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CHEMICAL AND PHYSICAL CHARACTERIZATION OF SOME TUNISIAN SMECTITES FOR HUMAN HEALING USE

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ABSTRACT
The use of clays for therapeutic purposes is mainly related to their high absorbent and adsorbent properties. In dermatology and cosmetics (topical applications), clays are used due to their high swelling, high plasticity, high specific surface and high ion exchange properties. In this paper, mineralogical, chemical and technological properties of some Tunisian smectitic clays are reported with the aim to assess their suitability to be used for therapeutic external applications. Properties of these clays have been compared to those of the bentonite of Porto Santo Island (PSBT) of the Madeira archipelago (Portugal), considered to be very interesting for therapeutic treatment on the basis of their technological characterization (CEC, specific surface, exchangeable cations, specific heat, cooling rate and abrasivity). Among the investigated clays HMD1, TFL1, BRD1 and AYD1 seem to be the most appropriate for topical applications as cataplasms or mud baths.

KEYWORDS: smectite, cooling kinetic, specific heat, topical application, Atlas domain, Tunisia

1. INTRODUCTION

The use of clay minerals for cosmetic and curative goals is almost as old as mankind itself. Clay minerals served in the past to combat several gastrointestinal epidemics, several cutaneous infections, poisoning and even they had been served for the mummification of pharaohs. At present, clay minerals are used for therapeutic purposes in pharmaceutical formulations, spas and aesthetic medicine. In pharmaceutical formulations, smectite, palygorskite, kaolinite and talc act as active principles or as excipients mainly due to their high specific area and their absorption/adsorption capacity, rheology, chemical inertness and low or no toxicity for the patient. In spas and aesthetic medicine, geotherapy, pelotherapy and paramuds, smectite and kaolinite are mostly used clay minerals. Favourable properties for those purposes are fundamentally represented by absorption/adsorption capacity, cation exchange capacity, plastic properties, rheology, grain size and cooling index. They are used in spas to treat dermatological diseases and to alleviate the pain of chronic rheumatic inflammations. In aesthetic medicine they are used as cosmetic products, in order to clean and moisturise the skin, as well as, to treat acne, cellulite and to combat compact lipodystrophies (Carretero, 2002).

This work is conducted to appraise the suitability of some Tunisian smectitic clays as therapeutic minerals through the investigation of the fundamental properties required in the case of external application of clays (cataplasms and mud baths).

2. MATERIALS

The raw materials investigated in this work come from twelve smectite clay deposits located in the Meridional Atlas domain (Fig. 1).Clays collected in Jebel Aidoudi (AYD1, AYD2) (El Hamma region) and in Jebel Berda (JBD1) are Coniacian to Santonian in age and belong to Aleg formation (Burrolet, 1956, Jamoussi, 2001). Those sampled in Oued Tefal (TFL1) (Jebel Stah), in Jebel Hamadi (HMD1) and Jebel Orbata (KB) are Campanian to Maastrichtian in age and belong to the middle member of Abiod formation. The clays from Jebel Chamsi (CHM1) and from Chebika (CHB1), Oum Khechab (OMK1) and Secteur 100 (SC100) localities are Maastrichtian-Pliocene in age and belong to El Haria formation.

3. METHODS

The investigated clays have been submitted to chemical and mineralogical identification and evaluated through chemical and physical characterization from therapeutic quality point of view. This characterization includes the determination of cationic exchange capacity, specific surface area, grain size distribution, abrasivity, plasticity, cooling kinetics and apparent specific heat. Research has been realized on the <63 μm fraction.

The determination of mineral composition was carried out by X-ray diffraction (XRD) using Philips X'Pert instrument, CuK_α radiation, and by the powder method and oriented aggregates treated with ethylene glycol and heated to 500 °C.

Chemical analysis of major elements has been carried out using X-ray fluorescence (XRF) and flame-spectroscopy methods.

The cation exchange capacity (CEC) was estimated by the ammonium acetate method (Gomes, 1986) which comprises saturating clays by ammonium acetate solution, where the non-adsorbed NH_4^+ ions are drained with 96 % ethyl alcohol and the ions fixed upon clays are dosed with 0.1 N hydrochlorid acid in the presence of green bromocresol as coloured indicator. The surface area was obtained by nitrogen sorption using a quantachrome Autosorb instrument. Prior to analysis, the samples were degassed under vacuum at 120 °C for overnight.

