

## IDENTIFICATION OF CERTAIN GEM-STONE MATERIALS BY THEIR EMISSION SPECTRA

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The application of petrographic methods, using thin sections and mineral fragments, for the identification of mineral species, frequently cannot be carried out with cut and polished gem-stone materials. The examination of this type of material must be conducted without serious damage to the specimen, and thus gemological tests are sometimes handicapped when the physical and optical data are insufficient to identify the species conclusively. This investigation was prompted by failure to identify a certain red gem-stone weighing 22.37 carats with a value of 1.716 for its index of refraction and 3.61 for its gravity. Absorption bands in the visible region,<sup>1</sup> indicative of pyrope, were observed using a Gaertner spectroscope. Since this index is possible for both garnet<sup>2</sup> and spinel<sup>2,3</sup> and the density may be a value of either mineral,<sup>2,3,4</sup> more information was required to definitely identify the specimen. Spectrograms were obtained of this stone, designated as sample No. 1, also of two spinels, samples No. 2 and 3, and of a garnet, sample No. 4. The examination was subsequently extended to specimens of tourmaline, andalusite, jadeite, nephrite, fibrolite and epidote. Kunz<sup>5</sup> states, "Sausurite is probably the most important of these materials easily mistaken for true jade. It is a compact, tough, heavy mineral with a hardness and gravity almost identical with jadeite, and this makes the differentiation difficult." He places fibrolite second in the list of minerals difficult of separation from jadeite and says, ". . . it is readily identified chemically being a practically pure silicate of aluminum." Others also give these minerals as difficult to identify.<sup>6</sup> Andalusite and tourmaline may like-

<sup>1</sup> These figures were given by R. M. Shipley, Jr., of the Gemological Institute of America, Los Angeles, Calif., whose idea prompted the initial experiment with garnet and spinel.

<sup>2</sup> Eppler, W. F., *Edelsteine und Schmucksteine*, Leipzig, 1934, p. 266 and p. 310.

*Dana's Textbook of Mineralogy*, 4th Edition, revised by Ford, 1932, pp. 592-594 and p. 488.

Kraus and Holden, *Gems and Gem Materials*, 1931, pp. 238-239 and pp. 246-247.

Winchell, A. N., *Elements of Optical Mineralogy*, 1933, pp. 176-177 and p. 62.

Spencer, L. J., *A Key to Precious Stones*, Glasgow, 1936, p. 186 and p. 167.

<sup>3</sup> Bauer, Max, *Edelsteinkunde*, 3rd Edition, revised by Karl Schlossmacher, Leipzig, 1932, p. 549.

<sup>4</sup> Chuboda, Karl, *The Gemmologist*, vol. 5, pp. 267-270, 1936. Bauer, Max, *ibid.*, p. 549 and p. 566.

<sup>5</sup> Kunz, G. F., *Encyclopaedia Britannica*, 14th Edition, 1929, vol. 12, p. 864.

<sup>6</sup> Bauer, Max, *ibid.*, pp. 650-652. Doelter, C., *Handb. Mineralchemie*, II, Pt. 1, p. 694, 1914.

wise be confused.<sup>7</sup> Ford<sup>8</sup> states that zoisite "includes the essential part of the mineral material known as saussurite (e.g., in saussurite-gabbro), which has arisen from the alteration of feldspar." Due to inability to obtain specimens of saussurite or zoisite, epidote was substituted and examined.

#### PREPARATION AND EXAMINATION OF SAMPLES

The samples of garnet and spinel for spectrographic study were removed from the fashioned gems by careful application of a corundum hardness point to one of the back facets of each stone, close to the girdle. The material abraded was deposited directly upon the spectrographic electrodes, and weighed approximately 0.1 mg. A slightly rounded point was found to be better for removing the samples than a sharp one as sufficient material was procured without cutting too deeply into the specimen.

The extension of this first work was conducted with samples obtained as just stated. However, a carborundum point was employed instead of corundum. The quantity used, in each case, was of the same magnitude. The aluminum contamination from the corundum point was not deemed serious in the garnet-spinel examination since silicon was to be the element of interest in showing the compositional differences between these two minerals. Silicon was expected to be present in the examinations in all the other minerals and thus very slight contaminations from the silicon carbide were not deemed serious. However, the use of a diamond point is recommended for this type of investigation. The spectrographic technique and the interpretation of the plates have been previously described.<sup>9</sup>

TABLE OF RESULTS

Sample Number	Large	Medium	Small	Very Small
Sample—No. 1	Mg Al	—	—	—
Spinel—No. 2	Mg Al	—	—	—
Spinel—No. 3	Mg Al	—	—	—
Garnet—No. 4	Mg Si Al	Fe Mn	—	—

<sup>7</sup> Bauer, Max, *ibid.*, p. 615. Eppler, W. F., *ibid.*, p. 277.

