

# Measurement of the Solid Dielectric Permittivity of Clay Minerals and Granular Samples Using a Time Domain Reflectometry Immersion Method

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## ABSTRACT

Both porosity and water content of rocks, sediments, and soils can be estimated from measurements of the effective dielectric permittivity. To achieve accurate modeling to obtain either water content or porosity the permittivity of the solid phase must be known. Until recently the most common method of obtaining the permittivity of the solid phase of granular materials relied on packing samples in air and using a mixing model to estimate the permittivity of the solid. This approach preassumes the correctness of the mixing models that we want to test. This work develops a recently proposed immersion methodology suitable for fine-grained mineral samples and clay minerals. Measured permittivity values were 4.4 for ground quartz, 9.1 for Iceland Spar calcite, 6.0 for biotite mica, 5.8 for phlogopite mica, 5.3 for talc, 5.1 for kaolin, 5.8 for illite, and 5.5 for montmorillonite. The methodology was found to work well other than for the high surface montmorillonite sample where the immersion polar fluid adsorbed to the clay.

G EOPHYSICAL PROSPECTING has benefited greatly from developments in radio and microwave technology. Electromagnetic techniques are used to estimate the characteristics of rocks such as porosity (Sen et al., 1981) and water content (Sakaki et al., 1998). Both invasive methods, such as time domain reflectometry (Topp et al., 1980; Robinson et al., 2003) and cross borehole radar (Hubbard et al., 1997; Binley et al., 2001), and noninvasive methods, such as ground penetrating radar (Huisman et al., 2001; Davis and Annan, 2002), are used. Common to all these techniques is the fact that electromagnetic wave propagation velocity depends on the dielectric properties of the rock or sediment deposit through which it travels. It is often convenient to consider the analogy of the propagation velocity of an electromagnetic plane wave, which depends on the materials electromagnetic properties through which it travels:

$$v_p = \frac{1}{\sqrt{\mu_o \mu_r \epsilon_o \epsilon_r}} = \frac{c}{\sqrt{\mu_r \epsilon_r}} \quad [1]$$

where  $c$  is the velocity of light ( $3 \times 10^8 \text{ ms}^{-1}$ ),  $\epsilon_r$  is the relative permittivity,  $\mu_o$  is the magnetic permeability of vacuum ( $1.257 \times 10^{-6} \text{ H}$ ), and  $\mu_r$  is the relative magnetic permeability. The relative magnetic permeability is unity in most rocks, with the exception of some iron oxides such as magnetite (Sharma, 1997).

Rocks and sediments can be considered as a two- or three-phase dielectric mixture, depending on whether they are saturated or unsaturated, respectively. The

temperature-dependent permittivity of both air and water (air: 1.0005; water: 78.54 [standard temperature and pressure]) are well known and can be found in standard reference works (Weast, 1984), but the permittivity of the solid phase is difficult to measure directly. Dielectric measurements have been proposed in the engineering literature as a good method of estimating porosity of saturated soils (Arulanandan, 1991). However, to obtain reliable estimates of porosity using this approach a reasonable value of the permittivity of the particle dielectric permittivity is required to input into the model. For the last 25 yr values of mineral permittivity based on the work of Olhoeft (1979; 1981) have provided the main comprehensive reference data for geological materials. These values were estimates based on packing samples to different densities and applying an empirical two-phase mixing model (Lichteneker, 1926) extrapolated back to zero porosity. This method has been used by a number of authors to estimate the permittivity of a range of materials (Olhoeft, 1981; Nelson et al., 1989; Nelson and You, 1990; Nelson, 1992). This method preassumes the correctness of the model and is thus undesirable if dielectric mixing models are to be tested rigorously. Results from the mixing model approach should not be dismissed, as they have provided broad insight as to the dielectric properties of many minerals. Table 1 gives a list of some permittivity values reported in the literature for some minerals. These values often depend on the method used to obtain them, and most are estimated. It is clear from these data that when values for moist montmorillonite of 207 are presented, more definitive values would be useful. Clay minerals are of economic importance and are a common constituent of many sedimentary deposits.

A direct measurement method, independent of the use of a mixing model, is desirable. In recent work Robinson and Friedman (2003) presented an immersion measurement method using time domain reflectometry and granular samples immersed in different dielectric solutions. The immersion method dates back to the beginning of the last century (Schmidt, 1902). However, perhaps due to limited application the technique had faded into relative obscurity, with only a few workers utilizing the technique (Takubo et al., 1953; Andeen et al., 1970). The method was very effective for measuring the permittivity of granular samples. The values of granular quartz (4.7) were in close agreement with measurements presented in the literature for quartz crystals. Previous methods and the method presented by Andeen et al. (1970) were suited to coarse-grained rock or sediment samples ( $>500 \mu\text{m}$ ). However, they were not suitable for fine-grained materials such as clays. Clay miner-

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**Abbreviations:** TDR, time domain reflectometer.

**Table 1. Average permittivity values of minerals found in the literature.**

|                 | Jones and<br>Friedman (2000)<br>100 Hz | Olhoeft<br>(1979)<br>1 MHz | Ficai<br>(1959)<br>2.5 MHz | von Hippel<br>(1954)<br>30 MHz | Keller (1989)<br>Radio<br>frequencies | Clarke (1966)<br>Not given | This work<br>(immersion method) |
|-----------------|--|----------------------------|----------------------------|--------------------------------|---------------------------------------|----------------------------|---------------------------------|
| Quartz          |  | 4.5                        |                            | 4.27–4.34                      | 4.19–5.00                             |                            | 4.4 ( $\pm 0.3$ )               |
| Calcite         |  | 8.8                        |                            |                                | 7.8–8.5                               |                            | 9.1 ( $\pm 0.3$ )               |
| Biotite mica    |  | 6.3                        |                            |                                | 6.19–9.30                             |                            | 6.0 ( $\pm 0.5$ )               |
| Phlogopite mica | 6.35                                   |                            |                            |                                | 5.90–6.50                             |                            | 5.8 ( $\pm 0.6$ )               |
| Talc            |  | 5.8                        |                            |                                |                                       | 5.8                        | 5.3 ( $\pm 0.7$ )               |
| Kaolin          |  | 11.8                       | 5.24                       |                                |                                       |                            | 5.1 ( $\pm 0.7$ )               |
| Illite          |  | 10                         | 8.44                       |                                |                                       |                            | 5.8 ( $\pm 0.2$ )               |
| Montmorillonite |  | 207                        | 10.41                      |                                |                                       |                            | 5.5 (extrapolated estimate)     |

als present the practical challenge of preventing air entrapment in a mixture of the granular material and the background solution. Often only small amounts of pure material are available for analysis, and the high surface area and charge of some clay minerals can bind polar molecules. This may reduce the permittivity of the immersion fluid, leading to errors in determining the solid permittivity. In this work a methodology is tested and found to overcome most of these problems, effectively extending the immersion measurement methodology for fine-grained mineral samples ( $<500 \mu\text{m}$ ).

