SPECTROGRAPHIC EXAMINATION OF SIAMESE ZIRCONS

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Although many chemical analyses of zircons have been made, few spectrographic investigations have been reported. Pereira-Forjaz[1] has examined spectrographically a Portuguese zircon, and Wild[2] has investigated the arc spectrum of red, brown and blue Siamese zircons. The cause of the color in zircons generally has been attributed to the presence of impurities, particularly iron, copper, titanium, chromium, vanadium, zinc, uranium, thorium, hafnium and magnesium[3,4,5]

Preparation of Samples

The Siamese zircons examined were said to have originated in the province of Annam, French Indo-China.[6] All specimens were water-worn and exhibited no crystal faces. Color comparisons were made by placing a number of fragments, approximately 1 mm. thick, with random orientation, on a piece of white paper and comparing with Ridgway's Standards.[7]

The brown zircons were mine-rough specimens, while the blue were said to have been recolored from brown mine-rough by the action of heat alone, and the water-white or colorless from brown mine-rough by the use of both chemicals and heat.[8]

Samples for spectrographic examination were prepared as follows: the zircons were crushed in an agate mortar and then examined under a

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[1] Pereira-Forjaz, A., *Compt. rend.*, vol. **164,** p. 102, 1917.

[2] Wild, Georg O., *Centralbl. Min.*, vol. **1933A,** pp. 75–77.

[3] Stevanovic, S., *Zeit. Krist.*, vol. **37,** pp. 247–256, 1903.
Eppler, W. F., *N. Jahrb. Min., Abt. A., Beil-Bd.* **55,** pp. 401–487, 1926–27.

[4] Spezia, G., *Zeit. Krist.*, vol. **33,** pp. 636–637, 1900.
Herman, *Zeit. anorg. Chem.*, vol. **60,** p. 369, 1908.
Brauns, R., *Centralbl. Min.*, vol. **1928A,** p. 343.
Strutt, R. J., *Proc. Roy. Soc.*, vol. **89A,** pp. 405–407, 1914.
Sandberger, *N. Jahrb. Min.*, vol. **1845,** pp. 143–144.
Klemm, R., *Centralbl. Min.*, vol. **1927A,** pp. 267–78.

[5] Doelter, C., *Das Radium und die Farben*, Dresden, **1910.**
Alexander, Jerome, *Colloid Chemistry. Theoretical and Applied*, vol. **III,** pp. 270–273, 1931.

[6] The material was supplied by Mr. C. A. Allen, Cranbury, N.J. Grateful acknowledgment of his kind and valuable co-operation is hereby made.

[7] Ridgway, *Color Standards and Color Nomenclature*, Washington, **1912.**

[8] Private communication from C. A. Allen. The heat treating is described in Gems and Gemology, Heat Treating Zircons, Allen, C. A., vol. **1,** pp. 341–344, 1935. The chemicals often employed are as follows: one ounce of arsenous acid, one ounce of silver nitrate and five ounces of soda hypophosphite, thoroughly mixed.

microscope. Only material free from inclusions and color spots, visible under a magnification of 35 ×, was selected. This material is designated as "clear" or "inclusion-free." Sample No. 10 was found to be coated with a grayish white glaze, presumably due to the chemicals used in heat-treating. This glaze was removed and spectrographically examined as sample No. 10a; the included black spots and zones of black material composed sample No. 10b. The inclusions removed from samples Nos. 1, 2, and 3 (brown mine-rough) were red in color, and in No. 2 black spots

TABLE 1.

Sample Number	Color	Ridgway's Standard (7)	Density
1.	Brown	13′ *j*.	4.738
1a.	Red (inclusions)	4 *j*.	—
2.	Brown	13‴ *a*.	4.744
2a.	Red (inclusions)	4 *j*.	—
	Black (inclusions)	—	—
3.	Brown	17‴ *f*.	4.628
3a.	Red (inclusions)	4 *j*.	—
4.	Blue	43″ *d*.	4.719
5.	Blue	44′ *d*.	4.710
6.	Blue	44 *e*.	4.734
7.	Blue	44′ *e*.	4.702
8.	Straw-yellow	14 *g*.	4.613
9.	Water-white	—	4.712
10.	Water-white	—	4.622
10b.	Black (inclusions)	—	—
11.	Water-white	—	4.644
11a.	Red (inclusions)	4 *j*.	—
12.	Water-white	—	4.622
12a.	Red (inclusions)	4 *j*.	—
13.	Water-white	—	4.710
13a.	Red (inclusions)	4 *j*.	—

were also found. The red spots corresponded with those of the clear water-white samples, with a color approximating 4 *j*.[7]

In all the zircons, distinct spots or zones, or both, appeared as inclusions when examined under a magnification of 35 ×. Separation of clear portions for samples, in the crushed material, was comparatively simple except in the case of the blue variety. Here the inclusions consisted of a relatively small number of black spots distributed throughout the entire sample. No separation was made, since the material as a whole was practically inclusion-free.

TABLE 2.

