OPTICAL, SPECTROGRAPHIC AND RADIO-ACTIVITY STUDIES OF ZIRCON.

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ABSTRACT. The results of spectrographic, radioactivity and optical studies of zircon are presented. The variations in physical properties of zircon may be due to breakdown of the crystal lattice by the action of radioactive elements included at the time of crystal formation. It is suggested that the type of zircon present in a granite is governed by the concentration of uranium in the magma at the time of formation of the zircon crystals.

INTRODUCTION.

RECENT studies of accessory minerals in pre-Cambrian granites of the Lake Superior region[1] have revealed that, in that area, granites belonging to at least three different periods may be distinguished from one another by the optical properties of the zircon which occurs in them. Studies in the Oxford House Area of Manitoba[2] showed that similar distinctions can be made between granites belonging to at least two periods of igneous intrusion.

Radioactivity has been postulated as the cause of the variation in optical properties and specific gravity of zircon by Chudoba and Stackelburg[3] and others. A relationship has been noted by von Hevesy[4] between radioactivity and hafnium content of zircon.

To test these hypotheses spectrographic analyses were made and the radioactivity and optical properties of several samples of zircon were measured.

The spectrographic analyses were performed by the junior author in the laboratories of the Department of Chemistry, University of Wisconsin. The radioactivity measurements were also made in these laboratories. The optical studies were performed in the laboratories of the Department of Geology, University of Wisconsin, by the senior author.

[1] Tyler, S. A., Marsden, R. W., Grout, F. F., and Thiel, G. A.: "Studies of the Lake Superior Pre-Cambrian by Accessory-Mineral Methods." Geol. Soc. Am. Bull., Vol. 51, pp. 1429-1538, 1940.

[2] Morgan, J. H.: "The application of accessory mineral methods to the pre-Cambrian rocks of the Oxford House Area." Dissertation, Wisconsin, 1940.

[3] Chudoba, K., and Stackelburg, M. von: "Optical properties, density and structure of zircon." The Gemmologist, Vol. VII, No. 76, pp. 193-196, 1937.

[4] Hevesy, Georg. von.: "Chemical analysis by X-rays and its applications." McGraw-Hill, N. Y., 1932.

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DISTINGUISHING CHARACTERISTICS OF ZIRCON.

The three varieties of zircon found in the granites of the Lake Superior region are distinguished by their optical characteristics, color, and crystal form. The Keweenawan, or normal type, is a clear, colorless euhedral zircon of high refringence and strong birefringence. The hyacinth variety is characteristic of the oldest known granites in both the Lake Superior region and in the Oxford House Area. This type varies from a light pink to purple color, is of slightly lower refringence and lesser birefringence than the normal variety, and commonly has a rounded crystal form. The third type is characteristic of the younger granite in the Oxford House Area, and of the late pre-Huronian and Huronian granites of the Lake Superior region. This variety is malacon, a form of zircon with relatively low refringence, weak birefringence, and a dirty, altered appearance.

RADIOACTIVITY.

A measure of the radioactivity of 20 zircon samples was made with a Geiger-Müller counter connected with a recording device. The results of these measurements are shown in column one of the table. The figures given to represent radioactivity are the number of units recorded by the counter calculated to the basis of the radioactivity of one gram of sample in one minute. The data given for samples low in radioactivity are not so accurate as those given for more radioactive ones, since the efficiency of the counter drops as the count approaches the background effect.

The malacon type shows a higher radioactivity than the hyacinth and normal types. The hyacinth and normal types overlap, but the hyacinth in general is slightly higher in radioactivity.

OPTICAL STUDIES.

Refractive indices were measured by a modification of the Emmons double variation procedure in 14 samples. An accuracy of measurement of ± 0.005 was obtained. The data are shown in column two of the table. It should be noted that the optical measurements were made on only one grain in each sample, whereas the radioactivity measurement is an average of thousands of such grains. It is known that there is some variation in the index within each sample, so that the optical measurement may not represent the average optical properties of the sample.

TABLE 1.

