

## MILESTONES IN SOIL CHEMISTRY

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**An array of pioneering research, dealing with various aspects of soil chemistry, has appeared in *Soil Science* for the past 90 years. In this review, two papers that have shaped the field forever are featured and discussed. The paper by Mattson (1931) and the many others that he published in *Soil Science* established the importance of variable or pH-dependent surface charge on colloids and soils and the pronounced impacts on various soil chemical processes and reactions. He proposed the idea that soil colloids have an isoelectric point, that ion selectivity exists on soil surfaces, and that ligand exchange was an important process affecting ion sorption. In the second paper, using X-ray diffraction, Hendricks and Fry (1930) definitively showed that the major portion of the inorganic fraction of soils was crystalline. They presented results of total chemical analyses, optical studies, and X-ray diffraction on geological specimens of montmorillonite, bentonite, halloysite, kaolinite, and dickite; the results were related to data on 23 samples of colloids from soils. Their landmark paper paved the way for numerous studies on clay mineralogy throughout the world. (*Soil Science* 2006;171:S47-S50)**

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**O**VER the 90-year history of the venerable journal *Soil Science*, many classic and landmark papers have appeared that cover many aspects of soil chemistry. Accordingly, it was a Herculean task to choose two papers that exemplify pioneering discoveries that forever changed soil chemistry. During the past century, seminal papers have appeared in *Soil Science* on topics that have been hallmarks in soil chemistry, including ion exchange (Kelley and Brown, 1925, 1926; Kelley et al., 1931, 1939a, 1939b; Vanselow, 1932), soil acidity (Kelley and Brown, 1926; Coleman and Craig, 1961; Rich, 1964; Rich and Black, 1964), soil organic matter chemistry (Ghosh and Schnitzer, 1980; Schnitzer, 1991; Schnitzer, 1997; Schulten and Schnitzer, 1997), and soil chemical methodologies (Chang and Jackson, 1957). For this anniversary edition, I have chosen two papers that have had a profound impact on the field, and as they are reread more than seven decades

after they were first published, they are truly remarkable.

Beginning in 1929, a Swedish soil chemist, Sante Mattson (1886–1980), who spent part of his career at the United States Department of Agriculture and at Rutgers University, published a series of remarkable papers in *Soil Science* with a lead title of “Laws of Soil Colloidal Behavior.” These papers, although revolutionary and indeed visionary at the time, fell on deaf ears for many years. However, as we shall see, Mattson’s ideas were later validated, and to this day, are among the most significant to ever appear in the soil chemistry literature.

Mattson (1927) had earlier presented some of his proposals on the role of the ratio of  $\text{SiO}_2/\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$  in soils on ion adsorption at the First International Soil Science Society meeting in Washington, DC in 1927 and in two papers published in 1926 in which he conducted cataphoretic studies (i.e., the rate of movement of colloids in an electric field) and formulated a method for removing cations and anions from clays (Mattson, 1926a, 1926b, respectively). In the landmark papers in *Soil Science*, Mattson explained cation exchange on the basis of

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ionization. He also proposed the idea that soil components have an isoelectric point (IEP) in which equivalent quantities of cations and anions are dissociated. He noted that below the IEP, the dissociation of OH anions exceeds that of cations, and in this pH range, anion adsorption can take place. At pHs above the IEP, cation dissociation predominates, and cation adsorption also predominates. Mattson had pioneered the idea of variable or pH-dependent charge. He also correctly noted that cation exchange capacity (CEC) could vary in soils with pH changes and that pH should be stated when the CEC is reported (Mattson, 1927, 1931, 1932). He beautifully illustrated that soils from the Southeastern United States contained variable charge colloids that carried a positive charge at acid pHs. With the advent of X-ray diffraction and the discovery that clay minerals possessed negative charge because of isomorphous substitution (Marshall, 1935; Ross and Hendricks, 1945; Kelley, 1945), some soil chemists felt that Mattson's idea of clay minerals having an isoelectric pH, below which they were positively charged, was incorrect. However, later studies conducted by Schofield and Samson (1953) and Mehlich (1952) appeared, emphasizing the importance of pH-dependent or variable charge soils in ion sorption.

In the paper that is republished in this anniversary volume of *Soil Science*, Mattson (1931) studied the colloidal fractions from four soils and the 2:1 clay/bentonite ratio. The soil colloids were treated by electrodialysis to remove diffusible ions; then,  $\text{NH}_4^+$  salts containing  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{PO}_4^{3-}$  were added to study the adsorption of anions over a range of pHs. The suspensions were shaken for two days; then, pH and cataphoretic measurements were made. Mattson (1931) showed that the Nipe soil, which was from Cuba and was high in iron oxides and low in organic matter, adsorbed low amounts of cations but adsorbed high amounts of anions. He attributed this to the important role that iron oxides play in anion adsorption. A number of other important conclusions were drawn in the paper. He found that increased anion adsorption occurred when  $\text{PO}_4^{3-}$  was present as compared with  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ , which he attributed to the ability of  $\text{PO}_4^{3-}$  to displace  $\text{OH}^-$  and silicate from the colloidal surfaces. Mattson had proposed essentially the idea of ligand exchange, which results in the formation of inner sphere adsorption complexes. This conclusion was not directly verified until *in situ* molecular scale spectroscopic

