

Geochemistry of the Plio-Pleistocene clay-sand suite from Orte (Viterbo, Central Italy)

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ABSTRACT. — In the disposal of radioactive wastes, the geochemical characters of the geological formation and their long term maintenance are fundamental with regards to the mobility of the radionuclides in the geosphere.

In order to study the variation of the geochemical conditions through the boundary between oxidized and reduced environment in the clay, geological, mineralogical, sedimentological and geochemical investigations were carried out in a quarry near Orte, where a clayey series is interbedded with sandy levels and in the upper part it is covered by oxidized sandy banks. The sedimentary sequence corresponds to a deltaic or near-deltaic environment. The series is cutted by two principal normal faults; minor faults and fractures are also associated with principal faults.

The geochemical analyses were performed both along the whole series and, in more details, in the upper part of the series at the boundary between the clay and the oxidized sand. The samples were analyzed for major, minor and trace elements as well as for organic substance and sulphur.

In order to get an indirect indication of the Eh value in the different levels Fe^{+2}/Fe^{+3} and Mn^{+2}/Mn^{+4} ratios were measured: the samples from the clayey-silt levels show a Fe^{+2}/Fe^{+3} ratio higher than that shown by the sands and the silty-sands.

Some correlations between major, minor and trace elements and their distribution in the whole rock as well as in the different grain-size fractions are related to the mineralogical composition of the samples.

Key words: geochemistry, radioactive waste disposal, clay-sand suite, redox potential, trace elements.

RIASSUNTO. — Ai fini dello smaltimento dei rifiuti radioattivi, in considerazione della mobilità degli elementi nella geosfera, giocano un ruolo di primaria importanza le caratteristiche geochimiche delle formazioni geologiche, scelte per ospitare i residui delle industrie nucleari, e le loro possibili variazioni per tempi anche assai lunghi. In particolare uno dei fattori più importanti in grado di condizionare la migrazione dei radionuclidi è rappresentato dal potenziale ossidoriduttivo.

Per studiare appunto la variazione e le tendenze evolutive delle condizioni geochimiche delle argille, al contatto fra ambienti ossidanti e riducenti, sono state espletate una serie di indagini geologiche, mineralogiche, sedimentologiche e geochimiche in una cava nei pressi di Orte. Qui affiora infatti una serie argillosa plio-pleistocenica interstratificata con livelli sabbiosi e ricoperta da banchi sabbiosi ossidati. La sequenza sedimentaria corrisponde ad un ambiente deltizio o quasi-deltizio. La serie è attraversata da due faglie normali principali, cui sono associate faglie minori e fratture.

Le indagini geochimiche di cui si riferisce nel presente lavoro, sono state condotte sull'intera serie e, con maggior dettaglio, nella sua parte superiore, al limite fra le argille e le sabbie ossidate. Le analisi sono state condotte sia per gli elementi maggiori che per quelli minori ed in tracce.

Per avere delle indicazioni, sia pure indirette, sui valori dell'Eh nei differenti livelli, sono stati misurati i rapporti $\text{Fe}^{2+}/\text{Fe}^{3+}$ e $\text{Mn}^{2+}/\text{Mn}^{3+}$: i campioni provenienti da livelli limo-argillosi mostrano un rapporto $\text{Fe}^{2+}/\text{Fe}^{3+}$ più alto rispetto a quelli misurati su materiali sabbiosi e sabbioso-limosi.

Vengono evidenziate alcune correlazioni fra elementi maggiori, minori ed in traccia, nonché la loro distribuzione nella roccia «in toto» e nelle differenti frazioni granulometriche, anche in relazione alla composizione mineralogica dei materiali.

Parole chiave: geochimica, rifiuti radioattivi, serie argillosa Plio-Pleistocenica, elementi in traccia.

Introduction

As a part of the ENEA research programme for radioactive waste disposal in the geological formations, a series of studies coordinated by the Environmental Geology Laboratory, focussed on the possibility offered by clay formation in Italy, are in progress (GERA et al., 1975; ANSELMi et al., 1981; BRONDI, 1984; CHAPMAN, 1985). A correct approach to such a problem implies a thorough knowledge of the geological framework of such formations. Accordingly it is mandatory to implement a basic investigation on their geology, paleogeography, hydrology, mineralogy, geochemistry and geotechnical characteristics (ANTONIOLI and BOCCOLA, 1983; ANTONIOLI and LENZI, 1984; LEONE et al., 1984; FONTANIVE et al., 1985).