	Sample Number	1. Radioactivity Count/gm./min.	2. Optical Data N_o			3. Hf:Zr ratio $\frac{Hf\ 3072.9\ Å}{Zr\ 3106.57\ Å}$	4. Y:Zr ratio $\frac{Y\ 3216.87\ Å}{Zr\ 3214.29\ Å}$	$\frac{Y\ 3327.9\ Å}{Zr\ 3306.2\ Å}$
			N_o	N_e	N_e-N_o			
Normal type	1*	35	1.924	1.977	0.053	0.53	0.79	0.59
	2	91	1.927	1.973	0.046			
	3	90	1.934	1.970	0.036	tr. of Hf	0.39	0.46
Hyacinth type	4	0	1.927	1.970	0.043	0.45	0.35	0.21
	5	0						
	6	77						
	7	110						
	8	117	1.903 1.914	1.936 1.945	0.033 0.031	0.30	0.63	0.56
	9	166				0.41	0.54	0.53
	10	193	1.924	1.950	0.026			
	11	344	1.921	1.963	0.042			
	12	478	1.904	1.921	0.017			
Malacon type	13	493	1.864	1.872	0.008	0.26	0.70	0.64
	14	508	1.820	1.827	0.007	0.25	0.38	0.30
	15	545				0.52	0.69	0.55
	16	624	1.862	1.868	0.006	0.70	0.63	0.51
	17	629						
	18	1074	1.786		very weak	0.42	0.59	0.52
	19	1255	1.814		very weak	0.53	0.56	0.51
	20	2852	1.782		very weak	0.51	0.73	0.59

*Numbers refer to samples listed on next page.

Samples.

1. Zircon concentrate from granite near Mellen, Wisconsin.
2. Macroscopic zircon crystal, location unknown.
3. Macroscopic zircon crystals from near Wausau, Wisconsin.
4. Zircon concentrate from granite, Oxford House Area, Manitoba.
5. Zircon concentrate from granite, Elbow-Morton Area, Manitoba.
6. Zircon concentrate from granite, Elbow-Morton Area, Manitoba.
7. Zircon concentrate from granite, Oxford House Area, Manitoba.
8. Zircon concentrate from granite pebble, Oxford conglomerate, Oxford House Area, Manitoba.
9. Macroscopic specimen of zircon from granite intrusive into Grenville limestone, near Andover, New Jersey.
10. Zircon concentrate from granite, Oxford House Area, Manitoba.
11. Macroscopic specimen of zircon from metamorphosed limestone near Diana, New York. Univ. of Wis. Geol. Mus., No. 20922.
12. Zircon concentrate from granite, Oxford House Area, Manitoba.
13. Macroscopic specimen of malacon from Cheyenne Canyon, Colorado. Univ. of Wis. Geol. Mus., No. 20914.
14. Zircon concentrate from granite, Oxford House Area, Manitoba.
15. Zircon concentrate from Algoman granite, north Minnesota.
16. Macroscopic specimen of alvite from Helle, Norway.
17. Zircon concentrate from granite, Oxford House Area, Manitoba.
18. Macroscopic specimen of malacon from Hybla, Ontario.
19. Zircon concentrate from pebble of quartz-feldspar porphyry, Oxford conglomerate, Oxford House Area, Manitoba.
20. Macroscopic specimen of cyrtolite from Bedford, New York. Univ. of Wis. Geol. Mus., No. 43090.

The samples of the normal variety which were measured show the highest indices and strongest birefringences and show low radioactivity. The hyacinth samples generally are of lower index, weaker birefringence and higher radioactivity than the normal type. The malacons are the lowest in index, weakest in birefringence, and show the highest radioactivity.

The ranges in index and birefringence shown by the measurements made are—

Normal type	N_o — 1.924-1.934
	N_e — 1.970-1.977
	N_e-N_o — 0.036-0.053
Hyacinth type	N_o — 1.903-1.927
	N_e — 1.921-1.970
	N_e-N_o — 0.017-0.043
Malacon type	N_o — 1.782-1.864
	N_e — 1.872-1.782
	N_e-N_o — 0-0.008

SPECTROGRAPHIC ANALYSES.

