An Attempted Determination of the Approximate Chemical Composition of the Livingston Volcanics by the Fused Bead Technique

Robert D. Geach
AN ATTEMPTED DETERMINATION OF THE APPROXIMATE CHEMICAL COMPOSITION OF THE LIVINGSTON VOLCANICS BY THE FUSED BEAD TECHNIQUE

by

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A Thesis
Submitted to the Department of Geology in Partial Fulfillment of the Requirements for the Degree of Bachelor of Science in Geological Engineering

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INTRODUCTION

Many fine-grained igneous rocks, basaltic and felsitic in character, are difficult to classify. In numerous cases, it is impossible to classify these types of rocks by quick methods of identification. It was hoped at the beginning of this study that refractive indices of glasses formed by quick artificial fusion of samples from selected suites of igneous rocks would show a close correlation in chemical composition. Since the determination of the index of refraction with a petrographic microscope, performed by the use of certain liquids or oils of known index of refraction, is a relatively simple operation which in time requires only a few minutes, the advantages gained by such an index-composition correlation are at once apparent. If this method could be used, correlation of two igneous rocks with similar chemical compositions, but with unrecognizable textures and mineral assemblages, could be readily done without the need for elaborate and expensive chemical analyses. Such a correlation would facilitate recognition of the more
acidic rocks, the more basic rocks, and the intermediate types.

As a test of the idea, a suite of nineteen rocks, mainly andesitic in composition, collected by Professor Robertson from the Hat Creek section of the Livingston volcanics near Elliston, Montana, were used by the writer in this study. Four of these rocks, ranging from the most acidic to the most basic, were selected for chemical analyses. Samples from these analyzed rocks were then powdered, subjected to complete fusion in a carbon arc, and their refractive indices obtained from the resulting glass beads by oil immersion methods. From these refractive indices, a correlation with the silica content of the analyzed rocks was attempted, and a curve showing index variations was prepared. If samples from the remaining fifteen rocks were fused, and their refractive indices obtained similarly, it was postulated that the silica content of these other rocks could be obtained by cross-correlation on a curve without the need for chemical analyses. With the silica content determined by this method, classification of these rocks by a simple petrographic means might be facilitated.

However, Mathews (3, p. 100) states that the technique is not without its limitations. For example, the coarser-grained rocks, and perhaps porphyries, are not amenable to this procedure. Since the advantage of the technique
lies in the rapidity with which a determination can be done (10 to 15 minutes), the time and effort in grinding coarser-grained rocks would minimize this advantage, and the possibility of variation in samples enters into the procedure. But still more important, application of the Wentworth stage in study of coarser-grained plutonites for mineralogical composition, which is a fairly reliable guide to chemical composition, can be exercised with ease and assurance, and this procedure is simpler and more satisfactory. But for the fine-grained rocks, the fusion-bead technique was hoped to be without a substitute as an adjunct to petrographic classification.

PREVIOUS WORK

That the index of refraction of a natural glass is undoubtedly related to its chemical composition, expressed in terms of a single variable (silica content), has long been known. Michael Stark (1904) and W. O. George (1924) attempted correlations of refractive indices of natural glasses with their silica content, but without any assurance of accuracy. Their observations show that two glasses (natural) with the same index might differ in silica content by as much as 14 per cent, or that two glasses with the same silica content might differ by as much as 0.065 in index. Furthermore, the early work of Stark and George does make it clear that the proportion of one con-
stituent alone does not determine the refractive index of a glass; however, each constituent should, and perhaps does, contribute according to its amount and properties.

Since few completely glassy rocks, directly suitable for index determinations, are commonly found in the field, Tesch (1903) suggested that partly crystalline rocks (aphantic rocks) could be artificially fused to produce glasses suitable for index-composition studies. Vital to the artificial fusion is the fact that important changes may be brought about in the composition of the rock by elimination of water, bringing iron to a uniform state of oxidation, and even perhaps by the loss of some constituents by volatilization.

