THE EXTRACTION OF RUBIDIUM AND CESIUM FROM LEPIDOLITE.

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SUMMARY.

A method is described for the preparation of rubidium chloride and cesium chloride of high purity from lepidolite. Comparison is made with methods found less satisfactory. The amounts of rubidium chloride and cesium chloride obtained correspond to a content of 0.67% Rb_2O and 0.16% Cs_2O in the lepidolite.

I. *Occurrence of Rubidium and Cesium in Lepidolite.*

Rubidium was discovered in lepidolite from Saxony by Bunsen (6) in 1861, and has subsequently been reported to occur in various lepidolites from different localities in amounts ranging from traces to 3.73% rubidium oxide, Rb_2O. Cesium has been reported to occur in lepidolite in amounts varying from traces to 0.72% cesium oxide, Cs_2O. Lepidolite from the Stewart mine at Pala, Calif., is said to contain about 0.3% Cs_2O (17).[3]

While engaged in a spectroscopic examination of certain minerals, strong rubidium and weaker cesium lines were observed in the spectrum of lepidolite obtained from the Sickler mine at Pala. The extraction of rubidium and cesium salts was accordingly undertaken.[4] A preliminary announcement of the occurrence of rubidium in this lepidolite has been made elsewhere (11).

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[2] Based on a thesis submitted to Claremont Colleges in partial fulfillment of the requirements for the degree of M.A. in Chemistry.

[3] For numerous references to the occurrence of rubidium and cesium in lepidolite, see Dana's System of Mineralogy, 6th ed., p. 624, and Doelter's Handb. d. Mineralchemie II, 2, 449, and III, 2, 106. Other occurrences have been observed.

[4] Since preparing this article for publication, there has come to the authors' attention an article by W. J. Schiefflen and T. W. Capon [J. Soc. Chem. Ind., 27, 549 (1908)] in which it is stated that during the preparation of lithia from Pala lepidolite, rubidium and cesium alums were obtained in one stage of the process. Schiefflen and Capon do not state, however, that rubidium and cesium occurred in the lepidolite.

II. *Spectroscopic Control Methods.*

Throughout the extraction and purification of the rubidium and cesium salts, spectroscopic examination of the various fractions was regularly made. Both the arc and flame were employed for the excitation of spectra. The less volatile samples, such as the raw or fused lepidolite, and the residue remaining after the extraction of the alkalies, were subjected to arc excitation; the extracted salts, such as the alums, chlorostannates, and bitartrates, were customarily examined by volatilizing and exciting in the flame, since this method was quicker. The most sensitive spectral lines[5] for potassium, rubidium and cesium, when excited in the flame, are as follows: potassium, 7699.01 Å, 7664.94 Å (5); rubidium, 4215.58 Å, 4201.81 Å (12); cesium, 3593.2 Å, 4555.3 Å (12).

III. *Decomposition of Lepidolite.*

The grayish-white lepidolite, crushed to pass through a screen with five meshes to the inch, was fused in a small, gas-fired furnace. The interior of this furnace, cylindrical in shape, was 15 cm. in diameter and 21 cm. high. An iron pipe 35 cm. long, with an inside diameter of 3.2 cm. was bent to an angle of about 45°, and mounted in the furnace so that its ends projected slightly beyond the top and side wall of the furnace. Crushed lepidolite was poured into this pipe (at A, in Fig. 1), and the furnace started. Additional lepidolite was added at intervals, and gently tamped down. The temperature of the melted material within the central portion of the pipe, as measured by means of a thermocouple, was about 1090°, ± 10° C.; the surface temperature of the viscous, fused material as it was slowly extruded from the pipe (at B, in Fig. 1) was approximately 700° C. By this means 2.8 kg. of raw lepidolite could be fused per hour. Since the fused or sintered lepidolite is isotropic, whereas the original mineral is anisotropic, it was possible to check the completeness of heat treatment by means of a petrographic microscope. Complete fusion was not essential, since merely sintering the lepidolite so that it formed a coherent mass was found sufficient to cause the lepidolite to become isotropic and capable of being decomposed readily by dilute sulphuric acid. If the lepidolite

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[5] The values for all wavelengths are those given in Kayser, "Tabelle der Hauptlinien der Linienspektra Aller Elemente," Julius Springer, Berlin, 1926.