## THEORY

### Two-Phase, Single Solid Dielectric in Dielectric Solution

The general approach used in this work has a good theoretical basis, as outlined in previous work (Robinson and Friedman, 2003). For the purposes of this paper we will present the theoretical basis for the methodology, which clearly demonstrates why no models are required to obtain the results. Simply stated, the method relies on the fact that when the effective permittivity of a dielectric mixture of solid and fluid is measured, the only point at which the effective permittivity of the mixture is the same as the permittivity of the fluid is

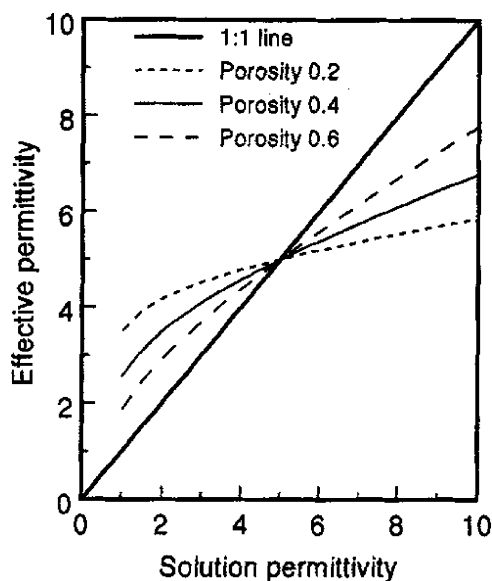
when the fluid and solid have the same value. If the permittivity of the solid is higher than the permittivity of the background fluid, then the permittivity of the mixture is greater than that of the fluid alone. If the permittivity of the solid is lower than the permittivity of the fluid, then the permittivity of the mixture is lower than that of the fluid alone.

The uniqueness of this measurement can be demonstrated using a two-phase dielectric mixing model. A suitable model for this purpose is the Maxwell Garnett (1904) model (Eq. [2]), based on the Lord Rayleigh (1892) formula.

$$\epsilon_{\text{eff}} = \epsilon_c + 3f\epsilon_c \left[ \frac{\epsilon_s - \epsilon_c}{\epsilon_s + 2\epsilon_c - f(\epsilon_s - \epsilon_c)} \right] \quad [2]$$

$\epsilon_{\text{eff}}$  is the permittivity of a two-phase dielectric mixture of spherical inclusions, of volume fraction  $f$  and permittivity  $\epsilon_s$  in a continuous dielectric background, or environment,  $\epsilon_c$  (Sihvola, 1999). More sophisticated models are available in the literature, such as the one presented in Sihvola and Kong (1988), and can be used to account for the effects of particle close packing and particle shape. However, that level of sophistication is not required in this demonstration, although it was used previously by Robinson and Friedman (2003). The model does not account for the effects of particle close packing, but this effect is minimal when the contrast ( $\epsilon_s/\epsilon_c$ ) between the two phases is small, as is the case here. The model assumes that the solid spherical inclusions “see” only the permittivity of the background. In practice in a densely packed granular mixture the background seen by the solid is some combination of solid and fluid and its respective permittivity. The Maxwell Garnett model provides an upper bound where the background has a higher permittivity than the inclusion and a lower bound when this is reversed.

Figure 1 shows the relationship between the effective permittivity,  $\epsilon_{\text{eff}}$ , and the fluid permittivity,  $\epsilon_c$ , for a granular sample with  $\epsilon_s = 5$ , packed to three different porosities. The 1:1 line is plotted on the diagram, and it can be seen that all the lines converge at the value of 5 when the solid and fluid have the same permittivity. Below this point the effective permittivity of the mixture is higher than the solution. Above this point the effective permittivity is lower than the permittivity of the immersion fluid. The main point demonstrated by the modeling is that the porosity of the mixture must be kept constant if measurements are to have a theoretical line fitted through to determine the permittivity of the solid.



**Fig. 1. Modeled effective permittivity (Eq. [2]) of a two-phase mixture plotted vs. the permittivity of the background solution. The unique crossing point occurs when the permittivity of the fluid matches the permittivity of the solid.**

## Two-Phase Mixing Models

The approach used in the past to estimate the permittivity of the solid relied on applying a mixing model to the data and extrapolating back to zero porosity. This approach is fraught with difficulty, as no single dependable two-phase dielectric mixing model has yet been demonstrated to fully capture the effective permittivity of two-phase dielectric mixtures. Olhoeft (1981) used the expression below (Eq. [3a]) (based on the Lichtenecker (1926) equation (Eq. [3b]), where  $\epsilon_e$  is assumed to be 1. This is a statistical mixing model that averages the logarithms of the permittivities, and it must be considered a power law approximation that lacks a rigorous physical base.

$$\epsilon_s = \epsilon_{\text{eff}}^{1-\phi} \quad [3a]$$

$$\ln \epsilon_{\text{eff}} = \phi \ln \epsilon_e + (1 - \phi) \ln \epsilon_s \quad [3b]$$

where  $\phi$  is the porosity and  $\epsilon_e$  is the permittivity of the background, 1 (as  $\epsilon_e$  is equal to 1 it is dropped in Eq. [4]–[6]). The so-called refractive index model (Birchak et al., 1974; Whalley, 1993) has been popular in soil science. It has a physical basis when derived for a series of dielectric layers (Schaap et al., 2003). However, for a granular material it must be considered an approximation:

$$\epsilon_s = \left[ \frac{\epsilon_{\text{eff}}^{1/2} + f - 1}{f} \right]^2 \quad [4]$$

Nelson et al. (1989) used the Looyenga (1965) mixing formula with reasonable results:

$$\epsilon_s = \left[ \frac{\epsilon_{\text{eff}}^{1/3} + f - 1}{f} \right]^3 \quad [5a]$$

$$\epsilon_{\text{eff}}^{1/3} = \phi \epsilon_e^{1/3} + f \epsilon_s^{1/3} \quad [5b]$$

The asymmetric effective medium approximation (Bruggeman, 1935) has also been a popular choice:

$$\epsilon_s = \frac{1 - f - \epsilon_{\text{eff}}^{2/3}}{1 - f - \epsilon_{\text{eff}}^{-1/3}} \quad [6]$$

