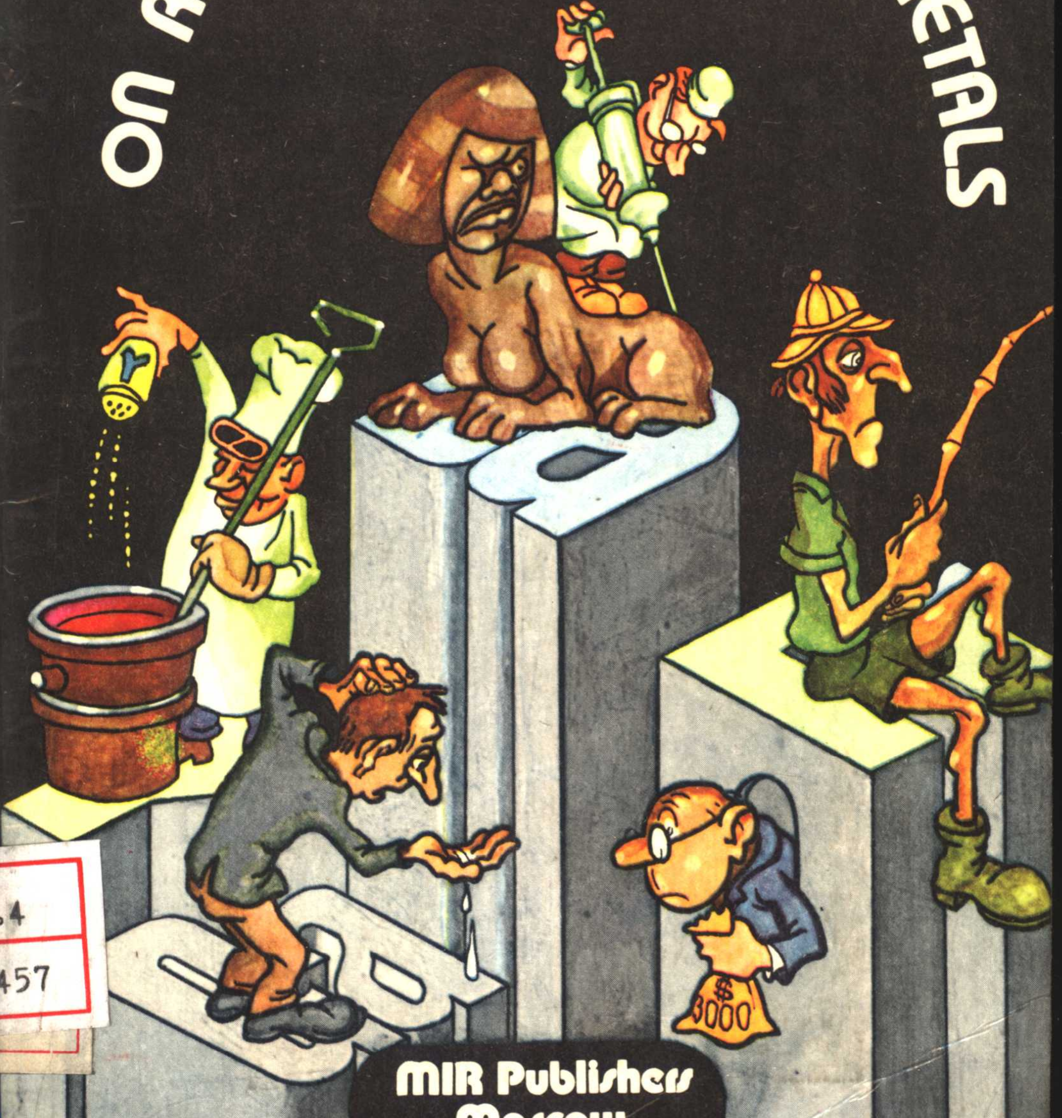
S. Venetsky

ON RARE AND SCATTERED METALS

Tales about Metals



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О РЕДКИХ И РАССЕЯННЫХ

Рассказы о металлах

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S. Venetsky

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Tales
about
Metals

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TO THE READER

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About This Book

Ours is an age of incredible breakthroughs in science and technology: man has blazed a trail into outer space, harnessed the energy of the atomic nucleus, built "thinking" machines and unravelled the mystery of the living cell.