Following this line of reasoning, C. W. Mathews (1951) artificially fused sixteen selected rocks from the same magmatic source in a carbon arc lamp; selected rocks, because the application of Harker's variation diagrams (2, pp. 118-125) to selected groups of igneous rocks, of one general locality and age, does show that within such groups two rocks with similar silica contents have similar bulk compositions and, if glassy, can be expected to have similar refractive indices. The maximum departure in Mathews' study was 0.007 in index and 1.8 per cent in silica content. Although these results are far from perfect, their accuracy seemed to justify the writer making a like investigation of his own.
LABORATORY PROCEDURE

The laboratory procedure, followed by the writer in his study, was developed by C. W. Mathews, and is outlined in the American Mineralogist, Volume 36, (1951). For the benefit of the reader, this procedure is cited as follows:

"...a rock chip of sufficient size to be representative within the limits of accuracy desired, i.e. yielding an error of less than 1 per cent in composition, is broken from the hand specimen. If the rock is homogeneous and fine grained or glassy a very small chip, weighing perhaps a couple of grams, is adequate; if, however, the rock is coarse grained or porphyritic of, the chip must be considerably larger, preferably of a size such that the addition or subtraction of a single grain or phenocryst would not materially affect the composition. The chip is then pulverized in a mortar until a fineness and degree of mixing is obtained such that any 10 mg. sample would differ from the mean composition of the mix by less than 1 per cent. At such a stage, again depending on the homogeneity and grain size of the original rock, most if not all the powder should be -200 mesh. It is desirable to split the sample, using an approved sampling technique, at several stages in the grinding in order to minimize the time and effort involved. A "diamond" mortar has proved better for pulverizing hard volcanic rocks than a cast iron mortar in which sufficient iron filings can be
produced during the grinding of a single chip to contaminate the sample effectively. An agate mortar, though unsuited for coarse grinding, is well adapted for the later stages of grinding and permits a more thorough mixing than does the diamond mortar. At first, until this part of the technique has been perfected, it is advisable to repeat determinations using different chips off the same hand specimen to establish the accuracy of sampling.

"The powdered sample is introduced into a broad crater cut with the point of a penknife to a depth of about 2 mm. in the upper end of the lower electrode of the carbon arc lamp. Uncored carbons, 7 mm. in diameter, and used after their ends have been tapered to about one half the original diameter by means of a pencil sharpener to reduce both the wandering of the arc and the heat loss from the vicinity of the crater. With this modification the powdered rock can be completely melted in the arc within several seconds, whereas with the full 7 mm. diameter persisting to the end of the electrode complete fusion can be obtained only with prolonged arcing. It is important to watch through a dark filter the powder in the process of melting to recognize the time at which fusion has reached completion and after which the arc should be switched off. If fusion is incomplete and the less fusible constituents remain undissolved, the glass will not have the composition of the anhydrous
rock. If fusion is unnecessarily prolonged differential boiling may lead to a loss of volatile constituents other than water and again the composition of the glass will not be that of the anhydrous rock. After prolonged heating, moreover, the melt is observed into the electrode and on cooling the glass is badly clouded with opaque grains of carbon. The composition of the glass itself is unaffected but the impurities make the refractive index determination difficult.

"The glass bead which forms in the crater of the electrode after the arc has been switched off is then crushed on a metal plate and the index of the glass fragments determined by the ordinary immersion methods in oils of known refractive index. Inasmuch as a maximum error of about 0.004 is permissible in routine determinations of the index of the glass, and as still greater accuracy is needed in the preparation of standard curves from analyzed samples, monochromatic light is virtually essential. Either a sodium vapor lamp or appropriately filtered white light can be used; unfiltered white light is unsatisfactory because of the vague color fringes it produces in place of the sharper Becke line when oil and glass have nearly the same index. Inasmuch as the refractive indices of oils change with age and vary with temperature they should be checked at the time of use with a refractometer to ensure the most accurate results."
The procedure, as stated before, was closely followed by the writer. Nineteen representative rock samples were pulverized in an ordinary mullite mortar, and the powdered material placed in appropriately labeled vials. Fusion of the samples was made with a spectrographic carbon arc, and the refractive indices were obtained by the use of a petrographic microscope and index of refraction liquid oils. However, instead of a monochromatic light source for use in conjunction with the petrographic microscope, the writer used unfiltered white light, which was the only type available.