<sup>8</sup> Dana's *Textbook of Mineralogy*, *ibid.*, p. 621.

<sup>9</sup> Kennard, T. G., and Howell, D. H., *Am. Mineral.*, vol. 21, pp. 721-726, 1936.

TABLE OF RESULTS (*Continued*)

Sample Number	Large	Medium	Small	Very Small
Jadeite—No. 1	Si	Al	—	Mg
Jadeite—No. 2	Si (Na)*	Al (Ca)	—	Mg
Jadeite—No. 3	Si	Al	—	Mg
Nephrite—No. 1	Mg Si	—	—	Al
Nephrite—No. 2	Mg Si	—	—	Al (Ca)
Nephrite—No. 3	Mg Si	—	—	Al
Epidote—No. 1	Si Al	Fe (Ca)	—	Mg
Epidote—No. 2	Si Al	Fe	—	Mg
Epidote—No. 3	Si Al	Fe	—	Mg
Sillimanite—No. 1	Si Al	—	—	Fe (Na) (Ca)
Sillimanite—No. 2	Si Al	—	—	Fe
Tourmaline—No. 1	Si Al	B	—	Fe Mn Mg
Tourmaline—No. 2	Si Al	B	—	Fe Mn Mg
Tourmaline—No. 3	Si Al	B	—	Fe Mn Mg

TABLE OF RESULTS (Continued)

Sample Number	Large	Medium	Small	Very Small
Andalusite—No. 1	Si Al	—	—	Fe Mg
Andalusite—No. 2	Si Al	—	—	Fe Mg
Andalusite—No. 3	Si Al	—	—	Fe Mg

\* The elements which are enclosed in brackets were recorded in the visible region.

Due to the technique employed and the very small quantity of material composing the spectrographic samples, traces of impurities are not recorded in the table of results.

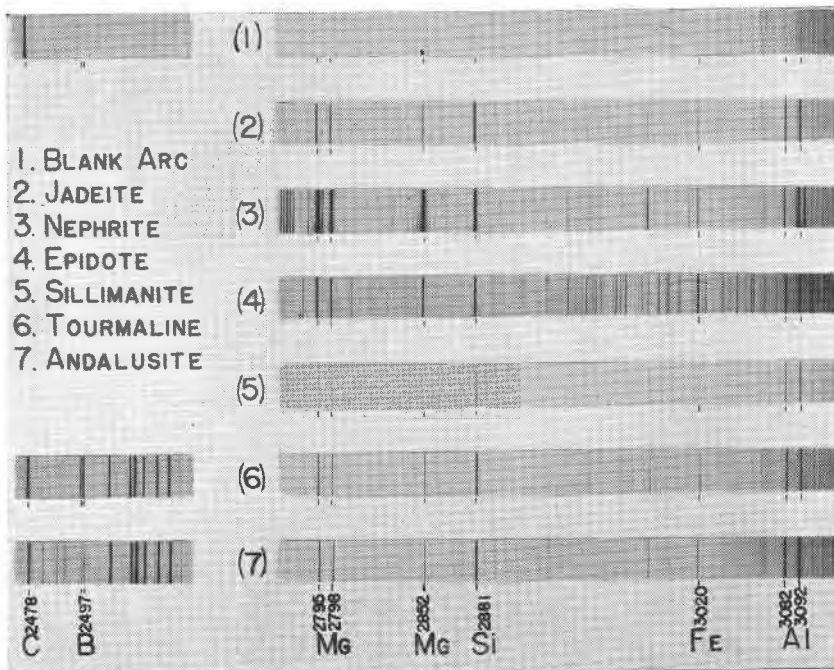


FIG. 1

## DISCUSSION OF RESULTS

The spectrum of sample No. 1 in the first group showed the presence of magnesium and aluminum with traces of silicon. This agreed with the spectra of two known spinels. Comparison of the spectra of sample No. 1 and sample No. 4, a garnet, showed a marked dissimilarity in composition. Thus, though the gravity and refractive index were insufficient to determine the gem's identity, spectroscopy showed the chemical composition of sample No. 1 to be that of a spinel rather than a garnet.

