USEFUL ASPECTS OF THE FLUORESCENCE OF ACCESSORY-MINERAL-ZIRCON*

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ABSTRACT

The mineral zircon has long been known to exhibit fluorescence when exposed to ultraviolet radiation. Hitherto little practical use appears to have been made of this phenomenon. Its application is here recommended in the inspection of commercial concentrates of zircon and of other minerals containing zircon as an impurity. Comparison of the fluorescent behavior of grains of zircon from igneous rocks of different ages, and from igneous as compared to sedimentary sources, reveals certain contrasts. The possible usefulness of such contrasts in the solution of a number of petrological problems is discussed. Reference is also made to the fluorescence of accessory-mineral apatite, and of certain other minerals found in association with zircon.

INTRODUCTION

Mineral fluorescence is generally regarded as little more than an interesting and spectacular phenomenon, and of but little practical value to the mineralogist or petrologist. A number of exceptions to this generalization might be enumerated however. Its usefulness in the control of grade of concentrates of New Jersey zinc ores (8) (12), and in the location and evaluation of tungsten ores (2) (22) (24), is well known. It also facilitates the sorting of a wide variety of other non-metallic minerals (1) (20) (23) (26). Other applications include the study of the occurrence and distribution of sodalite in alkaline igneous rocks (7) (10) (11) (16), and the localization of ore minerals in polished sections (27).

The fluorescence of zircon, although known for many years, does not seem to have received much attention. Zircon is frequently omitted from tabulations of the fluorescent minerals, and is said to be the most frequently overlooked of such minerals (26). Statements that zircon does not usually fluoresce (3), or that it fluoresces only under the shorter ultraviolet wave lengths (19), are at variance with the experience of the writer. Examination of hundreds of samples of fine-grained accessory-mineral zircon has demonstrated that, for this type at least, fluorescence is the rule rather than the exception, and may be exhibited under either short or long radiation or both.

Fluorescence in minerals depends upon the presence of elements in solid solution in certain optimum concentrations to function as activators, and the absence of appreciable amounts of other elements in solid solution which might poison or inhibit the activators (15). The precise

* Contribution from the Research Laboratories of the Ceramic Division of the Champion Spark Plug Company.
agent or agents responsible for fluorescence in zircon have not in all cases been determined, although it is probable that they are included among the elements of the rare earth and radioactive groups. The yellowish fluorescence of many zircons is perhaps suggestive of uranium, which with thorium is known to occur in zircon, even if only in the minutest traces. The red fluorescence of zircon has been ascribed to samarium and terbium, and the green fluorescence to dysprosium (9). Hafnium in zircon has been shown to vary from 0.2 to 16 per cent and to average three per cent (5), and the suggestion has been made that this element may be an activator of the fluorescence (4).

This paper is not concerned with the causal agents nor mechanism of zircon fluorescence. The sole purpose is to arouse an interest in its application to evaluate commercial concentrates and in its possible diagnostic value in heavy-mineral correlation studies. The results here presented are largely preliminary in character, yet they appear to indicate that further work is warranted. It is hoped that this initial study may prepare the way for more thorough studies by other workers.

Sources of Ultraviolet Radiation

The first requirement for such fluorescence studies is an adequate source of ultraviolet light for irradiating the specimens. It has been shown that the hue, intensity, and even existence of fluorescence in a particular mineral specimen depends on the wave length of the incident radiation (14). The ideal unit would be one capable of yielding essentially monochromatic radiations of high and uniform intensity over the wavelength band from about 2500 to 4000 angstrom units (A.U.). Such characteristics are not embodied in any commercial unit. Most currently available sources provide either a predominantly short-wave (2537 A.U.) or a predominantly long-wave (3650 A.U.) radiation. Unfortunately there is considerable variation in the intensity and degree of monochromaticity of different units. Accordingly, one should always specify the particular type of unit employed, in order to permit correlation with the work of other investigators. The possibility of any such correlation has been questioned on the grounds that not only are the lamps of a given manufacturer too variable in behavior, but a single lamp may display considerable change in output in service.* Such an extreme view should not be allowed to discourage fluorescence studies and comparisons, and it appears in no way to invalidate the general conclusions arrived at in this study.

