	3.3
Sandstones	0.45	1.7	7.0	3.8
Carbonates	2.2	1.7	9.0	0.77
Deep - sea clay	1.3	7.0	80.0	5.4

TABLE 2.14.

Uranium concentration in soil (B.Petrovic, R.Mitrovic, 1991).

Area	$\mu\text{g U/g}$
New Zealand	60
USA	0.2 - 47
France	1.2 - 37.6
Gabone	1 - 100
Poland	0.5 - 12.5
Former USSR	0.2 - 13
Japan	0.7 - 1.9
Serbia	0.08 - 5.9

Radionuclide Concentration in Water

In nature, all surface and groundwater contains radioactive elements (except thorium) in measurable quantities, i.e., it is radioactive to one

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thorium to be found in
., they account for the
radionuclide.

r Yugoslavia. 1- Marlovo; 2 -
; 7 - Janja; 8 - Bujanovac.

	7	8
3	6.4	1.9
5	29	4.5
2	4.5	2.4

sedimentary rocks (ppm).

Pb	Th/U
19.0	5.7
15.0	2.8
12.0	4.3
6.0	4.0
1.0	4.0
20.0	3.3
7.0	3.8
9.0	0.77
80.0	5.4

.Mitrovic, 1991).

g
7
7.6
0
2.5
3
.9
5.9

ins radioactive elements
, it is radioactive to one

extent or another. However, in the case of uranium behavior in the presence of water under exogenous conditions, we are dealing with very dynamic and often reversible processes of dissolution, transport, fixation, and renewed dissolution, the chemical nature of which has not yet been elucidated. These processes accordingly are hard to foresee, and predictions of places where they might occur are most often dubious. It is therefore understandable that uranium concentration in natural water fluctuates within a very wide interval, from 0.05 to 10 ppb. The average content of uranium in water is approximately 1.5 ppb. It is usually more than 200 ppb in groundwater that circulates through uranium - rich rocks. In the United States, for example, the concentration of Ra₂₂₆ varies within limits of from 370 mBq/m³ (Portland, Oregon) to 2.14 Bq/m³ (Joliet, Illinois). According to E.M. Durrance (1986), uranium content comprised 0.07 - 7 ppb (0.5 ppb on average) in 100 tested Russian watercourses; 0.1 ppb on average in American rivers; 1 - 10 ppb in surface water of uranium - bearing terrains; 1 - 150 ppb in groundwater of such terrains; and 15 - 400 ppb in water inside uranium deposits.

Radon Concentration in Rocks, Soil, and Groundwater

Radon is the heaviest of all inert gases, but like all of them it is exceptionally capable of migration. Of gases most often present in the Earth's crust, only CO₂ is more soluble than radon. For this reason, radon is often found in water, which is the main agent of distant transport of this gas. It is especially present in groundwater and (under special conditions) can be transported as far as many kilometers. The indicated high ability to migrate enables radon to move relatively easily and rapidly through rocks impermeable to water (schists for instance) and emanate from rocks into surrounding water or air. In tectonic zones, all gas formed from radium can be released from rocks (the coefficient of emanation is equal to 100%). Apart from groundwater, the main channels or conduits of radon transport are usually fault fissures⁵³. It should be kept in mind that the existence of most radon hydrochemical anomalies in the vicinity of tectonic zones is determined not only by migration of radon from greater depths, but also by the fact that the structure of such zones makes it possible for formations of uranium ore to come into contact with groundwater and be degraded by it.

Background concentrations of radon in the air of soil and in groundwater are of a predominantly local nature and most often depend on the rock substrate. Thus, for example, T. Tadolini and M. Spizzico (1998) cite experimental results from the karst region of Apulia in Italy,

⁵³ In the presence of pre-seismic tensions, fault fissures open and radon concentrations increase, which is why this gas is taken as one of the possible indicators (predictors) of earthquakes.

where they analyzed the ratio of radium in terra rossa (as the primary source of this gas) and radon 222 in groundwater (Fig. 2.36).

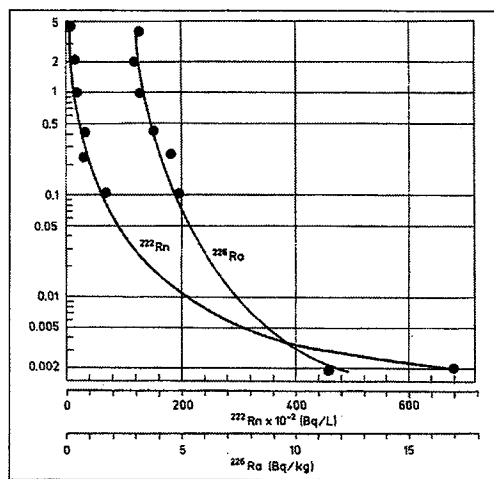


Fig. 2.36. Relation between grain - size and Ra_{226} activity in footwall of terra rossa and appropriate activities of Rn_{222} in water (T. Tadolini, M. Spizzico, 1998).

Radon content in groundwater varies from 3.7 to 1.11×10^3 Bq/l, the average approaching 74 Bq/l or somewhat exceeding it. The greatest concentration of this gas for different regions varies from 1.65×10^3 to 14.8×10^3 Bq/l. Groundwater with Rn concentration above 1.85×10^2 Bq/l is considered radioactive, while radon waters of high concentration contain more than 7.4×10^3 Bq/l. One of the extreme concentrations of this gas in water (20×10^3 Bq/l) was measured in the vicinity of Skopje in FYROM (Former Yugoslav Republic of Macedonia), and average content in water of springs in the immediate surroundings was of the order of 40 Bq/l. For the deep tectonic zones of the Caucasus, Ural, and Tien - Shan Mountains, S. L. Shvartsev et al. (1982) reported that radon concentration varies within an interval of from 133.2 to 277.5×10^3 Bq/l.