Humanity is moving into ever new and fascinating fields, but there is one field of activity which, while being old as the hills, is no less fascinating. This field is metallurgy, the production and working of metals and alloys.

At the dawn of civilization people were familiar with only a few metals. But as ages passed and ever more new elements were discovered, the range of useful metals extended as well. In the case of some metals scientists and engineers did not take long to acknowledge and appreciate them, with others, it took years before they began to be applied. There were valid reasons for their "idleness". First, the content of many of them in the earth's crust is minute and therefore, it is extremely difficult to extract them; some have no minerals of their own and occur only as impurities in other metals (such "scattered" elements belong to the group of trace elements). Second, up to a certain period science lacked information on most metals and since those we are going to discuss were used very rarely in industry, they were called rare metals.

The explosive development of technology is the hallmark of the 20th century, a time when instrument-making, chemistry, aviation, rocketry, electronics and nuclear power — all started to place orders for new materials with unique properties. This is what prompted scientists to delve deeper into the world of rare metals. A careful study of those "recluses" revealed that many of them were quite "gifted". Thus began the advent of rare metals in industry.

It would probably be correct to say that today not a single new area of technology can do without rare metals, their alloys or compounds. For example, fine-filament suspensions for navigation instruments of high precision are made from rhenium alloys; gallium goes into the manufacture of so-called liquid seals in vacuum equipment and high-temperature thermometers and pressure gauges; cesium is the most important component of photocells used in flaw detectors and some other instruments; hafnium is the material from which control rods of nuclear reactors are made and is also promising as a component of superalloys being developed for aviation and rocketry; a thin layer of indium deposited on ball-bearings protects them from erosion and increases their service life. Such examples could be listed indefinitely.

This book tells about some rare metals (including those called trace elements) and can be regarded as a second part of S. I. Venetsky's *Tales About Metals* (It was published in English by Mir Publishers, Moscow, in 1981).

The author follows the same principle as in his previous work: rather than giving the reader any exhaustive information about every chemical element he describes, to tell him some interesting facts, curious incidents and tales associated with rare metals, to tell about the thorny path of any major scientific discovery and about some paths yet to be trodden in the amazing world of metals.

The book is "peopled" by real and fictitious characters. Along with many outstanding scientists, it alludes to Napoleon, Agatha Christie, Karel Čapek and Sherlock Holmes. The stories associated with them are a background against which the author introduces his reader to achievements in metallurgy, physics and chemistry, to advances in the development of new processes of making metals and materials and to new instruments. It was only recently that experiments in space materials science were carried out on board the *Salyut-6* space station, but they too are mentioned in the book.

Many scientists and engineers make their first steps to the summits of science and engineering under the influence of popular science literature. It is my firm belief that this book will also help many young people with the crucial choice — their future occupation.

Academician A. F. Belov

Ga

THE TRIUMPH OF A GREAT LAW (GALLIUM)

Do not hasten to draw conclusions!— The first piece of evidence.— Irony of fate.— A violet stranger.— Was it a cock?— A scientific argument.— Different fates.— Shameful "discrimination".— A poor relative.— The wealth is hidden in the waste.— Gallium on the palm of a hand.— There will be no fire.— Lamps become better.— A great eccentric.— Beyond compare.— Not a good comrade.— Exceptional gifts.— No fool.— Experiments in space.— Why is the Sun shining?

