NANOPOROSITY CHARACTERISTICS OF SOME NATURAL CLAY MINERALS AND SOILS

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Abstract—Limited information is available on microporosity in soils. A study was undertaken to investigate the micropore characteristics of four soil samples, with different particle-size distributions, and four natural silicate clay minerals. Specific surface area and the differential micropore-size distribution were taken into account to characterize the microstructure of the soils and clays. The micropore-size distributions showed a maximum contribution to the total microporosity by pores having an effective pore radius of ~20 Å, thus indicating that that category of pore contributes more than others to the total microporosity of the system. For both soils and clays a good exponential correlation was found between the maximum contribution to the microporosity and their specific surface area. A linear relationship was also found between the microporosity of the soils and their clay content. It has been concluded that the micropore system formed by 20 Å pores is mainly located in the clay fraction of the soil, and contributes significantly to defining some of the most notable physicochemical properties of soils and clays.

Key Words— Clay Microporosity, Micropore-size Distribution, Soil Microporosity, Surface Area.

INTRODUCTION

Many of the fundamental chemical and physical properties of soils, such as soil structure and stability, water-storage capacity, hydraulic conductivity and the dynamics of nutrients or pollutants in soil, are strictly related to the size, shape and orientation of colloid particles. This arrangement depends on the mineralogical nature of the primary colloid particles present in the soil, and their association with other organic or inorganic constituents (Aylmore and Quirk, 1967; Ristori *et al.*, 1983; Murray *et al.*, 1985). The way in which they are organized is important to the suitability of the soil for crop production.

Limited information is available on soil microporosity, yet it is fundamental for the use and management of the soil (Quirk, 1999). Firstly, it is important to clarify the term 'microporosity'.

Several classifications of pores according to shape and size have been proposed: Aylmore and Quirk (1967) considered "micropore-size distributions" of compacted clay mineral systems to be those comprising pores <100 Å wide. Everett (1972) termed micro-, meso-, and macroporous, those systems which have pore-diameter ranges of <20, 20−500 and >500 Å, respectively. The largest pore radii suitable for analysis by the Kelvin equation are ~1000 Å (Lowell, 1979). Pores with radii greater than this are referred to as macropores. Pores in the Kelvin range from ~15 to 1000 Å, are referred to, by Dubinin (1960), as "transitional", and those with radii

<~15 Å are referred to as micropores (or in modern terminology, nanopores). According to the International Union of Pure and Applied Chemistry (IUPAC) classification, micropores are those with radii <10 Å (Marczewski, 2002). On the other hand, because of differences in the use of the terms macro- and micropores by different authorities, a system was suggested in which pores are described in relation to their function for plant growth. Pores with an equivalent cylindrical diameter (e.c.d.) >50 μm are described as transmission pores, those between 0.5 and 50 μm as storage pores, and those <0.5 μm as residual pores (Greenland, 1977; 1979).

The Kelvin equation was applied to calculate the effective pore radii of soil and clay-pore systems. Therefore, the term microporosity is applied to pores with radii in the range from ~5 to 50 Å, as reported by Aylmore and Quirk (1967).

Much of the available work on the micropore-size distributions of soil and clay mineral systems has been conducted by Aylmore and Quirk (1967), Quirk (1994) and co-workers. They found that a large proportion of microporosity of these systems was due to a high degree of parallel alignment of the clay-mineral particles. They observed two different regions of microporosity. The first group, up to 10 Å wide, exists between contact areas of overlapping crystal units. The second region of microporosity consists of slit- and wedge-shaped pores, up to 30 Å wide, resulting from the crystal units consisting of several elementary sheets giving rise to the formation of discrete pore-size distribution peaks at or near plate-thickness value.

In some preliminary investigations Aringhieri and Giachetti (1994, 1999) observed similarities in the

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Table 1. Selected characteristics of the investigated soils.