Natural Radionuclides and Risks

In their paper "**Two centuries since discovery of the chemical element uranium**" (1989), V. Omaljev and A. Antonovic wrote as follows: "*Uranium today is tasked with a heavy burden of guilt for current and future radioactive pollution of the planet. Especially worrying are uncertainties regarding possible (uncontrolled) mutagenic changes in living organisms, man above all. Systematic biological and medical investigations of this question for practical purposes began only after the atomic bombing of Japan, and a period of 45 years is too short to see the long - term risks.*" The authors ask whether this means the end of the rule of uranium.

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Together with economic and other global questions, safety is certainly a pressing concern, and most people hold it to be the most alarming problem of the present day. In the event that nuclear power plants prove to be faulty for any reason and radioactive substances are emanated into the environment or if nuclear tests are carried out and nuclear weapons used on a massive scale, the consequences could be catastrophic. *At the present level of civilization, the modern world is increasingly destructive, and the consequences are unfortunately moving ever closer to a state of catastrophe.* We note only what was done recently to the population and environment of Iraq, Yugoslavia, and Bosnia and Herzegovina by tens of tons of depleted uranium used in the making of projectiles.

The anthropogenic component of the biosphere's radiation background is what has raised this global question. However, even after eventual cessation of the use of uranium, there would remain a group of natural radionuclides with all potential risks to human health⁵⁴. According to the results of studies performed to date, natural radiation of the lithosphere (biosphere) is responsible for one fourth of the total *basic radiation load* of all living beings. To be specific, the role of natural radionuclides and their radiation as sources of radiation risk to the biocenosis has been present since the beginning of life on Earth. Thus, natural radionuclides have through radiomutations not only affected the evolution of living organisms, but also influenced the dynamics of equilibrium of ecological systems.

In contrast to the large doses of ionizing radiation produced predominantly by fabricated radionuclides, it is fairly logical to maintain that in the case of so - called *small doses*, i.e., doses that do not cause clinical symptoms but which exert distinct bionegative action, natural sources of radioactive radiation assume the leading role. It is known that opinions among radiobiologists are greatly divided about the effect of small doses. Still, many authors hold that a slight increase of absorbed radiation raises the probability of cataracts, increases the incidence of radiation illness, contributes to the formation of tumors, shortens life expectancy, and slows fetal development in the mother's uterus. Following the engagement of world experts on an international project during the period of 1980 - 1984, it was concluded (among other things) that: 1) ***small doses of ionizing radiation exert distinct bionegative action*** (boldface mine - M.K.); 2) *the bionegative action of small doses of ionizing radiation conforms to a linear dependence with no threshold*; 3) *since it is impossible to isolate small doses of ionizing radiation as one of a large number of carcinogenic factors, it is necessary to prevent increase in the level of all of the indicated*

⁵⁴ According to propositions of the International Committee for Radiation Protection published in 1976, *risk* means the probability that some organism will experience a certain harmful effect as a result of irradiation.

factors; and 4) *we need to monitor constantly the radiation load of the population through the whole food chain, including cultivated plants, livestock, and foods of plant and animal origin.*

Medical geology can make a great contribution in establishing natural preconditions for occurrence of small doses of ionizing radiation in rocks, soil, and water, and in planning measures designed to lower the level of carcinogenic factors. This is especially true because the content of radioactive elements in the natural environment is not always the same, and organisms inhabiting a given region are exposed to radioactive radiation of varying strength: greater in some cases, lesser in others. We shall therefore dwell in the text to follow on certain geological factors that deserve special attention.

The first and very important step in investigating a region of interest is to isolate **uranium - bearing rocks and formations** in it. We have already discussed the kinds of rocks (such as acidic granites) that are potential carriers of radionuclides. However, it was not stressed that uranium - bearing geological formations can potentially encompass enormous areas and thereby increase the natural radiation load of a large number of people. Thus, schists rich in organic substances and uraninite (for example, the Chittanunga formation in the states of Alabama and Kentucky, covering an area of the order of 100 thousand km²) occur in many regions of the world. In the United States, the Phosphoria formation (phosphate deposits with 0.003 - 0.03% uranium) and other formations on the Colorado Plateau and in Eastern Utah, Northeast Arizona, and Northwest New Mexico encompass an even greater area. The Francevillien formation in Gabon covers an area of about 35 thousand km². When it is taken into account that the Oklo deposit or phenomenon (a natural nuclear reactor) is found in that formation, it is easy to grasp the potential danger from constant reactions of fission in that region. Large amounts of thorium are found in sands of marine beaches in Southern India and (to some extent) Australia. By conducting regional geomedical investigation (mapping) of the natural radionuclides in rocks and soil in an area of interest to us, we are able to isolate *radioecogeological ranges* (regions) in which the biocenosis (including human beings) carries a certain radiation load. It is understandable that some regions of the world are well - known for high content of radioactive elements (the state of Kerala in India, the La Plata Plateau in Brazil, the wider region of the Oklo uranium mine in Gabon, etc.).

That man has been unable to adapt to natural radiation fields is shown by the results of international research indicating that regions with elevated content of natural radionuclides in rocks and soil are characterized by slow population increase, increase in the number of birth defects, increase in the number of organic diseases, and increased