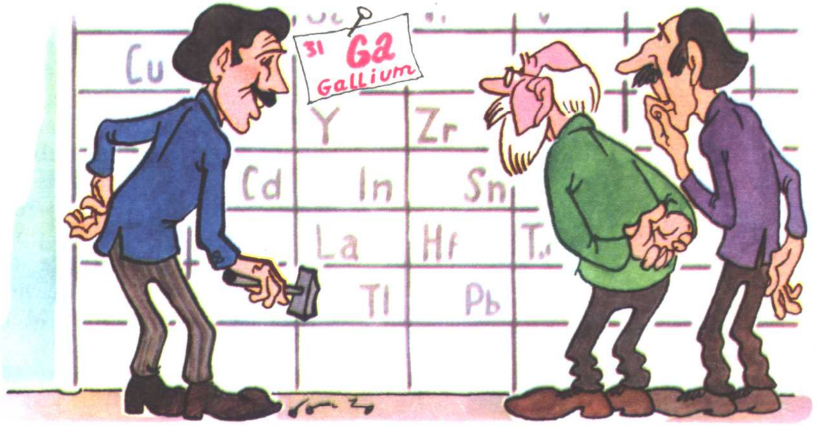
Dmitri Mendeleyev's discovery, in March 1869, of a periodic law which governs the behaviour of absolutely all chemical elements was given a hostile reception by some scientists. Even a chemist of such eminence as Robert Bunsen, one of the creators of spectral analysis, made this caustic remark: "One can draw any number of such generalizations on the basis of figures printed in stock-exchange bulletins."

Later Bunsen must have regretted his ill-considered remark on more than one occasion, but back in 1869 Mendeleyev was yet to prove his law. And he did prove it brilliantly. The greatness of the periodic law consisted in that it not only generalized and put in strict order whatever information about chemical elements scientists had at their disposal, but became something of a compass to the multi-thousand-strong army of experimenters seeking new islands in the boundless sea of chemistry: new elements, new bricks of the universe. On the basis of the periodic law Mendeleyev was able to predict the discovery of more than a dozen elements.

The first to prove Mendeleyev's correctness was gallium.

At the end of 1870, addressing a sitting of the Russian Physical and Chemical Society, Mendeleyev said that in the fifth row of the third group of elements there was a place for an element which was yet undiscovered but which definitely existed somewhere in nature. He described the properties of the new element in much detail and gave it the arbitrary name eka-aluminium (its place in the table of elements being beneath aluminium). He even expressed confidence that it would be discovered by spectral analysis. (There is irony of fate for you: could Bunsen ever expect the spectral method he worked out to play such a mean trick on him and furnish irrefutable proof of the fallacy of his premature denial of the periodic law?)

The news of discovery of the predicted element was not long in coming. In 1875 the French chemist Lecoq de Boisbaudran made a spectral study of a specimen of zinc blende, a well-known mineral



from Pieerefitte in the Pyrenees, discovering a stranger — a violet line which was an indicator that the mineral contained an unknown chemical element.

But it was one thing to discover the line and quite another, to isolate the element responsible for it. Not an easy task at all, considering that the content of the unknown element in zinc blende was minute. But the chemist was successful: his numerous experiments yielded a grain of the new metal weighing 0.1 gram.

The most difficult part over, Lecoq de Boisbaudran now had to give his metal a name. He called it gallium in honour of his country (Gallia is the Latin for France). True, some wicked tongues soon began to assert that gallium was the chemist's cleverly concealed hint at his own name: *gallus* in Latin means a cock and the French for cock is *le coq*, which makes the connection with Lecoq de Boisbaudran only too obvious, they said.

Soon the news of the discovery of gallium was published in a paper of the French Academy of Sciences. When it reached Mendeleyev he immediately realized that this was the eka-aluminium to which he had already assigned a place in the table of elements. In his letter to the French Academy Mendeleyev wrote: "... the method by which it was discovered and isolated and also the few properties described allow me to suggest that the metal is nothing else but eka-aluminium".