Grain size distribution was assessed using an X-ray particle size analyser (Sedigraph, Micromeritics 5100).

Abrasivity was carried out by the Einlehner AT-1000* abrasion tester. The used speed was $43.5 \cdot 10^3$ revolutions/ min.

Cooling kinetics of these samples was carried out by simple measuring of the cooling of crushed clays (<63 μm) previously heated at 60 °C in drying oven for at least two hours by means of thermometer. The measurements were taken every 30 seconds from 60 °C to 30 °C. Finally, specific heat was estimated from the DSC curves.

4. RESULTS

The mineralogical composition of the samples is shown in Table 1. Most of the samples consist of prevailing smectite (39 to 81 %), illite, interstratified illite/smectite phase and kaolinite. The latter is abundant in some samples (OMK1, SC100). Quartz, feldspars, calcite and dolomite are presented in subordinate quantities.

Chemical analyses of the samples are reported in Table 2 along with Na_2O/CaO ratio, an important parameter to distinguish swelling bentonite ($1<Na_2O/CaO<3$) from non swelling 2:1 clays ($Na_2O/CaO<1$) (Ravaglioli et al., 1989 in Cara et al., 2000). Chemical composition shows that clays are rich in iron (Fe_2O_3 is in the range of 4.38-8.27 %), CaO content is very variable. Its lower values (0.64 and 0.41 %) were observed in clays AYD2 and OMK1. The Na_2O/CaO ratio shows that AYD2 is that of Na bentonite type as well as OMK1 but the latter with higher Na_2O/CaO ratio (4.27) than the first.

Table 3 shows the results of technological tests. In smectitic clays CEC ranges between 33 and 59 meq/100g. The list of exchangeable cations is given in Table 4. Three groups of smectitic clays can be distinguished: the first one is of Ca type (BRD1, KB and CHB1), the second is of Ca-Na type (AYD1, TFL1, SC100 HMD1 and CHB1) and the third group is of Na type (AYD2 and OMK1).

The specific surface area of these clays ranges between 56 and 87 m^2/g (Table 3). These values highly depend on the mineral composition (the greater amount of clay mineral, especially of smectite, influences specific surface) and the particle size of clays.

The abrasivity of these clays is variable (Table 3) and depends on non clay minerals amount and on a type included, especially on quartz content with its high abrasiveness.

Grain size distribution determined in the grain fraction less than 0.063 mm of the clays, shows that the grain size less than 0.01 mm represents between 91 and 97 % (Fig. 2). Therefore, in textural terms, the investigated clays are extremely fine grained.

Figure 3 shows, in term of the heat attenuation and the corresponding cooling rate, the behaviour of the smectitic clays during cooling from a temperature of 60 °C to 30 °C. The obtained curves show the same appearance. The cooling rate depends upon many characteristics (texture, compositions, specific heat and heat diffusiveness of the clay) (Gomes, 2003). For the hot cataplasm application, good heat retention is required (Cara et al., 2000 b).

Table 3 gives the results of specific heat of the tested clays. These results are in the range of 1.01 to 2.72 J.G °C. It is clear from this table that the highest value (2.72 J.G °C) corresponds to the most smectite rich clay (AYD2) (Table 1).

5. DISCUSSION AND CONCLUSION

Clays investigated in this work are of smectitic type. The discussion about the suitability for their use in the therapeutic external application is done through comparison with bentonite of Porto Santo island (PSBT) of the Madeira archipelago (Portugal) which is considered to be very interesting for therapeutic treatment (Gomes and Silva, 2001) due to its high specific surface area (119 m^2/g), its high CEC (80 meq/100g), the presence of Ca and Mg as the main exchangeable cations and its low cooling rate (38 min. from 58 °C down to 30 °C). The tested clays show acceptable properties (CEC, S.BET, cooling kinetics, specific heat) (Table 3 and Fig. 3). The efficiency as curative minerals is highly related to their CEC. In fact, the higher CEC values enable higher absorption of the chemical elements fixed reversibly in the clay through the skin. It is based on the establishment of ion gradients and on ion exchange reactions.

