

Comparative analysis of Na⁺ and Ca²⁺ ion effects on the physical-chemical properties of Bentonite: Implications for industrial applications

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ABSTRACT

This study investigates the potential industrial applications of two types of bentonite - Calcium Bentonite (Ca-B) and Sodium Bentonite (Na-B) - from the Kert Basin in northern Morocco. The bentonite samples' structural characteristics, inclusions, and microcracks were examined using scanning electron microscopy. X-ray diffraction analysis of both the whole rock and clay fractions was conducted to determine the bentonite type and mineralogical composition. The chemical composition was assessed through X-ray fluorescence. The physico-chemical properties analyzed included cation exchange capacity, swelling index, colloidal index, water content, and pH. The plasticity index and liquid limit were determined using Atterberg limits tests. The results indicate that sodium bentonite exhibits superior absorption and plasticity compared to calcium bentonite, with a higher cation exchange capacity, particularly after activation. The analyzed bentonites contain high amounts of iron and silica, with moderate levels of calcium and aluminum. Quartz, feldspars, and clay minerals were identified in all samples, with smectite being the dominant clay mineral phase (80 %), along with traces of kaolinite, illite, and interstratified illite-smectite. These bentonites generally display high plasticity, making them well-suited for hydraulic drilling applications. Additionally, their low organic matter and calcium carbonate (CaCO₃) content may indicate mechanical strength, water sensitivity, and purity.

1. Introduction

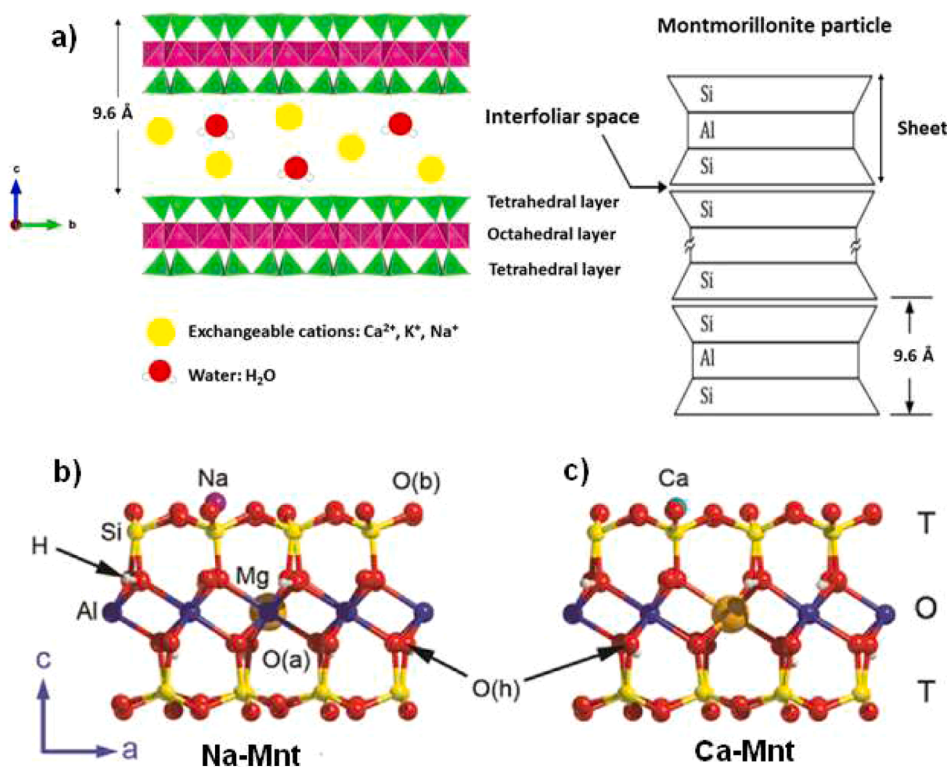
Clay minerals, depending on their nature and classification, are generally characterized by their water adsorption capacity, plasticity, and swelling index (Lyu et al., 2015; El Ouahabi et al., 2019). Among them, bentonite is widely used in industry due to its unique properties. It

is a volcanic clay rock formed through the alteration and hydrothermal transformation of volcanic ash rich in glass (Belousov and Karelina, 2022), leading to the neoformation of clay minerals. Originally deposited as volcanic ash in freshwater or saltwater millions of years ago, bentonite undergoes chemical transformation over time (Adamis and Williams, 2005). It is typically composed of >85 % montmorillonite,

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Silicon (Si), Aluminum (Al), Magnesium (Mg), Sodium (Na), Calcium (Ca), Oxygen (O), Hydrogen (H)
O(b), O(a), and O(h) refer to the basal, apical, and hydroxyl oxygen atoms, respectively.

Fig. 1. (a) Crystalline structure of montmorillonite, viewed along the [010] direction (Lambe, 1953); (b) Sodium montmorillonite (Na-Mnt); and (c) Calcium montmorillonite (Ca-Mnt) (Ulian et al., 2021).

along with impurities, including other clay minerals (e.g., chlorite, vermiculite) and non-clay minerals (e.g., quartz, feldspars, gypsum, calcite). Montmorillonite, the primary component of bentonite, is a clay mineral with a 2:1 tetrahedral-octahedral-tetrahedral (TOT) structure (Fig.1) (Holtz and Kovacs, 1981; Ulian et al., 2021). This structure contributes to its high adsorption capacity and swelling, making it valuable for various industrial applications.

The elementary layer consists of a thin section of alumina (octahedron) enclosed between two silica (tetrahedron) layers, where the aluminum in the octahedral layer is sometimes partially replaced by magnesium. Isomorphous substitutions on the surface of the layers result in an excess negative charge. This charge deficit is compensated by Ca²⁺ or Na⁺ cations to maintain electrical neutrality. Montmorillonites compensated by Ca²⁺ cations are called calcic montmorillonites (the most common), while those compensated by Na⁺ cations are called sodium montmorillonites.

In this context, numerous studies have shown that the presence of Ca²⁺ or Na⁺ as substituents within the montmorillonite structure influences the physicochemical properties and plasticity of bentonite (e.g., Huang et al., 2015; Krupskaya et al., 2017; Ulian et al., 2021; Barbieri et al., 2022; Et-Tayea et al., 2023). Increasing the Na/Ca ratio can significantly enhance bentonite's swelling capacities and plasticity-modifying properties. Understanding the difference between calcium and sodium bentonite is essential for selecting the appropriate type for specific applications. However, both are clay minerals that share several common characteristics. Their distinct properties make one more suitable than the other depending on the intended use.

Bentonites, particularly montmorillonite-rich varieties, are widely studied for their diverse industrial and environmental applications. Vincenzi et al. (2015) explored their adsorption of organic compounds,

relevant to the food industry. Thermal behavior studies by Sarikaya et al. (2000) revealed structural changes affecting adsorption properties, while Youcef and Achour (2004) demonstrated enhanced fluoride removal after acid activation, supporting water purification applications. Önal (2007) found that heating and acid activation modified cation exchange capacity (CEC) and swelling, influencing adsorption performance. Kaufhold et al. (2008) examined how carbonates and exchangeable cations impact bentonite suspension pH, while Benyounes et al. (2010) characterized Algerian bentonites, highlighting their industrial potential. Yener et al. (2012) confirmed excellent adsorption of methylene blue, relevant for waste management. Chalah et al. (2018) investigated the influence of polymers on drilling fluid rheology.

Moroccan bentonites have shown promise in adsorbing heavy metals and organic pollutants (Ait Hmeid et al., 2019, 2021a, b, c, d, 2022, 2025). Et-Tayea et al. (2023) highlighted their suitability for ceramics due to their high plasticity and swelling properties. Böhm et al. (2024) optimized adsorption studies for hydrophobic organic compounds, while Imgirne et al. (2025) explored their use in sustainable porous ceramics. The bentonites of northeastern Morocco result from volcanic activity in a semi-arid Mediterranean climate (Hernandez et al., 1987). Together, these studies underscore bentonite's versatility in water treatment, adsorption, drilling fluids, ceramics, and sustainable materials.