Indeed, the properties of the theoretical eka-aluminium and the really existing gallium were amazingly identical. The only difference was in their density: according to Mendeleyev, it had to be around 6 g/cm^3 and the French chemist estimated it to be 4.7 grams. Who was correct? The one who had never even seen the new metal or the other who not only held it on his palm but carried out various experiments with it? It was not the first time in the history of science that theory clashed with practice, the mind questioned the experiment.

To prove he was right Boisbaudran once more isolated a few grains of gallium, carefully cleaned them and made a new study. This time he found that the density of gallium was really close to 6 and publicly acknowledged the correctness of his Russian colleague. He wrote: "It seems there is no need to point out the exceptional importance the establishment of density of the new element has to confirming Mendeleyev's theoretical conclusions."

There is much similarity in the history of many metals. But just as among hundreds of people you know you will not find two whose biographies are identical, you will not find two metals with identical histories. Even twins like zirconium and hafnium or tantalum and niobium have different stories to tell. But the early stages in the life of most metals were equally uneventful: they patiently waited for some work to be found for them. Some were lucky and only a few years after discovery were leading active lives. For others the period of waiting lasted a long time. Gallium was among the unfortunate ones.

More than half a century had passed since Lecoq de Boisbaudran had announced to the world the discovery of gallium but the industrial world was still ignoring it. The 14th volume of the Great Soviet Encyclopaedia (1st Ed.) published in 1929 had exactly four words on the application of gallium: "Not used in technology". And that was that.

But what can explain such discrimination? Could it be that the metal which had played such an outstanding role in confirming the periodic law would find no other use but taking up residence in the 31st square of the table of elements? Could it be that it did not possess a single property capable of arousing the interest of designers, inventors and scientists?

The properties of gallium, as you will soon see for yourself, had nothing to do with it. But perhaps nature's stock of this element was too small and that explained all its misfortunes? Alas, that was not so either. The earth's crust contains tens of times more gallium than say, tantalum or tungsten, and hundreds of times more than mercury or silver.

The point is that, like some scattered elements, gallium did not "bother" to create its own deposits. Furthermore, it has practically no minerals of its own. It was fairly recently that the first gallium mineral was discovered in South-East Africa. Hallite, as the mineral is called, contains up to 37 per cent of gallium. But as a rule, hardly appreciable quantities of this element (a few hundredths of one per cent) are found "living" like "poor relatives" with aluminium and more seldom, with iron, zinc, copper and some other metals. It has been found that coal ash is comparatively rich in gallium. According to British scientists, one ton of coal mined in the British Isles contains an average of five grams of gallium. Is that all? It seems even this minute concentration is believed sufficient for its industrial recovery. (Everything is relative: iron ore, one ton of which contains some 300 to 400 kilograms of iron, is generally considered poor.)

The production of gallium has been expanding at a slow rate. The first 50 kilograms of this metal were produced in Germany in 1932. Some twenty-five years later gallium production had reached only 350 kilograms. Though modern output is measured in tons, even such a scarce metal as rhenium, the content of which in the earth's crust is tens of thousands of times less than that of gallium, has left it far behind in quantities produced.

The main source of gallium are... the waste products of the aluminium industry. But do not hurry to conclude that gallium is a cheap metal. Though the raw material costs nothing, the process of recovery of the metal is so complex (even the extraction from aluminium) that it turns out to be one of the most expensive metals on the world market. In the middle of the 1950s one kilogram of gallium cost 3 000 dollars — almost three times the price of gold. Just think, an ingot easily held on the palm of a hand at such a price!

As a matter of fact, holding gallium on one's palm is exactly what we shouldn't advise one to do, and not only because it is not a very reliable container for a very precious metal, but because the warmth of the human body is enough to transform it into a liquid state: the melting point of this silvery, soft metal (you can cut it with a knife) is extraordinarily low, 29.8°C. In this respect it is inferior only to the restless mercury which becomes immobile only at minus 40°C, and to some extent, to cesium melting at 28.5°C. Another reason why gallium

should not be held in a hand is that it is rather toxic (more so than mercury) and holding it may cause unpleasant consequences.

