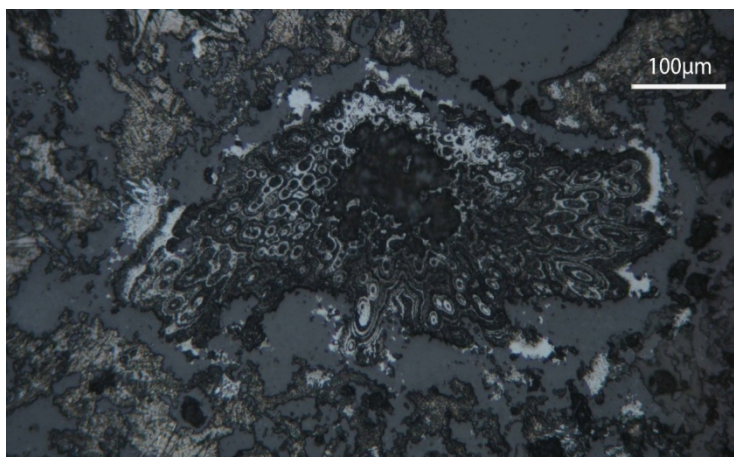




NATIONAL AND KAPODISTRIAN UNIVERSITY OF ATHENS

Surface area and porosity determination of natural todorokite-rich manganese (Mn) oxides, Cape Vani Mn deposit, Milos Island, Greece: implications for potential industrial applications

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ABSTRACT

Natural todorokite-rich Mn oxide ore samples derived from the Cape Vani Mn oxide deposit, Milos Island, Greece, were studied by means of N₂ BET specific surface area (SSA), and pore volume measurements. Cape Vani Mn oxide ores occur in a Pliocene-Pleistocene intravolcanic marine basin, they consist primarily of nanocrystalline and crystal defective todorokite, and δ -MnO₂, hollandite-cryptomelane-coronadite-manjiroite and pyrolusite that cement volcanoclastic sandstone, and are suggested to be derived from biogenic Mn oxide precursors. Todorokite which possesses many potential technological and industrial applications, has been identified in Cape Vani employing primarily high-resolution transmission electron microscopy (HR-TEM) ; moreover, the Milos todorokite has identical nanoparticle morphology to experimentally produced todorokite from birnessite (Atkins et al., 2014) under conditions analogous to marine diagenetic and hydrothermal settings. The determined SSA and porosity were compared to available relevant data from the published literature, i.e. natural and synthetic todorokite in order to evaluate its industrial and/or environmental application prospects.

The measured N₂ BET surface areas of the sandstone-hosted Cape Vani material range from 10.7 to 53.1 m²/g, and correspond largely to Mn oxides and primarily todorokite. The measured pore size that ranges 87.78 and 168.29 Å (8.7-16.8 nm) may suggest a tendency to mesoporosity (containing pores >20Å), and even for microporosity with rather complicated (the so called "bottleneck") type of pores. Generally, the SSA of the investigated todorokite-rich material is moderate, compared to other Mn oxide and oxyhydroxide sorbents in natural systems (≤ 360 m²/g), and deep-sea manganese nodules (102-130 m²/g). However, the obtained SSA values fall within the range of 19-59 m²/g reported in literature for natural and synthetic todorokites, as well as synthetic abiotic δ -MnO₂. Moreover, the determined SSA maximum value (53.1 m²/g) is very close to measured N₂ BET surface areas of experimentally produced nanocrystalline todorokite from birnessite (65.82 m²/g).

These results have important implications. Considering that birnessite has not been detected in the analyses, the Milos nanocrystalline todorokite may represent a time series product of birnessite transformation during diagenesis in a marine hydrothermal environment, in concurrence with the geological setting of the Cape Vani Mn ores. In cases of natural marine ore-grade Mn oxides precipitates containing intermixed other tunnel-structured Mn-oxides (hollandite-cryptomelane-coronadite-manjiroite, pyrolusite, ramsdellite) and predominant todorokite, like Cape Vani, the overall surface area of the rock is controlled by the predominant Mn oxide phase and may be used as a proxy for modal mineralogical composition. Mn oxide ore material from Milos is not characterized by very large SSA and therefore it probably does not hold particularly attractive sorptive properties compared to other Mn oxide and oxyhydroxide sorbents in natural systems. However, the combined: (1) moderate specific areas of up to 53.1 m²/g; (2) presence of abundant nanocrystalline todorokite; (3) total porosity that may include meso and micropores; and, (4) presence of biogenic

Mn oxides in the Milos material that may suggest strong sorbent quality for a variety of toxic trace metal cations, provide a scientific basis for further research, e.g. using X-ray absorption spectroscopy, in order to bringing new insights into the molecular-scale structure and reactivity of the Milos Mn oxide minerals for more promising results. This new knowledge may have important implications for the remediation of trace metal contamination.

Further research is needed to fully characterize the trace metal adsorption and other physical and chemical properties of biologically oxidized Mn in Milos and to establish the importance of biologically oxidized Mn in natural aquatic systems, using Cape Vani as a natural laboratory.

Keywords: Cape Vani, Milos, manganese oxides, specific surface area, BET N₂ method, pore size, todorokite, special applications

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ABSTRACT	3
<i>Acknowledgements</i>	5
<i>List of Abbreviations</i>	8
<i>List of Tables</i>	9
<i>List of Figures</i>	10
1. Introduction	12
1.1 Specific Surface Area	13
1.1.1 Definition. What is Specific Surface Area and how it is measured?	13
1.1.2 Why do we measure Specific Surface Area (SSA)?	13
1.1.3 How do we measure Specific Surface Area (SSA)?	15
1.1.4 Porosity	18
1.1.5 Pore Size distribution	18
1.2 Manganese	19
1.2.1 Manganese and Mn oxides: chemistry and geochemistry	19
1.2.2 Manganese Oxide structure and chemical properties	20
1.3 Manganese Oxide Formation	22
1.3.1 Biogenic Manganese Oxides	23
1.3.2 Synthetic Manganese Oxides	24
1.3.3 Todorokite	26
1.3.4 Todorokite from the Montenegro Mine, Cuba	27
1.4 Environmental Aspects	28
1.5 Applications	29
2. Scope	30
3. Geology	31
3.1 General Geology	31
3.2 Local Geology – Cape Vani geological setting	31
3.3 Geothermal activity and mineralization in Vani	32
3.4 The Cape Vani Mn ore-deposit	32
4. Previous work	35
5. Materials and Methods	38
5.1 Sampling	38
5.2 Sample Preparations	38
5.3. Specific surface area	38
5.4 Microscopy	38
6. Results	38

6.1 Mineralogy and Mn oxide textures	38
6.2 Surface area, pore size and pore size distribution	42
7. Discussion	47
8. Conclusions	50
9. References	51
10. Internet Sources	59
Appendix – Isotherms and Hysteresis Loops	60

List of Abbreviations

AAS	Atomic Absorption Spectroscopy
BCM	Biologically Controlled Mineralization
BET method	Brunauer-Emmett-Teller Method
BIF	Banded Iron Formations
BIM	Biologically Induced Mineralization
DFT	Density Functional Theory
EPS	Extracellular Polymeric Substances
FT-IR	Fourier-Transform IR
HR-TEM	High Resolution Transmission Electron Micrographs
HVA	Hellenic Volcanic Arc
INAA	Instrumental Neutron Activation Analysis
IR	Infrared Spectroscopy
MISS	Microbially Induced Sedimentary Structures
MOM	Manganese Oxide Mesoporous Structures
NLDFT	Non-Local Density Functional Theory
OMS	Octahedral Molecular Sieve
RL	Reflected Light Settings
SAED	Selected-Area Electron Diffraction
SEM-EDS	Scanning Electron Microscopy
SSA	Specific Surface Area
TEM	Transmission Electron Micrographs
TG/DTA	Thermogravimetric/differential Thermal Analysis
TL	Transmitted Light Settings
TPD	Temperature Programmed Desorption
VMS	Volcanic Massive Sulfides
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
XRF	X-ray Fluorescence

List of Tables

Table 1 Specific Surfaces Area values of different minerals (Sparks, 2003).....	15
Table 2 Useful definitions appearing throughout the text.....	19
Table 3 Manganese oxide mineral formulas (Post, 1999.	22
Table 4 Specific Surface Area data collected from literature, focusing on manganese oxides.	27
Table 5 Specific Surface Area as measured with N₂ BET method in natural manganese oxide samples from Cape Vani.....	43
Table 6 Pore size as measured with N₂ BET method in natural manganese oxide samples from Cape Vani.	43
Table 7 Summary of all available specific surface area data from literature, combined with current measurements from Cape Vani.....	48

List of Figures

Figure 1 Isotherm Linear Plot depicting the adsorption and desorption branches of an isotherm. When these two curves do not match (as above), a hysteresis loop is created between them (Condon, 2006).	17
Figure 2 The experimental process of nitrogen gas for the determination of porous materials. Illustration and stage description by Micromeritics Instrument Corporation.	17
Figure 3 The building block of manganese oxides, MnO_6. Source: http://minerals.gps.caltech.edu/ge114/Lecture_Topics/Mn_oxides/Mn_oxides3.htm.	21
Figure 5 Polyhedral representations of the crystal structures of (A) pyrolusite, (B) ramsdellite, (C) hollandite, (D) romanechite, and (E) todorokite, looking approximately parallel to the Mn octahedral chains, illustrations and description are reproduced from Post (1999).	21
Figure 4 Polyhedral representation of (A) lithiophorite showing alternately stacked layers of MnO_6 (blue) and $(Al, Li)(OH)_6$ (red) octahedra, (B) chalcophanite with Zn cations (green octahedra) occupying positions above and below vacancies in the Mn octahedral layers, and (C) Na-rich birnessite-like phase showing disordered H_2O/Na sites (yellow) sandwiched between the Mn octahedral sheets, by Post (1999).	21
Figure 6 Possible pathway of synthetic Mg-todorokite production, showing the timeframe and the transformation that take place and the final structural differences of the end product, which starts from a layer structure to a tunnel structure. This is a general synthetic scheme in a three-step procedure (modified after Ching et al., 1999).	26
Figure 7 Geological map of Milos Island and South Aegean volcanic arc (inset). The inset shows volcanic centres along the Hellenic Volcanic Arc. The geological map shows both the location of Cape Vani Mn oxide ore-deposit and main geological features in Milos. UPI – Upper Pleistocene; LPI – Lower Pleistocene; UPo – Upper Pliocene; LPo – Lower Pliocene; UMi – Upper Miocene; M – Mesozoic, modified after Fytikas et al. (1986).	32
Figure 8 Cape Vani terrain map. The terrain map depicts the layout of volcanoclastic sandstones/sandy tuffs (light brown shaded area) that are nested by submarine dacitic/andesitic lava domes. Red area indicates rhyolite intrusives on a faulted contact (blue line) with the lavas. The geology has been overlain on an aerial photograph (Kilias et al., 2016). The area is a magnification of the Inset in Figure 7.	34
Figure 9 Cape Vani stratigraphic column. Lithostratigraphic relationships of Cape Vani Mn ore-deposit, modified after Kilias (2011).	34
Figure 10. High-resolution transmission electron micrographs (HR-TEM) images of nanocrystalline todorokite. A and B. Isolated primary elongated striated particles of acicular todorokite; (OA) lateral oriented attachments of nanoparticles forming stable laths; (P) plate-like morphology of aggregated and attached todorokite laths, note trilling intergrowths (the white lines, indicating three orientations). Selected area electron diffraction (SAED) pattern in b shows diffraction rings at $2.4 \text{ \AA}$. C and D. Laterally aggregated todorokite laths showing structural defects in the form of spiral-like longitudinal dislocations; E. Todorokite showing lattice fringes at a spacing of $\sim 9.8 \text{ \AA}$; note tunnel-width inconsistencies observed as additional $\sim 6 \text{ \AA}$ spacings in the a direction. All images from Kilias et al. (2016).	37
Figure 11 Reflected and transmitted microscopy, Mn oxides as cement. A. & B. Photomicrographs of laminated texture of Mn oxide cement-supported structures (A in reflected light and B in transmitted light). The white arrows point to the limits of the lamina (scale bar 0.5 mm). C. Highly mineralized Mn sandstone/sandy layer with Mn oxide cement-supported texture, oval structures replaced by Mn oxide (microfossil relics?), reflected light settings, scale bar $150 \mu\text{m}$. D. Massive Mn oxides cementing volcanoclastic detritus (the dark grey angular clasts are K-feldspar). Around Mn oxides the texture is spongy (reflected light, scale bar $150 \mu\text{m}$). E. Massive crystalline pyrolusite (p) filling a vug; it overgrows thin wavy layers of microcrystalline Mn oxides (reflected light, scale $150 \mu\text{m}$). F. Same as A, pyrolusite anisotropy, high crystallinity degree (reflected light + crossed nicols, scale $150 \mu\text{m}$). G. & H. Thin colloform Mn oxide open space fillings; notespongy texture; H is a close up of G (reflected light, scale bar 0.5 mm).	40

Figure 12 A, B: Colloform banded Mn oxides. A: RL, scale bar 0.5mm; B is a close-up of A (framed area). (RL, scale bar 150 μ m) C. Colloform banded Mn oxides filling a vug. The center of the vug is filled by crystalline pyrolusite needles.) (RL, scale bar 150 μ m). D. A Unique photomicrograph of possibly unidentified microfossils. The central part of the structure is vacant (a hole), around which are several eight-figure-shaped (and multiple-eight) microstructures, some of which are elongated to the right, some are almost perfect circles, others are more oval-like. The aforementioned structures seem to follow more or less some orientation (RL, scale bar 100 μ m) E. Mn oxides cement volcanoclastic detritus and former microfossils (relic outlines). A vein is also filled with Mn oxides (reflected light, scale bar 0.5mm). F. Same as in E, transmitted light settings. Microfossil relic outlines are better distinguished. G. & H. Close-ups of abrupt transition from massive Mn oxides to acicular, cross-cutting fibrils (reflected light, oil, scale bar 25 μ m).....	41
Figure 13 Nitrogen adsorption-desorption isotherms at 77K in respect to the investigated manganese oxide material from Cape Vani. The plots are type IV. The hysteresis loops (H3) of the plots indicate that the material in question is mesoporous; interpretation according to Condon (2006) and Leofanti (1998).....	42
Figure 14 Pore size distribution (adsorption and desorption isotherm used) per sample.	44
Figure 15 The continuation of Figure 14.	45
Figure 16 Pore size distribution based on both adsorption and desorption isotherm data of all investigated samples from Cape Vani.	46
Figure 17 Chart summarizing literature data (Table 4), Cape Vani (Table 5). N ₂ BET SSAs, grouped by type (natural, synthetic and biological). The natural are distinguished by their symbols and the red oval shape surrounds their distribution.....	49

1. Introduction

Manganese (Mn) is the second most abundant redox active transition metal in the Earth's crust, and nature's solution to making O₂ via its incorporation and oxidation into the water splitting complex of photosynthetic organisms (Allen and Martin, 2007; Spiro et al., 2010). A key metal for the steel industry, Mn precipitates as (oxy)(hydr)oxides (hereafter Mn oxides), and to some extent as carbonate and silicate minerals (Post, 1999; Maynard, 2010). Manganese oxide minerals are ubiquitous in aquatic and terrestrial settings, and an important source of reactive mineral surfaces in the environment, and in nature are believed to form due to enzymatic catalysis by bacteria and fungi via oxidation of Mn²⁺ (Tebo et al., 2004; 2005; Spiro et al., 2010). They adsorb metal ions strongly, playing key roles in the biogeochemical cycles, bioavailability and distribution of many toxic and essential metals (and organic compounds) including priority pollutants (i.e. Pb, Cr, As etc.), thus stimulating interest in the development of Mn oxides for use in remediation applications (Tebo et al., 2004).

Todorokite, a 3 × 3 tunnel structure with corner-sharing triple chains of MnO₆ octahedra, is a naturally occurring Mn oxide found in terrestrial Mn ore deposits and marine Mn nodules (Turner and Buseck, 1981; Bolton et al., 1986; Yin et al., 1994). The presence of tunnels (micropores), with dimensions 6.9×6.9Å (Fron del et al., 1960), allows the lattice to accommodate water molecules as well as possibly exchangeable cations (e.g., Na⁺, Ca²⁺) like zeolites. Due to the superior characteristics of todorokite in ion exchange, specific surface area, thermal stability and molecule-sized tunnels (Shen et al., 1993), it has many potential industrial applications as molecular sieves, lithium-manganese-oxide cathode materials, heterogeneous catalysts and sensors (Shen et al., 1993; Vilen o et al., 1998; Ching et al., 1999; Feng et al., 1999); and it also plays an important role in cleaning up natural water and controlling the concentrations of heavy metals in soil solution (Post, 1999).

The specific surface area (SSA) is a determinant characteristic for the assessment of the sorption capacity of minerals. In addition to size, the accessibility of the surface area is very important, because it is primarily affected by porosity. This thesis is an attempt to characterize natural Mn oxides in terms of their specific surface area and porosity in order to decipher their suitability as materials for environmental and/or industrial applications, using the Cape Vani Mn oxide deposit, Milos island, Greece as a natural todorokite-rich material (Kilias et al., 2017).

1.1 Specific Surface Area

1.1.1 Definition. What is Specific Surface Area and how it is measured?

Specific surface area (SSA) is a property of solids defined as the total surface area of a material per unit of mass (McNaught and Wilkinson, 1997) (with units of m^2/kg or m^2/g) or solid (the SI Metric System of Units and SPE Metric Standard, SPE, 1984) or bulk volume (Tiggelaar et al., 2009) (units of m^2/m^3 or m^{-1} respectively). It is a derived scientific value that can be used to determine the type and properties of a material (e.g. soil or mineral). It has a particular importance for adsorption, heterogeneous catalysis, and reactions on surfaces. Specifically, the specific surface area (SSA) is a principle characteristic for the assessment of the sorption capacity of minerals. In addition to size, the accessibility of the surface area is of importance, which is primarily affected by porosity.

The SSA can be measured by adsorption using the Brunauer–Emmett–Teller (BET) isotherm. This has the advantage of measuring the surface of fine structures and deep texture on the particles. However, the results can differ markedly depending on the substance adsorbed. The Brunauer–Emmett–Teller (BET) theory aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of a material. In 1938, Stephen Brunauer, Paul Hugh Emmett, and Edward Teller published the first article about the BET theory in the Journal of the American Chemical Society.[1] The BET theory refers to multilayer adsorption, and usually adopts non-corrosive gases (like nitrogen, argon, carbon dioxide, etc.) as adsorbates to determine the surface area data. **Surface area of a solid reactant or catalyst.** If a reaction involves a solid with a gas or liquid, the surface area of the solid affects the reaction rate. Because the reaction occurs at the surface of the solid, the rate increases with increasing surface area. A wood fire burns faster if the logs are chopped into smaller pieces. Similarly, the surface area of a solid catalyst is important to the rate of reaction. The greater the surface area per unit volume, the faster the reaction' (Ebbing and Gammon, 2010). Surface area helps in the determination of phenomena as how solids burn, dissolve and react with other materials (Micromeritics Instrument Corporation).

1.1.2 Why do we measure Specific Surface Area (SSA)?

As already mentioned, the specific surface area (SSA) of a solid is a basic property which essentially affects its reactivity as a catalyst or sorbent, e.g. Feller et al. (1992). The larger the SSA the more surface sites are available, resulting in a higher reactivity or sorption capacity, of the solid. In case of porous solids, a large part of the SSA may be present inside pores, as pore surface area, e.g. Gregg et al. (1967). Thereby, their accessibility determines whether these parts of the SSA participate in the reaction or not. This is governed by the size of the pores.

According to the International Union of Pure and Applied Chemistry (IUPAC) pores are classified depending on the pore diameter into macropores ($>50\text{nm}$), mesopores ($2\text{--}50\text{nm}$) and micropores ($<2\text{nm}$) (e.g. (Sing, 1985; Davis and Kent, 1990; Rouquerol et

al., 1994). Especially for micropores the accessibility of the pore surface area to potential adsorptives may be limited because of size exclusion. In particular the size of the pore entrance is decisive of the accessibility of the ore surface area, see Heister (2016; and references therein). Lai et al. (2015) discuss that the reactive surface area controls interfacial processes between minerals and aqueous fluids in porous rocks.

This principle of the positive relationship between surface area and reactivity of the material has been demonstrated by Madden and Hochella Jr (2005) who found that Mn^{2+} oxidation reaction rates are up to two orders of magnitude faster on hematite nanoparticles with grain diameters of 7nm than 40nm. As reaction rate is defined the amount of product formed or the amount of reactant used up per unit of time (Ebbing and Gammon, 2010).

Surface area is important in geology because of the sorption i.e. the retention of metals, including alkali (e.g. K), alkaline earth (e.g. Ca), and transition (e.g. Cd and Ni) metals, on inorganic minerals (clay minerals, metal oxides and oxyhydroxides) and organic humic substances. This is an unambiguously important geochemical process, as surface area controls the fate, transport, and bioavailability of metals in soil and water environments (Sparks, 2005). Various metal sorption mechanisms can occur at natural surfaces, involving both physical and chemical processes (Sparks, 2005), as follows:

- *Chemisorption*: enhancement of the amount of gas molecules on the surface of a solid caused by covalent or ion bonding.
- *Physisorption (physical adsorption)*: enhancement of the amount of gas molecules on the surface of a solid phase caused by Van der Waals forces (includes dipole-dipole, dipole-induced dipole, London forces and possibly hydrogen bonding).

The terms of chemisorption and physisorption have been adapted from Condon (2006).

In natural systems (soils and sediments) the most important adsorbents and sorbents for metals are clay minerals and metal oxides and oxyhydroxides, and lastly humic substances associated with natural organic matter. These sorbents exhibit significant surface area and surface charge (Sparks, 2005). As sorbents are defined solid substances that adsorb and absorb another substance on their surface, while adsorbents are solid substances that adsorb another substance on their surface (Deng, 2006). In the following table (Table 1) (Sparks (2003) are presented the surface areas of several minerals.

Mineral	Chemical Formula	Specific Surface Area (m ² g ⁻¹)
CLAY MINERALS AND OTHER LAYER SILICATES		
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	7-30
Halloysite	Al ₂ Si ₂ O ₅ (OH) ₄	10-45
Pyrophyllite	Al ₂ Si ₄ O ₁₀ (OH) ₂	65-80
Talc	Mg ₃ Si ₄ O ₁₀ (OH) ₂	65-80
Montmorillonite	(Na, Ca) _{0.3} (Al, Mg) ₂ Si ₄ O ₁₀ (OH) ₂ •nH ₂ O	600-800
Diocahedral vermiculite	(K, Na, Ca) _{0.7} (Al, Mg, Fe) ₂ (Si, Al) ₄ O ₁₀ (OH) ₂ •nH ₂ O	50-800
Triocahedral vermiculite	Mg _{0.7} Mg ₃ (SiAl) ₄ O ₁₀ (OH) ₂ •nH ₂ O	600-800
Muscovite	KAl ₂ Al Si ₃ O ₁₀ (OH) ₂	60-100
Minerals of the biotite series	K(Mg, Fe, Al) ₃ (Si, Al) ₄ O ₁₀ (OH, F) ₂	40-100
Minerals of the chlorite group	[(Mg, Al, Li) ₂₋₃ OH ₃](Al, Mg, Li) ₂₋₃ (SiAl) ₄ O ₁₀ (OH, F) ₂	25-150
Allophane	Variable (amorphous hydrous aluminosilicates with a molar Si/Al ratio of 1.2:1 to 1:1)	100-800
METAL OXIDES AND OXYHYDROXIDES		
Aluminum oxides and oxyhydroxides		100-220
Bayerite	α-Al(OH) ₃	
Bohmite	γ-AlO(OH)	
Corundum	α-Al ₂ O ₃	
Diaspore	α-AlO(OH)	
Gibbsite	γ-Al(OH) ₃	
Iron oxides and oxyhydroxides		70-250
Akaganéite	β-Fe ³⁺ (O, OH, Cl) or Fe ₈ (OH, O, Cl) ₁₇	
Ferrihydrite	~Fe ₄₋₅ (OH, O) ₁₂	
Feroxyhyte	δ-FeO(OH)	
Goethite	α-FeO(OH)	
Hematite	α-Fe ₂ O ₃	
Lepidocrocite	γ-FeO(OH)	
Maghemite	γ-Fe ₂ O ₃	
Magnetite	Fe ²⁺ Fe ³⁺ ₂ O ₄	
Manganese oxides and oxyhydroxides		5-360
Birnessite	δ-MnO ₂ or (Na, Ca)(Mn ⁴⁺ , Mn ³⁺) ₄ O ₈ •3H ₂ O	
Manganite	γ-MnO(OH)	
Groutite	α-MnO(OH)	
Pyrolusite	β-MnO ₂	

Table 1 Specific Surfaces Area values of different minerals (Sparks, 2003).

1.1.3 How do we measure Specific Surface Area (SSA)?

Specific surface area is a physical property that cannot be directly measured. As a result, adsorption methods have been developed for the characterization of porous materials, in other words their specific surface area and their pore size. According to Sing (1998) (unless otherwise mentioned), no other type of adsorption method can characterize porous solids as gas adsorption. Liquid nitrogen at 77K (or -196.15°C) is the most widely used adsorptive for the characterization of porous materials. Other adsorptive gases used in different occasions include argon and krypton (Gregg and Sing, 1982). The Brunauer-Emmet-Teller (BET) method continues to be used as a standard procedure for the determination of surface area, although the Brunauer-Emmet-Teller (BET) theory is based on an over-simplified model of multilayer adsorption. The interpretation of the experimental data is complicated by the fact that both solute and solvent molecules are present at the solid-liquid interface. This is why there are some reasons that adsorption from solution is considered unreliable for the determination of surface area:

- Most surfaces are heterogeneous and the surface coverage is not uniform.

- The orientation of the adsorbate molecules may vary considerably from one surface to another and adsorbate-adsorbate interaction often determines the structure of the adsorbed phase.
- Adsorption of the solvent is dependent on its interaction with both adsorbent and adsorbate.

Despite the above shortcomings, the N₂ BET method continues to be the favoured procedure for determining the overall 'effective' surface area of adsorbents, catalysts and various other porous materials. It is generally agreed that the method is unreliable when applied to an ultramicroporous adsorbent, which contains pores of molecular dimensions (e.g. a molecular sieve carbon or zeolite). Also the decision as to which branch of the hysteresis loop should be used, remains arbitrary unless the pore shape and interconnectivity are known (Sing, 1998).

The full BET theory is described by Brunauer et al. (1938). The method in practice is applied as follows: at the beginning the sample is powdered. Then the sample has to be degassed (evacuation or purge with inert gas while heated) in order to remove all physisorbed material (moisture or other contaminants). Then the experimental isotherm curves are determined. The sample is exposed to low adsorptive (N₂ in our case) pressure. A monolayer starts to form as the adsorptive pressure increases and at the same time increases also the amount adsorbed. (The pressure is increased gradually after reaching equilibration.) **This part of the isotherm is used to calculate the BET surface area.** As the experiment progresses, the adsorptive pressure is further increased, which results in multilayer formation, which leads to mesopore filling (also known as capillary condensation), at which point the slope of the adsorption isotherm increases. The smaller pores are filled before the large ones. If the pores are not too large they can be completely filled and in this case the isotherm reaches a plateau value, which terminates the measurement for the adsorption isotherm. The inverse process is then followed to create the desorption isotherm, where the pressure is gradually lowered. In Figure 1 the adsorption and desorption isotherms are shown in a plot, in which y axis is the adsorbed amount and x axis the relative pressure. The step-by-step process is by Micromeritics Instrument Corporation and by Quantachrome Instruments. If the desorption branch is different from the adsorption, then hysteresis takes place and a hysteresis loop is created between the adsorption and desorption branch of the isotherm (Figure 1). Hysteresis indicates that the amount of adsorbate is greater for desorption (Condon, 2006). Isotherm types (I-VI) reveal macro-, meso-, microporosity, while hysteresis loops types (H1-H4), the pore shape of the material under investigation. Isotherm types and hysteresis loop types are reproduced in the box below, after (Sing, 1985). In this thesis this method will be applied to Mn oxide mineral phases. The surface area can be determined, using the linear part of the plot in Figure 1, by the equation: $A_s = n_m N_A a$, where:

- n_m is the number of moles of adsorbate in a monolayer
- a is the cross-sectional area of the adsorbate molecule
- N_A is Avogadro's number, $6.022 \times 10^{23} \text{ mol}^{-1}$.

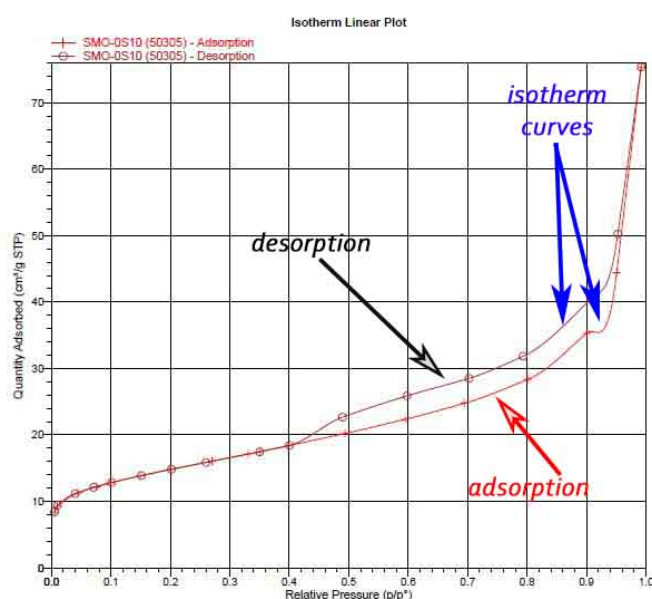


Figure 1 Isotherm Linear Plot depicting the adsorption and desorption branches of an isotherm. When these two curves do not match (as above), a hysteresis loop is created between them (Condon, 2006).

By extending the above process and allowing the adsorptive gas to condense into the pores, the material's pore structure can be determined. As adsorptive gas pressure increases, the gas condenses in the pores (in the smaller pores first) and the pressure is incrementally increased until saturation, at which point all pores are filled with liquid. Estimating then the adsorption and desorption branches of these isotherms and the hysteresis between them, information about pore size, pore volume and pore area is found out (Micromeritics Instrument Corporation). The stages of the whole experimental process are summarized in Figure 2:

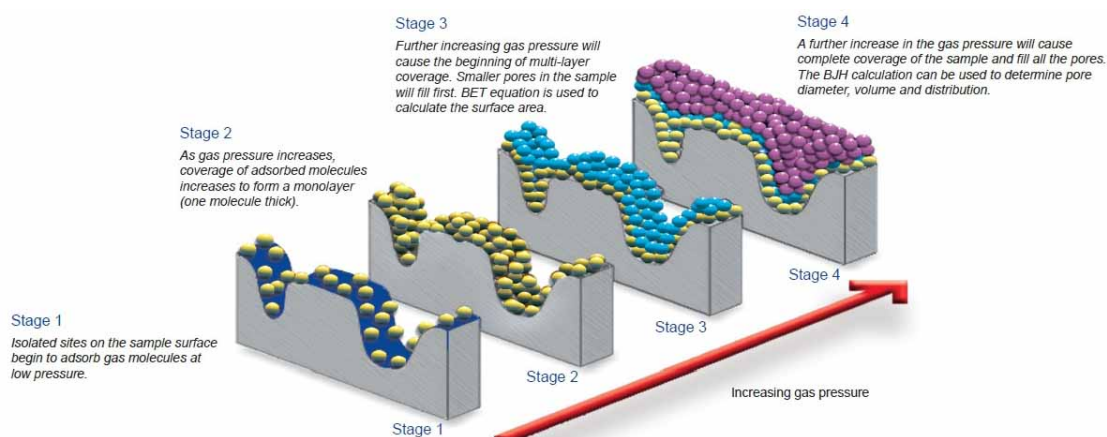
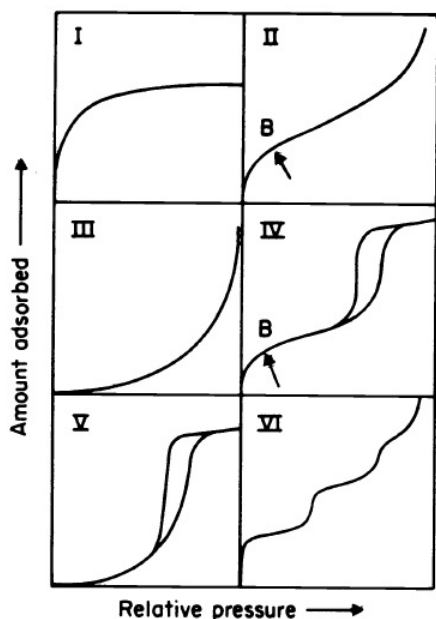
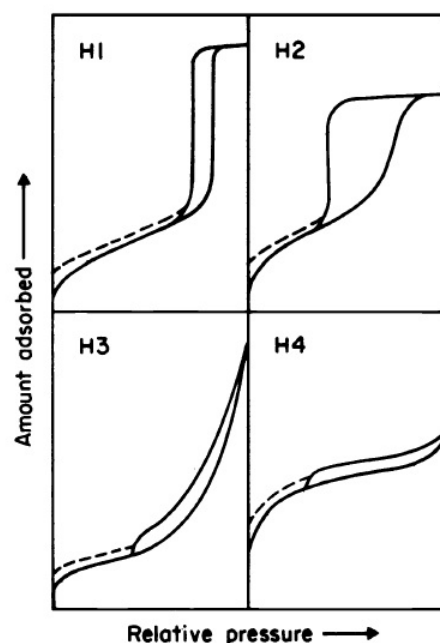


Figure 2 The experimental process of nitrogen gas for the determination of porous materials. Illustration and stage description by Micromeritics Instrument Corporation.