Soil location	Sand	Silt (%)	Clay	CEC* (cmol(+) kg^{-1})	OM** (%)	CaCO$_3$ (%)	pH	EC† (dS m^{-1})
Pian d'Alma	83	8	9	8.3	0.93	****	7.2	0.11
S. Piero (torretta)	66	19	15	11.5	1.09	8.7	7.9	0.15
Principina	44	35	21	16.3	1.86	13.8	8.1	0.35
La Foce (biancane)	20	36	44	14.2	0.92	16.3	8.2	0.57

* CEC: cation exchange capacity
** OM: organic matter
† EC: electrical conductivity

micropore-size distribution of different soils. In all cases the differential micropore-size distribution, $\Delta v_P/\Delta r_P = f(r_P)$, where v_P represents the volume of pores with an effective radius r_P, showed a maximum contribution to the total microporosity of the investigated systems by pores having an effective radius (r_P) of ~20 Å, thus indicating that these pores contribute more than others to the total microporosity. This tends to be true for the montmorillonite system (Aringhieri, unpublished data). Moreover, similar micropore-size distributions were reported for alumina (a group of substances, the main component of which is aluminum oxide, Al$_2$O$_3$), and silica gel (the partially dehydrated form of polymeric colloidal silicic acid, SiO$_2$.xH$_2$O) (Gregg and Sing, 1967; Ponec *et al*., 1974).

The present study was undertaken to investigate the micropore-size distributions of soils with different textures, and natural silicate clay minerals, to further our understanding of the origin and role of pores with an effective pore radius of ~20 Å.

MATERIALS AND METHODS

Four soil samples, chosen to represent different textures, as shown in Table 1, collected from the coastal plain of Tuscany (Italy), and four source clays obtained from Ward's Natural Science Establishment Inc. (montmorillonite # 22a, 48 W 1221, Amory, Mississippi; montmorillonite Wyoming, SWy-1; montmorillonite # 36, 48 W 1310, Cameron, Arizona; illite # 36, Morris, Illinois), were used in this study. The standard clay minerals were gently ground by hand with a pestle and mortar, and 2% suspensions were made by shaking with distilled water. The <2 μm equivalent Stokes diameter (ESD) fraction was separated by repeated sedimentation and decantation. In order to achieve the best separation of the clay fraction, ultrasonic vibration was applied to the suspensions for 15 min at 20 kHz ultrasonic energy with an output power of ~90 W, using a Sonifier model 250 by the Branson Ultrasonic Corporation. The clays were then made homoionic with Na$^+$ by the procedure of Parfitt and Greenland (1970), by washing the suspensions three times with 1 M NaCl at pH 3.0, twice with 1 M NaCl at pH 5.7, and then repeatedly with distilled water until the clay dispersed.

The suspensions were further washed with distilled water until they were free of Cl$^-$, as indicated by the AgNO$_3$ detection test. The Na-clays were separated by centrifuging for 30 min at 43,700 g.

All the samples were then investigated for their microstructural characteristics at the temperature of the N$_2$ boiling point (−196.5ºC). Specific surface area was
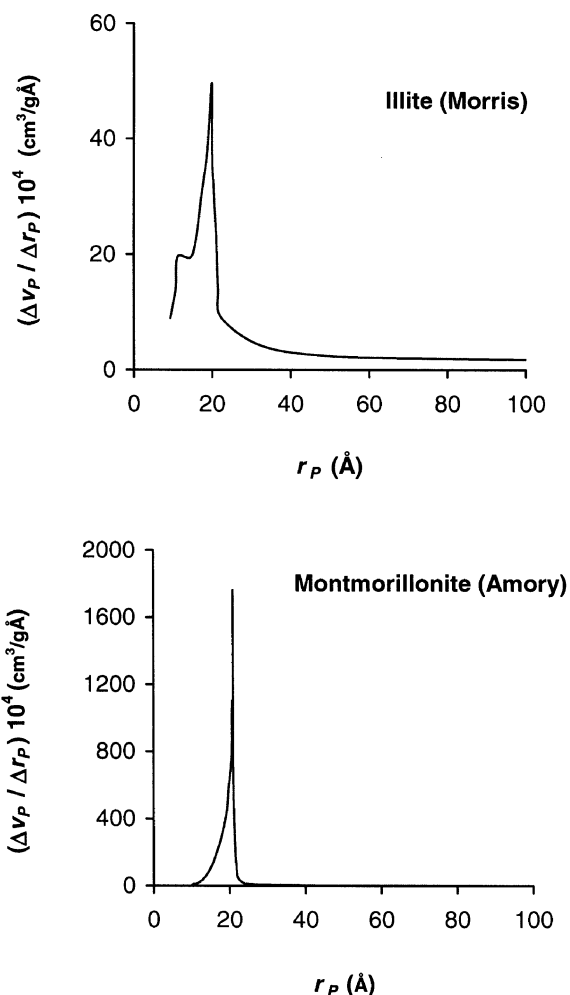