The spectrographic evidence for sample No. 4 points to a pyralspite garnet.<sup>10</sup> The presence of an appreciable amount of manganese indicates the spessartite variety. Laboratory tests gave the value 1.805 for the index of refraction and 4.05 for gravity which agree for garnets of this variety. The presence of iron and magnesium indicate an admixture of pyrope and almandine molecules.

The spectra produced by jadeite, nephrite and its substitutes are each distinctive. A portion of the spectrum using one sample from each group is reproduced in Fig. 1. The region from 2700Å to 3100Å was found to be satisfactory for establishing significant variations in the silicon, magnesium and aluminum contents. The table of results and the illustration show the silicon comparable in the spectra of jadeite and nephrite, but the aluminum content of the former is greater. In nephrite the reverse is true, for the five magnesium lines between 2777Å and 2783Å appear, indicating a large amount of this element. The aluminum content is approximately that of a trace or a very small amount. This variance in the aluminum, magnesium, silicon ratios is in accordance with the theoretical composition of these minerals.<sup>11</sup>

The spectrum of epidote shows strong iron lines, especially at 3020Å, and this is different from the two preceding spectra. The aluminum, magnesium, silicon ratios in this mineral are definitely not the same as those of either jadeite or nephrite. The intensities of the iron lines are such as to show this element to be present in considerable amount, while in the case of jadeite or nephrite it is present as an impurity in relatively small amount. In a similar manner sillimanite can be separated from jadeite and nephrite. The corresponding tri-element ratios in this aluminum silicate are markedly different.

The tourmaline-andalusite separation is easily made apparent by comparing the strength of the boron lines in the spectrum of each mineral. Tourmaline, a boro-aluminum silicate, gave very strong boron lines while andalusite showed boron to be present only in traces or in very small amounts.

<sup>10</sup> Winchell, A. N., *Elements of Optical Mineralogy*, 1933, vol. II, pp. 174-179.

<sup>11</sup> Doelter, C., *Handb. Mineralchemie*, II, Pt. 1, p. 651. 1914.

The mineral specimens previously sampled as jadeite, No. 2, nephrite, No. 2, epidote, No. 1, and sillimanite, No. 1, were resampled and spectrograms were made in the visible region. These same specimens of jadeite and nephrite were also examined in both the visible and ultra-violet portions of the spectrum, using a very large sample of each, weighing approximately 100 mg. These spectrograms taken in the visible region showed the sodium and calcium content of jadeite, nephrite, epidote and sillimanite. The very large sample of jadeite was of sufficient quantity to produce strong sodium lines at 3302Å. Comparison of the spectral lines of silicon, aluminum, magnesium and iron produced by the very large sample and the minimum samples showed no significant changes in the ratios of these elements but only a diminution of intensity in the small samples. Since analyses of jadeite and nephrite<sup>12</sup> show definitely a great dissimilarity in the aluminum and magnesium contents of these minerals, and since the sensitive spectral lines of these three elements lie in the ultra-violet region, this portion of the spectrum was employed and found satisfactory for differentiation between the ratios of these elements present in each species. The results showed that the identity of a mineral, having the color, physical and optical values possible for either jadeite or nephrite, could be determined by the type of spectrum produced and the tri-element ratios. The sensitive lines of the elements indicating the chemical composition of epidote and sillimanite likewise occur, with the exception of calcium, in the ultra-violet, as do the sensitive boron lines of tourmaline.

The technique just described, employing a very minute amount of a specimen, showed significant differences in the spectra of the specimens examined. These differences in composition may be quantitatively interpreted in terms of specific ratios which definitely separate one species from the other on the basis of chemical composition. The method may be employed to further a positive identification of cut and polished gem-stones, ornamental stones or archaeological artifacts as well as mineral specimens, using less material and causing less damage than is possible with a direct chemical analysis.

#### SUMMARY

(1) A technique is described whereby material sufficient for emission spectroscopy may be obtained without serious damage to valuable specimens.

(2) The method has been tested using specimens of garnet, spinel, jadeite, nephrite, epidote, sillimanite, tourmaline and andalusite and found to be satisfactory in distinguishing between the various species.

<sup>12</sup> Doelter, C., *Handb. Mineralchemie*, II, Pt. 1, pp 652-680, 1914.

(3) The procedure is considered to be applicable generally in distinguishing between species which have similar optical and physical properties, but different chemical composition.

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