A USEFUL METHOD FOR DETERMINING APPROXIMATE COMPOSITION OF FINE GRAINED IGNEOUS ROCKS

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Abstract

The refractive indices of glasses formed by artificial fusion of samples from *selected* suites of igneous rocks show a close correlation with chemical composition. Each of three suites studied has its own characteristic curves relating refractive index to composition of chemically analyzed samples, and these curves can be used to establish the approximate composition of other rocks from the same suites for which no chemical analyses are available. Similar relationships can be expected for the igneous rocks of many other suites and petrographic provinces.

Complete fusion of the powdered rock can be effected in a carbon arc using a small but representative sample. The glass formed from this fusion is crushed and its refractive index determined in immersion oils.

That the refractive index of a glass is determined by its chemical composition has long been known. Michael Stark (1904) and Walter George (1924), recognizing this relationship, attempted to correlate refractive indices of natural glasses with the content of their major constituent, silica, but with comparatively little success. According to their own observations two glasses with the same index might differ in silica content by as much as 14 per cent, or conversely two glasses with the same silica content might differ in index by as much as 0.065. Thus, although they demonstrated that indices are generally low if the silica content of the glass is high, and vice versa, they did not demonstrate a relationship sufficiently precise to provide a means of determining composition with any assurance of accuracy. The early work on refractive indices and composition, of which Stark and George were well aware, makes it clear that the proportion of any one constituent, even the major constituent, does not alone determine the refractive index of the glass, but instead each constituent contributes according to its abundance and to its specific properties. Thus, although the silica content of two natural glasses may be the same, as in a phonolite and an andesite, the proportion of other constituents may be markedly different and the refractive indices may, therefore, show no similarity. However, the application of Harker's variation diagrams (Harker, 1909, 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. Thus had Stark and George confined their studies to glasses of a single petrographic province or magmatic suite they could have expected a much closer distribution of plotted points on the silica-refractive index diagram along a smooth curve than anything they obtained (Fig. 1 lower left).

Few completely glassy rocks, suitable for refractive index determinations, are encountered in the field; but there is no reason, as Tesch indicated in 1903, why partly or wholly crystalline rocks could not be fused artificially to produce glasses suitable for composition-refractive index studies. The significant changes brought about in the composition of rocks as a result of artificial melting are essentially loss of the most volatile constituents, notably water, and change in the state of oxidation of iron. The presence of variable quantities of water in natural glasses may well have contributed to the deviations from George's silica-refractive index curve, for, as shown by Tilley (1922), this constituent even in small amounts can have a significant influence on refractive index.[1] Similarly, differences in the degree of oxidation of lavas during and after extrusion may also create deviations from the composition-refractive index curves for a particular suite. By artificially eliminating water and bringing iron to a uniform state of oxidation, however, a comparison of indices with composition in the suite may thus be aided.

Combining the two concepts outlined above, it would appear possible to correlate compositions of the members of a particular magmatic suite with the refractive indices, not merely of the naturally glassy rocks within the suite, but also with any artificially fused specimens of partly or wholly crystalline rocks. It would appear necessary only that the anhydrous compositions of the members of the suite can be expressed in terms of a single variable, that is that rocks representing comparable degrees of magmatic differentiation would contain similar amounts not merely of silica but also of alumina, iron, lime, and other essential constituents. The process of artificial fusion must be one that does not significantly alter the anhydrous composition of the specimens by faulty sampling, by contamination, by selective melting, or by differential boiling. If a reasonably close relationship can be established between composition and refractive index of the artificial fusion for a representative group of rocks from the magmatic suite in question, then the relationship can, in turn, be utilized in determining the approximate composition of other rocks from the same suite for which no chemical analyses are available. The degree of accuracy obtainable in the latter determinations is indicated by the scale of discrepancies between the mean curves on the composition-refractive index diagrams and the individual points corresponding to the analyzed rocks.

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[1] According to Tilley the index rises, other things being equal, at a rate of about 0.0033 for each additional per cent water up to at least 3.3 per cent; the density falls with increasing amounts of water.