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found. There is an increase in the number of birth
defects, diseases, and increased

mortality (especially among children). Complex studies on the question of
existence or non - existence of *radiogeochemical endemias* remain to be
carried out. In their book "**Radiation Hygiene in Biotechnology**" (1991),
B. Petrovic and R. Mitrovic state that there is research indicating decisive
significance of radiogeochemical endemias, but also work that negates
them. For example, English investigators maintain that elevated
concentration of radon Rn₂₂₂ in drinking water in the county of Devon
(Great Britain) represents the main cause of more frequent incidence of
malignant diseases among the population. Similar conclusions were
reached by American investigators who carried out radioepidemiological
studies on more than a million people in 111 cities in the states of Iowa
and Illinois: they assert that considerably elevated concentrations of the
indicated radionuclide in drinking water above the average level lead to
significant differences in mortality from malignant diseases of the bones
(which are manifested especially in persons more than 30 years old). Also,
Soviet investigators reported results of measuring natural radioactivity in
the bones of persons who died of leukemia and ones who died of various
injuries: the total activity of gamma - emitting radionuclides was more
than two times greater in bones of those who died of leukemia than in
bones of persons who died of traumatic causes. From the results of his
own investigations and reports of others, the French scientist Pincet
concludes that there exists a significant correlation between the level of
the radiation background in the biosphere and mortality due to malignant
diseases. It follows from all that has been said that familiarity with the
radiogeochemical regionalization of a certain area is very important in order
to establish the radiation load of the population in it: doctors need to pay
special attention to the most dangerous radioecological ranges.

Depending on the rocks from which it was formed and content of the
clay component, **soil** can be radioactively contaminated to a greater or
lesser extent. Natural radionuclides accumulated in the soil are
incorporated metabolically into plants and through contaminated food
find their way to the organism of man and animals. The given danger to
living beings understandably is especially expressed within
radioecological ranges marked by an elevated background of natural
radioactive elements. The problem is further complicated by the presence
of strontium, cesium, and other artificial products of *long - lived*
radionuclides, which will be discussed in a special chapter.

Uranium can be relatively easily transported, concentrated, and
carried away from its primary deposit, depending on geological
(hydrogeological) conditions. A very important role in this is played by
groundwater, since uranium from the moment of its oxidation and
dissolution in water moves almost freely through the Earth's crust (Fig.
2.37.). Uranium by itself is not necessarily all that dangerous, but the

products of its radioactive decay not only threaten nature with radioactive radiation, they are also toxic as elements⁵⁵. The role of aqueous solutions is therefore of primary significance for the creation of chemical dispersion aureoles of uranium and its decomposition in the surface clay layer of river sediments. We have in mind here *anomalous zones*, with uranium content of up to 200 ppb and more (as much as 400 ppb and sometimes ten times higher in mine waters). Under favorable hydrogeological conditions (for example, the presence of extended fault zones), uranium can be transported over very great distances, which must be kept in mind. Thus, for example, the origin of high uranium content (50 - 100 ppb) in one spring in Colorado is linked with rocks at least 100 km away. For all of these reasons, in hydrogeological investigations of a region, special attention must be paid to the content of radioisotopes in drinking water and water used for production of food, so as to prevent them from entering the human organism in this way.

Pollution of the environment by radioactive elements is certainly at the very top of the list of all problems that have ever existed and called for protection of nature and mankind. The complexity and danger of pollution of nature by radioactive elements have forced man to study in the minutest detail processes involving radioactive elements. Natural and artificial radionuclides introduced into the organism by ingestion or inhalation is distributed to individual organs in keeping with metabolism of the radionuclide itself and sensitivity of the organ to radiation. All of this is taken into account in estimating size of the contribution of radionuclides from drinking water, food products, and other sources of radiation to total irradiation of the population.

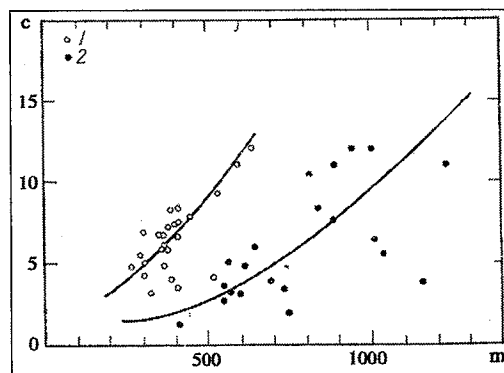
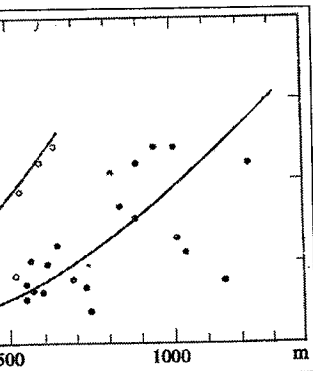


Fig. 2.37. Ratio of uranium concentration c ($\mu\text{g/l}$) and water mineralization m (mg/l) from Ogallala formation in Texas (USA)(S.N.Davis, R.J.M.de Wiest, 1966). 1- samples with HCO_3^- , over 50% of all anions; 2 - samples with HCO_3^- is less than 50% of all anions.

⁵⁵ It is interesting to note that when the most widespread U_{238} isotope of uranium is present in water, the danger of chemical toxicity causing diseases of the liver is greater than the danger from radiation.

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Radiation that from the place of its generation enters inhabited regions or regions not directly connected with production or utilization of nuclear energy should not exceed 0.5 *sieverts (Sv)*⁵⁶ per person annually. In regions with widespread radioactive minerals, the dose of background irradiation a man receives can be four times greater than the given limit, which must have greater or lesser harmful effects on human health⁵⁷. If some short-term radiation is involved, more considerable changes in the cardiovascular system can set in at a dose greater than 150 - 200 mSv, while a dose exceeding 700 - 1,000 mSv is usually fatal. The term *maximal permissible concentration* is used in practice, although it is highly questionable whether there exists a limit below which safety is guaranteed. Even if a maximal permissible dose of radiation is found, it remains for us to establish the action of individual radioisotopes, especially inasmuch as they emit different kinds of radiation and at different rates. Moreover, some elements have a tendency to accumulate in different parts of the human organism. Radioisotopes of such elements cause concentrated biological damage. For example, plutonium, radium, and strontium accumulate in the bones; iodine accumulates in the thyroid gland; and lead and water - soluble isotopes accumulate in the kidneys. The lungs are the critical organ in the case of radionuclides in undissolved form.

