Rapid Chemical Tests

FOR SOME HYPOTHERMAL AND PEGMATITE MINERALS OF ECONOMIC IMPORTANCE GENETICALLY RELATED TO GRANITES

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Introduction

MANY important hypothermal and pegmatite minerals are not always recognised with certainty by applying simple and well-known physical and/or chemical tests. Prospectors and others have identified molybdenite as graphite, ilmenite as wolfram and beryl as quartz and felspar, whilst scheelite has often been completely overlooked. Because of these facts, and because the minerals under reviw are not only of importance to many lode miners but to the majority of alluvial miners also, the author has written this paper.

The tests described for the minerals selected have been shown by considerable usage to be reliable and easy to carry out. Some are in the exact form as described by others, but the majority are new tests devised by the author. The chemical reactions utilised in these tests, have been developed by others.

Details of the tests :—

Cassiterite, SnO_2.

The well-known tinning test is the most useful way of identifying cassiterite providing the surface of the mineral is clean. Some untreated cassiterites are easier to tin than others but the author has yet to encounter a sample of clean cassiterite which does not react positively to this test, although it has been stated that such material exists.

To carry out the test, place the mineral in a zinc tray or on a zinc block and add 5N. HCl. After five to ten minutes the cassiterite, largely where it has been in contact with the zinc, is coated with grey metallic tin.

Cassiterite coated with secondary products such as limonite will not react unless first acid-cleaned by boiling with concentrated HCl or aqua-regia. Similarly, cassiterite which has been in contact with flotation reagents should be cleaned by boiling with a suitable reagent before submitting it to the tinning test.

Cassiterite grains are buoyant immediately after they are tinned, and by rotating the sample, having first diluted the acid somewhat, they will migrate to the centre. The area of the "tin-circle" in relation to that occupied by the whole sample, permits of an estimation to be made of the amount of cassiterite present.

The author has utilised the following semi-quantitative method with success when examining products from the Malayan and Nigerian alluvial fields :—Make a tray of thin sheet zinc of base $1\frac{1}{2}$ by $2\frac{1}{2}$ inches and with sides $\frac{1}{5}$ of an inch high. Weigh 0.5 g. of the ore and scatter the grains over the base of the tray. Half fill the tray with 5N. HCl. After ten minutes shake the tray so that the buoyant tinned cassiterite migrates to one corner. Carefully break down the corner, drain off the acid, and with the aid of a fountain-pen filler filled with water, and a sharpened match, transfer the cassiterite to a watch-glass. With a little care and experience an excellent separation can be made providing that the particles are not exceedingly small. Wash the tin-free fraction into a silica crucible, remove the rest of the water with a fountain-pen filler, add a few ml. of alcohol, and ignite. Complete the drying process over a bunsen burner. Brush out the dry grains and weigh. The difference between this weight and that of the original sample represents the amount of cassiterite in the sample. (1).

Cassiterite which has been treated to c. 1000° C. for 30 minutes changes colour and if originally magnetic, it loses its magnetic properties. Brown cassiterite becomes vermilion and practically white cassiterite becomes pink. (2).

These colour changes enable cassiterite in such heat-treated samples to be readily recognised. Such cassiterite is

very slow to tin. The tinning process, both of this and of normal cassiterite may be accelerated, either by covering the sample in the zinc tray with a sheet of lead, or by first depositing a little lead on the tray by treating it with a dilute solution of lead acetate. (3). Even with this treatment, heat-treated cassiterite is still much slower to tin than "normal" cassiterite. In view of the semi-quantitative results which can be obtained by making use of the tinning test, together with the fact that heat-treatment of columbite and magnetic cassiterite concentrate may become standard practice in Nigeria, the problems associated with the tinning of heat-treated cassiterite are worthy of further study.

The detection of tin in minerals.

The only simple and reliable test for tin in minerals generally is carried out as follows :—Mix a few mg. of the mineral to be tested with K_2Co_3 and KCN (POISON !) and melt the mixture on a magnesia stick. Dissolve the melt in a few ml. of conc. HCl. (Poisonous HCN gas is liberated). Spot a piece of drop-reaction paper with a drop of a saturated aqueous solution of cacotheline and place upon this a drop of the test solution. The presence of tin is indicated by the development of a purple spot or ring. (4).

The detection of wolfram, (Fe, Mn) WO_4.

(a) The sodium peroxide fusion method (5).