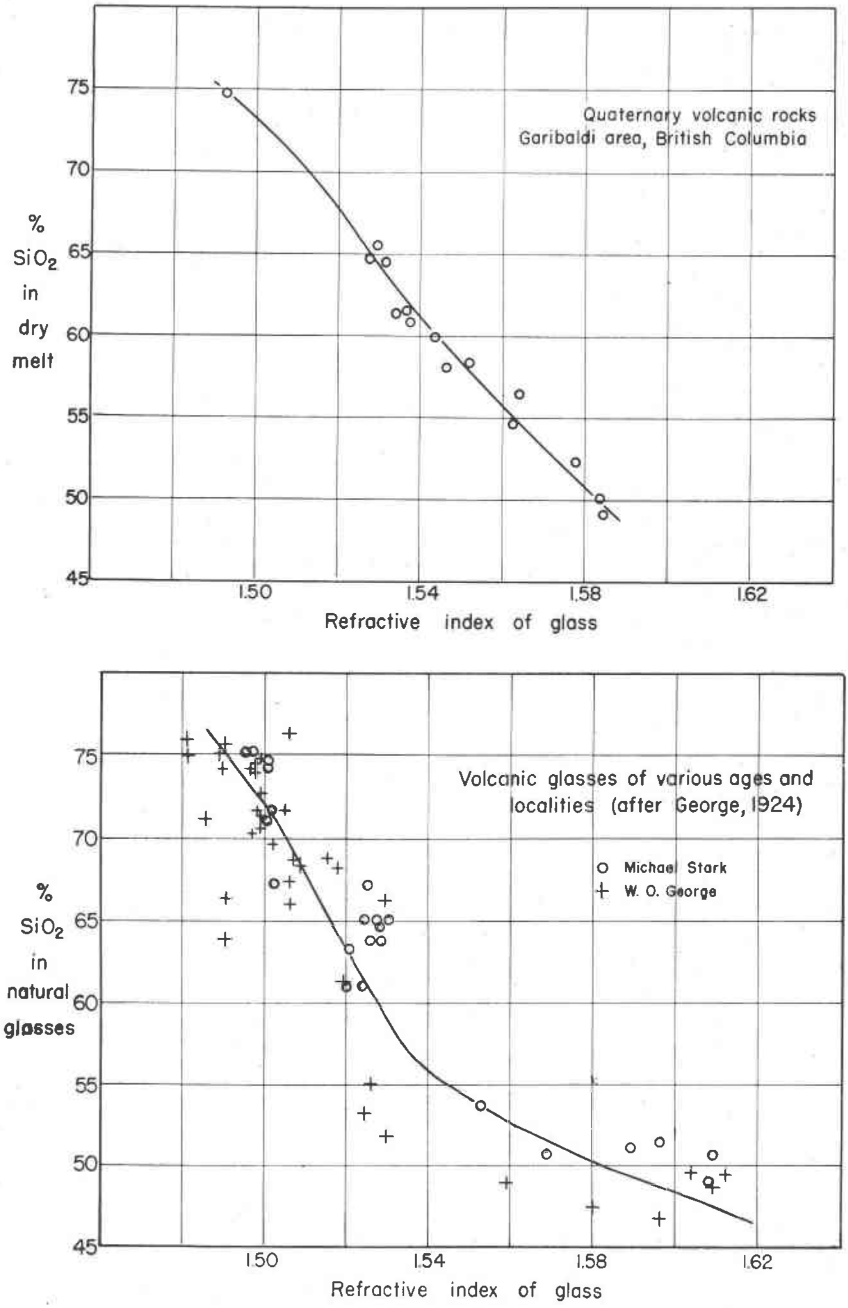
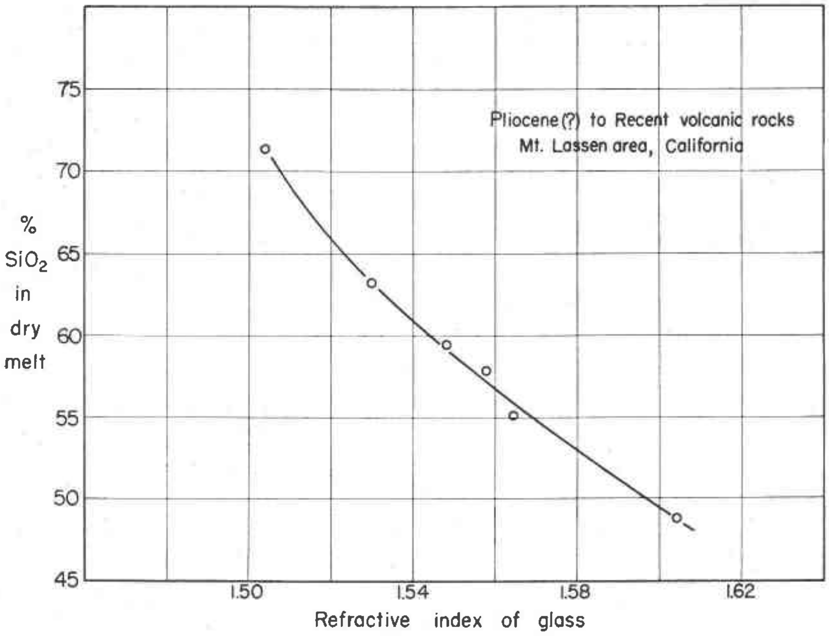