## Two-Phase, Binary Solid Dielectrics in Dielectric Solution

The effective permittivity of a material with inclusions of different volume fractions and different permittivities is analogous to the composition of sediment with mixed mineralogy. For this problem, Sihvola (1999) presented a simple Maxwell Garnett-based model for spherical inclusions. He demonstrated that the effective permittivity of the solid was not simply the arithmetic average of the solid permittivities and their respective volume fractions:

$$\epsilon_{\text{eff}} = \epsilon_e + 3\epsilon_e \frac{\left[ f_1 \left( \frac{\epsilon_1 - \epsilon_e}{\epsilon_1 + 2\epsilon_e} \right) + f_2 \left( \frac{\epsilon_2 - \epsilon_e}{\epsilon_2 + 2\epsilon_e} \right) \right]}{1 - \left[ f_1 \left( \frac{\epsilon_1 - \epsilon_e}{\epsilon_1 + 2\epsilon_e} \right) + f_2 \left( \frac{\epsilon_2 - \epsilon_e}{\epsilon_2 + 2\epsilon_e} \right) \right]} \quad [7]$$

where,  $\epsilon_e$  is the permittivity of the background,  $f_1$  is the fraction of solid with permittivity  $\epsilon_1$ , and  $f_2$  is the volume fraction of solid with a permittivity  $\epsilon_2$ . Robinson and Friedman (2002) presented work on the dielectric properties of mixtures of glass beads and quartz sand. They demonstrated that in the case of low contrasts ( $\epsilon_2/\epsilon_1 < 4$ ) between the inclusion permittivity values, as is the case with soil minerals, negligible error is expected when assuming the arithmetic average of the permittivity,  $\bar{\epsilon}_s$  of the minerals and their volume fractions:

$$\bar{\epsilon}_s = \epsilon_1 f_1 + \epsilon_2 f_2 \dots \quad [8]$$

This is an approximation for contrasts between minerals ( $\epsilon_2/\epsilon_1 < 4$ ).

## MATERIALS AND METHODS

### Minerals and Reference Materials

The minerals and reference clay minerals used in this study are shown in Table 2. Table 2 also shows the particle size used for each of the minerals and composition and crystallographic structure. Particle densities (Table 3) were determined using the excluded volume method described in Flint and Flint (2002). The minerals were obtained from a number of different sources, calcite, (USDA-ARS George E. Brown, Jr. Salinity Lab., Riverside CA), quartz (USDA-ARS George E. Brown, Jr. Salinity Lab.), phlogopite mica (Suzorite mica products, Boucherville, QC, Canada), biotite mica (Eimer and Amend, New York), and talc (Aldrich Chemical Co. Inc., Milwaukee, WI). The clay minerals, kaolin, bentonite, and Silver Hill illite came from The Soil Clay Minerals Repository, University of Missouri, Columbia. The minerals represent a spectrum of common minerals and clays. Ground quartz provides a reference and would be expected to have a permittivity value close to the value measured for single crystals, of 4.6 (Fontanella et al., 1974). Talc was chosen as a mineral with a layer silicate structure but no surface charge and low surface area to give confidence that no immersion dielectric was rotationally hindered by the surface. The more polar the immersion fluid becomes, the more likely it will bind with a charged layer silicate surface and possibly bias results.

### Dielectric Immersion Fluids

In applying this type of method one difficulty is finding fluids whose permittivities lie in a range between 1 and 15 to provide the dielectric background and do not show dispersion due to dielectric relaxation within the time domain reflectometry frequency bandwidth (0.001–1.75 GHz). In previous work Robinson and Friedman (2003) used air ( $\epsilon = 1$ ), penetrating oil (WD-40;  $\epsilon = 2.3$ ), dichloromethane ( $\epsilon = 9.1$ ), and acetone ( $\epsilon = 20.8$ ). They also found that the alcohols were unsuitable because of dielectric relaxation in the frequency bandwidth of interest. In this work mixtures of fluids were used to obtain the low permittivity background dielectric solutions. The main liquids used were air ( $\epsilon = 1$ ), corn oil ( $\epsilon = 2.4$ ), dichloromethane ( $\epsilon = 9.1$ ), and acetone ( $\epsilon = 20.8$ ), all at 25°C. The acetone and corn oil were miscible, so that any dielectric background solution could be made with a permittivity between 2.4 and 20.8.

### Measurement of the Effective Permittivity Using Time Domain Reflectometry

Time domain reflectometry is a broadband (0.001–1.75 GHz) electrical technique used extensively in soil science to estimate the water content of soils (Robinson et al., 2003). Originally developed for metallic cable testing to find faults on cables, it has been widely used to measure the dielectric properties of porous media (Hoekstra and Delaney, 1974; Topp et al., 1980; Topp and Ferre, 2002). Time domain reflectometry measures the propagation velocity of a step voltage pulse; the velocity of this signal is primarily a function of the permittivity of the material through which it travels (Eq. [1]). The velocity of the signal in a perfect dielectric is therefore

**Table 2. Mineralogy and particle size of mineral samples.**

| Mineral         | Composition  | Structure         | Denomination and particle size      |
|-----------------|--|-------------------|-------------------------------------|
| Ground quartz   | SiO <sub>2</sub>   | tectosilicate     | <50 μm                              |
| Calcite         | CaCO <sub>3</sub>  |                   | <500 μm                             |
| Biotite mica    | K-aluminum silicate  | 2:1 trioctahedral | <500 μm                             |
| Phlogopite mica |  | 2:1 trioctahedral | <250 μm                             |
| Talc            | hydrous magnesium silicate                                       | 2:1 trioctahedral | 2–20 μm                             |
| Kaolin          | Si <sub>2</sub> Al <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub> | 1:1 dioctahedral  | KGa-1, Washington County, GA, <2 μm |
| Illite          | aluminum silicate  | 2:1 dioctahedral  | Silver Hill, Cambrian Shale, <2 μm  |
| Bentonite       | Na-aluminum silicate   | 2:1 dioctahedral  | Greyball, Wyoming, <2 μm            |

$$v = \frac{2l}{t} \quad \text{and} \quad v = \frac{c}{\sqrt{\epsilon_r}} \quad [9]$$

where  $l$  is the length (m) and  $t$  is the time (s) for a round trip (back and forth). Equating these and rearranging gives the round trip propagation time ( $t$ ) of the wave as a function of both the length of transmission line ( $l$ ) and the permittivity of the material ( $\epsilon_r$ ):

$$t = \frac{2l\sqrt{\epsilon_r}}{c} \quad [10]$$

Hence it follows that the permittivity can be determined by measuring the time it takes the wave to traverse the time domain reflectometry probe embedded in a sample.

In this work a Tektronix (1502B, Tektronix, Beaverton, OR) time domain reflectometer (TDR) was used throughout the experiments to measure the effective permittivity. The TDR was connected to a PC, which was used to collect waveforms using software developed by Heimovaara and de Water (1993). For each pure fluid and each mixture, the average permittivity was calculated from the average of five waveforms.

