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Density determination of microcrystals in magnetic fluids

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Abstract

A technique employing magnetic fluids has been developed for measuring the density of microcrystals. The method has been used to determine the density of samples as small as 0.004 mg, an order of magnitude smaller than measurable by conventional techniques. The measurable density range extends to at least 21.4 g/ml, which is well beyond the range of heavy-liquid techniques. The experimental arrangement uses a standard Frantz Isodynamic Magnetic Separator with no equipment modifications.

Introduction

With the advent of the electron microprobe and single-crystal X-ray techniques such as the Gandolfi camera, descriptive mineralogy of microcrystals has become possible. However, the very small size of these crystals has made the determination of certain physical properties elusive. One such property is density. This fundamental property of a mineral is a necessary complement to the composition and cell-parameter data. These data collectively determine the number of formula units (Z) per unit cell by the relationship:

$$Z = (V\rho A)/FW$$

where Z = number of formula units per unit cell
V = volume of unit cell
ρ = density
A = Avogadro's number
FW = formula weight

The terms density (ρ) and specific gravity (G) are often used interchangeably; however, these terms are not equivalent. The density of a mineral is the ratio of its mass to volume, generally measured in g/ml. The specific gravity of a mineral is the ratio of the mass of the substance to the mass of an equal volume of water at 4°C. Other standard liquids may be used in specific gravity determinations, but their densities must be known to correct to the mass of water. Specific gravity is a dimensionless term. The specific gravity of a mineral has the same value as its density if the density of the water in which the determination is made exactly equals 1.0 g/ml. In this paper, the word density will be used throughout, although some of the methods described below actually measure specific gravity.

There are five standard methods of density determination: displacement, pycnometry, hydrostatic weighing, comparison with heavy liquids, and gas volumenometry. A good review of these methods with extensive references to specific studies is given by Muller (1977) and Mason (1944). The displacement method described by Muller (1960) (seen in Muller, 1977) requires at least 2 mg of sample. The pycnometer method described by May and Marinenko (1966) uses 9–12 mg of sample. The Kraus-Jolly spring balance (Hutchison, 1974, p. 236–238) and the Berman torsion balance (Berman, 1939; Hutchison, 1974, p. 239–241) are commonly used in the hydrostatic weighing methods and have minimum sample requirements of 1 g and 10 mg, respectively.

Heavy-liquid methods are limited to densities that do not exceed those of the heavy liquids. The most dense liquid available is the extremely toxic Clerici solution (thallous malonate/formate) whose density is about 4.3 g/ml at room temperature. The more easily handled methylene iodide has a density of about 3.3 g/ml. The rate at which small crystals rise or fall in these liquids is very slow; but by combining a heavy-liquid arrangement with a centrifuge to speed the movement of the grains, Bernal and Crowfoot (1934) obtained results for samples on the order of 0.05 mg with densities between 1.0 and 1.5 g/ml. Hauptmann and Schulze (1934) described a microscale gas volumenometry method suitable for volumes of 0.01 ml.

While the accuracy of the different methods varies,

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the displacement, pycnometry, and hydrostatic weighing methods are limited to sample sizes of at least 2 mg. The volumenometry method can be extended down to volumes of 0.01 ml. The heavy-liquid method when combined with a centrifuge can measure the density of 0.05 mg samples within the density range of heavy liquids.

The magnetic-fluid method described herein has been used to measure the density of single crystals at least as small as 0.004 mg. The principal advantages of this method are that (1) it measures the density of very small samples, at least an order of magnitude smaller than reported for other methods, (2) it extends the measureable range of densities beyond heavy liquids to at least 21.4 g/ml, and (3) it is easily performed with a Frantz Isodynamic Magnetic Separator or other suitable electromagnet.

Magnetic fluids

The following description of magnetic fluids is based on the reports of Moskowitz (1975) and Khalafalla and Reimers (1973a, b). Magnetic fluids were developed in the early 1960's at the National Aeronautics and Space Administration as a means of controlling fuel flow under weightless conditions. Magnetic fluids are ultrastable colloidal suspensions of 100A magnetite particles in a carrier fluid such as water, hydrocarbon (mineral oil or kerosene), or fluorocarbon. The magnetite particles are covered by a monomolecular elastic coating that prevents particle flocculation. Brownian motion within the carrier liquid keeps the particles suspended. When a magnetic field is applied, the particles instantly orient themselves, and the fluid acquires a magnetic moment. When the field is removed, magnetic fluids instantly demagnetize with no hysteresis effects. Moskowitz pointed out the uniqueness of magnetic fluids in that they simultaneously act as a magnetic solid and a liquid.

