residuals with other geophysical data, such as heat flow, geopotential variations, and surface topography, may indicate the presence or absence of some relation between these quantities, and may point to some common explanation of lateral heterogeneities. The spherical harmonic coefficients for the geopotential variations (*2*), heat-flow values (*1*), and "equivalent rock" topography of Earth's surface (*5*) are listed in Table 2.

Correlation coefficients between two sets of data are computed by use of the spherical harmonic coefficients and the equation

$$\rho = \sum_{n=0}^{3}\sum_{m=0}^{n}(C_{nm}\cdot C'_{nm} + S_{nm}\cdot S'_{nm}) \Big/ \left\{\left[\sum_{n=0}^{3}\sum_{m=0}^{n}(C^2_{nm} + S^2_{nm})\right]^{1/2} \cdot \left[\sum_{n=0}^{3}\sum_{m=0}^{n}(C'^2_{nm} + S'^2_{nm})\right]^{1/2}\right\}$$

This analytic representation of correlation is used rather than individual points, because the data sets do not always have common locations on Earth's surface.

None of the computed correlation coefficients (Table 3, as a matrix) is very high. First of all, the very small correlation coefficients between surface topography and seismic travel-time residuals or the geopotential variations indicate that, at least on a broad scale, the surface topography does not control the lateral variations of seismic and geoid data; the causes must be sought somewhere deep in the crust or in the mantle. Correlation between heat flow and topography is relatively good; higher surface areas seem to be characterized by higher heat flow; tectonic regions of continents and oceanic ridges seem to contribute to such a correlation. Heat flow and seismic waves seem to have a positive correlation coefficient indicating that areas of high heat flow are characterized by slower seismic arrivals. The apparently poor correlation between heat flow and geopotential variations contradicts Wang's results (*5*) from earlier data.

The best correlation among the data sets that we have considered is between seismic travel-time residuals and the gravitational potential (ρ, −0.58). The negative correlation signifies that, where there is a deficiency of mass, seismic travel times are longer or seismic velocities are lower—not an unexpected result; a linear relation between seismic velocities and densities exists for rocks and minerals of similar composition (*6*). Lack of larger correlation coefficients may reflect lateral variations in composition of the upper mantle; partly, insufficient and poorly distributed seismic data.

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21 August 1967

Stable Magnetic Remanence in Antiferromagnetic Goethite

Abstract. *Goethite, known to be antiferromagnetic, acquires thermoremanent magnetization at its Neel temperature of 120°C. This remanence, extremely stable, is due to the presence of unbalanced spins in the antiferromagnetic structure; the spins may result from grain size, imperfections, or impurities.*

In studying the magnetic properties of minerals one may usefully consider both antiferromagnetic and ferrimagnetic materials. Among the better-known magnetic minerals are magnetite and maghemite—both ferrimagnetic. On the other hand, minerals such as hematite are dominantly antiferromagnetic; its magnetic properties have always been difficult to understand. In large grain sizes it carries a strong spontaneous magnetization which is anisotropic; in small grains, about 1 μ or less, it has only a small spontaneous magnetization but does carry a weak isotropic remanence. This weak remanence probably results (*2*) from unbalanced spins due to grain-size effects,