The main objective of this study is to analyze the behavior of bentonite types from the Trebia Basin in northern Morocco, specifically calcium (Ca-B) and sodium (Na-B) bentonites. The study aims to understand the implications of their applications across various industries. The findings will offer essential insights into the utilization of these clay deposits, providing valuable information for the effective exploitation of both bentonite types based on their distinctive properties.

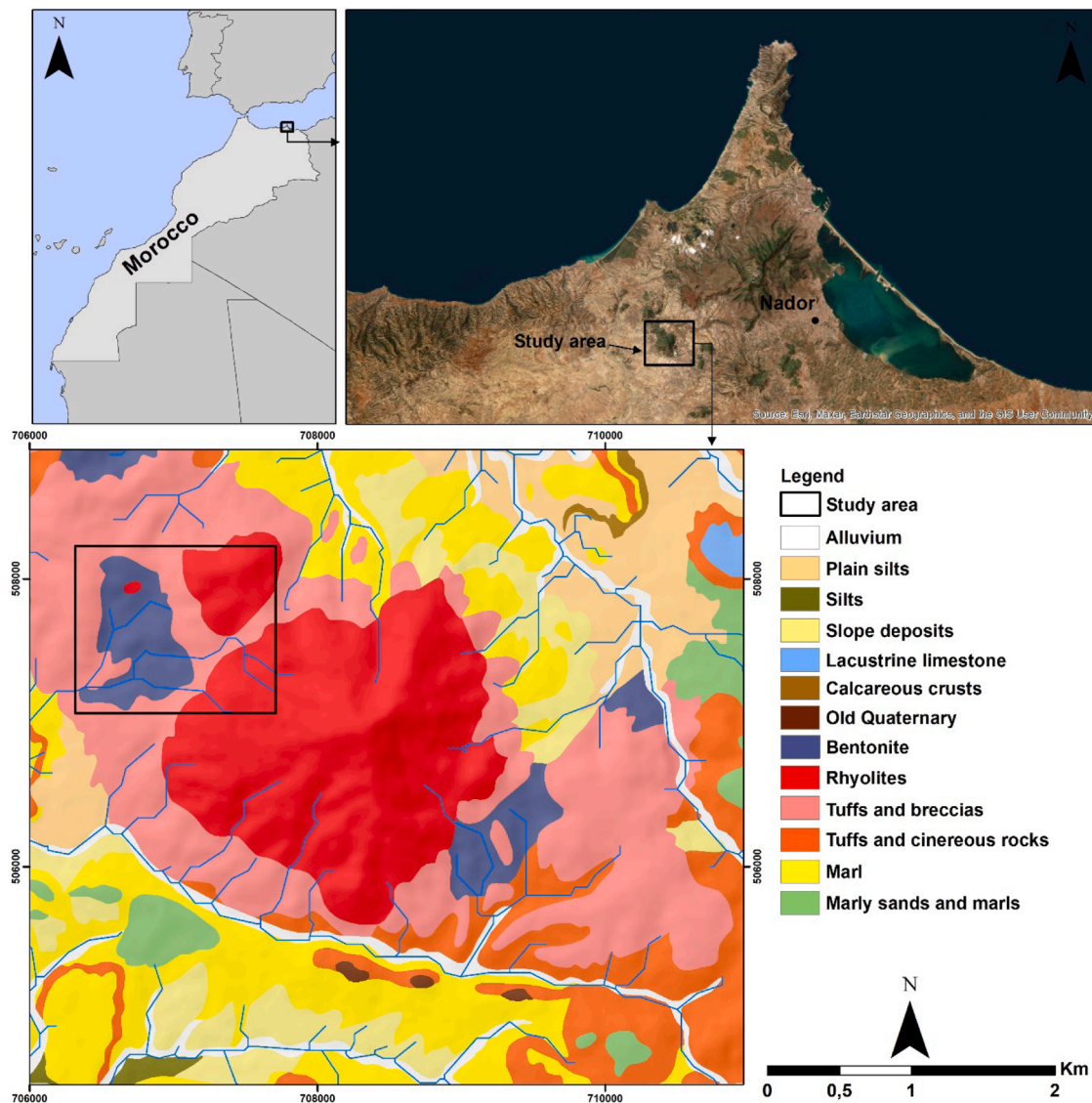


Fig. 2. Geological map of the Trebia deposit (modified from Chalouan et al., 2001), showing the locations where bentonite samples are collected. Extracted from the geological map of the Rif region/Zeghanghane (Scale=1:50,000).

2. Materials and methods

2.1. Geographical and geological overview of the study area

The Trebia deposit, located in the external domain of the Rif Mountain chain, lies on the western flank of the city of Nador, within the Neogene Kert Basin (Fig. 2). Geographically, it is situated southwest of the Tidiennit massif, approximately 18 km from Nador. This deposit showcases unique geological features, including large mineralized masses surrounded by pyroclastic materials and rhyolitic breccias, indicative of the intense volcanic activity that shaped the region during past geological periods. The surrounding geological formations are crucial for understanding the site's geological history. To the south, the deposit is bordered by the Providencia bentonites, while volcanic formations associated with Trebia mark its western boundary. This diverse range of materials enhances the study of the site. The Trebia bentonites are located on the northwest flank of the Tidiennit magmatic massif in the Nador region, part of the external domain of the Rif Mountain chain (Louaya and Hamoumi, 2010). This region is particularly significant due to its complex geological history, marked by major tectonic processes. Most of the sedimentary basins in the region were formed during the

Messinian to Pliocene period, a time characterized by subduction processes and intense volcanic activity. This volcanic activity was key in the formation of the Gourougou complex, a major volcanic massif in the region (Hernandez, 1983; El Bakkali, 1995; El Bakkali et al., 1998; Ddani et al., 2005). The intensity of this volcanic activity has left lasting geological traces, including deposits of volcanic ash, lava, and pyroclastic flows.

During the formation of the Neogene basins, lava flows, pyroclastic flows, and volcanic ash were gradually deposited. These materials then underwent hydrothermal alteration, transforming into bentonite deposits. This process occurred in an open system, where water circulated through the geological layers, facilitating the conversion of volcanic ash into clay rich in minerals such as montmorillonite, a key characteristic of bentonites (Hernandez and Bellon, 1985; El Bakkali et al., 1998; Ddani et al., 2005).

The Trebia bentonite deposit is bounded to the south by perlite formations and to the north by rhyolites, creating an intriguing geological juxtaposition between materials of varying volcanic origin (Fig. 3). In addition to its geological significance, the Trebia deposit is crucial for understanding volcanic dynamics and the processes of clay formation in this region of the Rif.