On a square-inch of asbestos paper resting on an asbestos mat place a cone of the powdered mineral and cover it with an equal volume of Na_2O_2. (The mineral cone should have a base of c. 7 mm. diameter.) Fuse the charge by applying a burning splint to it. Maintain contact between the splint and the charge until all the Na_2O_2 has been consumed. The presence of manganese in the mineral is indicated by the fusion product being blue-green in colour. (6). Cut out two portions of the obviously fused material and place each one in a separate depression in a spot-plate. To one add a few drops of conc. HCl and then a few drops of 10% KCNS solution. The presence of iron is indicated by the development of a red colour. To the other portion add one or two ml. of a

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p. 6, line 16 : **delete** K_2Co_3, **substitute** K_2CO_3.

p. 6, line 35 : **delete** conc. HCl, **substitute** 2N. HNO_3.

p. 7, line 2 : **delete** 2N. HNO_3, **substitute** conc. HCl.

p. 9, line 3 : **Formula for thorite should read** ThO_2. SiO_2.

p. 11, line 1 : **Formula for ilmenite should read** FeO. TiO_2.

to purple solution

hot solution prepared when needed by boiling a gram of granulated tin with C. 5 ml. of 2N. HNO_3 for three minutes. The presence of tungsten is indicated by the development of a blue precipitate.

An alternative and perhaps more convenient method is to carry out the fusion and the subsequent wet tests on a small inverted Pyrex pie dish. Such a dish is robust, easily cleaned and can be used repeatedly without deteriorating.

(b) The ammonium hypophosphite method. (7).

Mix a little of the powdered mineral with twice its volume of ammonium hypophosphite and place it in one end of an open-tube such as is used for the well-known open-tube tests. Heat the charge with a match. Whilst the charge is still warm add two or three drops of water to it and rotate the tube so that the solution runs along it. The presence of a deep-blue to purple solution is a certain indication of tungsten in ANY mineral.

The detection of scheelite, $CaWO_4$, and the identification of tungsten in this mineral.

Scheelite is best detected by means of a **short-wave** ultra-violet lamp. Pure scheelite fluoresces a strong blue, but with increasing quantities of the isomorphous mineral powellite ($CaMoO_4$), the colour grades from blue through pale blue, white to straw-yellow. Hydrozincite, mineral oil and scorpions fluoresce blue when similarly irradiated !

The presence of tungsten in scheelite or in any tungsten mineral, with the exception of members of the iron-manganese tungstate series, may be identified as follows :—Streak the mineral on a small portion of unglazed tile and cover the streak with zinc powder. Spot the zinc with a few drops of conc. HCl. then wash off the residual zinc. A blue streak indicates tungsten. Molybdenum minerals, which also produce blue reduction compounds under certain circumstances, do not do so when the above method is used. (8).

The presence of tungsten in **any tungsten** mineral may be shown by treating a streak on a portion of unglazed tile as

follows :—Place a few crystals of ammonium hypophosphite on the streak and holding the tile in a tongs gently heat the crystals and streak with the reducing flame of a blowpipe. Scheelite and other pale-coloured tungsten mineral streaks usually become pale-blue as a result of this treatment but molybdenum minerals may react similarly. However, if one or two drops of water are placed on the streak whilst it is still hot a purple to deep-blue halo immediately develops if the mineral contains tungsten. (9).

The detection of niobium and tantalum in such minerals as columbite and tantalite, (Fe, Mn) (Nb, Ta)$_2$O$_6$.

The following fairly quick test is entirely satisfactory for the detection of these much sought after elements :—Fuse the powdered mineral with $KHSO_4$ in a silica crucible. Cool, then half fill the crucible with 20% tartaric acid and warm to detach the melt. Transfer the melt and solution to a 250 ml. beaker and add more tartaric acid to bring the total used up to c. 25 ml. Heat to dissolve the melt and filter. Boil the filtrate with a quarter of its volume of conc. HCl. A white precipitate, usually separating after a few minutes boiling, but occasionally taking a considerably longer time, is a certain indication of the presence of tantalum and/or niobium.

The only other element which reacts under the same conditions is tungsten which results in the production of a **yellow** precipitate. It is often necessary to remove the precipitate by filtering in order to ascertain whether it is white or yellow as it is frequently suspended in a strong yellow solution.

If tungsten is present proceed as follows :—Fuse the powdered mineral with solid KOH in a nickel crucible. Extract the product with a little water and filter. Divide the filtrate into two portions. To one portion add enough NaCl (solid) to saturate it. A white crystalline precipitate strongly suggests the presence of the earth acids. Tungstates do not form a precipitate under these conditions but antimony does.

Acidify the other portion of the filtrate with H_2SO_4. If earth acids are present a white precipitate develops. To the suspension add an aqueous solution of tannin. The presence

of tantalum and/or niobium is confirmed by the precipitate becoming orange or yellow. Antimony does not react. (10).

The detection of Nigerian columbite and thorite, ThO_2, SiO_2, and uranium minerals.