A. Types of Physisorption



B. Types of hysteresis loops

A. Types of Physisorption

- The reversible Type I isotherm is concave to the p/p° axis and approaches a limiting value as $p/p^\circ \rightarrow 1$. Type I isotherms are given by microporous solids (e.g. activated carbons, molecular sieve zeolites and certain porous oxides), the limiting uptake being governed by the accessible micropore volume rather than by the internal surface area.
- The reversible Type II isotherm is the normal form of isotherm obtained with a non-porous or macroporous adsorbent. The Type II isotherm represents unrestricted monolayer-multilayer adsorption. Point B, the beginning of the almost linear middle section of the isotherm, is often taken to indicate the stage at which monolayer coverage is complete and multilayer adsorption about to begin.
- The reversible Type III isotherm is convex to the p/p° axis over its entire range and therefore does not exhibit a Point B. Isotherms of this type are not common, but there are a number of systems (e.g. nitrogen on polyethylene) which give isotherms with gradual curvature and an indistinct Point B. In such cases, the adsorbate-adsorbate interactions play an important role.
- Characteristic features of the Type IV isotherm are its hysteresis loop, which is associated with capillary condensation taking place in mesopores, and the limiting uptake over a range of high p/p° . The initial part of the Type IV isotherm is attributed to monolayer-multilayer adsorption since it follows the same path as the corresponding part of a Type II isotherm obtained with the given adsorbent on the same surface area of the adsorbent in a non-porous form. Type IV isotherms are given by many mesoporous industrial adsorbents.
- The Type V isotherm is uncommon; it is related to the Type III isotherm in that the adsorbent-adsorbate interaction is weak, but is obtained with certain porous adsorbents.
- The Type VI isotherm, in which the sharpness of the steps depends on the system and the temperature, represents stepwise multilayer adsorption on a uniform non-porous surface. The step-height now represents the monolayer capacity for each adsorbed layer and, in the simplest case, remains nearly constant for two or three

adsorbed layers. Amongst the best examples of Type VI isotherms are those obtained with argon or krypton on graphitised carbon blacks at liquid nitrogen temperature.

B. Types of hysteresis loops

Hysteresis appearing in the multilayer range of physisorption isotherms is usually associated with capillary condensation in mesopore structures. Such hysteresis loops may exhibit a wide variety of shapes. Two extreme types are shown as H_i (formerly Type A) and H₄ in Figure 3. In the former the two branches are almost vertical and nearly parallel over an appreciable range of gas uptake, whereas in the latter they remain nearly horizontal and parallel over a wide range of p/p° . In certain respects Types H₂ and H₃ (formerly termed Types E and B, respectively) may be regarded as intermediate between these two extremes. A feature common to many hysteresis loops is that the steep region of the desorption branch leading to the lower closure point occurs (for a given adsorptive at a given temperature) at a relative pressure which is almost independent of the nature of the porous adsorbent but depends mainly on the nature of the adsorptive (e.g. for nitrogen at its boiling point at p/p° 0.42 and for benzene at 25°C at p/p° 0.28).

Although the effect of various factors on adsorption hysteresis is not fully understood, the shapes of hysteresis loops have often been identified with specific pore structures. Thus, Type H₁ is often associated with porous materials known, from other evidence, to consist of agglomerates or compacts of approximately uniform spheres in fairly regular array, and hence to have narrow distributions of pore size.

Many porous adsorbents (e.g. inorganic oxide gels and porous glasses) tend to give Type H₂ loops, but in such systems the distribution of pore size and shape is not well-defined. Indeed, the H₂ loop is especially difficult to interpret: in the past it was attributed to a difference in mechanism between condensation and evaporation processes occurring in pores with narrow necks and wide bodies (often referred to as 'ink bottle' pores), but it is now recognised that this provides an over-simplified picture and the role of network effects must be taken into account.

The Type H₃ loop, which does not exhibit any limiting adsorption at high p/p° , is observed with aggregates of plate-like particles giving rise to slit-shaped pores. Similarly, the Type H₄ loop is often associated with narrow slit-like pores, but in this case the Type I isotherm character is indicative of microporosity.

With many systems, especially those containing micropores, low pressure hysteresis (indicated by the dashed lines in Figure B), may be observed extending to the lowest attainable pressures. Removal of the residual adsorbed material is then possible only if the adsorbent is outgassed at higher temperatures. This phenomenon may be associated with the swelling of a non-rigid porous structure or with the irreversible uptake of molecules in pores (or through pore entrances) of about the same width as that of the adsorbate molecule or in some instances with an irreversible chemical interaction of the adsorbate with the adsorbent.

1.1.4 Porosity

Porous materials are materials with pore space (cavities, channels or interstices). The characteristics of a porous material vary depending on the size, arrangement and shape of the pores, as well as the porosity (the ratio of the total pore volume relative to the apparent volume of the material) and composition of the material itself. Porous materials are classified into several kinds by their size. The recommendations of a panel convened by the International Union of Pure and Applied Chemistry (IUPAC) are: (i) microporous materials have pore diameters of less than 2 nm, (ii) mesoporous materials have pore diameters between 2 nm and 50 nm, and macroporous materials have pore diameters of greater than 50 nm (Rouquerol et al., 1994).

1.1.5 Pore Size distribution

Pore size distribution of a porous solid is based on the Kelvin equation,

$$\ln(p/p_0) = - (2\gamma w_m \cos\theta) / (RT r_c)$$

- o r_c represents the distance between walls for slit shaped pores
- o γ the surface tension
- o w_m the molar volume
- o θ the contact angle

making use of the capillary condensation region of Type IV isotherm and is only valid for this isotherm type (Gregg and Sing, 1982; and references therein). The Barrett-Joyner-Halenda (BJH) Method is used for the calculation of pore size distribution, which uses cumulative pore volume (cm^3/g) divided by pore size ($\text{\AA}$) versus pore size ($\text{\AA}$) to present the pore size distribution directly from the desorption isotherm (Barrett et al., 1951). The decision as to which branch of the hysteresis loop should be used (adsorption or desorption branch) for the calculation of the pore size distribution remains arbitrary (Gregg and Sing, 1982), unless the pore shape and interconnectivity are known (Sing, 1998). Newer computational methods are being developed, among which prevails DFT (Density Functional Theory), which benefits from specialized computer software and options regarding various statistical methods. Insights upon this method provide Landers et al. (2013). The NLDFT ('NL' stands for non-local) method is also able to analyze the adsorption branch for H2, H3 hysteresis loops, whose origin is not well understood (Trunschke, 2013).

Term	Definition	Reference
Adsorbate	The molecules adsorbed on the surface of the solid material.	
Adsorbent	The solid material upon which the adsorbate is adsorbed.	Condon, 2006
Adsorption	Addition of adsorbate to the adsorbent by increasing the adsorptive pressure.	
Adsorptive	The gas in equilibrium with the adsorbate.	

Desorption	Removal of adsorbate from the adsorbent by decreasing the adsorptive pressure.	
Degassing (Outgassing)	A process of cleaning a sample using either evacuation or an inert gas purge while heating to remove weakly adsorbed molecules.	Gregg and Sing, 1982
Physical adsorption	Enhancement of the amount of gas molecules on the surface of a solid caused by van der Waals forces (includes dipole-dipole, dipole-induced dipole, London forces and possibly hydrogen bonding).	
Chemical adsorption	Enhancement of the amount of gas molecules on the surface of a solid caused by covalent or ionic bonding.	
Isotherm	The plot depicting adsorbed amount-relative pressure.	Condon, 2006
Hysteresis	The phenomenon of the desorption isotherm being different from the adsorption isotherm. (The amount of adsorbate is greater for desorption.)	
Monolayer	A uniform liquid film of adsorbate one molecular layer thick.	
Pore size distribution	Pore volume vs pore size.	Leofanti et al., 1998
Saturated vapor pressure (Ps)	The vapor pressure over the flat surface of the liquid adsorptive.	Condon, 2006
Porosity	Ratio of the volume of open pores to the total volume of the solid.	Gregg and Sing, 1982
Micropores	pores with a diameter less than 2nm	
Mesopores	pores with a diameter 2-50nm	IUPAC
Macropores	pores with diameter greater than 50nm	

Table 2 Useful definitions appearing throughout the text.

1.2 Manganese

1.2.1 Manganese and Mn oxides: chemistry and geochemistry

Manganese (Mn) is a transition metal belonging to the VIIB group of the periodic table of elements. In nature it is found in valence states of 2, 3 and 4, which are the most prevalent. Mn is the 10th most abundant element in Earth's crust (Turekian and Wedepohl, 1961; Maynard, 2010). Recent publications state that Mn has been collected in cosmic dust (Brownlee, 2016; Taylor et al., 2016) and Mn oxides have been discovered in Mars (Lanza et al., 2016). Mn is the second most abundant transition metal next to iron and resembles it as far as geochemistry is concerned (multiple valence states in the environment) and they are both micronutrients for most

organisms (Tebo et al., 2004). Geochemically, Mn behaves also like Mg, Fe, Ni, Co and tends to partition into minerals that form in the early stages of magmatic crystallization, some quantities of Mn persist and can be concentrated in pegmatites. It is known that Mn is readily depleted from igneous and metamorphic rocks by interactions with surface water and groundwater and is highly mobile, as Mn(II), in acidic aqueous systems (Crerar et al., 1980).

Manganese is traditionally used in industry for steel production (Maynard, 2010), and except for steel, there is a variety of other uses. It is often mentioned to be used in a variety of industrial applications, but also as a water purifying agent. In brief, the different applications of Mn can be summed up as below: catalysts, colorants, metal sorbents and batteries (Saratovsky et al., 2006; Spiro et al., 2010). As Post (1999) mentions Mn (as Mn oxide ore) has been used even by the ancients for pigments and to clean glass. More specifically, pyrolusite was known to remove the green tint rendered by iron to glass (Varentsov, 2013). By the mid-19th century Mn was essential in steel making, deoxidizing, desulphuring and making hard-steel alloys (Post, 1999). Nowadays other uses incorporate: the production of special Al alloys, Mn chemicals, catalysts, water-purifying agents, additives to livestock feed, plant fertilizers, colorant for bricks and in batteries (primarily nsutite is used as the cathodic material in zinc-carbon dry-cell batteries (Post, 1999)). Still the most up-to-date applications include water and wastewater treatment, soil and sediment remediation (both of metals and organics), metal removal and recovery, sorbents and electrical conductors in the form of Mn oxides (Tebo et al., 2004). However, today emphasis is given in the manufacture of synthetic analogues of Mn oxides in the same fashion zeolites are synthesized for specific uses (Al-Sagheer and Zaki, 2004; Katranas et al., 2004). More in respect to synthetic Mn oxides and other uses follow.

1.2.2 Manganese Oxide structure and chemical properties

Mn oxides is a collective term including oxides, hydroxides, and oxyhydroxides (Tebo et al., 2004). Mn oxide minerals commonly occur as coatings and fine-grained aggregates with large surface areas; their small size and large surface area dramatically affect geochemical reactions (Sparks, 2005). The physical properties and reactivity of nanoparticles vary dramatically as a function of material size; nanoparticles typically have completely different properties than larger particles of the same material, this is the basis of nanoscience (Hochella and Madden, 2005). This is why they are considered important antipollutants and reactive substances, even though they are minor components in soils, their influence on the chemical properties is significant (Kampf et al., 2000).

Metals undergo an array of biogeochemical processes at reactive natural surfaces, including surfaces of clay minerals, metal oxides and hydroxides, humic substances, plant roots and microbes. Such processes control the solubility, mobility, bioavailability and toxicity of metals in the environment, because they affect the metal speciation (form) (Sparks, 2005). *Speciation* is termed both the chemical and physical

(spatial distribution) form an element takes in a geochemical setting (McNear et al., 2005). The basic building block of Mn oxides is the Mn^{4+}O_6 octahedron (Post, 1999) and its illustration is shown in Figure 3.

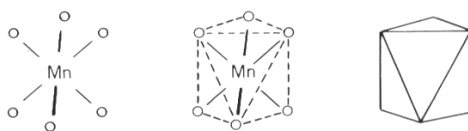


Figure 3 The building block of manganese oxides, MnO_6 . Source: http://minerals.gps.caltech.edu/ge114/Lecture_Topics/Mn_oxides/Mn_oxides3.htm.

These octahedra can be joined together by sharing corners or edges into a wide variety of structures that fall into two basic categories: *phylломanganates* (Figure 4), which

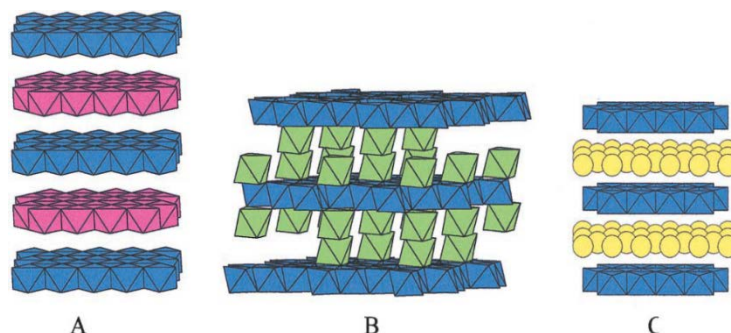


Figure 5 Polyhedral representation of (A) lithiophorite showing alternately stacked layers of MnO_6 (blue) and $(\text{Al}, \text{Li})(\text{OH})_6$ (red) octahedra, (B) chalcophanite with Zn cations (green octahedra) occupying positions above and below vacancies in the Mn octahedral layers, and (C) Na-rich birnessite-like phase showing disordered $\text{H}_2\text{O}/\text{Na}$ sites (yellow) sandwiched between the Mn octahedral sheets, by Post (1999).

are layer-structured and *tectomanganates* (Figure 5), which form tunnel and chain structures.

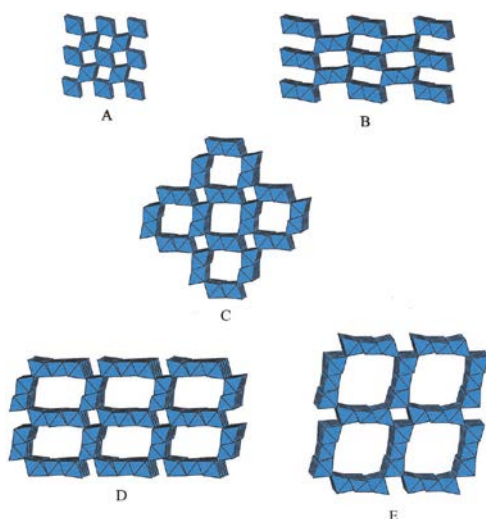


Figure 4 Polyhedral representations of the crystal structures of (A) pyrolusite, (B) ramsdellite, (C) hollandite, (D) romanechite, and (E) todorokite, looking approximately parallel to the Mn octahedral chains, illustrations and description are reproduced from Post (1999).

Tectomanganates are formed from single, double, or wider chains of MnO_6 octahedra that are linked into a framework thus forming tunnels (or channels) through the structures and these tunnels are occupied by large foreign cations (e.g. Na^+ , Ca^{2+} , Ba, Mg) and water molecules (Kampf et al., 2000). This is a key property of environmental significance. For phyllosulfates though, the unoccupied sites are relevant to the mineral in question. Layer and tunnel manganates can differ in their cation replacement series. The term ‘manganates’ includes both Mn(IV) oxides and mixed Mn(III,IV) (hydroxy)oxides, to emphasize their oxyanion properties (Tebo et al., 2004; and references therein)).

1.3 Manganese Oxide Formation

Mn oxides exhibit high surface area (SSA) values, which is an important physical property, and constitute highly reactive mineral phases participating in elemental biogeochemical cycles (Tebo et al., 2004). This is important, because on their specific surface area (SSA) are adsorbed trace elements such as Sb, Zn, As, Co etc. (Godelitsas et al., 1999) in a variety of environments ranging from deep ocean Mn nodules (Blöthe et al., 2015) to shallower environments (Hein et al., 2000; 2008), where Mn oxides form. Due to their high sorptive capacities Mn oxides adsorb a wide range of ions, such as Ca, Ni, Pb, Cr, As (Tebo et al., 2004), and this is why Goldberg (1954) referred to Mn oxides as “the scavengers of the sea”. Near the Earth’s surface, Mn is easily oxidized, and more than 30 known Mn oxide/hydroxide minerals are known (Post, 1999). They occur as fine-grained aggregates, in veins, marine and fresh-water nodules and concretions, crusts, dendrites, coatings on other mineral particles and desert varnish). In Table 3 important Mn oxide minerals are presented.

Table 3 Manganese oxide mineral formulas (Post, 1999.

Mineral	Chemical formula
Pyrolusite	MnO_2
Ramsdellite	MnO_2
Nsutite	$\text{Mn}(\text{O},\text{OH})_2$
Hollandite	$\text{Ba}_x(\text{Mn}^{4+},\text{Mn}^{3+})_8\text{O}_{16}$
Cryptomelane	$\text{K}_x(\text{Mn}^{4+},\text{Mn}^{3+})_8\text{O}_{16}$
Manjiroite	$\text{Na}_x(\text{Mn}^{4+},\text{Mn}^{3+})_8\text{O}_{16}$
Coronadite	$\text{Pb}_x(\text{Mn}^{4+},\text{Mn}^{3+})_8\text{O}_{16}$
Romanechite	$\text{Ba}_{.66}(\text{Mn}^{4+},\text{Mn}^{3+})_5\text{O}_{10} \cdot 1.34\text{H}_2\text{O}$
Todorokite	$(\text{Ca},\text{Na},\text{K})_x(\text{Mn}^{4+},\text{Mn}^{3+})_6\text{O}_{12} \cdot 3.5\text{H}_2\text{O}$
Lithiophorite	$\text{LiAl}_2(\text{Mn}^{4+},\text{Mn}^{3+})\text{O}_6(\text{OH})_6$
Chalcophanite	$\text{ZnMn}_3\text{O}_7 \cdot 3\text{H}_2\text{O}$
Birnessite	$(\text{Na},\text{Ca})\text{Mn}_7\text{O}_{14} \cdot 2.8\text{H}_2\text{O}$
Vernadite	$\text{MnO}_2 \cdot n\text{H}_2\text{O}$
Manganite	MnOOH
Groutite	MnOOH
Feitknechtite	MnOOH
Hausmannite	$\text{Mn}^{2+}\text{Mn}_2^{3+}\text{O}_4$
Bixbyite	Mn_2O_3
Pyrochroite	$\text{Mn}(\text{OH})_2$
Manganosite	MnO

The most extensive deposition of Mn oxides today occurs in the oceans as nodules, microconcretions, coatings and crusts (Crerar and Barnes, 1974). Ocean nodules are thought of as of potential commercial interest as apart from Mn, they additionally

contain significant amounts of Cu, Ni, Co and other strategic metals (several tenths to more than 1 wt%) (Chao and Theobald, 1976; Post, 1999). Deep-sea nodules are formed at relatively low accretion rates and this provides ample time and opportunity for adsorption of heavy metals and is consistent with observations that more rapidly growing nodules tend to have lower trace metal concentrations (Hein et al., 1997). Fe-Mn nodules and crusts also exist and display similar chemical properties (high specific surface area, 325 m²/g (Conrad et al., 2016), and contain concentrations of metals, for example platinum contents range between 70-328 ppb and palladium between 0.6-4.7 ppb (Cabral et al., 2009), tellurium is found on average 50 ppm in crusts with a maximum value of 205 ppm (Hein et al., 2013; and references therein).

Manganese oxides form in nature either abiotically (Bodeř et al., 2007) and/or biologically (Myers and Nealson, 1988; Ivarsson et al., 2015) and they may be synthesized either abiotically (Prélot et al., 2003; Atkins et al., 2014) or biologically (Nelson et al., 1999; Villalobos et al., 2003; Feng et al., 2010).

1.3.1 Biogenic Manganese Oxides

Since 1981, Chukhrov and Gorshkov (1981) have explained the occurrence of vernadite in a wide range of substrates as a product of rapid microbial oxidation of Mn²⁺. Also models of biotic oxidation of Mn (and Fe) are described by Ehrlich (1990); Ghiorse and Ehrlich (1992). It is not known exactly why bacteria oxidize Mn(II) (Tebo et al., 2005). Still, suggestions have been made, for example Mn(II) oxidation serves some explicit biological role or it could be an evolutionary holdover that no longer has physiological relevance (Edwards et al., 2003). There are possible benefits ranging from protective mechanisms (by coating themselves with Mn oxides, Mn(II) oxidizing bacteria can protect themselves from environmental parameters such as UV radiation, predation, viral attack or heavy metal toxicity (Tebo et al., 2005) to storage of an electron acceptor (Tebo et al., 1997). Notwithstanding the reason for the microbial catalysis of the oxidation of Mn(II) to Mn(III) and finally to Mn(IV), what is important is that microorganisms catalyze this redox reaction, which even though it is thermodynamically favoured, is otherwise sluggish (Spiro et al., 2010), due to its high activation energy (Tebo et al., 2004; and references therein), and in the absence of catalysts or photochemical enhancement and at neutral pH, it would require half a millennium to proceed (Spiro et al., 2010; and references therein).

Numerous studies link manganese oxide formation with microorganisms. Biogenicity sheds new light upon the formation and aging of Mn oxides, as they are associated with bacteria, such as *Bacillus sp strain SG-1* (Van Waasbergen et al., 1993; Van Waasbergen et al., 1996; Francis et al., 2002; Francis and Tebo, 2002; Webb et al., 2005b, a), *Leptothrix discophora SS-1* (Corstjens et al., 1997; Brouwers et al., 2000), *Pseudomonas putida strains MnB1 and GB-1* (Caspi et al., 1996; Brouwers et al., 1998; Caspi et al., 1998; De Vrind et al., 1998; Brouwers et al., 1999; De Vrind et al., 2003; Villalobos et al., 2006), *Pedomicrobium* (Larsen et al., 1999; Ridge et al.,

2007), *Erythrobacter*-like strain SD-21 (Francis and Tebo, 2001), *Shewanella* (Mn-oxidizing) and *Colwellia* (Mn-reducing species) (Blöthe et al., 2015) and fungi (*Plectosphaerella cucumerina* strain DS2psM2a2, *Pyrenochaeta* sp. DS3sAY3a, *Stagonospora* sp. SRC11sM3a, and *Acremonium strictum* strain DS1bioAY4a) (Santelli et al., 2011). Microorganisms participate actively in Mn-cycling in the natural environment. In polymetallic Mn nodules of the the Clarion and Clipperton Zone of the Pacific Ocean manganese-cycling microbial communities have been found; they are prevailed by Mn(IV)-reducing and Mn(II) oxidizing bacteria (Blöthe et al., 2015). Also biogeochemical redox processes are linked to manganese and atmospheric oxygen regarding the atmosphere-ocean system in Neoarchaeon-Palaeoproterozoic era (Tsikos et al., 2010). Even though not validated by modern evidence, Mn-based anoxygenic photosynthesis has been postulated to concentrate Mn in early Proterozoic sediments before the rise of cyanobacteria (Johnson et al., 2013; Fischer et al., 2015). So, the presence of Mn(III) and Mn(IV) often serves as a likely indicator of biological activity under conditions relevant to 'low-temperature' geochemistry. Whether microfossils can be recognized and whether they can be used to infer microbial origin (in conjunction with paleoenvironmental conditions, in particular oxygen concentration, pH and temperature), is yet to be proven. Still, todorokite, busserite and birnessite are some of the most commonly preserved Mn oxides and commonly invoked as products of microbial Mn(II) oxidation (Tebo et al., 2005). Phylломanganates may transform to tectomanganates in nature. Atkins et al. (2014) have demonstrated the experimental transformation of birnessite into todorokite in the marine environment. There are many types of environments where Mn oxide deposition may be microbially mediated. However, it cannot necessarily be concluded that from the identification of a specific mineral the origin is biogenic (Tebo et al., 2004).

1.3.2 Synthetic Manganese Oxides

The structure of biogenic Mn oxides has proven to be elusive due to their poorly crystalline nature that makes their structure difficult to study with traditional techniques like XRD (Webb et al., 2005b).

Our knowledge of the properties and structures of Mn(IV) oxide minerals is based largely on studies of oxides made synthetically using extreme conditions of pH, Mn(II) concentration, or temperature (Tebo et al., 2004). Al-Sagheer and Zaki (2004) report the synthesis of various todorokite-type Mn(IV)-oxides via hydrothermal treatment of corresponding synthetic busserite. The study of Mn oxides has been tough, as their typical occurrence as fine-grained mixtures makes their atomic structures and crystal chemistries problematic (Post, 1999) requiring the combination of modern techniques (XAS, XANES, EXAFS, XES, SR-XRD,)

It is crucial to mention that 10Å todorokite and/or busserite, 7Å (birnessite) manganates and possibly also vernadite δ -MnO₂ have similar X-ray diffraction reflections (Burns and Burns, 1977). Additionally, phylломanganates seem to have no

significant structural differences and thus 10Å buserite, 7Å birnessite, and vernadite are structurally similar and should all be called 10Å vernadite, 7Å vernadite and vernadite respectively (Manceau et al., 2007). The nomenclature problem report several researchers (Villalobos et al., 2003; Tebo et al., 2004; Manceau et al., 2007; Hein et al., 2008). Actually, it is a problem that stems from the very nature of Mn oxides, as they mostly occur as poorly crystalline mixtures (Post, 1999; Kampf et al., 2000). Lastly, according to (Villalobos et al., 2003), the nomenclature discrepancies have arisen in characterizing structural details of natural layer type Mn oxides, caused by poor crystallinity (Post, 1999; Villalobos et al., 2003; and references therein).

Initially, 10Å vernadite, buserite and todorokite were named as one phase under 10Å-manganite based on the *d* space of basal plane of diffraction (Buser and Grütter, 1956). 'Buserite' is not an official mineral, it is structurally related to birnessite (Tebo et al., 2004).

Several researchers (Ching et al., 1999; Bodeř et al., 2007; Feng et al., 2010; Xu et al., 2010; Atkins et al., 2014; Zhao et al., 2015) have synthesized and transformed in laboratory conditions a phyllomangate into todorokite (tectomanganate); the studies mentioned above, suggest possible pathways that this transformation could take place in nature. The trilling effect of todorokite has been explained as a consequence of the transformation from birnessite, since the birnessite octahedral sheet is characterized by pseudo-hexagonal symmetry, the resulting tunnel structure can have three orientations, leading to the trilling effect (Xu et al., 2010). In Figure 6, one of the possible pathways of the transformation is presented, as illustrated by Ching et al. (1999). The first to have produced synthetic todorokite are Golden et al. (1986); (1987), who have originally developed the method described in Figure 6, backed also by Post and Bish (1988) who provided more details on the matter. However, Post et al. (2003) report a way of todorokite further transforming into hausmannite. .

It should not be overlooked that through the transformation from less crystalline phases to more crystalline, the specific surface area is a property that adjusts. Poorly crystalline mineral phases exhibit higher surface area and vice versa (Stobbe et al., 1999). Atkins et al. (2014) monitored how the specific surface area changes from precursor to subsequent product.

In Table 4 are summarized the SSA values collected from literature, reflecting the wide range they display (0.0048-360m²/g). The data include crystalline powders (commercial chemical product), natural, synthetic, natural biological samples and natural samples of not definite origin (chemical or biological?).

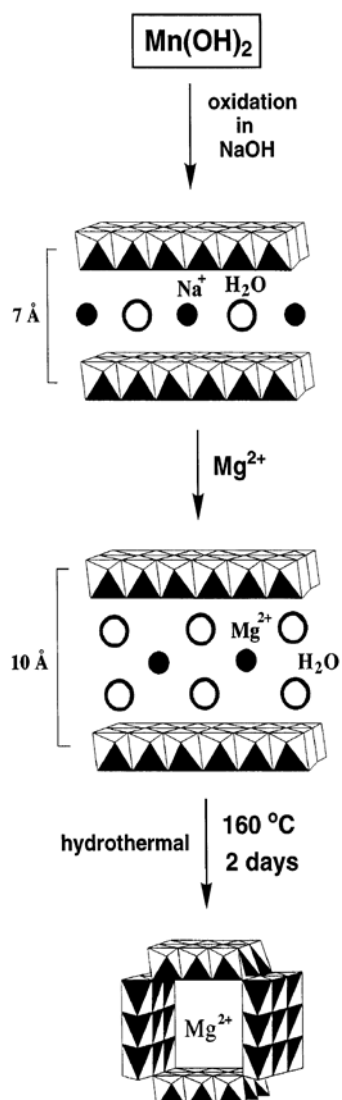


Figure 6 Possible pathway of synthetic Mg-todorokite production, showing the timeframe and the transformation that take place and the final structural differences of the end product, which starts from a layer structure to a tunnel structure. This is a general synthetic scheme in a three-step procedure (modified after Ching et al., 1999).

1.3.3 Todorokite

The following synthesis is based on Zhao et al. (2015, *and references therein*) Post (1999) and Shen (1993).