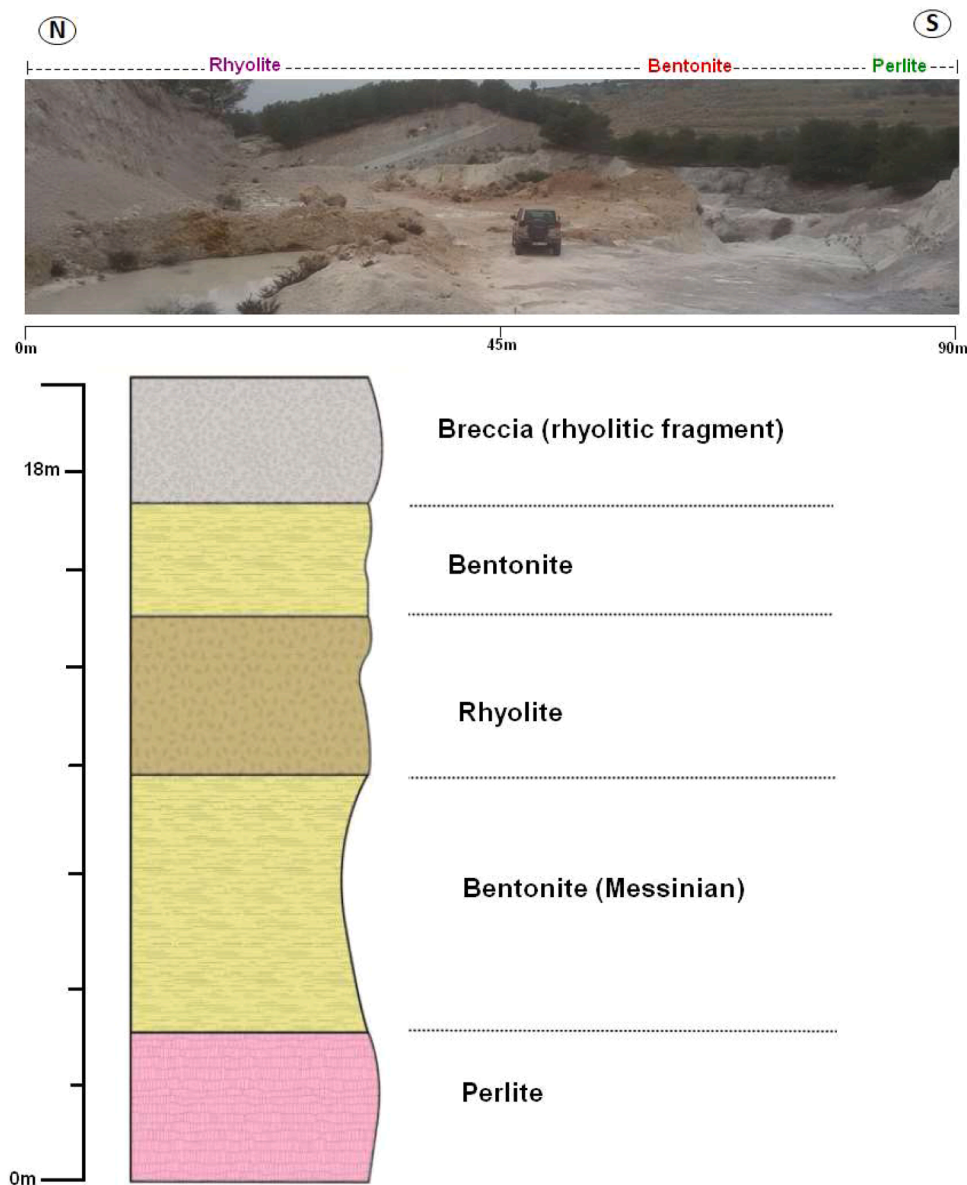


Fig. 3. View of the Trebia-Jbel Tidiennit deposit and a simplified stratigraphic log of the studied area.

The bentonite deposits are of great importance due to their unique properties, such as water absorption and moisture retention, making them highly sought after in various industries, including filtration, agriculture, and the cosmetic and pharmaceutical sectors. These characteristics endow the Trebia deposit with significant economic potential, in addition to its scientific value. The surrounding geological formations, particularly the rhyolites and perlites, further enrich the analysis of this site, offering insight into the complex geological evolution of the region and the interactions between different volcanic materials.

Thus, studying this deposit and the surrounding geological formations is essential for understanding geological processes in the Rif, as well as for the sustainable management and exploitation of the region's mineral resources. This deposit serves as a link between geological research and industrial applications, with important implications for both the local and national economy.

The sampling technique involved the systematic collection of six samples from the bentonite layer, using a 5-meter spaced grid. Three samples were calcium bentonite (Ca-B), while the other three were sodium bentonite (Na-B). This approach allowed for an in-depth comparative analysis of the characteristics specific to each variety

(Fig.3). The locations of the calcium and sodium bentonites were randomly distributed within the bentonite reservoir.

2.2. Methods

Distinct analysis methods were employed to investigate the various characteristics of the Trebia bentonites:

- The particle size distribution of Trebia samples was analyzed using a Horiba 300 laser diffraction instrument. A one-gram portion of the pre-prepared sample was disintegrated in demineralized water. Prior to analysis, the samples were placed on a magnetic stirrer to break up agglomerates (Bertrand et al., 2008).
- The water content was determined by dehydrating the samples in an oven at 105 °C for 24 h. The mass of the material after drying was considered the mass of solid particles (Ps). Water content was calculated according to standard NF P94-050 (Callaud, 2004; Holtz and Kovacs, 1981).

Table 1

Grain size distribution of studied samples.

	Particle-size distribution (wt.%)			D ₁₀ (mm)	D ₃₀ (mm)	D ₆₀ (mm)	Cu	Cc
	>60 μm	2–60 μm	<2 μm					
Na-B ₁	43.1	52.4	4.5	0.0113	0.089	0.047	4.13	14.81
Na-B ₂	77.5	20.8	1.7	0.0394	0.29	0.1	2.6	20.68
Na-B ₃	52.7	43.9	3.4	0.0179	0.213	0.057	3.18	44.52
Ca-B ₁	77.5	20.8	1.7	0.0395	0.29	0.103	2.6	20.68
Ca-B ₂	45	46.5	8.5	0.0051	0.23	0.039	7.8	26.96
Ca-B ₃	59.4	35.9	4.7	0.0168	0.23	0.065	3.9	49.69

*Caption = Na-B : Sodium Bentonite; Ca-B : Calcium Bentonite; >60 μm (%) : Sand (%); 2–60 μm (%) : Silt (%); <2 μm (%) : Clay (%); Dx (mm) : The effective particle diameter corresponding to x % passing; Cu : Hazen's uniformity coefficient ($Cu = D_{60} / D_{10}$); Cc : Curvature coefficient ($Cc = (D_{30}^2 / (D_{10} \times D_{60}))$).

- Calcium carbonate (CaCO₃) content was measured using the calcimetric method, based on the Bernard calcimeter protocol in accordance with standard NF P 94 048 (AFNOR, 1996).
- Organic matter (OM) content was calculated using the Loss on Ignition method, which involves heating the samples to 1000 °C for 2 h (Daoudi et al., 2018).
- pH values were measured with a basic 20+ pH meter, calibrated using buffer solutions at pH 4, 7, and 10.
- X-ray diffraction (XRD) characterizations were performed on both unoriented powders (to determine total mineralogy) and oriented slides (< 2 μm) to analyze the clay fraction. The analyses were conducted Both total mineralogy and clay mineralogy were determined using a Bruker D8-Advance diffractometer with a copper anticathode. Semi-quantitative analysis was performed following the method of Cook et al. (1975), using X'pert HighScore, and the international mineralogical database (ICDD), to detect mineral phases, with an estimated uncertainty of ±5 % (Cook et al., 1975; Moore and Reynolds, 1989; Marcoen et al., 2000; Fagel and Boës, 2008).
- The microstructure of the bentonites was examined using a Philips XL30 scanning electron microscopy (SEM). The average grain size of the bentonites was estimated using Image J software.
- Elemental composition was determined using a Panalytical Axios spectrometer equipped with an Rh tube, utilizing argon/methane gas.

The liquid limit (LL) is determined following the method described by Casagrande (1947) and Andrade et al. (2011), using the Casagrande apparatus following ASTM D3418 (1983). The plastic limit (PL) test involves rolling a soil sample into a 3 mm diameter thread, with the PL defined as the point at which the thread begins to crack upon this diameter, following the NF P 94–050 standard (AFNOR, 1996). By comparing the natural water content (W) with the Atterberg limits, the material's state can be assessed using the consistency index (CI), calculated as follows (Callaud, 2004):

$$CI = \frac{(LL - W)}{(LL - PL)} = \frac{(LL - W)}{(LL - PL)}$$

Where, LL : liquidity limit; PL : Plasticity limit; W : Natural water content; IP : Plasticity index.

The swelling index is measured by placing 2g of 63μm sieved

bentonite into a graduated tube, adding 100 ml of water, and shaking for one minute to suspend the clay particles. The height of the settled deposit is recorded after 24 h (Phanikumar 2006).

Colloidalilty is assessed by suspending 4g of bentonite in 100 ml of distilled water with the addition of 0.2g of MgO to promote deflocculation. After shaking for 5 min, the mixture is placed in a graduated tube, and after 24 h, the volume V (ml) occupied by the floating particles is measured (Gillot, 1968).

