THE ALTERATION OF RADIOACTIVE MINERALS

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Received March 14, 1941
(Communicated by N. L. Sharma, Esq.)

The soundness of the "lead-ratio" method of determining the age of a radioactive mineral (and hence of the formation where it occurs) is well established, as the lead ratios obtained from different radioactive minerals from the same locality have been practically identical in many cases. Nevertheless it has been observed by different workers that different radioactive minerals from the same locality, and sometimes from the same pegmatite, indicate different ages; also that the uranium minerals generally indicate a higher age than the thorium minerals and these latter have lead ratios varying greatly among themselves. The case of thorium minerals from Norway and Ceylon is prominently illustrative.

From a study of lead accumulated in thorium minerals Boltwood\(^1\) and later Holmes and Lawson\(^2\) came to the conclusion that lead was not the end product of the disintegration of thorium, and even if it was so, a part only of the lead was stable and the remainder further disintegrated into thallium. Soddy\(^3\) and Lawson\(^4\) considered that the thorium minerals were of a secondary nature and necessarily gave lower age indications than the primary minerals with which they were associated. Against this, Joly\(^5\) appeared to have found evidence that uranium might have disintegrated more rapidly in earlier times than to-day, and consequently uranium minerals would give higher age indications than normal, whereas thorium minerals disintegrating at a constant rate would give correct age values. None of these ideas have been found to be satisfactory and they have been dropped in course of time. The formulation of the above ideas shows the complex nature of the puzzle and how the disagreeing lead ratios of radioactive minerals have affected the development of the fundamentals of radioactivity.

In the opinion of the present writer, the essential condition about the unaltered nature of the mineral was lost sight of by many investigators. We shall consider in this paper how the radioactive minerals undergo alteration and how the lead ratio of such minerals are affected in consequence of the process of alteration. We shall also discuss some relevant points in the light of the ideas presented here.

261
The radioactive minerals have a great tendency to occur in the metamict state. This phenomenon was first observed by Brögger\(^6\) in the case of the rare earth minerals and was thought by him to be due to hydration. Later Mügge\(^7\) considered that the radioactive substances occurring in these minerals by their disintegration were responsible for the metamict state of the minerals. Goldschmidt\(^8\) noted that minerals that usually occur in the metamict state are mostly combinations of weak acids and weak bases and according to him, the percolating waters cause hydrolysis in the minerals, the components of which then exist as a solid solution of the oxides, and consequently the minerals occur in the metamict state. Vegard\(^9\) thought that such minerals were probably formed under very high pressure, and as they are exposed to the ordinary pressure the crystal lattice breaks up and the change to the metamict state is reached gradually. Probably all the above factors are involved in the transformation of a mineral to the metamict state, and such a mineral is very much likely to be altered in the process of this transformation or subsequent to it by external agencies.

I would like to point out that a mineral in the metamict state is not necessarily in the altered condition. The changes to the metamict state and to the altered condition are due to two different sets of causes. The change to the metamict state signifies a change in the physical condition of the mineral and its composition is unaffected, whilst the alteration of a mineral always changes the composition of the mineral, some of its constituents being removed and replaced by other substances. The transformation to the metamict state is brought about purely by physical agencies, such as, by the radiations from the radioactive elements present in the mineral, and is also probably partly due to a release from immense pressure. These two processes may lead to an increase in volume which destroys the arrangement of atoms in the crystal lattice, thus causing the mineral to behave like an amorphous substance, \textit{i.e.}, the mineral is then in the metamict state.

The presence of solutions is essential for altering a mineral. These solutions may contain metallic salts, silica and also some \(\text{CO}_3\) dissolved in them. When a radioactive mineral becomes subject to the action of such solutions any of the following changes may occur: (1) The solution may exert a solvent action on some of the constituents of the mineral. (2) Chemical reactions between dissolved substances in the solution and the mineral may occur. (3) Sorption of substances in the solution by the minerals may take place. (4) Ion exchange may take place. We shall discuss these possibilities individually.

(1) There is an old observation of Brande\(^{10}\) that hydrated uranium trioxide dissolves in an aqueous solution of \(\text{CO}_2\). That this solvent action
of CO₂ is also manifest in nature is seen from the occurrence of the mineral rutherfordine, which has been found as an yellow alteration product of the uraninite of the Uruguri Mountains, East Africa. The occurrence of sharpite, a radial fibrous, yellow-green carbonate from the Shinkolobwe deposit, Katanga, may also be due to the same cause. Simple solution is less likely to happen than solution involving chemical reactions. It is, indeed, very difficult to distinguish between the two.