Differences in the biological danger caused by different radioisotopes are generally great. For example, if we compare Ra_{228} and H_3 (both with a half - life of several years and emission of low - energy beta rays), we see that the time of their residence in the human organism is different. A large part of H_3 disappears from the organism after several weeks, whereas Ra_{228} remains in the bones forever. Several other specificities in behavior of the more important radioisotopes are examined below.

The most widespread **isotope of radium Ra_{226}** is the most toxic of all inorganic components and has very strong carcinogenic action. Its biological half - life is quite long, 45 years. Its chemical behavior is similar to that of calcium. By means of resorption from the soil, it readily enters plants and later reaches man by way of animals and food of animal and plant origin. Although the average concentration of this element introduced with food is 111 - 185 mBq/day, American investigators established great variability of its concentration in different kinds of food. For example, the very high activity and content of Ra_{226} in filberts as a natural phenomenon has occupied the attention of many investigators.

⁵⁶ The *sievert (Sv)* is the biological equivalent of the *roentgen* and corresponds to the value of absorption by the body of any ionizing radiation equivalent in its activity to absorption by man of one roentgen of X- or gamma radiation.

⁵⁷ It is known that the biological consequences of ionizing radiation can be divided into somatic consequences, which are manifested on the irradiated organism itself; and genetic consequences, which result from damage to the cell's genetic material and can appear as a reaction in the organism's progeny, often several generations later.

According to B. Petrovic and R. Mitrovic (1991), many workers have investigated the content of Ra²²⁶ in the human organism and attempted to determine the radiation load of this radionuclide. It has been established that in inhabitants of Europe and Central America, its average amount in bones is 0.37 - 0.55 mBq/g of ash (which for the average man corresponds to an activity of 1.11 - 1.48 mBq). This figure is somewhat higher in regions of North America and Asia.

The presence of **radon** in water is not dangerous to human health. However, radon in the gaseous state exerts undesirable influence. Radon is fixed in the lungs as the critical organ. The real danger of radon is from its short-lived products bismuth and polonium. Radon and its products emit predominantly alpha rays, which have a very limited range, but are energetically quite strong and within a diameter of less than 1 mm cause heavy damage to the lungs. The risk of cancer is directly dependent on the concentration of this gas in the space where man spends his time and is especially high for miners working in shafts in uranium deposits.

The positive influence of radon and unknown doses of alpha rays from products of its breakdown on the human organism is widely used in balneology. Radioactive (radon) waters alter the blood picture, lower blood pressure, affect certain allergic diseases, act on functioning of the central and vegetative nervous system, stimulate many compensatory - adaptive responses of the organism, etc.

Radioactive Elements in Rocks, Soil, and Groundwater on the Territory of Yugoslavia

In Yugoslavia, the first occurrences of uranium were discovered in 1947 at the confluence of the streams Dobroticka Reka and Vojnicka Voda south of Prokuplje (M. Ristic, 1965). The uranium mineral autunite (*autunite*) was found in crystalline schists in a pegmatite vein there. After this discovery, the Geological Institute in Belgrade (Geoinstitut - Beograd) conducted intensive investigation of uranium mineralization on the entire territory of former Yugoslavia. Already in 1947, the first measurements were performed in Permian sandstones in the vicinity of the peak Zirovski Vrh about 30 km west of Ljubljana. It was subsequently established that this is in practical terms the most interesting uranium deposit not just in the former Yugoslavia, but in Southeastern Europe as well, and its exploitation was launched. It also turned out that there are many other occurrences of uranium, including uranium-bearing coals near Sinj in Dalmatia and Rasa in Istria; uranium-bearing veins of Zletovska Reka east of Kratovo and south of Prilep; in rhyolites near Radovise and Strumica; in the granites of Bukulja and the Stara Planina Mountains; occurrences in the Golija region and along the upper course of the Pcinja River; in granites of the stream Slatinska Reka; occurrences on the southern slopes of Mt. Cer; and in trachytes south of Gnjilane. In different mineral associations and genetic types, uranium mineralization is found in virtually all metallogenic provinces of the given territory. Let us dwell on interesting localities on the territory of Serbia and Montenegro, where *the Carpatho - Balkanides, the Vardar Zone, and the southern half of the*

many workers have investigated to determine the level of radon in the air. The average concentration of radon in the air is 0.37 - 0.55 mBq/g of air and its activity is 1.11 - 1.48 mBq/g of air in the Balkans, the Caucasus and Asia.

Radon is a danger to human health. However, radon is found in the lungs as well as in its short-lived products, which are predominantly alpha rays, which are quite strong and within a few days reach the lungs. The risk of cancer is high in the space where man spends most of his life in uranium deposits.

High doses of alpha rays from radon are widely used in balneology. They lower blood pressure, affect the central and vegetative nervous systems of the organism, etc.

Water on the Territory of

Radon was first discovered in 1947 at the Vojnicka Voda south of the general autunite (*autunite*) vein there. After this the Geoinstitut - Beograd concentrated on the entire territory. The first measurements in the vicinity of the peak Zirovski were frequently established that there is a uranium deposit not just in Europe as well, and its presence indicates that there are many other uranium-bearing coals near Sinj in the veins of Zletovska Reka and the pegmatites near Radovise and the Stara Planina Mountains; in the upper course of the Pcinja there are occurrences on the south of Gnjilane. In different mineralizations is found in this territory. Let us dwell on the territory of Montenegro, where the southern half of the

Serbo - Macedonian Mass can be singled out as regions with many occurrences.