Sample Number	Large	Medium	Small	Very Small	Trace	Minute Trace
1. Brown (clear)	Zr Si	—	—	Hf	Ca	Mg Ba
1a. (inclusions)	Zr Si	—	—	—	Fe Ca	Mg Ba
2. Brown (clear)	Zr Si	—	—	Hf	Ca	Mg Ba
2a. (inclusions)	Zr Si	—	—	—	Fe Ca	Mg Ba
3. Brown (clear)	Zr Si	—	—	Hf	Ca	Mg Ba
3a. (inclusions)	Zr Si	—	—	—	Fe Ca	Mg Ba
4. Blue	Zr Si	—	—	Hf	Ca	Mg Ba
5. Blue	Zr Si	—	—	Hf	Mg Ca	Ba
6. Blue	Zr Si	—	—	Hf	Mg Ca	Ba Ti
7. Blue	Zr Si	—	—	Hf	Mg Ca	Ba
8. Straw-yellow (clear)	Zr Si	—	—	Hf Ag	Mg Ca Na	Ba
9. Water-white (clear)	Zr Si	—	—	Hf	Mg Ca	Ba
10. Water-white (clear)	Zr Si	—	—	Hf	Mg Ca Ag	Ba
10a. Glaze	Zr Si Na	Ag	—	Al Fe Mg Ca	Li V	Ba

TABLE 2. (*Continued*)

Sample Number	Large	Medium	Small	Very Small	Trace	Minute Trace
10b. (inclusions)	Zr Si Fe	Al	—	Hf Ag	Mg Ca Na	Ba
11. Water-white (clear)	Zr Si	—	—	Hf	Ca	Ba
11a. (inclusions)	Zr Si Fe	—	—	—	Ca	Ba
12. Water-white (clear)	Zr Si	—	—	Hf	Ca	Ba
12a. (inclusions)	Zr Si	—	Fe	Hf	Ca Ti	Ba
13. Water-white (clear)	Zr Si	—	—	Hf	Ca	Mg Ba
13a. (inclusions)	Zr Si	—	Fe	Hf	Ca Mg Cu	Ba

The spectrographic technique has been previously described by one of us.[9] The exposure time, however, was increased to 60 seconds. The long slit length of 7 mm. was found particularly advantageous in distinguishing spectral lines due to traces of impurities in the zircon from impurity lines in the electrodes. The results are given in Table 2.

DISCUSSION OF RESULTS

The refractive indices of the samples were checked by the use of high-refractive liquids,[10] for the purpose of identifying the material examined. No significant differences were found in the refractive indices of any of the samples and the values were approximately $\omega = 1.928 \pm 0.005$ and $\epsilon = 1.980 \pm 0.005$.

By examination of Table 1, for density and the indices of refraction obtained, it appears that the material investigated was the *b*- or normal modification of zircon, as classified by Stevanovic, Eppler and Simon, since the density, which varied from 4.613 to 4.744 (averaging 4.684),

[9] Kennard, T. G., *Am. Mineral.*, vol. **20**, pp. 392–399, 1935.

[10] West, C. D., *Am. Mineral.*, vol. **21**, pp. 245–249, 1936.

as well as the refractive indices, agreed with their data.[3,11] According to the classification of Bauer,[12] this is *alpha* zircon, which is the stable form as regards density and refraction changes due to the effects of heat.

Of especial interest is the similarity in composition of the various samples. It is noteworthy that no significant qualitative difference is shown in the spectra of the inclusion-free samples. Very small amounts of hafnium and traces of barium and calcium were found in all inclusion-free samples; in addition, very small amounts or traces of silver, magnesium, and sodium were found in one or more samples. With the exception of silver, the elements occurring in the samples are those generally found in zircons and have been previously reported.[13,14] The silver, observed in the spectra of four samples, i.e., two zircons, the glaze, and certain black spots, is probably due to the chemicals used in heat-treating, since the silver content is very prominent in the sample of the glaze.

Thus it would appear that there is no marked difference in the chemical composition of these brown, blue and colorless varieties of the normal or *b*-modification of zircon. This is in accordance with the spectrographic findings of Wild,[2] who, however, reports that no impurities were found. This is rather astonishing inasmuch as hafnium has been reported to be ever present in zircon.[15] As stated above, very small quantities of this element were found in all of the inclusion-free samples examined.

The blue and brown colors in the inclusion-free zircons are apparently not pigmental, but may be due to structure or colloids. Doelter, in particular, has favored the last-mentioned hypothesis for the coloration of many minerals, including zircon.[5] The red spots, however, contained a considerable amount of iron, which could have been responsible, at least in part, for their color.

Thorium was not found, nor did the photoluminescence test, described by Papish and Hoag,[16] show the presence of uranium. The absence of detectable quantities of lead agrees with these results.

Summary

1. Brown, blue and colorless Siamese zircons have been examined spectrographically.

2. The inclusion-free portions of these three color-varieties showed no

[11] Simon, *N. Jahrb. Min., Abt. A., Beil-Bd.* **61,** pp. 165–226, 1930.

[12] Bauer, Max, *Edelsteinkunde,* 3rd Edition, revised by Karl Schlossmacher, Leipzig, **1932,** p. 562.

[13] Venable, Francis P., *Zirconium,* **1922,** p. 98.

[14] Doelter, C., *Handb. Mineralchemie,* **III,** Pt. 1, p. 133, 1918.

[15] von Hevesy, *Chemical Analysis by X-Ray and Its Application,* **1932,** p. 217.

[16] Papish, Jacob and Hoag, L. E., *Proc. Nat. Acad. Sci.,* vol. **13,** pp. 726–728, 1927

differences in chemical composition, except for traces of magnesium, sodium and silver.

3. A very small amount of hafnium and traces of barium and calcium were found in all the inclusion-free samples; very small amounts or traces of silver, magnesium and sodium were found in one or more samples.

4. The black inclusions and red spots showed a marked difference in chemical composition from the inclusion-free material, being much richer in iron. Aluminum, copper and titanium were sometimes present.

5. The blue and brown colors in the inclusion-free zircons are not pigmental.