### Time Domain Reflectometry Probe Construction

The TDR was connected via a 0.75-m, (50-Ω RG 58) coaxial cable to a custom coaxial TDR probe (Fig. 2). It had an internal stainless-steel electrode (Fig. 2A) 0.003175 m in diameter and 0.16 m in total length, with 0.152 m projecting above the chemical-resistant Delrin probe head at the base (A), outer brass tube, 0.156 m long with an internal diameter of 0.0085 m. This had a brass collar soldered onto it at one end, so that a screw fitting (Fig. 2C) could tighten the coaxial cell onto the microwave electrical connector (Fig. 2E). This central electrode had a male end that fitted into the female microwave connector. The microwave electrical connector was high quality and rated to pass frequencies of up to 11 GHz. The coaxial TDR probe was designed with screw-and-push fit so it could be taken apart for cleaning. Such a small probe was developed to minimize the amount of clay mineral required for the measure-

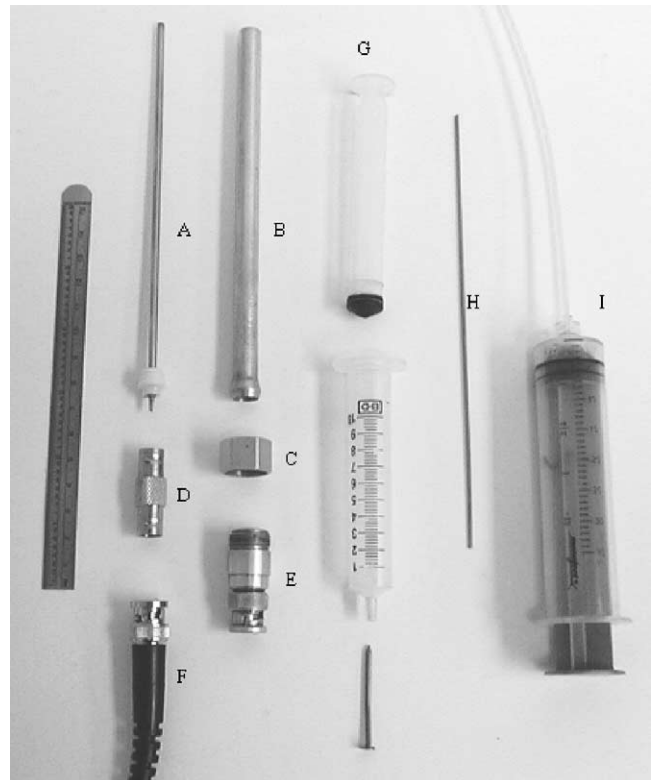
**Table 3. Values of physical mineral properties and textbook values of particle density from Weast (1984).**

| Mineral         | Bound water 50% humidity<br>g water 100 g <sup>-1</sup> soil | Particle density |                        |
|-----------------|--|------------------|------------------------|
|                 |  | Measured         | Literature value range |
| Ground quartz   | 0.02   | 2.60             | 2.65                   |
| Calcite         | 0.00   | 2.71             | 2.72–2.94              |
| Biotite mica    | 0.35   | 3.06             | 2.7–3.3                |
| Phlogopite mica | 0.00   | 2.86             | 2.76–2.90              |
| Talc            | 0.10   | 2.70             | 2.58–2.83              |
| Kaolin          | 0.23   | 2.58             | 2.61–2.68              |
| Illite          | 1.84   | 2.72             | 2.60–2.90              |
| Bentonite       | 4.90   | 2.67             | 2–3                    |

ment. The volume of the cell was determined to be 8.0134 cm<sup>3</sup>. The TDR probe was calibrated for effective length (0.154 m) using air and deionized water (Heimovaara, 1993). After calibration this method is expected to give a permittivity measurement accuracy of about 0.1.

### Measurement Procedure

The measurement procedure relies on making a suspension of the mineral in the background dielectric fluid. In the first step clay mineral samples were oven dried at 150°C overnight to drive off any bound water. Thermogravimetric analysis of the samples found that there was no loss of mass above 150 to 800°C, the upper limit of heating. The samples were removed from the oven and allowed to cool in a desiccator. A subsample (≈10 g) was removed and accurately weighed in a



**Fig. 2. Photograph of the equipment specifically made for soil dielectric measurements: internal stainless-steel electrode 0.003175 m in diameter and 0.16 m in total length with 0.152 m projecting above the chemical resistant Delrin probe head at the base (A), outer brass tube, 0.156 m long with an internal diameter of 0.0085 m (B), retaining nut fixing B to E (C), male connector (D), microwave electrical connector (E), coaxial cable (F), syringe assembly for mixing suspension (G), mixing rod (H), syringe used to draw fluid out of the coaxial cell (I). A similar syringe was used with a piece of Tygon tube to connect to G, to apply a tension to deair the suspension.**

plastic weighing boat on a four-point balance. The sample was then gently poured into the coaxial TDR probe until it was flush with the top. The weighing boat was then reweighed to determine the mass of sample poured into the probe. This mass of clay was used consistently for all subsequent mixtures to ensure constant bulk density and porosity. Five waveforms were collected for the material packed into the coaxial probe. The material was then removed from the coaxial probe, which was dismantled and cleaned. A second sample of material was accurately weighed out to give the same mass as the first. For the second measurement a suspension was to be made with corn oil, but first the permittivity of the corn oil was measured in the coaxial probe. For each measurement the fluid was measured first followed by the suspension made from the same fluid. A minimum amount of time was left between the measurement of the fluid and the making of the suspension for the subsequent measurement. We measured the temperature of the fluid and the suspension with a thermocouple, which matched to within 1°C. The importance of this is that if a long period of time is left between the measurements the temperature of the fluid and suspension may differ, so the background fluid in the suspension can no longer be assumed the same as when measured individually.

The corn oil was removed from the probe using a large syringe with a 0.16-m tube attached; this same material was used to make the suspension. The suspension was made in a 10-mL syringe (Fig. 2G). The nozzle of the syringe was blocked with a nail and 4 mL of oil was placed in the 10-mL syringe. The preweighed mineral sample was poured into the syringe and mixed using a stainless-steel stirring rod (Fig. 2H). The suspension sample was now made up to a mark on the syringe representing 8.0134 cm<sup>3</sup>. This method was found to work best, especially with the swelling montmorillonite, as only enough fluid was added so that the suspension filled the required volume. An advantage of measuring the permittivity in fluids of low dielectric permittivity is that swelling is minimized, since it depends largely on the permittivity of the fluid (Graber and Mingelgrin, 1994). The nail was removed from the nozzle and another syringe attached to the syringe with the suspension via a Tygon tube (Saint-Gobin, Paris). A small tension was applied using this syringe to draw out any remaining air. As bubbles formed the syringe with the suspension was gently tapped to remove these bubbles. This suspension was then injected into the coaxial TDR probe; this suspension had the same porosity as the sample measured with air as the background. If the sample was slightly short of reaching the top of the coaxial probe a little more background fluid was added until it was flush with the top of the probe. Measurements were again made with the TDR. Then the coaxial probe was dismantled and cleaned thoroughly. This procedure was then performed several more times with different background dielectric fluids. The measurement procedure is rather demanding, and to obtain high-quality measurements it is well worth practicing to get the correct technique. The measurements in this paper were obtained after several weeks of practice using ground quartz.