Figure 1. Micropore-size distributions for the illite (Morris) and montmorillonite (Amory) systems.
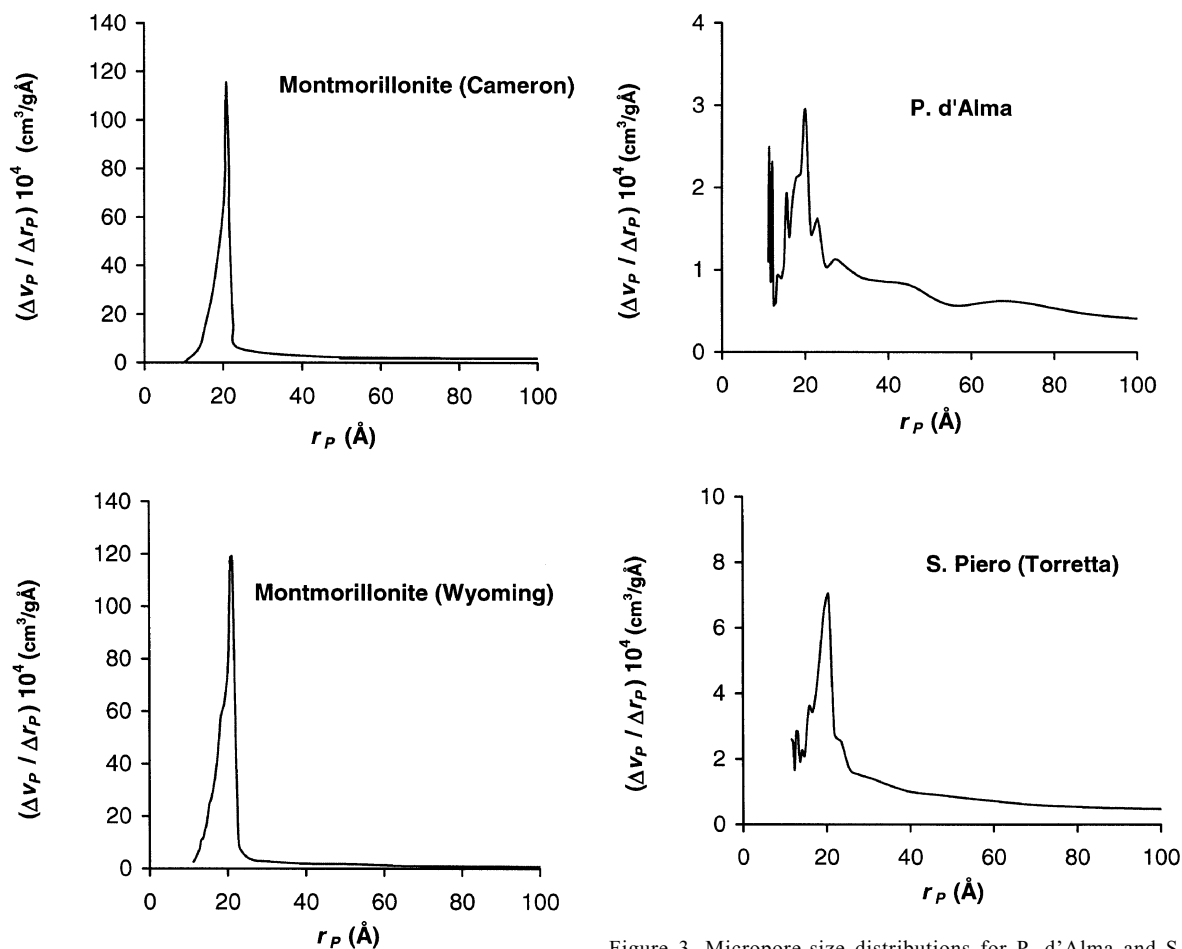
Figure 2. Micropore-size distributions for the montmorillonite (Cameron, and Wyoming) systems.

Figure 3. Micropore-size distributions for P. d'Alma and S. Piero soils.

determined by N_2-adsorption isotherms using a computerized volumetric gas instrument (Sorptomatic mod. 1900, C. Erba Instruments) after outgassing under vacuum at a temperature of 105°C. The surface area was calculated using the BET equation (Brunauer *et al.*, 1938). The differential micropore-size distributions $[(\Delta v_P/\Delta r_P) = f(r_P)]$, up to 1000 Å effective pore radius, were obtained from the adsorption-desorption isotherms using the Kelvin equation in the form:

$$r_p - t = 2\gamma \overline{V}/RT\ln(P/P_0)_{des}$$

where v_P represents the volume of pores with an effective radius r_P, t the thickness of the adsorbed layer, R the gas constant, T the absolute temperature, and P/P_0 the relative pressure. The terms γ and $\overline{V}$ are the surface tension and the molar volume of liquid nitrogen, respectively (Gregg and Sing, 1967; Lowell, 1979).