Todorokite, a 3×3 tunnel structure with corner-sharing triple chains of MnO_6 octahedra, is a naturally occurring manganese (Mn) oxide found in terrestrial Mn ore deposits, weathering products of manganese-bearing rocks, and marine Mn nodules. Todorokite, appears to be the most interesting of all naturally occurring Mn oxides with tunnel structures, i.e. hollandite with 2×2 tunnels, romanechite with 2×3 tunnels, and materials with larger tunnels like 3×4 and 4×5 ; this is because it has the largest tunnel ($6.9 \text{ \AA}$) as well as cation exchange behavior like zeolites. Due to the superior

<i>mineral/phases</i>	<i>Sample</i>	<i>sample type</i>	<i>BET Surface Area (m²/g)</i>	<i>Reference</i>
not mentioned	Crystalline β -phase MnO_2 (Fisher)	synthetic	0,0048	Nelson et al., 1999
MnO_2	β - MnO_2	synthetic	0,3	Stobbe et al., 1999
Mn_2O_3	α - Mn_3O_4 hausmannite	synthetic	1	Stobbe et al., 1999
not mentioned	Crystalline powdered MnO_2 (ICN)	synthetic	4,7	Nelson et al., 1999
Mn_2O_3	α - Mn_2O_3 hausmannite	synthetic	8	Stobbe et al., 1999
Birnessite	synthetic Mn Oxide - δ - MnO_2	synthetic	15	Kanungo and Mahapatra, 1989
Ni-Todorokite	Todorokite	synthetic	19	Al-Sagheer and Zaki, 2004
Cu-Todorokite	Todorokite	synthetic	25	Al-Sagheer and Zaki, 2004
Torokite	Todorokite	natural	25	Godelitsas et al., 2002
Mn_2O_3	α - Mn_2O_3	synthetic	26	Stobbe et al., 1999
Torokite	Todorokite	natural	37	Godelitsas et al., 2002
abiotic oxidation	Triclinic Na-Birnessite	synthetic	39	Villalobos et al., 2003
Torokite	Todorokite	natural	39	Godelitsas et al., 2002
reduction of permanganate	Acid birnessite	synthetic	40,5	Villalobos et al., 2003
Mg-Todorokite	Todorokite	synthetic	44	Al-Sagheer and Zaki, 2004
Birnessite	synthetic Mn Oxide - δ - MnO_2	synthetic	45	Burdige et al., 1992
mixed Mn mineral phases	Fresh Mn oxide precipitate (abiotic)	synthetic	58	Nelson et al., 1999
Torokite	Todorokite	natural	59	Godelitsas et al., 2002
Manganite	γ - MnOOH	synthetic	61	Friedrich et al., 2016
Birnessite	synthetic Mn Oxide - δ - MnO_2	synthetic	74	Ballistreri, 1982
<i>Pseudomonas putida</i> strain MnB1	Mn biooxide	biological	98	Villalobos et al., 2003
bulk Mn nodules	Mn nodules	natural	102	Bloethe, 2015
c-disordered birnesste	reflux product	synthetic	103,7	Atkins et al., 2014
Mg-phyllomanganate	reflux product	synthetic	104,9	Atkins et al., 2014
redox	δ - MnO_2	synthetic	121	Villalobos et al., 2003
bulk Mn nodules	Mn nodules	natural	130	Bloethe, 2015
Birnessite	synthetic Mn Oxide - δ - MnO_2	synthetic	137	Godtfredsen and Stone, 1994
OMS-1	todorokite-like	synthetic	140	Shen et al., 1993
reduction of permanganate	c-disordered H+-birnessite	synthetic	154	Villalobos et al., 2003
reduction of permanganate	δ - MnO_2 vernadite	synthetic	155	Villalobos et al., 2003
OMS-1	todorokite-like	synthetic	180	Shen et al., 1993
Birnessite	synthetic Mn Oxide - δ - MnO_2	synthetic	160	Loganathan and Bureau, 1973
<i>Leptothrix</i> -oxidized Mn	Biogenic Mn oxide	biological	224	Nelson et al., 1999
Birnessite	synthetic Mn Oxide - δ - MnO_2	synthetic	263	Murray, 1974
Birnessite	synthetic Mn Oxide - δ - MnO_2	synthetic	290	Catts and Langmuir, 1986
Birnessite	δ - MnO_2	synthetic	300	Healy, 1966
Mn oxides and oxyhydroxides	various	not mentioned	5-360	Sparks, 2005

Table 4 Specific Surface Area data collected from literature, focusing on manganese oxides.

characteristics of todorokite in ion exchange, specific surface area, thermal stability and molecule-sized tunnels (microporosity), it has many potential industrial applications as molecular sieves, lithium-manganese-oxide cathode materials, heterogeneous catalysts and electrochemical sensors, and it also plays an important role in cleaning up natural water and controlling the concentrations of heavy metals in soil.

1.3.4 Todorokite from the Montenegro Mine, Cuba

A todorokite natural specimen from the Montenegro Mine, Cuba has been examined using several analytical techniques by Godelitsas et al. (1999). The specific surface area (SSA), measured by means of N_2 BET method ranged from 25 m^2/g to 59 m^2/g . The maximum SAS value gave additional information on the porosity of the material, with

a tendency to mesoporosity (containing pores with diameter > 20 Å), or even microporosity with rather complicated (the so called "bottleneck") type of pores.

1.4 Environmental Aspects

Mn is one of the first elements released during weathering of primary minerals, which explains its common accumulation in saprolites. Most of the Mn oxides found in surface environments are compounds of Mn(IV) with some Mn(III) (Kampf et al., 2000).

In Latin America the environmental problem of ground and surface water contamination from geogenic arsenic, which is of the same magnitude as in SE Asia, has been attenuated using Mn oxides, converting the As-rich residue of the process to non-toxic waste (Bundschuh et al., 2010). Mn(III) and Mn(IV) oxide phases constitute some of the strongest oxidants found in the environment as they interfere with the reduced forms of other metals, such as Se, As and Cr affecting their availability via oxidative precipitation and solubilization (Tebo et al., 2004; and references therein). As for Cr, the oxidation of Cr(III) to Cr(VI) is sped up when manganese oxides are present (Ivarsson et al., 2011). Additionally they serve as strong oxidants for metalloids, for example, with a fungal Mn oxide present, metal cations as Zn(II) and Mn(II) influence the rate of As(III) oxidation, plus the sorption of resultant As(V) onto biogenic Mn oxides (Miyata et al., 2007).

Natural bacterial Mn-oxides nanoparticles and grain coatings are ubiquitous in the environment (met at a variety of geological settings, such as marine and terrestrial environments) and thoroughly impact the water quality and quality of sediments through their ability to degrade several categories of contaminants (toxic organic contaminants, including aromatic hydrocarbons) and sequester contaminants, apart from participating in nutrient and carbon cycling in the environment (Webb et al., 2005a, b). Their high sorptive capacities for many metal ions allow them to wield considerable influence on trace metal speciation, even when present as minor component of the host rock (Tebo et al., 2004; and references therein). The presence of only tiny amounts (e.g., a fraction of a weight percent of soil or sediment) of Mn oxide minerals might be enough to control distribution of heavy metals between earth materials and associated aqueous systems. Sequestration of dissolved heavy metals during Mn oxide biogenesis is believed to be a key mechanism for attenuation of contaminants in polluted waters (Webb et al., 2005b).

Bacteriogenic Mn oxides can strongly bind metal cations possessing coordination geometries as diverse as Zn(II), Pb(II) and U(VI) and this underscores their exceptional qualities as adsorbents (Spiro et al., 2010).

Mn oxides also play a role in the circulation of heavy metals and radionuclides in the geosphere (Katrana et al., 2004; and references therein).

Mn is not listed as health threatening metal (Adriano, 2001). On the other hand, Mn is an important trace nutrient, 'micronutrient' with respect to plants (among B, Cu, Fe, Zn, and Mo) (Sparks, 2005), required for a large number of cellular function (Tebo et al., 2005).

Heavy metal adsorption by biogenic iron and manganese oxides can be used not only in bioremediation, but also in geochemical exploration targeting metal anomalies in soils and sediments (Mann, 2010). Bioremediation is termed as the use of biological agents, such as bacteria or plants, to remove or immobilize contaminants in polluted soil or water (Elements, 2012). Additionally are needed a couple of more terms: BCM and BIM. BCM stands for biologically controlled mineralization and BIM, biologically induced mineralization. Briefly, in BCM, the nucleation and growth of crystals are genetically controlled by microbes; a typical example is magnetite in magnetosomes produced by magnetotactic bacteria, other examples include carbonates, phosphates, and silica in marine animals. In BIM, mineralization is not genetically controlled and occurs as a result of changes in microenvironments through microbial metabolism. Such examples include: clay minerals, (hydr)oxides, sulfides, carbonates and phosphates. Using the metabolic pathways indicated by microbes through redox reactions, the mobility of pollutants is influenced (Dong and Lu, 2012; and references therein). Bioremediation, as in the use of biological agents, such as bacteria or plants, to remove or immobilize contaminants in polluted soil or water (Elements, 2012). As Dong and Lu (2012) summarize, irrespective of the processes of mineral-microbe interactions are ancient or modern, microbial activity can cause significant changes in the mobility of heavy metals and radionuclides, which can result in the formation of metal deposits over geologic time or the immobilization of metals in modern contaminated sites.

The challenge for bioremediation is designing a system that is able to withstand natural variability, for example, storm events that can increase flow rates (overall metal loading) and potentially increase metal concentrations, but for bioremediation to work, new biomass must be produced to replace the cells that are lost (Southam, 2012). Using Mn oxides properties bioremediation can be backed-up, i.e. todorokite may incorporate water molecules or cations into the vacant spaces of its tunnel-structure (Post, 1999).

1.5 Applications

Besides the potential for the aforementioned biotechnological applications, Mn oxides offer potential for special industrial applications, as well. Todorokite is a Mn oxide with exclusive physicochemical properties, which due to its analogy to zeolites has attracted attention as a possible heterogeneous catalyst, concisely some examples of its industrial uses include the decomposition of H_2O_2 , the reduction of nitrogen oxides, desulfurization of topped petroleum crude in the presence of hydrogen (Katranas et al., 2004; and references therein), carbon monoxide, methane, butane catalytic oxidation (Shen et al., 1993; and references therein). It is suggested by Godelitsas et al. (1999) that more research concerning natural todorokite ought to be conducted as it is more valuable for specific applications rather than a common Mn ore. Al-Sagheer and Zaki (2004) suggest synthetic todorokite Mn(IV) Mn-oxides as shape selective oxidation catalysts with BET surface area 19-44 m^2/g .

Katranas et al. (2004) have shown that H-Todorokite exhibits lower amount of metal content, larger surface area and enhanced solid acid properties in comparison with its precursor (natural todorokite from Montenegro mine, Cuba). Both natural todorokite from Cuba and H-Todorokite have been used as catalysts and natural todorokite is effective in dehydrogenation, while H-todorokite proved better than a commercially available catalyst, suggesting that H-Todorokite could be a catalyst for the cracking of small alkanes. Both synthetic todorokites and their natural counterparts participate in cyclohexane functionalization (Wang et al., 1998), and ethanol dehydrogenation (Zhou et al., 1998). Last but not least, Mn oxides (todorokite) have been found to interact with actinides and to have the ability to remove them from solution (Misaelides et al., 2002).

It is notable to mention at this point, that synthetic Mn oxides can be produced, having certain specifications in order to serve a specific purpose, in the same way it is applied for zeolites. For example, Ali et al. (2001; 2002; and references therein), believe the synthetic tunnel-structured Mn(IV) oxides (cryptomelane, nsutite and todorokite-type) that they have produced, have accessible structural tunnels at their surface and that shape-selective oxidation catalysis may be attained at these surfaces, noting that structural tunnels can be possibly formed at various dimensions, from 1x1 to 3x3, (Ching et al., 1999).

Shen et al. (1993) have proposed electrochemical devices as a possible application area for synthetic manganese oxides such as OMS-1 (Octahedral Molecular Sieve, which resembles todorokite). OMS-1 and OL (Octahedral Layers, referring to birnessite) have unique properties of excellent semiconductivity and porosity, which is not a usual combination in materials, not to mention that conductivity is both ionic and electrical (Suib, 2008). Other synthetic manganese oxides showing adsorptive and catalytic properties are MOMs, an abbreviation for manganese oxide mesoporous systems, developed by Tian et al. (1997). A 2x2 synthetic cryptomelane is abbreviated as OMS-2. OMS-2 when treated with acid catalyzes the selective oxidation of alcohols to aldehydes. The rate of ion exchange in thin films of OMS-2 was boosted and the explanation given was the interconnection of mesopores and micropores (Suib, 2008; and references therein). OMS-2 has been efficiently tested for water oxidation, apart from amorphous manganese oxides and OL, which are known to be suitable (Iyer et al., 2012; and references therein).

Finally, todorokite can be used in lithium-manganese cathode materials and sensors (Suib, 2008; Zhao et al., 2015).

2. Scope

The scope of the current study is to characterize natural Mn oxides from Cape Vani in terms of their specific surface area and porosity as materials in order to decipher their suitability for environmental applications.

Towards this scope, the main objectives are:

- o The mineralogical study of natural Mn oxides using reflected and transmitted light microscopy.
- o Measurement of specific surface area and porosity of natural Mn oxides using the N₂ BET method.

My research hypothesis is to check the suitability of Cape Vani natural Mn oxide material in terms of specific surface area and porosity for environmental and/or technological applications.

Thus I apply the N₂ BET method, reflected and transmitted light microscopy to Mn oxides from Cape Vani, Milos Island.

3. Geology

3.1 General Geology

Milos Island, Southern Cyclades, belongs to the Hellenic Volcanic Arc (HVA), which starting in Methana peninsula (Eastern Peloponnese) includes the following subaerial and submarine (SSB) volcanoes: Sousaki, Aegina, Milos, Santorini, Kolumbo (SSB), Kos, Nisyros, Yali. Among these areas, separate groups can be distinguished. According to Nomikou et al. (2013) i) the Paphsanias submarine volcano in the Methana group, ii) three volcanic domes to the east of Antimilos Volcano and hydrothermal activity in southeast Milos, iii) three volcanic domes east of Christiana and a chain of about twenty volcanic domes and craters in the Kolumbo zone northeast of Santorini in the Santorini group, and iv) several volcanic domes and a volcanic caldera together with very deep slopes of several volcanic islands in the Nisyros group. Additionally, the HVA has migrated southwards, following the geodynamic evolution of the Hellenic orogenic arc (Royden and Papanikolaou, 2011). The current position of the HVA can be seen in Figure 7 (inset), accompanied by a geological map of Milos, where the exact location of Cape Vani is marked with a red frame.

3.2 Local Geology – Cape Vani geological setting

The Cape Vani Mn deposit is located in the NW extremity of Milos Island, a recently emergent (<2Ma) volcano of the active HVA, that is characterized by volcanism and geothermal activity occurring through thinned pre-Alpine to Quaternary continental crust, within a local transtensional to extensional tectonic regime (Kilias et al., 2013). Milos comprises an Upper Pliocene to Pleistocene compositionally and texturally diverse succession of calc-alkaline volcanic and volcanic-sedimentary rocks that record a transition from a relatively shallow submarine setting to subaerial one (Stewart and McPhie, 2006; and references therein). Calc-alkaline volcanic activity in Milos overlies

Neogene carbonate sedimentary successions and has evolved in four phases from Middle to Late Pliocene (3.5-2.7 Ma) to Late Pleistocene (<0.08 Ma) (Stewart and McPhie, 2006; and references therein). Extensional tectonics of Miocene to Pliocene resulted in a tectonic regime comprised of four main fault sets trending NW, N, NE,

and E, which created a series of horsts and grabens and has led the volcanic and hydrothermal activity of Milos (Alfieris et al., 2013).

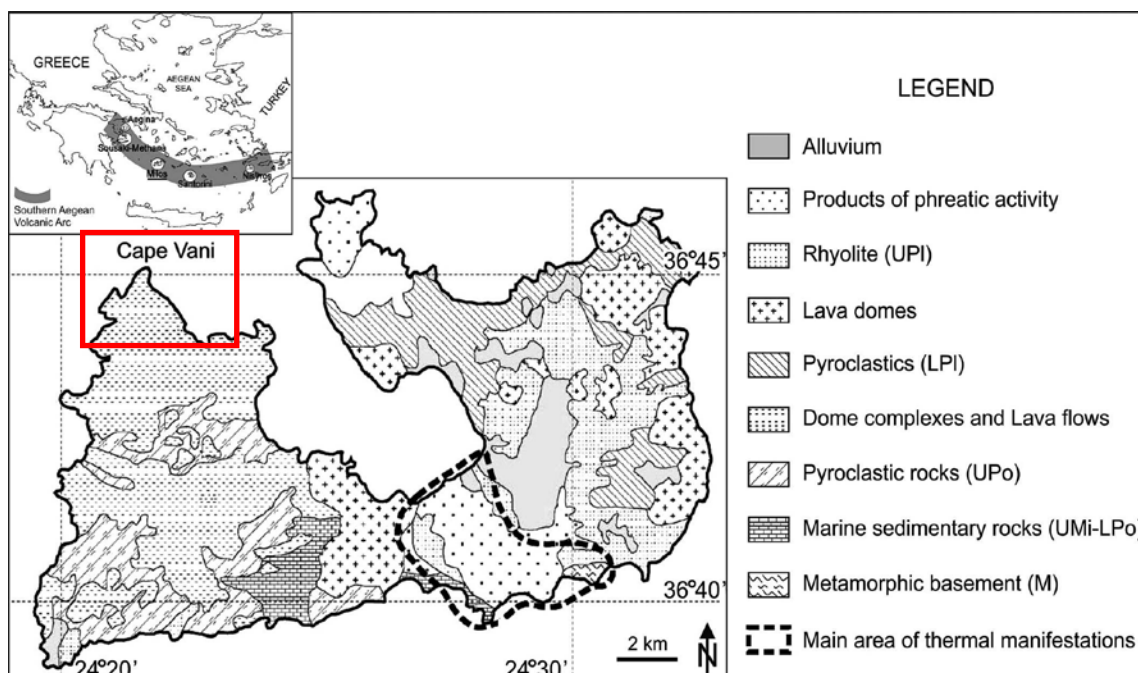


Figure 7 Geological map of Milos Island and South Aegean volcanic arc (inset). The inset shows volcanic centres along the Hellenic Volcanic Arc. The geological map shows both the location of Cape Vani Mn oxide ore-deposit and main geological features in Milos. UPI – Upper Pleistocene; LPI – Lower Pleistocene; UPo – Upper Pliocene; LPo – Lower Pliocene; UMi – Upper Miocene; M – Mesozoic, modified after Fytikas et al. (1986).

3.3 Geothermal activity and mineralization in Vani

The Milos geothermal activity is ~2 Ma (Stewart and McPhie, 2006). It is currently comprised of a shallow-marine to subaerial hydrothermal-vent system, which is also the largest of its kind described to date (Dando et al., 1995; Valsami-Jones et al., 2005; Wu et al., 2011). Extinct geothermal systems, produced hybrid polymetallic volcanic-hosted massive sulfide (VMS) and continental epithermal mineralization of Late Pliocene to Early Pleistocene age, which were controlled by magmatic heat, while the water origin was mixed (sea, meteoric and magmatic) (Kilias et al., 2001; Naden et al., 2005; Alfieris et al., 2013).

3.4 The Cape Vani Mn ore-deposit

Cape Vani operated as a Mn mine from 1886 and 1909 (220,000 tons of Mn) and 1916 to 1928 (Plimer, 2000). The deposit covers a surface of 1km², containing an inferred resource of 2.1 million tons with mean composition: 14.6% Mn, 12.8% BaSO₄, 62% SiO₂, 7.5% Fe₂O₃ (Liakopoulos et al., 2001; Kilias et al., 2017 ; and references therein). Its occurrence is within a 2.38±0.1 Myr old restricted intravolcanic marine rift basin, an inner shallow sea marginal to an andesite/dacite continental shelf. The basin is filled with >60m-thick volcanoclastic-pyroclastic sediments comprising Upper Pliocene to Lower Pleistocene sandstones/sandy tuffs, which host the Mn ore, and have been

shaped by episodic dacite volcanism, syndepositional rifting/faulting, deepening, tectonic uplift and emergence to 35 meters above sea level (Kilias et al., 2017; and references therein).

Siliciclastic host sediments were deposited in a shallow-marine/tidal-flat paleoenvironment (Kilias (2011), they are locally overprinted by a silica-K-feldspar-illite-barite assemblage due to hydrothermal diagenesis (Liakopoulos et al., 2001; Kilias, 2011; Kilias et al., 2017). The Mn oxide deposits exhibit a range of ore styles that in fact constitute Mn mineralized microbially induced sedimentary structures, often referred to with the abbreviation of 'MISS' (Noffke et al., 2001; Noffke, 2010; Kilias, 2011).

Mn mineralized (typically 2-3 wt% Mn) barite±silica-rich hydrothermal veins occur throughout the mineralized stratigraphy. Bedding-conformable barite (±Mn oxide, silica)-rich horizons underlain by discordant mineralogically similar pipe-like bodies occur locally within the sediments (Kilias, 2011). Where the veins meet the palaeosurface they project to white smoker-like chimney structures. In addition, discordant epithermal-like quartz-barite(±Mn oxide) stringer veins occur below the mineralized sediments within dacite/andesite basement (Kilias, 2011). Figures 7 and 8 provide a terrain map of Cape Vani and a stratigraphic column respectively (Kilias et al., 2017).

Whole rock geochemical data shows that the Mn-ores are enriched in K, Na, Mg, Ca, Al, Ti, Fe, Zr, Nb, Ce, Hf, and Th, and Ba, Pb, Zn, As, Sb, and W metal, whereas REE patterns are characterized negative Ce anomalies and positive Eu anomalies (Kilias et al., 2017; and references therein). The Mn oxide mineralogy include PXRD-poorly crystalline δ -MnO₂, pyrolusite, ramsdellite, cryptomelane-hollandite-coronadite, and in a lesser degree romancheite, jacobsonite, franklinite and hydrohetaerolite (Hein et al., 2000; Liakopoulos et al., 2001; Kilias et al., 2007; Kilias, 2011; Kilias et al., 2017 ; and references therein). Finally, Liakopoulos et al. (2001) mention also arseniosiderite, haematite, and traces of galena, pyrite and sphalerite.

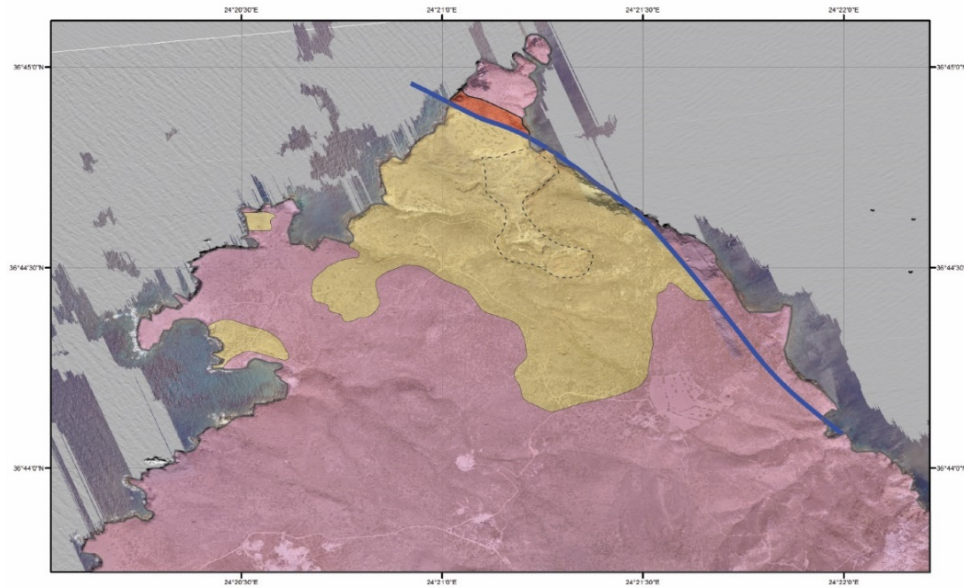


Figure 8 Cape Vani terrain map. The terrain map depicts the layout of volcaniclastic sandstones/sandy tuffs (light brown shaded area) that are nested by submarine dacitic/andesitic lava domes. Red area indicates rhyolite intrusives on a faulted contact (blue line) with the lavas. The geology has been overlain on an aerial photograph (Kilias et al., 2016). The area is a magnification of the Inset in Figure 7.

Lastly, recently a microbial iron banded rock formation in Cape Vani has been considered an analogue of Precambrian BIFs, both chemically and texturally (Chi Fru et al., 2013; Chi Fru et al., 2015).

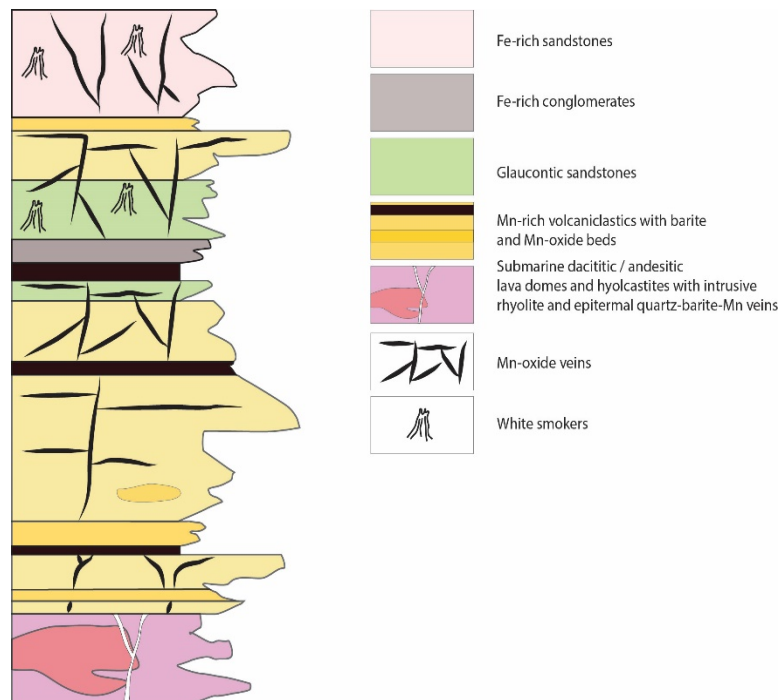


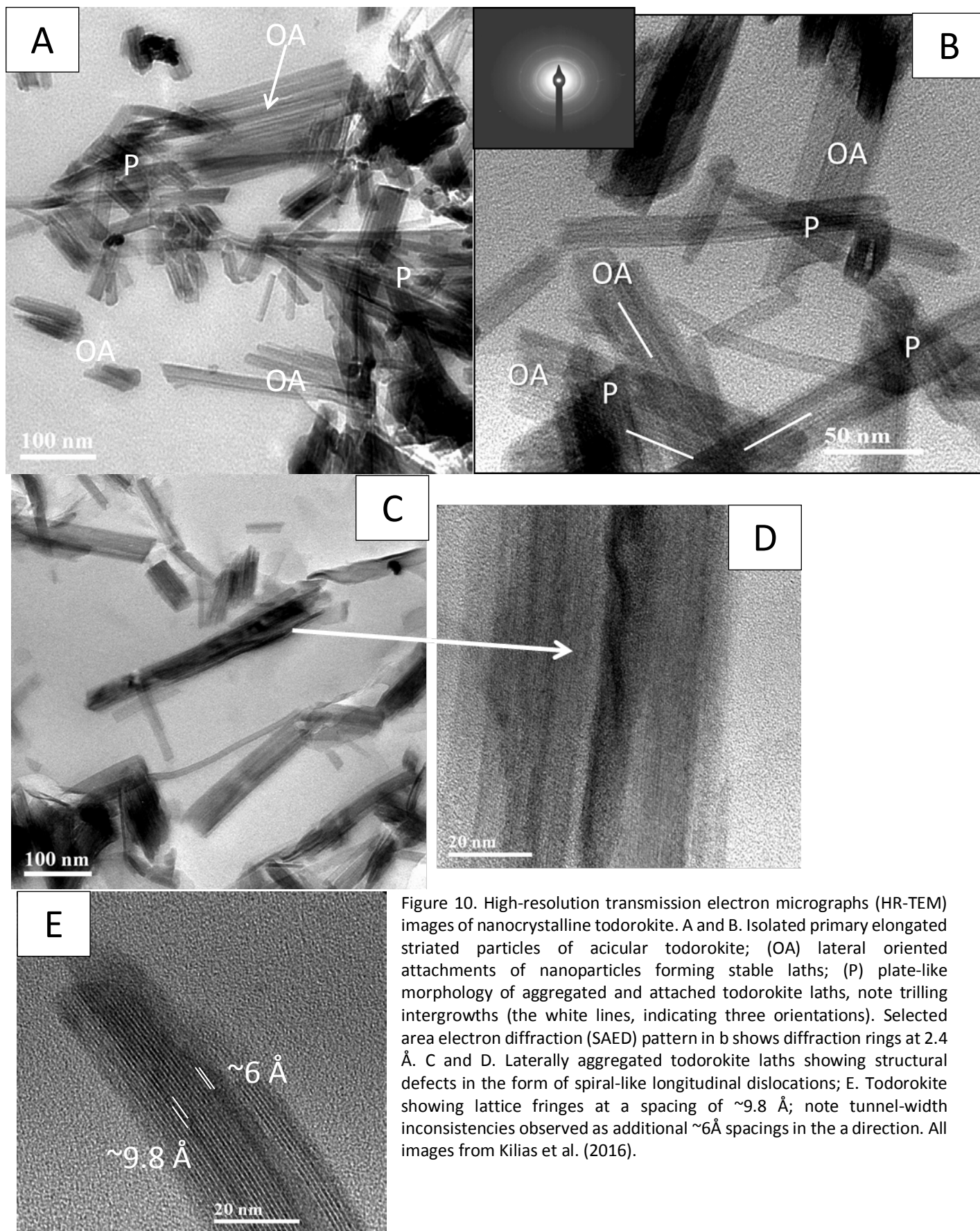
Figure 9 Cape Vani stratigraphic column. Lithostratigraphic relationships of Cape Vani Mn ore-deposit, modified after Kilias (2011).

4. Previous work

Focusing on manganese mineralization in Cape Vani, Hein et al. (2000) report that manganese-cemented volcanoclastic sandstone beds contain up to 60% MnO. Mn oxide cement is as a rule massive and mottled. The second generation cement, which is partly an alteration of first-generation cement and partly replaces first generation cement consisting of pyrolusite, ramsdellite, hollandite (and/or coronadite) and other minor Mn oxide phases. Mn oxides contain replaced shells, which exhibit little preservation of infrastructure, maintaining only their external form. Also the mineralization had been thought to have taken place along bedding planes and in porous, permeable volcanoclastic sandstone layers. Liakopoulos et al. (2001) have identified two generations of Mn oxides, the first comprised of pyrolusite and ramsdellite and the second comprised of cryptomelane-hollandite-coronadite plus hydrohetaerolite, delineated by high concentrations of K, Ba, Pb, and Zn respectively. It has been inferred that the Mn oxide minerals above are the product of a two-stage process, in which a second hydrothermal fluid of high salinity is responsible for the enrichment in Ba, Pb and Zn, which originated from the dissolution of sulphide minerals. In spite of Hein et al. (2000) position that no bacterial mats, mounds and chimneys were observed in Cape Vani, Kiliass et al. (2007) provide the first evidence of at least partial biogenicity in Cape Vani by finding Mn oxides pseudomorphically replacing spherical cell-like structures and branching filamentous constructions, plus silicified consortia of spherical, filamentous, sheathed, septate and spiral fossilized photosynthetic cyanobacteria in quartz. On top of that, the same researchers have found with XRD and EMD analyses amorphous hollandite group Mn oxide phases, vernadite, recorded also by Hein et al. (2000). Lastly todorokite has been identified by HR-TEM (Kiliass et al., 2016), a mineral of high-value for industrial/environmental applications (see below), and of inferred biological origin (Tebo et al., 2004; and references therein). Additionally to the evidence of Mn oxide biomineralization by Kiliass et al. (2007), microbial mat-related sedimentary structures (MISS) have been identified in Cape Vani (abandoned open pit mine premises) including: 1) mat-layer structures, 2) growth bedding structures and nodules, 3) wrinkle structures and exfoliating sand laminae, 4) cracks with upturned and curled margins, 5) roll-up structures, 6) fossil gas domes, 7) mat fragments and chips, and 8) mat slump structures, which further assist the notion of biomineralization in Cape Vani; however, it is unclear whether structures 1-8 were constructed by in situ photoautotrophic bacteria or cyanobacteria (Kiliass, 2011). It is also notable that in Cape Vani barite is ubiquitous (from host sediments to mat related structures etc), which suggests that microbial mats were associated with white smokers, which have functioned as the Mn(II) suppliers; Mn(IV) mineralization has been considered syngenetic and syngenetic (Kiliass, 2011). Further study by Kiliass et al. (2017; in review) using other techniques (EPR study on Mn oxides, lipid biomarker analysis, pure strain isolation from modern sediments (*Bacillus* species), carbon isotopes and oxygen isotopes of Mn oxides) to conclude that Mn oxides (todorokite, hollandite, manjiroite) have evolved from biogenic Mn oxide precursors, whose alteration via ageing and diagenesis is suggested to explain the crystallinity of Mn oxides which composed the Mn ore

deposit. HR-TEM analysis has shown that todorokite from Cape Vani is nanocrystalline, forming stable laths (Figure 10A), plate-like morphology of aggregated and attached todorokite laths plus trilling intergrowths (Figure 10B), structural defects in the form of spiral-like longitudinal dislocations (Fig. 10 C,D) and lattice fringes at a spacing of $\sim 9.8\text{\AA}$; also tunnel-width inconsistencies are observed as $\sim 6\text{\AA}$ spacings in the a direction (Figure 10E).