## RESULTS AND DISCUSSION

### The Measured Dielectric Permittivity of Mineral Samples

Four to five samples of mineral were mixed in background solutions of differing permittivity. As with previous work (Robinson and Friedman, 2003), an empirical power function of the form  $\epsilon_{\text{eff}} = b\epsilon_c^n$  was fitted to the data. The value of the solid permittivity was then deter-

mined from the intercept of this power function with the 1:1 line. In this section the results using the immersion method are compared with estimates previously published in the literature. It is important to stress that most of these previous estimates were obtained using mixing models. Values obtained in this way should be considered as guideline values but not as definitive because of possible errors in mixing models used. Figure 3 presents the results for the minerals quartz and calcite. The value obtained for quartz of 4.4 was in close agreement with the previous result of 4.7 obtained using this method (Robinson and Friedman, 2003) and is close to single crystal measurements made by Fontanella et al. (1974) who obtained  $\epsilon_s$  values of 4.64 and 4.52 for the two axes. The value is in the midst of values from various sources and methods presented in Table 1. A value of 9.1 was obtained for the Iceland Spar. Estimates from Table 1 put the value between 8 and 9, so the measured value for this sample was slightly higher than previous estimates. The sample had been obtained by crushing a calcite crystal, and X-ray diffraction analysis revealed that no aragonite peak was present. Estimates for aragonite give it a slightly higher permittivity than calcite. Estimated values given in Carmichael (1982) for calcite and aragonite are 7.8 to 8.5 and 6.5 to 9.7, respectively. One might expect that highly crystalline samples such as the calcite used in this study will provide the highest permittivity and that defects in the crystal structure will tend to reduce the permittivity.

Figure 4 presents results for the two micas and talc. Similar values were obtained for both the biotite (6.0) and phlogopite (5.8) mica. The value for the talc was determined to be 5.3. Due to the platy nature of these materials the packing tended to create high porosities (0.6–0.8). As a result the data tend to lie close to the 1:1 line, and the fitted curve and 1:1 line meet at an oblique angle. This creates more uncertainty in the determined values of solid permittivity. However, this anisotropy in the packing is only likely to affect the measured permittivity of the crystal if the crystal unit cell itself is strongly anisotropic. In the case of these micas the anisotropy in the refractive index is about 4% with values taken from Weast (1984), indicating that this is unlikely to have a significant impact. The permittivity values determined using this immersion method are presented in the final column of Table 1.

The derivative of the waveform was used to determine travel time and calculate permittivity. The absolute error in the determination of the travel time using the value at the peak of the derivative was  $\pm 8.15$  ps. This value was added or subtracted from the travel time obtained from the peak of the derivative, and the absolute error in permittivity was determined for each measurement. Lines were then fitted through the upper and lower permittivity values obtained for all the data points for a sample. The location at which these fitted lines intercepted the 1:1 line was used to give an error estimate for the measurements. Determining the error in this way indicates less uncertainty in the permittivity when the line fitted to the data and the 1:1 line cross at right angles. However, it indicates greater uncertainty

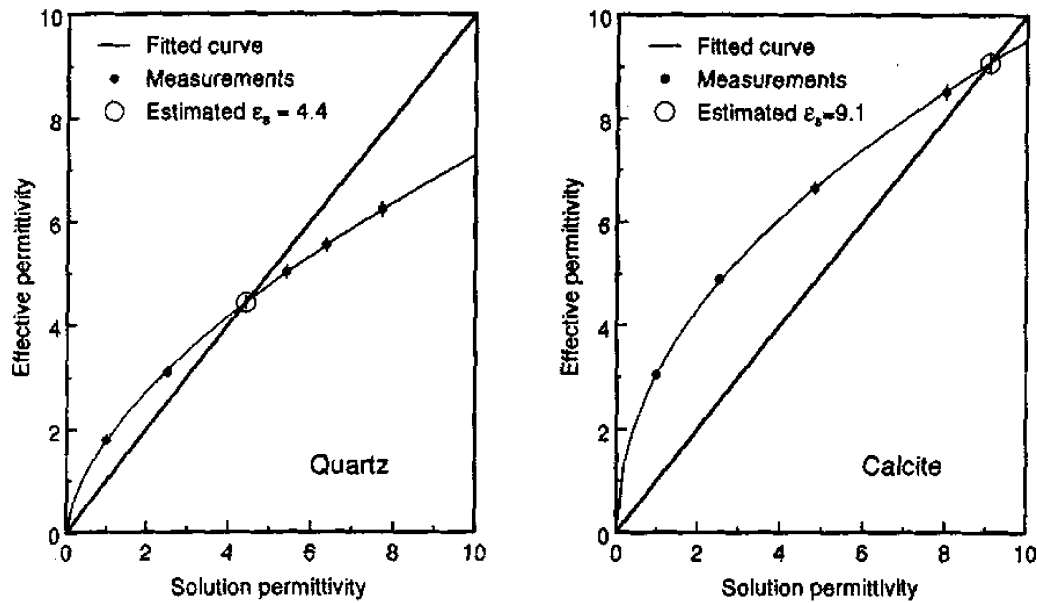


Fig. 3. The solid permittivity of quartz and calcite determined using the immersion method.

as the angle between the intercepting lines is reduced. This means that the data in Fig. 3 (calcite) have less error than the data in Fig. 4 (talc), since the angle of intercept between the curve fitted through the data and the 1:1 line is greater for the calcite. As the high-porosity packing (e.g., talc) results in smaller angles between the fitted curve and the 1:1 line this results in larger error values. In the case of low porosity ( $<0.6$ ) materials, permittivity error values of  $\pm 0.3$  and lower are to be expected using this length of TDR probe. However, this error rises to about  $\pm 0.7$  for the high-porosity materials ( $>0.6$ ). Increased accuracy may be obtained by reducing the absolute error in travel time determination by using a longer probe, but this leads to more difficulty packing the sample and requires a greater volume of material. Thus, there is a tradeoff between desired accuracy and sample size.

One of the major issues concerning fine-grained samples compared with coarse-grained samples is the removal of air trapped in the suspension. In the procedure described great care was taken in the preparation of

each measurement. Once the suspension was made an empty syringe was attached to the syringe containing the suspension, and a tension was applied to the sample to draw out any entrapped air. It was evident that a small amount of air was trapped in some of the samples, especially when the particle size was  $<50 \mu\text{m}$ . The syringe containing the suspension was tapped while under tension and it appeared that much of the air was removed. However, caution should be observed in interpreting the estimates for materials with a particle size  $<50 \mu\text{m}$ .