Qualitative spectrographic analyses of 24 samples of zircon show the presence of zirconium, silicon, hafnium, yttrium, cerium, lead, iron, and titanium. Germanium is present in 20 of the 24. Uranium is thought to be present also, but is not detectable by the method of excitation employed.

A semi-quantitive estimation of the amounts of hafnium and yttrium present in 12 samples was made in the following manner. Three milligrams of the sample were weighed into the crater of a graphite electrode which was used as the anode in a direct current arc. At 220 volts and 7 amperes, 90 seconds at 50 per cent light are sufficient to excite the sample so that lines of elements present in trace amounts are brought out. A large Bausch and Lomb Littrow type quartz spectrograph was used to make the spectrograms and a Bausch and Lomb non-recording densitometer to measure the densities of the lines. Eastman process plates and Eastman process developer were used.

The ratio of the densities of lines of hafnium and yttrium to zirconium lines is used to compare the relative quantities of these two elements in the 12 samples. Columns three and four of the table are the presentation of these ratios. In the sample of cyrtolite from Bedford, New York, the ratio of zirconium oxide to hafnium oxide is thought to be about 8 : 1. Analyses[5] of cyrtolite from the same locality showed this ratio to be fairly constant. Thus, the ratios larger than 0.51 in the table contain a greater ratio of hafnium to zirconium and those below, a lesser ratio than the cyrtolite sample.

SUMMARY AND CONCLUSIONS.

Von Hevesy[6] noted a rough relationship between hafnium content and radioactivity of zircon. The quantitative comparisons of hafnium content made in this study do not confirm the relationship noted by von Hevesy. No relation is apparent between yttrium content and radioactivity, nor between yttrium content and hafnium content.

[5] Lee, O. Ivan: "Mineralogy of Hafnium." Chem. Rev., Vol. 5, No. 1, pp. 17-37, 1928.

[6] Hevesy, Georg. von.: "Chemical analysis by X-rays and its applications." McGraw-Hill, N. Y., 1932.

X-ray studies by Chudoba and Stackelburg[7, 8, 9] suggest that zircon of low specific gravity, low refringence and weak birefringence, is in the metamict state. These workers also suggest that the metamict state is due to radioactive elements present in the zircon. The measurements of radioactivity made on 20 samples indicate a greater radioactivity in the malacon forms than in the hyacinth and normal varieties. The normal and hyacinth types are not sharply separated either in their radioactive properties or in their optical properties. It may be that a similar gradation exists between malacon and hyacinth.

It is thought that the data of this study indicate that content of radioactive elements is a major factor in the formation of meta-zircons, which is in agreement with the views of Chudoba and Stackelburg.

The type of zircon present in a granite may be dependent on the quantity of uranium available at the time of crystallization of the zircon. The quantity of uranium available apparently was very small when the Keweenawan or normal type zircon formed. A slightly greater quantity of uranium was available for inclusion in the crystals which formed the hyacinth variety. A still greater quantity of uranium was included in the zircon from which malacon formed.

This may imply that the concentration of uranium is greater in some magmas than in others, and may sometimes be indicative of concentration of uranium in the late stages of magmatic intrusion.

The concentration of uranium in granite magmas of one intrusive period may be similar over wide areas, since granite intrusives of similar time relationships can be distinguished by the zircon variety present in them. Such similarity in concentration of uranium may mean a common, deep-seated source for the magma.

[7] Chudoba, K., and Stackelburg, M. von.: "Dichte und Struktur des Zirkons." Zeit. Krist., 95, pp. 230-246, 1936.

[8] Chudoba, K., and Stackelburg, M. von.: "Dichte und Struktur des Zirkons II." Zeit. Krist., 97, pp. 252-262, 1937.

[9] Chudoba, K., and Stackelburg, M. von.: "Optical properties, density and structure of zircon." The Gemmologist, Vol. VII, No. 76, pp. 193-196, 1937.

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