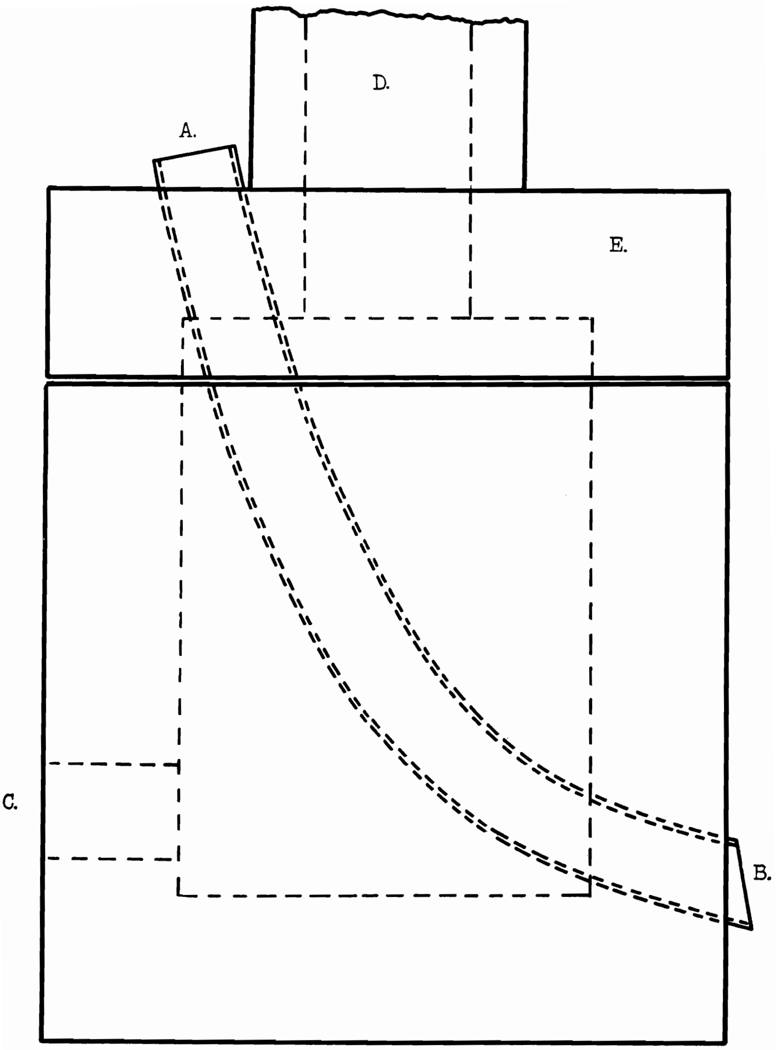

Fig. 1. Furnace.
AB—Iron pipe.
C—Tangential inlet for air and gas.
D—Vent.
E—Removable top.

was tamped too firmly into the pipe, the extruded mass contained a core of unaltered lepidolite, which was not completely decomposed by the subsequent treatment with acid.

In order to estimate the loss in weight on fusion, small samples of the raw lepidolite were ignited to constant weight in porcelain crucibles, heating to a bright orange. A loss in weight of 2.7% was found.

After being ground in a burr mill to pass a 40 mesh sieve, the fused lepidolite was decomposed with sulphuric acid. A typical run was as follows: 1 kg. of ground, fused lepidolite was suspended in a 5 liter, round-bottom flask with a total of 21. of water and washings from a preceding run. 850 cc. of concentrated, commercial sulphuric acid were slowly added. After the frothing subsided, the mixture was refluxed 45 minutes and immediately filtered, with suction. The residue was washed on the filter four times with 200 cc. portions of boiling water. The first filtrate was diluted with part of the washings to a volume of approximately 2.8 l., and was allowed to crystallize. The remainder of the washings was used in the next run.

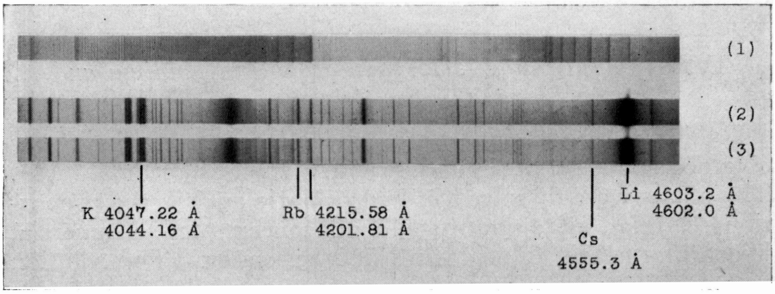

Fig. 2. (1) Spectrum of graphite electrodes. (2, 3) Spectra of raw lepidolite.

By this method about 900 g. of alums were obtained per kg. of fused lepidolite. A spectroscopic examination of these alums revealed the presence of relatively large amounts of potassium and rubidium, a small amount of cesium, and very small amounts of sodium and lithium. The mother liquor from which the alums separated showed traces of rubidium, but no cesium. The washed residue was found to be spectrographically free from rubidium and cesium.

Other methods of decomposing the lepidolite were tried, but found to be less satisfactory. (a) The ground, sintered lepidolite was decomposed with hydrochloric acid (13), and the alkalies, together with iron and aluminum, were obtained as chlorides. Trouble was experienced in filtering, and in extracting the rubidium and cesium (8, 14, 19). (b) Ground, raw lepidolite was heated with concentrated sulphuric acid (10) until heavy white fumes ceased to be evolved. Another batch was refluxed two hours with 7 *N* sulphuric acid. In both cases decomposition was incomplete. (c) Raw lepidolite was decomposed with calcium fluoride and sulphuric acid (3, 4, 16) and also with sodium fluoride and sulphuric acid. Decomposition was complete in both cases, but the use of a fluoride was objectionable on account of fumes.