Commercial applications of magnetic fluids have been made in the fields of magnetogravimetric separation of incinerated refuse (Khalafalla and Reimers, 1973a), zero-leakage seals, printing, and silencing of solenoids (Moskowitz, 1975).

The magnetic fluid used in this study was purchased from Ferrofluidics Corp. (144 Middlesex Turnpike, Burlington, Massachusetts). When obtained in February 1979, the material was available in 100 ml volumes (enough for 10,000 density determinations) at $150. The density of the fluid (nonmagnetized) is 1.05 g/ml, its magnetic saturation is 200 Gauss, and its carrier solvent is refined white mineral oil (catalogue #H01).

Density determination in magnetic fluids

The density determination technique using magnetic fluids takes advantage of the fact that the fluid acquires an increased apparent density when it is placed in an inhomogeneous magnetic field. The apparent density of the magnetic fluid varies directly with the value of the magnetic field gradient across the fluid (Khalafalla and Reimers, 1973a, b). For density determinations, the magnetic field gradient is oriented so that the levitation force is vertical and acts as an antigravity force.

There are two ways to vary the value of the magnetic field gradient across a vessel containing a magnetic fluid: (1) the vessel may be moved to intersect different magnetic field gradients within the field of a magnet of fixed pole strengths, or (2) the pole strengths of an electromagnet may be varied to change the magnetic field gradient across the vessel at a fixed position. By using an electromagnet instead of a permanent magnet, options 1 and 2 above can be applied to measure the widest range of density values of crystals contained in the vessel.

Figure 1 sketches the relationship between the poles of an electromagnet and a vessel containing the

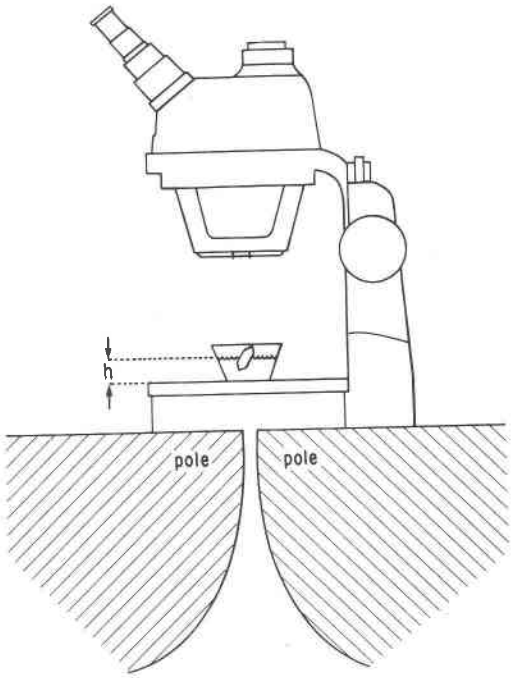

Fig. 1. Sketch of vertical cross-section perpendicular to the chute of the Frantz Isodynamic Magnetic Separator pictured in Fig. 2.

magnetic fluid and a test crystal. The apparent density of the magnetic fluid is varied by changing the height of the fluid surface above the electromagnet or by changing the pole strengths of the electromagnet.

Experimental procedure

An experimental configuration for density determination of microcrystals is easily obtained with no equipment modifications by using a standard Frantz Isodynamic Magnetic Separator (Model L-1, S. G. Frantz Co., Inc., 339 East Darrah Lane, Trenton, New Jersey) (Figs. 1 and 2). Any electromagnet of suitable strength can be used, but the Frantz Isodynamic Magnetic Separator is used in this description because it is available in most geologic laboratories.

The Frantz is set with 90° side tilt and 0° forward tilt. In this configuration, the top of the separator makes a convenient platform on which a microscope can be placed. We used an aluminum microscope. It is important to use the same microscope throughout the study, as the metal in the microscope may cause variations in the magnetic field, and these variations should be constant for all samples. A diameter of the field of view of the microscope should coincide with the chute of the magnetic separator. This configuration centers the sample in the magnetic field and allows a small sample container to intercept a magnetic field gradient strong enough to measure a wide range of densities.