Its low melting point makes gallium the base of many fusible alloys. For example, an alloy of gallium (67 per cent) with indium (20.5 per cent) and tin (12.5 per cent) cannot remain solid even at room temperature: its melting point is 10.6° C. Such alloys have an extensive use in engineering, in particular, in fire-alarm systems. Once the air in the building warms up to a certain point, the gallium-alloy column fixed in a relay begins to melt, closing the electrical contacts and giving a sound or a light alarm signal. This device is much more reliable than any human guard.

Low-melting gallium alloys (and gallium itself) are also characterized by good wetting properties, which is why they are widely applied instead of mercury in vacuum seals. Gallium seals maintain a vacuum more effectively than mercury ones.

Alloys of gallium with indium and tin are used as lubricants, interlayers in joining parts made of quartz, glass and ceramics and also for pressure bonding. A gallium-indium coating of ball bearings considerably prolongs their service life. As mentioned earlier, gallium is very toxic, but in company with nickel and cobalt it fails to demonstrate its poisonous nature and is even used for dental fillings of high quality.

The cathodes in the ultra-violet lamps applied in medicine, which were formerly made from mercury, are now made from an alloy of aluminium with gallium. It has been found that this alloy is much better suited for the job as its flux contains more ultra-violet rays.

Most metals melt and solidify at the same temperature. The unique property of gallium is that it can remain liquid for months in a supercooled state. If a drop of gallium is left on ice it will not solidify for a long time. But when it finally does its volume will have expanded considerably. Therefore, metal or ceramic containers must not be filled with liquid gallium — they will burst as the metal becomes solid. It is usually stored in small gelatin or rubber cylinders. It has been suggested that the ability of gallium to grow in volume on solidification (all the other metals except antimony and bismuth "lose weight" as they transform from the liquid to solid state) should be used in ultrahigh pressure equipment.

But the main advantage of gallium is that it remains liquid over a vast temperature range, and here no other low melting metal can compare with it. Molten gallium begins to boil only heated to a temperature of 2 230°C. It is this amazing property that determines its main role in technology — high-temperature thermometers and pressure gauges. Gallium thermometers can be used for temperatures of 1 000°C and over, a level mercury thermometers cannot even approach: mercury boils already at 357°C.

The low melting point combined with the wide temperature range of its melt makes gallium a potential heat-transfer agent for nuclear reactors. But liquid gallium is not a good comrade to structural materials with which it might come into contact in the reactor: at high tempera-

tures it dissolves and destroys most metals and alloys. This is why at present the important role of heat-transfer agent is usually played by sodium and potassium. But it is possible that scientists will find a way of coping with this problem: it has been found, for instance, that tantalum and tungsten easily survive the contact with gallium even at 1 000°C. It is an interesting fact that small additions of "aggressive" gallium (up to 5 per cent) to magnesium enhance the latter's corrosion resistance and strength.

Another interesting fact is that electric resistance of gallium crystals depends to a considerable degree on whether the current is passed through their horizontal or vertical axes. The maximum-minimum resistance ratio is 7, which is far greater than that of any other metal. The same is true of its heat expansion coefficient which changes by a factor of three depending on the current direction.

Gallium's outstanding ability to reflect light explains its successful application in the manufacture of mirrors, and it must be stressed, that gallium mirrors do not dim even at high temperatures. The oxide of the metal is essential for production of special glasses characterized by a high refractive index, allowing for a free transmission of infrared rays.

Super-pure gallium (no less than 99.999 per cent) serves as an alloy addition to germanium and silicon, increasing their semiconducting properties. Not long ago gallium itself was shown to be "no fool" in this respect. Some of its compounds — with antimony, phosphorus, and especially, arsenic — reveal semiconducting qualities.