Tunisian smectitic clays take 20 to 24 min. to pass from 60 °C to 30 °C. Their cooling rate is

Table 1 Mineralogical composition of the studied clays (Sm = smectite, Ill = illite, Kao = kaolinite, I/S = interstratified illite-smectite, Qz = quartz, Cal = calcite, Fd = feldspars, Dol = dolomite) in %

Samples	Sm	Ill	I/S	Kao	Qz	Fd	Cal	Dol
AYD1	77	3	-	9	5	1	5	-
AYD2	81	5	-	9	4	1	-	-
BRD1	66	8	-	8	5	3	8	2
TFL1	80	5	-	-	3	2	8	2
HMD1	77	1	-	2	3	1	13	3
KB	50	12	-	13	9	3	13	-
CHB1	64	6	-	16	5	2	6	1
CHM1	64	-	-	13	7	2	13	1
OMK1	39	4	8	36	8	5	-	-
SC100	40	-	-	51	3	1	1	4

Table 2 Chemical compositions of the studied clays and bentonite of Porto Santo island (PSBT) in %

Samples	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	SO_3	LOI	Na_2O/ CaO
AYD1	49.02	20.61	7.41	3.97	2.29	1.80	1.75	1.02	0.34	0.04	-	11.27	0.45
AYD2	53.93	21.73	8.27	0.64	2.38	1.64	1.58	1.06	0.36	0.03	-	7.98	2.56
BRD1	49.37	20.51	8.18	6.37	2.82	0.71	1.80	1.00	0.43	0.02	-	8.34	0.11
TFL1	45.06	13.91	5.36	1193	3.74	1.85	1.25	0.70	0.57	0.02	-	15.14	0.08
HMD1	44.62	13.68	5.42	12.98	3.17	1.05	1.04	0.64	0.60	0.03	-	16.16	0.08
KB	49.04	16.79	6.45	8.32	2.47	0.67	1.29	0.89	0.37	0.02	-	13.21	0.08
CHB1	49.52	19.96	7.36	4.46	2.85	0.84	1.95	1.00	0.40	0.02	-	11.15	0.18
CHM1	43.27	18.07	6.27	9.98	2.26	1.83	1.53	0.91	0.24	0.02	-	15.11	0.18
OMK1	50.78	23.16	7.56	0.41	2.27	1.75	2.06	0.97	0.33	0.02	-	10.24	4.27
SC100	47.91	22.77	7.36	2.39	3.10	1.25	1.37	0.98	0.33	0.02	-	12.08	0.52
PSBT	45.01	18.57	10.85	5.97	3.86	2.37	0.45	2.77	1.76	0.86	0.11	7.54	0.39

Table 3 Technological properties (CEC, S.BET, Abrasion, Specific Heat) of the studied clays and bentonite of Porto Santo island (PSBT)

Samples	CEC (meq/100g)	S.BET (m^2/g)	ABRASION (g/m^2)	SPECIFIC HEAT
AYD1	48.2	87	35.4	1.84
AYD2	56.7	86.8	29.3	2.72
BRD1	45.9	64	66.8	1.65
TFL1	47.5	76.8	66.8	1.88
HMD1	59	-	75.4	2.2
KB	45	56	114.7	2.08
CHB1	46.5	83	52.1	2.07
CHM1	33	74	32.8	1.01
OMK1	40.8	84	33.1	1.56
SC100	48	85.18	50.8	1.81
PSBT	80	119	0.11	3.55

Table 4 Exchangeable cations of the studied clays

Samples	Na (ppm)	K (ppm)	Ca (ppm)	Mg (ppm)
AYD1	1392.29	200.39	1032	164
AYD2	1092.04	147.79	1	229
BRD1	651.11	235.45	1390	150
TFL1	2529.94	273.02	1588	275
HMD1	1182.12	460.87	1963	425
KB	260	74.8	592	231
CHB1	891.88	205.40	1551	125
CHM1	2004.51	265.51	1157	251
OMK1	1932.73	190.37	72	175
SC100	1452.34	200.39	987	350