1. A large number of occurrences and deposits of uranium are found in the region of the **Carpatho - Balkanides**. The area of the *Stara Planina* Mountains has been evaluated as especially promising due to elevated content of uranium in granitoids and in surface and groundwater. Granitoid massifs on western slopes in the central part of these mountains are characterized by interesting mineralization. The Janje ore field extends over an area of about 30 km² (S. Gertik, 1978). Uranium content in ore bodies here is exceptionally high, about 300 g/t (300 ppm). Investigation of up to 30 km of mine corridors was carried out in the exploratory phase. During trial exploitation from 1960 to 1966, the amount of uranium ore extracted from the deposits in Gabrovnici and Mezdreji comprised 90 thousand tons. Also known in the *Stara Planina* Mountains are uranium mineralizations in the vicinity of Inovska Reka and Tumba near Kalna, with average content of this element in the range of 300 - 700 g/t (300 - 700 ppm).

The attention of investigators has been attracted as well by a formation of Permian red sandstones developed on an area of about 800 km². Systematic radiometric investigations were carried out in the *Zaplanje region* south of the Nisava River, where about 130 anomalies with increased radioactivity were isolated. A significant number of these anomalies are secondary dispersion aureoles. The more important occurrences include Gadzin Han, where uranium is found in Permian sandstones and conglomerates (with up to 200 g/t of uranium and gamma radioactivity of up to 1,500 nR/h); occurrences in sandstones of Neogene age in Donje Prisiane (up to 300 g/t of uranium) and in Gornje and Donje Dragovlje; and occurrences in sandstones with coals along the Mlaka River (more than 800 g/t in coals) (S. Visic, 1969). Several tens of radioactivity anomalies have been registered in black Paleozoic schists on an area of about 100 km² in the neighborhood of Mts. *Kucaj* and *Beljanica*, where more than 60% of surface and groundwater samples had higher than permissible radium concentration and some were in good measure contaminated by radon.

2. Apart from the Kratovo - Zletovo volcanogenic region in Macedonia, the *Pcinja region* can be singled out within the **Serbo - Macedonian Mass** as an area with a considerable number of uranium mineralizations. High levels of uranium, thorium, and potassium have been established in the Slatinska Reka granites (on slopes of Mt. Kukavica). Marked by anomalies with elevated uranium content are granitoids of the *Surdulica Massif*; the pegmatites of *Vidojevica* and *Dobrotic* near Prokuplje; and the *Grbko* gneisses near Stalac (up to 260 g/t of uranium). Characterized by anomalies with elevated thorium content are monazites from granitoids in the vicinity of *Stalacki Visovi* (2,300 ppm of uranium and 50 thousand ppm of thorium); sphene from the granodiorites of *Surdulica* (up to 380 ppm of thorium); gneisses of the *Poljno* locality near Krusevac; etc.

3. Radiometric measurements in Sumadija have shown that granites, volcanites, Paleozoic schists, and some lacustrine sediments of Tertiary basins are uranium - bearing. The situation is similar at many localities in the remainder of the **Vardar Geotectonic Zone**, from Mt. Cer in the northwest through Mt. Golija and Brzec to Gnjilane in the south. The *Bukulja granitic massif*, with an area of about 40 km², has been extensively investigated. Up to 10 m thick and more than 1 km long, the Paun Stena and Cigankulja veins have been isolated within that massif. Also of interest in the Sumadija region are the *Brajkovac granitic massif* and the volcanites of *Medvednjak*, *Rudnik*, and *Borac*, with high average content of uranium and thorium. High uranium content is especially characteristic of volcanites in the western part of *Mt. Golija* (the region of Muhovo) and is also recorded in surface and groundwater there, as well as in clayey alluvial sediments (10 - 75 g/t). On the western slopes of *Mt. Cer* (Iverak near Dragnice), uranium is linked with lignite residues in lacustrine sediments of Neogene age. On the opposite side of this geotectonic unit, trachytes near *Stublovaca* south of Gnjilane contain appreciably more thorium than uranium.

From what has been said above, it is possible to discern regions or geological formations with enhanced uranium - bearing mineralization on the territory of Yugoslavia. These areas with increased risks to human health are appreciably expanded as a result of transport of natural radionuclides by surface and groundwater running from regions with mined uranium. Thus, for example, springs formed in fault zones in the region of the hydrochemical radon anomaly near Mt. Kitka south of Skopje (FYROM) are marked by exceptionally high content of this isotope (up to 19,640 Bq/l), even though they are fairly far removed from the anomaly. Or in the case of an anomaly in the granitoids of Mt. Cer, the spring Majur - Slatina in 1978 had radon content of the order of 3,600 Bq/l.

In order to illustrate the dangers of radioactive contaminants, let us dwell on waters of terrains that have been investigated. In the eastern part of the *Bukulja granitic massif*, from which water gravitates toward the Malo Jezero lake (a source of water supply for the town of Arandjelovac), all water analyses showed radon content of more than 10 Bq/l, 55% of the samples contained more than 100 Bq/l, and some samples had even as much as 462 Bq/l of radon. In the southern part of the massif, around the lake Garasko Jezero (formed above the western part of the Paun Stena uranium deposit), radon content in half of the samples of groundwater was 120 - 126 Bq/l. In the domain of the Cigankulja deposit in the massif's western part, close to 80% of 64 samples of groundwater contained more than 7 Bq/l of radon, 11 samples contained more than 100 Bq/l, and even levels of 500 to 1000 Bq/l were recorded in 8 samples. In view of the fact that this region is fairly densely populated, the cited data emphasize the need for geological (geomedical) studies and

appropriate protective measures⁵⁸. Elsewhere, underground and surface water in the region of black schists on the mountains *Kucaj* and *Beljanica* predominantly contains radium in amounts greater than permissible and is also in good measure contaminated with radon. In the *Stara Planina Mountains*, several occurrences and deposits of uranium have been investigated in the Dojkinci - Brlog - Jelovica - Lokve region southeast of Kalna. It was established that levels of radioactive elements (U, Ra, and Rn) in groundwater are elevated (U up to 40.9 µg/l, Ra up to 0.294 Bq/l, and radon up to 63.2 Bq/l). Of the many water samples tested, about 38% had increased content of uranium, while about 34% were with increased content of radium. Radioactivity anomalies were isolated northwest of Dojkinci (Dojkinci - Paleski Vrh), in the Brlog - Jelovica region, and north of Ponor (J. Kovacevic, 1999). Due to high radon content, the "*Skolska Cesma*" Spring and water from travertine around the spa Niska Banja are extremely radioactive (about 766 Bq/l). The *Studenica Mineral Spring* near Usce also has significant radioactivity (407 Bq/l).