In particular, the physico-chemical characters of the geological formations have to be considered as the main factors conditioning the migration of the radionuclides within the geosphere. With the aim of evaluating such characters as well as their evolutive trend within clay formations, detailed information have to be acquired on the processes occurring at the boundary between reduced and oxidized environments.

Among various clay formations, the Orte quarry suite has been chosen for a training cooperative work, as it possesses an optimal situation, whereby a clayey material sequence is interbedded with more or less sandy layers, and it is cut by two principal normal faults, associated with minor fractures (FAREBEGOLI, 1983), ensuring enough circulation for aqueous solutions.

From the geochemical point of view, the presence of sandy layers (apparently oxidized)

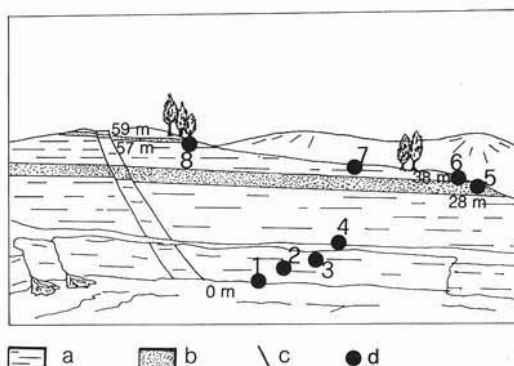


Fig. 1. — Cross section of the Orte quarry outcrop: a = clayey and silty rocks; b = sandy layer; c = fault; d = sampling points.

interbedded with clayey horizons (apparently unoxidized), gives the opportunity to study the distribution and the behaviour of major and trace elements in different environments. A trial was also made to record information on the redox character of the environments, by measuring the $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Mn}^{2+}/\text{Mn}^{3+}$ ratios.

Sampling

Sampling of the Orte series was aimed at obtaining general information on the variations of lithological, mineralogical and geochemical characteristics along the series, and at checking the behaviour of the clay material in relation to the redox processes occurring at the boundary between the apparently oxidized sandy layers and the apparently unoxidized clay layers. It can be then confirmed that the geochemical characters of a thin clay layer can be preserved, even if it is interbedded with oxidized sands.

From the front of the Orte quarry outcrop, section of which is shown in fig. 1, a set of samples (numbered 1 to 8) was selected as the most representative ones of the series. A second set was sampled in more detail within a sandy layer (n. 5 of the first set), which appears to be oxidized (fig. 2). Some thin lenticular pelitic layers are also present in it, with a thickness of a few centimeters; their grey colour is expected to be related to reducing conditions.

Samples n. 6A and 6B are two sandy layers respectively on the bottom and on the top of a clay layer (n. 6).

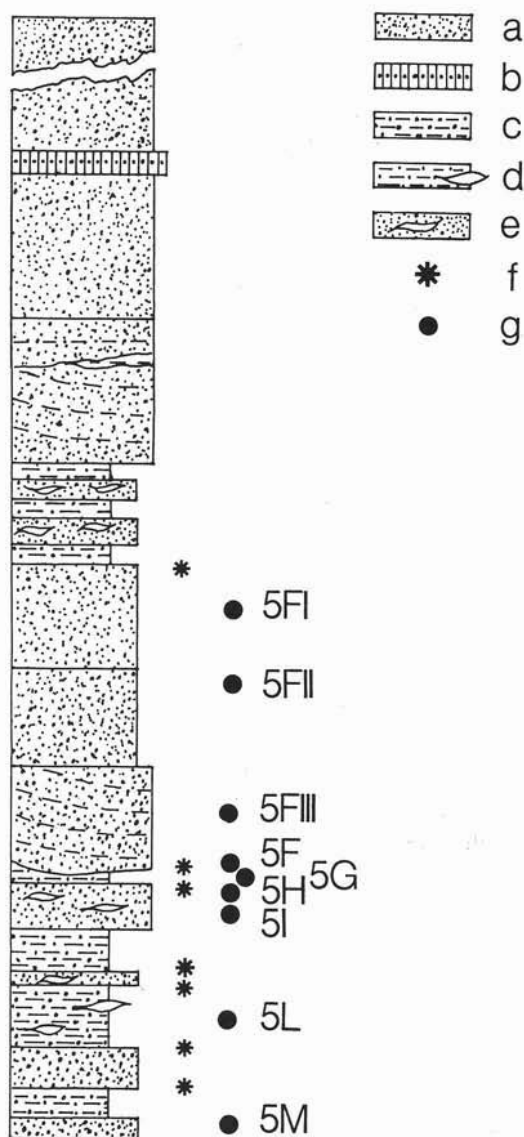


Fig. 2. — Detail of sampling within the sandy layer: *a* = sand; *b* = marl; *c* = sandy silt; *d* = lenticular stratification; *e* = stratified flaser; *f* = iron oxides hard-ground; *g* = sampling points.

