

FIRST DATA ON CLAY MINERAL ASSEMBLAGES AND GEOCHEMICAL CHARACTERISTICS OF TOARCIAN SEDIMENTATION IN THE UMBRIA- MARCHE BASIN (CENTRAL ITALY)

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(Received 19 December 1991; revised 21 September 1992)

ABSTRACT: A moderate to high rate of clay sedimentation is characteristic of the Toarcian sequences in the Umbria-Marche basin. The clay mineral assemblages and geochemical characteristics indicate that the Marne di Monte Serrone Formation and the Rosso Ammonitico Umbro-Marchigiano Unit were deposited in a shallow marine environment. In this general palaeogeographic scheme, a reducing subenvironment must have existed in which black shale-type facies were deposited resulting in geochemical anomalies in As, Sb, Zn, Co, Cu, Pb, V, Cr, and Ba, among other elements. The high values of both the detrital index and the Ce/Ce* ratio reveal the influence of proximal emerged reliefs. It is suggested that the palaeosoils that developed on the Liassic carbonate Laziale-Abuzzese platform were the source area of these sediments, following a palaeogeographic scheme analogous to that proposed for the Betic Cordilleras (Spain) during the Middle Domerian to Middle Toarcian. The positive and negative Eu anomalies are due to the decisive influence of the weathering process in which sediments with heterogeneous Eu anomaly size were mixed. The final distribution pattern of REE is the result of the different environments to which the clay minerals were subjected and the differences in intensity of weathering.

The Toarcian sequences of the Umbria-Marche basin are characterized by a moderate to high rate of clay sedimentation. According to the variability of local subsidence and bottom morphology, “condensed”, “intermediate” or “extended” clayey sequences were formed (Colacicchi *et al.*, 1988). The “condensed” sequences were deposited in areas of elevated structural zones where the formations are absent or very thin. “Intermediate” sequences, which are defined as normal because they are very common, were located on slightly tilted fault blocks, forming wide, relatively stable structural surfaces, and on the slightly sloping sea-bottom. The extended sequences, which present the greatest thickness and probably the deepest facies, are scarcer than the intermediate ones; they indicate areas with rapid subsidence and represent structural, but not morphological depressions. During the Toarcian, abundant clay materials entered the basin and were deposited in this type of depression.

Some of these argillaceous sequences contain abundant detrital beds 0.5–100 cm thick. In some cases these detrital intervals are represented by calcareous turbidites showing the classic Bouma BC sequence. In other cases, sharp-based hummocky cross-stratified (HCS) calcarenites are interbedded or overlie turbiditic materials (Monaco, 1992). Locally, slumps and pebbly mudstones are present. The depositional environment of HCS beds usually seems not to exceed the major storm wave base depth, unlike turbiditic deposits. Vertical

transition from turbidites to HCS deposits should therefore prove to be useful in the reconstruction of the variations in basin depth and the relations with tectonics and sea-level changes in regressive shelf sequences.

The detailed study of mineralogical characteristics, particularly of clay minerals and of the geochemistry of the Marne di Monte Serrone (MS) Formation and the Rosso Ammonitico Umbro-Marchigiano (RAUM) Unit has contributed significantly to the exact determination of the depositional environment and the palaeogeography of the depositional basin.

GEOLOGICAL SETTING AND STRATIGRAPHY

The Umbria-Marche (U-M) basin is located in the Northern Apennines (Central Italy) between the front of the Trasimeno-Falterona-Cervarola nappe and the Pliocene Adriatic foredeep (Fig. 1-I). It consists of a Mesozoic and Cenozoic carbonatic-siliciclastic sequence which varies greatly in thickness from South to North (between 2000 m and ~3500 m) and

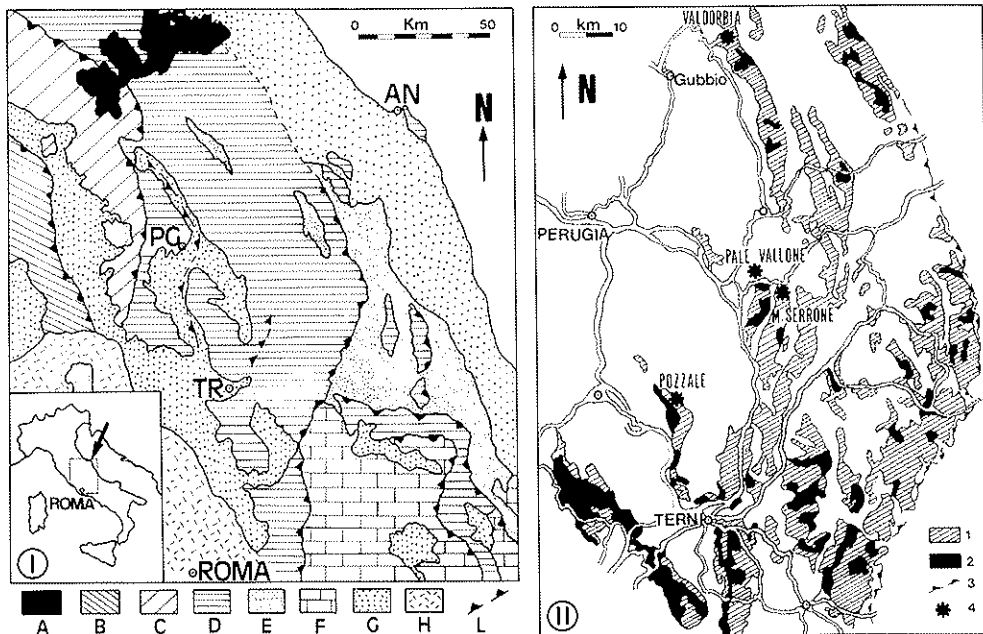


FIG. 1. Location of the sequences studied.

