ABUNDANCE OF TUNGSTEN IN IGNEOUS ROCKS.

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OUR present knowledge of the tungsten content of igneous rocks is largely based on the results of an investigation by von Hevesy and Hobbie(1).* These authors, using an X-ray spectrographic method after preliminary chemical concentration of the element, found 69 parts per million of tungsten in a mixture of 282 central European igneous rocks of Caledonian and Variscian age(2), 83 p.p.m. in a specimen of granite (Schwarzwald), and 24 p.p.m. in a mixture of 67 gabbros and norites. The molybdenum content of these samples is also given. A few values for tungsten in rocks, comparable in magnitude with those of von Hevesy and Hobbie, were reported by I. and W. Noddack in connection with a study of the geochemistry of rhenium(3). They found 4, 30, and 20 p.p.m. of tungsten in granites from the Harz, Norway, and the Andes respectively; 20 p.p.m. in the lava of Vesuvius; 20 p.p.m. in basalt from Kaiserstuhl and 5 p.p.m. in basalt from Sweden; and 3 p.p.m. in kimberlite. In addition, the tungsten (and molybdenum) contents of many minerals are stated. Details regarding the methods of concentration and determination of the traces of tungsten and other elements are not given, but presumably the final determination was made by X-ray spectrography. It is stated that the results may be in error by ± 25 per cent in general.

The above values for tungsten in igneous rocks are higher than might be expected and it seemed desirable to determine the element by a different method in a series of composite samples. Further work on the abundance of tungsten appeared necessary also because von Hevesy and Hobbie's figures for the amount of molybdenum in igneous rocks do not agree well with the values found for a series of American rocks(4), the respective average contents being 15 and approximately 2.5 p.p.m.

METHOD OF ANALYSIS.

The procedure used in determining tungsten in silicate rocks is described in detail elsewhere(5). In brief the method is the

* Numbers in parentheses indicate the references at the end of the article.

following. The sample (0.8 to 1.0 gram) is decomposed with hydrofluoric, sulfuric, and nitric acids. Iron, titanium, and some other elements are removed by double precipitation with excess sodium hydroxide. Molybdenum is then precipitated as the sulfide, antimonic sulfide being used as a collector. Tungsten is determined colorimetrically in the final solution by adding thiocyanate, excess hydrochloric acid, and stannous chloride to form a yellow thiocyanate complex of tungsten in a lower valence state, which is extracted with ether. The color of the ether is compared against standards in small tubes having a cross-sectional area of approximately 1 square centimeter. It is possible to detect 0.5 p.p.m. of tungsten with certainty when a 1-gram sample is taken.

The method was tested on natural and synthetic rock samples to which known amounts of tungsten were added. The best results are obtained with silicic rocks in which the percentages of iron and titanium are low. As the amounts of the latter increase, the recovery of tungsten progressively decreases. Useful results (approximately 80 per cent recovery of tungsten) can still be obtained with a rock containing 6 per cent total iron oxides, 0.9 per cent TiO_2, 3 per cent MgO, 5 or 6 per cent CaO, and 0.25 per cent P_2O_5. Approximately one-half of the added tungsten (a few parts per million) is recovered from a sample containing 13 per cent total iron oxides and 1.75 per cent of TiO_2; the remainder of the tungsten is lost by coprecipitation in the precipitate produced by sodium hydroxide, especially in the hydroxides of titanium and iron. The method cannot, therefore, be applied to a typical basic rock, except perhaps for the purpose of obtaining a rough value for the amount of tungsten present. In general, the method is applicable to rocks in the silica range above 60 per cent.

With the exception of vanadium, no element is known, which in amounts likely to be encountered in igneous rocks, will yield a color similar to tungsten under the conditions of the determination. Vanadium produces a color approximately 1/300 as strong as an equal weight of tungsten. In other words a sample containing 0.015 per cent V (0.022 per cent V_2O_3) would show an apparent tungsten content of 0.5 p.p.m. In silicic rocks for which the method is primarily intended the vanadium content will be less than this and the effect of this element can be disregarded. Even in intermediate rocks with a silica percentage greater than 60, it is unlikely that this value for vanadium will be exceeded. If necessary the vanadium content of the sample can be found by a simple colorimetric method and the requisite amount of vanadium can then be added to the colorimetric standards in the tungsten determination.

SAMPLES.

Most of the samples analyzed were composites of plutonic rocks. The composites were prepared on the basis of silica content for the most part. In order to see whether there might be a regional factor involved in the distribution of tungsten, several composites having similar silica ranges (average about 72 per cent) were made up from granites from Canada, New York state, Minnesota, and Africa respectively. The results of the analyses of the composites are given in Table I.

TABLE I.

Tungsten in Composites of Igneous Rocks.

Silica Range % SiO_2	Average Silica % SiO_2	Type of Rock	No. of Samples	Region	Tungsten P. p. m. W
81.5–75.1	77.4	Granite*	20	Various†	2.0
77.4–71.5	74.1	‡	9	California	1.4
76.8–68.2	73.1	Granite	5	Texas (Llano region)	1.8§
74.3–70.6	72.6	Granite	7	Canada	1.4
73.9–70.0	72.0	Granite	9	Africa	1.3
73.3–70.7	72.0	Granite	6	New York	1.0
....	...	Granite	5	Minnesota	1.1
69.6–65.5	68.4	¶	14	‖	1.3
66.4–64.8	65.6	Quartz monzonite	2	California	1.6
65.7–52.7	62.0	Diorite	7	Oregon and California	1.2
64.1–56.0	60.3	Syenite	6	New York and Minnesota	1.9Δ

* Includes 1 quartz porphyry, 1 quartz monzonite.

