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PRELIMINARY LABORATORY INVESTIGATION OF RADIOACTIVE FERRUGINOUS SANDSTONE FROM MADIGANS PROSPECT, BYNOE HARBOUR, N.T.

by

W.B. Dallwitz.

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SUMMARY

Specimens of radioactive ferruginous sandstone from Madigan's Prospect, Bynoe Harbour, N.T., have been examined by autoradiographic, mineragraphic, mineralogical, and petrographic methods, and tested treated, and analysed chemically; radiation measurements have been made at appropriate stages in the investigation to ascertain the behaviour and distribution of the radioactive material.

It has been established that the radioactivity is due almost entirely to thorium, and it is likely that this metal was precipitated colloidally((?) with iron hydroxide) at the time when the beds of sandstone were laid down. Subsequent migration and marked concentration of iron oxides and thorium have taken place in some, if not all, places in the more highly radioactive parts of the deposit.

In the specimens examined it seems possible that the thorium exists as the orthophosphate or as silicophosphate.

Samples of less radioactive (and less ferruginous) sandstone adjacent to the highly radioactive parts of the beds have not been studied. Investigation of this sandstone, and further study of the highly radioactive rock, should be undertaken.

INTRODUCTION

Specimens of strongly radioactive ferruginous sandstone from Madigan's Prospect, near Bynoe Harbour, N.T., have been submitted for laboratory examination by R. S. Matheson and Dr. N.H. Fisher. Matheson's specimens represent highly ferruginous material near and in joint planes in a less radioactive and less ferruginous sandstone. Dr. Fisher's specimen was taken from a massive uniformly ferruginous and radioactive sandstone, in which there appears to have been no secondary concentration of either iron oxides or the radioactive substance.

The object of this investigation was to identify the material responsible for the strong radioactivity noted in the samples.

PETROGRAPHIC, MINERAGRAPHIC, AND MINERALOGICAL OBSERVATIONS

The rocks examined so far are coarse to medium ferruginous sandstones.

Ultraviolet light inspection reveals the presence of very rare, small, isolated, specks of a green-fluorescing presumably uraniferous mineral; there is not sufficient of this mineral to enable identification. Thin films of a white substance, some of which has a bluish fluorescence, and some yellow-green, are more abundant. The white, green-fluorescing mineral was tested for uranium by W.M.B. Roberts with negative result, and its identity has not yet been established.

Autoradiographs have been prepared from some of Matheson's material. These show that radioactivity is distributed almost uniformly throughout the ferruginous cement; stronger activity is shown at and near the edges of parts of the samples, suggesting relative abundance of the radioactive substance near smaller cracks and joints within a rock which itself owes its richness in iron oxides and radioactive substance to concentration in and near major joints (Rosenhain, 1953).

Specimens of these rocks contain from 40 to 70 per cent. iron oxides by volume. Most of the oxide is dark brown in hand-specimen, but patches and irregular bands are light rust-coloured.

Thin sections show that the rock consists almost entirely of iron oxides and detrital quartz grains. The iron oxides have migrated into cracks in the quartz and have also "eaten into" the grains marginally, so that their rounded shapes are partly destroyed. Some parts of the rock are much richer in iron oxides than are others, and probable argillaceous material is mingled with the ferruginous minerals. A few books of chlorite or bleached biotite are scattered through the rock, and a single book of muscovite occurs in a quartz grain.

W.M.B. Roberts prepared four polished sections of the rock, and he reports, in part, as follows:

"The matrix is a mixture of iron oxides consisting of an anisotropic oxide which differed from hematite in that it showed less anisotropism, and etched with $SnCl_2$ and HCl; this conforms to the hydrated oxide, goethite. It occurs as fine-grained aggregates, and as areas up to 0.3 mm. showing a colloform texture. Hematite and magnetite, in lesser amounts, are the other two oxides present. No evidence of a separate uranium mineral was found in any of the sections.

The oxides are all closely intergrown, and much altered to a limonitic material. It was not possible to separate them for microchemical tests, so these were done on a mixed powder. Of three tests made, one showed a definite uranium reaction with sodium and zinc acetate, and the remaining two were negative."

Roberts also carried out four additional zinc acetate tests for uranium on a strongly radioactive portion of a specimen from which an autoradiograph was prepared, and all were negative.

Dr. Fisher has collected ex situ a specimen of a massive, dark brown, ferruginous sandstone wherein radioactivity does not appear to have been concentrated along joints by secondary processes. It is this specimen which shows the thin white film of yellow-green-fluorescing mineral.