Lastly, a most recent study (Papavassiliou et al., 2017) compares Cape Vani manganese deposit to hydrothermal manganese deposit in Aspro Gialoudi, describing Aspro Gialoudi as the deepest part of Cape Vani. These two deposits are found alike in terms of geology, mineralogy and geochemistry (formed almost contemporaneously between 2.18 and 1.44 Ma, etc.) according to the same authors.



5. Materials and Methods

5.1 Sampling

Fieldwork and sampling took place during several consecutive field seasons between 2004 and 2014. The volcanoclastic sandstones consist of grains of K-feldspar, altered volcanic rock fragments, volcanic glass, barite and insignificant quartz and clay minerals. In order to minimize the effect of volcanoclastic grains to N₂ BET surface area measurements, analyzed samples were carefully selected to represent the most advanced mineralized and relatively pure Mn oxide samples that contained only scarce volcanoclastic grains.

5.2 Sample Preparations

The Mn oxide samples have been powdered in an agate mortar (mem approximately 20µm).

5.3. Specific surface area

The bulk powder (sample mass approximately 0.18g) was measured in order to determine the specific surface area and porosity of Mn oxides from Cape Vani, by nitrogen sorption isothermally at 77K using a Sorptomatic 1900 instrument. Prior to the determination of the sorption isotherms the sample was degassed for 3h at different temperatures (150, 250, 350 and 450°C) under a 1x10⁶ mbar vacuum. This was done in order to test the effect of pretreatment temperature on the surface area and porosity of the material.

5.4 Microscopy

Thin section of the Mn oxide material from Cape Vani has been studied using an optical microscope (reflected and transmitted light).

6. Results

6.1 Mineralogy and Mn oxide textures

The Cape Vani manganese deposit is comprised of manganese oxides which cement the volcanoclastic sandstone. Manganese oxides exhibit laminated texture (Fig. 11 A & B) and cement the volcanoclastic detritus (Figure 11 A,B,C,D), which can be grain-supported (Figure 11 A,B,C) or (locally) cement-supported (Figure 11 D). The laminae often are wavy (Figure 11 A,B) and their thickness varies, their boundaries can often be gradually diffuse (either on a single or both sides of the lamina). Manganese oxides may replace possible microfossil relics (Figure 11 C), which cannot be identified. K-feldspars are common in the volcanoclastic detritus, as well as spongy texture (Figure 11 D). Some parts of Mn oxides are well-crystallized, forming typical pyrolusite cores (Figure 11 E & F), which are surrounded by microcrystalline Mn oxides. Colloform banding of Mn oxides is also frequent (Figure 11 G & H), which occurs as open-space filling; pyrolusite is exclusively found at the centres of such open-space fillings, surrounded by microcrystalline Mn oxides overgrowing the colloform-banded Mn oxides which line the vug walls. Colloform-banding occurs at various scales (Figure 12

A, B & C), which engulf volcanoclastic detritus (Figure 12 B) and occur as rounded, closed, colloform assemblages (Figure 12 A), overgrown by Mn oxides cross-cutting fibrils. Cross-cutting fibrils are also found in central parts of wavy bands of microcrystalline Mn oxides (Figure 12 C). Mn oxides form an uncommon oval pattern, void in its centre (Figure 12 D). Mn oxides fill veinlets (Figure 12 E &F), microfossils can be seen below the veinlet, which as previously stated, cannot be identified. The fibrils develop perpendicular to the edge of massive Mn oxides and they cross-cut each other, they maintain this geometry, whether they surround, for example a colloform banding as in Figure 12 B or are surrounded by multiple wavy Mn oxide bands as in Figure 12 C. The porosity of these structures is high.

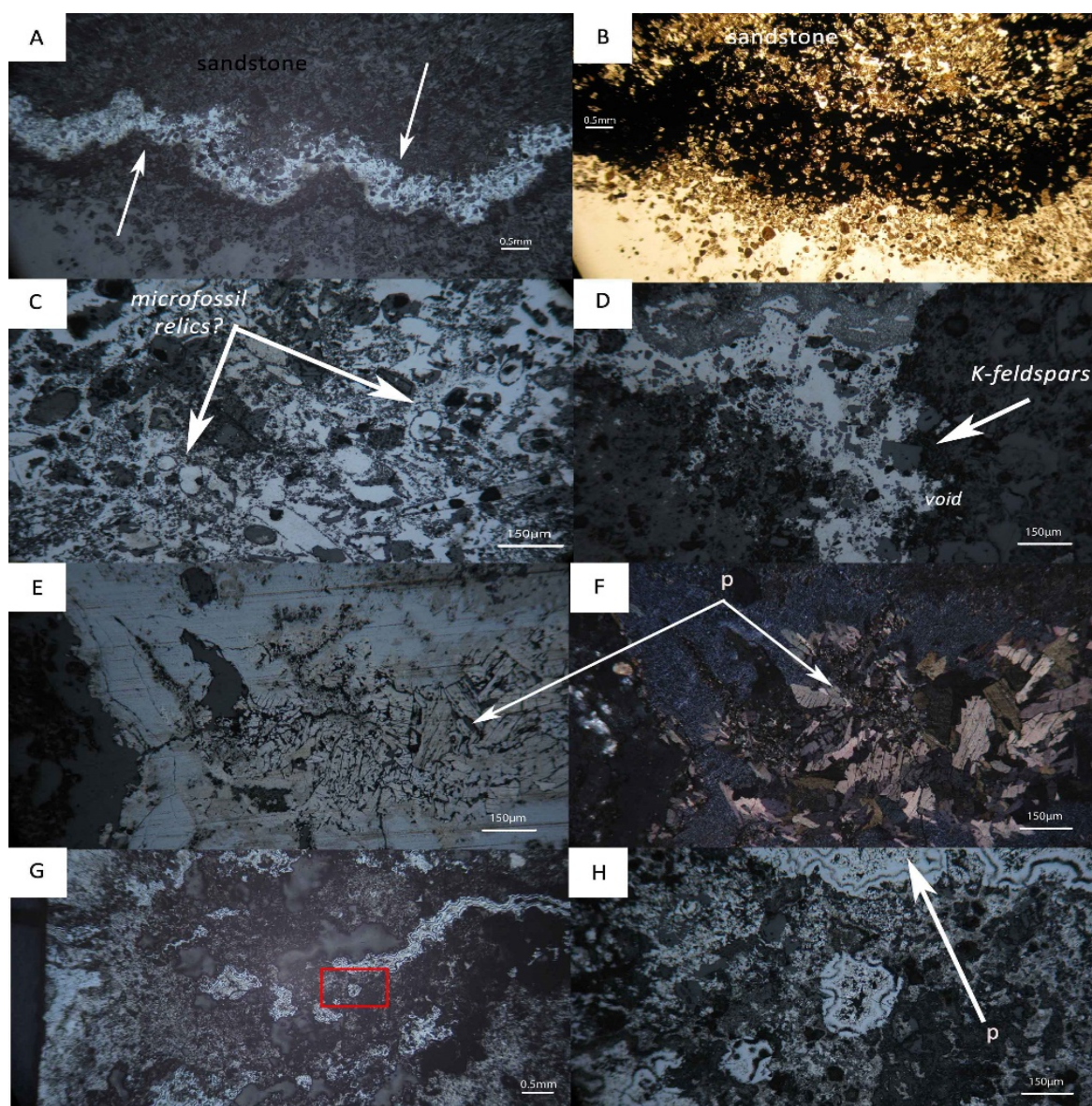


Figure 11 Reflected and transmitted microscopy, Mn oxides as cement. A. & B. Photomicrographs of laminated texture of Mn oxide cement-supported structures (A in reflected light and B in transmitted light). The white arrows point to the limits of the lamina (scale bar 0.5mm). C. Highly mineralized Mn sandstone/sandy layer with Mn oxide cement-supported texture, oval structures replaced by Mn oxide (microfossil relics?), reflected light settings, scale bar 150µm). D. Massive Mn oxides cementing volcaniclastic detritus (the dark grey angular clasts are K-feldspar). Around Mn oxides the texture is spongy (reflected light, scale bar 150µm). E. Massive crystalline pyrolusite (p) filling a vug; it overgrows thin wavy layers of microcrystalline Mn oxides (reflected light, scale 150µm). F. Same as A, pyrolusite anisotropy, high crystallinity degree (reflected light + crossed nicols, scale 150µm). G. & H. Thin colloform Mn oxide open space fillings; notespongy texture; H is a close up of G (reflected light, scale bar 0.5mm).

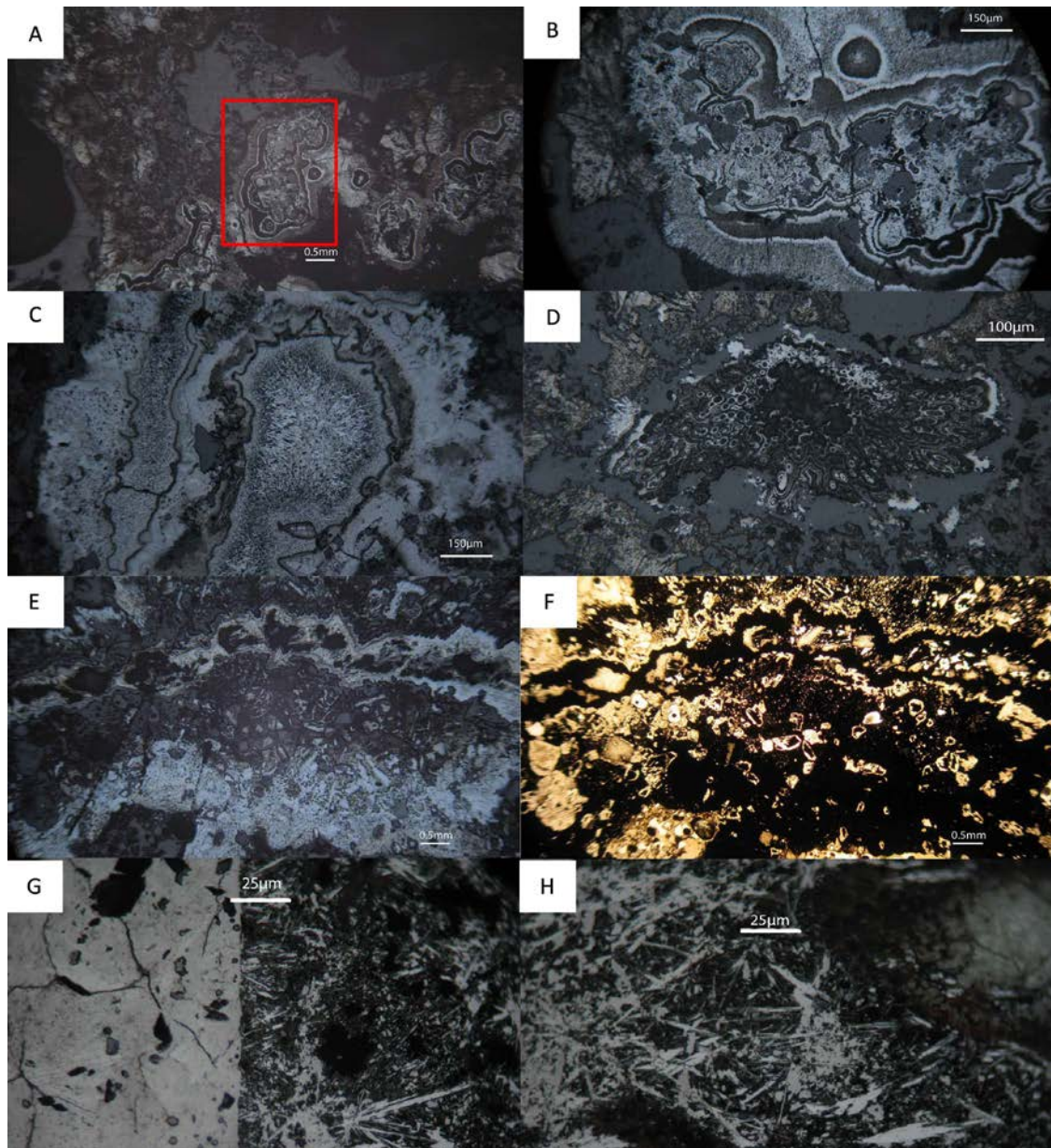


Figure 12 A, B: Colloform banded Mn oxides. A: RL, scale bar 0.5mm; B is a close-up of A (framed area). (RL, scale bar 150 μ m) C. Colloform banded Mn oxides filling a vug. The center of the vug is filled by crystalline pyrolusite needles.) (RL, scale bar 150 μ m). D. A Unique photomicrograph of possibly unidentified microfossils. The central part of the structure is vacant (a hole), around which are several eight-figure-shaped (and multiple-eight) microstructures, some of which are elongated to the right, some are almost perfect circles, others are more oval-like. The aforementioned structures seem to follow more or less some orientation (RL, scale bar 100 μ m) E. Mn oxides cement volcaniclastic detritus and former microfossils (relic outlines). A vein is also filled with Mn oxides (reflected light, scale bar 0.5mm). F. Same as in E, transmitted light settings. Microfossil relic outlines are better distinguished. G. & H. Close-ups of abrupt transition from massive Mn oxides to acicular, cross-cutting fibrils (reflected light, oil, scale bar 25 μ m).

6.2 Surface area, pore size and pore size distribution

Surface area is determined by the adsorption-desorption isotherms and the hysteresis loops shown in the Isotherm Linear Plots of Figure 13. (Quantity Adsorbed cm^3/g STP vs Relative Pressure (p/p_0)). Figure 13 illustrates the N_2 BET method of measuring surface area for from the Cape Vani Mn oxides samples. The shown adsorption-desorption isotherms match with type IV model, which indicates mesoporosity (8.78-16.84 nm, see Table 6), as mesoporosity is defined between 2 and 50 nm by IUPAC

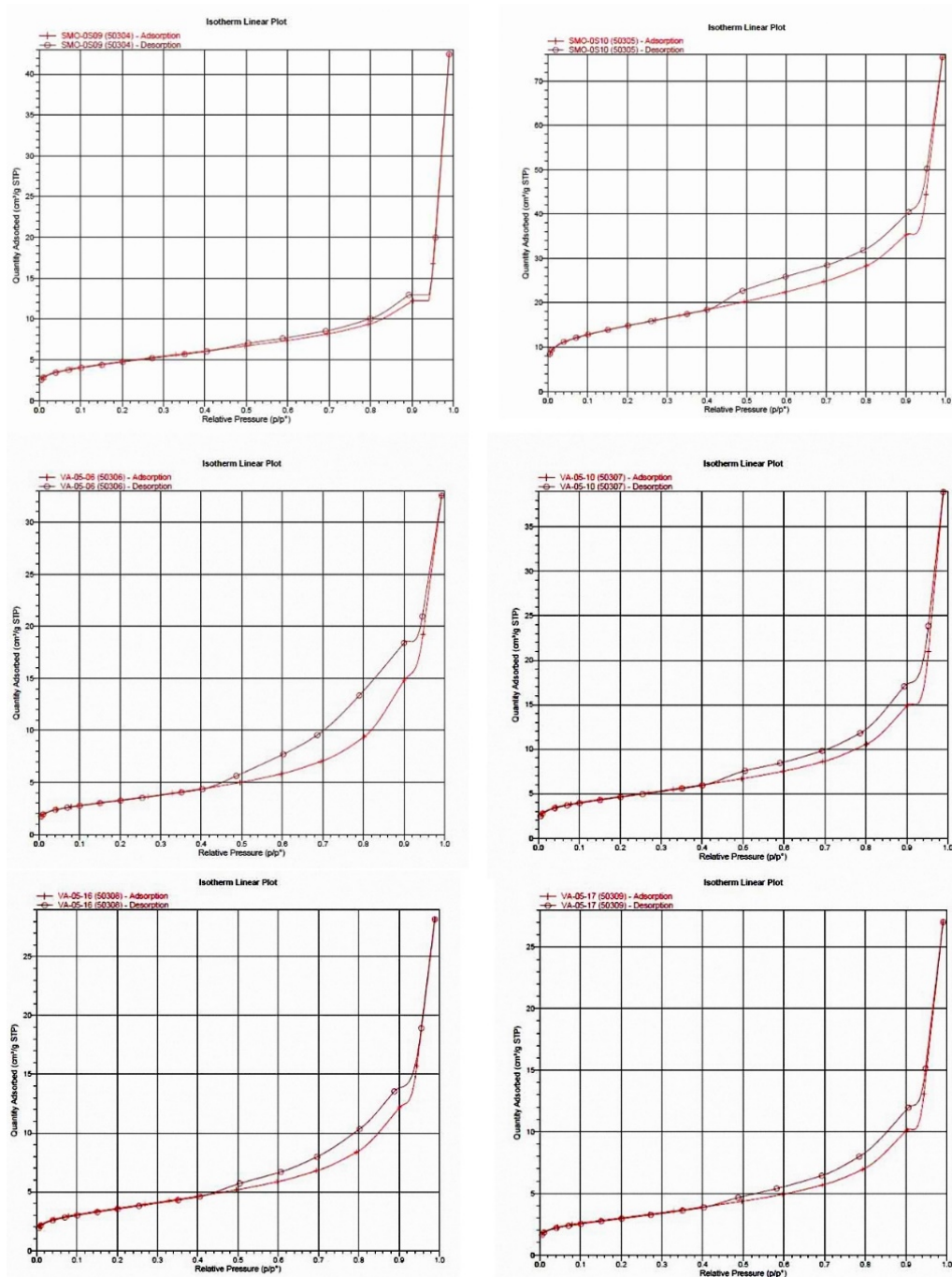


Figure 13 Nitrogen adsorption-desorption isotherms at 77K in respect to the investigated manganese oxide material from Cape Vani. The plots are type IV. The hysteresis loops (H3) of the plots indicate that the material in question is mesoporous; interpretation according to Condon (2006) and Leofanti (1998).

standard. Additionally, their corresponding hysteresis loops match with type H3, which indicates slit-like pores, according to template curves by Condon (2006) and Leofanti et al. (1998).

The specific surface area measured is determined by the above plots, and is summarized in Table 5 below.

Table 5 Specific Surface Area as measured with N₂ BET method in natural manganese oxide samples from Cape Vani.

Sample	Specific Surface Area (m²/g)
VA-05-17 (50309)	10.7695
VA-05-06	11.96
VA-05-16 (50308)	12.9974
VA-05-10 (50307)	16.2603
SMO-0S09	17.356
SMO-0S10	53.1284

The pore size measurements results are presented in Table 6.

Table 6 Pore size as measured with N₂ BET method in natural manganese oxide samples from Cape Vani.

Sample	Pore size (Å)	Pore size (nm)
SMO-0S10	87.7863	8.77863
VA-05-16 (50308)	134.1234	13.41234
VA-05-10 (50307)	143.3479	14.33479
SMO-0S09	151.3762	15.13762
VA-05-17 (50309)	155.2831	15.52831
VA-05-06	168.423	16.8423

The pore size distributions are presented in Figure 14 and Figure 15 (Figure 14 continued), where for each sample the adsorption and desorption isotherm data have been used.

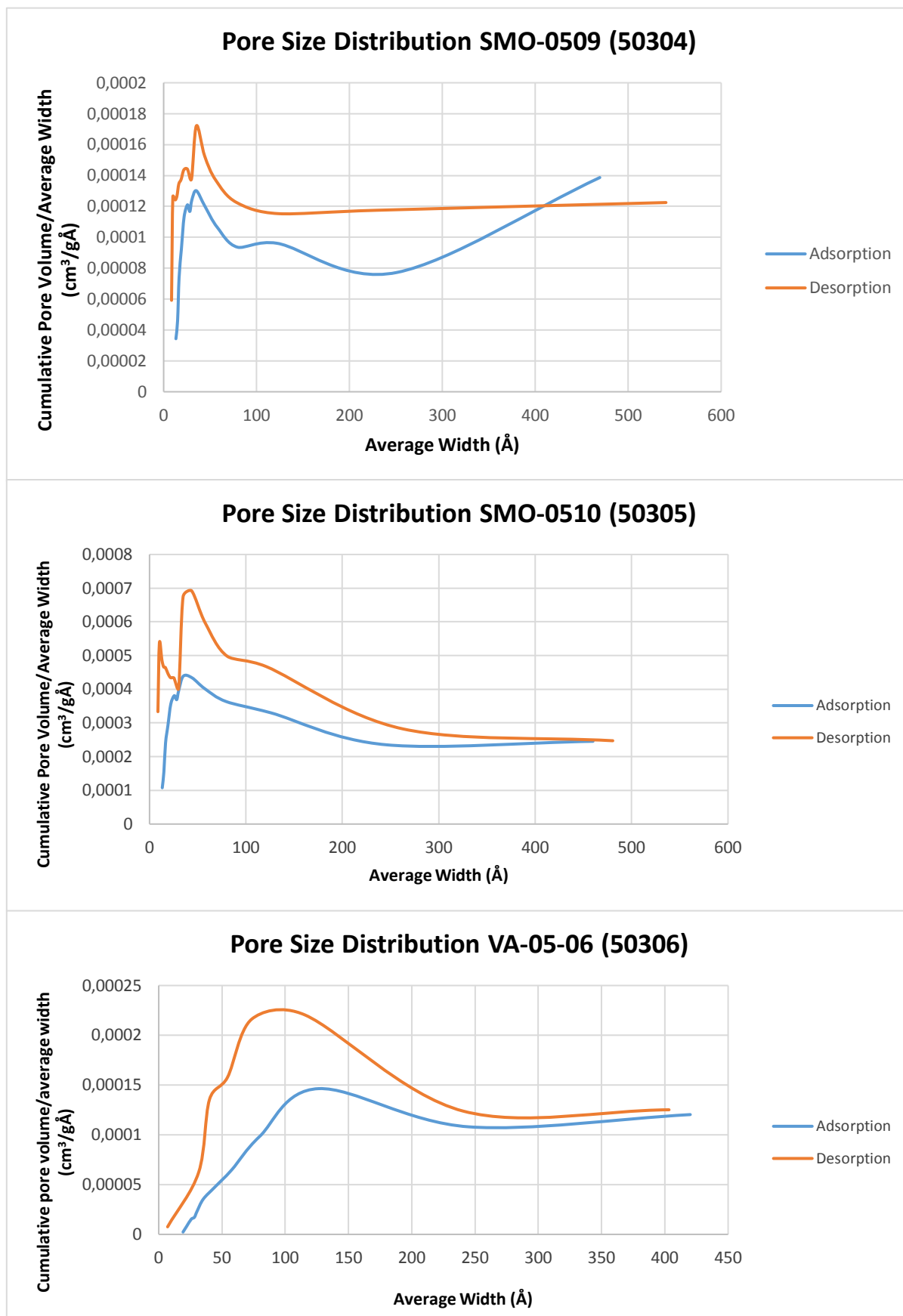


Figure 14 Pore size distribution (adsorption and desorption isotherm used) per sample.

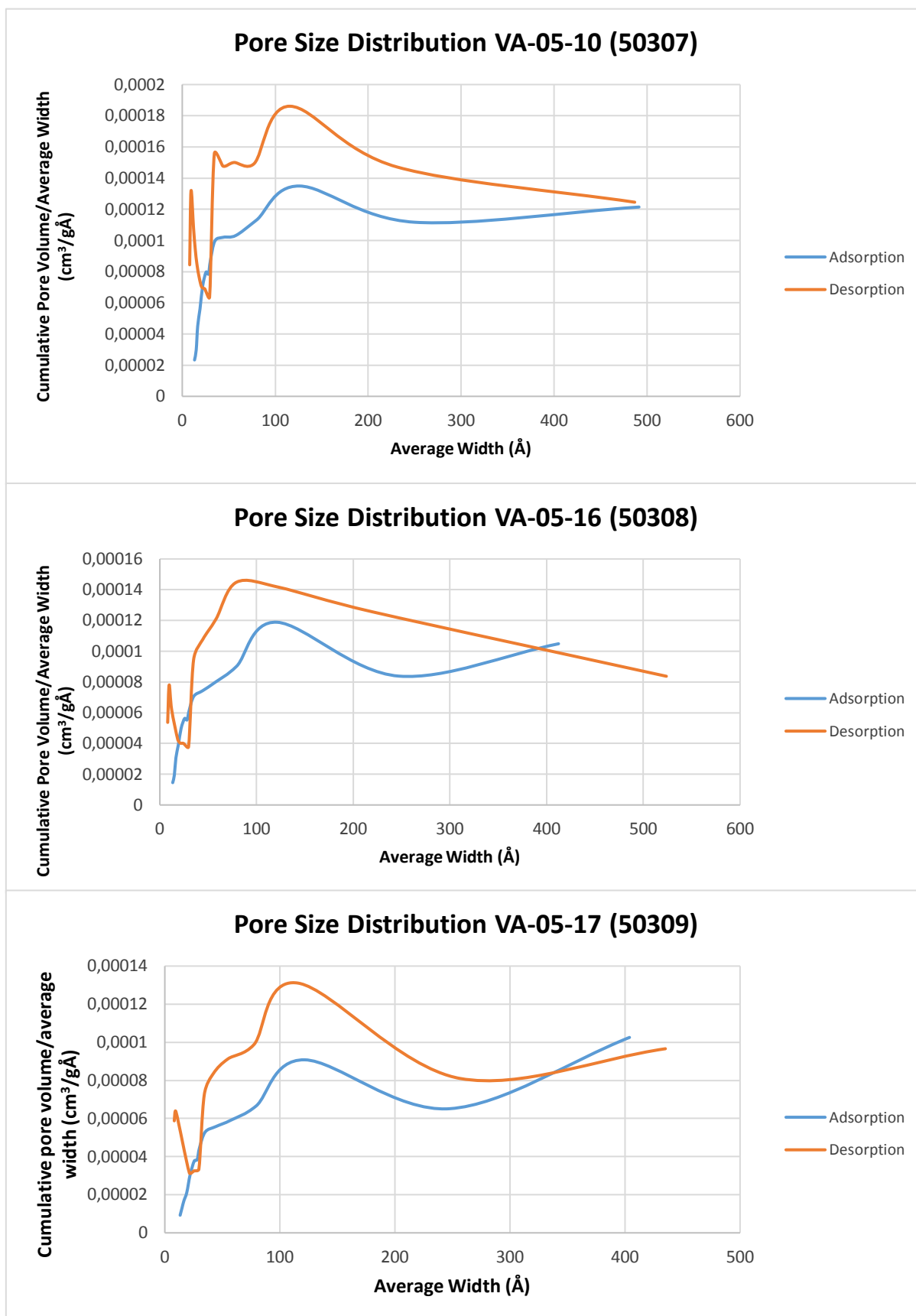


Figure 15 The continuation of Figure 14.

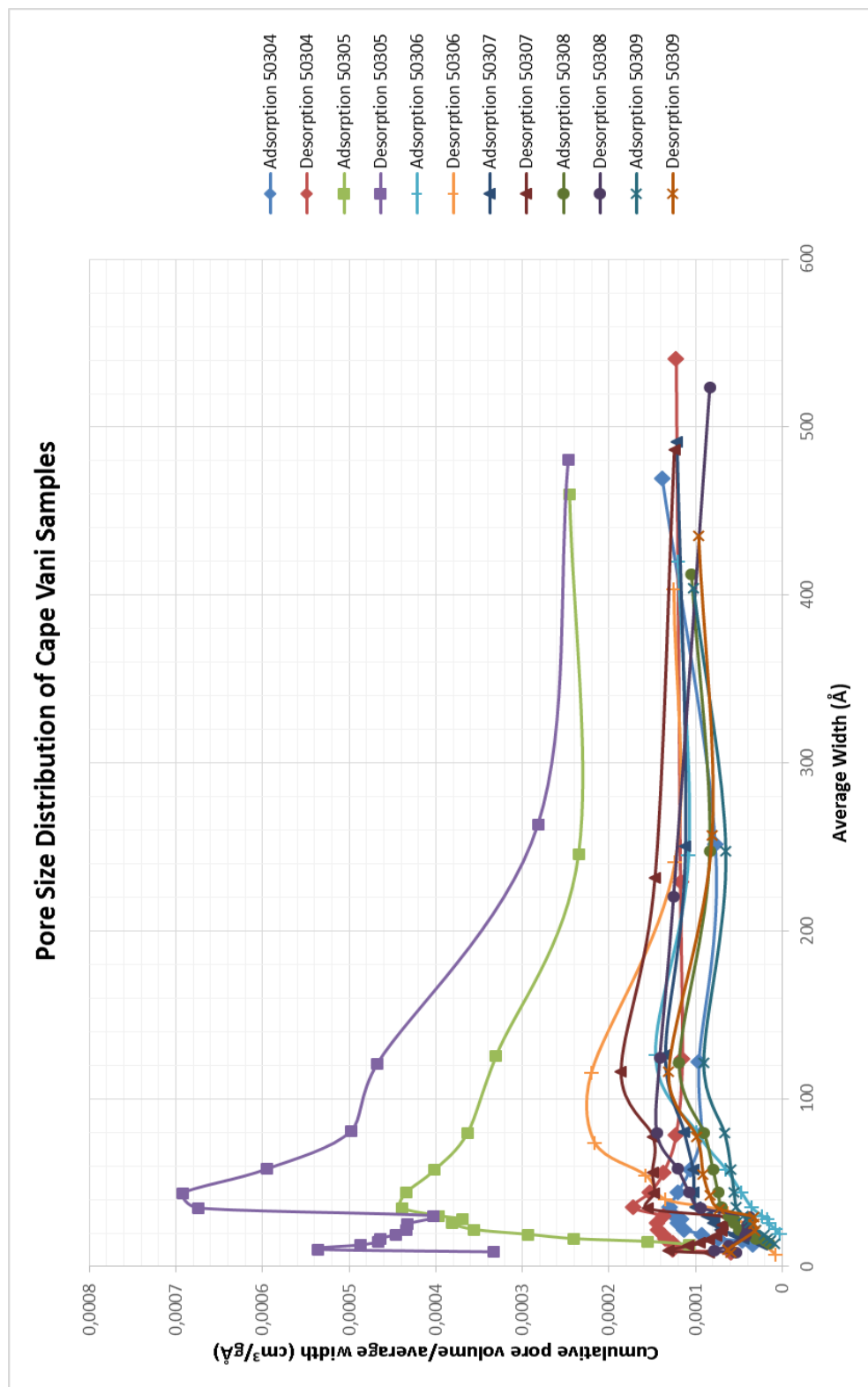


Figure 16 Pore size distribution based on both adsorption and desorption isotherm data of all investigated samples from Cape Vani.

Figure 16 is a synthesis of data from the previous figures (Figure 14 & Figure 15).

7. Discussion

The Cape Vani manganese oxide ore comprises natural Mn oxide precipitates containing intermixed other tunnel-structured Mn oxides (hollandite-cryptomelane-coronadite-manjiroite, pyrolusite, ramsdellite) (Liakopoulos et al., 2001; Kiliyas et al., 2017; and references therein) and predominant todorokite. Todorokite is the most remarkable phase among them due to its unique properties and promising technological applications (see section 1.5).

The N₂ BET method isotherms (Quantity Adsorbed (cm³/g) vs Relative Pressure p/p_0) (Figure 13) are of type IV (Sing, 1985; Leofanti et al., 1998; Condon, 2006), which reveals mesoporosity. The interpretation of the hysteresis loops, exhibited in the isotherm diagrams (not matching adsorption and desorption branches), are of type H3 and they indicate slit-shaped pores, non-rigid aggregates of plate-like particles (Trunschke, 2013; and references therein) and non-uniform size and shape (Leofanti et al., 1998).

Comparing current study's specific surface area measurements to literature (Table 7 and Figure 17). The SSA results of Cape Vani match better to naturally occurring specimens, Montenegro Mine, Cuba conducted by Godelitsas et al. (1999). Synthetic Mn oxides are developed in ideal conditions and therefore it is inevitable that they display much higher SSA values. Sparks (2005) gives a range 5-360m²/g without mentioning categories (tectomanganates, phyllomanganates, synthetic, natural, abiotic, biological). Shen et al. (1993) have produced a todorokite-like phase with a specific surface area of 180m²/g. But natural Mn oxides, as those from Cape Vani, are naturally occurring and undergo geological processes, such as diagenesis, which can alter their initial inferred properties.