(2) That chemical reactions between substances dissolved in the percolating waters and a mineral may occur is easily understandable; here the law of mass action would decide the course of the reaction. Even very dilute solutions of acids and alkalies would cause considerable damage to a rock or mineral by prolonged action. The acid waters would easily dissolve uranium minerals, whilst alkaline waters would react with silicate and phosphate minerals, such as, allanite, monazite, etc. The presence of CO₂ dissolved in water together with salts of metals (such as those of alkalies and alkaline earths) would mostly determine the pH of the solution due to the formation of carbonates and bicarbonates. Of course, the presence of silica and other salts in the solution will cause secondary and complex reactions to take place, and of the many reaction products some will be noticeable in the alteration products of the minerals concerned and others are lost in solution.

The solvent action of acid water on uranium minerals and subsequent precipitation of uranium as phosphate is noticeable in the case of alteration of pitchblende from Gaya District, Bihar (India), and also of uraninite from Ruggles mine, near Grafton Centre, New Hampshire (U.S.A.). The solvent action of alkaline water has been found to be mainly responsible for the formation of thorogummite from yttrialite, of tengerite from gadolinite, hellandite and yttrialite, and for the alteration of allanite. Further, if the percolating water is alkaline and carries silica, it is possible that when it comes in contact with the radioactive mineral, it will lose its alkalinity, and silica as such may be deposited in the mineral. This may quite happen in cases of minerals like monazite where the alkaline solution may attack the phosphate and some silica can get in. Besides these, oxidation due to oxygen dissolved in the solution and hydrolysis (in Goldschmidt's sense) may also take place. These are possibly important steps in the process of alteration of a mineral.

(3) A radioactive mineral seems to be particularly suited for sorbing substances from solution. The transformation of such a mineral to the metamict state brought about by radiations from radioactive substances and also by release from immense pressure, presumably renders the mineral somewhat porous; loss of helium from the mineral may be another cause of
its porosity. Due to the porous nature of the mineral there is greater surface, greater capillary action, Langmuir forces are more operative and the process of absorption takes place readily. Further, the sorbed salts and the compounds formed in the mineral by reaction with percolating water exert a sort of wedge action in disrupting the internal structure of the mineral; and this is one of the principal factors involved in the alteration of a mineral.

(4) The presence of $\text{UO}_3$ in most uranium minerals shows that a part of the uranium exists as uranate in the minerals; it may easily be conceived that part of the lead in a radioactive mineral exists as plumbate. In a mineral where uranate and plumbate ions are present, silica present in percolating waters as silicate, may easily be able to displace these ions. In uranium minerals the displacement of uranium by silica is more easily effected than that of lead because the uranate ions are present in much greater numbers than the plumbate ions. In thorium minerals where there is little uranium, lead is lost to a considerable extent. The same is also true of the thorium minerals, such as brøggerites and uranothorites, which contain comparatively large quantities of uranium. The presence of water in these minerals may be explained by supposing that hydroxyl ion replaces the acid radical.

Of the above four factors involved in the alteration of a radioactive mineral, the last one is the most important. This factor may explain why uranium minerals, suspected to be altered, tend to give higher lead ratios than pure unaltered minerals and why similar thorium minerals tend to give low results. We can also explain why the weathering of uraninite has been found to be selective in the removal of uranium, and how uranium minerals of secondary origin are formed. The mode of alteration of uraninites is what would be expected from the view put forward here. We have seen why thorium minerals which have undergone alteration give low age indications, and we have an explanation for Holmes' finding that "the higher lead ratios of thorium minerals are, like the higher helium ratios, most likely to approach the true index to age". We may expect that thorianites being less liable to alteration through ion exchange—these being oxidic minerals—would give higher age indications than the thorites, which are likely to be altered much more easily. This has, in fact, been found to be the case by Holmes in the case of minerals from Ceylon. We also understand the raison d'être of the "silica test" of the freshness of titanio-tantalo-niobate minerals, which Ellsworth found out as a result of his considerable experience, and why such minerals containing silica have too low lead ratios.

In the alteration of phosphate minerals, like monazite, tetra-co-ordinated phosphate ion may easily be replaced by tetra-co-ordinated silicate ion.
The Alteration of Radioactive Minerals

The effect of alteration on the lead ratios of monazite and similar minerals would be expected to lower the lead ratios according to the ideas put forward in this paper. Such will indeed be the case if the mineral is considerably altered. When the alteration is slight, the silicate ion will mostly replace the phosphate ion, while the plumbate ion, being much less in number, will not be replaced. From this reasoning, the age indications of slightly altered monazites may be reliable.

