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Full Length Research Paper

Mineralogical and geochemical study of mud volcanoes in north Moroccan atlantic margin

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The gulf of Cadiz is one of the most interesting areas to study mud volcanoes and structures related to cold fluid seeps since their discovery in 1999. In this study, we present results from gravity cores collected from Ginsburg and Meknes mud volcanoes and from circular structure located in the gulf of Cadiz (North Atlantic Moroccan margin) during the cruise TTR14 in 2004 on board of the R/V *Logachev*. The clay mineralogical analysis by XRD shows a difference in clay mineral amounts mainly in smectite between the different studied structures. Ginsburg MV shows high percentage of smectite with an average of 44% whereas Meknes MV displays illite rich clay association, smectite average percentage is about 16%. In circular structure, amount of smectite is about 13%. This variation in clay mineralogy association between the mud volcanoes suggests different nature and depth of parent layers and fluids feeding the mud volcanoes in gulf of Cadiz.

Key word: Mud volcano, clay mineralogy, geochemistry, mud breccias, North Moroccan Atlantic margin.

INTRODUCTION

The study of marine mud volcanoes is of large interest for several reasons: (i) they provide precious information about deeper units inaccessible by coring; (ii) they constitute a probable source of energy by accumulation of gas hydrates and (iii) for their contribution in climate changes by liberation of greenhouse gases like methane.

The mud volcanoes results from the extrusion of argillaceous material on the earth's surface or the sea floor (Dimitrov, 2002). The material extruded (mud breccias) consists of fine-grained sediments, water, gases and by rock fragments from the deeper units (Cita et al., 1981).

Since 1999, many mud volcanoes and diapirs were discovered in the gulf of Cadiz and North Atlantic Moroccan margin. In July 2004, several cores were extracted from the gulf of Cadiz and collected during the TTR14 (Training Through Research) on board R\V Professor Logashev. In the framework of a large cooperation including several teams and laboratories, we worked on five cores: two were recovered from the crater of Ginsburg mud volcano 521G and 522G. One core 535G from the slope of Meknes mud volcano, and two cores 531 and 532G from the top of the diapiric ridge near the Kidd mud volcano (Table 1, Figure 1).

We develop in this study two aspects: mineralogical and geochemical study in order to determine the source of the organo-mineral material.

Study area

The gulf of Cadiz is a tectonically active area, situated in front of the betic rifain arc. It is bounded by the Iberian Peninsula to the North and the African continent to the south (Figure 1). It is characterized by a very intricate geological history linked to the Africa Eurasia convergence directed NW-SE since the Cenozoic (Ribeiro et al., 1996).

This region underwent several episodes of rifting since the Mesozoic (Maldonado et al, 1999).The emplacement of the olistostrome complex occurred in the Miocene, following the west ward migration of the Gibraltar arc into the gulf of Cadiz (Bonnin et al., 1975). According to Lonergan and White, (1997) and Maldonado et al. (1999) this westward movement ceased before the Pliocene. This olistostrome body includes a tremendous volume of mud and salt diaparism of Triassic salts units under com-

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Table 1. Data of gravity cores (Kenyon et al. IOC- UNESCO, 2006)

Cores	Site	Latitude(°N)	Longitude(°E)	Water depth(m)	Recovery(cm)
521G	Carter of Ginsburg MV	35°22.284	7°05.276	919	216
522G		35°22.417	7°05.299	912	202
531G		35°26.078	6°46.485	518	80
523G	Circuler Structures	35°26.130	6°46.832	518	107
535G	Slope of Meknes MV	34°59.034	7°04.552	718	281