The following test, developed and utilised successfully by Mackay (11) both for the detection and for the approximate estimation of columbite and of thorite in Nigerian alluvial material, must not be regarded as one necessarily suitable for the examination of columbite from other fields. It can, however, be utilised for the detection of uranium in any uranium-rich mineral and the results obtained will be similar to those obtained with thorite.

The test :—Place a quantity of flux, the preparation of which is described below, in a flat nickel dish about three inches in diameter, or on the cover of a tobacco tin, and heat until it has melted. Tilt the dish until only a thin coating of melt covers the bottom of the container and cool, then place the grains to be tested on it. Ideally, each grain should be as far apart from neighbouring grains as possible. Re-heat until the flux is molten and continue heating for about 30 seconds. Cool to room temperature and examine under either long or short wave ultra-violet light. Nigerian columbite grains will be surrounded by a pale-yellow halo, as will the quite distinctive monazite, whilst thorite and uranium-rich mineral grains will be surrounded by an intense-yellow halo. Zircon grains, both before and after treatment may fluoresce yellow. Care must be taken not to confuse yellow fluorescing grains with yellow halos. Too much flux and prolonged heating destroy the value of the test from a quantitative point of view as the fluorescent material then pervades much of the flux.

Mackay's flux has the following composition :—

Sodium fluoride ..... 5% by weight.
Sodium bisulphate ..... 2% by weight.
Sodium carbonate) balance in equal parts.
Potassium carbonate)

The detection of monazite, (Ce, La, Yt)PO_4 with ThO_2.

This important mineral which is obtained in economic

quantities from alluvial and marine placers is usually easily recognised under the microscope and is generally of a honey-yellow colour. However, it may be green, white, plum-coloured, etc., and the author has seen pink monazite in lode material from Llallagua (Bolivia) which fluoresces blue under the short-wave ultra-violet lamp, and in this respect it resembles scheelite.

The following simple but little-known test developed many years ago by Ohly (12), serves as a useful confirmatory test for the mineral. Place a drop of conc. H_2SO_4 on a grain of the mineral on a microscopic slide. Warm gently over a micro-flame until the test area is nearly dry, then cool and examine under a microscope. The presence of double ball-shaped clusters of radiating needles, or of minute crystals shaped like cucumber seeds, indicates that the mineral is monazite. Better crystals are usually obtained if a drop of water is added to the nearly dry test area and recrystallisation allowed to proceed in a desiccator.

The detection of beryllium in beryl, $Be_3Al_2Si_6O_{18}$. (13).

Place a 7 mm. diameter conc of a 1 : 1 mixture of the powdered mineral and $KHSO_4$ on an inverted Pyrex dish. Cover the cone with an equal volume of Na_2O_2 and fuse by applying a burning splint to it. Add several drops of 5N. NaOH to the product of fusion and disintegrate the latter with a glass rod. Place two drops of p-nitrobenzeneazoorcinol solution on a double thickness of spot-reaction paper and to the wet spot add a drop of 25% KCN (very poisonous !). To the wet, orange-coloured spot, add a drop of the test solution. The presence of beryllium is indicated by the development of a pink to peach-red spot or ring.

No elements interfere and it is an ideal test for distinguishing rapidly between beryl and somewhat similar minerals such as quartz and felspar.

To prepare a solution of the organic reagent, dissolve 0.025 g. p-nitrobenzeneazoorcinol in 100 ml. 4% NaOH solution. A fresh solution should be prepared fortnightly.

The detection of titanium in ilmenite, FeO TiO_2, and rutile, TiO_2. (14).

Cover a 1 : 1 mixture of mineral and $KHSO_4$ with Na_2O_2 exactly as in the beryllium test and fuse. Dissolve a portion of the product in a solution of HCl and stannous chloride prepared by boiling metallic tin with conc. HCl as indicated in the wolfram section. To the acid test solution add one or two drops of a freshly prepared 5% aqueous solution of the sodium salt of chromotropic acid. The presence of titanium is indicated by the solution becoming dull-red. The colour may be more clearly appreciated by taking up some of the solution on filter-paper.

The detection of zirconium in zircon, $ZrSiO_4$. (15).

Cover a cone of powdered mineral on an inverted Pyrex dish with an equal volume of Na_2O_2 and fuse as in the above tests. Dissolve a portion of the product in 2N. HCl. Place a drop of the acid test solution on a piece of spot-reaction paper which has been impregnated with the organic reagent below, and dried. Wash the paper for one minute in hot (c. 60° C.) 2N. HCl. The presence of zirconium is indicated by a brown to orange spot on the paper.

The organic reagent is prepared by dissolving 0.1 g. p-dimethylaminoazophenylarsinic acid in a mixture composed of 95 ml. ethyl alcohol and 5 ml. conc. HCl.