The current thesis investigated the Mn oxides' properties from Cape Vani considering their potential technological/industrial or other special applications. Todorokite is a known catalyst (Katranas et al., 2004) and can be produced in the same fashion zeolites are, to serve specific industrial-technological needs (Al-Sagheer and Zaki, 2004). However, more research should be conducted focusing on Mn oxides from Cape Vani, to test the suitability in particular for each potential application, as Mn oxides have to be pure to be used (Suib, 2008). This knowledge could expand the application field.

	mineral/phases	Sample	sample type	BET Surface Area (m ² /g)	Reference
1	not mentioned	Crystalline β -phase MnO ₂ (Fisher)	synthetic	0,0048	Nelson et al., 1999
2	MnO ₂	β -MnO ₂	synthetic	0,3	Stobbe et al., 1999
3	Mn ₂ O ₃	α -Mn ₂ O ₃ hausmannite	synthetic	1	Stobbe et al., 1999
4	not mentioned	Crystalline powdered MnO ₂ (ICN)	synthetic	4,7	Nelson et al., 1999
5	Mn ₂ O ₄	α -Mn ₂ O ₄ hausmannite	synthetic	8	Stobbe et al., 1999
6	mixed Mn mineral phases	VA-05-17 (50309)	natural	10,7695	current study
7	mixed Mn mineral phases	VA-05-06 (50306)	natural	11,96	current study
8	mixed Mn mineral phases	VA-05-16 (50308)	natural	12,9974	current study
9	Birnessite	synthetic Mn Oxide - δ -MnO ₂	synthetic	15	Kanungo and Mahapatra, 1989
10	mixed Mn mineral phases	VA-05-10 (50307)	natural	16,2603	current study
11	mixed Mn mineral phases	SMO-0509 (50304)	natural	17,356	current study
12	Ni-Todorokite	Todorokite	synthetic	19	Al-Sagheer and Zaki, 2004
13	Cu-Todorokite	Todorokite	synthetic	25	Al-Sagheer and Zaki, 2004
14	Todorokite	Todorokite	natural	25	Godelitsas et al., 1999
15	Mn ₂ O ₃	α -Mn ₂ O ₃	synthetic	26	Stobbe et al., 1999
16	Todorokite	Todorokite	natural	37	Godelitsas et al., 1999
17	abiotic oxidation	Triclinic Na-Birnessite	synthetic	39	Villalobos et al., 2003
18	Todorokite	Todorokite	natural	39	Godelitsas et al., 1999
19	reduction of permanganate	Acid birnessite	synthetic	40,5	Villalobos et al., 2003
20	Mg-Todorokite	Todorokite	synthetic	44	Al-Sagheer and Zaki, 2004
21	Birnessite	synthetic Mn Oxide - δ -MnO ₂	synthetic	45	Burdige et al., 1992
22	mixed Mn mineral phases	SMO-0510 (50305)	natural	53,1284	current study
23	mixed Mn mineral phases	Fresh Mn oxide precipitate (abiotic)	synthetic	58	Nelson et al., 1999
24	Todorokite	Todorokite	natural	59	Godelitsas et al., 1999
25	Manganite	γ -MnOOH	synthetic	61	Friedrich et al., 2016
26	Birnessite	synthetic Mn Oxide - δ -MnO ₂	synthetic	74	Balistreri, 1982
27	<i>Pseudomonas putida</i> strain MnB1	Mn biooxide	biological	98	Villalobos et al., 2003
28	bulk Mn nodules	Mn nodules	natural	102	Bloethe et al., 2015
29	c-disordered birnessite	reflux product	synthetic	103,7	Atkins et al., 2014
30	Mg-phyllomanganate	reflux product	synthetic	104,9	Atkins et al., 2014
31	redox	δ -MnO ₂	synthetic	121	Villalobos et al., 2003
32	bulk Mn nodules	Mn nodules	natural	130	Bloethe et al., 2015
33	Birnessite	synthetic Mn Oxide - δ -MnO ₂	synthetic	137	Godtfredsen and Stone, 1994
34	OMS-1	todorokite-like	synthetic	140	Shen et al., 1993
35	reduction of permanganate	c-disordered H ⁺ -birnessite	synthetic	154	Villalobos et al., 2003
36	reduction of permanganate	δ -MnO ₂ vernadite	synthetic	155	Villalobos et al., 2003
37	Birnessite	synthetic Mn Oxide - δ -MnO ₂	synthetic	160	Loganathan and Bureau, 1973
38	OMS-1	todorokite-like	synthetic	180	Shen et al., 1993
39	<i>Leptothrix</i> -oxidized Mn	Biogenic Mn oxide	biological	224	Nelson et al., 1999
40	Birnessite	synthetic Mn Oxide - δ -MnO ₂	synthetic	263	Murray, 1974
41	Birnessite	synthetic Mn Oxide - δ -MnO ₂	synthetic	290	Catts and Langmuir, 1986
42	δ -MnO ₂	δ -MnO ₂	synthetic	300	Healy et al., 1966
43	10Å manganite	3MnO ₂ ·Mn(OH) ₂ ·nH ₂ O	synthetic	30-50	Buser and Graf, 1954
	Mn oxides and oxyhydroxides	various	not mentioned	5-360	Sparks, 2005

Table 7 Summary of all available specific surface area data from literature, combined with current measurements from Cape Vani.



8. Conclusions

- ◆ The specific surface area measurements of Cape Vani manganese oxides range between 10.7 and 53.1 m²/g.
- ◆ The pore size of Cape Vani manganese oxides ranges between 87.78 and 168.2831 Å.
- ◆ Mn oxides from Cape Vani can be potentially used as catalysts etc for special technological and industrial applications but before that further experiments for the characterization of this material should be performed (XRD, AAS, EXAFS, differential scanning calorimetry, infrared spectroscopy, thermogravimetric / differential thermal analysis, resistivity and magnetic studies).

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10. Internet Sources

<https://www.youtube.com/watch?v=sqGJsIVCvq8>

<http://www.quantachrome.com/technical/dft.html>

<http://www.micromeritics.com/>

http://minerals.gps.caltech.edu/ge114/Lecture_Topics/Mn_oxides/Mn_oxides3.htm

Appendix

Sample: SMO-0S09 (50304)
 Operator: Olga
 Submitter: TRIANTAFYLLIDES
 File: C:\...\2007\50304.SMP

Started: 10/5/2007 10:34:48
 Completed: 10/5/2007 6:58:37
 Report Time: 14/5/2007 4:16:55
 Warm Free Space: 7.4296 cm³ Measured
 Equilibration Interval: 50 s
 Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
 Analysis Bath Temp.: 77.300 K
 Sample Mass: 0.1751 g
 Cold Free Space: 22.2549 cm³ Measured
 Low Pressure Dose: None
 Automatic Degas: No

Isotherm Tabular Report

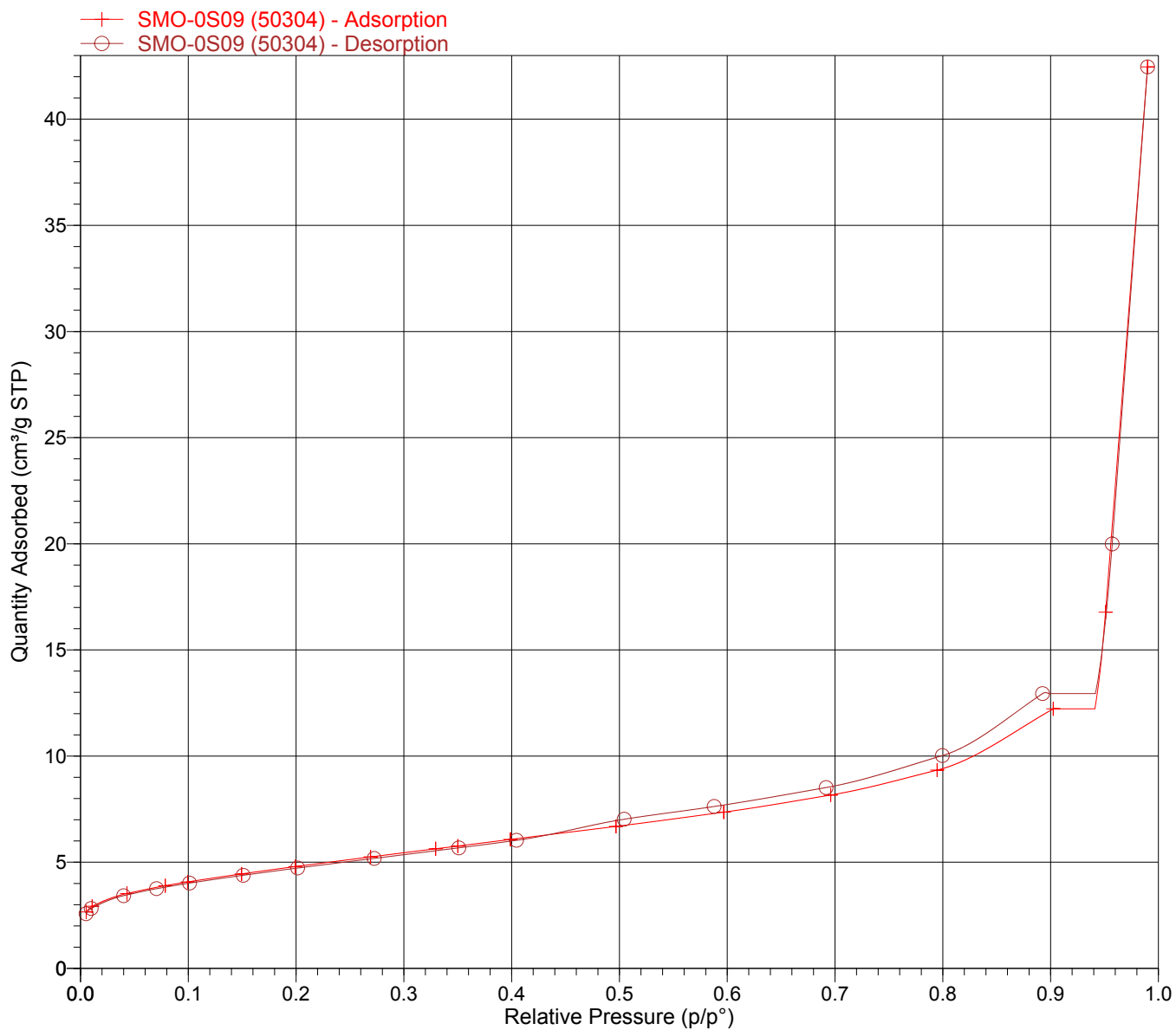
Relative Pressure (p/p°)	Absolute Pressure (kPa)	Quantity Adsorbed (cm ³ /g STP)	Elapsed Time (h:min)	Saturation Pressure (kPa)
			01:24	101.580089
0.005320933	0.540664	2.6574	02:26	
0.010827377	1.100220	2.9248	02:34	
0.043138102	4.383653	3.5260	02:43	
0.078611915	7.988818	3.8934	02:52	
0.099363702	10.098128	4.0718	03:01	
0.149429958	15.186922	4.4491	03:10	
0.199328798	20.259046	4.7949	03:18	
			03:25	101.639777
0.269112316	27.352129	5.2490	03:27	
0.329500955	33.487799	5.6332	03:36	
0.350015217	35.570439	5.7617	03:45	
0.398881560	40.534208	6.0728	03:53	
0.496819508	50.483417	6.6875	04:02	
0.596771491	60.635998	7.3591	04:11	
0.696047085	70.718566	8.1660	04:20	
0.794711882	80.737796	9.3391	04:29	
0.902475429	91.679420	12.2240	04:39	
0.950912888	96.593185	16.7796	04:49	
0.990007319	100.547305	42.4632	05:13	
			05:25	101.553562
0.957102294	97.194414	19.9905	05:29	
0.892549153	90.631988	12.9439	05:40	
0.799550038	81.182885	10.0239	05:50	
0.691733901	70.231252	8.5184	05:59	
0.587917367	59.687476	7.6257	06:07	
0.504345012	51.199671	7.0249	06:16	
0.404471536	41.058201	6.0318	06:25	
0.351002119	35.628227	5.6771	06:34	
0.272461027	27.654411	5.1805	06:42	
0.201352959	20.435749	4.7262	06:51	
0.150965421	15.320838	4.3854	07:00	
0.101097160	10.259271	4.0177	07:09	
0.070585763	7.162542	3.7542	07:18	
			07:25	101.467900
0.040086363	4.067479	3.4253	07:29	
0.009901113	1.004645	2.8208	07:43	
0.005125797	0.520104	2.5716	07:56	

Sample: SMO-0S09 (50304)
Operator: Olga
Submitter: TRIANTAFYLLIDES
File: C:\...\2007\50304.SMP

Started: 10/5/2007 10:34:48
Completed: 10/5/2007 6:58:37
Report Time: 14/5/2007 4:16:55
Warm Free Space: 7.4296 cm³ Measured
Equilibration Interval: 50 s
Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
Analysis Bath Temp.: 77.300 K
Sample Mass: 0.1751 g
Cold Free Space: 22.2549 cm³ Measured
Low Pressure Dose: None
Automatic Degas: No

Isotherm Linear Plot



Sample: SMO-0S09 (50304)
 Operator: Olga
 Submitter: TRIANTAFYLLIDES
 File: C:\...\2007\50304.SMP

Started: 10/5/2007 10:34:48
 Completed: 10/5/2007 6:58:37
 Report Time: 14/5/2007 4:16:55
 Warm Free Space: 7.4296 cm³ Measured
 Equilibration Interval: 50 s
 Sample Density: 1.000 g/cm³

Analysis Adsorptive: N₂
 Analysis Bath Temp.: 77.300 K
 Sample Mass: 0.1751 g
 Cold Free Space: 22.2549 cm³ Measured
 Low Pressure Dose: None
 Automatic Degas: No

BET Surface Area Report

BET Surface Area: 17.3560 ± 0.0184 m²/g
 Slope: 0.248428 ± 0.000263 g/cm³ STP
 Y-Intercept: 0.002390 ± 0.000037 g/cm³ STP
 C: 104.928246
 Qm: 3.9870 cm³/g STP
 Correlation Coefficient: 0.9999989
 Molecular Cross-Sectional Area: 0.1620 nm²

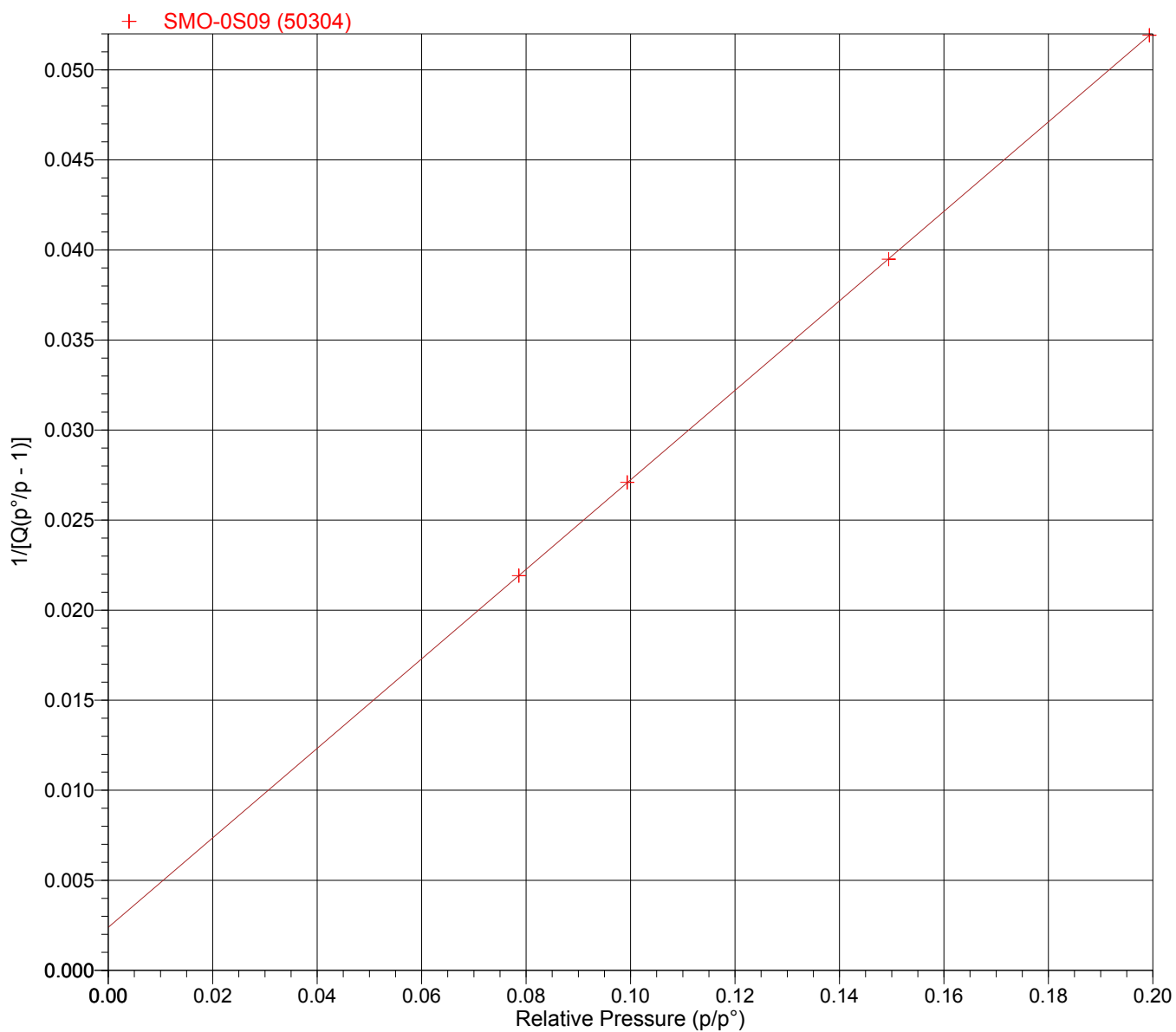
Relative Pressure (p/p°)	Quantity Adsorbed (cm ³ /g STP)	1/[Q(p°/p - 1)]
0.078611915	3.8934	0.021914
0.099363702	4.0718	0.027095
0.149429958	4.4491	0.039487
0.199328798	4.7949	0.051921

Sample: SMO-0S09 (50304)
Operator: Olga
Submitter: TRIANTAFYLIDIS
File: C:\...\2007\50304.SMP

Started: 10/5/2007 10:34:48
Completed: 10/5/2007 6:58:37
Report Time: 14/5/2007 4:16:55
Warm Free Space: 7.4296 cm³ Measured
Equilibration Interval: 50 s
Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
Analysis Bath Temp.: 77.300 K
Sample Mass: 0.1751 g
Cold Free Space: 22.2549 cm³ Measured
Low Pressure Dose: None
Automatic Degas: No

BET Surface Area Plot



Sample: SMO-0S09 (50304)
 Operator: Olga
 Submitter: TRIANTAFYLLIDES
 File: C:\...\2007\50304.SMP

Started: 10/5/2007 10:34:48
 Completed: 10/5/2007 6:58:37
 Report Time: 14/5/2007 4:16:55
 Warm Free Space: 7.4296 cm³ Measured
 Equilibration Interval: 50 s
 Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
 Analysis Bath Temp.: 77.300 K
 Sample Mass: 0.1751 g
 Cold Free Space: 22.2549 cm³ Measured
 Low Pressure Dose: None
 Automatic Degas: No

t-Plot Report

Micropore Volume: 0.000877 cm³/g STP
 Micropore Area: 2.3342 m²/g
 External Surface Area: 15.0218 m²/g
 Slope: 0.971151 ± 0.012622 cm³/g·Å STP
 Y-Intercept: 0.566905 ± 0.064402 cm³/g STP
 Correlation Coefficient: 0.999747
 Surface Area Correction Factor: 1.000
 Density Conversion Factor: 0.0015468
 Total Surface Area (BET): 17.3560 m²/g
 Thickness Range: 1.5000 Å to 8.0000 Å
 Thickness Equation: Harkins and Jura

$$t = [13.99 / (0.034 - \log(p/p^\circ))] ^{0.5}$$

Relative Pressure (p/p°)	Statistical Thickness (Å)	Quantity Adsorbed (cm ³ /g STP)
0.199328798	4.3645	4.7949
0.269112316	4.8125	5.2490
0.329500955	5.2062	5.6332
0.350015217	5.3438	5.7617
0.398881560	5.6831	6.0728

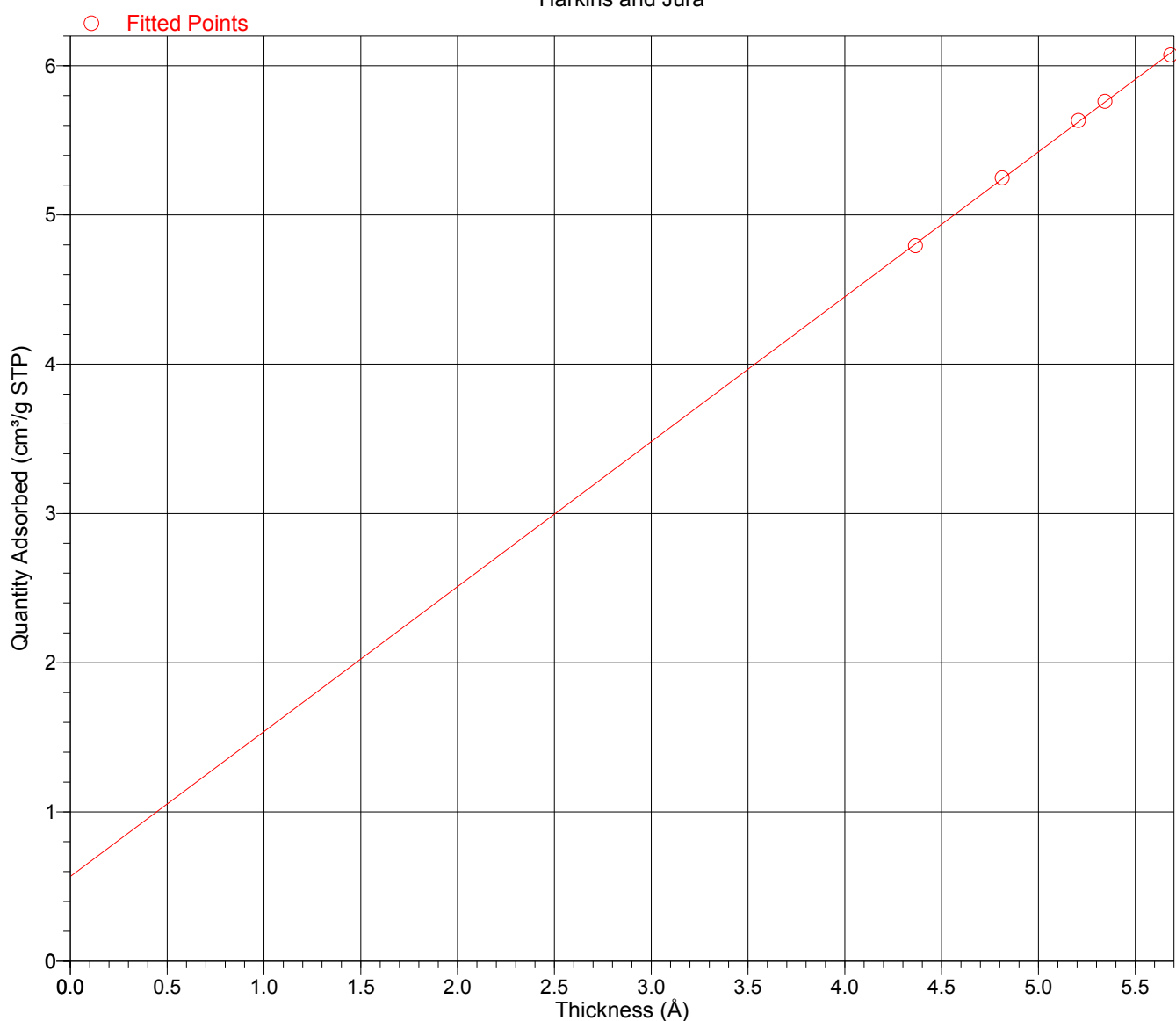
Sample: SMO-0S09 (50304)
Operator: Olga
Submitter: TRIANTAFYLIDIS
File: C:\...\2007\50304.SMP

Started: 10/5/2007 10:34:48
Completed: 10/5/2007 6:58:37
Report Time: 14/5/2007 4:16:55
Warm Free Space: 7.4296 cm³ Measured
Equilibration Interval: 50 s
Sample Density: 1.000 g/cm³

Analysis Adsorptive: N₂
Analysis Bath Temp.: 77.300 K
Sample Mass: 0.1751 g
Cold Free Space: 22.2549 cm³ Measured
Low Pressure Dose: None
Automatic Degas: No

t-Plot

Harkins and Jura



Sample: SMO-0S09 (50304)
Operator: Olga
Submitter: TRIANTAFYLLIDES
File: C:\...\2007\50304.SMP

Started: 10/5/2007 10:34:48	Analysis Adsorptive: N2
Completed: 10/5/2007 6:58:37	Analysis Bath Temp.: 77.300 K
Report Time: 14/5/2007 4:16:55	Sample Mass: 0.1751 g
Warm Free Space: 7.4296 cm ³ Measured	Cold Free Space: 22.2549 cm ³ Measured
Equilibration Interval: 50 s	Low Pressure Dose: None
Sample Density: 1.000 g/cm ³	Automatic Degas: No

Summary Report

Surface Area

Single point surface area at $p/p^\circ = 0.199328798$: 16.7124 m²/g

BET Surface Area: 17.3560 m²/g

t-Plot Micropore Area: 2.3342 m²/g

t-Plot External Surface Area: 15.0218 m²/g

BJH Adsorption cumulative surface area of pores
between 1.000 Å and 3000.000 Å width: 16.9272 m²/g

BJH Desorption cumulative surface area of pores
between 1.000 Å and 3000.000 Å width: 22.3974 m²/g

Pore Volume

Single point adsorption total pore volume of pores
less than 1936.044 Å width at $p/p^\circ = 0.990007319$: 0.065682 cm³/g

t-Plot micropore volume: 0.000877 cm³/g

BJH Adsorption cumulative volume of pores
between 1.000 Å and 3000.000 Å width: 0.065087 cm³/g

BJH Desorption cumulative volume of pores
between 1.000 Å and 3000.000 Å width: 0.066207 cm³/g

Pore Size

Adsorption average pore width (4V/A by BET): 151.3762 Å

BJH Adsorption average pore width (4V/A): 153.805 Å

BJH Desorption average pore width (4V/A): 118.241 Å

Sample: SMO-0S10 (50305)
 Operator: Olga
 Submitter: TRIANTAFYLLIDES
 File: C:\...\2007\50305.SMP

Started: 10/5/2007 10:34:48
 Completed: 10/5/2007 6:58:37
 Report Time: 15/5/2007 10:26:54
 Warm Free Space: 7.0962 cm³ Measured
 Equilibration Interval: 50 s
 Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
 Analysis Bath Temp.: 77.300 K
 Sample Mass: 0.1783 g
 Cold Free Space: 20.8380 cm³ Measured
 Low Pressure Dose: None
 Automatic Degas: No

Isotherm Tabular Report

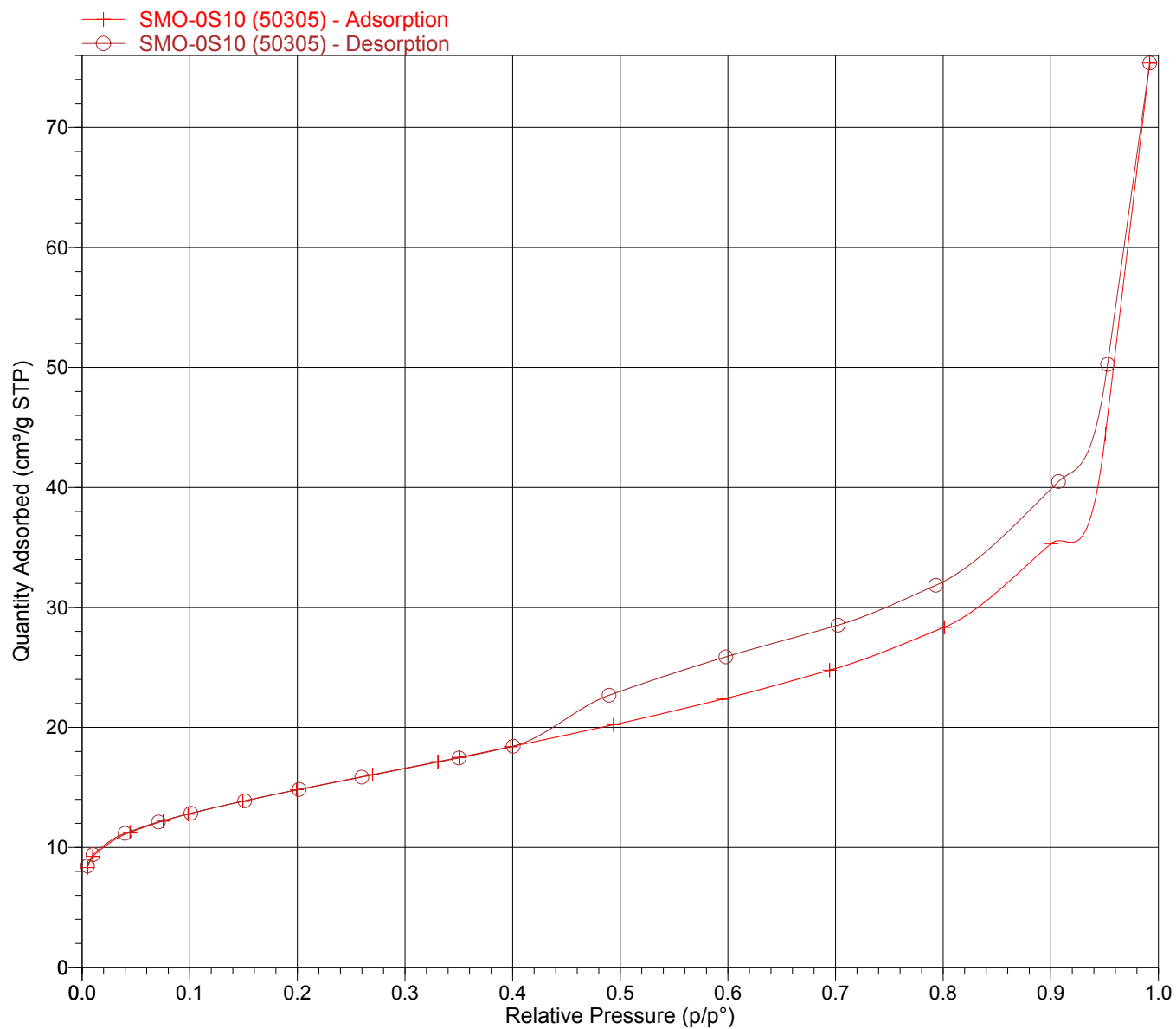
Relative Pressure (p/p°)	Absolute Pressure (kPa)	Quantity Adsorbed (cm ³ /g STP)	Elapsed Time (h:min)	Saturation Pressure (kPa)
			01:24	101.580089
0.005033940	0.511408	8.3059	01:48	
0.009902304	1.006048	9.2518	01:59	
0.044470187	4.518273	11.2631	02:09	
0.075574745	7.678940	12.2068	02:19	
0.098475067	10.006264	12.7782	02:29	
0.149347966	15.176231	13.8489	02:38	
0.199461962	20.269629	14.8042	02:48	
0.269866311	27.425424	16.0710	02:57	
0.330634879	33.602556	17.1501	03:06	
0.350797177	35.653216	17.5158	03:15	
0.398370296	40.490071	18.3945	03:24	
			03:25	101.639777
0.493836671	50.190611	20.2281	03:33	
0.595395727	60.508189	22.3647	03:43	
0.694505722	70.575934	24.7690	03:52	
0.801037631	81.395416	28.3523	04:03	
0.900137965	91.458133	35.3110	04:14	
0.950796259	96.595684	44.4555	04:28	
0.991891849	100.750104	75.3805	04:57	
0.952812917	96.768391	50.2613	05:15	
			05:25	101.553562
0.907186121	92.126039	40.4948	05:28	
0.793231386	80.547545	31.8422	05:39	
0.702373514	71.316499	28.5222	05:49	
0.598054178	60.720016	25.8815	05:59	
0.489564405	49.694293	22.6811	06:30	
0.400461535	40.646569	18.4352	06:41	
0.350043301	35.526904	17.4561	06:50	
0.259907414	26.376898	15.8597	07:00	
0.201636116	20.461896	14.8289	07:09	
0.151128191	15.335523	13.8811	07:17	
			07:25	101.467900
0.101055239	10.253863	12.8508	07:27	
0.070853245	7.189330	12.1224	07:36	
0.039951688	4.053814	11.1756	07:46	
0.010102219	1.025051	9.3908	08:02	
0.005051110	0.512525	8.4480	08:22	

