Magnetic Properties of Sheet Silicates; 1:1 Layer Minerals

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Abstract. Three iron-rich 1:1 clay minerals, greenalite [Si3][Fe2+3+2(OH)]4, berthierine [Si, Al]2{Fe2+, Mg, Fe3+, Al}3 O2(OH)4 and cronstedtite [Si, Fe3+]2{Fe2+, Fe3+}2O2(OH)4 have been studied by Mössbauer spectroscopy, magnetization measurements and neutron diffraction to determine their magnetic properties. The predominant magnetic coupling is ferromagnetic for pairs of ferrous ions in the octahedral sheet, but antiferromagnetic for ferric pairs. The crystal field at Fe2+ sites in greenalite and berthierine is effectively trigonal with an orbital singlet $I_\text{F}=0$ as ground state. These mainly ferrous minerals order magnetically at 17 K and 9 K respectively. The magnetic structure of greenalite consists of ferromagnetic octahedral sheets, with the moments lying in the plane, coupled antiferromagnetically by much weaker interplane interactions. The ratio of intraplane to interplane coupling is of order 50, so the silicate has a two-dimensional aspect, both structurally and magnetically. Although the overall magnetic order is established as antiferromagnetic by neutron diffraction, the magnetization curves resemble those of a ferromagnet because of the very weak interplane coupling. Cronstedtite orders antiferromagnetically around 10K. Moments within the planes are antiferromagnetically coupled. The magnetism has no particular two-dimensional character because exchange paths between the layers are provided by the ferric cations present in the tetrahedral sheets.

Introduction

Magnetism in minerals is related to the presence of transition metal ions which themselves carry a magnetic moment in their incompletely filled 3d-shells. Far and away the most common is iron whose abundance in the crust is approximately 40 times that of all the other magnetic elements together. The magnetic properties of minerals are therefore essentially due to the iron they contain.

If the iron in a silicate is sufficiently dilute, magnetic exchange interactions, which tend to align the moments of neighbouring cations parallel or antiparallel, may be neglected and the magnetic susceptibility follows a Curie law (Morris 1965):

$$\chi = \frac{C}{T - \theta}$$

where $C = \frac{Ng^2\mu_B^2(S+1)}{3k}$ is the Curie constant. Here $N$ is the number of ions per gram of material, $k$ is Boltzmann's constant, $\mu_B$ is the Bohr magneton, $S$ is the spin quantum number and $g$ is the Landé factor. $g\mu_B S$ is the maximum magnetic moment which can be measured on the ion.

At greater concentrations of iron, magnetic interactions cannot be neglected because is the possibility of finding magnetic cations on adjacent sites where their spins are coupled by direct or superexchange interactions. These interactions may be most simply represented by an exchange field $H_\text{E}$.

The susceptibility then follows a Curie-Weiss law

$$\chi = \frac{C}{T - \theta}$$

when $T > \theta$. The paramagnetic Curie temperature $\theta$ is related to the strength and sign of the dominant interactions. At some lower temperature $T_c$, long range magnetic order may set in, provided the iron content exceeds the "percolation threshold", the limiting concentration where there appears an infinite path through adjacent iron sites which connects most of the iron ions. The simplest forms of magnetic order are ferromagnetism, like iron metal itself, where the moments of adjacent atoms are all aligned parallel, and antiferromagnetism, like goethite, where adjacent moments align antiparallel. A positive or negative sign of $\theta$ indicates whether the dominant interactions are ferromagnetic or antiferromagnetic.

In only a few iron-rich oxides and sulphides (e.g. magnetite, hematite, goethite, pyrrhotite) are the exchange interactions sufficiently strong to produce magnetic order at room temperature. However, a number of iron-rich silicates such as fayalite (Kündig et al. 1967), staurolite (Regnard 1976) laihunite (Kan et al. 1980) and certain amphiboles (Borg and Borg 1974, 1980) do order magnetically at lower temperature.

As far as we are aware there have been no previous reports of magnetic order in sheet silicates or related clay minerals. These materials are of potential interest magnetically because of their layer structures and the possibility of intercalation (Ballet 1979).