I. Schematic geological setting of the Umbria-Marche area (Monaco, 1989). A: Tosco-Emiliani Allochthonous Complex; B: Toscana facies; C: Trasimeno-Falterona-Cervarola allochthonous sediments; D: Mesozoic and Cenozoic sediments of the Umbria-Marche basin; E: Upper Tertiary syn- and postorogenic siliciclastic rocks; F: Laziale-Abruzzese carbonate platform; G: Pliocene-Pleistocene postorogenic sediments; H: Tosco-Laziale volcanic province; L: Major thrusts; AN: Ancona; PG: Perugia; TR: Terni.

II. Jurassic outcrops and sequences studied (Monaco, 1992). 1: Jurassic sediments including the COR, RAUM and CP Units, and MS Formation from Sinemurian to Aalenian. 2: Early Jurassic carbonate platform (Hettangian to Sinemurian). 3: Major thrusts. 4: Studied sequences. VD: Valdorbria; PLV: Pale Vallone; MS: Monte Serrone; PO: Pozzale.

is at present organized in an acute fold belt. The basin was rapidly downwarped in the Early Lias, when extensional faulting fragmented a nearly isolated passive continental margin (a large southern Tethyan carbonate platform) commonly referred to as Adria (Channell *et al.*, 1979). This brought about a turning point in the type of Liassic sedimentation, changing from neritic-type carbonates (Calcere Massiccio Formation), where sediment production occurs mainly on the shallow-sea bottom, to sediments produced in the water mass (from the Corniola to Calcari a Posidonia Units) (see the extensive literature summarized in Colacicchi *et al.*, 1970, 1988; Centamore *et al.*, 1971; Farinacci *et al.*, 1981; Farinacci & Elmi, 1981; Cresta *et al.*, 1988, 1989).

The marly and marly-argillaceous Marne di Monte Serrone (MS) Formation (Fig. 1-II) (Late Domerian–Middle Toarcian) (Pialli, 1969) represents a moderate to thick clayey deposit. Black shales with organic rich intervals formed during the “Toarcian anoxic event” (Early Toarcian) are common (Jenkins & Clayton, 1986; Jenkins, 1988; Bartolini *et al.*, 1992). The MS unit ranges in thickness from a few metres to 80 m in the intermediate and extended sequences of the Umbria-Marche area. The microfacies (Cresta *et al.*, 1988) indicate a circalittoral to upper bathyal environment in the type section (Monte Serrone). The deposition depth and the thickness of the MS Formation are consequently extremely variable in the Umbria-Marche area and reflect a differentiated topography of the basin.

The MS Formation is overlain by reddish nodular marls with ammonite-rich horizons of the Rosso Ammonitico Umbro-Marchigiano (RAUM) (Colacicchi *et al.*, 1988), which is mainly Middle–Late Toarcian in age (Cresta *et al.*, 1988; Cecca *et al.*, 1990). The microfacies of the RAUM in general indicate a shallower and more oxygenated environment than that of older deposits, which range from the Late Sinemurian to the Early Toarcian.

Figure 2 shows the location of the samples studied in stratigraphic correlation between Pozzale (PO), Valdorbia (VD), Monte Serrone (MS) and Pale Vallone (PLV) sequences. Thirty two representative samples were studied in palaeontologically well-dated stratigraphical sequences, thus permitting accurate correlations between them.

METHODS

The whole samples and clay fractions were examined by X-ray diffraction (XRD) using a Philips PW 1710 diffractometer equipped with graphite monochromator and automatic slit (Department of Mineralogy and Petrology, University of Granada). The reflecting factor, calculated for this equipment and its instrumental conditions on the basis of the data by Schultz (1964) and Barahona (1974) were for random powder samples—phyllosilicates, 0.09; quartz 1.43; calcite 1.05; dolomite, 1.08; feldspar, 1.03; for oriented powder samples—illite, 0.36; smectites, 0.93; chlorite, kaolinite, 0.98.

The morphological study of the minerals was carried out by scanning electron microscopy (SEM) using a Zeiss DSM 950 (Technical Services of the University of Granada). The microanalyses of the clays were obtained using a Jeol JSM-820 fitted with a Link Analytical microanalysis system (University of Cádiz, Spain).

Analyses of the major and minor elements and the rare-earth elements (REE) were carried out using X-ray fluorescence (XRF), neutron activation (NA), inductively coupled plasma (ICP) and atomic absorption spectrometry (AAS) at the X-Ray Assay Laboratories in Ontario, Canada.