The technical characteristics of our instrument enabled us to obtain pore-size distributions ranging from 5 to 1000 Å r_P. The minimum detectable surface area was 1 m^2/g, and the average reproducibility obtained by several analyses was equal to ±2%.

RESULTS AND DISCUSSION

Some of the physicochemical characteristics of the soils studied are given in Table 1. The micropore-size distribution curves are reported in Figures 1–2 for the clay minerals, and in Figures 3–4 for the soils. Although we limited the graphical representations to a maximum of 100 Å, only one peak at ~20 Å was always observed in a range from 5 to 1000 Å effective pore radius (r_P). The main difference observed in the micropore-size distributions of both natural standard silicate clay minerals and soils was the height of the peak, namely in the contribution of these pores to the total microporosity.

The pore-size distribution curves showed a maximum contribution to the total microporosity of both soils and clay minerals by pores of ~20 Å effective radius $[(\Delta v_P/\Delta r_P)_{max} = (\Delta v_P/\Delta r_P)_{20\ Å}]$. Therefore, the results indicate that this size of pore contributes more than other size categories to the microporosity of the investigated systems.

Studies of Ca-montmorillonite have shown the presence of slit-shaped pores between lamellae which are ~9 Å wide. Another set of pores ~40 Å in size,
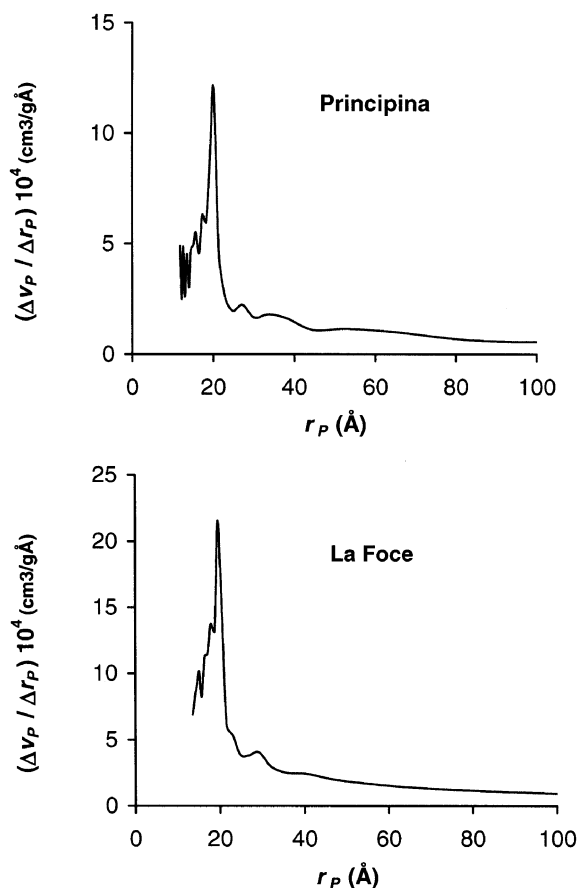
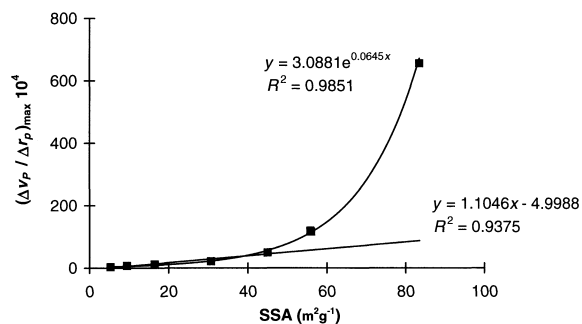Figure 4. Micropore-size distributions for Principina and La Foce soils.

Figure 5. Relationship between the maximum contribution to the microporosity, $(\Delta v_P/\Delta r_P)_{max}$, of soils and clay minerals and the respective specific surface area.

resulting from discontinuities in the quasi-crystals between sub-stacks of perfectly oriented lamellae, has also been reported (Oades, 1986). Aylmore and Quirk (1967) found a separation of some 30 Å between illite surfaces within a domain, even on complete drying, which was unaffected by exchangeable cations present on the clay surface.