Sample: SMO-0S10 (50305)
Operator: Olga
Submitter: TRIANTAFYLIDIS
File: C:\...\2007\50305.SMP

Started: 10/5/2007 10:34:48
Completed: 10/5/2007 6:58:37
Report Time: 15/5/2007 10:26:54
Warm Free Space: 7.0962 cm³ Measured
Equilibration Interval: 50 s
Sample Density: 1.000 g/cm³

Analysis Adsorptive: N₂
Analysis Bath Temp.: 77.300 K
Sample Mass: 0.1783 g
Cold Free Space: 20.8380 cm³ Measured
Low Pressure Dose: None
Automatic Degas: No

Isotherm Linear Plot



Sample: SMO-0S10 (50305)
 Operator: Olga
 Submitter: TRIANTAFYLLIDES
 File: C:\...\2007\50305.SMP

Started: 10/5/2007 10:34:48
 Completed: 10/5/2007 6:58:37
 Report Time: 15/5/2007 10:26:54
 Warm Free Space: 7.0962 cm³ Measured
 Equilibration Interval: 50 s
 Sample Density: 1.000 g/cm³

Analysis Adsorptive: N₂
 Analysis Bath Temp.: 77.300 K
 Sample Mass: 0.1783 g
 Cold Free Space: 20.8380 cm³ Measured
 Low Pressure Dose: None
 Automatic Degas: No

BET Surface Area Report

BET Surface Area: 53.1284 ± 0.1515 m²/g
 Slope: 0.081411 ± 0.000233 g/cm³ STP
 Y-Intercept: 0.000527 ± 0.000023 g/cm³ STP
 C: 155.566891
 Qm: 12.2044 cm³/g STP
 Correlation Coefficient: 0.9999918
 Molecular Cross-Sectional Area: 0.1620 nm²

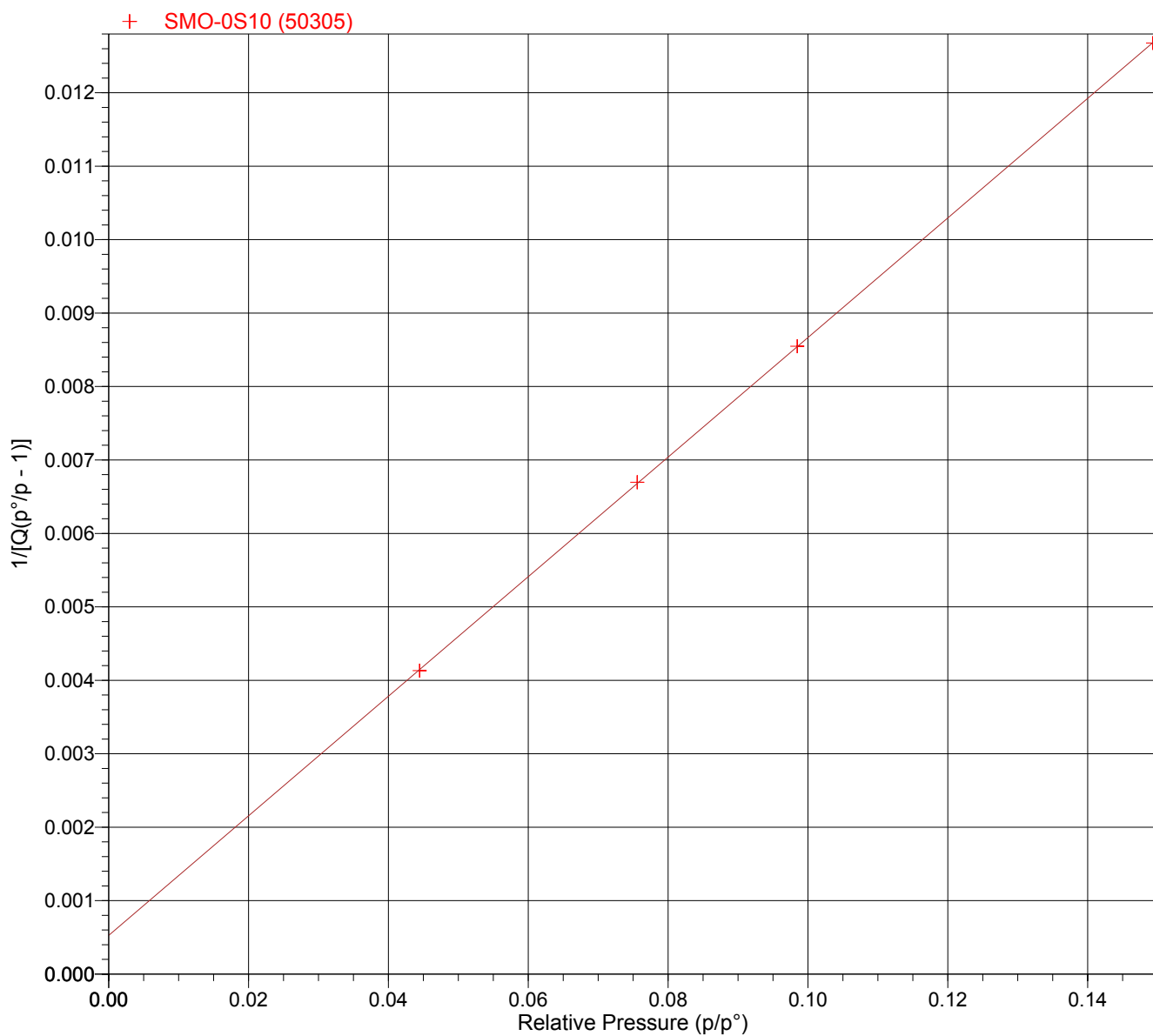
Relative Pressure (p/p°)	Quantity Adsorbed (cm ³ /g STP)	1/[Q(p°/p - 1)]
0.044470187	11.2631	0.004132
0.075574745	12.2068	0.006697
0.098475067	12.7782	0.008548
0.149347966	13.8489	0.012677

Sample: SMO-0S10 (50305)
Operator: Olga
Submitter: TRIANTAFYLIDIS
File: C:\...\2007\50305.SMP

Started: 10/5/2007 10:34:48
Completed: 10/5/2007 6:58:37
Report Time: 15/5/2007 10:26:54
Warm Free Space: 7.0962 cm³ Measured
Equilibration Interval: 50 s
Sample Density: 1.000 g/cm³

Analysis Adsorptive: N₂
Analysis Bath Temp.: 77.300 K
Sample Mass: 0.1783 g
Cold Free Space: 20.8380 cm³ Measured
Low Pressure Dose: None
Automatic Degas: No

BET Surface Area Plot



Sample: SMO-0S10 (50305)
 Operator: Olga
 Submitter: TRIANTAFYLLIDES
 File: C:\...\2007\50305.SMP

Started: 10/5/2007 10:34:48
 Completed: 10/5/2007 6:58:37
 Report Time: 15/5/2007 10:26:54
 Warm Free Space: 7.0962 cm³ Measured
 Equilibration Interval: 50 s
 Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
 Analysis Bath Temp.: 77.300 K
 Sample Mass: 0.1783 g
 Cold Free Space: 20.8380 cm³ Measured
 Low Pressure Dose: None
 Automatic Degass: No

t-Plot Report

Micropore Volume: 0.004078 cm³/g STP
 Micropore Area: 10.0619 m²/g
 External Surface Area: 43.0665 m²/g
 Slope: 2.784230 ± 0.018033 cm³/g·Å STP
 Y-Intercept: 2.636610 ± 0.086230 cm³/g STP
 Correlation Coefficient: 0.999937
 Surface Area Correction Factor: 1.000
 Density Conversion Factor: 0.0015468
 Total Surface Area (BET): 53.1284 m²/g
 Thickness Range: 1.5000 Å to 8.0000 Å
 Thickness Equation: Harkins and Jura

$$t = [13.99 / (0.034 - \log(p/p^\circ))] ^{0.5}$$

Relative Pressure (p/p°)	Statistical Thickness (Å)	Quantity Adsorbed (cm ³ /g STP)
0.149347966	4.0338	13.8489
0.199461962	4.3654	14.8042
0.269866311	4.8173	16.0710
0.330634879	5.2138	17.1501
0.350797177	5.3491	17.5158

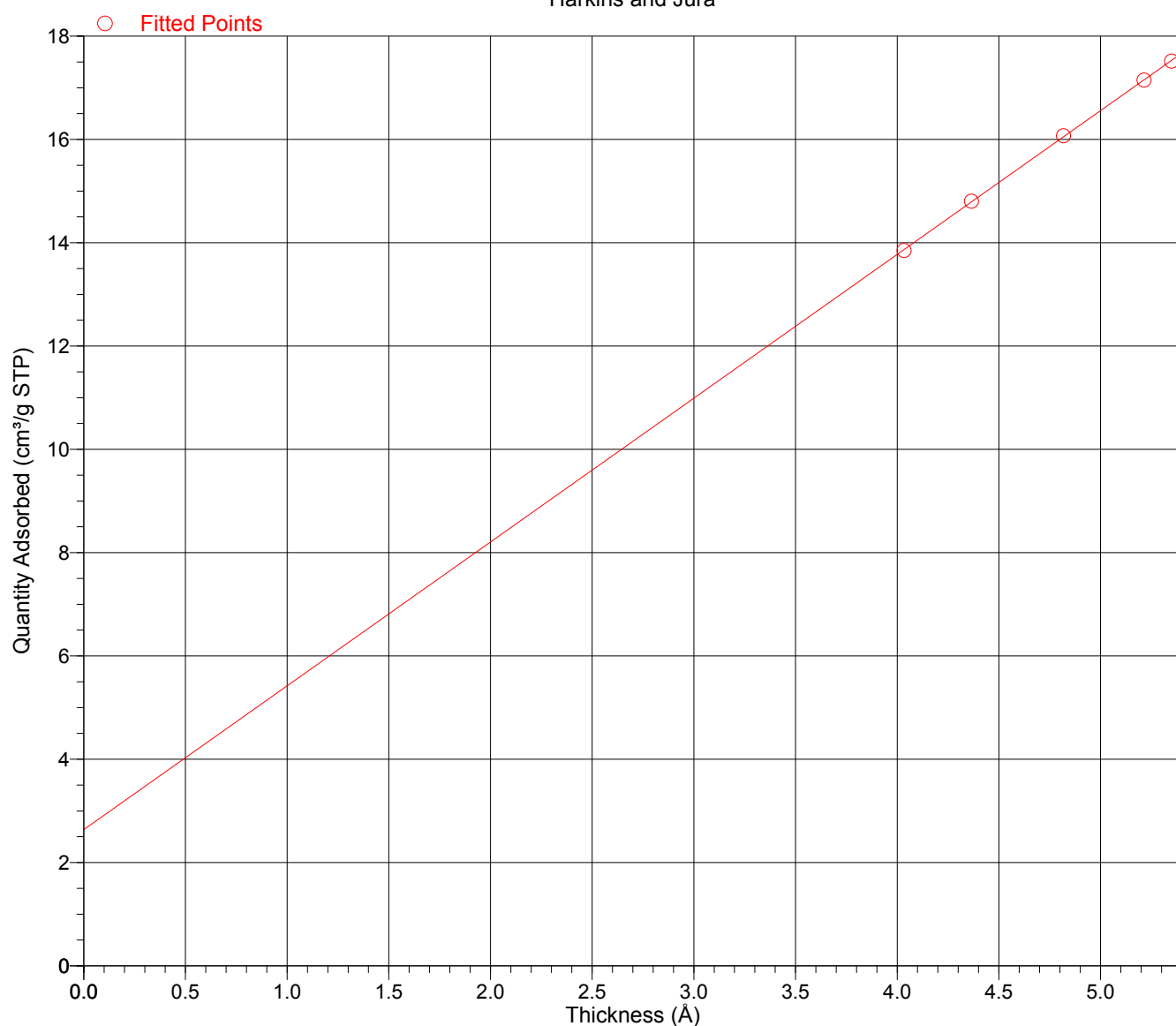
Sample: SMO-0S10 (50305)
Operator: Olga
Submitter: TRIANTAFYLIDIS
File: C:\...\2007\50305.SMP

Started: 10/5/2007 10:34:48
Completed: 10/5/2007 6:58:37
Report Time: 15/5/2007 10:26:54
Warm Free Space: 7.0962 cm³ Measured
Equilibration Interval: 50 s
Sample Density: 1.000 g/cm³

Analysis Adsorptive: N₂
Analysis Bath Temp.: 77.300 K
Sample Mass: 0.1783 g
Cold Free Space: 20.8380 cm³ Measured
Low Pressure Dose: None
Automatic Degas: No

t-Plot

Harkins and Jura



Sample: SMO-0S10 (50305)
Operator: Olga
Submitter: TRIANTAFYLLIDES
File: C:\...\2007\50305.SMP

Started: 10/5/2007 10:34:48	Analysis Adsorptive: N2
Completed: 10/5/2007 6:58:37	Analysis Bath Temp.: 77.300 K
Report Time: 15/5/2007 10:26:54	Sample Mass: 0.1783 g
Warm Free Space: 7.0962 cm ³ Measured	Cold Free Space: 20.8380 cm ³ Measured
Equilibration Interval: 50 s	Low Pressure Dose: None
Sample Density: 1.000 g/cm ³	Automatic Degas: No

Summary Report

Surface Area

Single point surface area at $p/p^\circ = 0.149347966$: 51.2833 m²/g

BET Surface Area: 53.1284 m²/g

t-Plot Micropore Area: 10.0619 m²/g

t-Plot External Surface Area: 43.0665 m²/g

BJH Adsorption cumulative surface area of pores
between 1.000 Å and 3000.000 Å width: 48.5882 m²/g

BJH Desorption cumulative surface area of pores
between 1.000 Å and 3000.000 Å width: 73.6667 m²/g

Pore Volume

Single point adsorption total pore volume of pores
less than 2379.789 Å width at $p/p^\circ = 0.991891849$: 0.116599 cm³/g

t-Plot micropore volume: 0.004078 cm³/g

BJH Adsorption cumulative volume of pores
between 1.000 Å and 3000.000 Å width: 0.112965 cm³/g

BJH Desorption cumulative volume of pores
between 1.000 Å and 3000.000 Å width: 0.118802 cm³/g

Pore Size

Adsorption average pore width (4V/A by BET): 87.7863 Å

BJH Adsorption average pore width (4V/A): 92.998 Å

BJH Desorption average pore width (4V/A): 64.508 Å

Sample: VA-05-06 (50306)
 Operator: Olga
 Submitter: TRIANTAFYLLIDES
 File: C:\...\2007\50306.SMP

Started: 10/5/2007 10:34:48
 Completed: 10/5/2007 6:58:37
 Report Time: 15/5/2007 10:37:09
 Warm Free Space: 6.7069 cm³ Measured
 Equilibration Interval: 50 s
 Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
 Analysis Bath Temp.: 77.300 K
 Sample Mass: 0.1912 g
 Cold Free Space: 19.3681 cm³ Measured
 Low Pressure Dose: None
 Automatic Degas: No

Isotherm Tabular Report

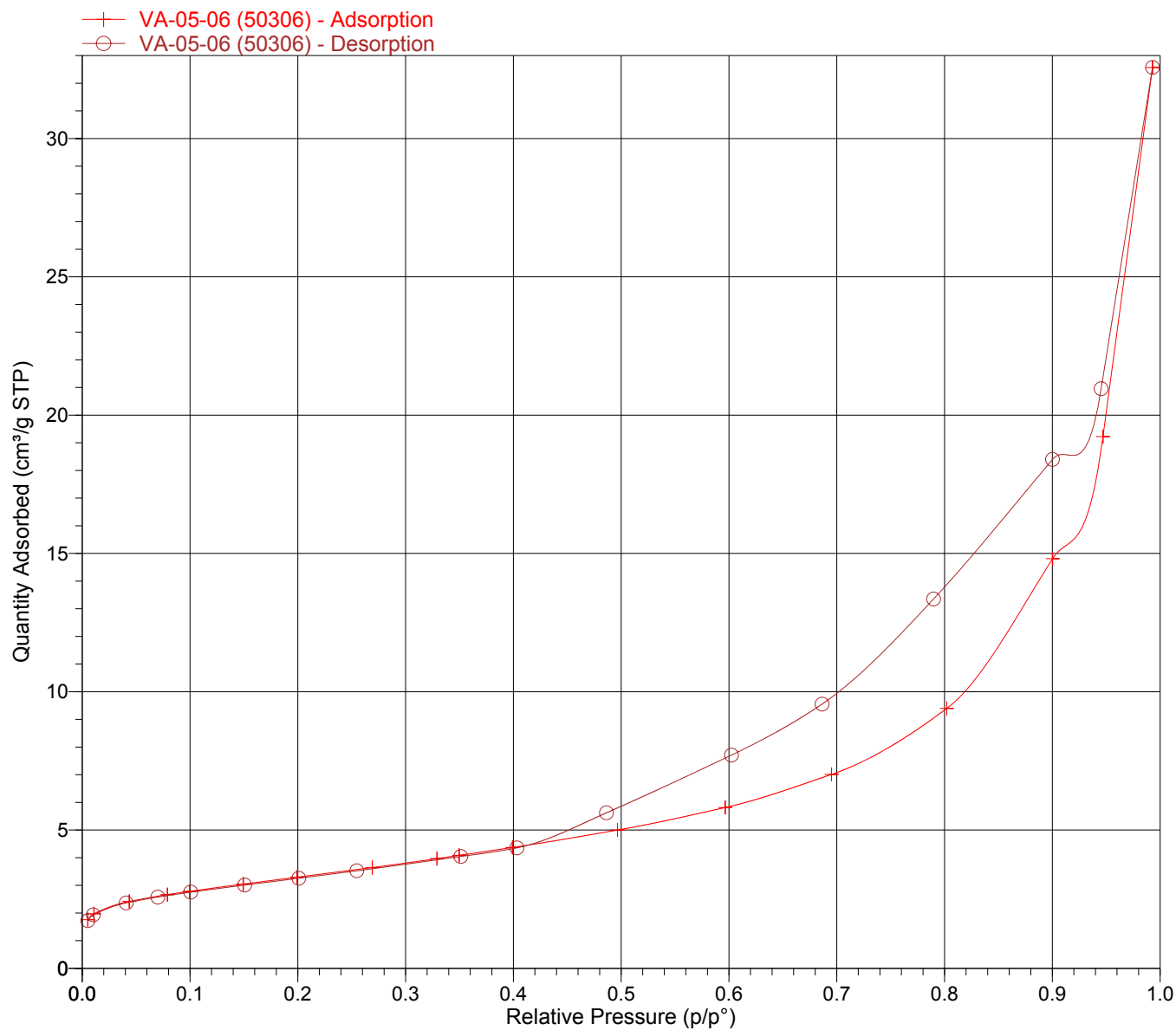
Relative Pressure (p/p°)	Absolute Pressure (kPa)	Quantity Adsorbed (cm ³ /g STP)	Elapsed Time (h:min)	Saturation Pressure (kPa)
			01:24	101.580089
0.005184809	0.526852	1.7612	02:34	
0.010777185	1.095167	1.9742	02:43	
0.043601901	4.430978	2.4194	02:52	
0.079002594	8.028832	2.6662	03:00	
0.099468315	10.109152	2.7844	03:09	
0.149424406	15.186947	3.0471	03:18	
			03:25	101.639777
0.199293860	20.255897	3.2961	03:27	
0.269085582	27.347672	3.6454	03:36	
0.329130063	33.448213	3.9674	03:44	
0.349693367	35.535721	4.0847	03:53	
0.399039998	40.547729	4.3703	04:02	
0.496512519	50.449012	5.0000	04:11	
0.596496258	60.604604	5.8156	04:19	
0.695059097	70.613692	7.0117	04:29	
0.802054702	81.478019	9.3965	04:39	
0.900256012	91.446195	14.8098	04:51	
0.946911868	96.177920	19.2287	05:02	
0.992943680	100.840534	32.5687	05:20	
			05:25	101.553562
0.945253060	95.987742	20.9552	05:34	
0.900162731	91.402522	18.3973	05:44	
0.789841819	80.194335	13.3536	05:55	
0.686364995	69.682721	9.5543	06:06	
0.602325598	61.146381	7.7107	06:16	
0.486405292	49.371537	5.6235	06:36	
0.403273631	40.930843	4.3560	06:45	
0.351245810	35.647947	4.0449	06:54	
0.254639643	25.841749	3.5277	07:03	
0.200863380	20.383049	3.2587	07:12	
0.150653287	15.287010	3.0111	07:20	
			07:25	101.467900
0.100609779	10.208663	2.7548	07:29	
0.070104297	7.113336	2.5779	07:38	
0.040846501	4.144609	2.3665	07:47	
0.010232057	1.038225	1.9329	08:00	
0.005094235	0.516901	1.7238	08:12	

Sample: VA-05-06 (50306)
Operator: Olga
Submitter: TRIANTAFYLIDIS
File: C:\...\2007\50306.SMP

Started: 10/5/2007 10:34:48
Completed: 10/5/2007 6:58:37
Report Time: 15/5/2007 10:37:09
Warm Free Space: 6.7069 cm³ Measured
Equilibration Interval: 50 s
Sample Density: 1.000 g/cm³

Analysis Adsorptive: N₂
Analysis Bath Temp.: 77.300 K
Sample Mass: 0.1912 g
Cold Free Space: 19.3681 cm³ Measured
Low Pressure Dose: None
Automatic Degas: No

Isotherm Linear Plot



Sample: VA-05-06 (50306)
Operator: Olga
Submitter: TRIANTAFYLIDIS
File: C:\...\2007\50306.SMP

Started: 10/5/2007 10:34:48
Completed: 10/5/2007 6:58:37
Report Time: 15/5/2007 10:37:09
Warm Free Space: 6.7069 cm³ Measured
Equilibration Interval: 50 s
Sample Density: 1.000 g/cm³

Analysis Adsorptive: N₂
Analysis Bath Temp.: 77.300 K
Sample Mass: 0.1912 g
Cold Free Space: 19.3681 cm³ Measured
Low Pressure Dose: None
Automatic Degas: No

BET Surface Area Report

BET Surface Area: 11.9644 ± 0.0286 m²/g
Slope: 0.360046 ± 0.000861 g/cm³ STP
Y-Intercept: 0.003798 ± 0.000120 g/cm³ STP
C: 95.792119
Qm: 2.7484 cm³/g STP
Correlation Coefficient: 0.9999943
Molecular Cross-Sectional Area: 0.1620 nm²

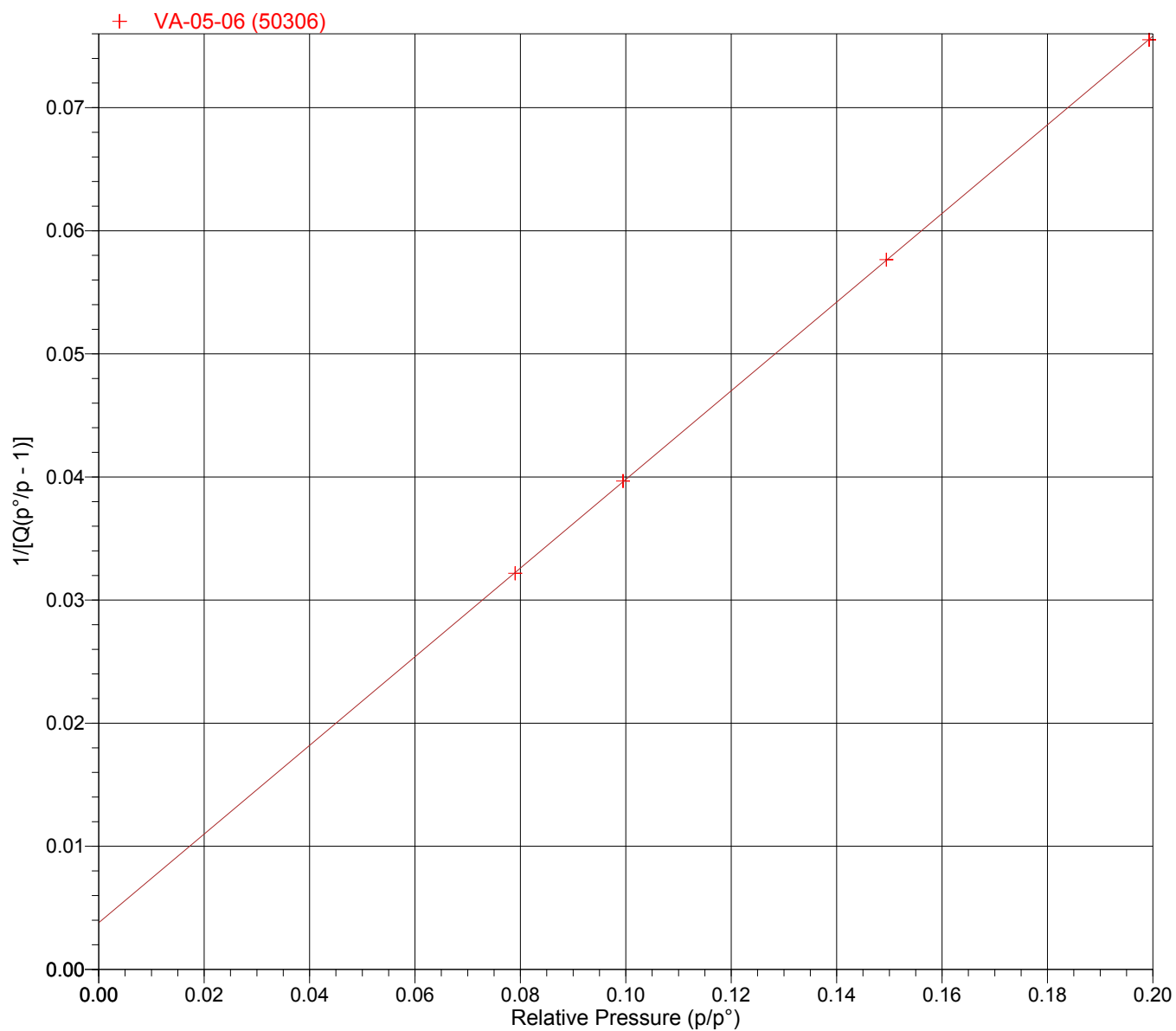
Relative Pressure (p/p°)	Quantity Adsorbed (cm ³ /g STP)	1/[Q(p°/p - 1)]
0.079002594	2.6662	0.032173
0.099468315	2.7844	0.039669
0.149424406	3.0471	0.057652
0.199293860	3.2961	0.075512

Sample: VA-05-06 (50306)
Operator: Olga
Submitter: TRIANTAFYLIDIS
File: C:\...\2007\50306.SMP

Started: 10/5/2007 10:34:48
Completed: 10/5/2007 6:58:37
Report Time: 15/5/2007 10:37:09
Warm Free Space: 6.7069 cm³ Measured
Equilibration Interval: 50 s
Sample Density: 1.000 g/cm³

Analysis Adsorptive: N₂
Analysis Bath Temp.: 77.300 K
Sample Mass: 0.1912 g
Cold Free Space: 19.3681 cm³ Measured
Low Pressure Dose: None
Automatic Degas: No

BET Surface Area Plot



Sample: VA-05-06 (50306)
 Operator: Olga
 Submitter: TRIANTAFYLLIDES
 File: C:\...\2007\50306.SMP

Started: 10/5/2007 10:34:48
 Completed: 10/5/2007 6:58:37
 Report Time: 15/5/2007 10:37:09
 Warm Free Space: 6.7069 cm³ Measured
 Equilibration Interval: 50 s
 Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
 Analysis Bath Temp.: 77.300 K
 Sample Mass: 0.1912 g
 Cold Free Space: 19.3681 cm³ Measured
 Low Pressure Dose: None
 Automatic Degas: No

t-Plot Report

Micropore Volume: -0.000413 cm³/g STP
 Micropore Area: *
 External Surface Area: 12.6013 m²/g
 Slope: 0.814667 ± 0.007872 cm³/g·Å STP
 Y-Intercept: -0.266735 ± 0.040157 cm³/g STP
 Correlation Coefficient: 0.999860
 Surface Area Correction Factor: 1.000
 Density Conversion Factor: 0.0015468
 Total Surface Area (BET): 11.9644 m²/g
 Thickness Range: 1.5000 Å to 8.0000 Å
 Thickness Equation: Harkins and Jura

$$t = [13.99 / (0.034 - \log(p/p^\circ))] ^{0.5}$$

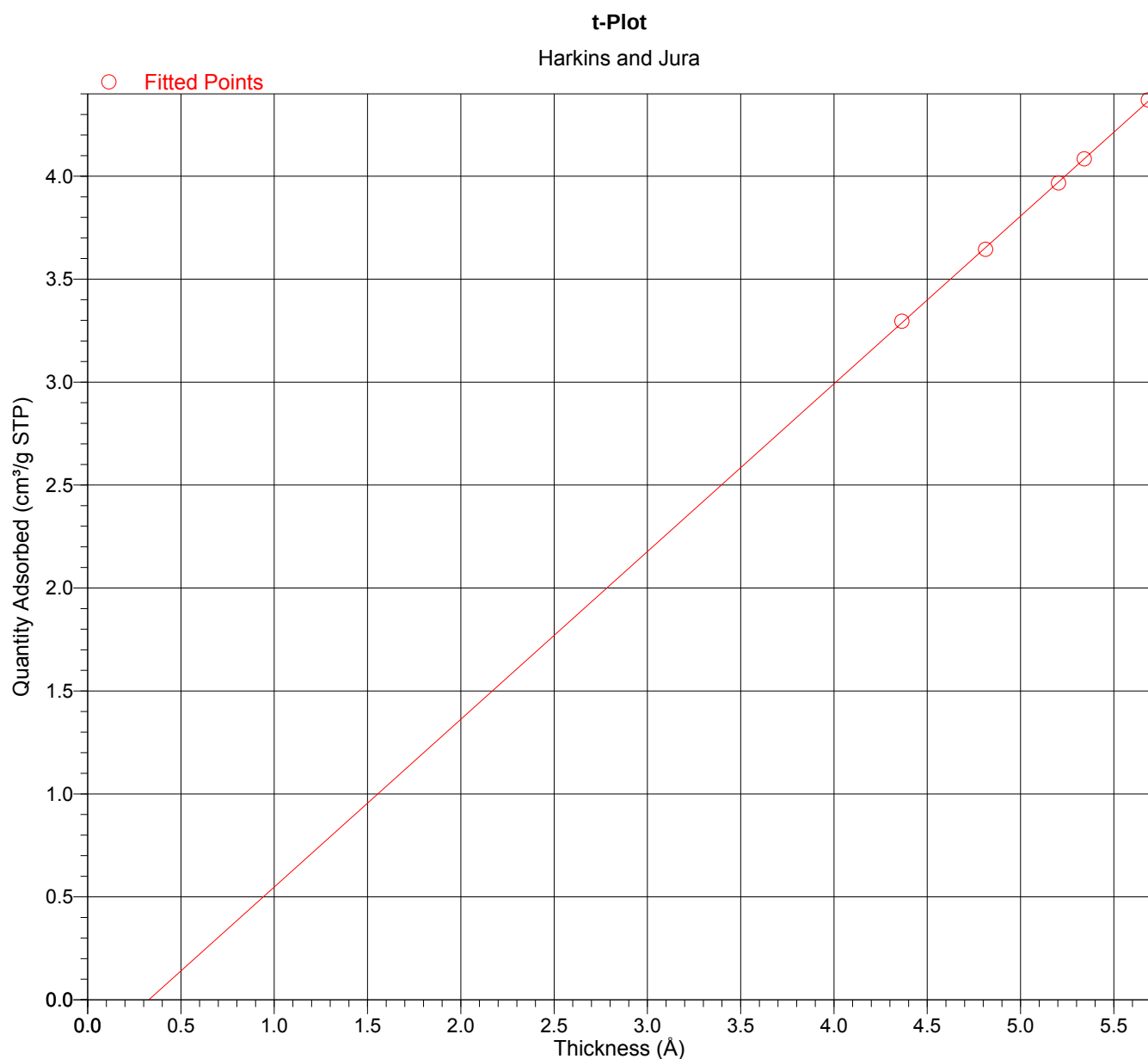
Relative Pressure (p/p°)	Statistical Thickness (Å)	Quantity Adsorbed (cm ³ /g STP)
0.199293860	4.3643	3.2961
0.269085582	4.8123	3.6454
0.329130063	5.2038	3.9674
0.349693367	5.3416	4.0847
0.399039998	5.6842	4.3703

* The micropore area is not reported because either the micropore volume is negative or the calculated external surface area is larger than the total surface area.