Where groundwater is concerned, it can be concluded from the health standpoint that the results of radiohydrogeological investigation of the indicated large areas are alarming, especially in the case of the densely populated Bukulja massif (B. Ilic and J. Kovacevic, 1996).

How do things stand with the radionuclide concentration in crops, food, and the organisms of domestic animals and man? In attempting to answer this question, we rely on the book "**Radiation Hygiene in Biotechnology**" (B. Petrovic and R. Milivojevic, 1991), which provides abundant data on the radiation load of biocenoses on the territory of Serbia⁵⁹. Primarily due to lithologic heterogeneity, the activity of Ra₂₂₆ in soil of this territory is highly variable, ranging from 18.5 mBq/kg to 10.5 Bq/kg. For all crops tested (except onions), activity of Ra₂₂₆ in plants is linearly dependent on its activity in soil. It is therefore understandable that activity of this element in crops grown in different parts of Serbia is highly variable. As for soil, it is in general appreciably greater on untilled land than on tilled land. Table 2.15. gives the average activity of this isotope in several crops. Like uranium, Ra₂₂₆ accumulates best in onions, while in beans its concentration can vary greatly.

⁵⁸ Omaljev (1996) cites two cases where farm families live above fairly intensive anomalies: 1) the Kostovic house in the settlement of Ljuljac on the southern slopes of Mt. Golija is located in the middle of a strong radon anomaly posing high risks to humans; and 2) composed of the volcanic rocks of Borac, the entire hill above the Jakovljevic house has elevated radioactivity, and rocks from local quarries are used in construction of farmhouses.

⁵⁹ As a part of the carbonate Dinarides, the territory of Montenegro is characterized by a far lower background of natural radioactivity.

TABLE 2.15.
Activity of Ra₂₂₆ in plant cultures at the territory of Serbia
(B. Petrovic, R. Mitrovic, 1991).

Type of plant culture	mBqRa ₂₂₆ /kg of fresh sample
Bean	7.4 - 303.4
Wheat	3.7 - 162.8
Corn	7.4 - 111
Cabbage	7.4 - 88.8
Potato	7.4 - 7.7
Onion	18.5 - 980

Macro- and Microelements in Rocks, Soil, and Water: Biological and Medical Role and Geochemical Risks

Selective accumulation of microelements in organisms has been of exceptionally great significance throughout the entire evolution of life. The role of metals was especially conspicuous here. To be specific, it is known that the first organisms that arose in the hydrosphere 3.4 billion years ago were surrounded by a solution of different metals that must have affected their metabolism. Many ions were absorbed into the tissue of living cells and participated in biochemical reactions. Metals played a large part in the evolution of redox processes of the cell during different periods of transition from anaerobiosis to aerobiosis (M. Jaredic and J. Vucetic, 1982).

Today it is known that about 60 elements are found in the human organism, 36 of which are metals. With the improvement of analytical methods, it becomes possible to detect new metals in organisms, even ones that are present in extremely small quantities.

Both metals and all elements of interest from the biological and medical standpoints will be treated in the text to follow. They include above all the so - called *essential macroelements*, without which plant and animal life would not be able to survive: C, H, O, N, P, S, Ca, Na, K, Mg, and Cl (Fig. 2.38.)⁶⁰. In addition to the listed macroelements, life also

⁶⁰ According to E. J. Underwood (1981), 15 microelements (Fe, I, Cu, Mn, Zn, Co, Mo, Se, Cr, Ni, Sn, Si, V, As, and F) are essential for animals and man. Their *essential nature* is based on the following criteria: 1) they must be present in living matter; 2) they must be capable of interacting with living systems; and 3) their deficit in nutrition must lead to a reduction of biological function, which can be prevented or restored by introducing physiological amounts of the microelements in question. Of those listed, the last six are ones with a relatively recently discovered role, and their practical significance in human and animal nutrition has not yet been defined. The etiology of certain endemic diseases

requires the presence of *essential microelements*: Co, Cu, Mn, Mo, Se, Zn, B, Fe, I, and F, as well as (to some extent) Ni, Li, Si, V, Sr, Sn, and Cr (Fig. 2.39). Opposed to these elements are *non - essential* and *harmful elements*: Cd, Hg, Pb, Ti, Be, Ba, Al, As, Sb, Bi, U, Th, and others that threaten life, even though the certain biochemical and biological role of some of them (As, Hg, etc.) cannot be ignored. The differentiation of elements into essential and harmful categories is a consequence of long evolutionary selection and development of unsuccessful and successful (resistant) species, i.e., ones that do not survive and ones that do.

Whereas macroelements constitute the bulk of living material, microelements are present in the organism in insignificant quantities of the order of 10^{-1} to $10^{-120\%}$ ⁶¹. Nevertheless, the biological importance of many microelements is very great. Deficits of some of them lead to diseases of animals and plants, and the disease symptoms can be successfully removed simply by adding the missing ingredient to the diet. Deficiencies of microelements in food and water can also cause serious pathological processes in humans and animals.

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<p>Legend: H-essential; Hg-toxic; Fe-essential or toxic Ba-partially essential</p>																																													

Fig. 2.38. Essential (black) and toxic (grey) elements.

