The Radioactivity of the Rocks.¹

By Prof. JOHN JOLY, D.Sc., F.R.S.

THE subject of the radioactivity of the rocks is one which offers to the geologist considerations of the first importance respecting the history of the surface features of the globe. To the chemist it offers considerations even more fundamental in character, for it appears to throw a certain amount of light on the past history of the chemical elements during geological ages—knowledge attainable in no other way at the present time.

The fact that the radioactive elements of the uranium family are widely, indeed universally, distributed in the rocks was determined, in the first instance, by the present Lord Rayleigh, who in 1906 published an extensive research on rocks of various kinds. Later it was found that elements of the thorium family are just as widely distributed; and further, it was found that there appears to be a certain well-sustained relation between the amounts of these elements present in igneous rocks when the uranium and the thorium content of the same chemical division of the rocks are compared.

Lord Rayleigh in his earliest paper came to the conclusion that the acid rocks contained more radium than the basic rocks. This result has been confirmed by subsequent work. He found that the mean content of the igneous rocks was considerably greater than that of the sediments. This result, which has also been confirmed, throws light on the high radioactivity of the more slowly collecting oceanic deposits—the red clay and the radiolarian ooze. Similar results have been arrived at for the thorium content of rocks.

I have already referred to the fairly constant ratio which exists in the quantities of uranium and thorium in igneous rocks. When we estimate the uranium from the radium, using the equilibrium factor 3.4×10^{-7} , we find in basalts about 0.44×10^{-5} gm. of uranium and 0.9×10^{-5} gm. of thorium. In intermediate rocks the corresponding ratio is 0.76:1.64. In the acid rocks (granites) the ratio is 0.8:2.0. For acid intrusives it is 1.1:2.3. The mean of all acid rocks affords 0.9:2.0. In short, we find a ratio which does not vary much from 1:2. In individual rock specimens this ratio is often seen to hold; but exceptions are found. It is best revealed in the general means, as, under the conditions, might be expected. To what may this fairly constant ratio be ascribed?

The rate of decay of uranium is nearly three times as fast as that of thorium. Obviously the precise numerical value of the ratio referred to must have been changing throughout geological time and must continue to change. The uranium will have dwindled to insensible amounts long before the thorium. But the fact that there appears to be a numerical ratio which is preserved through the chemical divisions of the rocks, although the actual amounts involved may differ largely, must be significant of some controlling condition.

Now if all rock families derive their origin from some world-magma by certain processes of differentiation which do not select between the parent radio-

active substances, uranium and thorium, then we can account for the observed constancy of ratio. For if granites, for example, take from the parent magma a certain quantity of both the parent radioactive elements without disturbing their primal ratio, and if diorites and syenites take a different quantity, but still without disturbing the original ratio, then in subsequent ages the ratio of uranium to thorium, varying in the same manner both in granites, diorites, syenites, and the mother magma, will continue to be alike in all.

This subject naturally leads us to the interesting conclusion reached by Lord Rayleigh that the first formed silicate in rocks—zircon—is most exceptionally rich in radium. We seem to know little about mineral genesis in rocks. Hence we find here a tempting field for speculation. The oxide of zirconium is isomorphous with the oxides of uranium and thorium. It seems probable that herein is some explanation of the accretion by zircon of radioactive elements from the magma. The radioactive centre thus originating becomes the centre of a minute field of intense ionisation. These conditions may be supposed to be favourable to the crystalline growth of molecules around it. The radioactive nuclei are small and their field of influence is restricted, but the surrounding chaos is trembling on the verge of equilibrium and there is unlimited time. Of the chemical effects of radioactivity Soddy says: "The great chemical reactivity of otherwise inert substances in presence of the radioactive materials must always be remembered in the interpretation of their action." In fact it has been supposed by workers on this subject that there is first a dissociation of molecular aggregates and temporary formation of free atoms under the influence of the radiations, rendering the substance highly reactive, as in the nascent state. Much experimental evidence for this statement might be quoted. In some such way the growth of mica or hornblende around zircons may originate.

This concentration of radioactive elements gives rise to the radioactive haloes found in certain rock-forming minerals of early consolidation—notably the brown micas. These very beautiful manifestations of radioactivity in the rocks raise many questions. It is remarkable that the earlier observers regarded these minute objects as organic in origin. The only basis for this view appears to have been their behaviour when the containing mineral was heated to a high temperature. The halo then vanished or lost all definition.