The methylene blue V_{BS} value is determined using the filter paper staining method, following the P 18–592 standard. The Cation exchange capacity (CEC) and specific surface area are then calculated from the V_{BS} value, based on formulas proposed by Medjnoun (2014) and Arab et al. (2015).

3. Results

3.1. Grain size distribution

The particle size analysis reveals that Trebia samples consist of 60 % sand fraction (>60 μm), 30 % silt fraction (2–60 μm), and 10 % clay fraction (<2 μm) on average (Table 1). The uniformity coefficient values exceed 2, indicating a significant proportion of particles between 1 and 2 μm, which are classified as colloidal particles. The uniformity and curvature coefficients, with a uniformity coefficient < 5 and a curvature coefficient > 3, suggest that the Trebia deposit exhibits an ungraded grain distribution. These results confirm that the texture of Trebia samples is primarily silty sand.

3.2. Physico-chemical parameters

The Trebia bentonites contain moderate amounts of CaCO₃, with values ranging from 6 to 11 %. Total inorganic carbon (TIC) and organic matter are present in low quantities (< 1 %), while the loss on ignition at 950 °C varies between 1 and 10 % (Table 2). The pH values range from 6.94 to 9.23, indicating the material's significant alkalinity. The studied bentonites have water contents ranging from 15.74 to 36.95 %, which can be attributed to their hygroscopic nature and high porosity (Rollet and Bouaziz, 1972).

Table 2

Physico-chemical parameters of the studied bentonites.

	CaCO ₃	MO	COT	LOI 950 °C	CIT	Weight (g) 550 °C	Weight (g) 950 °C	W	pH
Na-B ₁	11	0.08	0.61	9.9	2.7	139.8	129.9	16.28	9.23
Na-B ₂	6	0.12	0.79	1.01	0.2	141.3	139.9	36.95	7.54
Na-B ₃	8	0.05	0.71	9.8	2.7	144.3	130.1	36.41	7.14
Ca-B ₁	7	0.1	0.56	5.4	1.4	161.1	152.4	15.74	9.17
Ca-B ₂	7	0.03	0.51	10.08	2.7	140.9	130.9	30.63	6.94
Ca-B ₃	7	0.12	0.87	4.8	1.3	164.9	156.9	16.45	8.92

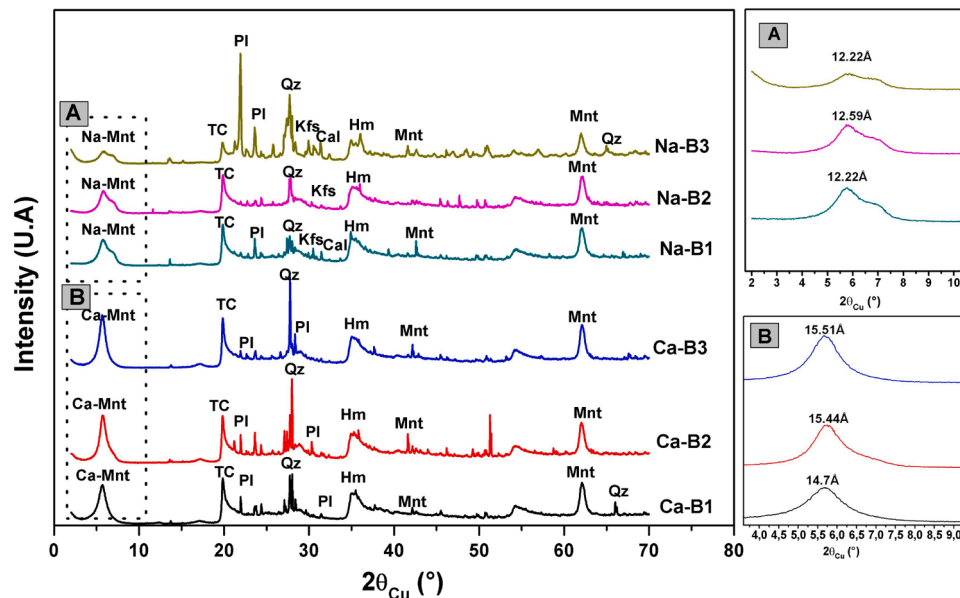
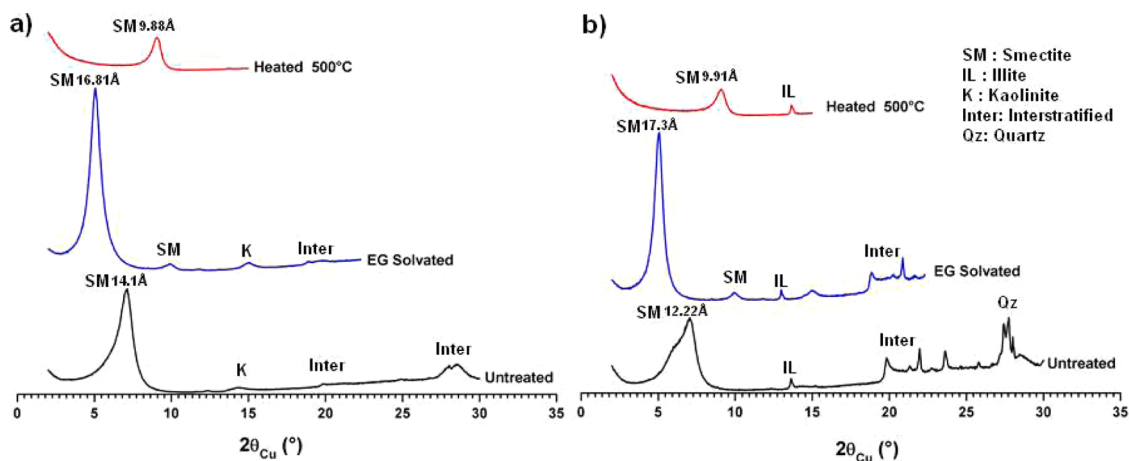
*Caption = CaCO₃ (%) : Calcium carbonate rate; MO (%) : Organic matter content; COT (%) : Total organic carbon content; CIT (%) : Total inorganic carbon content; LOI 950 °C : Loss on Ignition at 950 °C; W (%) : Water content; pH (dimensionless) : potential of hydrogen.

Table 3

Mineralogical composition of the bulk samples and clay fraction of Trebia bentonite (wt.%).

	Kaolinite	Illite	Smectite	K-feldspar	Quartz	Plagioclases	Calcite	Dolomite	Hematite
Na-B ₁	3.5	8.2	24.3	20	11	10.2	3.3	1.1	18.4
Na-B ₂	2.7	5.2	24	20.6	14.3	10	3	1.3	18.9
Na-B ₃	1.3	5.1	24.9	24.2	12.1	9	4	1.1	18.3
Ca-B ₁	1.1	2.4	24	28.5	12.1	9.6	3.9	2.1	18.9
Ca-B ₂	0.3	0.6	24.1	20.1	26	10.1	4.4	1.1	19
Ca-B ₃	1.5	2	27.2	20	11.9	11.5	3.5	3.7	18.7

*Explanatory Note: The percentages are expressed relative to the total weight of the sample.

**Fig. 4.** XRD pattern of Ca-B and Na-B (a & b). Na-Mnt = sodium montmorillonite; Ca-Mnt = calcium montmorillonite; TC = total clays; Qz = quartz; Kfs = K-feldspar; PI = plagioclase; M = montmorillonite; Hm = hematite; Cal = calcite.**Fig. 5.** XRD patterns of the studied clay fractions (<2 μm) with three different treatments (N: untreated; EG: saturated with ethylene glycol; H: heated at 500 °C for 4 h). (a) Ca-B sample; (b) Na-B sample.

3.3. Mineralogical and chemical composition

The total mineralogical composition, determined by X-ray diffraction, reveals that the clays of Trebia are primarily composed of montmorillonite (24 to 27.2 wt.%), K-feldspar (20 to 28.5 wt.%), quartz (11 to 26 wt.%), hematite (18.3 to 19 wt.%), and plagioclase (9 to 11.5 wt.%). Calcite is present in small quantities (3 to 4.4 wt.%) and dolomite is found in trace amounts (1.1 to 3.7 wt.%) (Table 3).