The general dependence of geochemical composition of the *soil* on rocks in the substrate was stressed earlier. Excesses of heavy metals generally occur on soils formed from minerals rich in heavy metals.

and some "diseases of civilization" (such as cardiac ischemia, diabetes, osteoporosis, and many malignant diseases) is not yet known, but multifactor analyses have shown that diet is very important. For this reason, it is impossible to exclude a potential role for microelements recently found to be "essential," as well as ones whose role is yet to be established (Z. Maksimovic, 1985). *All the indications are that medical geology will make a very great contribution in this field of scientific research.*

⁶¹Relatively large amounts of essential macronutrients (above 100 mg every day) are needed for human life.

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Among other things, soils formed on sulfate, copper, and silicate minerals or on serpentinites are characterized by elevated content of nickel and chromium, while ones formed on sedimentary and metamorphic rocks are characterized by a high share of cadmium. We are especially interested in sedimentary rocks, since they account for approximately 75% of all lithological products on the Earth's surface. The concentration of microelements in these rocks depends on minerals and adsorptive characteristics of the basic rock and the concentration of metals in the water in which sediments were formed. For example, clays are characterized by high concentrations of many elements, which is a consequence of their ability to adsorb metal ions. Concentration range of metals found in agricultural soil in different parts of the world is noticeable. A more detailed treatment of the geochemical origin of individual microelements and their chemical behavior in soil is given in the book "**Heavy Metals in the Environment**" (Ed. by R. Kastori, 1997).

Land that as a rule is highly populated and farmed, *river valley sediments* represent the hypsometrically lowest base for concentration of transported products of rock weathering and soil erosion, as well as for accumulation of water. The appreciable concentration of heavy metals formed in this way in the overlying clay horizon of alluvial sediment can threaten human health⁶². For example, systematic measuring of heavy metal content in the clay fraction of Danube river sediment in Germany revealed pronounced anomalies of cadmium (up to 45 ppm), lead (100 - 200 ppm) and zinc (500 ppm) (U. Fortsner and D. T. W. Wittmann, 1981). Anomalous levels of mercury in the sediment of this river course have been established both in Germany and in Austria and Hungary. Downstream, the problem of concentration of metals and other toxic elements in Danube sediments appeared immediately after construction of the Iron Gate Dam, when changes occurred in the entire aquatic system (Z. Maksimovic and M. Rsumovic, 1988). Just the question of the form of binding of heavy metals in aquatic sediments is today very pressing.

The content of individual microelements in *groundwater*, mineral and thermal waters above all, was likewise considered in a special chapter. It was stressed that such waters are characterized by considerable diversity of composition, depending on the rocks in which they move. However, exceptionally high concentrations of microelements sometimes occur, for example, in the waters of fumarole springs in regions of New Zealand with current volcanism (11,350 mg/kg of Fe^{2+} , 2,018 mg/kg of Al^{3+} , and 871 mg/kg of F); in waters of regions where saline solutions occur (up to 3,000

⁶² The geography of endemic nephropathy is known to be almost exclusively linked with alluvial valleys of stream courses on the territory of Serbia, Republic Srpska, Romania, and Bulgaria. However, the main cause of that disease has not yet been established, although it is logical to assume that geological factors play a decisive role.

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and farmed, *river valley* base for concentration of soil erosion, as well as for concentration of heavy metals of alluvial sediment can automatic measuring of heavy river sediment in Germany (up to 45 ppm), lead (100 - 150 ppm) (T. W. Wittmann, 1981). Some parts of this river course have been studied in Austria and Hungary. The concentration of metals and other toxic elements has increased lately after construction of the entire aquatic system. The question of the form of iodine deficiency is today very pressing.

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Iodine deficiency is almost exclusively linked with the regions of the Republic Srpska, Romania, and Bulgaria, as has not yet been established, although it plays a decisive role.

- 6,000 mg/l of Br, up to 2,000 - 6,000 mg/l of Sr, up to 500 - 700 mg/l of Fe, and up to 100 - 700 mg/l of Mn); and in brines of fault zones (with anomalously high content of Zn, Pb, and Cu).

The application of scientific principles in study of vital practical problems showed that a relationship exists between the supply of microelements and health of humans and animals, and enabled man to conquer such illnesses as pernicious anemia and Kashin disease (Z. Maksimovic, 1985). However, much remains to be done in attempting to correct imbalances of microelements in man, especially in growing children (Fig. 2.39.) The risks that lead to abnormal mental and physical development of children and to the appearance of certain chronic diseases later in life have been poorly defined, except in the case of exposure of children to high concentrations of lead (W. Mertz, 1981). Significant in this connection is the discovery of a high percentage of anomalies in the kidneys, ureters, and urinary bladders of children in families with endemic nephropathy, which indicates the action of unknown harmful factors in their development (N. Calic - Perisic et al., 1981).

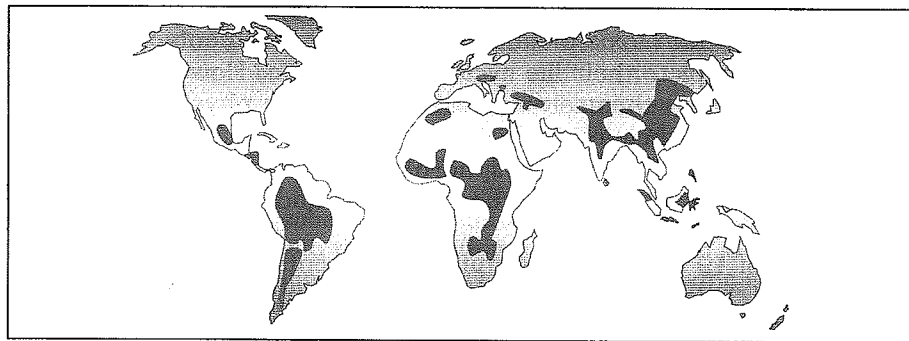


Fig. 2.39. Areas of iodine deficiency in the Earth (Dunn and van der Haar, 1999).