It is likely that some of the entrapped air may remain. Equation [7] is useful for determining the likely effect that this would have on measured permittivity values. The effective permittivity was determined for a volume fraction of solid of 0.6 with a range of permittivity values representative of measurements made. It was assumed that the permittivity of the solid and liquid matched having the same permittivity; the results then apply to any volume fraction of solid. The results are presented in Fig. 5 with the effective permittivity plotted as a

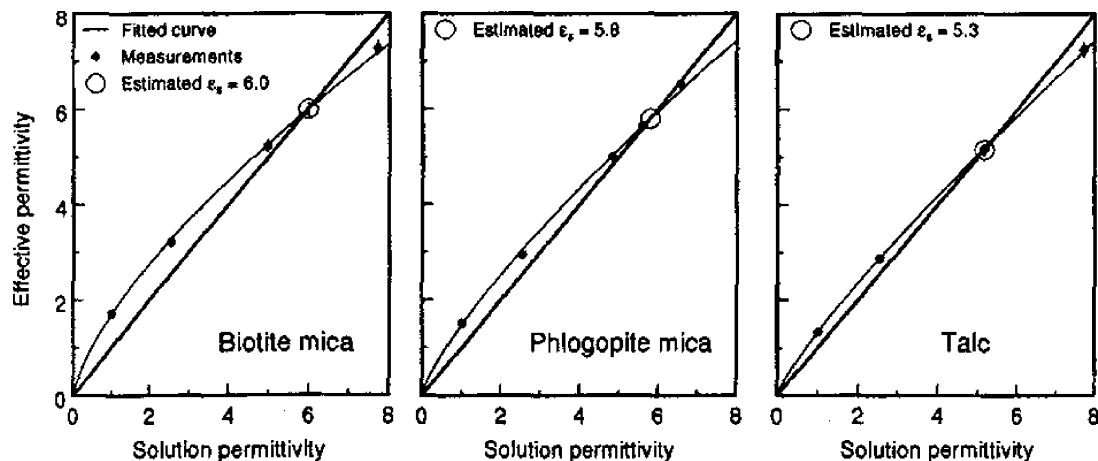


Fig. 4. The solid permittivity of biotite mica, phlogopite mica, and talc determined using the immersion method.

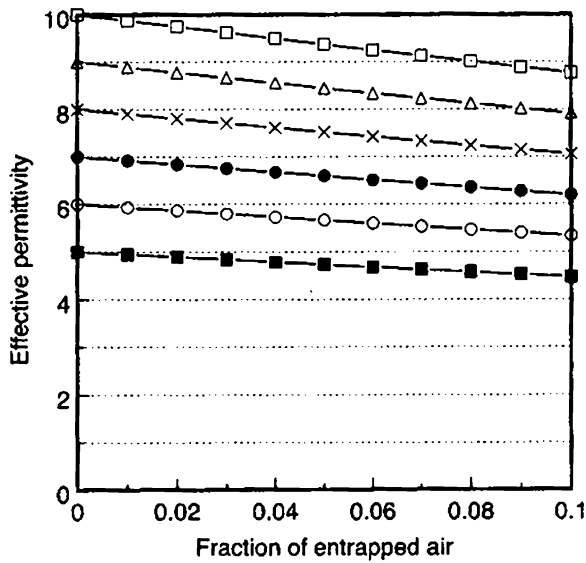


Fig. 5. The predicted effective permittivity as a function of the quantity of entrapped air.

function of the quantity of air entrapped in the sample. The data indicate that for effective permittivity values measured up to 6, which includes most of the samples in this work, even 10% entrapped air would only reduce effective permittivity values by about 0.6. Hence one might conclude that a few percent entrapped air is likely to cause less than a 0.5 reduction in the measured value of the permittivity. A 0.5 error in the determined permittivity for a mineral with a permittivity of 5 is about a 10% error. This is still considerably lower than the maximum 45% error observed by Robinson and Friedman (2003) when the method of repacking in air was used with a hematite sample.

### Clay Mineral Samples

Figure 6 presents results for three of the most common clay minerals, kaolin, illite, and montmorillonite. The results indicate that the permittivity of these minerals is reasonably similar, between 5 and 6. The value for illite was very similar to that of the micas, which is to be expected of hydrous-mica. In the case of the

montmorillonite some difficulties in obtaining measurements were encountered. The value of permittivity had to be extrapolated from the measurements in air and oil because the measurements made with mixtures of oil and acetone appeared unrealistically low. The form of the empirical model that was extrapolated,  $\epsilon_{\text{eff}} = b\epsilon_c^c$  has previously been found to provide an accurate empirical model to describe the data (Robinson and Friedman, 2003).

We considered that the acetone within the background dielectric solution adsorbed to the surface of the montmorillonite. Polar molecules can adsorb to the surface of a mineral, forming a monomolecular layer with different properties from the bulk solution. In most materials with low surface area this has no significant impact, but in a montmorillonite a significant amount of the fluid may be in contact with the surface and have a reduced mobility in the TDR frequency bandwidth. This has been observed for water in montmorillonites in studies using dielectric spectroscopy (Ishida et al., 2000). Because of this the permittivity of the background solution would no longer be the same as measured independently of the solid. We do believe that the extrapolated value of 5.5 is not unreasonable considering the crystal structure and is in keeping with the values for the other clay minerals. This value is a substantial improvement over the wet clay values of 207 presented in the literature (Table 1).

The data in this paper present strong evidence that many of the clay minerals will have permittivity values between 5 and 6, substantially lower than the values of 8 to 10 obtained from previous estimates (Table 1). The case of montmorillonite highlights one of the limits of this measurement method: unreliable estimates may be obtained in clay minerals with high surface area capable of binding polar molecules. In the future this may be overcome by measuring at low frequencies where relaxation has not occurred. The choice of background dielectric becomes critical, since liquids with a low permittivity like the oil may not be affected as much as acetone. However, many of the low permittivity liquids (<5) are organic solvents and undesirable for use because of their harmful nature.

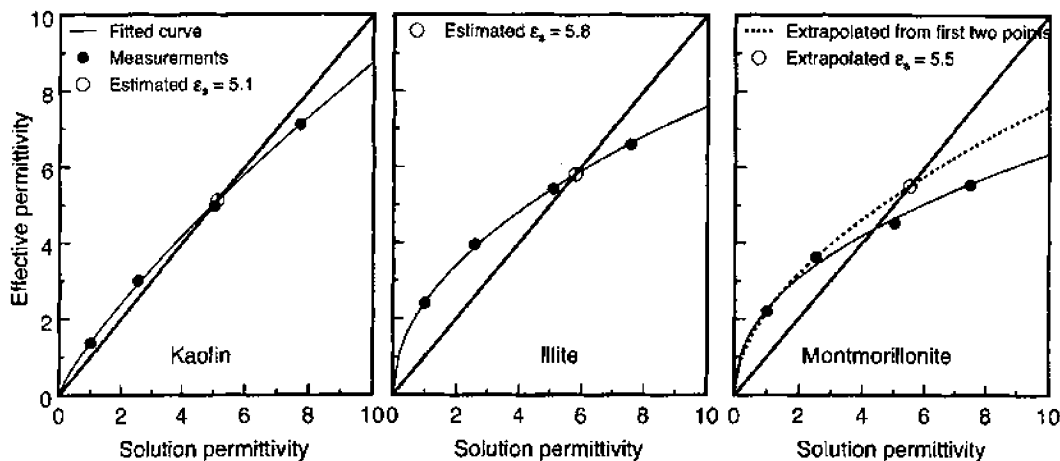


Fig. 6. The effective permittivity of kaolin, illite, and montmorillonite used to determine solid permittivity.