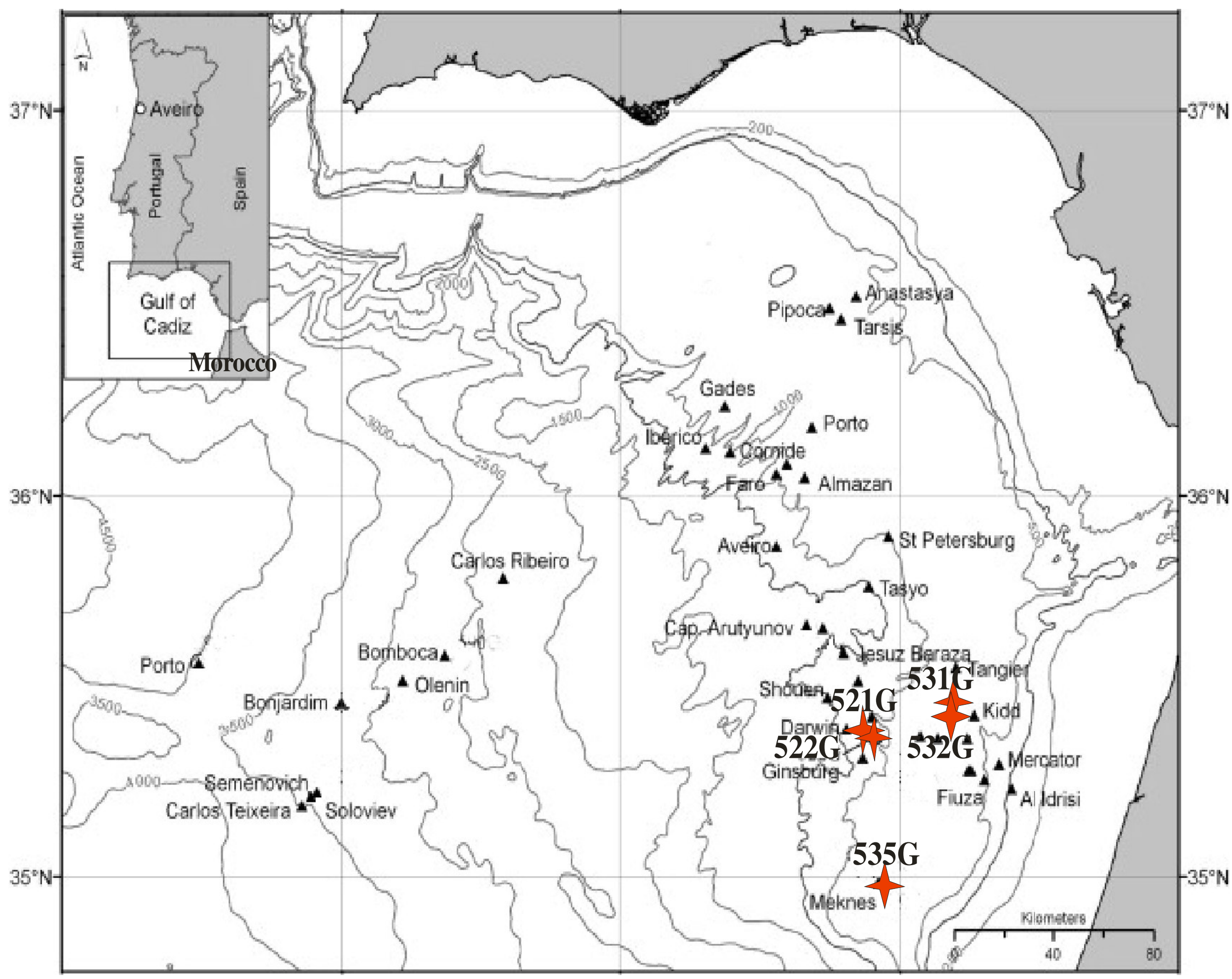

Figure 1. Location of gravity cores (map after Mieiro et al., 2007). *Triangles* mud volcanoes, *stars* gravity cores.

pacted early middle Miocene plastics marl (Maldonado et al, 1999). Presently the dominant tectonic in this area is characterized by moderate tectonic subsidence and local transpressive tectonics (Maldonado et al, 1999).

In the last years, several extensive mud volcanoes were discovered in the gulf of Cadiz (Gardner, 2000, 2001) and were intensively investigated and studied. Most of them are located in the shallowest part of the accretionary wedge (Gutscher et al., 2007), and they result from neo-tectonism (Garàcia et al., 2003).

MATERIALS AND METHODS

The clay minerals were identified by X- ray diffraction. After removal carbonate, every sample was washed with distilled water and centrifuged several times. The clay fraction under 2 µm was separated by centrifuging and deposited onto glass slide. The oriented clay aggregates were dried under air condition and analyzed, then treated with ethylene-glycol for 24 h in a desiccator and reanalyzed.

The geochemical analysis was carried out only on four samples (fraction <63 µm) of each core: sampling from the top, the base and the middle only. The hot acid extraction under reflux method was used to determine the amount of metals in sediments. The digestion procedure was applied to 0.5 g of grinded sediments, a solution of HNO_3 and H_2O_2 was added to each sample on the vigreux tube, and was inserted in the digester at 120℃ for 2 h. After centrifugation the supernatant was transferred in polyethylene bottles and analyzed using Inductively Coupled Plasma Atomic Emission Spectrography (ICP, AES)

Clay minerals and geochemical results

The results of the clay mineral analysis of sediments of the five cores along with the granulometry analysis's are listed in Figures 2, 3 and 4. The geochemical analyses of the four samples of every core are shown in Table 2.

Meknes mud volcano

The Meknes mud volcano was newly discovered during this survey. Its crater is at a depth of approximately 650 m and the base is at 710 m. The width of the volcano is about 1 km. Core 535G was sampled from the slope of the mud volcano. It presents an intercalation of brownish grey, light grey dark greenish grey, and dark greenish clayey silt with shell fragments, corals and foraminifera (Kozlova et al., 2006). A thin layer of brown clayey sand covers the core (Figure 2).

The clay content ranges from 20 to 60%, silts from 8 to 20% and sand from 10 to 50% (Figure 2). The three fractions show a strong fluctuation along the core without a systematic trend.

The clay mineral association consists of smectite, illite, kaolinite and chlorite. It is dominated by illite with an average of 70%. In the interval 0 – 105 cm all the clay minerals are relatively constant, illite 68%, smectite 14%, chlorite10% and kaolinite 8%. At the lower part of core (105-257cm), the values of clay minerals are strongly variable (Figure2).