Facilities for an exhaustive comparison of the effect of a wide variety of ultraviolet sources on the fluorescence of ziron were not available, nor

* Hugh S. Spence, personal communication.
did such a comparison appear necessary, for this preliminary investigation. Attention was confined to several units which happened to be at hand. These included a Magnaflux ZB22 Blacklight, a General Electric B-H-4 bulb, and an R & M unit. The two former are classed among the so-called long or near ultraviolet sources, and give their predominant emission at 3650 A.U. The third is a representative of the short or far ultraviolet sources, its radiation being concentrated at a wave length of 2537 A.U. Of the two long-wave sources the Magnaflux unit was found to give much the more intense radiation, and was used almost exclusively when 3650 A.U. radiation was required. The R & M lamp did not furnish as intense a radiation as might be desired. Another lamp of the same type, the Mineralight, apparently has a much higher radiation intensity, but unfortunately it was not available. Undoubtedly other sources superior to even the best of the above-mentioned lamps will before long be obtainable, particularly if studies such as the present one demonstrate a need for them.

**Method of Study**

No fixed method of sample preparation was followed for these studies. In most cases the condition of the sample as examined was that in which it was received, and included highly concentrated, partially concentrated, and unconcentrated conditions.

*Highly Concentrated Samples:* Commercial zircon samples are already highly concentrated. The manner in which they are evaluated for industrial use is described in a later section. These concentrates furnished excellent material for studying the variety of fluorescent responses displayed by zircon. A high degree of concentration is particularly desirable for critical comparison of the responses of zircons of various rock types and ages. Fortunately, some of the samples lent to the writer were received in this condition.

*Partially Concentrated Samples:* Some samples were received in the form of heavy-mineral concentrates in which the often minor zircon is accompanied by the usual accessory mineral associates. In order to protect these borrowed samples from depletion, contamination, or change in mineral proportions they were studied without any attempt at further concentration. Permanent grain mounts, if embedded in Canada balsam or any of the other customary media, are not amenable to direct study, since the fluorescence of the mounting medium masks that of the zircon. It has been suggested to the writer that the mounting medium can be readily dissolved with acetone, if desired.

*Unconcentrated Samples:* Although some degree of concentration is

† S. A. Tyler, personal communication.
desired, it is by no means mandatory. Considerable information can be obtained from rock chips, despite the minuteness of the grain size and the quantity of zircon in its host rock. A number of rock chips presenting reasonably smooth though not necessarily plane or polished surfaces should be available for such direct examination. Such a step is a worthwhile preliminary to the study of any suite of rocks for which zircon concentrates are not already available. Background fluorescence due to the enclosing rock is seldom so pronounced as to obscure the response of the zircon grains, especially if the rock is fresh. A single rock thin section generally presents too restricted an area to reveal the characteristic response of the zircon. Thin sections, too, suffer from the same disadvantage as permanent grain mounts on account of the fluorescence of the mounting medium.

The examination procedure is extremely simple, and observations can be rapidly made. The sample is merely exposed directly to the radiation from the ultraviolet source. The visible light thereupon emitted by the sample can usually be detected with the unaided eye, and in some cases direct examination is satisfactory. In most cases, however, it is preferable to make the observations under the low magnification (10X or thereabouts) of a binocular microscope. For sparse granular samples, it is well to use a black non-fluorescing background. In general, where glass or plastic-capsule containers are used the samples must be removed therefrom. Glass, although transmitting the longer ultraviolet wave lengths, cuts out the shorter radiation, whereas plastic capsules are themselves fluorescent. A general rule to be followed in the comparison of a series of samples is that the conditions of observation and of the samples be the same throughout.

**GENERAL OBSERVATIONS**

The pronounced variation in fluorescent response exhibited by zircon is strikingly evident if one examines but a single sample of commercial granular zircon under the binoculars with ultraviolet illumination. Close examination of many such samples has given rise to the descriptive classification presented in Table 1. Admittedly, it is very qualitative and leaves much to be desired if one is interested in a rigorous approach to the problem of fluorescence in zircon. Yet it is quite satisfactory for present purposes, where one is interested primarily in general trends in behavior among the zircons from different sources.

As regards the hue of fluorescence quite a few types can be recognized under the same lamp. The more intense Magnaflux lamp reveals sharper distinctions in hue than do the weaker R & M and General Electric B-H-4 lamps. Intensity of fluorescence under a given lamp shows all
possibilities from imperceptible to intense. Where the response is faint, it is difficult if not impossible to assign to it any definite hue. It is significant that the weaker R & M short-wave unit reveals intensities every bit as great (although not necessarily in the same zircon grains) as does the stronger Magnaflux long-wave source.