**Table 4. Comparison of mineral permittivity values measured using the immersion method and estimated by applying different two-phase dielectric mixing models using air dry (RH = 50%) and oven-dry samples. The number in parentheses is the standard deviation in the permittivity measurement.**

|                        | Immersion method | Lickteneker (Eq. [3]) | Looyenga (Eq. [5]) | Birchak (Eq. [4]) | Bruggeman (Eq. [6]) | Maxwell Garnett (Eq. [2]) |
|------------------------|------------------|-----------------------|--------------------|-------------------|---------------------|---------------------------|
| <b>Kaolin</b>          |                  |                       |                    |                   |                     |                           |
| air dry                |                  | 9.1 (2.1)             | 5.6 (0.9)          | 4.9 (0.7)         | 8.9 (2.5)           | 12.6 (5.0)                |
| oven dry               | 5.1              | 8.4 (2.1)             | 5.4 (0.9)          | 4.7 (0.7)         | 8.5 (2.7)           | 12.1 (5.5)                |
| <b>Illite</b>          |                  |                       |                    |                   |                     |                           |
| air dry                |                  | 7.3 (0.2)             | 5.7 (0.2)          | 5.2 (0.2)         | 6.6 (0.1)           | 8.9 (0.3)                 |
| oven dry               | 5.8              | 7.3 (0.2)             | 5.7 (0.1)          | 5.3 (0.1)         | 6.6 (0.1)           | 9.0 (0.3)                 |
| <b>Montmorillonite</b> |                  |                       |                    |                   |                     |                           |
| air dry                |                  | 48.7 (6.8)            | 18.3 (1.3)         | 14.2 (0.8)        | –                   | –                         |
| oven dry               | 5.5              | 3.1 (2.3)             | 2.8 (0.1)          | 2.7 (0.1)         | 2.9 (0.1)           | 3.0 (0.2)                 |

### Comparison of Immersion Measurement with Mixing Model Predictions of the Solid Permittivity

Table 4 compares permittivity values obtained for clays using the immersion method and values predicted using clay samples packed to five bulk densities in air and applying the two-phase mixing models. In previous work Nelson and You (1990) found that the Lichteneker model used by Olhoeft (1979) (Eq. [3]) overpredicted values of solid permittivity for low permittivity plastics. They instead preferred the Looyenga model (Eq. [5]). Dube (1970) also tested the Looyenga model for powders, demonstrating that the error in predicting the solid permittivity could be as much as 8% for the mixtures studied in his work. In the work of Robinson and Friedman (2003) both Eq. [3] and [6] tended to overestimate the permittivity of the sample of hematite ore, whereas Eq. [4] and Eq. [5] tended to underestimate the permittivity. Assuming reasonable accuracy for the measured permittivity values of the kaolin, illite, and montmorillonite, our results show a similar pattern. Results collected from air-dry and oven-dry samples also indicate the importance of bound water in determining the estimated permittivity using a mixing model. In the case of the air-dry samples Eq. [2], [3], and [6] overestimate the permittivity. Both Eq. [3] and [5] are in reasonable agreement for kaolin and illite but overestimate the montmorillonite. In the case of the oven-dry samples there is little effect on the kaolin and illite results, but oven drying has a huge impact on the values predicted for montmorillonite. The oven-dry permittivity for the montmorillonite gave a value with all models of about 3. The large difference between solid permittivity estimated using an air-dry and oven-dry sample indicates the importance of bound water contributing to the estimate in the case of the air-dry samples. The importance of this comparison is that none of the models could correctly predict all of the solid permittivity values. Hopefully the immersion method and the new values for the permittivity of clay minerals will allow for more rigorous testing of dielectric mixing models and their continued improvement.

### CONCLUSIONS

A refined method of determining the permittivity of clays and fine-grained mineral samples (<500  $\mu\text{m}$ ) is presented. It relies on the suspension of the mineral

solid in a number of dielectric fluids. Results are presented for mineral samples (quartz, calcite, biotite mica, and phlogopite mica) and four clay mineral samples (talc, kaolin, illite, and montmorillonite). The values for the clay minerals fall consistently between 5 and 6, suggesting previous estimates of 8 to 10 were too high and obtained due to the predictive deficiencies of the mixing models used to predict the permittivity of the solid.

The method worked well with all the mineral samples; however, the high surface area montmorillonite appeared to adsorb the immersion dielectrics, with higher permittivity values resulting in a low estimate of 3 for the mineral permittivity. The swelling of the sample made it difficult to pack. It appeared that the acetone from the immersion fluid mixture adsorbed to the mineral surface, which reduced its permittivity in comparison with the bulk solution. This lowered the values of effective permittivity measured. The method will require more refinement if accurate solid permittivity values are to be obtained from high surface area clays. However, as the crystal structure of montmorillonite varies little from other clay minerals we believe the extrapolated value of 5.5 is realistic.

Permittivity values determined using the immersion methodology suggest that existing dielectric mixing models do not successfully predict the permittivity of all the clay mineral samples. The provision of directly measured mineral permittivity values should allow dielectric mixing models to be more thoroughly tested, as the permittivity of all the phases should be determinable.

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### REFERENCES

- Andeen, C., J. Fontanella, and D. Schuele. 1970. Accurate determination of the dielectric constant by the method of substitution. *Rev. Sci. Instrum.* 41:1573–1576.
- Arulanandan K. 1991. Dielectric method for prediction of porosity of saturated soil. *J. Geotech. Eng.* 117:319–330.
- Binley, A.P., P. Winship, R. Middleton, M. Pokar, and L.J. West. 2001. High-resolution characterisation of vadose zone dynamics in the Sherwood sandstone using cross-borehole radar. *Water Resour. Res.* 37:2639–2652.
- Birchak, J.R., C.Z.G. Gardner, J.E. Hipp, and J.M. Victor. 1974. High