Polished sections reveal that the rock is very similar to that forwarded by Matheson. In thin section the only recognizable difference is that much more iron oxide occurs in cracks in the quartz grains; in general these cracks occur in a definite pattern, and must, therefore, be related to tectonic stresses to which the rock has been subjected. The iron oxides have migrated into the quartz from the matrix by replacing silica, for some grains of quartz have been more than half replaced. No radioactive mineral was recognizable in the slides. A dish concentrate made in the field by Dr. Fisher consisted apparently only of iron oxide and a few quartz grains.

Four zinc acetate tests for uranium, carried out on a representative sample of the specimen, gave negative results, and a definite, though rather weak, reaction for copper was obtained with potassium mercuric thiocyanate.

D.A. White performed three sodium fluoride bead tests for uranium on the same sample, two with negative result; presumably the positive test was obtained through the fortuitous presence of a grain of the secondary uranium mineral noted during ultraviolet light inspection.

CHEMICAL ANALYSES AND TESTS

A chemical analysis on material from Madigan's Prospect has been carried out for Mr. S. Mazlin by W.H. Roache, assayer, of Brisbane. Results of the analysis are as follows:

	%
SiO_2	16.8
ThO_2	9.57
P_2O_5	2.81
Al_2O_3	4.00
Fe_2O_3	58.8
Ignition loss	7.20
Total:	99.18

To check some of these results a portion of the specimen collected by Dr. Fisher has been forwarded to the Director of Mines, Adelaide. He has been asked for determinations of uranium, thorium, silica soluble in hydrochloric acid, and phosphate. W.M.B. Roberts has carried out an approximate determination of ThO_2 on part of the same sample, and he arrived at the figure of 2.3 per cent.

Dr. Fisher's specimen has been subjected to certain simple chemical treatments in order to get more information about the nature and distribution of the main radioactive substance in the rock.

To test the possibility that the radioactivity is due to resistant, detrital thorium-bearing minerals, a powdered portion of the specimen was digested in boiling concentrated hydrochloric acid. No such minerals had been observed in the thin section - though it was possible that they were masked by iron oxides - and none was seen in the insoluble residue from the acid treatment. This residue consisted of quartz and a small quantity of an isotropic or slightly doubly-refracting clay mineral - probably halloysite - whose refractive index is 1.47±; all trace of iron oxide had been removed, even from within the quartz grains, and no radioactivity remained in the residue.

In a second test a more representative bulk sample was treated with hydrochloric acid for a shorter period. The insoluble residue in this case consisted of quartz, white clay, iron-stained clayey or sericitic material, accessory rutile, and rather rare zircon, and gave a 120 counts per minute, whereas the sample before digestion gave 1600 counts per minute; the residual radioactivity almost certainly emanated from the iron-stained clayey material.

Next a less drastic procedure was adopted. An attempt was made to remove iron oxide by a method described by Leith (1950), who applied it particularly to cleaning mineral grains in sediments. A small portion of the sample was crushed to pass through a 40-mesh sieve, and then boiled for 40 minutes in a 5 per cent. solution of oxalic acid containing a cylinder of sheet aluminium. By this method, Leith found even calcite to be only slightly attacked, and so it was hoped that its use would leave the radioactive substance unscathed. Accordingly, 2.6 gm of sample, giving 950 counts per/minute on a ratemeter were digested as described. The insoluble residue was washed repeatedly by decantation, dried, and found to weigh 0.75 gm; it gave 550 counts per minute, consisted of quartz, iron oxides coated and mingled with an off-white substance (possibly a clay mineral), and rare zircon, and was contaminated with ferrous oxalate. The filtrate was evaporated almost to dryness, and, in this state, gave 160 counts per minute.

The total radioactivity measured in the evaporated solution and in the insoluble residue is several hundred counts per minute short of that recorded in the original sample. This is due to three factors:

(1) Loss of finely, divided radioactive material during washing of the insoluble residue by decantation.

(2) Reduced concentration of radioactive material in insoluble residue through dilution with ferrous oxalate.

(3) Relatively low concentration of soluble radioactive material in the evaporated solution due to dispersion in a large volume of aluminium oxalate, ferrous oxalate, and oxalic acid.