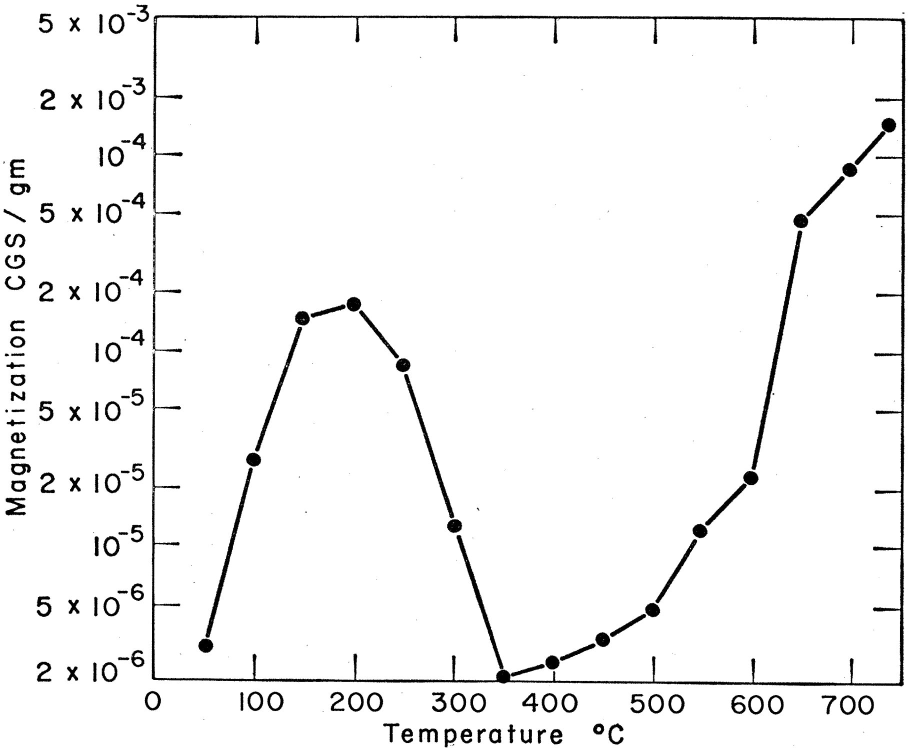

Fig. 1. Thermoremanent magnetism acquired during cooling, from temperatures shown, in Earth's magnetic field (sample No. 4A).

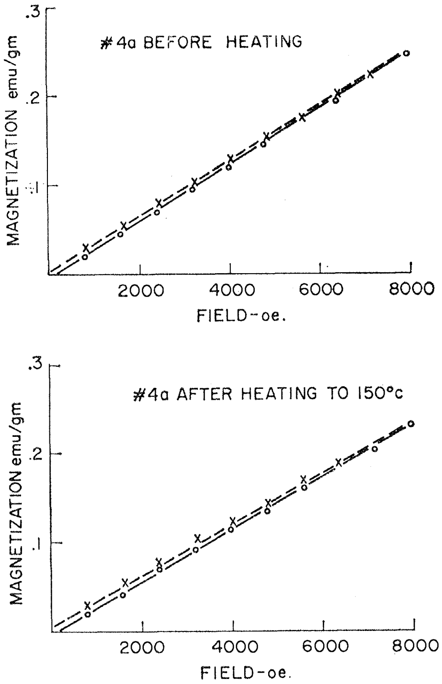

Fig. 2. Hysteresis loops before and after heating to 150°C (sample No. 4A).

imperfections, or impurities (*3*). Smith and Fuller (*4*), after studying hematite, point out that it has a stable magnetic remanence resulting from spin unbalance, a fact made evident by experimental studies at both high and low temperatures. Stable remanence is acquired at 725°C, the Neel temperature of hematite, and it is not lost on cooling below −20°C, the Morin transition. A less-stable ferromagnetism is acquired on cooling to 675°C, the Curie temperature, but is lost at −20°C.

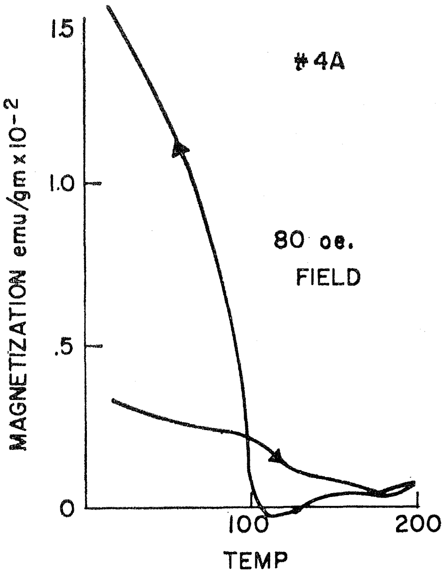

Fig. 3. Thermoremanent magnetism acquired during cooling to room temperature in the field shown.

Thus hematite has two magnetic properties: The first is a low-stability ferromagnetism that occurs only in grains larger than 0.5 μ (*2*) and only between −20° and 675°C (*4*). The second is a high-stability remanence that occurs in grains as small as 20 Å (*5*), is acquired at 725°C, and is not lost at −20°C; it is believed to result from unbalanced spins in a typical antiferromagnetic structure.

We now report the existence of spin unbalance remanence in another common mineral. Goethite is known to be antiferromagnetic (*6*), but extensive studies of it at low temperature have not revealed its remanence properties (*7*). We have examined various properties of naturally occurring goethites in an attempt to understand the processes involved. Creer (*7*) showed that, in particles about 20 Å in size, goethite becomes superparamagnetic; that is, thermal agitation disrupts the magnetic ordering in these very small grains.