The geochemical analysis of the metals shows a high Ti ratio, around 120 µg/g, and an increasing trend for As, Mo, Cd, Ag and U at the lower part of the core. The Arsenic and Manganese have a high ratio at the top of the core 10 µ and 400 µg/g respectively (Table 2).

Ginsburg mud volcano

This mud volcano, discovered during the TTR-9 cruise in 1999, is among the largest and active volcanoes of this area. It has one central dome, over 200 m high and about 4 km in diameter in a water depth of about 1200 m (Gardner, 2000; 2001).

The Ginsburg mud volcano was broadly studied since its discovery: the chemical composition of pore water, the gas hydrate, the petrography of clasts and micropaleontological studies (León et al., 2006; Mazurenko et al., 2003; Niemann et al., 2006; Pinheiro et al., 2003).

Both cores, 521G and 522G, were collected from the crater of the mud volcano. The core 521G is composed by intercalation of grey, greenish and grey greenish mud breccia with clasts of different lithology mixed with clayey matrix. Core 522G is composed only of sequences of grey mud breccia witch has a strong smell of H2S at the sampling (Kozlova et al., 2006). A veneer of hemipelagic sediments covers both cores (Figure 3).

The granulometry percentage of both cores is similar: the clay dominant fraction varies between 45 and 70%. The sand ranges from 3 to 40%. It is abundant at the top of both cores (0 – 4 cm for core 521G and 0 – 44 cm for core 522G) and at70 cm at the core 521G. The silt occurs in percentage of 26 to 37% (Figure 3).

Ginsburg mud volcano presents the same clay mineral association as at Meknes mud volcano, but their relative percentage is completely different. Both cores 521 and 522G show a clear increase of smectite in favor of illite in comparison with 535G (Figures 2 and 3).

The distribution pattern of clay minerals at the upper part of both cores (hemipelagic unit) is different from the lower part (mud breccia unit). In hemipelagic unit of both cores illite show an increasing trend from > 30 to 52%, while the smectite shows a slight decreasing trend from 42 to 29%. The kaolinite and chlorite ratio are relatively constant around 10 and 7% respectively (Figure 3).

At the lower part of both cores (mud breccia unit), smectite has fluctuating concentrations between 40 and 50%, the illite show a slight increasing trend from 38 to 42% for 521G and from 30 to 42% for 522G. The kaolinite and chlorite show the same amount as the upper part except at 522G between 63 and 108 cm both minerals have strongly fluctuating concentrations (Figure 3).

The metals contents show a decrease in the Ti ratio, about 50 µg/g. A difference in the rate of some elements between the two cores was noticed: core 522G presents a high composition of Zn and As at the top, 230 and 14µg/g respectively, an increase in the rate of Mo and U at 41cm depth 12 and 4 µg/g respectively. Whereas in core 521G there is an increase of Cu 42 µg/g and Mn at 34 cm depth and high concentrations of As 11 µg/g at the top of the core (Table 2).

The circular structures near Kidd mud volcano

Two highs structures which possibly are tops of mud diapirs were identified on the crest of Vernadsky ridge by sides can sonar (Kozlova et al., 2006) (Figure 4). The south easternmost one rise 60 m above the sea floor, its base has a width of 2.4 km (Kozlova et al., 2006). The top is nearly flat and shows only moderate to low reflectivity. The northwesternmost feature is a highly reflective area made up of linear to lobate ridges up to 20 m high (Kozlova et al, 2006).

Two cores were sampled from a high backscatter area on the top of the ridge (Figure 4). The core 531G consists of an upper interval of brown sand (0 – 20 cm) overlying an interval of light grey clayey sand (20 – 30 cm) and below which is a thick interval of stiff light grey clay (30 – 80 cm) (Figure 5) . The core 532G consists of an upper

Table 2. The major and trace element concentration at Ginsburg and Meknes mud volcano and the circular structure.