Far-fetched as such an explanation may appear, we must remember that the real history of these objects was at that period absolutely undecipherable. It required a generation of scientific discovery and the brilliant advances which brought to light radioactivity, the transforming atom, and the phenomena of material radiation, before the real explanation was possible. Sollas, before the period of these discoveries, suggested that they were in some way caused by the presence of rare elements in the nuclear zircon which is in most cases to be found in the halo. To go any nearer to the truth was then impossible. The

¹ Hugo Müller lecture (slightly abridged), delivered before the Chemical Society on February 28.

wonderful similarity of dimensions and structure revealed by these objects seems to have escaped notice.

With the advent of radioactivity the explanation is simple. In this new domain, which borders at once upon radioactivity, chemistry, petrology, and geology, many curious facts have come to light. For the first time we can determine by direct visual observation the presence of radioactive elements in the rocks, and, given the halo, a single measurement of its radius tells us at once whether it was generated by uranium or by thorium. Some haloes there are which are generated in a curious way from the passage of the gaseous emanation of the uranium family which has wandered from the radium whence it originated and has become occluded in certain nuclei. These then have become centres of development of haloes possessing characteristic dimensions telling of their exotic origin. These are the only three sorts of haloes reconcilable with the known sources of radioactivity.

It is desirable to recall here the foundations upon which our knowledge of haloes is built. The fundamental assumption is that the α -ray is the all-sufficient source of the halo. For example, the atomic *débâcle* from uranium to lead takes place in fifteen stages. Of these, eight are attended by the expulsion of a helium atom as an α -ray carrying a charge of two units of positive electricity. The range in air of these rays varies from 2.7 cm. (in the case of the ray from uranium-1) to 6.97 cm. (in the case of radium- C_1). If the atomic disintegration occurs within a mica flake, these ranges are reduced some two thousand times.

We know something about what happens along the track of the ray in gases. The particles of the gas are ionised. Bragg plotted the curve of ionisation. He found that the curve was alike in form for α -rays of long range and of short range, and that the ionisation rapidly increased just before the ray lost so much of its kinetic energy as to be no longer effective. The range of the ray is measured to the point where—effectively—it comes to rest.

Suppose now that in the brown micas the ionisation is attended with certain chemical changes—for example, affecting the iron present—so that the mica is darkened in colour. Then this darkening intensifies along the path of the ray and is darkest just at the approaching end of its trajectory. If uranium is contained in a minute particle—a crystal of zircon most generally—the eight rays will all act upon the surrounding mica within a certain spherical volume which has the zircon at its centre and the outermost boundary of which is defined by the path of the helium atom discharged from radium- C_1 , the most penetrating of the rays. The radius of the uranium halo will therefore be about the two-thousandth part of 6.97 cm.—or, say, 0.035 mm. In the case of an emanation halo the outer dimension will be the same, for the penetrating ray of radium- C_1 decides its boundary, but the effects of the four least penetrating rays of the uranium family will be absent. If thorium be in the nucleus,

then seven rays operate on the mica and the outer dimension is determined by the range of thorium- C_1 , which is 8.62 cm. in air and becomes 0.041 mm. in biotite. Uranium and thorium haloes are thus readily distinguishable.

To determine the inner features, we lay out the ionisation curves of the eight rays of the uranium family, or the seven rays of the thorium family, or the four rays which generate the emanation halo and add the ordinates at sufficiently close distances. This gives us the integral curves of ionisation, and these curves we find bear close comparison with the actual halo. The apices of the curves correspond to the rings of darkened mica which lie around the nucleus. The depressions of the integral curve are depicted in the mica as annular areas of feeble darkening. But here a difficulty arises. Our method of arriving at these curves assumes that the rays affect the mica as if they travelled in parallel lines. But in fact they diverge, and when we plot the integral curve so

FIG. 1.—Ionisation curve for uranium haloes.

FIG. 2.—Ionisation curve for thorium haloes.

FIG. 3.—Ionisation curve for emanation haloes.

as to allow for this divergence, we get a curve not at all accordant with the halo.

In order to explain why the halo does not exhibit the effects of the divergence of the rays, we may assume that something like photographic reversal or solarisation occurs when one ray traverses the path followed by a preceding ray. This weakens the density of the inner parts more than it affects the outer parts of the halo, and it follows that the ultimate effect is much the same as if the rays had been parallel. This view also explains the early appearance of the outermost ring of all; for a minimum of reversal affects this. It is not at all an improbable assumption that reversal plays an important part in the generation of the halo as we see it.