Sample: VA-05-06 (50306)
Operator: Olga
Submitter: TRIANTAFYLIDIS
File: C:\...\2007\50306.SMP

Started: 10/5/2007 10:34:48
Completed: 10/5/2007 6:58:37
Report Time: 15/5/2007 10:37:09
Warm Free Space: 6.7069 cm³ Measured
Equilibration Interval: 50 s
Sample Density: 1.000 g/cm³

Analysis Adsorptive: N₂
Analysis Bath Temp.: 77.300 K
Sample Mass: 0.1912 g
Cold Free Space: 19.3681 cm³ Measured
Low Pressure Dose: None
Automatic Degas: No



Sample: VA-05-06 (50306)
Operator: Olga
Submitter: TRIANTAFYLLIDES
File: C:\...\2007\50306.SMP

Started: 10/5/2007 10:34:48	Analysis Adsorptive: N2
Completed: 10/5/2007 6:58:37	Analysis Bath Temp.: 77.300 K
Report Time: 15/5/2007 10:37:09	Sample Mass: 0.1912 g
Warm Free Space: 6.7069 cm ³ Measured	Cold Free Space: 19.3681 cm ³ Measured
Equilibration Interval: 50 s	Low Pressure Dose: None
Sample Density: 1.000 g/cm ³	Automatic Degas: No

Summary Report

Surface Area

Single point surface area at $p/p^\circ = 0.199293860$: 11.4891 m²/g

BET Surface Area: 11.9644 m²/g

t-Plot External Surface Area: 12.6013 m²/g

BJH Adsorption cumulative surface area of pores
between 1.000 Å and 3000.000 Å width: 12.6416 m²/g

BJH Desorption cumulative surface area of pores
between 1.000 Å and 3000.000 Å width: 18.5595 m²/g

Pore Volume

Single point adsorption total pore volume of pores
less than 2730.434 Å width at $p/p^\circ = 0.992943680$: 0.050377 cm³/g

t-Plot micropore volume: -0.000413 cm³/g

BJH Adsorption cumulative volume of pores
between 1.000 Å and 3000.000 Å width: 0.050549 cm³/g

BJH Desorption cumulative volume of pores
between 1.000 Å and 3000.000 Å width: 0.050477 cm³/g

Pore Size

Adsorption average pore width (4V/A by BET): 168.4230 Å

BJH Adsorption average pore width (4V/A): 159.945 Å

BJH Desorption average pore width (4V/A): 108.790 Å

Sample: VA-05-10 (50307)
 Operator: Olga
 Submitter: TRIANTAFYLLIDES
 File: C:\...\2007\50307.SMP

Started: 11/5/2007 2:18:41ii
 Completed: 11/5/2007 10:33:50ii
 Report Time: 15/5/2007 11:07:58di
 Warm Free Space: 7.7563 cm³ Measured
 Equilibration Interval: 50 s
 Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
 Analysis Bath Temp.: 77.300 K
 Sample Mass: 0.1769 g
 Cold Free Space: 23.5509 cm³ Measured
 Low Pressure Dose: None
 Automatic Degas: No

Isotherm Tabular Report

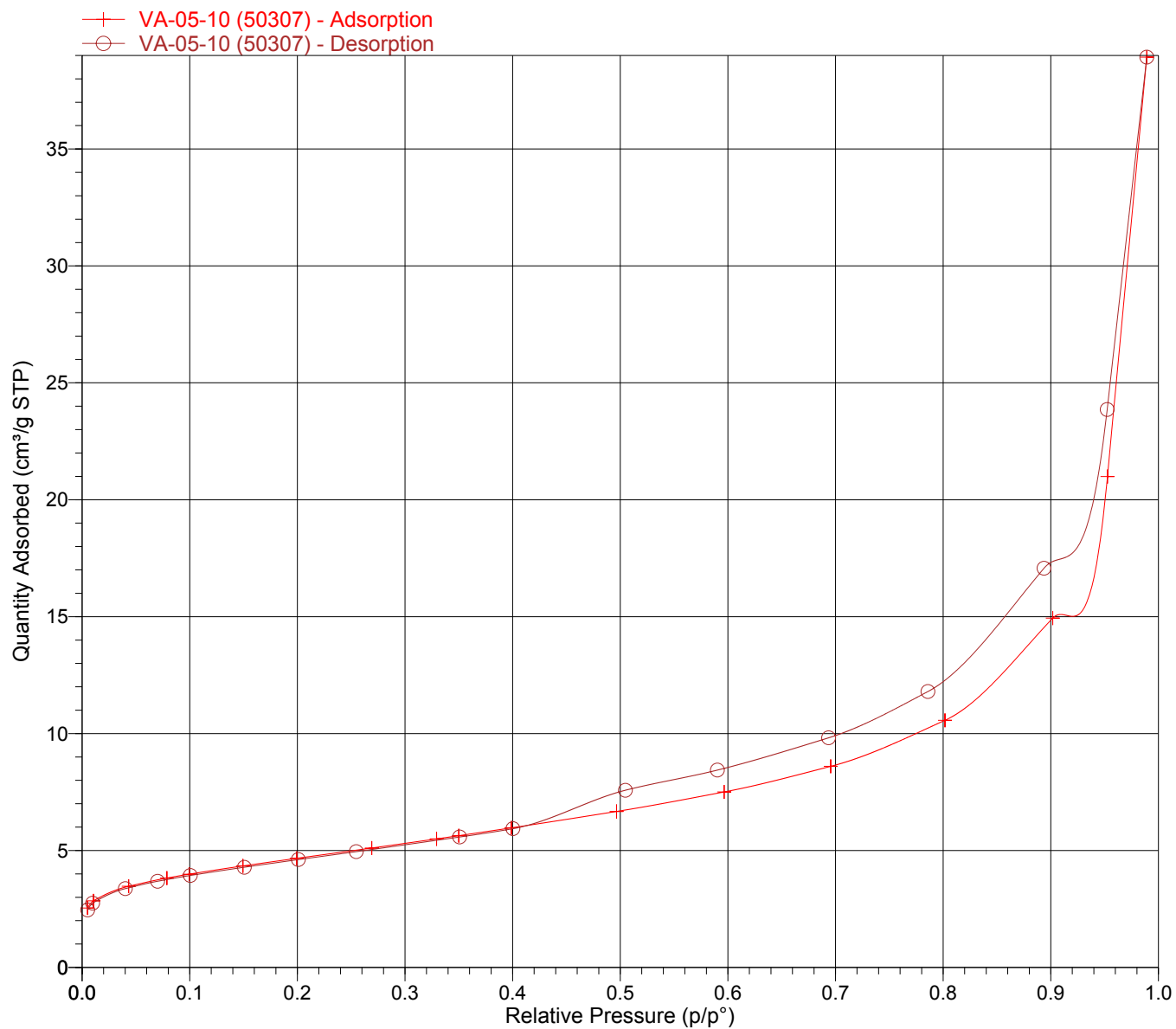
Relative Pressure (p/p°)	Absolute Pressure (kPa)	Quantity Adsorbed (cm ³ /g STP)	Elapsed Time (h:min)	Saturation Pressure (kPa)
			01:24	101.414633
0.005044198	0.511744	2.5397	02:31	
0.010520549	1.067383	2.8509	02:40	
0.043203001	4.383439	3.4701	02:48	
0.078795447	7.995095	3.8224	02:57	
0.099468242	10.093189	3.9884	03:06	
0.149455073	15.166176	4.3404	03:15	
0.199354834	20.230828	4.6653	03:24	
			03:25	101.482059
0.269076996	27.305785	5.1063	03:32	
0.329360967	33.422263	5.4973	03:41	
0.349878534	35.503131	5.6342	03:50	
0.398877809	40.473882	5.9697	03:59	
0.496489929	50.377041	6.6708	04:07	
0.596486667	60.521347	7.5049	04:16	
0.695520732	70.567309	8.5996	04:25	
0.801675858	81.334484	10.5686	04:36	
0.901820504	91.491016	14.9375	04:47	
0.952691722	96.647356	20.9921	05:00	
0.989169316	100.340136	38.9293	05:21	
			05:25	101.437295
0.952352389	96.601787	23.8573	05:37	
0.893750005	90.655334	17.0727	05:49	
0.785851899	79.709243	11.7985	06:00	
0.693553712	70.346168	9.8192	06:09	
0.590247602	59.866807	8.4387	06:19	
0.504812361	51.200501	7.5776	06:28	
0.400306002	40.600011	5.9336	06:40	
0.350649868	35.563140	5.5777	06:49	
0.254636585	25.825006	4.9517	06:57	
0.200900055	20.374739	4.6119	07:06	
0.150717413	15.285083	4.2851	07:15	
0.100565874	10.198760	3.9333	07:24	
			07:25	101.413526
0.070097652	7.108850	3.6858	07:32	
0.040105892	4.067280	3.3709	07:43	
0.009747047	0.988482	2.7486	07:58	
0.005084463	0.515633	2.4589	08:14	

Sample: VA-05-10 (50307)
Operator: Olga
Submitter: TRIANTAFYLIDIS
File: C:\...\2007\50307.SMP

Started: 11/5/2007 2:18:41ii
Completed: 11/5/2007 10:33:50ii
Report Time: 15/5/2007 11:07:58di
Warm Free Space: 7.7563 cm³ Measured
Equilibration Interval: 50 s
Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
Analysis Bath Temp.: 77.300 K
Sample Mass: 0.1769 g
Cold Free Space: 23.5509 cm³ Measured
Low Pressure Dose: None
Automatic Degas: No

Isotherm Linear Plot



Sample: VA-05-10 (50307)
Operator: Olga
Submitter: TRIANTAFYLIDIS
File: C:\...\2007\50307.SMP

Started: 11/5/2007 2:18:41ii
Completed: 11/5/2007 10:33:50ii
Report Time: 15/5/2007 11:07:58di
Warm Free Space: 7.7563 cm³ Measured
Equilibration Interval: 50 s
Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
Analysis Bath Temp.: 77.300 K
Sample Mass: 0.1769 g
Cold Free Space: 23.5509 cm³ Measured
Low Pressure Dose: None
Automatic Degas: No

BET Surface Area Report

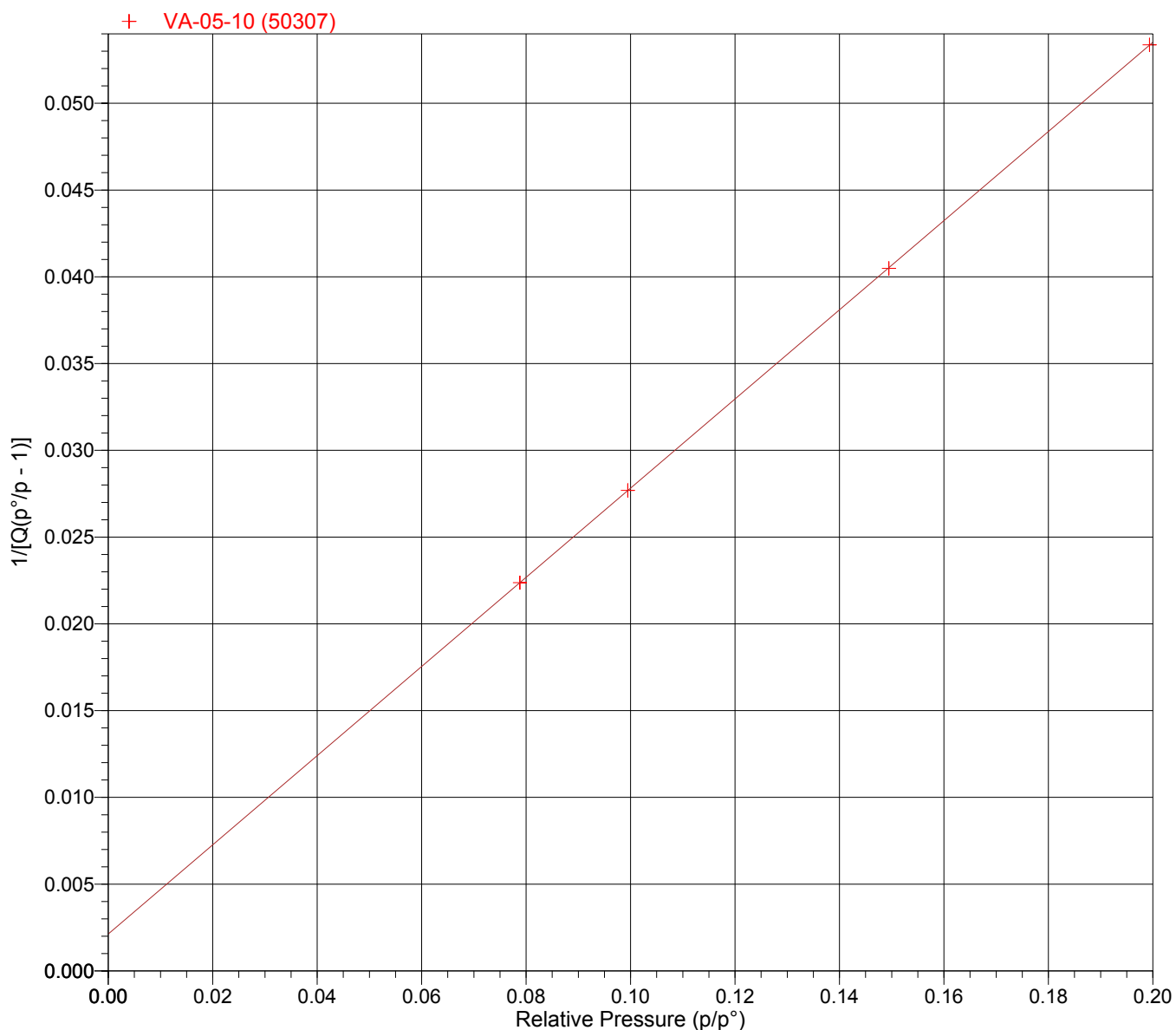
BET Surface Area: 16.8027 ± 0.0249 m²/g
Slope: 0.256954 ± 0.000381 g/cm³ STP
Y-Intercept: 0.002123 ± 0.000053 g/cm³ STP
C: 122.019531
Qm: 3.8598 cm³/g STP
Correlation Coefficient: 0.9999978
Molecular Cross-Sectional Area: 0.1620 nm²

Relative Pressure (p/p°)	Quantity Adsorbed (cm ³ /g STP)	1/[Q(p°/p - 1)]
0.078795447	3.8224	0.022378
0.099468242	3.9884	0.027694
0.149455073	4.3404	0.040484
0.199354834	4.6653	0.053371

Sample: VA-05-10 (50307)
Operator: Olga
Submitter: TRIANTAFYLIDIS
File: C:\...\2007\50307.SMP

Started: 11/5/2007 2:18:41ii
Completed: 11/5/2007 10:33:50ii
Report Time: 15/5/2007 11:07:58di
Warm Free Space: 7.7563 cm³ Measured
Equilibration Interval: 50 s
Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
Analysis Bath Temp.: 77.300 K
Sample Mass: 0.1769 g
Cold Free Space: 23.5509 cm³ Measured
Low Pressure Dose: None
Automatic Degas: No

BET Surface Area Plot

Sample: VA-05-10 (50307)
 Operator: Olga
 Submitter: TRIANTAFYLLIDES
 File: C:\...\2007\50307.SMP

Started: 11/5/2007 2:18:41ii
 Completed: 11/5/2007 10:33:50ii
 Report Time: 15/5/2007 11:07:58di
 Warm Free Space: 7.7563 cm³ Measured
 Equilibration Interval: 50 s
 Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
 Analysis Bath Temp.: 77.300 K
 Sample Mass: 0.1769 g
 Cold Free Space: 23.5509 cm³ Measured
 Low Pressure Dose: None
 Automatic Degas: No

t-Plot Report

Micropore Volume: 0.000736 cm³/g STP
 Micropore Area: 1.8845 m²/g
 External Surface Area: 14.9182 m²/g
 Slope: 0.964453 ± 0.009382 cm³/g·Å STP
 Y-Intercept: 0.475767 ± 0.051811 cm³/g STP
 Correlation Coefficient: 0.999858
 Surface Area Correction Factor: 1.000
 Density Conversion Factor: 0.0015468
 Total Surface Area (BET): 16.8027 m²/g
 Thickness Range: 1.5000 Å to 8.0000 Å
 Thickness Equation: Harkins and Jura

$$t = [13.99 / (0.034 - \log(p/p^\circ))] ^{0.5}$$

Relative Pressure (p/p°)	Statistical Thickness (Å)	Quantity Adsorbed (cm³/g STP)
0.269076996	4.8122	5.1063
0.329360967	5.2053	5.4973
0.349878534	5.3429	5.6342
0.398877809	5.6831	5.9697
0.496489929	6.4327	6.6708

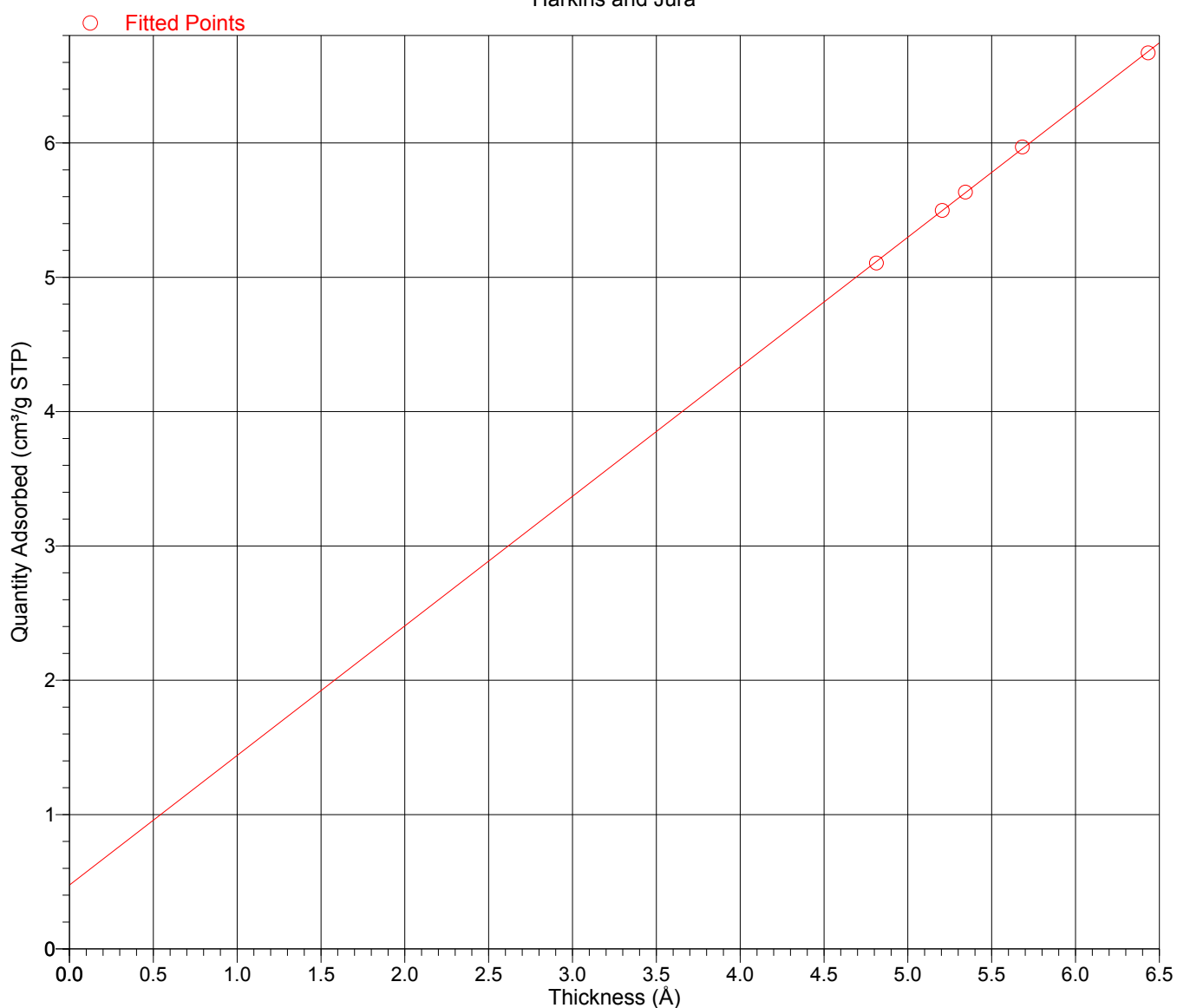
Sample: VA-05-10 (50307)
Operator: Olga
Submitter: TRIANTAFYLIDIS
File: C:\...\2007\50307.SMP

Started: 11/5/2007 2:18:41ii
Completed: 11/5/2007 10:33:50ii
Report Time: 15/5/2007 11:07:58di
Warm Free Space: 7.7563 cm³ Measured
Equilibration Interval: 50 s
Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
Analysis Bath Temp.: 77.300 K
Sample Mass: 0.1769 g
Cold Free Space: 23.5509 cm³ Measured
Low Pressure Dose: None
Automatic Degas: No

t-Plot

Harkins and Jura



Sample: VA-05-10 (50307)
Operator: Olga
Submitter: TRIANTAFYLIDIS
File: C:\...\2007\50307.SMP

Started: 11/5/2007 2:18:41ii	Analysis Adsorptive: N2
Completed: 11/5/2007 10:33:50ii	Analysis Bath Temp.: 77.300 K
Report Time: 15/5/2007 11:07:58di	Sample Mass: 0.1769 g
Warm Free Space: 7.7563 cm ³ Measured	Cold Free Space: 23.5509 cm ³ Measured
Equilibration Interval: 50 s	Low Pressure Dose: None
Sample Density: 1.000 g/cm ³	Automatic Degas: No

Summary Report

Surface Area

Single point surface area at $p/p^\circ = 0.199354834$: 16.2603 m²/g

BET Surface Area: 16.8027 m²/g

t-Plot Micropore Area: 1.8845 m²/g

t-Plot External Surface Area: 14.9182 m²/g

BJH Adsorption cumulative surface area of pores
between 1.000 Å and 3000.000 Å width: 16.4459 m²/g

BJH Desorption cumulative surface area of pores
between 1.000 Å and 3000.000 Å width: 22.8201 m²/g

Pore Volume

Single point adsorption total pore volume of pores
less than 1788.279 Å width at $p/p^\circ = 0.989169316$: 0.060216 cm³/g

t-Plot micropore volume: 0.000736 cm³/g

BJH Adsorption cumulative volume of pores
between 1.000 Å and 3000.000 Å width: 0.059661 cm³/g

BJH Desorption cumulative volume of pores
between 1.000 Å and 3000.000 Å width: 0.060607 cm³/g

Pore Size

Adsorption average pore width (4V/A by BET): 143.3479 Å

BJH Adsorption average pore width (4V/A): 145.109 Å

BJH Desorption average pore width (4V/A): 106.233 Å

Sample: VA-05-16 (50308)
 Operator: Olga
 Submitter: TRIANTAFYLLIDES
 File: C:\...\2007\50308.SMP

Started: 11/5/2007 2:18:41ii
 Completed: 11/5/2007 10:33:50ii
 Report Time: 15/5/2007 11:12:27di
 Warm Free Space: 7.6669 cm³ Measured
 Equilibration Interval: 50 s
 Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
 Analysis Bath Temp.: 77.300 K
 Sample Mass: 0.1795 g
 Cold Free Space: 23.2029 cm³ Measured
 Low Pressure Dose: None
 Automatic Degas: No

Isotherm Tabular Report

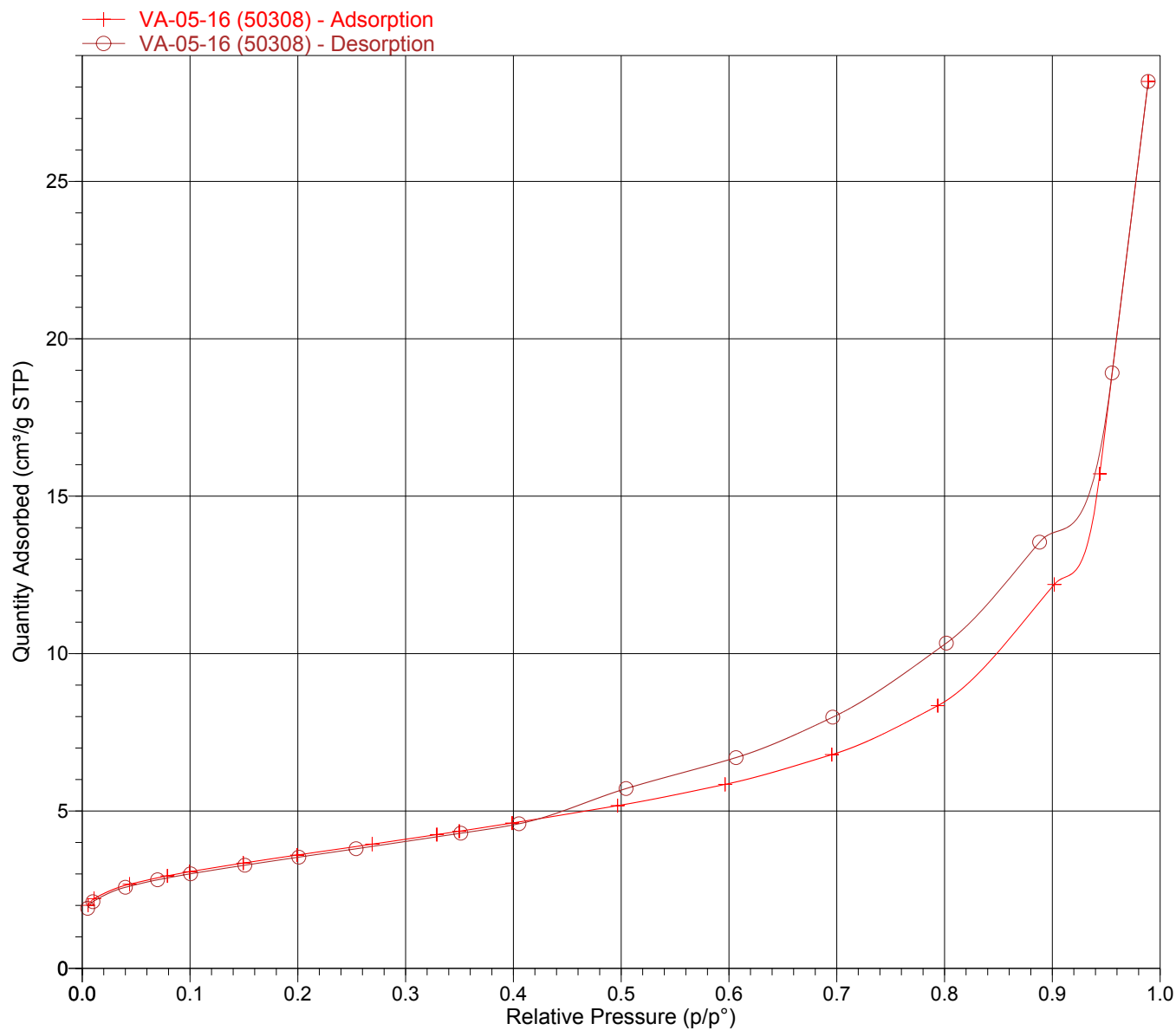
Relative Pressure (p/p°)	Absolute Pressure (kPa)	Quantity Adsorbed (cm ³ /g STP)	Elapsed Time (h:min)	Saturation Pressure (kPa)
			01:24	101.414633
0.005399389	0.547733	2.0020	02:16	
0.010996578	1.115588	2.2165	02:25	
0.043929049	4.456762	2.6730	02:34	
0.079045240	8.019824	2.9396	02:43	
0.099483885	10.093945	3.0687	02:51	
0.149438785	15.163274	3.3447	03:00	
0.199300627	20.223661	3.6002	03:09	
0.268963240	27.293894	3.9452	03:18	
			03:25	101.482059
0.328980269	33.385472	4.2497	03:26	
0.349749664	35.492011	4.3567	03:35	
0.398792343	40.467441	4.6177	03:44	
0.496617666	50.392596	5.1693	03:53	
0.596358622	60.511692	5.8449	04:01	
0.695364324	70.555331	6.7900	04:10	
0.793646900	80.524638	8.3459	04:20	
0.901817340	91.496077	12.1963	04:31	
0.944044162	95.776781	15.7098	04:41	
0.988969698	100.328003	28.1752	04:59	
0.955487135	96.927020	18.9191	05:11	
0.888143428	90.091530	13.5406	05:23	
			05:25	101.437295
0.801699231	81.321090	10.3331	05:32	
0.696301050	70.628550	7.9802	05:42	
0.606557602	61.524439	6.6966	05:51	
0.504527571	51.174514	5.7112	05:59	
0.405184156	41.097334	4.5938	06:08	
0.351260197	35.627266	4.2933	06:17	
0.253999146	25.761917	3.7991	06:26	
0.200957834	20.381833	3.5338	06:35	
0.150868138	15.301325	3.2778	06:43	
0.100501540	10.192872	3.0048	06:52	
0.069917502	7.090913	2.8132	07:01	
0.040026933	4.059376	2.5755	07:12	
			07:25	101.413526
0.009898141	1.003805	2.1186	07:26	
0.005031739	0.510286	1.9070	07:38	

Sample: VA-05-16 (50308)
Operator: Olga
Submitter: TRIANTAFYLIDIS
File: C:\...\2007\50308.SMP

Started: 11/5/2007 2:18:41ii
Completed: 11/5/2007 10:33:50ii
Report Time: 15/5/2007 11:12:27di
Warm Free Space: 7.6669 cm³ Measured
Equilibration Interval: 50 s
Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
Analysis Bath Temp.: 77.300 K
Sample Mass: 0.1795 g
Cold Free Space: 23.2029 cm³ Measured
Low Pressure Dose: None
Automatic Degas: No

Isotherm Linear Plot



Sample: VA-05-16 (50308)
 Operator: Olga
 Submitter: TRIANTAFYLIDIS
 File: C:\...\2007\50308.SMP

Started: 11/5/2007 2:18:41ii
 Completed: 11/5/2007 10:33:50ii
 Report Time: 15/5/2007 11:12:27di
 Warm Free Space: 7.6669 cm³ Measured
 Equilibration Interval: 50 s
 Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
 Analysis Bath Temp.: 77.300 K
 Sample Mass: 0.1795 g
 Cold Free Space: 23.2029 cm³ Measured
 Low Pressure Dose: None
 Automatic Degas: No

BET Surface Area Report

BET Surface Area: 12.9974 ± 0.0134 m²/g
 Slope: 0.331972 ± 0.000343 g/cm³ STP
 Y-Intercept: 0.002956 ± 0.000048 g/cm³ STP
 C: 113.296654
 Qm: 2.9857 cm³/g STP
 Correlation Coefficient: 0.9999989
 Molecular Cross-Sectional Area: 0.1620 nm²