In a second digestion with oxalic acid and aluminium 5.45 gm of representative bulk sample were treated from the same specimen. This sample gave 1,600 counts per minute before treatment. The insoluble residue was not washed by decantation, but was filtered and washed so that any finely divided radioactive material would be retained. This residue consisted of quartz, iron oxides coated and mingled with a probable clay mineral, indefinite sericitic or clayey material, accessory rutile, and rare zircon, and gave 850 counts per minute. The retention of the sericitic or clayey material, previously largely lost through washing by decantation, must have been responsible for the increased count (850 per minute) as compared with 550 recorded in the residue from the first oxalic acid - aluminium digestion. The count would have been even higher if the concentration of radioactive material had not been reduced by a very large amount of ferrous oxalate, a substance which was mostly lost in the first test through washing by decantation.

The solution from the second digestion was evaporated almost to dryness, and the mixed salts registered 300 counts per minute.

W.M.B. Roberts carried out microchemical tests for phosphate on both the insoluble residue and the solution, but obtained a positive reaction only from the latter. Probably the negative reaction for phosphate in the insoluble residue is due to the fact that (?) thorium phosphate is intimately associated with iron oxides (see also part 5 of report), which are insoluble in nitric acid (used to bring substance into solution for phosphate test). Sodium fluoride and zinc acetate tests for uranium on the soluble salts, after evaporation to dryness, were negative.

INTERPRETATIONS AND CONCLUSIONS

From the results described above the following deductions and conclusions as to the state, nature, and possible origin of the radioactive substance have been made.

Autoradiographs show that the radioactive substance is distributed almost uniformly through the ferruginous matrix of the rocks examined. Petrographic and mineragraphic examination contribute nothing further to the solution of the problem; the rare grains of zircon noted in the chemically treated samples can be dismissed as contributing only infinitesimally to the recorded radioactivity.

Uranium is probably present in minute amounts of secondary mineral, but the failure to obtain consistently reproducible positive uranium tests in such a strongly radioactive rock indicates that that metal is very far from being the main source of activity. In fact, the results of the Brisbane assayer and of Roberts' chemical analysis and other tests show almost beyond doubt that the radioactivity is due nearly entirely to thorium.

The hydrochloric acid and oxalic acid-aluminium treatments indicate that the radioactive element is present in a fairly easily soluble form. On prolonged boiling with concentrated hydrochloric acid it is, apparently, removed simultaneously with the last trace of iron oxide, as shown by the fact that the iron-free residue is non-radioactive, whereas those residues which still contain some iron oxide are radioactive.

The chemical analysis by W.H. Roache, of Brisbane, is of interest in that calculation shows that the phosphate present falls short of satisfying the thorium oxide, as determined, by only 16 to 17 molecular per cent., if the formula $Th_3(PO_4)_4$ - the orthophosphate - is assumed. The remaining thorium oxide may be satisfied by silica, to give a thorium silicophosphate; to provide a lead on this possibility a determination of acid-soluble silica is desirable. According to the Handbook of Chemistry and Physics (1947), artificial thorium orthophosphate is a non-crystalline, gelatinous, white substance, soluble in 30 per cent hydrochloric acid.

From the above data it is tentatively suggested that the radioactivity in the rocks examined is due to thorium phosphate or silicophosphate distributed more or less uniformly in a finely divided state through the iron oxide matrix. Secondary processes have clearly been responsible for enrichment in iron oxides and radioactive substance along joint planes in some, if not all, parts of the deposit. According to Rankama and Sahama (1950, p.591), who quote the results of Dietz, Emery, and Shepard (1942), phosphates are deposited inorganically in shallow seas from colloidal suspension.

Rankama and Sahama (p.573) refer also to the work of Pettersson (1939), who found that thorium, in a marine environment, tends strongly to be precipitated with the hydroxides of iron and manganese; however, from the context, it is clear that the quantity of thorium so deposited is measurable as parts per million rather than as percentage. Nevertheless it is possible that both iron hydroxides and thorium phosphate were colloidally deposited in the rocks at Madigan's prospect, and that, during a tectonic episode, migration and concentration of those substances took place along joints. Microscopic evidence of migration is provided by the presence of abundant iron oxides as crack-fillings in quartz grains.

FUTURE WORK.

The investigation and results described above are, in some respects, preliminary and tentative. Autoradiographic and mineralogical studies could be carried out on residual iron-oxide-rich radioactive particles at various stages of digestion with acids. It should also be possible to separate such particles, with the isodynamic and electrostatic separators, and carry out chemical analyses on them.

The exact course of future investigation is difficult to outline at this stage. However, it seems virtually certain that it will be impossible to isolate the radioactive substance in a pure form, so that conclusions will depend, not on direct tests on a relatively simple compound, but on deductions made from experimental work on a mixture of compounds.

Samples of less radioactive sandstone, which are the host rocks for the highly radioactive material, also remain to be examined,

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