We see, then, that we can foretell the appearance and dimensions of the inner parts of a halo according as it originates from uranium, thorium, or radium emanation. If we find haloes not in accordance with these dimensions, we must conclude that we are dealing with new radioactive elements, unless some means of reconciliation be forthcoming. Herein we find an important application of the radioactivity of the rocks to the advance of chemical science.

When we look at the integral curves of uranium, thorium, and emanation haloes, we see that in the case of uranium and emanation (Figs. 1, 2, and 3) a single conspicuous crest occurs which must appear in

the halo as an inner ring of small radius. In the case of thorium, two such crests appear close together. Those early rings are the first appearance we find. Their measurement will tell us what elements we are dealing with, although the halo is only in an incipient stage of development. Such rings are found well developed and easily measurable around nuclei of extreme minuteness.

We possess in haloes a means of identifying the presence of radioactive substances in rocks which much transcends in sensitiveness any other known method. The electroscope transcends in sensitiveness chemical gravimetric methods of detection many thousands of times. The billionth of a gram of radium per gram of rock may be detected by the electroscope. But we may have a zircon nucleus of the five-thousandth of a millimetre in diameter. We may suppose it endowed with a radium richness twenty-five times as great as obtained in the richest zircons measured by Lord Rayleigh. Then the mass of radium involved is only 3×10^{-18} gm. or the millionth of the billionth of a gram. Such nuclei may show a perfectly measurable and identifiable ring.

The reason for this extraordinary sensitivity is obvious. The halo is always old—often very old, and through all the successive ages of geological time the ionisation effect is slowly adding up. It is, in fact, not found in the younger rocks. We perceive the final effects of such feeble radiation exactly as we may detect on the photographic plate, after long exposure, stars which are for ever invisible to the eye.

On this account, also, the halo is important to chemical science. It gives us a means of exploration, almost uncanny, into the past history of the chemical elements. By its help we may answer questions which may not be approached in any other way. We can tell if the known radioactive elements formerly differed in their mode of disintegration or if other radioactive elements existed in the remote past. The important question as to whether during geological time radioactivity has been a diminishing phenomenon may be answered by the halo. For the halo is, in fact, a sort of hieroglyphic, a writing in the rocks, which admits of interpretation based on to-day's experience of what radioactivity involves. All this is equally important to the geologist. For he wants to know, as vital to the past history of the surface changes of the earth, whether the known radioactive elements evolved thermal energy as they do to-day, or whether in the past notably more or notably less energy from this source affected the earth.

That halo-reversal is an actual and definite phenomenon seems certain. We cannot, indeed, be sure that it is quite similar in character to photographic reversal; but it acts much in the same manner and there is considerable probability that the two phenomena are very much the same in character.

The theory of photographic reversal may be stated in a few words. The action of light on the photographic plate is photo-electric in nature. Electrons are released from the silver halide each bearing a certain quantum of energy derived from the absorbed luminous vibratory energy. These electrons penetrate a certain distance from the illuminated point, which remains positively electrified, and create around it

a negative electrostatic field. This ionised system constitutes the latent image. It may persist for months or years. If we apply a developer, the energy, potential in the latent image, is expended in promoting chemical interaction between the ionised silver halide and the developer. In this process the silver is liberated and is built up in the ionised region to form the visible image. Such is the typical course of events in the case of normal exposure.

Suppose, however, we prolong the exposure or use a very powerful source of illumination. The electrostatic field around the illuminated point grows stronger and stronger until finally the insulation breaks down. There is then re-combination of positive and negative ions and the plate is restored to its original state. At this stage development gives no visible image. The image has, in fact, been reversed, the former latent image having disappeared. This is the first

FIG. 4.—Uranium haloes in various stages of development. $\times 76$. From Leinster Granite (Devonian).

reversal. If exposure be continued beyond the point of reversal, the original phenomena are repeated and a new latent image is formed like the first one, and so with continuous exposure the events in the film are repeated. The successive reversals may be demonstrated by exposing for increasing periods consecutive areas of a photographic plate.