Our experiments were concerned with the acquisition of thermoremanent magnetism (TRM) in weak fields. We heated various samples and cooled them in Earth's magnetic field. In all instances but one, weak magnetization was acquired at 120°C (Fig. 1). This temperature is so close to the temperature of 97°C reported for the Neel temperature of goethite that one is tempted to relate the TRM to the antiferromagnetic properties of goethite and to assume that the Neel temperature is in fact 120°C. When hysteresis loops were run on this material before and after heating to various temperatures (Fig. 2), in the fields of 8000 oersteds available there was no indication of spontaneous magnetization of the bulk material, since essentially no hysteresis and no saturation effects appeared. The TRM may be due to the presence of some common impurity, or to a weak ferromagnetization of the kind discussed in hematite, or to the presence of unbalanced spins in the antiferromagnetic structure; or it may be related to a spin canting effect.

It seems unlikely to be due to impurities, since heating to 350°C invariably eliminates ability of the sample to acquire this TRM (Fig. 1); the fact that this is the temperature at which goethite dehydrates to form hematite (*8*) almost certainly means that the TRM is a property of the goethite. Figure 1 shows that the TRM decreases after heating above 200°C, as the goethite starts to break down to hematite; it is unlikely to be a fundamental ferromagnetism of the type found in hematite, and it is probably the result of unbalanced spins in the goethite. We have also experimented with this TRM in higher fields. Figure 3 shows the TRM acquired when one allowed the sample to cool from 200°C in an 80-oersted field: the magnetization is about 0.014 emu/g for the particular sample (Table 1). A small decrease in the magnetization observed in a few instances just before the TRM was acquired is probably related to the antiferromagnetic properties.

Table 1. Peak TRM values acquired by samples of geothite heated above 150°C before cooling in Earth's magnetic field.

Sample		TRM (10^{-6} emu/g)
No.	Source	
1	Marquette, Mich.	5.3
6(3114)	Houghton, Mich.	Present only in larger fields
3126	Harz Mountains, Ger.	5.8
3129	Michigan	14
3124	Lake Superior area	45
4A	Unknown	260
2	Santa Eulalia, Mex.	94
3113	Iron Mountain, Mich.	6700
4238	Pikes Peak, Colo.	210

We have also tested the stability of this TRM by a-c demagnetization. In fields of 1000 oersteds our inability to alter the TRM even slightly indicated that it is extremely stable.

Goethite is a common mineral in many environments; we have here a very simple way of detecting its presence in various samples. Moreover, goethite can acquire a highly stable TRM simply by heating to 120°C. Goethite that has never been heated may possibly carry remanent magnetization, probably as chemical remanent magnetism.

Smith and Fuller (*4*) point out that antiferromagnetic materials other than hematite should carry stable remanence; goethite is one such substance that may be of considerable importance in natural systems.

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Membranes of Valonia ventricosa: Apparent Absence of Water-Filled Pores

Abstract. *Osmotic and diffusional permeabilities to water have been measured in internally perfused cells of* Valonia ventricosa. *The osmotic and diffusional permeability coefficients for the protoplast are identical, 2.4 × 10⁻⁴ centimeter per second. Thus, both osmotic and diffusional flows can occur by the same mechanism, that is, by diffusion; and there is no need to postulate the existence of water-filled pores in the membranes of this cell. Supporting evidence for this conclusion is the absence of solvent-solute interactions, that is, "solvent drag," for water, urea, and methanol crossing the protoplast of* Valonia.

A popular hypothesis concerning the structure of cell membranes holds that pores or channels through the membrane facilitate the penetration of water and small hydrophilic solutes. Two main lines of evidence for the presence of these water-filled pores in a membrane are (i) a discrepancy between the osmotic and diffusional permeabilities to water and (ii) frictional interaction between water and solutes, that is, "solvent drag." The evidence for and against the existence of water-filled pores in biological membranes is reviewed by Dainty and House (*1, 2*) and Dick (*3*).