	Cores	Depth (cm)	Ti µg/g	V µg/g	Cr µg/g	Mn µg/g	Fe µg/g	Co µg/g	Ni µg/g	Cu µg/g	Zn µg/g	As µg/g	Mo µg/g	Ag µg/g	Cd µg/g	Sb µg/g	Tl µg/g	Pb µg/g	U µg/g
Ginsburg mud volcano		0-2	56,25	**102,92**	82,63	364,52	31276,8	11,33	28,23	26,48	64,98	**11,83**	0,58	0,106	0,128	0,177	0,29	14,11	1,71
	521G	33-35	52,51	90,65	102,3	735,94	34026,1	17,28	40,63	42,82	68,27	2,41	0,48	0,152	0,140	0,185	0,32	9,59	1,54
		100-101	51,84	85,45	98,48	749,40	32360,0	16,66	41,65	41,83	58,89	2,25	0,38	0,111	0,115	0,173	0,27	10,50	1,45
		160-170	35,80	76,24	91,47	732,88	30303,3	15,50	36,54	38,09	66,56	2,15	0,32	0,143	0,113	0,168	0,26	9,45	1,41
		0-4	58,64	**104,66**	85,14	520,10	33371,1	12,93	30,86	29,77	**232,99**	**14,14**	0,75	0,109	0,132	0,187	0,30	**17,50**	1,58
		42-44	50,63	97,20	90,79	648,44	33906,3	13,89	34,65	39,88	73,64	**10,18**	**12,61**	0,092	0,191	0,174	0,33	9,99	4,03
	522G	82-84	45,35	84,13	99,62	744,34	33113,4	17,27	41,14	44,53	68,84	2,38	0,38	0,130	0,123	0,182	0,29	9,58	1,46
		184-186	42,00	79,41	90,81	661,90	30060,0	15,58	37,00	38,25	63,74	2,14	0,33	0,132	0,093	0,172	0,27	8,69	1,36
circular structure		0-2	**114,17**	80,43	65,97	**605,24**	**31067,2**	**13,08**	**37,08**	**26,29**	**128,66**	**8,34**	0,55	0,160	0,173	0,184	0,28	18,44	1,51
	531G	26-27	92,19	95,17	69,35	305,89	27654,4	10,70	34,38	21,58	85,74	5,27	1,22	0,157	0,398	0,188	0,57	12,41	5.47
		50-52	38,34	87,97	68,40	299,13	24874,0	9,09	26,82	16,33	45,86	4,11	4.41	0,083	0,174	0,175	0,24	8.86	**2.81**
		60-62	40,72	84,68	68,57	298,73	24266,1	8,97	26,27	16,30	50,02	3,79	5.58	0,205	0,144	0,173	0,23	8.69	**2.34**
		0-3	**128,04**	83,24	65,71	**446,28**	**31346,2**	**12,21**	**34,35**	**28,92**	**190,86**	**9,69**	0,74	0,231	0,199	0,242	0,30	**18,44**	2.42
		30-32	44,82	94,26	76,81	304,86	23283,7	9,57	28,91	16,15	47,50	3,33	2.85	0,062	0,190	0,176	0,25	12,41	3.26
	532G	57-59	40,42	91,40	73,75	280,74	26487,0	10,66	33,50	17,07	52,13	5,34	**1.92**	0,052	0,159	0,175	0,26	8,86	2,15
		92-94	41,38	87,00	72,37	252,97	22719,8	9,35	27,59	16,68	49,61	3,10	**3.20**	0,098	0,164	0,174	0,23	8,69	2,51
Meknes mud volcano		6-8	**125,31**	71,75	58,29	407,16	29062,5	12,35	32,52	18,35	60,43	8,31	0,45	0,073	0,188	0.140	0,22	**9.31**	1.77
		57-61	**116,81**	74,04	66,09	279,88	29778,7	11,48	32,87	18,30	59,62	3,06	0.28	0,063	0,192	0,189	0,27	11.33	2.13
	535G	151-153	**114,69**	78,21	63,98	256,37	25547,8	9,80	31,22	19,68	71,17	3,40	0.23	0,106	0,300	0,189	0,26	9,69	2,66
		255-257	**138,44**	75,27	50,88	361,49	29090,4	11,30	29,20	22,94	71,76	10,58	**4.88**	0,162	0,385	0,202	0,25	9,65	**6.22**