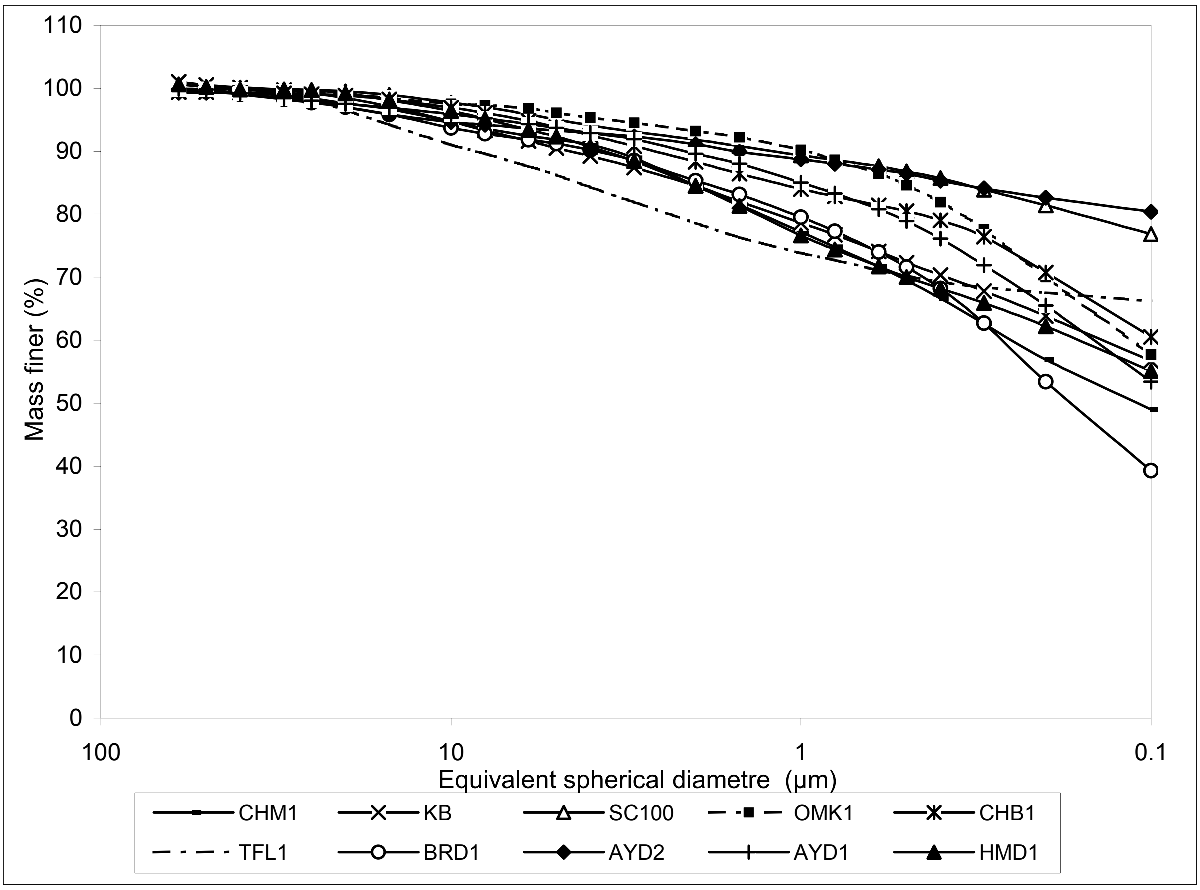

Fig. 2 Grain size distribution curves of the studied clays

suitable since the application of clay mixed water on the surface of the skin as cataplasm or mud bath takes 20 to 30 min. The studied clays also exhibit an easy handling due to their high plastic character. The only quality which may constitute an obstacle for their topical application, is their abrasiveness. It appears to be higher compared to that of Porto Santo bentonite (Table 3). This abrasiveness is mainly related to the presence of quartz (3 to 6 %), but these contents are lower than those of many muds used in spas. We can take an example of the Benetutti mud (Cara et al., 2000a) in which quartz is counted among the main minerals. Its sand content is 32.4 wt % which indeed influences its CEC that is only 30 meq/100g.