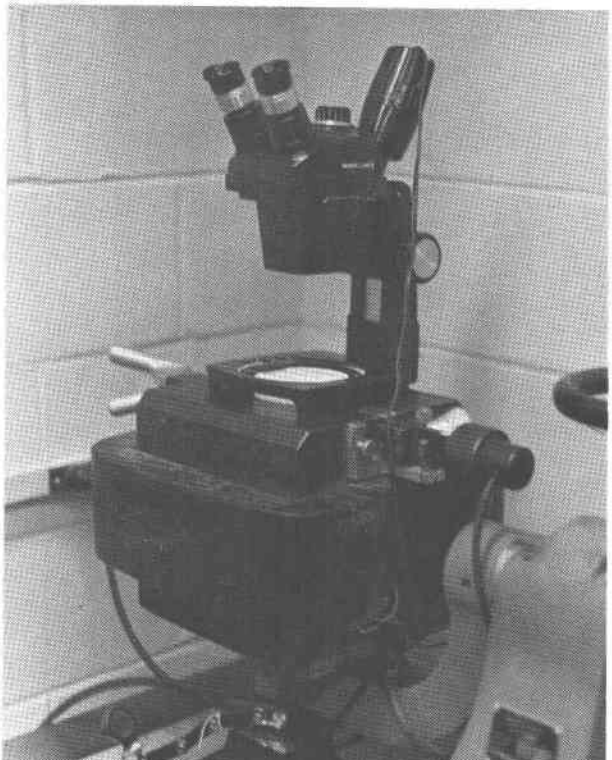

Fig. 2. Experimental configuration of microscope and Frantz Isodynamic Magnetic Separator used in magnetic-fluid method of density determination. Forward tilt of separator = 0°, side tilt = 90°.

The unique feature of the electromagnet in the Frantz is the isodynamic magnetic field in the air gap between the poles where the mineral separation chute is located. However, this method utilizes the inhomogeneous magnetic field region above the air gap.

In our study, the sample container is a plastic biological culture tray (#3034 tissue culture plate, Falcon, 1950 Williams Drive, Oxnard, California) which contains 60 individual wells. Each well has the shape of a truncated cone with the following approximate dimensions: 4 mm top diameter, 2 mm bottom diameter, and 1.5 mm depth. The wells each hold 0.01 ml of magnetic fluid. A single grain or several grains of the test mineral are introduced into an individual well. The vessel is then filled with magnetic fluid (0.01 ml) and centered under the field of view of the microscope. No more than one sample should be in the field at a time, because the presence of another magnetic substance (the fluid) near the vessel being examined will cause aberrations in the field gradient. The height of the sample vessel above the platform provided by the magnetic separator will depend on the density range of the sample and standards to be examined, but it must be constant for all specimens examined for a single determination. If all specimens are at a constant height above the magnet and centered in the microscope's field of view, a reproducible magnetic field gradient is insured. All samples should be approximately the same size.

The current through the magnetic coil is then increased to its maximum (1.7 amps). The crystal should float to the surface as it is displaced by the magnetic fluid. If it does not float, the sample vessel must be lowered to intersect a higher field gradient. In the present study, a height of approximately 1.5 cm above the magnet was found sufficient to measure a density range of about 2–5 g/ml. Densities greater than 21.4 g/ml were obtained at a height of 6 mm. The current is then decreased slowly until the crystal just sinks below the liquid surface. This value of the current is recorded, and the next sample is prepared and examined.

By successively examining a series of standards, a regression line is obtained from a plot of current *vs.* density. This allows the prediction of a density value for the unknown based on the current value when it just sinks. The entire procedure takes about 10–15 minutes.

Results

Five minerals were chosen *ad hoc* as standards: halite ($\rho = 2.16$), quartz ($\rho = 2.65$), spodumene ($\rho = 3.18$), topaz ($\rho = 3.50$), and barite ($\rho = 4.50$). To cover this range of density values, the sample vessel was placed 1.5 cm above the magnet platform. The minerals were sized between 100 (0.15 mm) and 140 (0.11 mm) mesh. Assuming a cube 0.13 mm on a side, individual grains were thus 0.002 mm^3 in volume and with masses between 0.004 and 0.009 mg. This is not the minimum detection limit, however. The practical limit of the method is the resolution of the microscope used to examine the vessel to determine when the crystals sink.