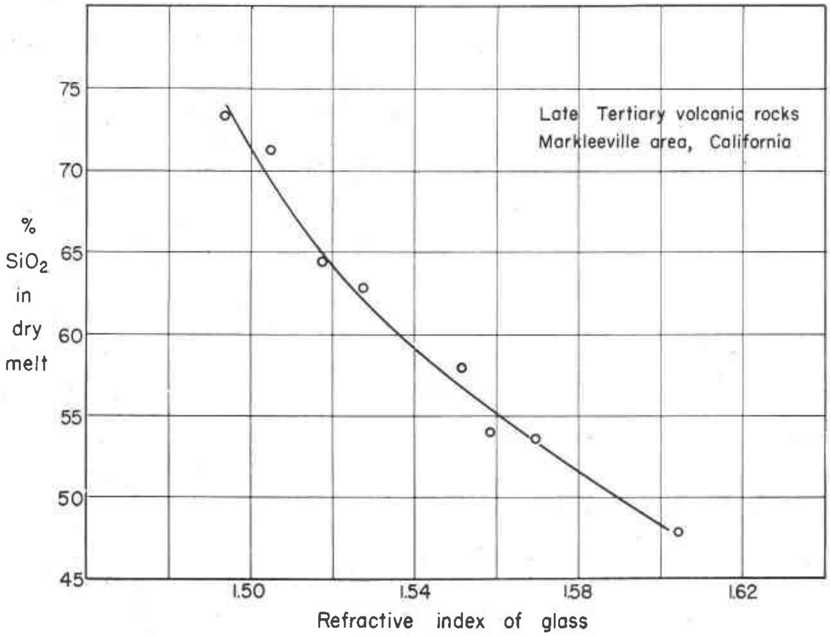