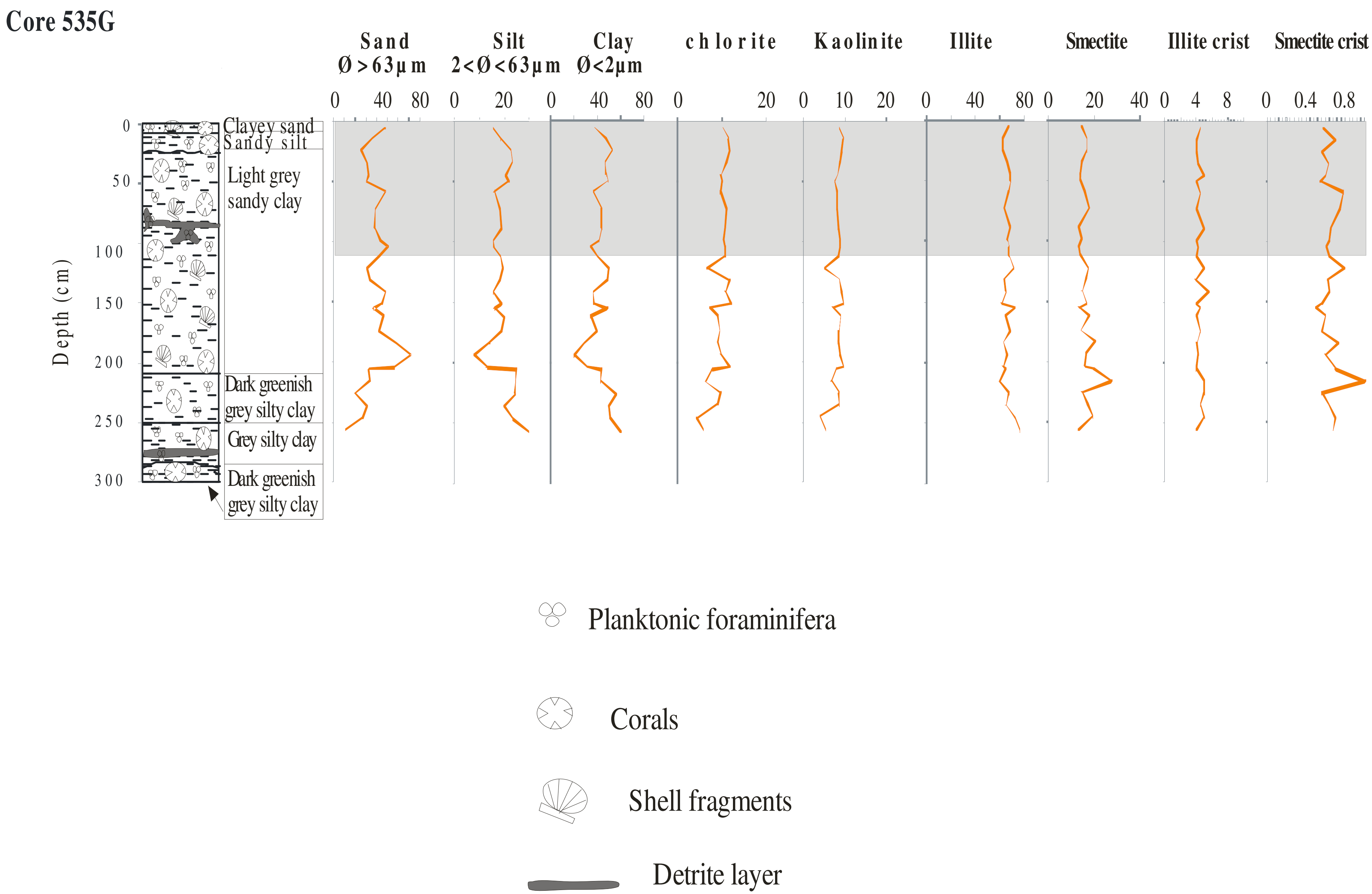

Figure 2. Main lithologic unit, granulometry and clay minerals at Meknes mud volcano. Smectite cryst: smectite crystallinity; illite cryst: illite crystallinity.