The change in fluorescence intensity of a given zircon grain with change from the short-wave to the long-wave source may follow one of three general patterns. Thus, cases have been noted in which fluorescence was enhanced, diminished, or remained essentially unchanged in changing from a short to a long-wave source. As demonstrated in a later section, these patterns may prove very useful and significant in distinguishing zircons from rocks of different ages. Some zircons actually show a stronger response under the weaker R & M unit than under the strong Magnaflux lamp. This is mentioned to emphasize the fact that, although inherently a poorer representative of the short-wave units than is the Magnaflux lamp of the long-wave class, the R & M unit nevertheless is not without merit in revealing varying types of fluorescent response.

Another feature which is considered highly significant in the petrological applications is the uniformity or lack of uniformity of bulk fluorescence. Thus, igneous zircon concentrates tend to be very similar in response from grain to grain, giving a uniform bulk response, whereas sedimentary zircon concentrates tend to be very non-uniform. Further reference will be made to this feature in a later section.

In the decoloration of zircon by chemical means iron is said to be one of the elements removed (25). Since iron is reputed to be a poison or inhibitor of fluorescence in certain minerals, it was decided to determine if
chemical treatment of zircon would perceptibly influence its fluorescence. Accordingly, samples in the form either of granular concentrates or rock chips were subjected to overnight heating on a steam bath with 20% oxalic acid solution. In the few such tests carried out, not only was the color removed but also the fluorescence was increased, in some cases pronouncedly. Treatment by oxalic acid, or other chemical reagents, would thus appear to be a promising preliminary step in the study of samples which give little or no response if untreated.

**Some Fluorescent Associates of Zircon**

It is necessary to keep in mind that certain common associates of zircon, in both igneous and sedimentary modes of occurrence, may be expected to fluoresce. No difficulty need be experienced, however, because of similarity of response to that of zircon. Apatite is almost universally present in granitic rocks, and many rock chips show fluorescent grains of this mineral. The grains are commonly larger and less regular than those of zircon, and the fluorescence is usually dingy greenish-yellow (sometimes brown or whitish) of only moderate intensity. Sodalite often exhibits an intense orange-red emission somewhat similar to that of certain zircons, but is more prone to occur within the light-colored constituents of the rock, and as less regular grains. Calcite sometimes displays an intense yellowish fluorescence. Oil-coated quartz grains and one type of corundum also give a yellow response easily mistaken for that of zircon. All of these minerals are readily distinguished from zircon microscopically.

Fluorite rarely if ever resembles zircon in fluorescence. Corundum, spinel, and kyanite, minerals which often accompany zircon in sediments, frequently emit a pink or red fluorescence not easily to be mistaken for that of zircon. Monazite and xenotime, the minerals most easily confused with zircon petrographically, do not appear to resemble it in fluorescent behavior. Tests on monazite from India and Brazil were negative, and it has recently been reported that xenotime from New Zealand gave no response to ultraviolet excitation (6). The foregoing enumeration is believed to include most of the fluorescent minerals which might cause confusion in zircon studies. It is always well to confirm the identity of any fluorescent grains presumed to be zircon, particularly in the case of rock chips, in which apatite is so often also present. With a little care a fluorescent grain can readily be pried loose with an oil-dipped needle and mounted for microscopic check.

**Evaluation of Commercial Concentrates**

Of recent years zircon has become an important raw material in the ceramic industry (12) (21). It is because of such desirable properties as
chemical stability, high refractoriness and mechanical strength, good electrical insulating characteristics, low thermal expansion, and good resistance to thermal shock that the demand for zircon for enamels, refractories, spark plug insulators and special porcelains has steadily increased. Zircon is also the source material for zirconia, another ceramic raw material, and for zirconium. It is because of these demands that the microscopic grains of zircon which constitute but a fraction of a per cent of both solid and unconsolidated rocks can be economically concentrated. It may come as a surprise to many mineralogists to learn that zircon, obtained largely by the beneficiation of beach sands already considerably concentrated by tidal action, may be purchased in carload lots of practically 100 per cent in purity.

Commercial grades of zircon vary considerably in the nature and extent of the impurities, of which the chief are rutile, tourmaline, and quartz. The dark color of the first two renders them easily visible. Samples containing quartz as the sole or chief impurity, however, give a false impression of high purity because the colorless quartz is indistinguishable from the zircon. A test based on the fluorescence of zircon and the non-fluorescence of quartz furnishes a simple and rapid means for evaluating such samples. As practiced in the writer's laboratory, the average sample obtained from each shipment is placed in an eight ounce bottle so as to fill the latter no more than about three-fourths, and turned over and over under the Magnaflux Blacklight. Such action causes the quartz to segregate into dark purple swirling strands, which contrast sharply with the yellowish background of the fluorescing zircon. The sensitivity of this test is high: as little as one tenth of one per cent of quartz can be readily detected. With practice in the use of prepared standards for comparison, it is possible to estimate the quartz content to the nearest one-half per cent, at least up to a five per cent limit, which is rarely exceeded by commercial samples.