FIG. 1. Four composition-





refractive index diagrams.

As a test of the idea, 16 unaltered Quaternary volcanic rocks from the Garibaldi area of southwestern British Columbia were fused, and the refractive indices of the resulting glasses compared with the rock analyses. The analyses had already indicated that composition could be expressed, with but a small error, in terms of a single variable. The results of the test are indicated in Fig. 1 (upper left.) The maximum departure of any point from a smooth mean curve on the silica-refractive index diagram is 0.007 in index and 1.8 per cent in silica content. The maximum departure from a smooth alumina-refractive index curve is 1.6 per cent alumina, and from a potash-refractive index curve only 0.25 per cent potash for 15 of the 16 analyzed rocks, and 0.40 for the 16th. The accuracy of the results, though by no means perfect, was far superior to any obtained by George and was sufficient to justify the effort involved in making the observations.

Similar refractive index measurements have been made by Messrs. G. H. Curtis and D. B. Slemmons of the University of California for two other volcanic suites, one of late Tertiary rocks from the Markleeville area (Fig. 1 upper right) in the northern Sierra Nevada, and one of Pliocene (?) to Recent rocks from Mount Lassen (Fig. 1 lower right). For both suites a close relationship is indicated between refractive index and the silica content of the water-free glass as calculated from the chemical analyses of the original rocks.

A comparison (Fig. 2) of the four available silica-refractive index diagrams[2] shows (1) that the mean curve for the Garibaldi suite diverges appreciably over a part of its range from the curve for the Markleeville lavas, (2) that for glasses of the same refractive index those from the Lassen area are regularly about 2 per cent richer in silica than those from the Markleeville area, and (3) that not one of the three curves corresponds to the one derived by George from a large but indiscriminately chosen set of volcanic glasses. The volcanic suites of the Garibaldi, Markleeville, and Lassen areas are all calcic (Peacock, 1931). Had alkaline suites been included in the studies we might expect to find other curves differing markedly from those already established, and in all probability lying on the opposite (left) side of the average curve prepared by George. Such variations show clearly how unsafe it is to assume that a composition-refractive index curve for one suite of rocks should necessarily apply for a suite of some other locality or age.

It should be emphasized that for each of the three suites so far studied

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[2] Note, however, that the diagrams for the rocks from the Garibaldi, Markleeville, and Lassen areas are based on the silica content of *water-free* glasses, whereas George's diagram is based on the silica content of natural glasses, many of which may be rich in water. The last mentioned diagram is not, therefore, strictly comparable with the other three.

it had been established by at least 8 chemical analyses that composition of the rocks could be expressed, with but a minor error, in terms of a single variable, such as silica content. Where more than one process of magmatic differentiation operated simultaneously and at independently varying rates in the development of these magmatic suites such a relationship might fail to develop. Had solfatarized, weathered, or otherwise metasomatized rocks been included in the suites, again no such relationship could be expected to hold, and the observations plotted on a silica-refractive index diagram would, almost certainly, have been widely scattered. Should the rocks have been metamorphosed without alteration of chemical composition, however, the close distribution of points along the silica-refractive index curves would have been unaffected.

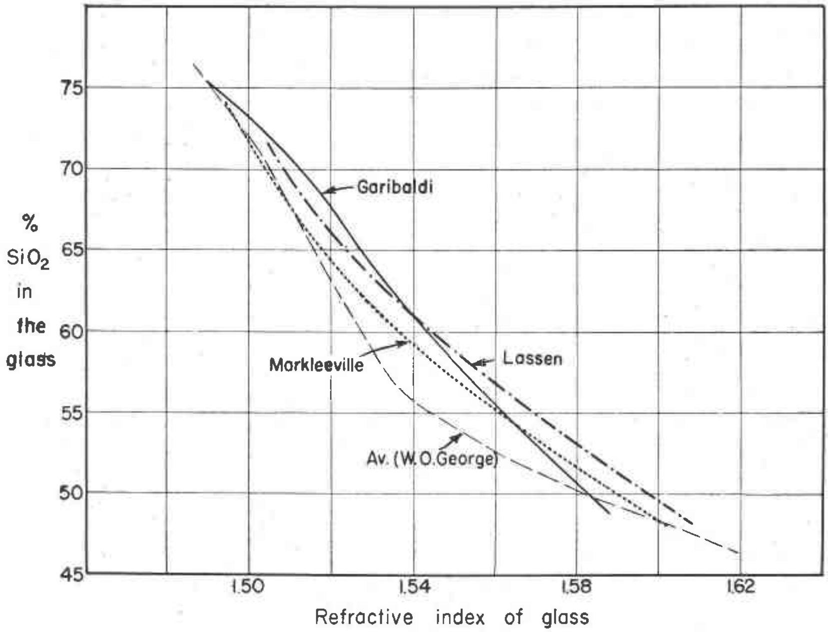

FIG. 2. Four composition-refractive index curves superimposed.