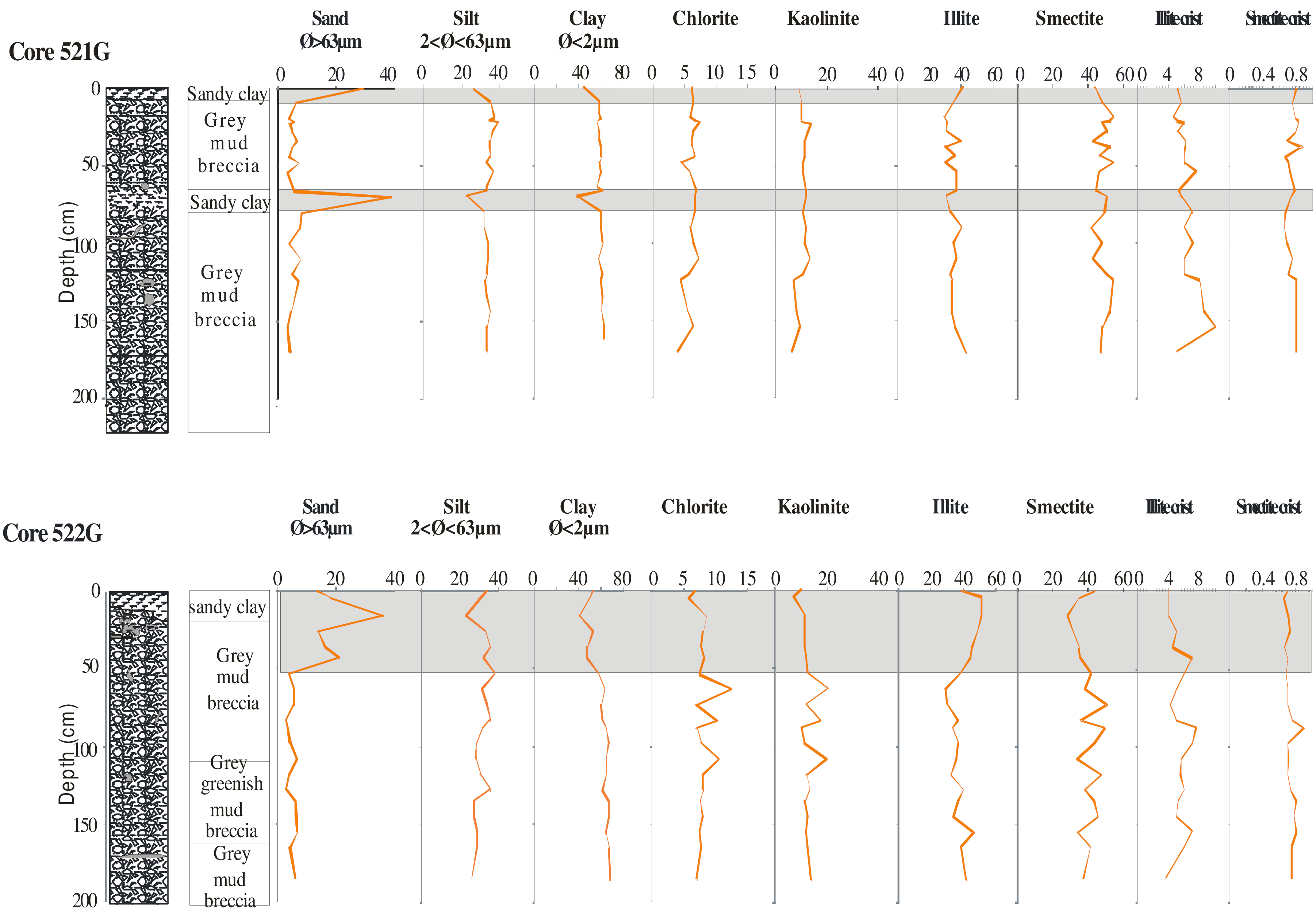

Figure 3. Main lithologic unit, granulometry and clay minerals at Ginsburg mud volcano.

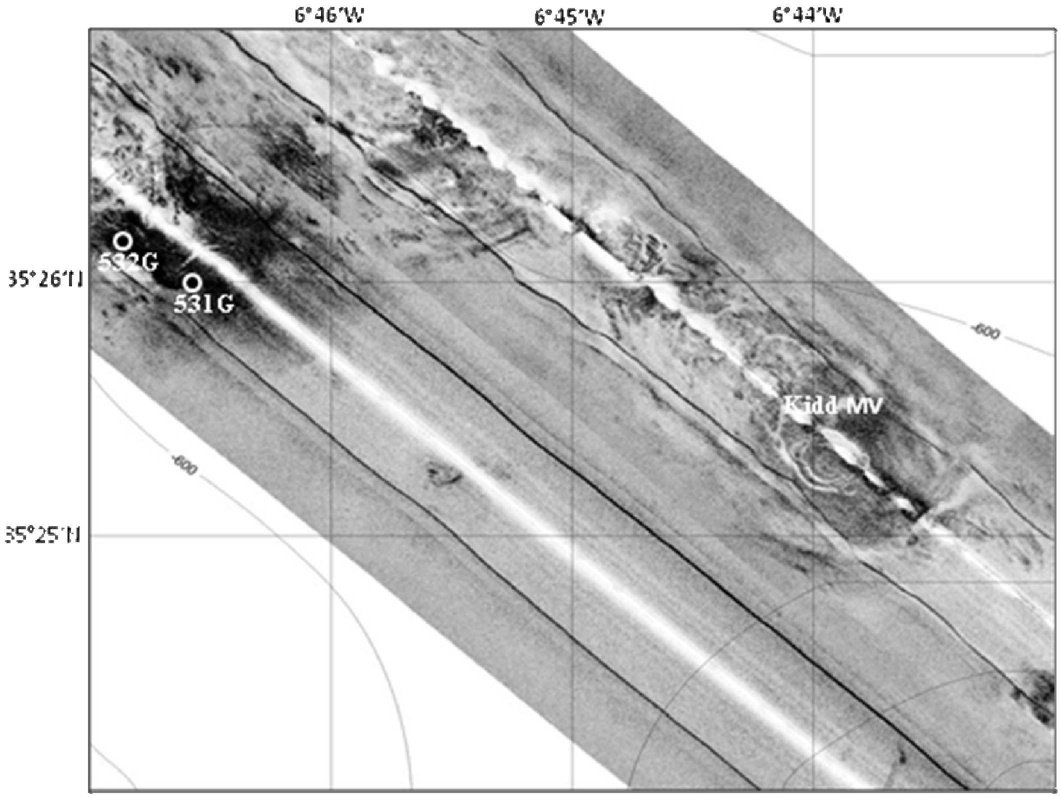

Figure 4. Location of sampling 531G and 532G.

unit of brown sand and a lower unit of grey clay.

The granulometry composition is similar at both cores. At upper part of cores the sand shows a trend of important increasing from 20 to 80%, while the clay and silt present a decreasing trend. At the lower part of cores, the three fractions are relatively constant clay with 78%, silt 20% and sand ≤ 2%.

All the clay minerals show the same distribution pattern and same concentrations at 531G and 532G. The illite principal mineral and chlorite are constant along both cores with 60% and 10% respectively. The Kaolinite presents a slight decreasing trend at the upper part of cores from 18 to 10%; at the lower part, it shows slight fluctuation with an average concentration of 20%. While the smectite shows at the upper part a slight increasing trend from 10 to 15%. At the lower part the smectite concentration ranges between 10 and 20%.

At the top of both cores the geochemical analysis shows an elevated concentration of Ti, Zn, As and Mn, and a high concentration of Cu 29 µg/g and Pb 22 µg/g at the top of core 532G only.

DISCUSSION AND CONCLUSION

The clay mineral assemblage in all studied structures, include smectite, illite, chlorite and kaolinite, but with different concentrations (Figure 6). The most marked change is perceptible at smectite percentage.