- dielectric constant microwave probes for sensing soil moisture. *Proc. IEEE* 62:93–98.
- Bruggeman, D.A.G. 1935. The calculation of various physical constants of heterogeneous substances. I. the dielectric constants and conductivities of mixtures composed of isotropic substances. *Ann. Phys.* 24:636–664.
- Carmichael, R.S. 1982. *Handbook of physical properties of rocks*. CRC Press, Boca Raton, FL.
- Clark, S.P. 1966. *Handbook of physical constants*. Geographical Society of America, New York.
- Davis, J.L., and A.P. Annan. 2002. Ground penetrating radar to measure soil water content. p. 446–463. *In* J.H. Dane and G.C. Topp (ed.) *Methods of soil analysis*. Part 4. SSSA Book Ser. 5. SSSA, Madison, WI.
- Dube, D.C. 1970. Study of Landau-Lifshitz-Looyenga's formula for dielectric correlation between powder and bulk. *J. Phys. D: Appl. Phys.* 3:1648–1652.
- Ficai, C. 1959. Caracteristiques des matieres argileuses etablies en mesurant les constants et les pertes dielectriques dans le domaine de frequence compris entre 30 kHz et 3 MHz. *Bull. Soc. Franc. Ceram.* 42:7–16.
- Flint, A.L., and L.E. Flint. 2002. Particle density. p. 229–240. *In* J.H. Dane and G.C. Topp (ed.) *Methods of soil analysis*. Part 4. SSSA Book Ser. 5. SSSA, Madison, WI.
- Fontanella, J., C. Andeen, and D. Schuele, 1974. Low-frequency dielectric constants of  $\alpha$ -quartz, sapphire,  $MgF_2$ , and  $MgO$ . *J. Appl. Phys.* 45:2852–2854.
- Graber, E.R., and U. Mingelgrin. 1994. Clay swelling and regular solution theory. *Environ. Sci. Technol.* 28:2360–2365.
- Heimovaara, T.J. 1993. Design of triple wire time domain reflectometry probes in practice and theory. *Soil Sci. Soc. Am. J.* 57:1410–1417.
- Heimovaara, T.J., and E. de Water. 1993. A computer controlled TDR system for measuring water content and bulk electrical conductivity of soils. Rep. 41. Laboratory of Physical Geography and Soil Science, University of Amsterdam, The Netherlands.
- Hoekstra, P., and A. Delaney. 1974. Dielectric properties of soils at UHF and microwave frequencies. *J. Geophys. Res.* 79:1699–1708.
- Hubbard, S.S., J.E. Peterson, E.L. Majer, P.T. Zawislanski, K.H. Williams, J. Roberts, and F. Wobber. 1997. Estimation of permeable pathways and water content using tomographic radar data. *Leading Edge* 16:1623–1628.
- Huisman, J.A., C. Sperl, W. Bouten, and J.M. Verstraten. 2001. Soil water content measurements at different scales: Accuracy of time domain reflectometry and ground-penetrating radar. *J. Hydrol. (Amsterdam)* 245:48–58.
- Ishida, T., T. Makino, and C. Wang. 2000. Dielectric-relaxation spectroscopy of kaolinite, montmorillonite, allophane, and imogolite under moist conditions. *Clays Clay Miner.* 48:75–84.
- Jones, S.B., and S.P. Friedman. 2000. Particle shape effects on the effective permittivity of anisotropic or isotropic media consisting of aligned or randomly oriented ellipsoidal particles. *Water Resour. Res.* 36:2821–2833.
- Keller, G.V. 1989. Electrical properties. p. 359–428. *In* R.S. Carmichael (ed.) *CRC practical handbook of physical properties of rocks and minerals*. CRC Press, Boca Raton, FL.
- Lichtenecker, K. 1926. Die dielektrizitatskonstante natuerlicher und kunstlicher mischkorper. *Physikalische Zeitschrift* 27:115–158.
- Looyenga, H. 1965. Dielectric constants of mixtures. *Physica* 31:401–406.
- Lord Rayleigh. 1892. On the influence of obstacles arranged in rectangular order upon the properties of the medium. *Philos. Mag.* 34: 481–502.
- Maxwell-Garnett, J.C. 1904. Colours in metal glasses and in metallic films. *Philos. Trans. R. Soc. London A* 203:385–420.
- Nelson, S.O., D.P. Lindroth, and R.L. Blake. 1989. Dielectric properties of selected minerals at 1–22 GHz. *Geophysics* 54:1344–1349.
- Nelson, S.O., and T.-S. You. 1990. Relationships between microwave permittivities of solid and pulverized plastics. *J. Phys. D: Appl. Phys.* 23:346–353.
- Nelson, S.O. 1992. Estimation of permittivities of solids from measurements of pulverized or granular materials. p. 231–271. *In* A. Priou (ed.) *Dielectric properties of heterogeneous materials PIER 6*. Progress in Electromagnetics Research. Elsevier, Amsterdam.
- Olhoef, G.R. 1979. Tables of room temperature electrical properties for selected rocks and minerals with dielectric permittivity statistics. USGS Open File Rep. 79-993. USGS, Reston, VA.
- Olhoef, G.R. 1981. Electrical properties of rocks. p. 298–329. *In* Y.S. Touloukian and C.Y. Ho (ed.) *Physical properties of rocks and minerals*. McGraw-Hill/CINDAS Data Series on material properties Vol. II-2. McGraw-Hill, New York.
- Robinson, D.A., and S.P. Friedman. 2002. The effective permittivity of dense packing of glass beads, quartz sand and their mixtures immersed in different dielectric backgrounds. *J. Non-Crystalline Solids* 305:261–267.
- Robinson, D.A., and S.P. Friedman. 2003. A method for measuring the solid particle permittivity or electrical conductivity of rocks, sediments, and granular materials. *J. Geophys. Res. B.* 108(B2): 2076. doi:10.1029/2001JB000691.
- Robinson, D.A., S.B. Jones, J.M. Wraith, D. Or, and S.P. Friedman. 2003. A review of advances in dielectric and electrical conductivity measurement using time domain reflectometry in soil science. Available at [www.vadosezonejournal.org](http://www.vadosezonejournal.org). *Vadose Zone J.* 2:444–475.
- Sakaki, T., K. Sugihara, T. Adachi, K. Nishida and W. Lin. 1998. Applications of time domain reflectometry to determination of volumetric water content in rock. *Water Resour. Res.* 34:2623–2631.
- Schaap, M., D.A. Robinson, S.P. Friedman, and A. Lazar. 2003. Measurement and modelling of the dielectric permittivity of layered granular media using time domain reflectometry. *Soil Sci. Soc. Am. J.* 67:1113–1121.
- Schmidt, W. 1902. Bestimmung der dielektricitatskonstanten von krystallen mit elektrischen wellen. *Ann. Physik* 9:919–937.
- Sen, P.N., C. Scala, and M.H. Cohen. 1981. A self-similar model for sedimentary rocks with application to the dielectric constant of fused glass beads. *Geophysics* 46:781–795.
- Sharma, P.V. 1997. *Environmental and engineering geophysics*. Cambridge University Press, Cambridge, UK.
- Sihvola, A., and J.A. Kong. 1988. Effective permittivity of dielectric mixtures. *IEEE Trans. Geosci. Remote Sens.* 26:420–429.
- Sihvola, A. 1999. *Electromagnetic mixing formulas and applications*. IEEE Electromagnetic Waves Ser. 47. IEE, Stevenage, Herts, UK.
- Takubo J., Y. Ukai, and S. Kakitani. 1953. On the dielectric constants of minerals. *Minerol. J.* 1:3–24.
- Topp, G.C., J.L. Davis, and A.P. Annan. 1980. Electromagnetic determination of soil water content: Measurements in coaxial transmission lines. *Water Resour. Res.* 16:574–582.
- Topp, G.C., and P.A. Ferre. 2002. Water content. p. 417–421. *In* J.H. Dane and G.C. Topp (ed.) *Methods of soil analysis*. Part 4. SSSA Book Ser. 5. SSSA, Madison, WI.
- von Hippel, A.R. 1954. *Dielectrics materials and applications*. (ed.) MIT Press, Cambridge, MA.
- Weast, R.C. 1984. *Handbook of physics and chemistry*. CRC Press, Boca Raton, FL.
- Whalley, W.R. 1993. Considerations on the use of time domain reflectometry (TDR) for measuring soil water content. *J. Soil Sci.* 44:1–9.