The structures of sheet silicates (Bailey 1980) are built up from one of two basic layers types. We are concerned here with 1:1 layer minerals of the serpentine-kaolin group. The basic layer is a double one composed of a two-dimensional sheet containing mainly silicon atoms tetrahedrally coordinated by oxygen and another sheet containing di- or trivalent cations such as Fe2+, Fe3+, Mg2+ or Al3+, octahedrally...
coordinated by four hydroxyl ions and two oxygens. The oxygens are in cis positions and also constitute the apices of SiO$_4$ tetrahedra, so they are common to both sheets. A fragment of the 1:1 layer is illustrated in Fig. 1. Layers are electrically neutral, and are held together by hydrogen and van der Waals bonds. Several different stacking sequences are possible. The same mineral may exist in different forms (polymorphs) having different stacking sequences. The minerals of the 1:1 family differ from each other mainly by the extent of substitution of Al$^{3+}$ or Fe$^{3+}$ for Si in the tetrahedral sheet, and by the cation valence and site occupancy in the octahedral sheet. Minerals are termed ‘trioctahedral’ when all available octahedral sites are filled, and ‘dioctahedral’ when only two thirds of them are occupied.

Aspects of the structure which are of importance here are the large separation of octahedral cations in adjacent 1:1 layers (>7 Å), the much smaller separation within the octahedral sheet (~3.2 Å), and the metal-ligand-metal bond angle of approximately 90°. Magnetic interactions between iron cations in different octahedral sheets should therefore be much weaker than those within the same sheet on account of the difference in cation separations, so the magnetism of sheet silicates may be expected to have some two-dimensional character. Magnetic properties are expected to depend sensitively on the structure and cation distribution, hence there is a prospect of using the magnetism to derive structural information.

In this article, and a following one on 2:1 and 2:1:1 families of layer silicates (Ballet and Coey, in preparation), we study the magnetism of iron-rich minerals belonging to the main families of sheet structures. Experimental methods used are susceptibility and magnetization measurements, magnetic neutron diffraction, and Mössbauer spectroscopy of $^{57}$Fe. The latter technique provides valuable information on a microscopic scale and its application to the clay minerals has recently been reviewed by one of the present authors (Coey 1980).

Fig. 1. Structure of the 1:1 layer minerals

The 1:1 samples are described in the following section and the magnetic, Mössbauer and neutron results are presented in Sect. 3. A discussion of the magnetic order is given in Sect. 4.

Materials

Three different iron-rich 1:1 layer clay minerals were used in this work, greenalite, berthierine and cronstedtite. Samples of greenalite and berthierine (chamosite) were provided by Dr. Weber (Centre de Sedimentologie et Géochimie de la Surface, Strasbourg). They come respectively from Moanda in Gabon (Weber 1973) and iron deposit in Lorraine, France. Both are trioctahedral 7 Å minerals, rich in ferrous iron. A more nearly dioctahedral sample of Romanian cronstedte, a 7 Å mineral rich in ferric iron, was obtained from the Smithsonian Institution (No R7807).

The clay grade (<2 μm) greenalite sample also contained quartz and siderite which were identified by X-ray diffraction. The greenalite diffraction pattern showed it to be the simple 1T polytype (Bailey 1980). Amounts of quartz and siderite present were respectively deduced from the paramagnetic Curie constant and room temperature Mössbauer spectrum. The relative proportion of the three phases, greenalite, quartz and siderite, was found to be 55:35:10. Chemical analysis indicates that the greenalite has a composition close to the ideal formula:

$$\left[\text{Si}_6\right]\left[\text{Fe}^{3+}\right]O_4(\text{OH})_4$$

[ ] and { } include cations on tetrahedral and octahedral sites respectively.

The presence of siderite is undesirable for an investigation of magnetic properties because FeCO$_3$ itself orders antiferromagnetically at 38K (Jacobs 1963). It was therefore eliminated chemically. Treatment for two hours in the dark with a mixture of 0.2 M oxalic acid and 0.2 M ammonium oxalate solutions also removes any associated non-crystalline hydroxides (Landa and Gast 1973). An alternative method for removing siderite effectively was washing in 0.1 M acetic acid or 0.05 M hydrochloric acid.

Measurements of the Curie constant after oxalic acid/ammonium oxalate treatment indicate that much of the greenalite is also lost, presumably the finest fraction. Nevertheless the magnetic and Mössbauer results show no significant difference in any intensive parameter for treated and untreated samples. Much of the magnetic data was obtained on samples treated in this way, whereas the neutron diffraction and some magnetization measurements were performed on samples washed in dilute HCl. The room temperature Mössbauer spectrum of treated samples (Fig. 2a) shows the presence of some ferric iron. Significantly more ferric iron was present in the spectrum of the untreated sample. The acid-soluble fraction is likely to have been ferric hydroxide whereas the remainder is probably situated in the greenalite lattice. Its location, wheth-

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1. We indicated previously that the octahedral sheet in greenalite was not completely occupied by iron, because we failed then to take account of the associated quartz (Coey and Ballet 1978). Almost no aluminium and little magnesium were found in the chemical analysis (0.2% Al$_2$O$_3$, 1.8% MgO) (Weber 1973).