In the process of alteration due to ion exchange, both the cations and anions are involved. Ion exchange involving cations does not seem to be of much importance as regards the removal of lead, uranium or thorium, though the possibility of the removal of thorium and uranium by calcium and that of lead by potassium is not denied; but it is thought that such exchange would be important for indicating that the mineral has been subjected to the action of percolating water. Alkalies are usually not present in such minerals, and their presence would indicate alteration of the mineral. It has been observed that in secondary uranium minerals, silication and hydration are quite common; alkalies have also been found when sought for. Generally speaking, in pitchblendses, an increased silica content is accompanied by hydration, and alkali salts are usually present in such cases. The hydration is not always in evidence; when the alteration is not serious alkalies are absent, silica and water are low and one of these may be very low or absent altogether. The presence of alkalies in addition to silica and water in relatively large quantities is a sure indication that the mineral has been considerably altered. In thorianites—these being oxidic minerals—ion exchange is not possible and consequently we find little water, practically no silica and no alkalies at all; in contrast to these, thorites often contain large amounts of water (6–10 per cent.) and appreciable amounts of alkalies (0.25–0.82 per cent.). Uranothorites also contain water (9.3–12.0 per cent.) and alkalies (0.11–0.77 per cent.). The decomposition products of thorites, e.g., calciothorites, freyalite eukrasite and mackintoshite contain appreciable quantities of alkalies (0.7–2.5 per cent.). The same is true of the zirconium minerals and the titano-tantalo-columbates.28

In the case of monazites it is rather difficult to ascertain from analytical data whether they have undergone any alteration. It is not justifiable to think that the silica is present in monazite as thorite,24 and the absence of thorite from monazite (in thin sections) does not mean that the presence of silica is a result of alteration. In monazite silica is as much a primary constituent as is phosphate. Water is almost always found; Johnstone25 observed that combined water in monazites varied from 0.2 to 1.2 per cent.
In such a case the presence of alkali salts in the mineral may be considered as an indication of the altered nature of the mineral. I want to emphasise the point that the presence of small quantities of silica and water in a mineral is no indication of its alteration. The age calculated from such minerals may be reliable. When comparatively large quantities of silica and/or water are present, the mineral may be considered to have undergone alteration; in all such cases alkalis will be found to be present in the minerals. The presence of alkalis is the only sure criterion by which a suspected mineral normally containing silica and water may be judged to have undergone alteration.

It is to be noted that our ideas as regards the process or mechanism of alteration is a general one and applicable not only in the case of the radioactive minerals but in the case of other minerals also. To give an example: all titanium minerals which contain appreciable quantities of water and silica contain alkalis; these minerals are to be regarded as altered.

It would thus seem that from a chemical analysis silica, water and alkali content of a mineral would be a fair indication whether its lead ratio would be reliable or not. The relative abundance of $\text{UO}_3$ over $\text{UO}_2$ in a mineral is due to auto-oxidation; and it would be rash to consider it as indicative of the altered nature of a mineral. The preponderance of $\text{UO}_3$ over $\text{UO}_2$ may be caused by alteration, but is not necessarily a sign of it.

Holmes in 1926 suggested "that the discrepancies in thorium minerals are due to the fact that lead present as oxide or silicate would be more easily removed by percolating waters and kinetic exchange than the lead in uranium minerals, which may be present actually or potentially as a highly insoluble uranate". This was as a result of the study of the lead ratios obtained from many thorium minerals and a smaller number of uranium minerals from Norway, Ceylon and U.S.A., and based on the atomic weight of the lead and the amounts of uranium and thorium present in the mineral as found by analysis. He calculated the amounts of thorium-lead and uranium-lead and found that the age as deduced from the accumulation of thorium-lead is, in practically all cases, lower than that deduced from the accumulation of uranium-lead. Almost all the minerals examined by Holmes were altered specimens. In short, Holmes' selective leaching hypothesis recognises that the minerals concerned have undergone leaching and thorium-lead (also to a much less extent uranium-lead) has been leached out as a consequence.

He later on recognises that "the hypothesis cannot, of course, represent the whole truth, for it is not to be supposed that while lead was being leached out of a mineral the proportion of uranium and thorium would continue to remain unchanged". Herein lies the greatest weakness in Holmes' theory.
and the chief difficulty in our accepting it. Holmes' hypothesis is based on results deduced from admittedly altered minerals and cannot find acceptance. Gleditsch and Quiller's corroboration of Holmes' idea is not tenable as their investigation was carried out with quite altered minerals. R. C. Wells has adversely criticised Holmes' idea as it postulated different behaviours of the isotopes of the same element, namely, uranium-lead and thorium-lead, towards circulating water, and has suggested, following Ellsworth, the alternative explanation that uranium has been leached out relative to other elements. It also follows that Holmes' idea that "when lead is lost it provides solutions that are relatively rich in thorium-lead, and when lead is gained the latter presumably derived from the same solutions—is also relatively rich in thorium-lead" becomes unacceptable.