The diffractograms of the disoriented powder show both sodic and calcic montmorillonites (Fig. 4). When the diffraction peak (001) of montmorillonite appears with a 14–15 Å spacing, it represents the calcic pole (Ca-Mnt). In contrast, a 12 Å peak indicates the sodic pole (Na-Mnt) (Inglethorpe, 1993). The other three peaks are located at 4.48 Å (d_{110}), 2.16 Å (d_{200}), and 1.49 Å (d_{060}). The d_{060} reflection at 1.49 Å confirms the dioctahedral nature of smectite (Inglethorpe, 1993; Kumpulainen and Kiviranta, 2010). Analysis of the oriented powder (N-EG-H500)

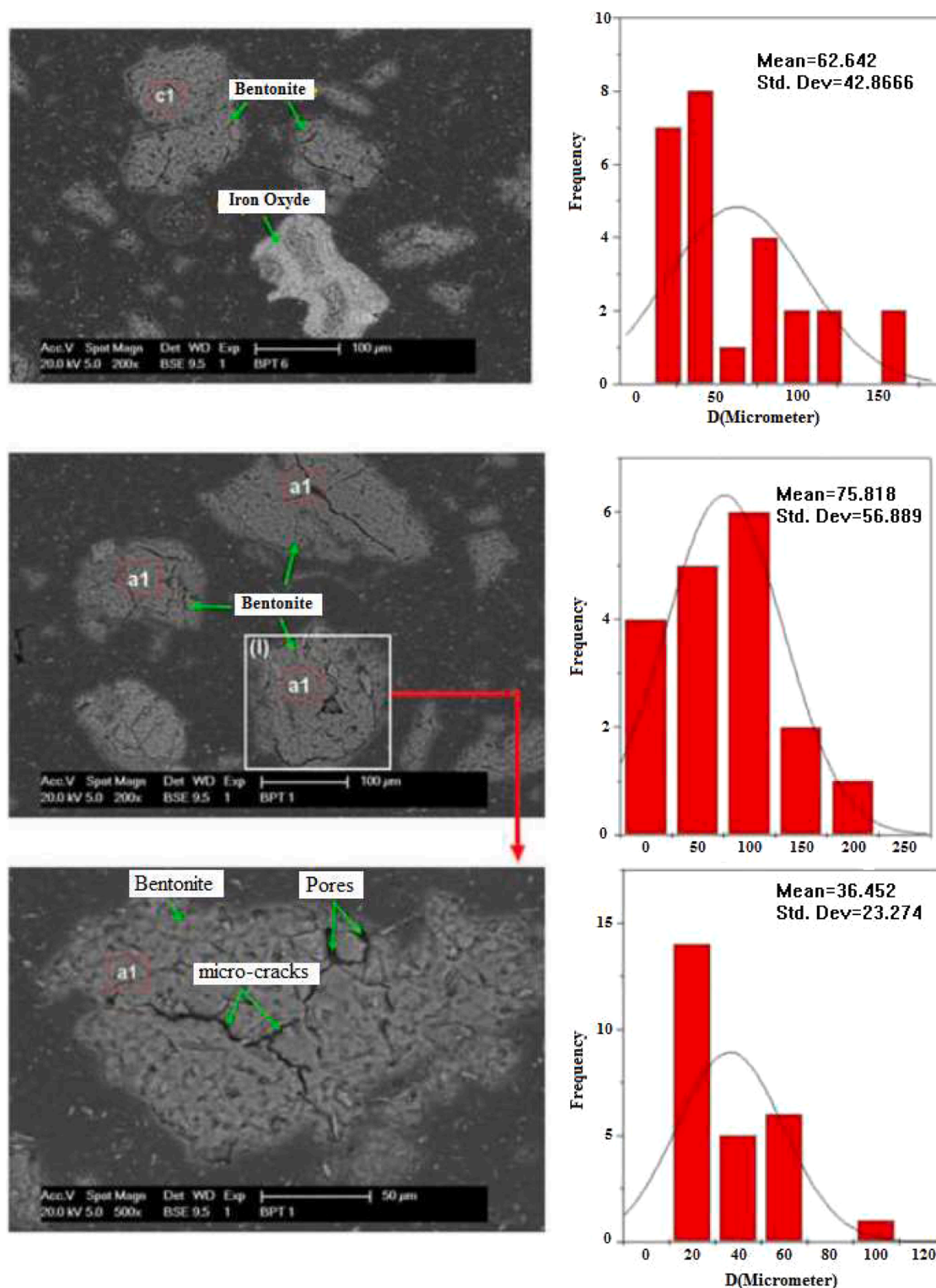


Fig. 6. SEM images and particle distribution of bentonites extracted from the Trebia deposit.

shows a clay fraction predominantly composed of smectite (Fig. 5), which constitutes over 80 % of the clay fraction, along with illite, kaolinite, and interstratified 10–14 Å minerals.

The presence of smectite in large quantities has been confirmed by a scanning electron microscope (SEM), which reveals spherical particles with heterogeneous dimensions. SEM images also highlight the presence of feldspar, plagioclase, and iron oxides (Fig. 6). At higher resolution (50 µm), the distribution of grains within the structure, along with pores and

micro-cracks, can be observed.

Table 4 shows that the elemental composition of Trebia bentonites is characterized by a high iron content, ranging from 37.5 % to 42.3 %, which is attributed to the presence of hematite (Fe_2O_3), as identified by X-ray diffraction (XRD) analysis. The silica content ranges from 9.9 % to 16.7 %, corresponding to quartz, feldspar, and clay minerals. Aluminum (Al) content ranges from 5.5 % to 12 %, while calcium (Ca) content ranges from 9.6 % to 18.3 %. These elements serve as compensating ions

Table 4

Chemical composition of Trebia bentonites (%).

	* Fe	* K	* Ca	Na	Mg	* Si	Al	P	S	Ti	Mn
Na-B ₁	48.81	5.06	15.1	1.12	ND	13.38	8.74	3.86	1.844	1.29	<1
Na-B ₂	37.51	3.34	9.65	0.01	26.36	9.86	5.49	2.68	1.29	1.3	1.43
Na-B ₃	41	5.7	17	ND	ND	14.8	11	4	2	2.7	<1
Ca-B ₁	42.3	5.6	18.3	ND	ND	15	9.5	4	2.1	1.6	<1
Ca-B ₂	42.1	5.8	16	ND	ND	15.7	10.3	4.1	2	1.5	1.1
Ca-B ₃	37.7	5.4	16.6	ND	ND	16.7	12	4.5	2.3	1.6	1.7

Note:.

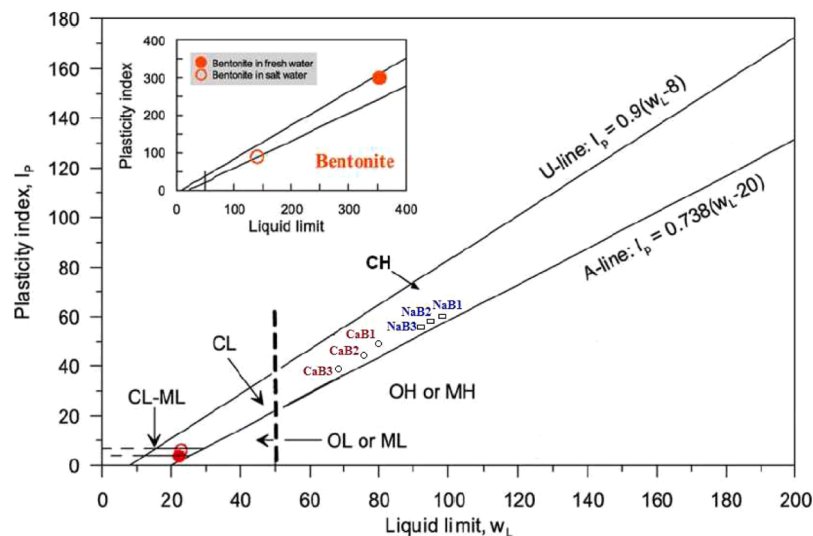
* major component; ND = not detected.