My report deals mainly with the first criterion for the presence of water-filled pores—a comparison of osmotic and diffusional permeabilities to water. If osmotic flow of water across a membrane occurs by diffusion, then it can be easily shown (*4*) that $L_pRT/\overline{V}_w = P_d$, where P_d (centimeters per second) is the diffusional permeability coefficient obtained from a self-diffusion tracer experiment, L_p (centimeters per second per atmosphere) is the hydraulic conductivity, R is the gas constant, T is the absolute temperature, and $\overline{V}_w$ (cubic centimeters per mole) is the partial molar volume of water. The expression $L_pRT/\overline{V}_w$ is often called the osmotic permeability coefficient, P_{os}, for water. If $L_pRT/\overline{V}_w$ is greater than P_d, a bulk flow of water through continuous channels in the membrane is indicated, and the equivalent radius of these channels can be estimated from the size of the discrepancy (*3*, pp. 83–126).

Both P_{os} and P_d have been measured in many biological membranes, and P_{os} is always greater than P_d, which suggests the presence of water-filled pores. A similar discrepancy appears in artificial phospholipid membranes (*5*). Dainty and House (*1, 2*) have questioned the reported values for P_d, however, pointing out that P_d was usually underestimated because the effects of the unstirred layers of solution adjacent to the membrane were not taken into account. Thus, in most cells and tissues, the presence of aqueous pores, based on this criterion, is still in doubt.

The marine alga *Valonia* (*8*), in contrast to erythrocytes (*6*) and the freshwater algae *Nitella* and *Chara* (*7*), is relatively resistant to water flow under an osmotic-pressure gradient. The high resistance to osmotic flow suggested to me that *Valonia* might be particularly suitable for a study of water permeability, because the effects of the unstirred layers on the apparent permeability should be relatively small. Another advantage of these giant cells is that they can be perfused internally, which facilitates permeability measurements with rapidly penetrating substances. A third advantage is that the important correction for the diffusional resistance of the cell wall and unstirred layers can be made on each cell after the protoplast has formed aplanospores (*9*).

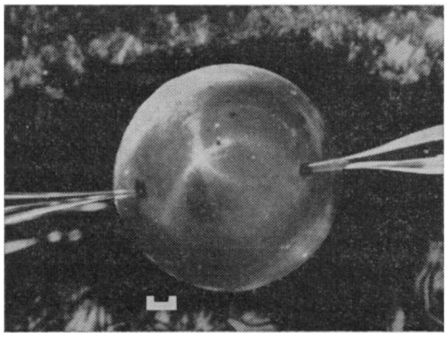

Fig. 1. A single cell of the marine alga *Valonia ventricosa* perfused internally by means of two micropipets inserted into the vacuole. Scale is 1 mm.

Cells of *Valonia ventricosa* about 1 cm in diameter were shipped by air from Jamaica and maintained in laboratory cultures as described previously (*10*). The method of perfusing the vacuole of *Valonia* is also described elsewhere (*8*). Briefly, a spherical cell is held with waterproof putty in a dish of seawater (*11*) on the stage of a dissecting microscope. Two micropipets are inserted through the cell wall and underlying protoplasm into the vacuole (Fig. 1). After a 1- to 2-hour recovery period the vacuole is perfused with artificial sap (*11*) at a rate of 100 to 300 μl/min. The outer solution is stirred gently with a Pasteur pipet. Rapid stirring is impossible because of the fragility of the cytoplasmic seal around the micropipets.

The potential difference between vacuole and seawater is monitored continuously and provides a sensitive indicator of the condition of the cell. Serious leaks which occasionally develop cause an immediate drop in the potential difference to near zero. The vacuole potential of these cells was +16±1 mv (13 cells) (*12*), which is the normal value for *V. ventricosa* bathed in seawater (*10*).

I measured the diffusional permeability to water by adding water labeled with tritium (THO) to the inflow reservoir and allowing about 40 minutes for the THO efflux to attain a steady value. Then 30 ml of seawater was placed outside the cell, and five 0.5-ml samples of this solution were removed at 2-minute intervals and counted by liquid scintillation. The total counts in the outside solution were plotted against time, and the gradient of this curve, $V_o{\cdot}dC_o^*/dt$, was determined. The permeability coefficient, P_d (centimeters per second), is equal to $V_o{\cdot}dC_o^*/dt{\cdot}A{\cdot}C_i^*$, where C_i^* and C_o^* are the THO concentrations inside and outside (counts per minute per cubic centimeter), A is the surface area of the spherical cell (square centimeters), V_0 is the volume