In Ginsburg mud volcano, the dominant mineral is smectite (44 - 53%), while in Meknes mud volcano, illite is the dominant mineral with 66% and smectite varies between 13% and 20%. In circular structure illite is also the dominant mineral with 62%, smectite has low concentration than Meknes mud volcano (10 - 13%) (Figure 6).

Cores 531 and 532G cover only the hemipelagic sequence. The sedimentation is not interrupted by any mud intrusion or extrusion. Hence, the distribution pattern of clay minerals at both cores could be related to climatic variation.

The elevated percentage of smectite found mainly in Ginsburg mud volcano, is unusual compared to the average regional values. High amounts of smectite were also found in mud volcanoes at the Mediterranean (Zitter et al., 2001; Zitter, 2004), in mud volcanoes at the gulf of Cadiz from the Tasyo field in the Spanish margin (Table 3) (Puertas, 2004; Puertas et al., 2004; Puertas et al., 1970).

Analysis of the fluid geochemistry of different mud volcano demonstrate that the origin of the fluid and over pressuring result from the clay mineral dehydration by the transformation of the smectite to illite (Dählmann and De Lange, 2003; Hensen et al., 2007; Sheppard and Gilg, 1996) at depth 5 – 6 km and under temperatures bet-

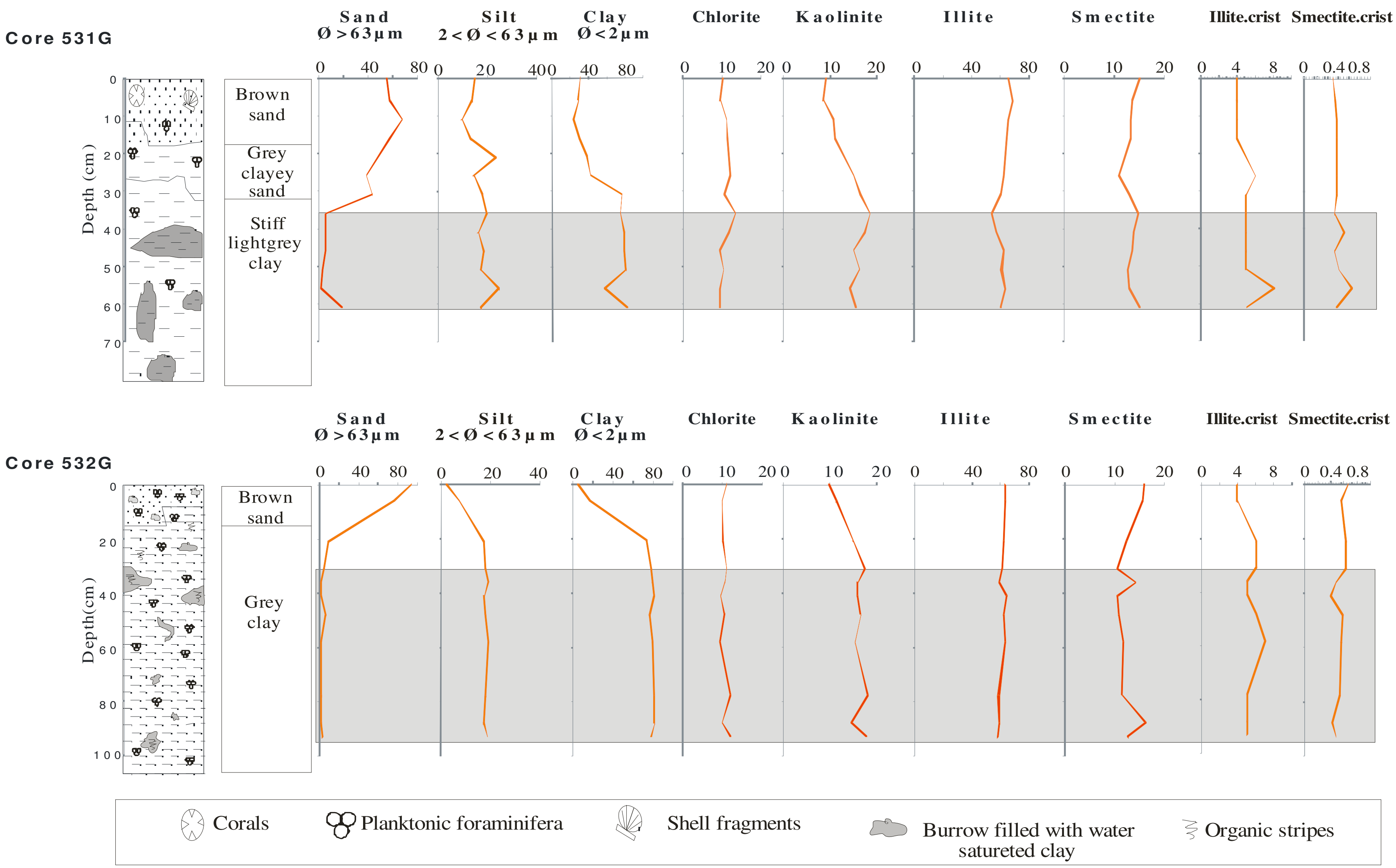

Figure 5. Main lithologic unit, granulometry and clay minerals at circular structure

