SULFUR IN CYRTOLITE AND ITS INDICATION OF GALENA

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In an effort to account for the low atomic weight of the lead from Bedford Cyrtolite I, as compared with that from another sample of Bedford Cyrtolite, designated as Bedford Cyrtolite II, Baxter and Alter[1] had polished sections made of both cyrtolites, and found that both contained a small quantity of galena crystals. The area of galena, as estimated by Moehlman (included in the article by Baxter and Alter), in Bedford Cyrtolite I, is 0.05%. They were not able from an examination of the sections to detect such a difference between these two samples of cyrtolite as to account for the difference in the atomic weights of the lead.

Kerr[2] likewise polished a number of specimens of Bedford cyrtolite. These he studied under the microscope and reports what he calls "U-galena." In an analysis made for him and reported in his paper, the amount of lead and sulfur is in the ratio of one atom of lead to one of sulfur, that is, just enough sulfur to combine with the lead as lead sulfide. The statement is made that: "It is probable, therefore, that all of the lead in the Bedford cyrtolite is combined with the sulphur in the form of galena." This is referred to as U-galena. The analysis reported by Kerr shows the amounts of lead and sulfur as follows: Pb = 0.33%, S = 0.05%. Most of the Bedford cyrtolite is of such a mixed nature that it is unlikely that two different samples would yield the same percentage of lead. The samples selected for age determinations were carefully chosen samples of the black "unaltered" material. Even with careful sampling of so called unaltered pieces, samples prepared by different individuals show a slight difference in the values for lead and uranium, as is illustrated by Bedford Cyrtolite I and II. The lead-uranium ratio, nevertheless, in the case of these two samples is the same.

Since the original materials used in previous age determinations were still available at the University of Missouri (portions of each had been saved), and in view of the importance of the amount of work that has already been done on these cyrtolites, it was decided that a careful sulfur determination on these samples would be of interest and possibly of some value.

SAMPLES

The samples were a part of the same ground and prepared materials which were used in the different age determinations. Bedford Cyrtolite

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[1] Baxter and Alter, *Jour. Am. Chem. Soc.*, vol. **57**, p. 467, 1935.

[2] Kerr, *Am. Mineral.*, vol. **20**, p. 443, 1935.

I[3] was part of the sample which gave Baxter and Alter an atomic weight of 205.93 for the lead. Bedford Cyrtolite II[4] was also part of the sample prepared by Baxter and Alter. The Hybla cyrtolite[5] was likewise of the same sample as that used for the age and atomic weight determinations of its lead. The analysis of the Henvey cyrtolite has just been completed and will be reported in detail in the near future.

The following table is a summary of the more important data on these cyrtolites compiled from the various references listed above:

Cyrtolite	Pb	U	Th	Pb/U	At. Wt. of Pb.	Approx. age in millions of Yrs.
Bedford I	0.374	7.29	0.0	0.0513	205.931	400
Bedford II	0.351	6.73	0.0	0.0522	206.072	400
Hybla	0.043	0.529	0.080	0.078	206.20	600
Henvey	0.036	1.83	0.01?	0.019	—	140

METHOD OF ANALYSIS

Total Sulfur

A one gram sample was fused with sodium peroxide in a nickel crucible which was protected from fuel gases by means of an asbestos board with a hole to receive the crucible. The crucible was leached and washed with water and finally with a small amount of hydrochloric acid. The liquid was then heated to boiling, filtered by suction through a buchner funnel and washed with water containing a little sodium peroxide. The filtrate was then acidified with hydrochloric acid and evaporated to 10–20 ml., permitting the salts to crystallize. The suggestions of W. A. Turner, as given by Hillebrand and Lundell,[6] were followed so as to reduce considerably the error due to the large amount of sodium chloride formed from the decomposition of the peroxide by hydrochloric acid.

Twenty-five ml. of concentrated hydrochloric acid were then added. In cases where the salts were difficult to remove from the sides of the beaker, a little water was used. Another 25 ml. of hydrochloric acid were

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[3] Baxter and Alter, *loc. cit.*
Muench, *Am. Jour. Sci.*, vol. **21**, p. 350, 1931.

[4] Baxter and Alter, *loc. cit.*
Muench, *ibid.*, vol. **56**, p. 1536, 1934.

[5] Muench, *Am. Jour. Sci.*, vol. **25**, p. 487, 1933.
Baxter and Alter, *loc. cit.*

[6] Hillebrand and Lundell, *Applied Inorganic Analysis*, p. 812.

added, and then filtered through a small buchner funnel containing a carefully washed asbestos mat. The residue was washed carefully with about 50 ml. of concentrated hydrochloric acid. The filtrate was transferred to a beaker and evaporated to 5–10 ml. An equal volume of water was added and filtered if necessary. It was diluted to 200 ml., heated to boiling and about 5 ml. of a 10% barium chloride solution added very slowly. After simmering on an asbestos covered hot plate for 1–3 hours, it was allowed to stand 18 hours. After filtering through a filter paper, and washing with a small amount of water to remove the barium chloride, the residue was ignited and weighed in a platinum crucible. It was then treated with a drop of hydrofluoric acid and sulfuric acid and evaporated, ignited and weighed. Four comparison blanks were run with the samples.