Role of Elements in Plant Nutrition

Plant nutrition has been a subject of interest and study since the earliest times. The first investigations were aimed at discovering factors that determine soil fertility and substances of which plants are made. Our current knowledge in this area is a result of the work of scientists from the oldest times to the present day. Knowledge about the role of individual elements in plant nutrition has expanded and deepened noticeably in the last decades, especially owing to the application of modern physico-chemical methods in the area of plant physiology. During that period, investigators have increasingly studied the role of individual elements in vital processes of plants and the nature of morphological and anatomical changes caused

by their deficiency or excess. In writing the following brief discussion of the given material, we relied on the work "**The Role of Elements in Plant Nutrition**" (R. Kastori, 1983).

Elements entering the composition of plants do not have the same significance: some are essential, without which plants cannot complete their life cycle; others behave in a stimulative way; and one group of elements (especially non - essential heavy metals) in higher concentrations exert very toxic action on plants. They affect the vital processes, anatomical and morphological structure, chemical composition, yield, and distribution of plants.

Plants play an important role in the circulation of heavy metals in nature. Heavy metals for the most part enter the food chain through plants. For this reason, knowledge of the ecology and mechanisms of accumulation, distribution, and metabolism of heavy metals in plants is of great ecological, scientific, and practical significance. On the other hand, the creation of varieties and hybrids characterized by lower accumulation of heavy metals would greatly reduce the chances of their entering the food chain.

Essential microelements are found in the dry matter of plants in far greater amounts than toxic metals and other microelements. Plants could not normally complete their life cycle without them. However, they differ significantly among themselves with respect to physico - chemical characteristics and their role in physiological and biochemical processes of plants. Whereas nitrogen, phosphorus, and potassium often limit the organic production of plants, carbon, oxygen, and hydrogen rarely limit the yield of cultivated plants.

The role of 19 of the most significant elements in plant nutrition will be considered below. These elements can be relegated to one of the following four groups: 1) *essential macroelements* (N, P, S, K, Ca, and Mg); 2) *essential microelements* (Fe, Cu, Mn, Zn, B, Mo, and Co); 3) *certain microelements that can exert physiological action* (Ni, F, and Li); and 4) *useful elements* (Na, Si, and Cl).

Essential Macroelements. Nitrogen. Nitrogen enters the composition of many compounds important for the vital processes of plants, compounds such as proteins, nucleic acids, nucleotides, chlorophyll, etc. Owing to this, its role in physiological processes of plants is significant and multifold. Its high mobility and capacity for transport are properties that enable nitrogen to be rapidly and repeatedly involved in processes of synthesis and breakdown of organic compounds, whereby the importance of nitrogen in circulation of plant substances becomes all the greater.

An adequate amount of nitrogen in the nutrient substrate is needed for normal and harmonic growth and development of plants. Insufficient nitrogen nutrition very quickly causes specific changes in the metabolism and

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Essential substrate is needed for
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morphological and anatomical structure of plants: growth is reduced, tips and edges of leaves die, the stem shortens, the root system lengthens, fruits shrink in number and size, and their quality deteriorates. Symptoms of nitrogen deficiency are partly specific for individual species and even varieties of plants.

Like nitrogen deficiency, a surplus of nitrogen has an unfavorable effect on plant productivity. Excessive nitrogen nutrition promotes growth of vegetative organs and bushiness of plants, increase of stooling in grain, shortening and thickening of the roots, retardation of ripening, decline of plant resistance to disease and drought, etc.

Use of greater doses of nitrogen in certain vegetable plants can cause accumulation of nitrates, which with longer standing are reduced to nitrites. Nitrites act very unfavorably on human and animal health. Examples of poisoning with serious consequences are known in the literature, especially poisoning by nitrate-rich spinach (*spinach meth - hemoglobinemia*).

Phosphorus. Phosphorus is a constitutional element because it enters the composition of important organic compounds. Many significant physiologic - biochemical reactions in living organisms cannot proceed without the participation of different phosphorus compounds. Phosphorus deficiency is manifested in cessation of growth, formation of tender and unresisting stems, and decrease in the yield and quality of production. Contrary to nitrogen surplus, an excess of phosphorus very rarely occurs in plants because its ions are quickly bound in soil.

Sulfur. Sulfur also belongs to the group of essential constitutional elements. Its role in plant metabolism is multifold: in addition to structural and catalytic functions, sulfur is involved in maintaining equilibrium of redox processes in the cell, is linked with the chain of electron transport, etc. Symptoms of sulfur deficiency are rarely observed on plants in nature. Plants in industrial regions and near larger cities usually are adequately supplied with sulfur due to the increased share of SO₂ in the atmosphere. Symptoms of rare occurrences of sulfur deficiency have much in common with those of nitrogen deficiency, and it is for this reason sometimes difficult to distinguish them. On the other hand, the surplus of SO₂ in the air has lately been posing a constantly increasing threat to the plant world.

Potassium. An alkaline metal, potassium is considered to be a *functional element*. Owing to its role in specific activation, i.e., as a co - factor of enzymes, potassium directly or indirectly affects many physiologic - biochemical processes, as a result of which it is of exceptionally great significance in the life of plants. Due to the multiple role of potassium in vital processes, a deficiency of this cation causes far - reaching changes in metabolism and thereby in the growth and development of plants. A potassium surplus can cause effects that are indirectly unfavorable.

Calcium. Calcium is one of the most widespread elements in nature. It plays a multiple role in vital processes of plants. Although it does not enter the composition of organic compounds, it plays a very important part in plant metabolism. It affects physico - chemical characteristics of protoplasm, stability of cell membranes, activity of certain enzymes, etc. Calcium deficiency can affect plants directly (if plants do not contain this element in sufficient quantity) and indirectly (if its content in the soil is insufficient). Calcium deficiency in nature has been observed to date in lettuce, cabbage, peanuts, potatoes, flax, tomatoes, and