RESULTS OBTAINED

The index of refraction data obtained during the course of the study did not result in a standard or symmetrical curve, in which the writer had confidence. When the first samples were fused and their indices determined, the writer noticed that different glass particles from the same bead yielded indices of refraction greatly different. Differences in index as much as 0.06 were recorded, which for the petrographer is a variation of 16 per cent or more than that desired. Successive runs in making fusions were then conducted on a time study; on a time study, because the time of exposure to a temperature of 3000° F. (the temperature of a carbon arc) would make possible the elimination of elements in the rock, such as water and the alkalies, by the simple process of volatilization. Several beads were made from one sample (specimen no. 29-9-4) with 23217.
the carbon arc at times ranging from 1 to 20 seconds. Yet, with this time factor, the variation in refractive index proved too great for satisfactory composition correlation (see Plate 1). However, in a general way, the final result of the study did indicate that acidic rocks, or those high in silica content, yielded lower refractive indices than the basic rocks. These results are summarized in Table 1, and shown in the accompanying refractive index-composition diagram (Plate 2).

<table>
<thead>
<tr>
<th>Specimen No.</th>
<th>Rock Type</th>
<th>SiO₂ Content</th>
<th>Refractive Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>28-155-1</td>
<td>Dacite vitrophyre</td>
<td>69.2%</td>
<td>1.495 ± 0.01</td>
</tr>
<tr>
<td>24-57-2-1</td>
<td>Trachyte</td>
<td>69.4%</td>
<td>1.500 ± 0.005</td>
</tr>
<tr>
<td>20-7-4-2</td>
<td>Andesite</td>
<td>58.7%</td>
<td>1.545 ± 0.03</td>
</tr>
<tr>
<td>20-7-4-2</td>
<td>Andesite</td>
<td>50.4%</td>
<td>1.570 ± 0.01</td>
</tr>
</tbody>
</table>

Conclusions and Future Recommendations

Since the data recorded during the course of the study indicates that the refractive index of a bead differed for the same time, and also despite the length of time of fusion, it was suggested by Professor Robertson that a slag film developed over the surface of the bead during the shorter times of fusion in the carbon arc. Consequently, this slag formation would prevent subsequent thorough mix-
DIAGRAM SHOWING VARIATION OF REFRACTIVE INDICES OF FUSED ROCKS REGARDLESS OF TIME
Diagram showing relationship of refractive indices of fused acidic and basic rocks.
ing of the constituents in the melt, and, as a result, variation in refractive index would be expected in the sample as a whole, which in analysis was the material examined for index of refraction. Another factor which might have entered into the fusion is that the carbon of the electrodes might have reacted with some of the rock constituents, particularly silica, and have formed silicon carbide, thus resulting in a new compound, instead of remaining neutral as assumed. A third factor, suggested by Dr. Perry, is that volatile constituents may have been driven off, thereby, changing the composition of the original rock; for example, water of crystallization may have been eliminated, and even some of the metallic constituents, such as sodium, calcium, and potassium may have been volatilized and lost.

In final conclusion, the results of this study did not yield the results hoped for, results which would be of aid in investigation of fine-grained rocks. The study does, however, show to future workers that this procedure in research has many limitations which detract from its use and value in rock identification.

Several future recommendations are offered by the writer for the benefit of those people whose interest might lie in conducting future research along these lines:

1. The specific gravity of non-vesicular samples obtained by the use of a pycnometer, and coupled with
refractive indices might ensure a higher degree of accuracy, than, as found out in this study, refractive indices alone.

2. Fusion points of paper-match-stick-sized rock samples, mounted in a non-fusible base, somewhat in the manner of segger cones used in a ceramics laboratory, might be taken for determination of the ratio of fusing to refractory material present in the rock, and thus prove to be an aid for rapid determination of the amount of some of the major constituents in the rock. Although this procedure appeared to offer possibilities of favorable results, the time available did not permit the writer to follow through the rather time-consuming experimental work needed.
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