Soluble Sulfates, Insoluble Sulfides, Soluble Sulfides and Insoluble Sulfates

The method given by Hillebrand and Lundell was followed. This in part involves the following procedure: the sulfur of all soluble sulfates was extracted by boiling with hydrochloric acid in an atmosphere of carbon dioxide, and finished as quickly as possible to reduce the error resulting from the oxidation of sulfide sulfur to sulfuric acid by any ferric salts that may be dissolved. The soluble sulfate sulfur found in the hydrochloric acid extraction was determined in the usual manner.

In the residue from the hydrochloric acid extractions, the sulfur of the insoluble sulfides was determined, after oxidation with nitric acid. The sulfur of soluble sulfides and insoluble sulfates was calculated by subtracting the sulfur in the above fractional sulfur determinations from the total sulfur.

The two samples of Bedford cyrtolite show the same percentages of sulfur. The analyses throw no light on the cause of the low atomic weight of the lead that Baxter and Alter obtained for Bedford Cyrtolite I, for sulfur does not, according to the above results, serve to distinguish between the two cyrtolites, nor to indicate any difference in the lead. There are practically no soluble sulfates nor insoluble sulfides present in any of the four samples. The amounts are too low (for the small samples taken for analyses), to have any particular significance, except that the cyrtolites are low in soluble sulfates and insoluble sulfides (such as pyrite, etc.). Larger samples should be taken to obtain very reliable results on these two sulfur determinations.

Most of the sulfur from lead sulfide is shown under soluble sulfides. There is not enough total sulfur in the Bedford and Hybla cyrtolites for all of the lead to be there as lead sulfide.

Sulfur in the Cyrtolites

Cyrtolite	Analysis	Total Sulfur % S	Soluble Sulfates as % S	Insoluble Sulfides, pyrite, etc. % S	By Difference Soluble Sulfides and Insol. Sulfates % S
Bedford No. I	1	0.027	0.004	0.005	0.018
	2	0.030	0.006	0.004	0.020
Bedford No. II	1	0.030	0.006	0.005	0.020
	2	0.030	0.005	0.006	0.019
Hybla	1	0.004	0.004	0.001	.....
	2	0.005	0.003	0.001	0.001
Henvey	1	0.079	0.009	0.005	0.065
	2	0.078	0.005	0.007	0.066
Average of each of two samples above					
Bedford No. I		0.029	0.005	0.004	0.019
Bedford No. II		0.030	0.005	0.005	0.020
Hybla		0.005	0.004	0.001	.....
Henvey		0.079	0.007	0.006	0.066

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NOTE BY A. C. LANE

The geologist may be surprised at the suggestion that galena can be separated from pyrite by HCl but Muench writes: "I was of the opinion that galena was insoluble in HCl when I planned the scheme of analysis. I tried some galena from Joplin, Mo., and found that some of it dissolved upon warming with 1–1 or even less concentrated HCl. The amount dissolved is considerable when it is a question of small quantities of galena such as are possibly present in Bedford cyrtolite. In such small quantities I feel that practically all of the galena is dissolved. The pyrite seems to be practically insoluble in the HCl, provided it is not in an oxidizing atmosphere, and the treatment is of short duration so that there is no appreciable amount affected by the ferric salt. Of course there is not a clean-cut separation of these fractions of sulfur and that is why I brought out the fact that there is not even enough total S for all the lead to be present as galena. I tried different concentrations of HCl in an attempt to prevent the galena from going into solution. The finely divided condition of the powder is also a contributing factor to the solubility . . . The addition of nitric acid of course will dissolve all the pyrite present in such small amounts, and all the galena that is left, if any.

"Grinding possibly oxidized some of the sulphur in the samples but probably very little. All that is reported in the total S."

The protection from sulphur gases in the fuel is noteworthy, since F. Hecht calls attention of its importance, and the advantage of using electric heat.

Taking the approximate age of the materials, as given by the lead ratio of these and other analyses from the same localities, and other considerations, we can estimate how much radio-lead there must be. The Bedford cyrtolite, should certainly be early paleozoic.

Taking the age as 360 million years and using the formula:

Age in million years $=15600 \log (1+1.156 \text{ RaG} \div \text{U})$ we have RaG $=.344$.

The atomic weight shows that there is no ordinary lead present so that whatever galena there is must be "U-galena" to at least nine tenths of the amount in the first sample. In the second lot the atomic weight and the age indicate the RaG to be .316 and .324, respectively.

In the Hybla cyrtolite the lead required to convert all the S into galena is .026 to .032 which is less than the lead present. Only about .002 of the lead need be thorium lead (ThD), about .007 ordinary lead, and .034 RaG. This would reduce the age to 485 million years. But in any case there is enough RaG to convert all the S into galena.

It is probably not a mere coincidence that the lead ratio in the Henvey cyrtolite (from the "Besner mine" in Henvey Township) is abnormally low, only about a sixth of that of the uraninite in the same mine. There has probably been some leaching of lead, possibly just after the Triassic uplift. At any rate there is more than one sign of abnormal conditions.