MINERALOGY

A graphic representation of the results obtained is presented in Fig. 3. The whole mineralogy consists of calcite, feldspars, quartz and clay minerals; gypsum (VD sequence), or dolomite and celestite (PLV sequence) were detected exceptionally in some samples. The clay minerals found in the sequences and lithofacies studied were illite (I), smectites (Sm) and kaolinite (K). Chlorite (Chl) was detected exceptionally in the PLV-11.5 sample in quantities <5% (Fig. 3).

The Marne di Monte Serrone Formation is characterized by the assemblages illite-smectite-kaolinite. Illite is the most abundant mineral, its mean proportions ranging from 76% (VD and MS sequences) to 93% (PLV sequence). Scanning electron microscopy suggests the existence of inheritance and diagenetic transformation processes, following the hypotheses of Pollastro (1985) and Ortega Huertas *et al.* (1991a). Dioctahedral smectite ($Fe/Al = 0.4$; $Al > Fe > Mg$) is the next most abundant mineral and is present in all the stratigraphic sequences, except the PLV sequence. The mean contents and range of variation are: VD sequence (19%, 7–25%), PO sequence (13%, <5–23%), MS sequence

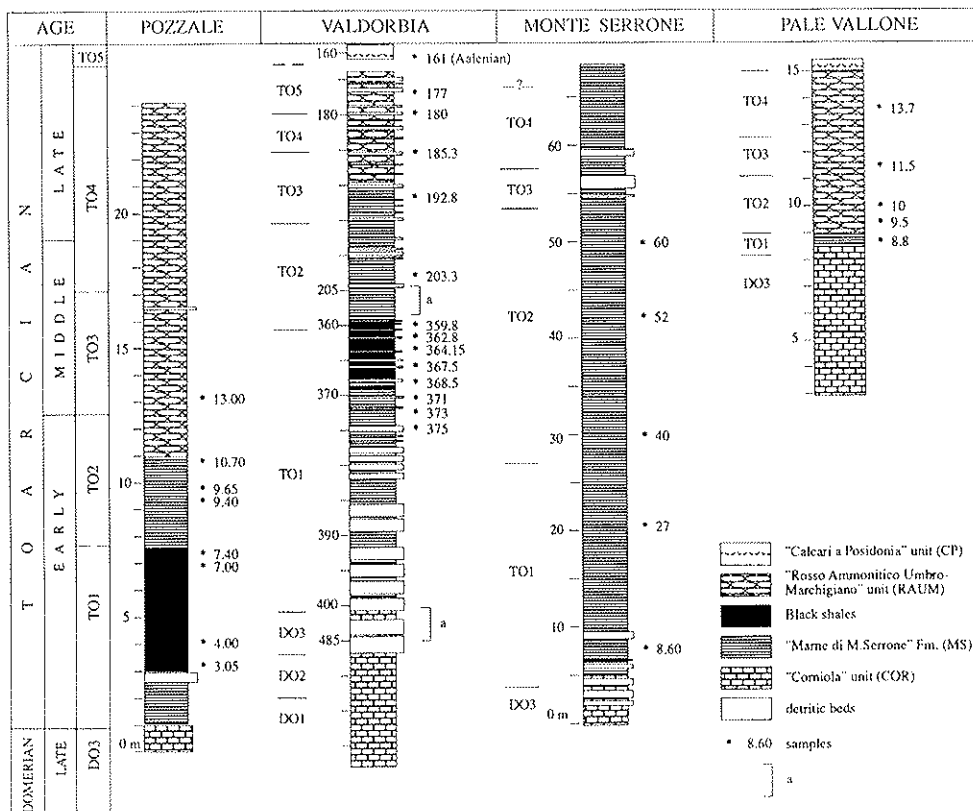


Fig. 2. Stratigraphy of the sediments studied. Informal subdivisions of the Domesian and Toarcian intervals are after Cantaluppi (1970) and Venturi (1990). a: The sequence is continuous and the difference in metres is not real but is due to the paleomagnetic sampling that is indicated here (Channell *et al.*, 1979).

(18%, 10–30%). Kaolinite is also present in all samples studied, the mean contents usually being not >7%, although they can reach 17% (PO-25).

In some sequences, the black-shale lithofacies appears within the Marne di Monte Serrone Formation. It is characterized by large quantities of illite, ranging from 70–76% in the VD sequence and from 70–85% in the PO sequence; significant amounts of smectite in the VD sequence (17–25%, average value 22%) and in the PO sequence (10–22%, average value 17%), and minor quantities of kaolinite, which are invariably <5%, except for sample PO-7.40, whose content is 8%. Overall this lithofacies is homogeneous from a mineralogical point of view. By SEM the smectite presents characteristic crinkly, ridged, honeycomb-like textures.

Figure 4 represents a general view of the quantitative variations of the whole mineralogy and the clay minerals during the Early Toarcian in the different stratigraphic sequences studied. The mean calcite content varies from 30% in VD to 81% in PLV, and is very similar in the PO (39%) and MS (41%) sequences. The values of the variation coefficient (V) reveal great diversity in the calcite content, which is high in the VD sequence ($V = 55$), normal in PO ($V = 17$) and low ($V = 8$) in the MS and PLV sequences. The detrital contribution (quartz, feldspare and most of the clay minerals) is more homogeneous throughout the different stratigraphic sequences. The illite proportion is very homogeneous in all the sequences, whereas those of smectite and kaolinite are very heterogeneous within all the sequences and also comparatively between them.