IV. *Concentration and Purification of Rubidium and Cesium Salts.*

Rubidium and cesium were concentrated from the alums obtained above by precipitating with stannic chloride (7, 18). The alums were dissolved in hydrochloric acid in the proportion of 1 kg. of alums to 440 cc. concentrated commercial hydrochloric acid diluted with 360 cc. water. The solution was heated to 95° C., and a slight excess of stannic chloride reagent, prepared by saturating concentrated hydrochloric acid with crystallized stannic chloride, $SnCl_4.5H_2O$, was added. The precipitate was allowed to digest while cooling slowly to 55° C. The crystals were then readily separated by decanting off most of the clear liquor, and filtering. A spectroscopic examination of this precipitate showed the presence of large amounts of rubidium and cesium, considerable potassium, and a little thallium. The mother liquor showed traces of rubidium, but no cesium. The precipitate was recrystallized from approximately 1 *N.* hydrochloric acid until no potassium lines were visible upon examination in the flame. The crystals of rubidium cesium chlorostannate, $(Rb, Cs)_2SnCl_6$, still contained a little thallium, as evidenced by the presence of the green thallium line.

The crystals were dissolved in water, and the tin and thallium were removed by precipitating with hydrogen sulphide. The resulting rubidium and cesium chlorides were evaporated with twice their weight of tartaric acid to a thick syrup, thus dispelling considerable hydrochloric acid. The syrupy mass was dissolved in water, and rubidium bitartrate was crystallized out (1, 20). Since these first crystals showed traces of cesium, they were recrystallized from water until the cesium lines could no longer be seen. The rubidium bitartrate was readily converted to the chloride by charring, igniting gently, and extracting with dilute hydrochloric acid.

The mother liquor from the bitartrate recrystallizations was similarly converted to the chloride and filtered. The filtrate was evaporated nearly to dryness, and dissolved in the minimum amount of 3 *N* hydrochloric acid. A slight excess of a saturated solution of antimony trichloride disolved in 3 *N* hydrochloric acid was then added (9, 20). The precipitate of cesium antimony chloride showed traces of rubidium, and was recrystallized from 3 *N* hydrochloric acid until the rubidium lines could no longer be seen. Pure cesium chloride was obtained from the antimony double chloride by the usual method. The mother liquor from the cesium antimony chloride recrystallizations was reworked to obtain additional rubidium bitartrate, after first removing the antimony by hydrolysis and hydrogen sulphide.

A total yield of 89.1 g. of rubidium chloride, spectrally free from cesium and potassium, and 19.8 g. of cesium chloride, spectrally free from rubidium and potassium, was obtained from 10 kg. of sintered lepidolite. In addition, 2.5 g. of mixed chlorides of potassium, rubidium and cesium were obtained from the residual mother liquors resulting from the chlorostannate and subsequent fractionations. This mixture showed, in the flame, the presence of a large amount of potassium, a small amount of rubidium, and a trace of cesium.

Other methods of separating and purifying the rubidum and cesium were tried. (a) The crude alums were fractionally recrystallized (3, 4, 16). Twelve recrystallizations were needed to obtain a rubidium cesium alum spectroscopically free from potassium. Twenty-one recrystallizations were needed to obtain a second crop of crystals of equal purity from the mother liquors. No attempt was made to obtain a pure cesium alum from the potassium-free rubidium cesium alum. The fractionation of the alums was found much more laborious and time consuming than the chlorostannate method of purification. Both the alums obtained from sintered lepidolite which had been decomposed with sulphuric acid, and those from raw lepidolite decomposed with sodium fluoride and sulphuric acid were readily recrystallized. However, when calcium fluoride was used instead of the sodium fluoride, a little calcium sulphate accompanied the alums, and a certain amount of difficulty was encountered in the recrystallizations. (b) An attempt was made to precipitate the rubidium and cesium as the triple nitrite, $(Rb, Cs)_2NaBi(NO_2)_6$ (2, 15). Difficulty was encountered due to excessive frothing, even though sodium hydroxide had been added to the alums to reduce the acidity. The precipitate contained considerable potassium. Three reprecipitations were needed to obtain a product spectroscopically free from potassium. (c) An attempt was made to separate rubidium chloride and cesium chloride from potassium chloride by means of alcohol and hydrochloric acid (8, 14, 19), using the salts resulting from the decomposition of sintered lepidolite with hydrochloric acid (13). Difficulty was encountered, both in extracting most of the rubidium chloride from the large amount of potassium chloride, and in obtaining a rubidium cesium chloride concentrate free from potassium.

V. *Rubidium and Cesium Content of Pala Lepidolite.*

The quantities of rubidium chloride and cesium chloride extracted from the lepidolite correspond to the following calculated percentages of oxides in the raw material: Rb_2O — 0.67%; Cs_2O — 0.16%.

The actual rubidium and cesium content of the lepidolite was probably slightly higher than this, since perceptible traces of rubidium were lost in the mother liquors from the alums, and from the chlorostannate precipitation. Also, a small amount of rubidium and a trace of cesium remained in the mother liquors left from the chlorostannate and subsequent fractionations.

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