The α -ray carries a certain quantum of energy according to its initial velocity when it leaves the transforming atom. The ray consists of a helium atom carrying two unit positive charges. In its passage through the mica it does work of ionisation. The original chemical bonding is disturbed, and under the influence of the ionisation, atomic systems are built up which are stable just as the latent image is stable. But it is conceivable that a second ray traversing the same or a nearly adjacent region may destroy this equilibrium and cause a reversion to the original equilibrium or to some new state of atomic equilibrium. The former case would result in the restoration of the original state of the mica: the latter may involve a new chemical bonding. As a matter of observation the new bonding appears, at least in some cases, to result in bleaching of the mica. Possibly successive "images" and reversals may occur. In experiments

on the age of haloes, Rutherford produced very intense coloration in biotite by exposing it to strong α -ray radiation. It might be possible to obtain some definite knowledge as to what actually happens by continuing such intense α -radiation for long intervals of time.

In the oldest rocks we certainly find plentiful evidence of bleaching around radioactive nuclei. If these particles happen to be sufficiently isolated, we get a

FIG. 5.—X-halo. $\times 256$. Radius = 0.0294 mm. Ytterby mica. (Archaean.)

halo which may show some of its circular bands not as darkened areas but as colourless areas. If the particles are arranged in line and are sufficiently close together we get a bleached band, in the axis of which the particles are distributed. Outside the bleached band we see the effect of normal exposure in the darkening of the mica. Sometimes we find a halo very beautifully reversed or bleached where normally there would be successive dark rings.

In the study of haloes we have to bear other conditions in mind besides these changes brought about by reversal. Side by side in the oldest mica, embryonic haloes and "over-exposed" haloes are to be found, the former merely as a delicate ring of small radius surrounding a very minute nucleus, and the latter as a disc sometimes of almost impenetrable blackness (Fig. 4). Why is this? The answer is simple. The stage of development attained depends on two conditions: the age of the rock and the radioactive richness of the nucleus. These conditions correspond to duration of exposure and strength of illumination in the case of photography. Another obvious fact must also be borne in mind. The halo presented to us in the flake of mica may be a section off the centre of the halo-sphere, for serial sections of haloes in mica demonstrate that they are spherical. Rock sections revealing haloes contained in sections crossing the cleavage support this conclusion.

The phenomena attending bleaching have also to be held in view when studying these radiographs in very ancient rocks; for it may happen that certain outer or inner features may be obliterated thereby. In drawing the conclusion that a halo cannot be

reconciled with known varieties, further evidence than the external dimensions of a few examples is required.

In the micas of Ytterby, which are of mid-Archæan age (pre-Huronian), I have found haloes which cannot be reconciled with haloes originating from known radioactive elements. These haloes I have called X-haloes (Fig. 5). There appear to be two varieties. I distinguish them as X_1 - and X_2 -haloes. They are fairly numerous. Sometimes, while free from any sign of bleaching, they look pale and washed-out. This is due possibly to some effect of over-exposure, just as an over-exposed plate lacks strength. Or, possibly, it is due to the remarkable metamorphic effects which this mica has generally experienced. In places such faded haloes may crowd together so as to overlap. They vary somewhat in dimensions, both externally and internally. But this effect may be due merely to different stages of development. Generally they consist of a central dark disc surrounded by two or three consecutive wide bands, the innermost one of which may be reversed. I do not think it is possible to ascribe X-haloes to thorium. Moreover, the thorium haloes which occur in this mica are always easily identifiable.

Here, then, is an example of the peculiar use we may make of these radiographs. If my conclusions are correct, we here find evidence either for an unknown element which has radioactively vanished off the earth, or for an undiscovered radioactive element.

In this same mica of Ytterby—but of extreme rarity—certain haloes of minute dimensions and all completely reversed or bleached also occur. I have called these "hibernium" haloes (Fig. 6). The majority are very uniform in dimensions, the radius being 0.0052 mm. A larger size—less abundant—seems present. These are closely 0.0086 mm. in radius. Now the earliest inner ring of a thorium halo is 0.011

FIG. 6.—"Hibernium" haloes. Radii, 0.0052 mm. and 0.0086 mm. $\times 1064$. Ytterby mica. (Archaean.)

and of a uranium halo 0.014. If the conversion factor in this mica be taken as roughly 2000, the range in air of the rays responsible for the smaller hibernium halo would be a little more than 1 cm.

Each of these minute halospheres contains a nucleus accurately centred. If two such nuclei are sufficiently adjacent, the resulting halo is of the form of intersecting spheres. Three adjacent nuclei may give rise to a pear-shaped halo. There seems no doubt that their development is controlled by the nucleus in every case. As the bleaching is no objection to their radioactive origin, but in fact supports it, I see no alternative to the view that they are true haloes but of remarkably small dimensions. A prolonged search for other swarms of these haloes has proved unavailing.