The Rosso Ammonitico Umbro-Marchigiano Unit shows a very homogeneous clay

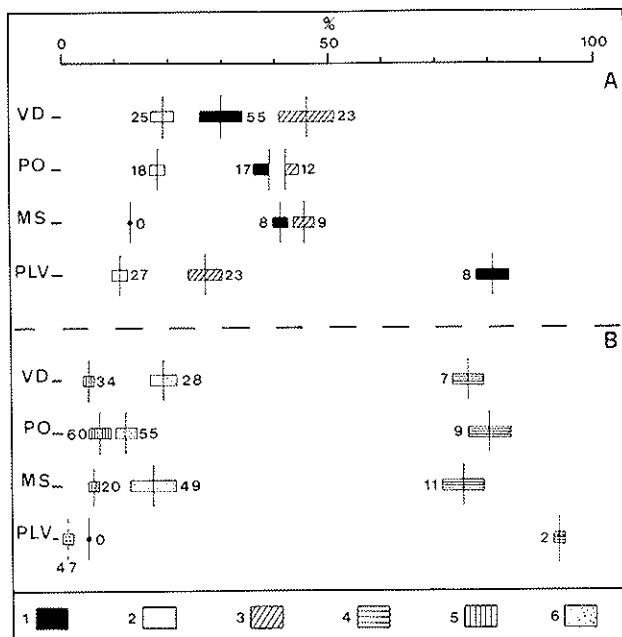


FIG. 4. Quantitative variations in the whole mineralogy (A) and the clay minerals (B) in the MS Formation during the Early Toarcian. The standard deviation is indicated by the bar, the arithmetic average by the cross-bar and the coefficient of variation by number. 1: calcite; 2: quartz; 3: clay minerals; 4: illite; 5: kaolinite; 6: smectite. VD, PO, MS and PLV: stratigraphic sequences.

mineral content whether its lithology is calcareous or marly-limestone (Fig. 3). This facies is very largely made up of illite (from 82% in PO to 92% in PLV), with minor proportions of smectites (5–10%) and kaolinite (5–8%). This fact, together with the aforementioned mineralogical homogeneity of the carbonate, quartz and clay mineral content, seems to indicate sedimentation occurring under homogeneous palaeogeographic and tectonic conditions, in which modifications to the sedimentary parameters would have caused the presence of carbonate or marly levels.

GEOCHEMISTRY

The chemical analyses of the whole samples are presented in Tables 1 and 2. In general, the trace elements are mainly concentrated in the clay fraction, except for Sr, Y and Zr. The Sr must be related to the abundance of carbonates, and the Y and Zr are mainly transported with the accessory minerals (especially zircon).

It is important to point out the significant positive correlation shown by As, Sb and Zn contents. The highest values appear in the same samples (from VD-368.50 to VD-362.80, PO-7, PO-7.40, PLV-8.8 and PLV-9.50), all of which can be stratigraphically correlated within the Early Toarcian. These geochemical anomalies are also clear for the same

TABLE 1. Chemical analyses of the whole samples (wt%).

Samples	Lithology*	SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	Fe ₂ O ₃	MnO	TiO ₂	P ₂ O ₅	LOI
VD-161	3	19.00	4.11	38.60	1.27	0.09	1.12	1.84	0.04	0.20	0.09	33.80
VD-185.30	2	26.00	7.70	29.50	1.57	0.22	2.69	4.68	0.02	0.42	0.10	27.20
VD-180	2	11.70	3.28	44.40	1.21	0.08	1.00	1.27	0.03	0.17	0.06	37.20
VD-177	2	29.10	8.44	27.20	1.65	0.18	3.15	4.71	0.02	0.49	0.14	25.20
VD-203.30	1	30.10	7.91	27.00	1.71	0.24	2.66	3.19	0.03	0.43	0.08	26.80
VD-362.80	1	51.10	12.90	6.83	2.11	0.29	4.49	5.11	0.04	0.76	0.09	16.50
VD-364.15	1	48.50	12.30	7.44	2.05	0.28	4.79	5.13	0.06	0.76	0.11	17.60
VD-368.50	1	41.70	10.50	14.90	1.97	0.28	3.99	5.10	0.15	0.61	0.19	18.60
VD-371	1	29.10	7.19	29.10	1.41	0.17	2.74	2.98	0.25	0.41	0.07	25.20
PO-13	1	36.70	9.72	20.20	2.04	0.27	3.32	3.80	0.41	0.58	0.10	21.80
PO-9.65	1	35.60	10.20	20.90	1.79	0.19	3.72	5.51	0.08	0.59	0.10	21.70
PO-9.40	1	27.00	7.68	29.70	1.64	0.16	2.79	3.88	0.09	0.42	0.07	26.90
PO-7.40	1	42.30	11.50	14.30	2.19	0.21	4.19	4.33	0.22	0.64	0.12	19.20
PO-7	1	46.40	12.50	10.80	2.28	0.19	4.59	4.35	0.17	0.73	0.10	17.80
PO-4	1	36.60	9.42	19.40	1.91	0.17	3.18	3.33	0.56	0.55	0.09	24.10
MS-60	1	36.10	9.75	22.10	1.90	0.20	2.87	3.75	0.02	0.50	0.30	22.80
MS-52	1	35.70	9.85	21.80	1.93	0.24	2.91	3.86	0.03	0.51	0.41	22.90
MS-40	1	37.10	9.51	20.80	1.95	0.30	2.82	4.47	0.06	0.54	0.09	22.80
MS-27	1	30.70	7.60	27.00	1.63	0.18	2.11	3.19	0.06	0.41	0.08	26.70
MS-8.60	1	39.60	11.30	17.60	2.08	0.28	3.36	4.38	0.03	0.61	0.09	21.10
PLV-13.70	2	18.50	5.76	37.90	1.20	0.14	2.04	2.91	0.03	0.31	0.08	31.50
PLV-11.5	2	22.40	7.12	32.30	1.59	0.17	2.54	3.63	0.03	0.38	0.07	29.30
PLV-10	1	21.90	6.88	34.90	1.29	0.20	2.45	2.08	0.03	0.36	0.07	29.80
PLV-9.50	1	25.70	7.94	31.40	1.47	0.14	3.29	2.59	0.03	0.43	0.09	26.40
PLV-8.80	1	40.10	12.70	16.70	2.50	0.28	4.76	4.88	0.02	0.70	0.13	16.20