Any technique for the complete fusion of a representative sample of the rock without affecting its anhydrous composition is suitable for the application of the principles discussed above. The fusion temperatures of most igneous rocks are, however, so high that complete melting calls for special facilities; the ordinary Bunsen burner, Meeker burner, or blowpipe flame is inadequate. Reaction between sample and container might, moreover, render unsatisfactory the slow melting of the sample in a high-temperature oven. Tesch (1903) found it possible to fuse rock samples in bone ash cupels using a gas-oxygen flame, but he did not eliminate the dual problem of complete fusion of sample without reaction with the container. I found it possible to melt completely small quantities of the powdered rock in a crater cut in the lower electrode of a carbon arc lamp. During the early part of the arcing cycle the molten bead rests in the electrode like water on a hot stove, and the contact between melt and container is so slight and the carbon so inert that contamination of the glass by reaction can be neglected. The technique thus adopted overcomes the difficulties mentioned above and necessitates only such facilities as are commonly present in a well equipped petrographic laboratory. One drawback exists, however, with this method: the amount of material that can be treated in the arc, perhaps 10 milligrams at a time, though sufficient for the determination of refractive index by oil immersion technique, is so small that extreme care is necessary to obtain accurate sampling. Experience in quantitative spectrochemical analysis shows, however, that sampling with the desired degree of accuracy is possible after fine grinding of the original rock and thorough mixing.

For the first step in this technique 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 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, are 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 absorbed 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 (Johannsen, 1914, p. 249 et seq.) 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 sharp 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 time involved in grinding and fusing a sample, determining the index of the resulting glass, and cleaning mortar, pestle, electrodes, and slides preparatory to a new determination can be as little as 10 to 15 minutes in routine work. If the fusion and index determinations of the powdered sample are repeated to obtain greater accuracy a few more minutes are required for each rock. In the preparation of the standard composition-refractive index curves from analyzed samples greater care is necessary and the determinations should be made in triplicate; such determinations involve correspondingly greater periods of time. A large number of determinations can, nonetheless, be completed in an uninterrupted day's work and the information provided by these determinations seems well worthy of the time spent.

Applications of the results of this technique are at once apparent. The correlation of two igneous rocks having similar chemical composition but different cooling histories, and hence distinct textures and possibly distinct mineralogical compositions, can be facilitated without the time and expense of additional chemical analyses; conversely the recognition of dissimilarity of two rocks of different chemical composition but alike in physical appearance is aided. The volumetric or stratigraphic distribution of acid to basic igneous rocks within a volcanic succession can be determined without resort to a large number of chemical analyses, or to tedious and commonly uncertain microscopic determinations. In the selection, from some igneous suite, of rocks for chemical analysis the technique can be of material assistance for it permits the recognition of the most acid rocks, the most basic, and a representative group of intermediate types.

This technique is not offered as a substitute for, but rather as an adjunct to, the microscopic examination of fine grained igneous rocks. The refractive index of a glass yields a minimum of information on the petrogenesis of the rock from which it has been made, and information on petrogenesis as well as on composition is the objective of petrographic studies. The technique is not offered, moreover, as a suitable one for the study of the coarser grained igneous rocks. For these the time and effort of grinding a representative chip sample minimizes the advantages of the method, and other techniques are better adapted for the solution of the problems. Specific gravity of non-vesicular samples, for example, can be obtained with greater ease than refractive index of a fusion and can be used in precisely the same way for the determination of approximate composition of holocrystalline rocks. In such rocks, moreover, mineralogical composition is a fairly reliable guide to chemical composition and the essential minerals of the rock can be recognized with ease and assurance with the naked eye or with low magnifications after the staining of a sawn section (Keith, 1939). For the coarse grained rocks, therefore, these other methods are simpler and more satisfactory, but for the finer grained and especially for the partly glassy rocks they form no substitute for the refractive index of glass from artificial fusions as a guide to composition.

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