Table 5

Textural parameters, colloidal, and swelling properties of the studied bentonites.

	V _{BS}	A _{CB}	S _{ST}	CEC	IG _b	IG _a	C	LL	PL	PI	CI
Na-B ₁	15.4	4.9	321.9	98.6	72.5	500	55	107.7	61.1	46.6	1.96
Na-B ₂	17.6	5.5	346.7	74.5	45	652	41	137	51	86	1.16
Na-B ₃	15.3	5.2	288.1	88.2	50	750	45	113	45	68	1.12
Ca-B ₁	23.1	11.5	488.2	49.5	25	375	45	84	37	47	1.45
Ca-B ₂	21.2	5.9	405.8	55.4	73.33	400	56	95	39	56	1.14
Ca-B ₃	23.9	6.3	512.3	42.6	59.18	410	40	89	39	50	1.45

*Caption = V_{BS} : Methylene blue value; A_{CB} : Clay activity ($A_{CB} = V_{BS} / \text{fraction}_{<2 \mu m}$); S_{ST} (m²/g) : Total specific surface area; CEC (meq/100g) : Cation Exchange Capacity; IG_b (%) : Gross swelling index; IG_a (%) : Activated swelling index; C (%) : Colloidal; LL (%) : Liquidity limit; PL (%) : Plasticity limit; PI : Plasticity index (PI = LL-PL); CI : Consistency index.

**Fig. 7.** Position of bentonite samples on the plasticity diagram (Holtz and Kovacs, 1981).

for the charge deficit between the smectite layers, specifically montmorillonite (Na, Ca)_{0.3}(Al, Mg)₂Si₄O₁₀(OH)₂(H₂O).

3.4. Textural properties, cation exchange capacity, and swelling index

Sodium bentonites (Na-B) are characterized by methylene blue V_{BS} values ranging from 15.4 to 17.6, which correspond to a clay activity (A_{CB}) ranging from 4.9 to 5.5. In contrast, calcium bentonite (Ca-B) exhibits relatively higher V_{BS} and A_{CB} values, ranging from 21 to 24 and 5.9 to 11.5, respectively (Table 5). For specific surface areas, sodium montmorillonite clays show values of 288.1, 321.9, and 346.7 m²/g, whereas calcium montmorillonite clays have higher values of 405.8, 488.2, and 512.3 m²/g.

The bentonite content significantly influences the cation exchange capacity (CEC) of smectitic clays. The average measured CEC is around 68.1 meq/100g, with Na-B samples exhibiting a remarkable increase, with the maximum value reaching 98.6 meq/100g, compared to Ca-B clays, where the maximum CEC value is 55.4 meq/100g.

The gross swelling index (IG_b) shows similar values between the two types of montmorillonite, whereas the activated swelling index (IG_a) reveals higher values for Na-B clays. Regarding the colloidal index (C), there is no significant difference between the two types of montmorillonite.

3.5. Plasticity and Atterberg limits

Several factors influence the plasticity properties of clay materials, including the origin of the geological formation, mineralogical composition, particle size distribution, impurities (non-clay minerals), and organic matter (Daoudi et al., 2014; El Halim et al., 2022).

Bentonites are characterized by very high liquidity limits compared to other clay minerals. Therefore, the liquidity limit index can serve as a sensitive indicator of the response of calcium (Ca) or sodium (Na) exchange. Calcium bentonites typically exhibit plasticity index (PI) values lower than those of sodium bentonites (Inglethorpe, 1993).

Trebia bentonites display high plasticity, with PI values ranging from

Table 6

Comparison of the mean values of the studied parameters between Na-montmorillonite (Na-Mnt) and Ca-montmorillonite (Ca-Mnt).

Properties	Na-Mnt	Ca-Mnt
Textural parameters, colloidal and swelling properties		
V _{BS}	16.1 ± 3	22.73 ± 5
A _{CB}	5.2 ± 2	7.9 ± 3
S _{ST} (m ² /g)	318.9 ± 4	468.76 ± 3
CEC (meq/100g)	87.1 ± 3	49.17 ± 2
IG _b (%)	55.83 ± 2	52.5 ± 3
IG _a (%)	634 ± 2	395 ± 3
C (%)	47 ± 4	47 ± 4
Chemical composition (%)		
Fe	42.44 ± 4	40.7 ± 3
K	4.7 ± 5	5.6 ± 4
Ca	13.91 ± 2	16.96 ± 4
Na	0.56 ± 4	ND
Mg	26.36 ± 3	ND
Si	12.68 ± 2	15.8 ± 5
Al	8.41 ± 4	10.6 ± 4
P	3.51 ± 3	4.2 ± 4
S	1.14 ± 4	2.1 ± 5
Ti	1.23 ± 2	1.56 ± 4
Mn	<0.9 ± 5	<1.14 ± 4
Plasticity and Atterberg limits		
LL (%)	119.23	89.33
PL (%)	52.36	38.33
PI	66.86	51
CI	1.41	1.34
Physico-chemical parameters		
CaCO ₃ (%)	8.33	7
MO (%)	0.083	0.083
COT (%)	0.7	0.65
CIT (%)	1.86	1.8
W (%)	28.88	20.94
pH	7.97	8.34
Mineralogical composition (%)		
Kaolinite	2.5	0.96
Illite	6.16	1.67
Montmorillonite	24.4	25.1
K-feldspar	21.6	22.87
Quartz	12.46	16.56
Plagioclases	9.73	10.4
Calcite	3.43	3.93
Dolomite	1.17	2.3
Hematite	18.5	18.87

46 to 86 (Table 5, Fig. 7). The plasticity is more pronounced in sodium bentonites, which have PI values between 46 and 86, whereas calcium bentonites show PI values ranging from 47 to 56. Notably, all samples have a consistency index (CI) greater than 1, varying between 1.12 and 1.96, and a natural water content (W%) below the plasticity and liquidity limits (Table 2), suggesting that these bentonites maintain stability in their natural state.

4. Discussion

4.1. Relationship between bentonite type, physicochemical characteristics, and textural properties

A comprehensive analysis of the collected bentonite samples reveals distinct physico-chemical properties, highlighting the following key characteristics:

- The studied bentonites exhibit a significant swelling ability, forming viscous and gelatinous masses in the presence of water. The swelling index values (55.83 % for Na-bentonite and 52.5 % for Ca-bentonite on average; Table 6) confirm this characteristic. Swelling behavior is primarily influenced by the proportion of smectitic minerals (Fig. 8a), particularly calcium montmorillonite (Fig. 8b).
- The swelling capacity is greatly improved by sodium activation (Fig. 8c), which involves replacing Ca²⁺ ions with Na⁺ ions,

converting calcium bentonite to sodium bentonite. Sodium bentonite accommodates multiple water layers due to its interlayer Na⁺ ions, whereas calcium bentonites can sustain a maximum of two water layers (Lagaly and Ziesmer, 2003; M'bodj et al., 2004; Komadel and Madejová, 2006; Heuser et al., 2014; Barclay, 2023). This structural modification results in superior properties in sodium bentonite. Research has shown that sodium and calcium concentrations directly affect the internal arrangement of smectite layers, influencing bentonite properties (Stawinski et al., 1990; Macheca et al., 2022). The swelling index, a critical section criterion for bentonites, significantly increases after sodium carbonate (Na₂CO₃) treatment (Inglethorpe, 1993; Dixon et al., 1996; Kaufhold et al., 2015). Sodium bentonite, due to its strong water-absorbing ability, qualifies as a high-swelling smectite (Davis, 1927; Pandey, 2017).