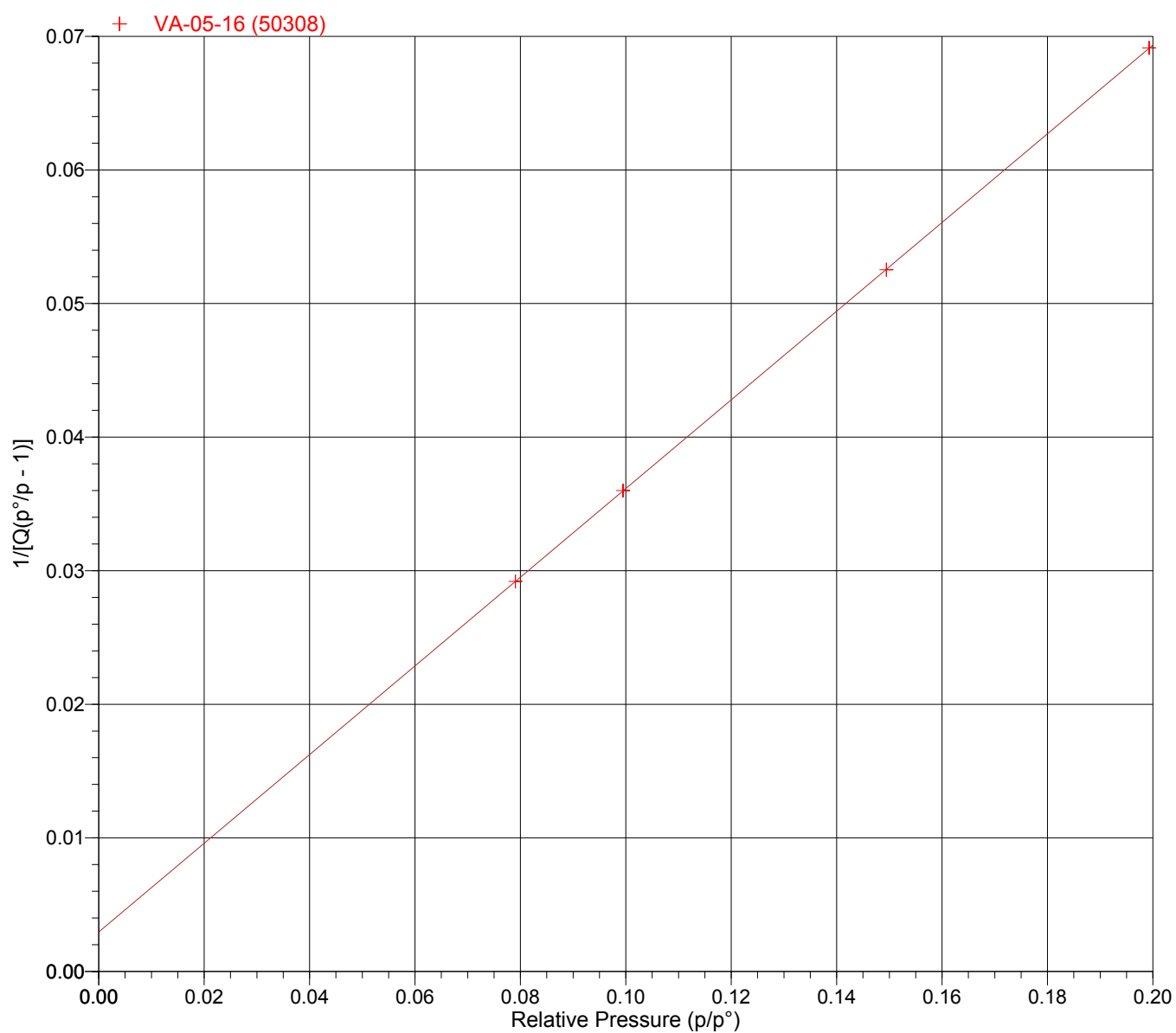
Relative Pressure (p/p°)	Quantity Adsorbed (cm ³ /g STP)	1/[Q(p°/p - 1)]
0.079045240	2.9396	0.029198
0.099483885	3.0687	0.036000
0.149438785	3.3447	0.052529
0.199300627	3.6002	0.069137

Sample: VA-05-16 (50308)
Operator: Olga
Submitter: TRIANTAFYLIDIS
File: C:\...\2007\50308.SMP

Started: 11/5/2007 2:18:41ii
Completed: 11/5/2007 10:33:50ii
Report Time: 15/5/2007 11:12:27di
Warm Free Space: 7.6669 cm³ Measured
Equilibration Interval: 50 s
Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
Analysis Bath Temp.: 77.300 K
Sample Mass: 0.1795 g
Cold Free Space: 23.2029 cm³ Measured
Low Pressure Dose: None
Automatic Degas: No

BET Surface Area Plot



Sample: VA-05-16 (50308)
 Operator: Olga
 Submitter: TRIANTAFYLLIDES
 File: C:\...\2007\50308.SMP

Started: 11/5/2007 2:18:41ii
 Completed: 11/5/2007 10:33:50ii
 Report Time: 15/5/2007 11:12:27di
 Warm Free Space: 7.6669 cm³ Measured
 Equilibration Interval: 50 s
 Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
 Analysis Bath Temp.: 77.300 K
 Sample Mass: 0.1795 g
 Cold Free Space: 23.2029 cm³ Measured
 Low Pressure Dose: None
 Automatic Degas: No

t-Plot Report

Micropore Volume: 0.000353 cm³/g STP
 Micropore Area: 1.0460 m²/g
 External Surface Area: 11.9515 m²/g
 Slope: 0.772657 ± 0.001272 cm³/g·Å STP
 Y-Intercept: 0.228325 ± 0.006488 cm³/g STP
 Correlation Coefficient: 0.999996
 Surface Area Correction Factor: 1.000
 Density Conversion Factor: 0.0015468
 Total Surface Area (BET): 12.9974 m²/g
 Thickness Range: 1.5000 Å to 8.0000 Å
 Thickness Equation: Harkins and Jura

$$t = [13.99 / (0.034 - \log(p/p^\circ))] ^{0.5}$$

Relative Pressure (p/p°)	Statistical Thickness (Å)	Quantity Adsorbed (cm³/g STP)
0.199300627	4.3643	3.6002
0.268963240	4.8115	3.9452
0.328980269	5.2028	4.2497
0.349749664	5.3420	4.3567
0.398792343	5.6825	4.6177

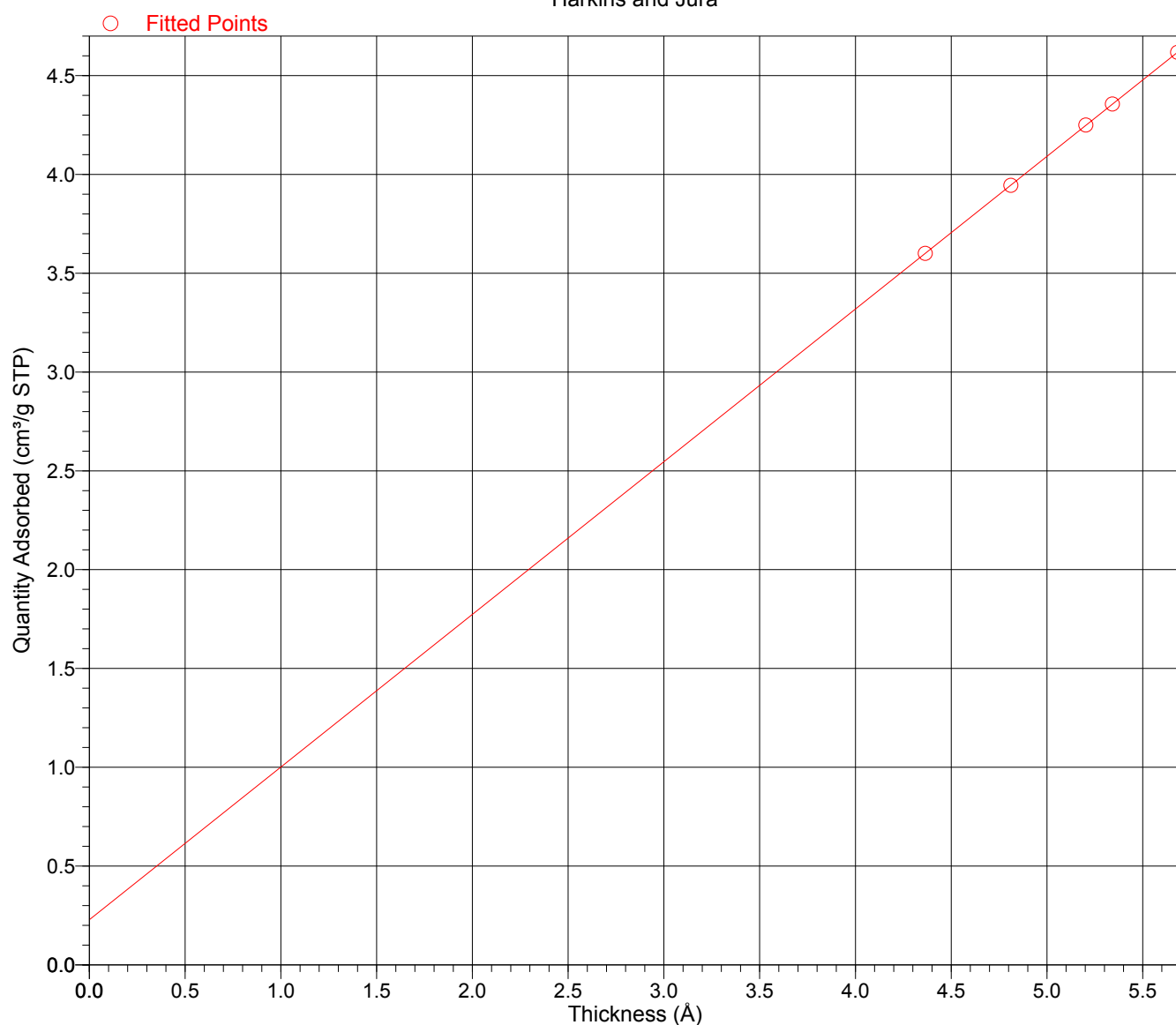
Sample: VA-05-16 (50308)
Operator: Olga
Submitter: TRIANTAFYLIDIS
File: C:\...\2007\50308.SMP

Started: 11/5/2007 2:18:41ii
Completed: 11/5/2007 10:33:50ii
Report Time: 15/5/2007 11:12:27di
Warm Free Space: 7.6669 cm³ Measured
Equilibration Interval: 50 s
Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
Analysis Bath Temp.: 77.300 K
Sample Mass: 0.1795 g
Cold Free Space: 23.2029 cm³ Measured
Low Pressure Dose: None
Automatic Degas: No

t-Plot

Harkins and Jura



Sample: VA-05-16 (50308)
Operator: Olga
Submitter: TRIANTAFYLIDIS
File: C:\...\2007\50308.SMP

Started: 11/5/2007 2:18:41ii
Completed: 11/5/2007 10:33:50ii
Report Time: 15/5/2007 11:12:27di
Warm Free Space: 7.6669 cm³ Measured
Equilibration Interval: 50 s
Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
Analysis Bath Temp.: 77.300 K
Sample Mass: 0.1795 g
Cold Free Space: 23.2029 cm³ Measured
Low Pressure Dose: None
Automatic Degas: No

Summary Report

Surface Area

Single point surface area at $p/p^\circ = 0.199300627$: 12.5489 m²/g

BET Surface Area: 12.9974 m²/g

t-Plot Micropore Area: 1.0460 m²/g

t-Plot External Surface Area: 11.9515 m²/g

BJH Adsorption cumulative surface area of pores
between 1.000 Å and 3000.000 Å width: 12.8416 m²/g

BJH Desorption cumulative surface area of pores
between 1.000 Å and 3000.000 Å width: 16.7207 m²/g

Pore Volume

Single point adsorption total pore volume of pores
less than 1756.389 Å width at $p/p^\circ = 0.988969698$: 0.043581 cm³/g

t-Plot micropore volume: 0.000353 cm³/g

BJH Adsorption cumulative volume of pores
between 1.000 Å and 3000.000 Å width: 0.043232 cm³/g

BJH Desorption cumulative volume of pores
between 1.000 Å and 3000.000 Å width: 0.043849 cm³/g

Pore Size

Adsorption average pore width (4V/A by BET): 134.1234 Å

BJH Adsorption average pore width (4V/A): 134.661 Å

BJH Desorption average pore width (4V/A): 104.897 Å

Sample: VA-05-17 (50309)
 Operator: Olga
 Submitter: TRIANTAFYLLIDES
 File: C:\...\2007\50309.SMP

Started: 11/5/2007 2:18:41ii
 Completed: 11/5/2007 10:33:50ii
 Report Time: 15/5/2007 11:38:01di
 Warm Free Space: 6.8139 cm³ Measured
 Equilibration Interval: 50 s
 Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
 Analysis Bath Temp.: 77.300 K
 Sample Mass: 0.2037 g
 Cold Free Space: 19.7344 cm³ Measured
 Low Pressure Dose: None
 Automatic Degas: No

Isotherm Tabular Report

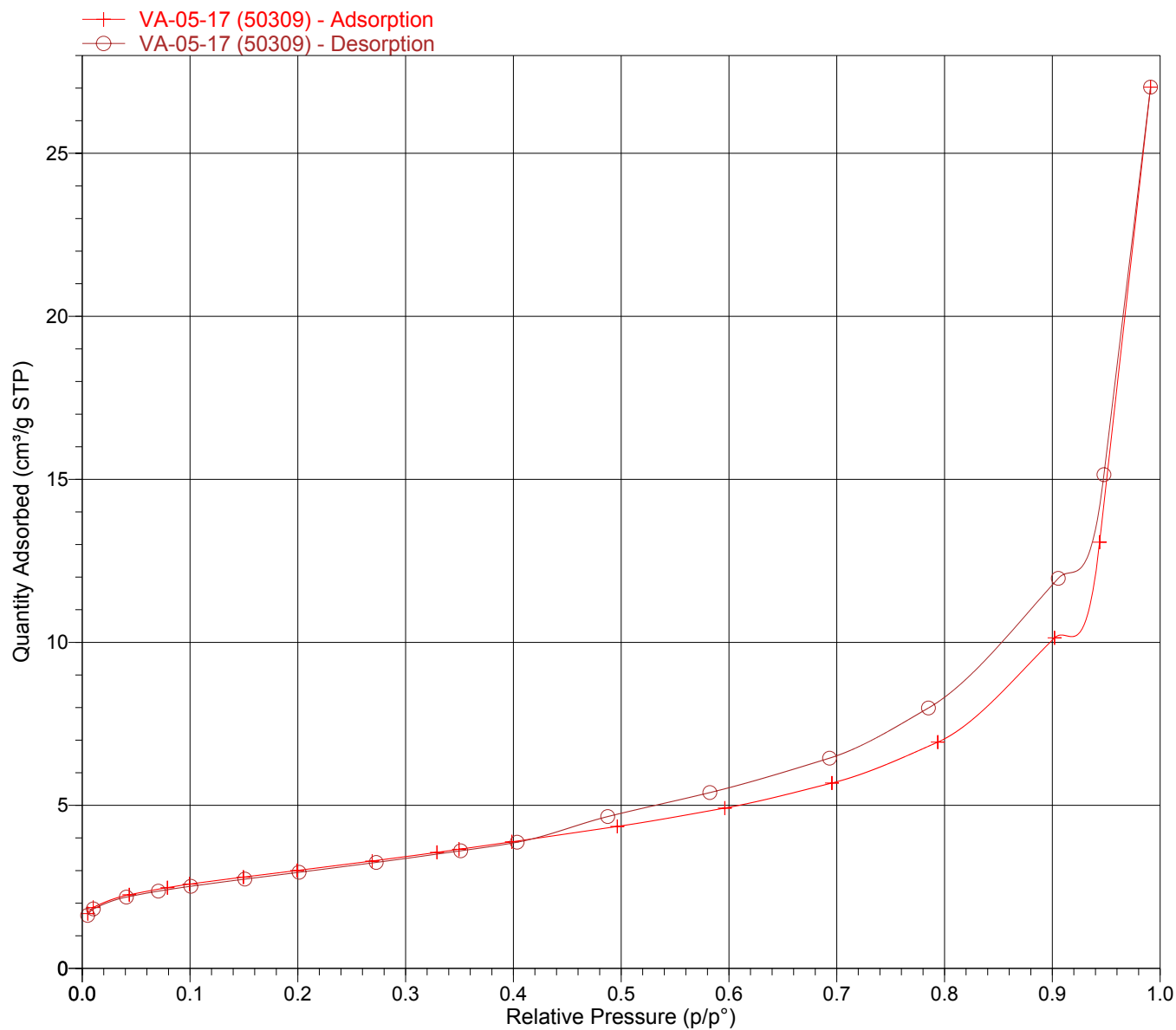
Relative Pressure (p/p°)	Absolute Pressure (kPa)	Quantity Adsorbed (cm ³ /g STP)	Elapsed Time (h:min)	Saturation Pressure (kPa)
			01:24	101.414633
0.005172702	0.524640	1.6788	01:42	
0.010225039	1.037117	1.8685	01:50	
0.043645022	4.427095	2.2585	01:59	
0.079050917	8.018858	2.4768	02:08	
0.099504951	10.094197	2.5837	02:17	
0.149586007	15.175295	2.7994	02:25	
0.199421815	20.232069	3.0028	02:34	
0.269042934	27.296734	3.2937	02:43	
0.329040427	33.385649	3.5578	02:52	
0.349531651	35.466517	3.6520	03:01	
0.398647083	40.451972	3.8824	03:09	
0.496410188	50.374791	4.3538	03:18	
			03:25	101.482059
0.596092085	60.492207	4.9176	03:27	
0.695556391	70.583640	5.6853	03:36	
0.793714311	80.541841	6.9392	03:45	
0.902057126	91.532183	10.1366	03:56	
0.943890610	95.773526	13.0725	04:06	
0.991074128	100.555540	27.0288	04:21	
0.947821881	96.162166	15.1437	04:35	
0.905568805	91.871624	11.9639	04:46	
0.785066205	79.643485	7.9871	04:56	
0.693257968	70.327127	6.4486	05:06	
0.582286831	59.067556	5.3914	05:16	
			05:25	101.437295
0.487508661	49.451560	4.6564	05:26	
0.403436824	40.923540	3.8698	05:35	
0.351089519	35.613571	3.6064	05:44	
0.272767449	27.668792	3.2504	05:52	
0.201094397	20.398472	2.9469	06:01	
0.150785365	15.295260	2.7375	06:10	
0.100727043	10.217479	2.5188	06:19	
0.070621201	7.163624	2.3694	06:28	
0.040891410	4.147914	2.1854	06:37	
0.010246015	1.039328	1.8224	06:50	
0.005079407	0.515241	1.6244	07:02	

Sample: VA-05-17 (50309)
Operator: Olga
Submitter: TRIANTAFYLIDIS
File: C:\...\2007\50309.SMP

Started: 11/5/2007 2:18:41ii
Completed: 11/5/2007 10:33:50ii
Report Time: 15/5/2007 11:38:01di
Warm Free Space: 6.8139 cm³ Measured
Equilibration Interval: 50 s
Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
Analysis Bath Temp.: 77.300 K
Sample Mass: 0.2037 g
Cold Free Space: 19.7344 cm³ Measured
Low Pressure Dose: None
Automatic Degas: No

Isotherm Linear Plot



Sample: VA-05-17 (50309)
 Operator: Olga
 Submitter: TRIANTAFYLIDIS
 File: C:\...\2007\50309.SMP

Started: 11/5/2007 2:18:41ii
 Completed: 11/5/2007 10:33:50ii
 Report Time: 15/5/2007 11:38:01di
 Warm Free Space: 6.8139 cm³ Measured
 Equilibration Interval: 50 s
 Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
 Analysis Bath Temp.: 77.300 K
 Sample Mass: 0.2037 g
 Cold Free Space: 19.7344 cm³ Measured
 Low Pressure Dose: None
 Automatic Degas: No

BET Surface Area Report

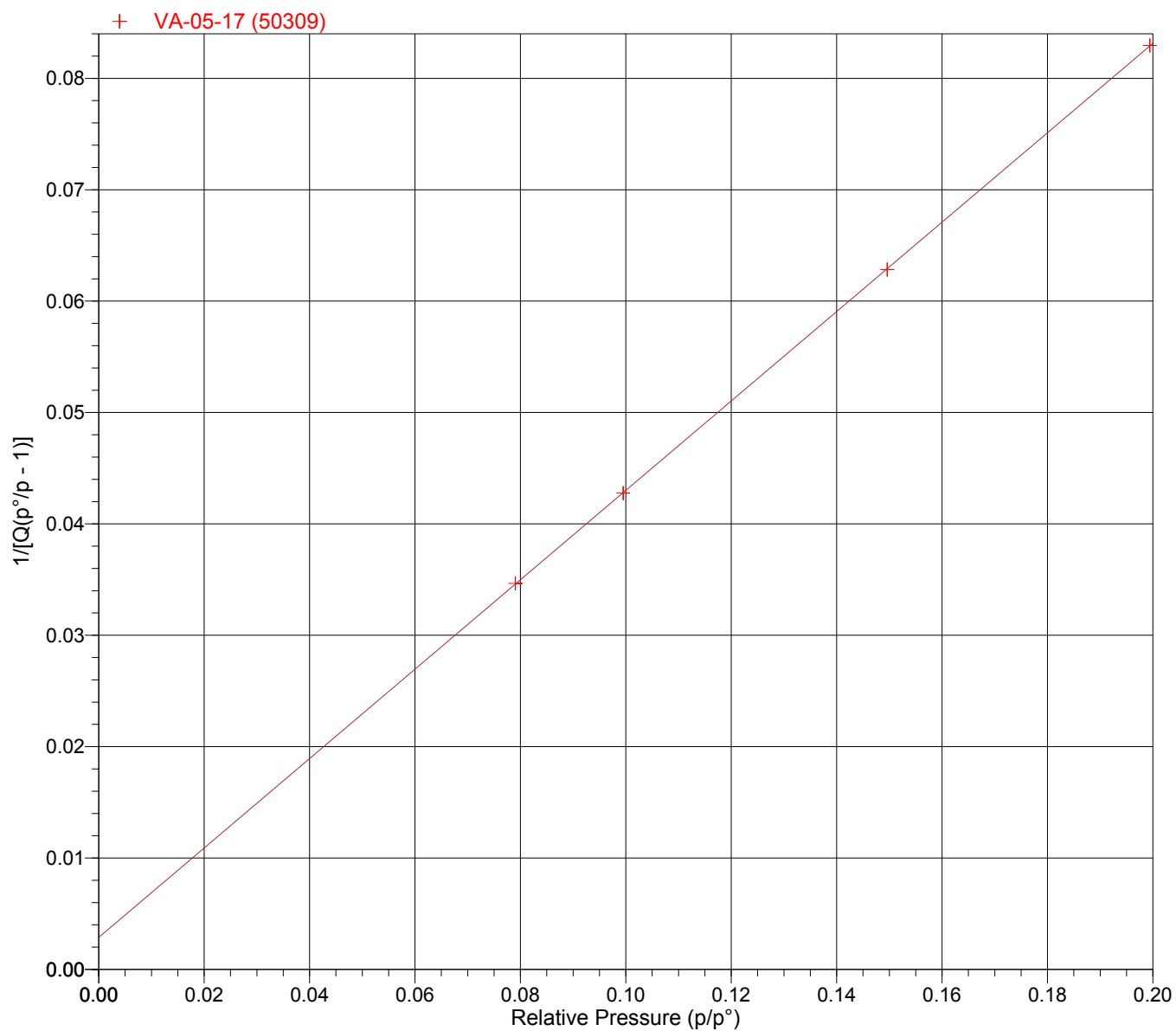
BET Surface Area: 10.7695 ± 0.0225 m²/g
 Slope: 0.401345 ± 0.000835 g/cm³ STP
 Y-Intercept: 0.002869 ± 0.000117 g/cm³ STP
 C: 140.871364
 Qm: 2.4739 cm³/g STP
 Correlation Coefficient: 0.9999957
 Molecular Cross-Sectional Area: 0.1620 nm²

Relative Pressure (p/p°)	Quantity Adsorbed (cm ³ /g STP)	1/[Q(p°/p - 1)]
0.079050917	2.4768	0.034656
0.099504951	2.5837	0.042768
0.149586007	2.7994	0.062835
0.199421815	3.0028	0.082954

Sample: VA-05-17 (50309)
Operator: Olga
Submitter: TRIANTAFYLIDIS
File: C:\...\2007\50309.SMP

Started: 11/5/2007 2:18:41ii
Completed: 11/5/2007 10:33:50ii
Report Time: 15/5/2007 11:38:01di
Warm Free Space: 6.8139 cm³ Measured
Equilibration Interval: 50 s
Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
Analysis Bath Temp.: 77.300 K
Sample Mass: 0.2037 g
Cold Free Space: 19.7344 cm³ Measured
Low Pressure Dose: None
Automatic Degas: No

BET Surface Area Plot

Sample: VA-05-17 (50309)
 Operator: Olga
 Submitter: TRIANTAFYLLIDES
 File: C:\...\2007\50309.SMP

Started: 11/5/2007 2:18:41ii
 Completed: 11/5/2007 10:33:50ii
 Report Time: 15/5/2007 11:38:01di
 Warm Free Space: 6.8139 cm³ Measured
 Equilibration Interval: 50 s
 Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
 Analysis Bath Temp.: 77.300 K
 Sample Mass: 0.2037 g
 Cold Free Space: 19.7344 cm³ Measured
 Low Pressure Dose: None
 Automatic Degass: No

t-Plot Report

Micropore Volume: 0.000123 cm³/g STP
 Micropore Area: 0.4222 m²/g
 External Surface Area: 10.3473 m²/g
 Slope: 0.668949 ± 0.003790 cm³/g·Å STP
 Y-Intercept: 0.079196 ± 0.019330 cm³/g STP
 Correlation Coefficient: 0.999952
 Surface Area Correction Factor: 1.000
 Density Conversion Factor: 0.0015468
 Total Surface Area (BET): 10.7695 m²/g
 Thickness Range: 1.5000 Å to 8.0000 Å
 Thickness Equation: Harkins and Jura

$$t = [13.99 / (0.034 - \log(p/p^\circ))] ^{0.5}$$

Relative Pressure (p/p°)	Statistical Thickness (Å)	Quantity Adsorbed (cm³/g STP)
0.199421815	4.3651	3.0028
0.269042934	4.8120	3.2937
0.329040427	5.2032	3.5578
0.349531651	5.3405	3.6520
0.398647083	5.6814	3.8824

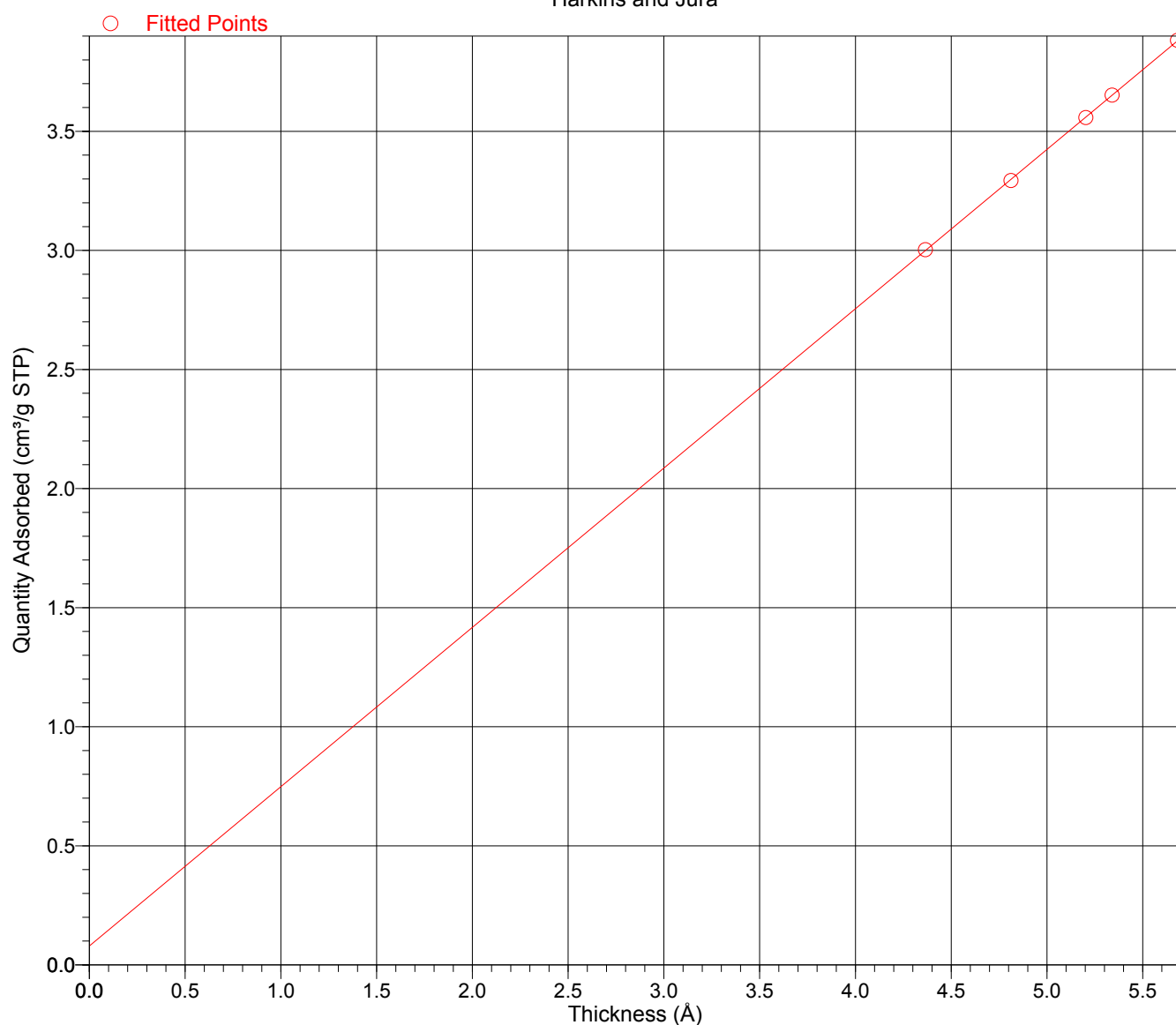
Sample: VA-05-17 (50309)
Operator: Olga
Submitter: TRIANTAFYLIDIS
File: C:\...\2007\50309.SMP

Started: 11/5/2007 2:18:41ii
Completed: 11/5/2007 10:33:50ii
Report Time: 15/5/2007 11:38:01di
Warm Free Space: 6.8139 cm³ Measured
Equilibration Interval: 50 s
Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
Analysis Bath Temp.: 77.300 K
Sample Mass: 0.2037 g
Cold Free Space: 19.7344 cm³ Measured
Low Pressure Dose: None
Automatic Degas: No

t-Plot

Harkins and Jura



Sample: VA-05-17 (50309)
Operator: Olga
Submitter: TRIANTAFYLIDIS
File: C:\...\2007\50309.SMP

Started: 11/5/2007 2:18:41ii	Analysis Adsorptive: N2
Completed: 11/5/2007 10:33:50ii	Analysis Bath Temp.: 77.300 K
Report Time: 15/5/2007 11:38:01di	Sample Mass: 0.2037 g
Warm Free Space: 6.8139 cm ³ Measured	Cold Free Space: 19.7344 cm ³ Measured
Equilibration Interval: 50 s	Low Pressure Dose: None
Sample Density: 1.000 g/cm ³	Automatic Degas: No

Summary Report

Surface Area

Single point surface area at $p/p^\circ = 0.199421815$: 10.4652 m²/g

BET Surface Area: 10.7695 m²/g

t-Plot Micropore Area: 0.4222 m²/g

t-Plot External Surface Area: 10.3473 m²/g

BJH Adsorption cumulative surface area of pores
between 1.000 Å and 3000.000 Å width: 10.4437 m²/g

BJH Desorption cumulative surface area of pores
between 1.000 Å and 3000.000 Å width: 14.0789 m²/g

Pore Volume

Single point adsorption total pore volume of pores
less than 2164.250 Å width at $p/p^\circ = 0.991074128$: 0.041808 cm³/g

t-Plot micropore volume: 0.000123 cm³/g

BJH Adsorption cumulative volume of pores
between 1.000 Å and 3000.000 Å width: 0.041421 cm³/g

BJH Desorption cumulative volume of pores
between 1.000 Å and 3000.000 Å width: 0.042039 cm³/g

Pore Size

Adsorption average pore width (4V/A by BET): 155.2831 Å

BJH Adsorption average pore width (4V/A): 158.644 Å

BJH Desorption average pore width (4V/A): 119.437 Å