It is possible that the microporosity due to 20 Å pores, which characterize the investigated systems, might be associated with the presence of both slit- and wedge-shaped pores, with a predominance of the latter. Moreover, these findings are very similar to the microporosity characteristics of alumina (Al_2O_3, sample

7C), and silica gel (SiO_2, sample IC), as reported by Gregg and Sing (1967). These systems present, in fact, a single peak at ~20 Å (r_P). It is therefore possible to suggest that voids due to the particle arrangement of aluminosilicate clay minerals reflect the structure of their main constituents.

Tables 2 and 3 show the microstructure parameters for the clay minerals and soils, respectively. The micropore-size distribution was the same for the Cameron and Wyoming montmorillonites, as we can see in Figure 2 and Table 2. The system with the highest microporosity was the Amory montmorillonite, whereas the illite represented the less porous system. As for the soils, the results reported in Table 3 show a relationship between specific surface area (SSA) and the maximum contribution to the total microporosity. The higher the maximum contribution to the microporosity of the soil, $(\Delta v_P/\Delta r_P)_{max}$, the higher was its specific surface area.

For both soils and clay minerals, the results showed a good exponential correlation (coefficient of determination $r^2 = 0.9851$) between the maximum contribution to the total microporosity, $(\Delta v_P/\Delta r_P)_{max}$, and specific surface area of the system, even though a linear relationship ($r^2 = 0.9375$) between these two parameters exists in the range of specific surface area up to 50 m^2g^{-1} (Figure 5). A linear relationship was also found between the maximum contribution to soil microporosity and clay content (Figure 6). This means that the maximum contribution region of micropores is from the clay-sized category of the soil. Similar micropore-size distributions have been observed, in

Table 2. Characteristic parameters of the microporosity of clay minerals.

Clay minerals	SSA* $(m^2\ g^{-1})$	r_P (Å)	$(\Delta v_P/\Delta r_p)_{max}\ 10^4$ $(cm^3\ g^{-1}\ Å^{-1})$
Mont. (Amory)	112.3	20.9	1761.2
Mont. (Wyoming)	55.8	21.0	119.0
Mont. (Cameron)	56.0	20.9	115.7
Illite (Morris)	45.0	20.0	49.6

* specific surface area

Table 3. Characteristic parameters of the microporosity of soils.

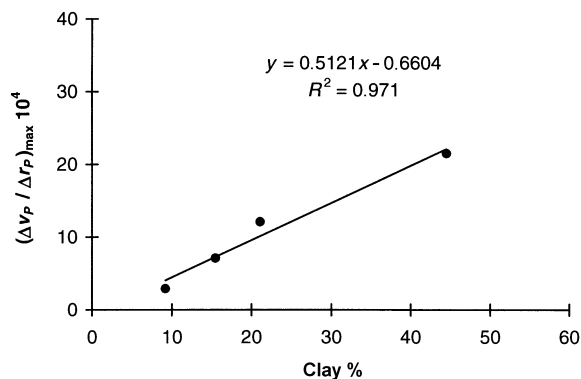| Soil location	SSA* $(m^2\ g^{-1})$	r_P (Å)	$(\Delta v_P/\Delta r_p)_{max}\ 10^4$ $(cm^3\ g^{-1}\ Å^{-1})$
Pian d'Alma	5.3	20.1	2.9
S. Piero (torretta)	9.5	20.5	7.1
Principina	16.5	20.1	12.1
La Foce (biancane)	30.7	19.5	21.5

* specific surface area

Figure 6. Relationship between the maximum contribution to the microporosity, $(\Delta v_P/\Delta r_P)_{max}$, of the soils and their clay content.

preliminary investigations, after organic matter destruction (Aringhieri, unpublished data).

According to these observations, the micropore system around 20 Å represents well defined pores that are common to soils and clays. Quirk (1994) also concluded that a pore size <30−50 Å wide, found for a Vertisol and Willalooka illite, is a common feature of clay soils. These pores are mainly located in the finest mineral fraction of the soil and, because of their fine structure, they can be expected to contribute more than other pore sizes in determining some of the most important physicochemical properties of both soils and clays.

CONCLUSIONS

In the Kelvin range (from ~15 to 1000 Å), pores of ~20 Å effective radius (r_P) contribute more than other pore sizes to the total microporosity of both soils and clays. Similar micropore-size distributions were also observed for alumina (Al_2O_3) and silica gel (SiO_2), which are the basic components of natural aluminosilicate clay minerals. The micropore system formed by 20 Å pores is closely related to both clay content and specific surface area. These pores can play an important role in many of the fundamental processes taking place in soils and sediments.

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