The irregularities in lead ratios shown by different minerals from the same locality may actually indicate different periods of their formation, as has been thought by Hess and others and for which Hess and Wells seem to find a support. Following the same current of idea, Kirsch suggested rejuvenation of magma as explaining the erratic lead ratios of the bröggerites from Moss, Norway. Holmes' comment on the idea is "that a very top-heavy superstructure has been raised on extremely slender and inadequate supports," but he admits of the possibility of there being two periods of bröggerite formation. He further says "that the lead ratios of certain other suites of minerals also suggest that the latter were the products of two periods of igneous activity rather than one; such are the uraninites of Morogoro with ratios 0.084 and 0.091 and possibly the thorianites and uraninites of Ceylon with respective ratios of Ca 0.08 and 0.065".

Kirsch in collecting his data of the lead ratios of the bröggerites from Moss, Norway, included the lead ratios of altered minerals and of those which had not been analysed sufficiently accurately for the purpose. The inclusion of such lead ratios invalidates any theory based on such data. That the minerals of a pegmatite may be changed long after its formation by later igneous activity in the same place is a possibility that is not denied, but irregular lead ratios shown by radioactive minerals of the same pegmatite is not necessarily a proof of such rejuvenation of magma. In my opinion Kirsch's idea as regards Moss bröggerites is not tenable and even Holmes' modification of the same idea is not warranted by the existing data.

The reasons for assuming that common lead is present in radioactive minerals seem to be the following: (1) Kirsch found that the atomic weight of lead derived from some radioactive minerals differed from that calculated from the uranium and thorium content of the minerals, and he ascribed this
T. C. Sarkar

difference to the presence of common lead in the minerals. (2) Kovarik\textsuperscript{36} argued that since Joachimsthal pitchblende contained common lead, other radioactive minerals would similarly contain it to some extent. (3) He tried to support his argument with the observation that the ratio $\lambda_u: \lambda_{Th}$ calculated from different radioactive minerals of different geological ages, was not a constant as it ought to be.

Ellsworth\textsuperscript{37} as well as Holmes,\textsuperscript{21} on mineralogical evidence, do not entertain the idea that common lead occurs in radioactive minerals derived from pegmatites. Ellsworth also points out that Kirsch's finding may be due to the altered nature of the minerals examined. Kovarik's first argument is not tenable, because the amorphous nature of the Joachimsthal pitchblende, its mode of occurrence and the associated minerals, all go to make its case a special one, and not representative of the radioactive minerals derived from pegmatites. His second argument would have been valid if the minerals he examined were perfectly fresh and unaltered, which they were not. In such minerals naturally the ratio $\lambda_u: \lambda_{Th}$ which is equal to $\frac{206}{208} \cdot \frac{208-A}{A-206}$ would not be a constant. Incidentally the reason why Kirsch's\textsuperscript{38} method of determining $\lambda_{Th}$ gave an incorrect value lies in the fact that the Ceylon thorianite, which Kirsch utilised, was not quite fresh and consequently gave unreliable data.\textsuperscript{39}

We may then accept that no common lead is present in radioactive minerals derived from pegmatites, and it is therefore unnecessary to determine the atomic weight of lead from a mineral. Such a determination would only indicate whether a mineral is altered or not. The altered character of a mineral can easily and definitely be known from physical and chemical examinations, without taking the trouble of an atomic weight determination.

\textit{Summary}

The discordant lead ratios of uranium and thorium minerals gave rise to a number of unsuccessful but interesting ideas to explain them. A fresh attempt has been made here based on the alteration of radioactive minerals. The alteration of a radioactive mineral is distinguished from its transformation to the metamict state. The latter is entirely caused by physical agencies, whereas the presence of solution is essential for altering a mineral. Such a solution may exert (1) a solvent action; or (2) chemically react with a mineral; (3) sorption of substance from the solution as well as (4) ion exchange may take place. Each of these possibilities has been considered individually.

In (4) the supposition is made that part of lead in the radioactive minerals is present as plumbate just as uranium is partly present as uranate.
Silica present in percolating waters as silicate may displace plumbate and uranate ions. This idea successfully explains (1) the high lead ratio obtained from altered uranium minerals, (2) low lead ratios from all altered minerals containing small quantities of uranium, (3) the alteration of uraninites, and (4) the raison d'être of the "silica test" for the freshness of titano-tantalo-columbates.

Reasons are given for the belief that age indications of slightly altered monazites may be reliable, that the presence of alkalies in a primary radioactive mineral is a sign of its alteration, and that the process of alteration as considered here is a general one and applicable to non-radioactive minerals as well.

Holmes' selective leaching hypothesis, Kirsch's idea of magmatic rejuvenation to explain erratic lead ratios of Moss bröggerites and the idea of possible presence of common lead in radioactive minerals have been discussed and found unacceptable.

Acknowledgements

My thanks are due to Principal C. Forrester of the Indian School of Mines, Dhanbad, for encouragement in the earlier stages of the work, and also to Dr. P. K. Ghosh of the Geological Survey of India and Mr. N. L. Sharma of the Indian School of Mines, for kindly going through the manuscript of the paper.

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