It is of interest to notice that these haloes may be—not impossibly—generated by one of the known elements, for they must originate from a substance so feebly radioactive that no known method of observation would detect its radioactivity. This follows from the extremely small trajectory of the responsible α -rays. It will be remembered that Rutherford long ago pointed out that there existed a connexion between the initial velocity with which an α -ray was expelled and the period of the element giving rise to it. Geiger and Nuttall showed that a definite relation was deducible, most simply shown by plotting the logarithm of the constant of transformation against the logarithm of the range of the α -particle. Thus treated, the elements of each radioactive family are distributed approximately along a specific right line, and the lines for the uranium, thorium, and actinium series are sensibly parallel. From this investigation Geiger inferred that elements emitting α -particles of very small ranges would possess so slow a rate of transformation

that no known instrumental method would reveal the fact that they were radioactive.

The age-long integration effected in the halo, however, can reveal radioactive phenomena far beyond the power of instrumental measurement. It is, therefore, not impossible that in these haloes we detect the radioactivity of some of those rare elements which this mica first revealed to science.

Lastly, one conspicuous fact is everywhere forced upon us in our studies of haloes—the scarcity of visible radioactivity in the rocks and the immense antiquity of that which we observe. In the absence of this mode of tracing radioactivity into the past, we might quite reasonably have argued that in former geological times many of the known elements were in process of radioactive genesis. The study of haloes rules out this view. Again, what radioactivity we are acquainted with has not originated in recent times. It dates back into the oldest rocks. The appearances which I have endeavoured to describe show this clearly. The reversed or blackened-up haloes of the Archæan are entirely different in appearance from those of Lower Palæozoic age. Indeed the geologist may by these appearances derive strong evidence as to the relative antiquity of the rocks he deals with. We arise from halo-study more than ever impressed with the immense age of the elements, and yet we know that some of them are to-day perishing off the earth and that a definite period is placed to their existence. What the halo ultimately shows is the remoteness of those past ages which probably witnessed the evolution of the elements.

The Malarial Treatment of General Paralysis.

FOR many years it has been realised that the intercurrent of an acute specific fever, such as erysipelas, in cases of general paralysis of the insane, is frequently followed by marked improvement in the general condition, and attempts have been made to procure remissions by the induction of an artificial pyrexia. In 1917, von Jauregg introduced the method of inoculation with malaria. About 5 c.c. of blood are taken from the vein of a patient suffering from benign tertian malaria and immediately injected subcutaneously, intravenously, or intramuscularly into the general paralytic. The average incubation period is about ten days, after which typical malarial attacks appear. When the patient has passed through ten or twelve attacks, the malaria is arrested by the administration of quinine and a course of neosalvarsan is given. Improvement is observed soon after the cure of the malaria, and in early cases of general paralysis the patient may become as capable as before the onset of the disease. Von Jauregg obtained prolonged remissions in more than fifty per cent. of his cases, the most noticeable features being the cessation of fits, better articulation, and general improvement in the mental and physical conditions. Other European observers have reported equally good results; in a series of 296 cases, Gerstmann found remissions in sixty-eight per cent.; Weigandt obtained improvement in forty-four out of fifty patients. In Great

Britain the number of patients hitherto treated is small; Worster-Drought found improvement in all except one of twelve early cases; in a series of asylum patients, in whom the disease would be more advanced, improvement has been reported in six out of nine cases.

In dealing with syphilis of the central nervous system, the cerebro-spinal fluid affords an indicator of the inflammatory changes taking place in the brain and spinal cord, and the efficiency of treatment may be estimated by the resultant alterations in the fluid. So long as a positive Wassermann or any other abnormal reaction is given by the fluid, it cannot be considered that the disease has been eradicated. In cases of general paralysis, treatment by drugs has very little influence on these reactions; neither has it been found that inoculation with malaria, although producing remissions, has any effect in diminishing the intensity of the Wassermann and colloidal gold reactions. No patients have been observed for sufficient length of time to determine what period of improvement may be anticipated, but it must be remembered that spontaneous remissions are common during the course of general paralysis, and that relapses invariably follow. In view of the persistence in the cerebro-spinal fluid of the evidence of active syphilis, it cannot be expected that remissions following malarial inoculation will differ from those which arise spontaneously.