* 1: Marne di Monte Serrone Formation; 2: Rosso Ammonitico Umbro-Marchigiano Unit; 3: Calcari a Posidonia Unit.

TABLE 2. Chemical analyses of the whole samples (p.p.m.).

Samples	Lithology*	Rb	Sr	Y	Zr	Nb	Ba	V	Cr	Ni	Co	Cu	Zn	As	Se	Sb	B	U	Pb
VD-161	3	40	407	12	26	13	100	62	25	36	11	16	32	<2	<3	0.5	50	0.6	<2
VD-185.30	2	62	201	<10	72	17	127	78	46	30	7	9	45	3	<3	0.9	70	1.0	<2
VD-180	2	30	252	<10	25	<10	100	38	26	21	9	12	33	<2	<3	0.5	20	<2	<2
VD-177	2	80	204	40	89	15	120	76	61	60	12	20	69	2	<3	0.7	60	1.0	<2
VD-203.30	1	72	294	15	86	26	162	76	46	19	7	16	37	<2	<3	0.4	60	1.0	4
VD-362.80	1	95	233	12	162	24	752	140	83	53	18	47	92	11	<3	1.7	100	2.5	8
VD-364.15	1	100	180	26	142	16	989	160	85	44	19	46	69	12	<3	1.8	110	2.5	8
VD-368.50	1	74	241	<10	121	<10	166	100	68	49	19	46	71	11	<3	1.3	80	1.8	4
VD-371	1	52	353	26	70	15	157	76	42	22	10	22	37	4	<3	0.8	60	1.1	2
PO-13	1	73	197	39	103	15	258	110	62	36	13	38	48	9	<3	1.0	70	2.3	2
PO-9.65	1	83	267	13	120	22	200	94	61	38	11	24	65	5	<3	0.9	90	1.4	4
PO-9.40	1	61	203	<10	81	16	117	68	45	28	7	23	50	3	<3	0.7	60	1.0	<2
PO-7.40	1	98	331	27	127	21	145	140	76	49	18	41	88	11	<3	1.5	100	1.9	6
PO-7	1	103	289	23	167	22	194	150	79	40	15	45	72	14	<3	2.0	90	2.6	10
PO-4	1	76	244	25	97	11	450	100	60	29	14	37	69	5	<3	0.7	80	1.6	2
MS-60	1	82	355	21	90	25	195	80	54	31	7	27	56	3	<3	0.6	70	2.0	4
MS-52	1	82	356	22	85	26	200	88	58	30	9	29	59	3	<3	0.8	70	2.2	4
MS-40	1	74	469	18	97	19	106	82	54	36	7	27	56	<2	<3	0.6	70	1.2	6
MS-27	1	60	304	<10	60	<10	120	66	44	23	5	26	47	3	<3	0.6	40	1.2	2
MS-8.60	1	93	353	<10	102	27	114	94	62	31	8	32	51	2	<3	0.7	80	1.4	12
PLV-13.70	2	40	185	10	47	17	114	56	32	32	9	11	47	<2	<3	0.6	70	0.5	4
PLV-11.5	2	60	242	14	77	<10	100	54	38	30	9	9	46	3	<3	0.6	70	0.7	2
PLV-10	1	50	237	<10	62	16	1000	64	36	32	8	9	48	2	<3	0.7	80	0.7	2
PLV-9.50	1	58	240	<10	81	<10	153	72	51	43	21	18	130	6	<3	1.0	90	1.0	14
PLV-8.80	1	110	238	15	168	28	114	96	75	83	50	25	64	7	<3	1.3	150	1.1	6

* 1: Marne di Monte Serrone Formation; 2: Rosso Ammonitico Umbro-Marchigiano Unit; 3: Calcarei a Posidonia Unit

stratigraphic levels on comparison of their contents of Co, Cu, Pb, V, Cr, Ba or B (Table 2) with those of other samples from the sequences studied.