These properties are strikingly demonstrated in heterojunctions ensuring high efficiency of semiconductor instruments. A heterojunction is a junction between two semiconductors with different chemical characteristics formed in a single crystal. Scientists have long since theoretically proved that this kind of "life under the same roof" holds interesting prospects for semiconductor engineering. The main difficulty lay in selecting a pair of materials for such "coexistence". Experimenters tried dozens of various combinations but all of them were far from ideal and only too often demonstrated open incompatibility. It was then suggested that the arsenides of gallium and aluminium could be a likely combination. Their crystalline lattices were similar like two drops of water and that was encouraging. But a new obstacle arose: in a humid atmosphere aluminium arsenide was so unstable that it became decomposed before one's very eyes.

Was it final defeat? Gallium saved the situation: atoms of gallium introduced in aluminium arsenide gave it adequate stability. The problem of heterojunctions was solved and numerous sophisticated instruments were designed on their basis.

The field of application of gallium compounds is constantly extending. Today one comes across them in computers, radars, thermocouples in solar batteries and in semiconductor devices for rocket-borne equipment. They are used in lasers and luminescent substances, and also as a strong catalyst involved in many important processes in organic chemistry.

Only recently the fictitious "engineer Garin's hyperbolloid" (a controlled concentrated ray of light invented by the main character of Alexey Tolstoy's well-known novel) seemed pure fantasy and the "hyperbolloids" of today, the lasers, are now becoming quite common. Gallium arsenide was one of the first laser materials. According to Western specialists, the simple, compact and effective lasers based on gallium arsenide were proposed for space apparatus, particularly for communications between the ship and the astronauts during their extravehicular activity, or between two space stations travelling in near space. There were also plans to use such a laser for the ship attitude control during the "landing" on the Moon.

Owing to weightlessness outer space is a unique setting for extensive technological experimentation. Interesting results were reported from the American *Skylab* whose crew succeeded in growing a gallium arsenide crystal 25-mm long. Here on earth it has yet been impossible to grow a crystal longer than two or three millimetres. Successful experiments along the same lines were also carried out on board the Soviet *Salyut-6*. Apart from that, the Soviet spacemen experimented with alloying gallium and molybdenum (by means of an installation called *Splav*). The point is that molybdenum is almost twice as heavy as gallium and under ordinary conditions the two cannot mix evenly: when the melt solidifies its upper layers appear to be rich in gallium and the lower ones, in molybdenum. But in weightlessness gallium and molybdenum are "equal" and the alloy is a homogeneous composition.

It is quite probable that gallium will provide science with an explanation as to why the Sun emits light. Incredible as it may seem, so far we have had nothing but conjectures about the nature of the colossal energy the Sun has been generating for thousands of millions of years. One of the more widely accepted and seemingly more authentic hypotheses asserts that this is the result of the unceasing processes of thermonuclear synthesis taking place in the Sun's interior. But how is this to be proved?

Neutrinos, the particles produced during thermonuclear reactions could serve as the most convincing, even if indirect, proof. But this piece of evidence is too elusive to get hold of easily. Even Wolfgang Pauli, the Swiss physicist who theoretically predicted the existence of neutrinos back in 1933, suggested that no one would ever be able to prove their existence experimentally, since they have neither mass nor electric charge.

On the other hand, it is a fact that neutrinos possess certain energy and a tremendous penetrating power. Released from the Sun's nucleus, they easily travel through the bulk of solar matter and rush down to earth (and other celestial objects, naturally) in a huge flux. It is believed that more than 60 000 million neutrinos bombard each square centimetre of the surface every second. But it is practically impossible to record them: they effortlessly pass through any substance as if it were an empty space. Nevertheless, physicists have been able to find some materials in which neutrinos should leave a trace. The nucleus of an atom of chlorine-37, absorbing a neutrino, releases an electron and transforms into an atom of argon with the same atomic mass. But this reaction can be effective only with neutrinos possessing great energy, the ratio of which in the flux coming from the Sun is extremely small (less that one ten-thousandth). Hence, almost sterile conditions are needed to capture the evasive particles.