There appears to be no reason why the above technique could not be used with profit in following the course of beneficiation of zircon-bearing sands, and as a prospecting method for the location of beach deposits of workable grade. Examination in ultraviolet light is also useful in revealing the extent to which granular concentrates of other minerals are contaminated by zircon. Thus commercial grades of rutile, ilmenite, chromite sillimanite, monazite, and glass sand may be profitably studied by this method. In these instances the scattered grains of zircon, even though their fluorescent response is faint, show up quite clearly against the non-fluorescing background of the predominant mineral. At the same time the presence of corundum, spinel, or kyanite may be revealed by the red fluorescence sometimes shown by these minerals.
Of recent years, too, zircon has assumed an important role in the solution of a variety of petrological problems. Numerous workers, after careful study of accessory-mineral suites, have singled out zircon as a mineral of particular promise in this regard. In view of the extent to which the other varietal features of zircon have been critically studied, it is somewhat surprising that its fluorescence has been completely neglected by heavy-mineral workers. Even the limited observations of the present study suggest that this property may possess a diagnostic value equal to, or greater than, that of the other varietal characteristics so far studied.

There appears to be a distinct tendency on the part of zircon from igneous rocks to display a uniform bulk fluorescence, whereas zircon from sedimentary sources is as a rule variable in response from grain to grain. This tendency is doubtless to be attributed on the one hand to the uniform physico-chemical environment in which zircon forms in a given igneous rock, and on the other to the heterogeneous origin of the material contributing to a given sedimentary occurrence. The above generalization is not without exceptions, and the latter may perhaps be accounted for as follows. Sedimentary zircon derived from the weathering of a single igneous intrusive would tend to be uniform. Furthermore, an igneous rock may contain several generations of zircon, or may acquire zircon present in the intruded rocks in addition to its own primary zircon.

The fact that zircon from a given igneous rock tends to be very uniform in fluorescence is believed to be highly significant in correlation studies. Thus, preliminary studies on a limited number of rock specimens from the Sawatch Range in Colorado give promise of success. The two Precambrian granites and one Tertiary batholith recognized in this area (17) (18) appeared to offer a means of testing the technique. Concentrates were not available, so the isolated zircon grains in rock chips, presenting about twelve square inches of surface, were carefully studied. Although the conditions of observation and comparison were thus not the best obtainable, yet a distinctive fluorescent response could be discerned for each of the three ages of intrusives. The older of the two Precambrian intrusives (the Pikes Peak granite) reveals no fluorescent zircon in either long or short ultraviolet light. Occasional grains of dingy greenish-yellow fluorescent apatite are observed. Under long ultraviolet the younger Precambrian intrusive (the Silver Plume granite) displays numerous bright orange zircon grains, which become imperceptible to faint under short wave length. Many grains of dingy yellow apatite are also visible. In sharp contrast to both of these are the rock chips of the
Tertiary Mt. Princeton batholith. No fluorescent apatite is seen, while the zircon not only displays a bright orange response in the long-ultraviolet but shows an even brighter yellow at the shorter wave length.

The above observations on the contrast in the zircons of the three Sawatch Range intrusives are summarized in Table 2, as are also additional results on some igneous rocks from several other areas. Some excellent samples in the form of concentrates were available for the Valverde tonalite and the Rubidoux Mountain granite of the Southern California batholith. Three samples were at hand for each of the two rock types, and for each rock the behavior of the three samples was identical. Thus the Valverde tonalite samples displayed a very uniform bulk fluorescence of a bright to intense yellow under both long and short radiation. In contrast the Rubidoux Mountain granite samples showed a rather non-uniform bulk response, faint under the short-wave source and faint to bright under the long-wave source, and of a decidedly orange rather than yellow hue. Careful examination of slices of granite of Killarnean age from Killarney Bay, Ontario, revealed no visibly fluores-