As regards REE distribution in the stratigraphic sequences studied (Table 3), the REE patterns in the samples are controlled, in our opinion, by the grain size, the whole mineralogy and the presence of heavy minerals. All of the REE should be related to the clay fraction, although there is no direct correlation with clay mineralogy, since trivalent REE may be accommodated in most clay minerals according to Cullers *et al.* (1975). Regarding the mineralogy of our samples, the quartz and calcite contain very low proportions of REE resulting in a dilution effect, and a negative correlation is observed between the calcite content and the REE content. In the sediments studied, the mean contents of Zr and Ti (Table 2) are high, indicating the presence of the heavy minerals (zircon and rutile) with abundant REE. This factor therefore affected the distribution of the REE content in the different samples and stratigraphic sequences studied. Figure 5 summarizes the REE contents, normalized to NASC, of the sediments studied; these data agree with those of MacLennan (1989) for sediments in similar geological environments.

TABLE 3. Geochemical data of the whole samples.

Samples	Lithology*	Total REE (p.p.m.)	CaCO ₃ %	Ce/Ce*	D	La/Lu	Eu/Sm
VD-161	3	76.79	73	absent	0.75	12.10	0.28
VD-185.30	2	93.13	37	"	0.75	11.75	0.31
VD-180	2	50.94	75	"	0.75	11.28	0.31
VD-177	2	102.87	50	"	0.74	11.56	0.25
VD-203.30	1	91.24	43	1	0.75	10.21	0.17
VD-362.80	1	146.87	9	1	0.76	11.00	0.23
VD-364.15	1	140.58	10	1	0.76	9.90	0.17
VD-368.50	1	167.95	23	0.85	0.74	10.57	0.28
VD-371	1	103.45	51	1	0.75	11.20	0.20
PO-13	1	137.42	36	0.97	0.74	10.72	0.26
PO-9.65	1	127.40	48	0.95	0.70	11.14	0.25
PO-9.40	1	95.33	36	1	0.70	11.05	0.25
PO-7.40	1	160.85	48	0.98	0.75	11.49	0.21
PO-7	1	166.87	30	1	0.75	11.51	0.22
PO-4	1	127.33	32	0.89	0.75	10.52	0.28
MS-60	1	119.22	45	0.90	0.77	12.20	0.24
MS-52	1	145.38	39	0.89	0.76	12.21	0.22
MS-40	1	100.05	46	1	0.70	11.08	0.15
MS-27	1	97.64	41	1	0.75	10.54	0.30
MS-8.60	1	121.98	37	1	0.76	11.68	0.25
PLV-13.70	2	72.79	81	0.91	0.70	10.47	0.20
PLV-11.5	2	88.51	82	absent	0.70	11.29	0.28
PLV-10	1	83.61	68	"	0.80	10.49	0.30
PLV-9.50	1	101.54	57	"	0.76	10.99	0.22
PLV-8.80	1	144.24	44	0.96	0.75	10.97	0.21

* 1: Marne di Monte Serrone Formation; 2: Rosso Ammonitico Umbro-Marchigiano Unit; 3: Calcari a Posidonia Unit.

D (detrital index) = Al/Al + Fe + Mn.

PALAEOGEOGRAPHY OF THE BASIN

Several papers have been published since the early 1980s comparing the stratigraphical characteristics of the Jurassic facies deposited in continental margin environments corresponding to Alpine domains, such as the Betic Cordilleras (Spain) and the Apennines (Italy) (e.g. Jenkyns, 1980; Vera, 1981). From a mineralogical and geochemical point of view, knowledge of Early Jurassic facies in the Betic Cordilleras is exhaustive (Palomo, 1987; Ortega Huertas *et al.*, 1991b). This paper presents the first data on identical lithofacies in the Apennines. The overall study of the mineralogy and geochemistry, and the previous knowledge of similar lithofacies in the Betic Cordilleras, allow us to infer the following general facts about the environment of the basin. Figure 6 shows the most significant mineralogical and geochemical characteristics of the studied lithofacies.

The sedimentation of the MS Formation and the RAUM Unit took place in depositional environments of similar palaeogeographic characteristics, with shallow marine, neritic sedimentation clearly affected by nearby emerged reliefs. However, the Early Toarcian sedimentation began in deeper marine conditions which became progressively shallower towards the Middle and Late Toarcian. This fact is common to all the sequences studied, as is shown by the systematic presence and greater abundance of kaolinite towards the top of the sequences.

This hypothesis is also supported by the La/Lu values found in these sediments (Table 3).