Considering all properties established for smectitic clays, four samples appear to be the most adequate for external application and the most benefit for the body (HMD1, TFL1, BRD1 and AYD1). These clays exhibit the best results since they have the highest CEC, the highest specific surface and the largest amounts of Ca and Mg as exchangeable cations. AYD2, despite its high quality (CEC, S.BET, low abrasion and high specific heat) is poor in Ca as an exchangeable cation (Table 4). The main

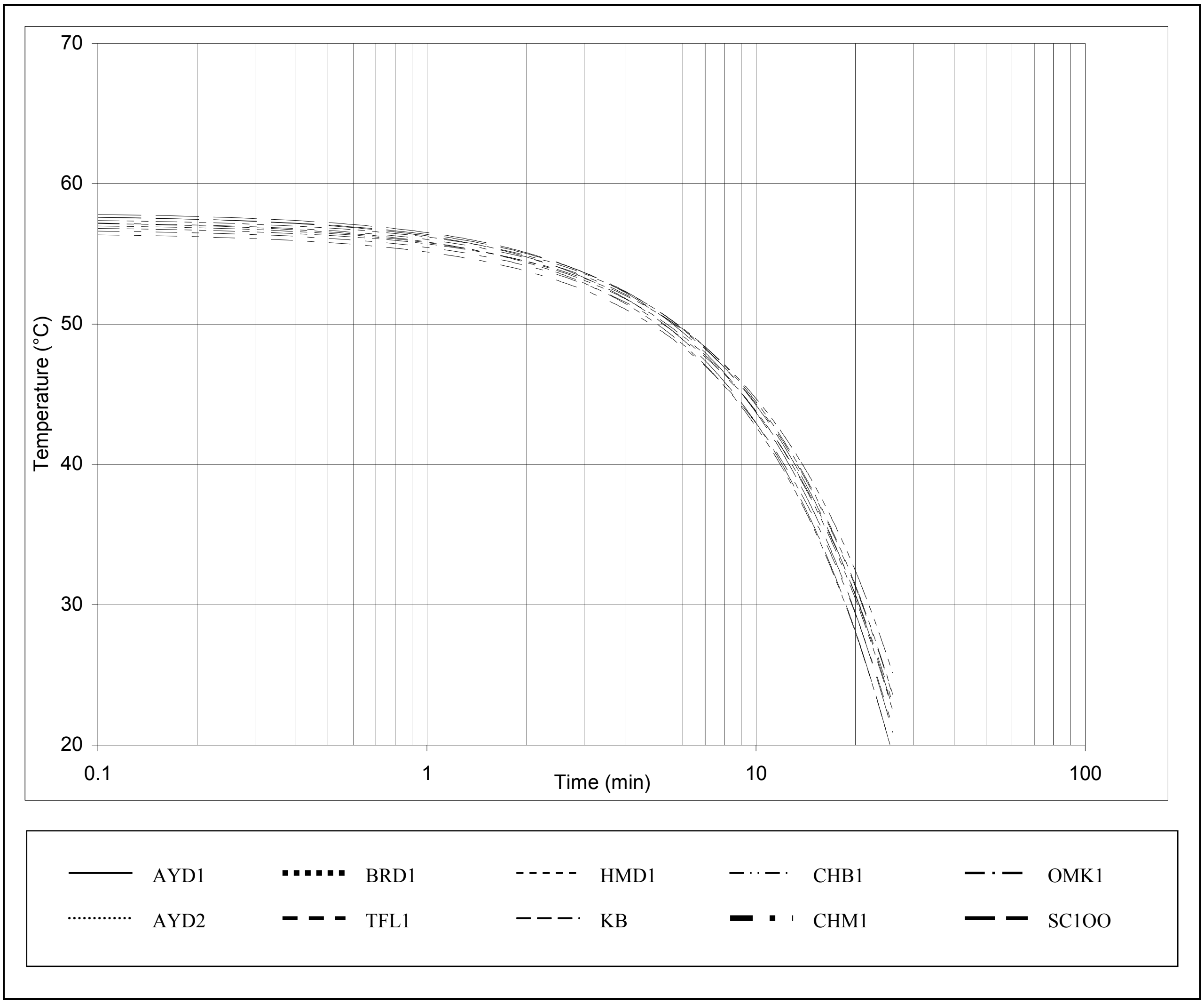

Fig. 3 Cooling kinetics of the studied clays

exchangeable cation of this clay is Na. KB is also inadvisable for this type of application due to its high abrasion power.