<table>
<thead>
<tr>
<th>Source-Rock and Locality</th>
<th>Age</th>
<th>Sample Type</th>
<th>Fluorescence Short (2537 A.U.)</th>
<th>Fluorescence Long (3650 A.U.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pikes Peak Granite</td>
<td>Earlier Pre-cambrian</td>
<td>Rock Chip</td>
<td>imperceptible</td>
<td>imperceptible</td>
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<tr>
<td>Sawatch Range, Colo.</td>
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<td></td>
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</tr>
<tr>
<td>Silver Plume Granite</td>
<td>Later Pre-cambrian</td>
<td>Rock Chip</td>
<td>faint</td>
<td>bright orange</td>
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<td>Sawatch Range, Colo.</td>
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<td></td>
<td></td>
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<tr>
<td>Princeton Batholith</td>
<td>Tertiary</td>
<td>Rock Chip</td>
<td>bright yellow</td>
<td>bright orange</td>
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<tr>
<td>Sawatch Range, Colo.</td>
<td></td>
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<tr>
<td>Valverde Tonalite</td>
<td>Cretaceous</td>
<td>Concentrate</td>
<td>bright yellow</td>
<td>bright yellow</td>
</tr>
<tr>
<td>Southern Calif.</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Rubidoux Mt. Granite</td>
<td>Cretaceous</td>
<td>Concentrate</td>
<td>faint</td>
<td>faint to bright orange</td>
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<tr>
<td>Southern Calif.</td>
<td></td>
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<tr>
<td>Killarney Granite</td>
<td>Killarnean</td>
<td>Rock Chip</td>
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<td>imperceptible</td>
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<tr>
<td>Killarney Bay, Ont.</td>
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<tr>
<td>Nepheline Syenite</td>
<td>Killarnean (?)</td>
<td>Rock Chip</td>
<td>bright orange-yellow</td>
<td>bright orange-yellow</td>
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<tr>
<td>French River, Ont.</td>
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</table>
cent zircon. Nepheline syenite from French River, Ontario, thought by Quirke* to belong also to the Killarnean, revealed bright-orange zircon under both long and short wave. This contrast in behavior suggests the possible need for reconsideration of the age of the syenite, which Quirke admitted was not too definitely established.

The above examples illustrate the manner in which zircon fluorescence studies may possibly aid in the correlation of igneous rocks. Although no work has been done in this direction, the method may possibly be of service in distinguishing meta-igneous from meta-sedimentary rocks, through the contrast in uniformity of bulk fluorescence of the two groups. Interesting information as to the igneous source rocks of sedimentary beds may also be forthcoming. In certain cases ore deposits, particularly such non-metallic "ore" deposits as the sillimanite minerals (andalusite, kyanite, sillimanite, dumortierite, topaz) and others, may possibly be tied in with the parent igneous intrusives. For example, a distinct yellow to orange-yellow fluorescence is shown by the zircon from both the andalusite deposits of White Mountain, California, and from the dumortierite deposits of Oreana, Nevada. It does not appear to be venturing too far into the realm of conjecture to suggest that each of these hydrothermal deposits might be correlated with its proper igneous intrusive.

A further comment might not be amiss regarding the reproducibility of results by different workers using different ultraviolet units. If the sole purpose of their studies is to characterize the fluorescence exactly as to hue and intensity, they might not agree in their descriptions of the responses observed. On the other hand, if the purpose is simply to classify the fluorescence according to general behavior patterns, different workers should be able to obtain essentially the same contrasts. Assuming each uses similar types of units (even although not from the same manufacturer) the broad conclusions as to uniformity or non-uniformity of the fluorescence, its strength or weakness, and the nature of the intensity change (increase, decrease, or no change) with change in wavelengths, should be quite similar.

**Summary and Conclusions**

Accessory-mineral zircon, such as occurs as tiny crystals and grains in igneous and sedimentary rocks, has been found to exhibit fluorescence to a considerably greater extent than one would conclude from the few literature references to the phenomenon.† A rather wide variety of fluorescent responses can be detected, even with the ordinary com-

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* T. T. Quirke, personal communication.
† Whether this applies also to gem and pegmatitic zircons was not investigated.
A crude classification of response-patterns has been presented, and a simple procedure for study has been outlined. Associated minerals which also fluoresce have been discussed. A rapid but very sensitive test for the detection of quartz in commercial zircon concentrates has been outlined. Associated minerals which also fluoresce have been discussed. A rapid but very sensitive test for the detection of quartz in commercial zircon concentrates has been outlined.

Interesting possibilities of the successful use of zircon fluorescence in the solution of a number of petrological problems have been suggested. The preliminary nature of the study from this standpoint has been emphasized. No sweeping claims for the method in such problems can be made, and any real appreciation of its value must await more careful application to specific problems. The probable utility of the method in any given case can be evaluated with a minimum of time and effort. The technique as outlined can doubtless be greatly improved upon. Rejection of the method on the ground that presently available ultraviolet units are unsatisfactory appears unwarranted.

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