An attempt to create such conditions was undertaken in the United States a few years ago. In order to safeguard against the influence of other space particles a huge tank containing tetrachloroethylene (a common cleaning fluid) was placed underground at a depth of about one and a half kilometres, in an abandoned gold mine in South Dakota. According to theoretical calculations, every 48 hours three atoms of chlorine-37 were to transform into atoms of argon-37, and it was believed, that two such transformations would be owing to neutrinos and the third owing to other radiations filtering even through one and a half kilometres of the earth crust. Alas, only one atom of argon was

detected every two days which meant that most likely the Sun's messengers had nothing to do with it.

Does this mean that no neutrinos come to earth and the thermonuclear theory of the origin of solar energy is wrong? Soviet physicists do not think the experiment described above is enough reason to refute the concept that the Sun is a gigantic thermonuclear reactor. Apparently, to be successful such experiments require even greater accuracy. Besides, theory asserts that the neutrinos in the flux hitting the Earth possess relatively low energy to register which the chlorine-argon method is simply no good. This is where gallium looks a likely prospect. It seems it can serve as a good target (detector, to use the physical term) for low-energy neutrinos. It is suggested that the nuclei of isotope gallium-71 will readily absorb these particles and transform into the nuclei of germanium-71. Having estimated the number of atoms of germanium-71, scientists will be able to measure the Sun's neutrino flux. True, at present it is only a theory, but a gallium-germanium installation has already been built in the Soviet Union and a deep adit for a neutrino observatory has been sunk in the gorge of the Baksan river (Northern Caucasus). Though the installation will require a few tons of gallium, which is quite expensive, the metal will remain practically intact throughout the experiment. It is probable that several years from now gallium will help to shed light on one of the major problems of modern astrophysics.

Rb

AN EVIL GENIE (RUBIDIUM)

If one is to believe the Bible.— The old rocks of Greenland.— The Himalayas grow younger.— A clock that does not tick.— A find in the spectrum.— A brief outline.— Bunsen evaporates a lake.— A quarter of a century later.— In a prison cell.— Clashing with ice.— Far from the nucleus.— Prospect of a power struggle.— A pleasant job.— On the world market.— Related professions.— The clocks chime on time.— Twenty centuries and one second.— Underground treasure troves.— On the banks of the river Kama.— Who dyed the salt?— In the lagoons of the Black Sea.— Protect your men!

How old is our planet? Unfortunately, no "birth certificate" has been preserved while she herself carefully conceals her age (like any woman no longer young). But where there is a secret there will always be people who will want to guess it. The argument concerning the time our "abode" appeared in the universe has lasted for many centuries now. If one is to believe the Bible, it happened quite recently, some six millennia ago. The modern scientific view, however, is that it is about 4 500 000 million years old.

Some of the supporting evidence is provided by ancient mountain rocks. Until recently the rock species found in the region of Transvaal in South Africa were believed to be the oldest on earth: their age is estimated at around 3 400-3 500 million years. But in 1966 Macgregor, a scientist from New Zealand, discovered some rocks at the mouth of Ameralik Fjord in Greenland which are at least 500 million years older. This fact was established by means of the so-called rubidium-strontium "clock". What is it?

In early 20th century the great British physicist, Ernest Rutherford, suggested that the age of minerals and rocks could be determined through radioactivity, a phenomenon discovered a few years previously. His point was that the atoms of radioactive chemical elements contained in terrestrial material constantly emit some or other nuclear particles, while themselves transforming into atoms of other elements. Interestingly, the speed of this transformation does not depend either on temperature or on pressure, or on any other factor. But every radioactive substance is characterized by its own half-life period, that is, a period during which exactly one half of the radioactive element decays. With some elements this period lasts a few millionths of a second and with others it takes hundreds of billions of years.

The half-life of one of the "centenarians", rubidium-87 (its pro-