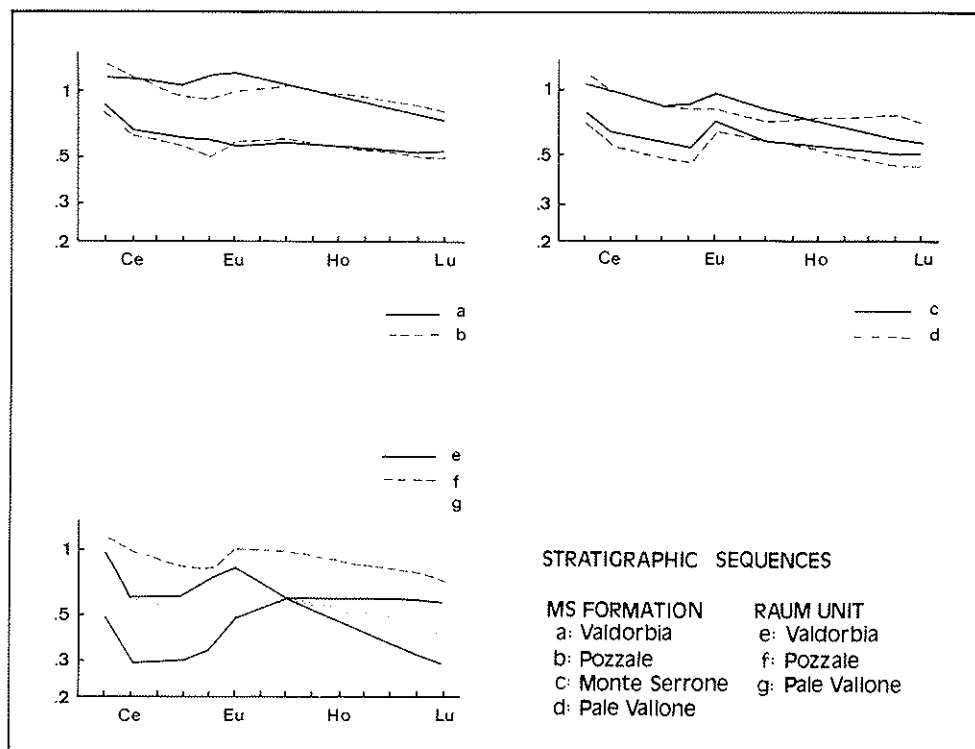


Fig. 5. NASC-normalized REE content. The curves correspond to the samples with maximum and minimum values.

Several authors (e.g. Ronov *et al.*, 1967) have established that the La/Lu ratio normalized to chondrites gives values of 21.8, 14.5 and 9.4 as typical of continental, nearshore marine and pelagic sediments, respectively. In our case, the values of the La/Lu ratio reveal that, as an overall consideration, the MS Fm and RAUM Unit were deposited in palaeogeographic conditions intermediate between those of a pelagic and a nearshore marine environment. The data for the Eu/Sm ratio (Table 3) also confirm this interpretation. Nonetheless, the deposition of the RAUM Unit could correspond to a shallower environment than that of the MS Fm., as can be deduced from the general trend of the La/Lu ratio to increase in the samples of the RAUM Unit (Table 3). A similar interpretation must be made for the fact that the Ce anomaly is absent in most of the samples of this lithology (Table 3).

Sedimentological data seem to concur with mineralogical and geochemical data. A vertical transition from classic turbidites presenting a BOUMA BC sequence in the Early Toarcian to sharp-base hummocky cross-stratified deposits at Valdorbja in the Middle Toarcian (Monaco, 1992) seems to indicate a trend for shallowing-upwards at this time. This trend can be referred to the general sea-level fall as shown by Hallam (1988), approximately during the Middle Toarcian. In addition, the microfaunal content indicates a transition from an upper bathyal/outer shelf to a middle shelf environment. Highly packed concentrations of bivalve shells (Pozzale sequence) and abrasion tests of benthic foraminifera in the Middle-Late Toarcian suggest a variable flow regime at the major wave base as a result of a storm event.

In this palaeogeographic context geological subenvironments characterized by reducing conditions must have existed. Specifically, this type of sedimentation must have occurred

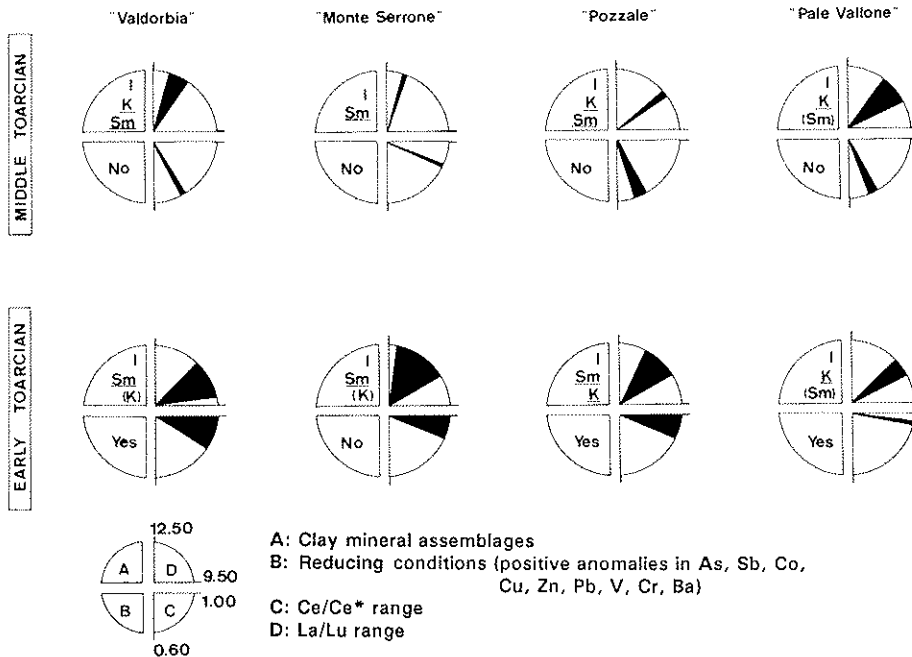


Fig. 6. Mineralogical and geochemical representative features of the Toarcian sedimentation.