The properties of these clays can be improved (especially plasticity, capacity of absorption, cooling index and grain size) through the maturation process (Veniale et al., 1999; Sanchez et al., 2000b; in Carretero, 2002) which consists of mixing clays with thermal spring water or sea water. Such mud is then designated as peloid. The therapeutic treatment is then named peloidtherapy.

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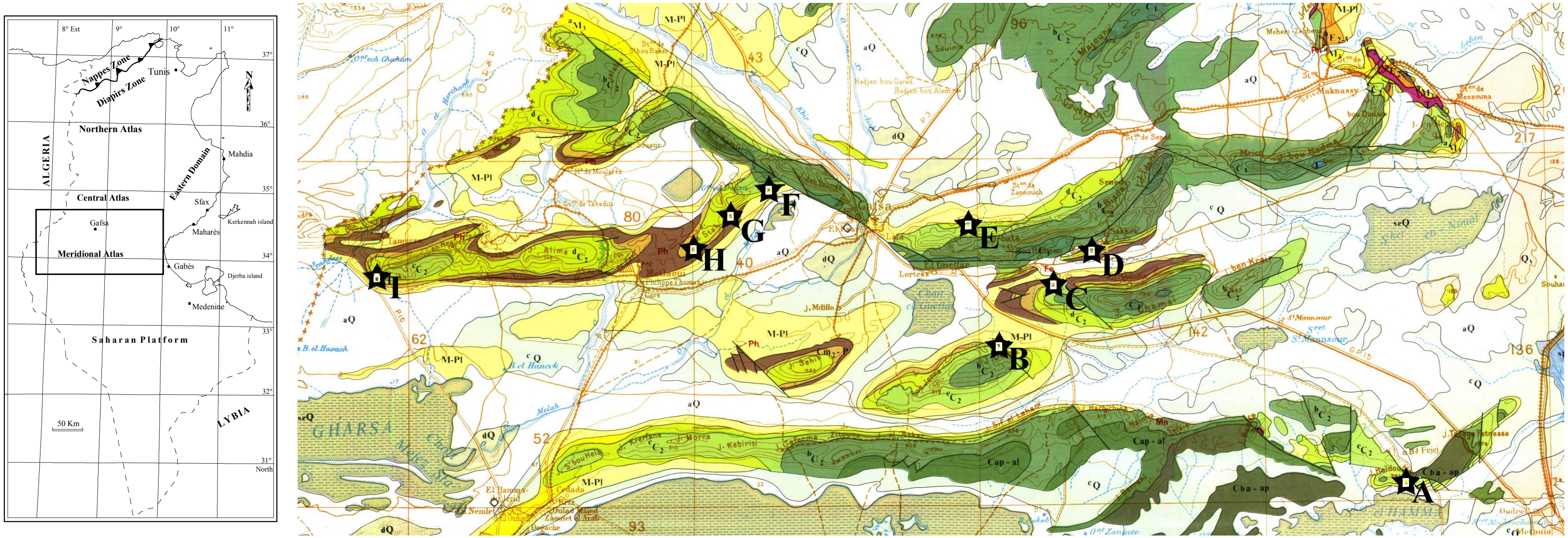

A: J. Aïdoudi (AYD1) (AYD2)	**E:** J. Orbata (KB)	**I:** Oum Kckeb (OMK1)
B: J. Berda (BRD1)	**F:** J. Sehib(SHB1)	**J:** Kef Eddour (KFED1)
C: J. Chamsi (CHM1)	**G:** OuedTefal (TFL1)	**K:** Chbika (CHB1)
D: J. Hamadi (HMD1)	**H:** Secteur 100 (SC100)	

Fig. 1 Localisation map of the studied clays