- The CEC of montmorillonite is highest in sodium bentonite, owing to higher isomorphic substitution in the octahedral and tetrahedral layers, leading to greater ionic deficiency (Kumari and Mohan, 2021). In contrast, calcium bentonite exhibits lower plasticity and liquidity indices, though its CEC can be enhanced through heat treatment, acid activation, or additive incorporation (Fig. 8d) (Krupskaya et al., 2019; Kumari and Mohan, 2021). These modifications enhance its suitability for industrial applications, including water purification, geotechnics, and construction (Önal, 2007).
- The dominant exchangeable cations in bentonite interlayers are Ca²⁺ and Mg²⁺, ensuring charge neutrality. However, some bentonites – like Wyoming clays – contain a higher proportion of Na⁺ ions, contributing to their superior swelling and rheological properties (Grim and Güven, 1978; Benhachem et al., 2024). Studies have demonstrated that sodium carbonate treatment effectively replaces Ca²⁺ and Mg²⁺ with Na⁺, further improving the material's properties (Hofmann and Endell, 1934).
- The colloidal nature of the studied bentonites exceeds 47 % on average (Table 6), indicating a high negative surface charge. This deflocculation effect promotes the formation of a stable suspension, which is beneficial for clay fraction purification by facilitating the removal of high-density non-clay impurities via sedimentation (Plaschke et al., 2001; Kaufhold and Dohrmann, 2008; Christidis, 2010; Heckroodt, 1991).
- The liquid limit and plasticity index differ between sodium and calcium bentonites (Tables 5 and 6), with higher values in sodium bentonite (average 66.86 % for Na-bentonite vs. 51 % for Ca-bentonite, Fig. 8e). High liquid limits are a distinctive feature of bentonites, making Atterberg limit tests a reliable indicator of calcium (Ca) or sodium (Na) dominance (Inglethorpe, 1993). The high plasticity index correlates with the montmorillonite content, which is strongly influenced by cation exchange properties (Bain, 1971; Mapossa et al., 2023).
- The natural water content varies between 28.88 % (Na-bentonite) and 20.94 % (Ca-bentonite) on average, consistently lower than the liquid limit and plasticity index values. The consistency index (CI) remains greater than 1, ranging from 1.41 for Na-bentonite to 1.34 for Ca-bentonite, confirming the material's solid-state stability.

The studied bentonite exhibits high plasticity and density, characteristics that can be attributed to the interaction of multiple factors, including mineral composition, formation conditions, particle size distribution, and organic matter content. Variations in these properties across different levels of the deposit result from the following influences:

- a. The proportion and type of clay minerals, particularly sodium and calcium montmorillonite, play a crucial role in determining bentonite properties. Sodium montmorillonite dominance significantly enhances swelling capacity compared to calcium montmorillonite (Fig. 8c). This is due to the higher hydration potential of Na⁺ ions in the interlayer space, which allows for greater water absorption and expansion.

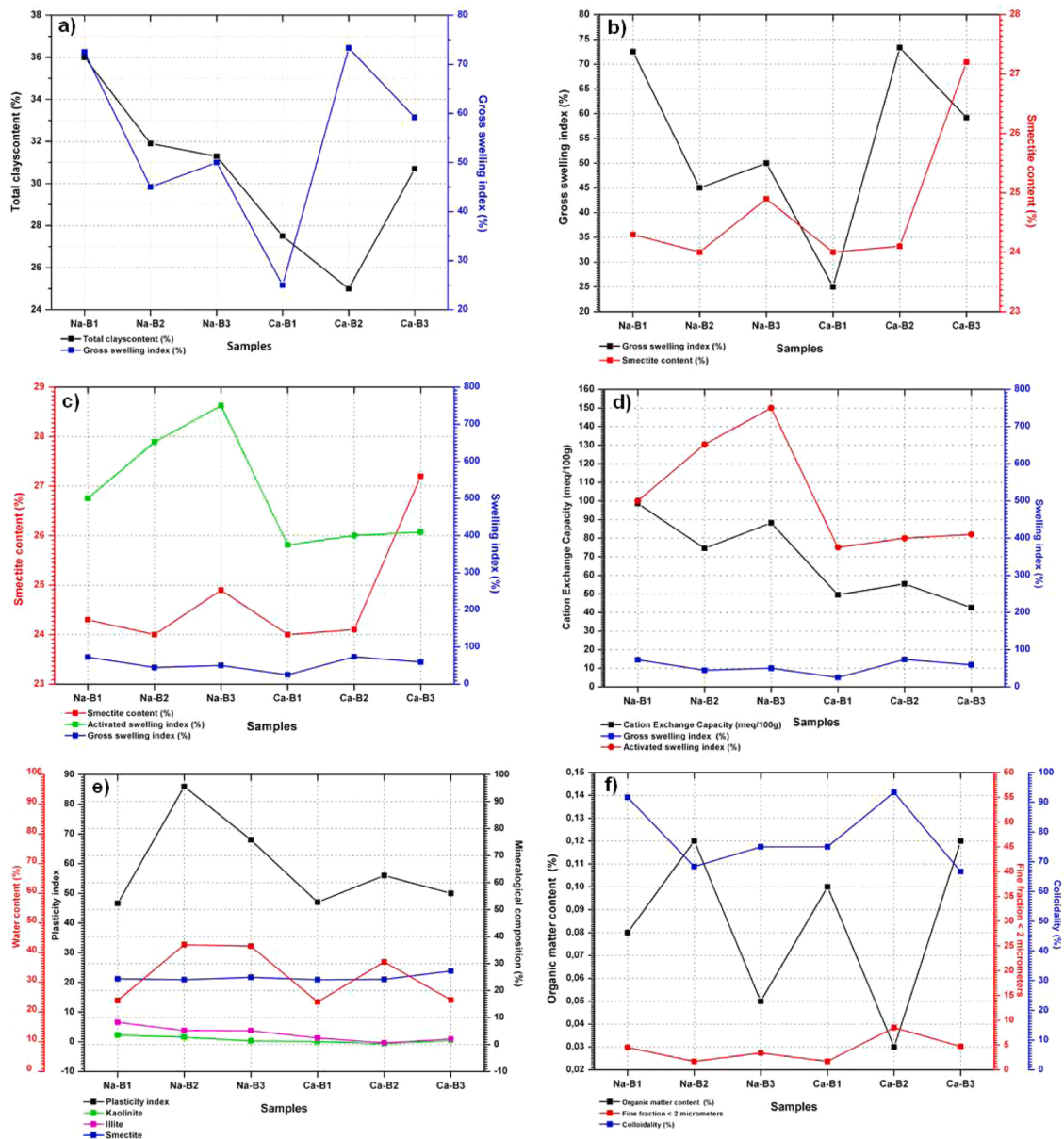


Fig. 8. Variation of different parameters influencing the properties of bentonite.

- b. The genesis of the studied bentonites is closely linked to volcanic activity and hydrothermal alteration. These materials, sometimes classified as "volcanic rocks", formed through successive volcanic events and hydrothermal reactions in a submarine environment characterized by tectonic instability, intense volcanic activity, and hydrothermal circulation. This dynamic setting facilitated the formation of smectite-rich bentonite deposits, often associated with hydroxides and trace minerals exhibiting smectite-like behaviors (Olloqui, 2020; Al-Ani and Sarapää, 2008; Galán, 2006). The element-rich environment may have promoted ion exchange and substitution within clay particles, potentially explaining negative correlations observed between smectite content and swelling/plasticity in certain areas (Fig. 8f) (Velde, 2000; Liu et al., 2022).
- c. The textural properties of bentonite, including particle size distribution, influence its microstructure (e.g., microporosity, intra- and inter-aggregate spaces), which in turn affects parameters such as V_{BS} , IG, and PI (Fig. 8f). The combination of high water affinity (inherent to clay mineralogy) and microstructural accounts for bentonite's exceptional swelling capacity (Villar, 2021).

- d. The studied bentonite contains 0.083 % organic matter, which may influence catalytic and adsorption properties through the formation of organo-clay complexes. Organic compounds (e.g., alkylammonium ions) can integrate into the interlayer space of montmorillonites, producing organophilic bentonite with enhanced adsorption capacity (Cuadros, 2017). This makes organophilic bentonite an excellent material for pollution remediation (Jordan, 1949; Akçay and Akçay, 2004). However, its catalytic efficiency at high temperatures ($>300\text{ }^{\circ}\text{C}$) is significantly reduced, as thermal degradation of organic components leads to the deterioration of the organo-bentonite structure.