The detection of molybdenum in molybdenite, MoS_2. (16).

Cover the mineral with an equal volume of Na_2O_2 and fuse as in the tests above. Dissolve a portion of the product in 5N. acetic acid and to the acid test solution add a small fragment of potassium ethyl xanthate. The presence of molybdenum is indicated by the solution becoming reddish-purple.

The detection of native dismuth and of bismuth in bismuthinite Bi_2S_3. (17).

Streak the mineral on a portion of unglazed tile and press the streak for two minutes against a piece of spot-reaction paper impregnated with 1 : 1 HNO_3 and resting on a por-

celain plate. Remove the portion of tile and place a drop of cinchonine and potassium iodide reagent on the paper. The presence of bismuth is indicated by the development of an orange print. As nitric acid has been used as an attacking reagent, some iodine is also liberated, but this causes no trouble.

The reagent is prepared by adding 1 g. cinchonine to 100 ml. water containing a little nitric acid and warming to dissolve. Cool, and add 2 g. potassium iodide.

The presence of sulphide ion in bismuthinite, or any other sulphide, may be shown by adding a drop of sodium azide/iodine solution to a streak of the mineral on a piece of ground glass. The sulphide ion causes a rapid evolution of bubbles of nitrogen. (18).

When examining minerals this test is specific for the sulphide ion. The reagent, which is stable, is prepared by dissolving 3 g. sodium azide in 100 ml. 0.1 N iodine solution.

The detection of tellurides, e.g. calaverite, (Au, Ag) Te_2.

Streak the mineral on a sheet of tin or on the lid of a tobacco tin and place a drop of conc. H_2SO_4 on it. Heat. The presence of tellurium is indicated by the development of a red to purple solution.

Alternatively, streak the mineral on a piece of unglazed tile and place a drop of 1 : 1 HNO_3 on the streak. After ten seconds, or when the acid has sunk into the tile, place a drop of a hydrochloric acid-stannous chloride solution on the streak. The preparation of this latter solution is detailed in the wolfram section. The presence of tellurium is indicated by the streak becoming black. (19).

NOTES AND REFERENCES

(1) K. F. G. Hosking, unpublished studies.

(2) The author is of the opinion that naturally occurring vermilion cassiterite, such as is encountered in some areas of Nigeria and Mexico, has been heat-treated during volcanic activity.

(3) K. F. G. Hosking, unpublished studies.

(4) F. Feigl, "Qualitative Analysis by Spot Tests," Elsevier Pub. Co. Inc., N. York, 1947, pp.87-88 and p.432.

(5) K. F. G. Hosking, unpublished studies.

(6) This test is an excellent one for identifying Mn. in any mineral in which it occurs in considerable quantity.

(7) This test has been developed by the author from a reaction for tungsten utilised by Van Valkenburgh and Crawford of the University of Colorado and described by De Ment and Dake in their book "Rarer Metals," Chem. Pub. Co. Inc., N. York, 1946, p.204.

(8) K. F. G. Hosking, unpublished studies.

(9) K. F. G. Hosking, unpublished studies.

(10) W. R. Schoeller and A. R. Powell, "The Analysis of Minerals and Ores of the Rarer Elements," Griffin & Co. Ltd., London, 1940, pp.161-162.

(11) R. A. Mackay, "The Detection of Columbite by Ultra-violet Light," Bull. Inst. Min. Met., vol. 60, pt. 4, 1950-51, pp.129-131.

(12) J. Ohly, "Analysis, Detection and Commercial Value of the Rare Metals," The Mining Reporter Pub. Co., Denver, Colorado, U.S.A., 1907, p.169.

(13) This test, devised by the author, is based on a test for beryllium which was developed by A. S. Komarowsky and N. S. Poluektoff, Microchemie, 14, 1933, p.315.

(14) This test, devised by the author, is based on a test for titanium which was first described by K. A .Hofmann, Ber. 45, 1912, p.2480 and later modified by F. Feigl and others.
(See Feigl, op. cit. pp.151-152.)

(15) This test, devised by the author, is based on a test for zirconium which was developed by F. Feigl, P. Krumholz and E. Rajmann, Mikrochem, 9, 1931, p.395.

(16) This test, devised by the author, is based on a test for molybdates which was developed by S. Malowan, Z. Anerg. allgem. Chem., 108, 1914, p.73.

(17) This test, devised by the author, is based on a reaction for bismuth which was developed by E. Leger, Z. anal. Chem., 28, 1889, p.374.

(18) F. Feigl, op. cit. pp.227-229 and p.301.

(19) K. F. G. Hosking, unpublished studies.