for levels VD-368.50 to VD-362.80 and the correlative levels in the PO stratigraphic sequence (PO-7, PO-18), in which geochemical anomalies are found in the contents of As, Sb, Zn, Co, Cu, Pb, V, Cr and Ba, among other elements (Table 2). This deposit was produced both in an environment intermediate between nearshore and pelagic sedimentation and in a clearly pelagic environment (sample VD-364.15, La/Lu = 9.90), which is indicative of the existence of small (local) tectonic adjustments in the basin. The deposition of the black-shale level, which is quite manifest in the PO and VD (TO1) sequences, must have occurred in this environment, although reducing conditions also existed in other parts of the basin (Table 2). Specifically, samples PLV-8.8 and PLV-9.5 (TO1) show identical geochemical characteristics to those of the black shale, even though they are lithologically different.

The source area of the sediments studied must have been quite homogeneous lithologically and the input of material to the basin must have been rather constant throughout the geological period. The constant presence of the I-Sm-K mineral assemblage and its scarce quantitative variations are evidence of this, and our suggestion is that the I is mainly inherited from the source area rocks, whereas the Sm and K originated in the soils developed on the rocks.

The hypothetical proximal influence of emerged reliefs caused a considerable detrital effect in the sedimentation. This can be seen by the high values for the detrital index (D) and the high concentration of REE (Table 3), both of whose values are much greater than those found in equivalent sediments from other correlative geological environments (Ortega Huertas *et al.*, 1991b). As a parameter indicative of the degree of detrital influence in a basin, the data provided by the Ce/Ce* ratio agree with the foregoing. In all those samples in which this ratio has been established, the values range from 0.81 to 1. In addition, in several of the stratigraphic levels studied (Table 3), the Ce/Ce* ratio is absent, which some authors (Courtois & Hoffert, 1979) consider to be characteristic of sediments very close to coasts.

The mineralogical and geochemical data presented concur with the possibility that the source area of the MS Fm and the RAUM Unit corresponded to the Liassic Laziale-Abruzzese carbonate platform. In fact, the regional geological data reveal the existence of local emersions during the Late Lias (upper part of Domerian and lower part of Toarcian) (Colacicchi, 1967, 1987; Praturlon, 1968; Carbone, 1984). In this context, karstification and pedogenetic processes took place on islands within the passive continental margin and these in turn affected the mineralogy and geochemistry of the nearby shallow deposits. Identical palaeogeographical situation have been described by Vera *et al.* (1989) in similar lithofacies of the Betic Cordilleras (Spain) during the Middle Domerian to Middle Toarcian.

Given the present state of knowledge, we can state with reasonable certainty that the weathering processes in the source area must have been of similar intensity, since the La/Lu ratio (just as the expression of the LREE/HREE ratio) does not show significant variations between the different stratigraphic sequences.

Both positive and negative Eu anomalies are found in the sediments studied. An Eu anomaly appears relative to other REE in samples studied in chondrite-normalized and NASC-normalized curves. We have determined the size of this Eu anomaly by comparing its absolute value with the absolute value of a precisely determined element (Sm). These anomalies could have originated in the source area of the sediments, in which case at least one of the following situations must have applied, as pointed out by Cullers *et al.* (1975): (a) the rocks of the source area could have had Eu anomalies; (b) the chemical weathering

processes may have removed the Eu in preference to other REE, which would have given rise to some sediments depleted in Eu compared to other REE; (c) some samples could contain detrital minerals with a high REE content and negative Eu anomalies. In the cases studied here, we consider that the anomaly initially existing in the source area rocks was modified during the sedimentary process, in which sediments with heterogeneous Eu anomaly size were admixed. This decisive influence of the weathering process is very clear in the sequences studied, since samples are found with positive Eu anomalies, together with samples with negative anomalies of differing intensity.

Many of the variations in the absolute REE content (Table 3) among the different samples and stratigraphic sequences studied in this paper could be due to differences in the source area in which the clay minerals originated. However, the original REE distribution pattern could have been modified by ion exchange when the clay minerals were subjected to a different environment. This sort of phenomenon could have been the cause of the enrichment in REE shown by some specific stratigraphic levels of the MS Fm, as there are no significant quantitative mineralogical variations (particularly for clay minerals) compared with the rest of the stratigraphic series. Such an hypothesis could indeed help to explain the REE contents detected in the levels related to a reducing environment, as mentioned above, in the VD, PO, and PLV sequences. The distribution of the REE content could have been modified by differences in intensity and duration of weathering during sedimentation, and by contamination of the clay minerals with small amounts of detrital minerals in REE.

ACKNOWLEDGMENTS

This research was financed by Research Group 4056 of the Junta de Andalucía, Spanish-Italian Joint Action 9A/1992, Research Project (DGICYT) PB87-0271 and MPI (40% R. Colacicchi). We are grateful to Dr. Ian MacCandless of the University of Granada for his assistance in translating the original text.

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