Two unknowns, both later determined to be calcite ($\rho = 2.71$), were chosen and sized similar to the standards. Two calibration runs and determinations of unknowns were made by each of the authors for a total of four individual standardization runs and eight unknown (calcite) determinations. The Pearson's r statistic for the four individual standard runs varied from 0.969 to 0.999. However, much of the random error within the four runs is eliminated by examining the average current value over the four runs for each standard and unknown. These data are presented in Figure 3. The Pearson's r statistic for the averaged current *vs.* density pairs is 0.998. The density values obtained for the two calcite unknowns were 2.83 and 2.77 g/ml. Using the interval estimation technique of Cox (1971) for estimating sample variance, a standard deviation of 0.07 g/ml is obtained for the values [note that formula 3.3 of Cox (1971) is misprinted, as the second term in the expanded equation should be divided by N]. The slope of the best-fit line was 0.230 (amps)/(g/ml). A first-order line is suitable for describing the current *vs.* density data, as the experiment was performed in essentially linear regions of the saturation curves of the electromagnet (McAndrew, 1957) and the magnetic fluid.

Additional experiments were conducted to test the range of densities which can be determined by the magnetic fluid method. By lowering the sample container to 6 mm above the magnet surface a much higher magnetic field gradient is intercepted. Using this experimental arrangement, an impure sample of native gold (ρ = 15.3–19.0 g/ml, exact value unknown) was lifted by the fluid at a current value of 0.62 amps, and a pure specimen of platinum (ρ = 21.45 g/ml) was lifted at 1.13 amps. Thus, densities which can be determined by this method extend beyond the range required by the mineralogist and well beyond the range possible with conventional heavy liquids.

A cautionary rider on the use of magnetic fluids with Fe-bearing minerals must be added. The presence of iron in a mineral will cause aberrations in the magnetic field and subsequent erroneous density determinations. Khalafalla and Reimers (1973a) noted this in their magnetogravimetric magnetic-fluid separation technique of non-ferrous incinerated refuse. In theory, an amperage correction term could be devised which would be proportional to Fe concentration, but this has not yet been attempted.

Summary

Density is the fundamental property of a mineral which relates its chemical composition to the volume of its unit cell. Conventional methods of microcrystal density determination are limited to samples at least as large as 0.05 mg, and are further constrained within the limited range of toxic heavy liquids. The magnetic-fluid method described herein extends the minimum mass requirement by at least an order of magnitude and can be used over the density range of geologic materials.

Numerous other applications of the method are possible. For example, the method provides a rapid determinative test for the fineness of electrum. In electrum, the density is a function of the gold/silver

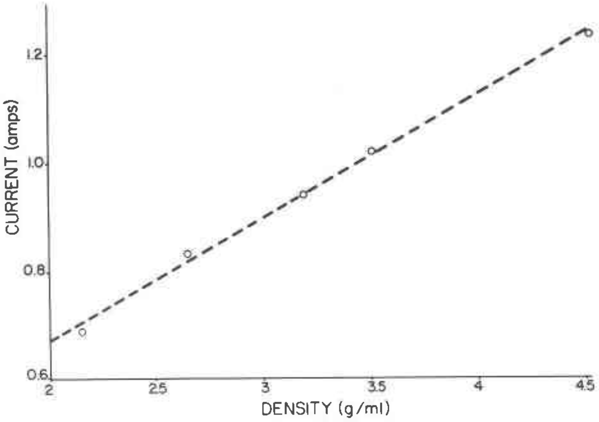

Fig. 3. Plot of average current from four runs *vs.* density for five standards. Standards in order of increasing density are halite, quartz, spodumene, topaz, and barite.

ratio. The high density and small sample size of this gold/silver alloy previously precluded fineness determinations by specific gravity, but these measurements can now be made in magnetic fluids. Another application, which we have used, is the determination of the homogeneity of a group of microcrystals. Finally, on a larger scale, the method could be employed to replace currently used heavy-liquid techniques of mineral separation. Khalafalla and Reimers' (1973a) proposed method for separation of incinerated refuse by density fractionation could be easily applied to mineral separations.

With the refinement of the techniques presented here and the advancement of new ones, magnetic fluids can provide a new analytical tool with numerous applications for the mineralogist.

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