studies were initiated in the mid-1980s to late 1980s (Sparks, 2002, 2006). Mattson (1931) also showed that anion adsorption increased as pH decreased and that the anion selectivity for the colloidal surfaces was  $\text{Cl}^- < \text{SO}_4^{2-} < \text{PO}_4^{3-}$ . With bentonite, which is a constant charge mineral in which ionic substitution is the source of the negative charge, he found little, if any,  $\text{Cl}^-$  adsorption and much less  $\text{PO}_4^{3-}$  adsorption than the other colloids he studied. He attributed this to the low iron content of bentonite. He also verified that soil colloids can be amphoteric, sorbing more cations as pH is increased and adsorbing more anion as pH is decreased. He called the pH at which anion adsorption equals cation adsorption as the pH of exchange neutrality. Interestingly, he also addressed the idea that the IEP is affected by ions in addition to  $\text{H}^+$  and  $\text{OH}^-$  (as potential determining ions) that hinted at the impact of "specifically" sorbed ions on shifting the IEP value.

Unfortunately, the perceptive observations of Mattson were largely ignored until the late 1950s and 1960s when Coleman et al. (1959) and Rich (1968) rediscovered the importance of Mattson's seminal studies. However, because much of the soil chemistry research was being conducted in areas where constant (permanent) charge soil minerals dominated, the chemistry of variable charge soils did not receive the attention it deserved (Sumner, 1998). This resulted in practices such as liming and soil analyses methodologies being transferred to parts of the world such as Africa, Asia, and South America where these practices were not appropriate. For example, the idea of measuring the CEC at pH 7 by extracting with 1 M ammonium acetate solution (a standard and widely used procedure), although appropriate for soils dominated by constant charge minerals such as montmorillonite and vermiculite, is not proper for CEC measurements on highly weathered soils high in kaolinite and aluminum and iron oxides. In short, Mattson's seminal papers brought to the forefront the importance of the chemistry and mineralogy of variable charge colloids in soils and the role they play in many significant soil chemical/mineralogical processes. During the 1960s and 1970s, more attention was given to the chemistry of variable charge systems and the importance of anion sorption on variable charge minerals and soils (Sumner, 1963a, 1963b; van Raji and Peech, 1972; Gillman, 1974, 1979; Fey and Roux, 1976; Thomas, 1977; Sparks, 2006). These studies provided useful information on

the effects of pH and ionic strength on the chemistry and physics of variable charge soils. The first textbook devoted to the chemistry and physics of variable charge soils appeared in 1981 (Uehara and Gillman, 1981).

#### CLAY MINERALOGY

Robinson and Holmes (1924) proposed that soils could be classified based on their silica/sesquioxide ratios. Robinson and Holmes (1924) also suggested that much of the silicon, aluminum, iron oxides, and water in soils may be parts of minerals such as kaolinite, nontorite, halloysite, or pyrophyllite. Robinson and Holmes (1924) noted that "With a further development of X-ray methods, it may be possible to decide definitively whether complex mixtures such as soil colloids are composed ultimately of crystals and what compounds, if any, are present." This perceptive statement was a reality several years later in the independently conducted studies of Hendricks and Fry (1930) and Kelley et al. (1931). Using X-ray diffraction, these investigators definitively showed that the major portion of the inorganic fraction of soils was crystalline (Thomas, 1977). It should not be surprising that Sterling Hendricks (1902–1981) should have made this landmark discovery which shaped the fields of soil chemistry and mineralogy for decades to come. Hendricks was a student of the great chemist and two-time Nobel, Linus Pauling (1901–1994), at the California Institute of Technology. Pauling made fundamental discoveries on the formation of chemical bonds in molecules and crystals and formulated Pauling's Rules that were the basis for understanding the structures of minerals such as clay minerals. The doctoral dissertation of Hendricks entitled, "Crystal Structure Determinations" (1926) delineated the crystal structures of aluminum and iron oxides. Hendricks went on to spend an illustrious career at the United States Department of Agriculture in Beltsville, was elected to the National Academy of Sciences, and was the recipient of the Presidential Medal of Science.

In the pioneering paper of Hendricks and Fry (1930), which is reprinted here, results of total chemical analyses, optical studies, and X-ray diffraction on geological specimens of montmorillonite, bentonite, halloysite, kaolinite, and dickite were presented; the results were related to data on 23 samples of colloids from soils. Hendricks and Fry (1930) indicated that the

diffraction patterns showed "the presence of only one crystalline component in each soil" and that "none of the primary soil minerals such as micas, feldspars, and quartz are shown as crystalline components of the colloid fraction." For the next 12 years, Hendricks and Alexander, (1939) and Ross and Hendricks, (1945) published many papers on clay mineral structures and their physical properties. Kelley et al. (1931, 1939a, 1939b), Hoffman et al. (1933), Marshall (1935), and Coleman and Jackson (1945) also made significant contributions in delineating the crystal structures of clay minerals and the types of clay minerals found in US soils. Jackson (1956) also developed many standard procedures for soil particle fractionation and separation and phyllosilicate identification. Jacob et al. (1935) analyzed the clay minerals found in soils around the world, and Nagleschmidt et al. (1940) determined the clay minerals in soils of India. From these investigations, it was discovered that in most soils, more than two clay minerals were present with kaolinite, montmorillonite, and mica, each being common. These researchers and others, based on clay mineralogical analyses, concluded that weathered soils were dominated by kaolinite, whereas grassland soils were dominated by montmorillonite.

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