† Origin as follows: Canada 3, New York 5, Texas 3, 8 from unspecified U. S. or Canadian localities, Africa 1.

‡ 4 granites, 2 quartz monzonites, 1 monzonite, 2 granodiorites.

§ Average of separate determinations, Table II; analysis of a composite sample gave 2.0 p.p.m. W.

¶ 6 granites, 1 granite porphyry, 1 felsite porphyry, 1 porphyry, 1 quartz monzonite, 1 granodiorite, 1 diorite. 2 dacites.

‖ Canada 2, New York 1, Texas 2, Montana 2, Wyoming 1, California 2, 4 from unspecified U. S. or Canadian localities.

Δ Not corrected for vanadium which may be present in appreciable amount so that true value for tungsten may be slightly lower.

Five granitic rocks from the Llano region of Texas(6) were analyzed individually (Table II). In addition a rhyolite from

Cook County, Minnesota, was found to contain 2.4 p.p.m. of tungsten.

The values for tungsten have been recorded to 0.1 p.p.m., but in comparing results it should be borne in mind that an error of 0.2 or 0.3 p.p.m. is possible in comparing colors. To this must be added any systematic errors of the method. For rocks with more than 70 per cent silica the results are believed to be essentially correct as judged by the recovery of tungsten added to known samples, but as already stated the values may be slightly low with the less silicic samples. Basic rocks which are definitely known to give low results for tungsten by the method applied have not been analyzed.

TABLE II.

Tungsten in Silicic Rocks of the Llano Region, Texas.

	SiO_2 %	W P.p.m.
Granite, Bear Mountain	76.8	2.4
Granite porphyry (llanite)	75.2	2.6
Granite, Granite Mountain	73.0	1.6
Granite, Cassaday	72.2	1.5
Granite, Town Mountain	68.2	1.1

DISCUSSION.

The results obtained point to an average tungsten content of approximately 1.5 p.p.m. for silicic and intermediate igneous rocks (silica range 80 to 60 per cent). In general it appears that the amount of tungsten in an igneous rock increases with the silica content. This trend is quite clear in the case of the Texas granites which have a common origin. The parallelism is less regular, as might be expected, but still perceptible, in the composites.

It seems natural to correlate tungsten, as an acidic element, with silica in igneous rocks. The ionic radius of hexavalent tungsten is small, probably being slightly less than 0.5 A. With the exception of silicon, all the major elements of the magma have ionic radii greater than this value, the radius of silicon equalling 0.39 A. (The next largest ion, aluminum, has a radius of 0.57 A according to Goldschmidt.) Because of the magnitude of the difference in the radii of tungsten and silicon it may be supposed that tungsten will have relatively little tendency to separate with the early crystallizing silicates and that, therefore, it will be concentrated in the residual liquid as the magma crystallizes. However, the concentration of tungsten in the silicic rocks does not appear to be very striking. The present method unfortunately does not allow the partition coefficient of tungsten between acidic and basic rocks to be determined. It may be noted that von Hevesy and Hobbie found about one-third as much tungsten in the basic rocks (gabbros and norites) as in their igneous rocks as a whole. The behavior of tungsten is similar to that of molybdenum, so far as rather scanty data indicate, which is to be expected from the similar ionic radii of hexavalent tungsten and molybdenum. A thorough study of the distribution of tungsten in silicate rocks must await the development of a better analytical method than any now available, whether spectrographic or chemical.

There is no evidence of any significant regional variation in the tungsten content of the rocks examined. Although the data are insufficient to allow any positive statement to be made, there is no indication of a radical difference in the tungsten contents of pre-Cambrian and later silicic rocks (California composite).

The results obtained permit a rough estimate of the tungsten content of the upper lithosphere. The maximum content is not likely to exceed greatly the value 1.5 p.p.m. found for the silicic and intermediate rocks analyzed. Although the total number of samples examined is comparatively small, the general similarity of the tungsten values found for rocks from different areas lends considerable support to the belief that the upper limit cannot be far from this value. It would be surprising if another series of plutonic rocks should give a value of 10 p.p.m., or even 5 p.p.m. There is thus a large discrepancy between von Hevesy and Hobbie's value for igneous rocks as a whole (69 p.p.m.) and the present value for rocks with a silica range of 60 to 80 per cent. The lower limit for the relative amount of tungsten in the lithosphere cannot be fixed very exactly on the basis of the results obtained in the present work. If it is assumed that rocks with silica content less than 60 per cent contain no tungsten and that these rocks compose as much as one-half of the lithosphere, the average would be 0.75 p.p.m. of tungsten. But there must be some tungsten in the less silicic rocks, so that the average value for the upper lithosphere must be greater than this. We may accordingly take 1 p.p.m. as the most likely tungsten content of igneous rocks as a whole on the basis of the results here reported. If this value for tungsten is accepted as being not far from the truth, it follows that tungsten is one of the least abundant elements of the crust of the earth. It would then be scarcer than beryllium (6 p.p.m.), scandium (5 p.p.m.), arsenic (5 p.p.m.), cesium (7 p.p.m.) as well as most of the rare earths, if the figures for these elements are substantially correct (7). The question whether tungsten or molybdenum is more abundant in igneous rocks cannot be answered definitely at the present time. Analysis of a relatively small number of samples from various areas of the United States gave an average value of 2.3 p.p.m. of molybdenum, silicic and subsilicic rocks being weighted equally(4). This figure may be too high. At any rate the relative amounts of tungsten and molybdenum in the upper lithosphere are not greatly different.

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