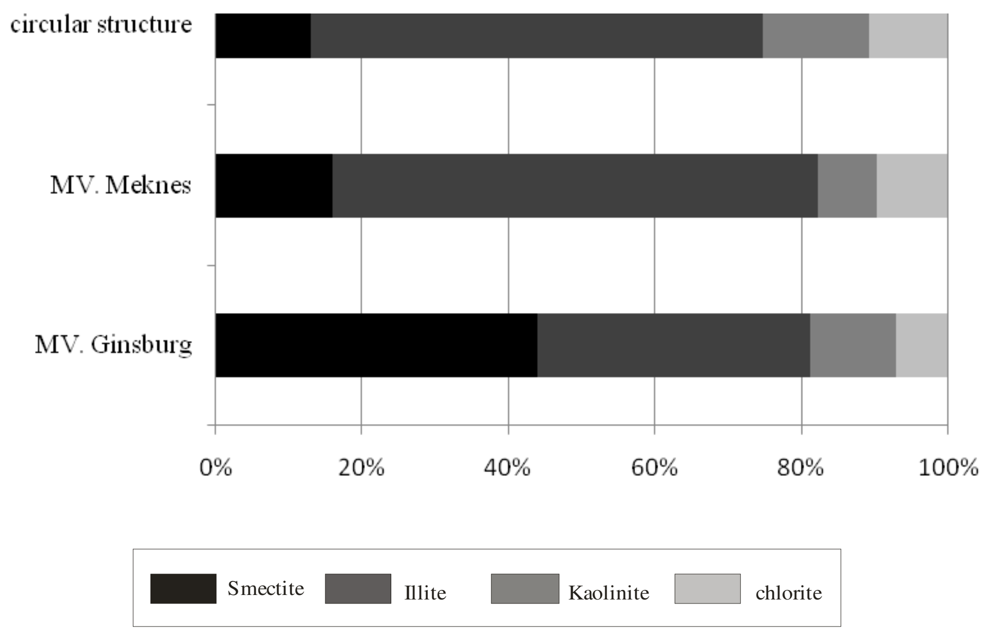

Figure 6. Comparative of average percentages of clay minerals from clay fraction of Ginsburg, Meknes mud volcano and circular structure.

Table 3. Comparative of average percentages of clay minerals from mud volcanoes of Spanish Atlantic margin (after Martin Puertas et al, 2007) and Moroccan Atlantic margin(in this study)

Clay minerals	Atlantic Moroccan margin (in this study)	Atlantic Spanish margin (Martin Puertas et al., 2007)
smectite	30	18
Illite	52	42
Kao+ cht	18	40

ween 60 and 150°C. Hence, the high amount of the smectite and the low amount of illite at the Ginsburg is not opposing the deep smectite-illite transformation. Because the reaction occurs at several kilometers deep and its products are transported along fault system causing the liquefaction of sediments and formation of mud volcanoes (Dählmann and De Lange, 2003). In other words, fluids and parents layers could have different depths and origins. Therefore, the significant difference in clay mineral concentrations between Ginsburg and Meknes mud volcano, essentially in smectite amount, may be related to different depth of source of the original material feeding the both volcanoes.

Considering an average geothermal gradient of 25 - 30°C at gulf of Cadiz, source material rich in smectite should not exceed a depth of 3km (Merriman and Peacor, 1999). then the clay mineralogy of Ginsburg mud volcano indicate a shallowest source of the material feeding the volcano which don't undergo the burial diagenesis, witch could be reflected by very well crystallinity of smectite (Figure 3), while for Meknes mud volcano, the clay mineralogy association is illite rich and most smectites and illites are moderately crystalline (Figure 2). It could indicate a deeper source than Ginsburg mud volcano and smectite evolved into an illite, or because the initial source is not rich in smectite.

This dissimilarity in clay mineralogy association between mud volcanoes of same area confirms different origins and depths of diapirs and fluids feeding mud volcanoes.

The geochemistry analysis of the fraction under 63 µm shows a high content of Ti, Zn, Mn and As at the top of the cores 531 and 532G. A high concentration of Zn and As for core 521G. At Meknes mud volcano high amounts of Ti are observed along the core. As, Mo, Cd, Ag and U present a negative trend. The elements V, Cr, Fe, Co, Ni and Sb are constant at all the cores.

The elements showing an increase at the top of the cores could suggest continental contribution by the wind transport (aerosol) or by suspension. The element showing an increase at the bottom of the cores can be explained by local production.

In conclusion, the high amount of smectite and minor illite content at the Ginsburg mud volcano indicate a shallow source of the matrix that does not undergo the burial diagenesis transformation (from smectite to illite) (Zitter et al., 2001) . The source of the original material of Meknes mud volcano could be deeper than the Ginsburg mud volcano witch explain the high amount of illite and low amount of smectite. The geochemical analysis shows that some elements have negative trend, which could be related to local production, and others have positive trend indicating a continental input.

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