Recent studies suggest that Ca^{2+} and Na^{+} contents have minimal impact on geotechnical stability, making the distinction less relevant for road engineering. The performance of calcium and sodium bentonites was found to be comparable in reducing permanent deformation and colloidity (Barbieri et al., 2022).

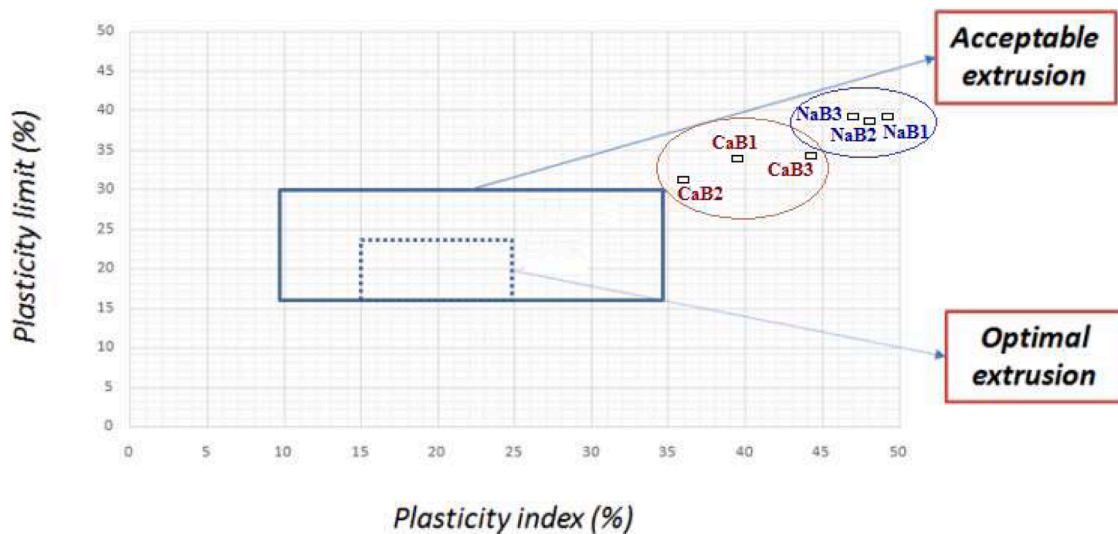


Fig. 9. Expected extrusion performance of Trebia clays based on the Atterberg limits (Marsigli and Dondi, 1997).

4.2. Trebia bentonites for industrial applications

The Atterberg identification characteristics indicate that the studied clays exhibit highly plastic and significant swelling potential, impacting their use in hydraulic engineering and construction. However, their hygroscopic nature makes them excellent adsorbents, offering a cost-effective alternative to other adsorption materials due to their natural abundance. Sodium bentonite (Na-B), with its high swelling index, is particularly suitable for drilling fluids (Pusch, 2015; Nurmuniira and Sumi, 2022). Additionally, the plasticity of these materials allows them to serve as additives in ceramics and cement, improving their moldability and shaping proprieties.

For ceramics and pottery, the extrusion ability of both sodium and calcium bentonites is limited due to their high plasticity (Fig. 9). However, calcium bentonite can be made more suitable for extrusion by incorporating non-plastic materials. The pottery industry generally requires materials with a plasticity index between 10 % and under 35 %, with plasticity limits ranging from 15 % to 30 % (Marsigli and Dondi, 1997; Ryan, 2013).

The high colloidal nature of these bentonites reflects the strong distribution of negative charges at the edges of montmorillonite particles. This property is crucial for extraction and purification processes, as bentonites disperse into colloidal particles, increasing their specific surface area. As a result, they are valuable for stabilizing emulsions and transporting chemical substances.

Additionally, Trebia bentonites are low in organic matter and calcium carbonate (CaCO_3), making them mechanically strong, water-resistant, and highly purity (Ben Azouz Ahmed, 2010; Jeddi et al., 2016). Their high alkalinity, resulting from the presence of soluble basic salts, is consistent with findings from bentonite deposits in Milos Island (Greece), the Paris Basin (France), and Maghnia (Algeria).

5. Conclusion

This study examines the influence of sodium and calcium bentonites on their physico-chemical and textural properties and their suitability for industrial applications. Sodium bentonite from the Trebia clay deposit exhibited remarkable plasticity, absorption capacity, and cation exchange capacity (CEC), particularly after activation. These properties make it highly suitable for drilling fluids, ceramics, and other applications. Research has also focused on modifying calcium bentonite to enhance its swelling capacity, making it more comparable to sodium bentonite for practical use.

The bentonite deposits studied demonstrate how microstructural

effects significantly influence plasticity and swelling behavior. The observed differences between sodium and calcium bentonites are attributed to multiple factors, including:

- Clay composition, particularly the smectitic complex.
- Formation conditions and particle size distribution (textural properties).
- Intrinsic water affinity and mineral/organic content.

The Trebia bentonite deposit displayed distinct physico-chemical characteristics that influence its industrial behavior. Sodium bentonite exhibited a higher swelling capacity (55.83 %) than calcium bentonite (52.5 %), primarily due to its mineralogical composition, particularly the dominance of smectite. Sodium activation further enhanced this swelling by promoting the formation of additional water layers between montmorillonite sheets, increasing its cation exchange capacity (CEC). In contrast, calcium bentonite requires activation treatments (e.g., heat or acid treatment) to improve its CEC and plasticity.

The random distribution of sodium and calcium bentonites within the same deposit results in property variations across different zones. The study also confirms their high colloidal properties (average >47 %), which enhance purification processes by forming stable suspensions that facilitate impurity removal. The Atterberg limits were found to be high for both bentonites, with plasticity primarily attributed to montmorillonite content. Additionally, the deposit contains 0.083 % organic matter, forming organo-clay complexes that improve adsorption capacity, making these bentonites effective for pollution remediation. However, the organic content also modifies the catalytic properties, limiting their use in high-temperature reactions (>300 °C).

The origin of these bentonites is linked to volcanic events and hydrothermal alteration within a complex geodynamic environment, significantly influencing their mineral composition and CEC properties. Moreover, particle size distribution plays a crucial role in microstructure formation, including intra- and inter-mineral microporosity, which directly affects key properties like swelling and plasticity.

This study highlights the importance of CEC, particle size distribution, and organic content in determining the industrial suitability of sodium and calcium bentonites. The findings contribute to a better understanding of their applications in pollution remediation, geotechnics, and construction.

CRedit authorship contribution statement

Hanane Ait Hmeid: Writing – review & editing, Writing – original

draft, Visualization, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Mustapha Akodad**: Writing – review & editing, Visualization, Validation. **Mouhssin El Halim**: Writing – review & editing, Visualization, Validation. **Fatima Ezzahra Omd**: Writing – review & editing, Visualization, Validation. **Mourad Baghour**: Writing – review & editing, Visualization, Validation. **Ali Skalli**: Writing – review & editing, Visualization, Validation. **Chaouki Sadik**: Writing – review & editing, Visualization, Validation. **Hicham Gueddari**: Writing – review & editing, Visualization, Validation. **Mohamed Chahban**: Writing – review & editing, Visualization, Validation. **Yassine El Yousfi**: Writing – review & editing, Visualization, Validation. **Mohamed Abioui**: Writing – review & editing, Visualization, Validation, Formal analysis. **Lahcen Daoudi**: Writing – review & editing, Visualization, Validation.

Declaration of competing interest

The authors declare to the *Ore & Energy Resource Geology* that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper titled: "*Comparative Analysis of Na⁺ and Ca²⁺ Ion Effects on the Physical-Chemical Properties of Bentonite: Implications for Industrial Applications*". As corresponding authors (H. Ait Hmeid & M. Abioui), we confirm that the manuscript has been read and approved for submission by all the named authors.

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Data availability

The data supporting this study's findings are available from the corresponding authors, H. Ait Hmeid and M. Abioui, upon reasonable request.

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