Experimental procedures

The determination of the grain-size characteristics of the materials were preceded by dispersion with sodium esametaphosphate (0.025 %); then the sample was wet-sieved at 0.063 mm and weighed. The fraction < 0.063 mm was analyzed by sedigraph. The mineralogical composition was studied

on the whole rock and the grain-size fraction < 0.5 μm by XRD. The identification of clay minerals was performed treating the sample with ethylen glycol and heating at 550° C.

Chemical analyses were performed as follows:

- total carbonates by CO_2 absorption on sodium asbestos after hot concentrated H_3PO_4 attack;
- silica by ICP after fusion by Na_2O_2 ;
- Na, K, Ca, Mg, Al, and total Fe by ICP and/or AAS after dissolution by $\text{HF} + \text{HClO}_4 + \text{HNO}_3$;
- Sr, Rb, Zn, Mn, Cr, and Ti by XRF;
- B by Optical Emission Spectrography (Be as internal standard);
- Cu, Zn, Cr, Ni and Mn by AAS;
- Pb, Cd, Co, V, As, and Mo by GFAAS;
- U by fluorimetry after fusion by Na_2O_2 and ion-exchange separation;
- $\text{Fe}^{2+}/\text{Fe}^{3+}$ by spectrophotometry (α -adi-piridile method) after dissolution in PTFE sealed container by $\text{HF} + \text{H}_2\text{SO}_4$;
- $\text{Mn}^{2+}/\text{Mn}^{4+}$ by AAS after differential dissolution for reduced (Mn^{2+}) and easily reducible (Mn^{4+}) forms by $(\text{NH}_4)\text{COO}-\text{CH}_3 + \text{CH}_3\text{COOH}$ (pH = 5) and by $(\text{NH}_4)\text{COO}-\text{CH}_3 + \text{CH}_3\text{COOH} + \text{NH}_2\text{OH}\cdot\text{HCl}$;
- U, Th and Ra by γ -spectrometry.

Results and discussion

Lithology

In table 1 the data related to the major, trace elements, carbonates content and grain-size distribution are reported. The distribution of samples according to their grain-size composition (fig. 3) implies that they can be roughly classified as clayey-silt, sandy-silt and sand; the detailed classification is as follows (PETTIJOHN, 1975):

Sand: samples n. 5, 5FI, 5FII, 5FIII, 5I and 5M.

Silty-sand: sample n. 6A.

Sandy-silt: samples n. 5H and 5L.

Clayey-silt: samples n. 1, 2, 3, 4, 7, 8, 5G, and 6B.

Silty-clay: sample n. 6.

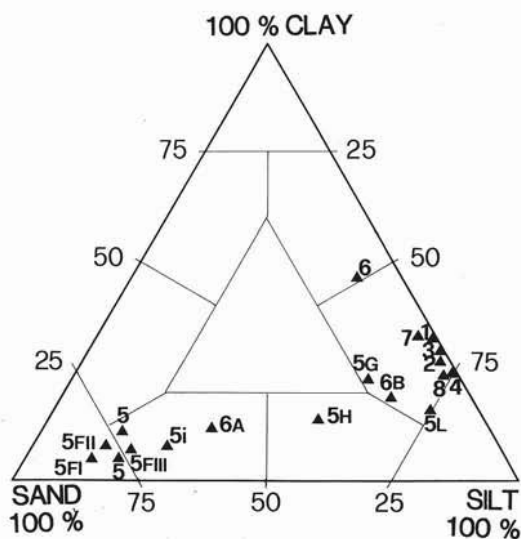


Fig. 3. — Grain size composition of the samples.

It is worthwhile mentioning, however, that within the so-called « silt » fraction (63μ to 2μ), the fine fraction (20μ to 2μ) is clearly prevailing.

The carbonates content generally falls in the 12% - 30% range, with the exception of sample n. 6 that shows a CaCO_3 content of about 3%. It is evident that the carbonate occurs either as fragments of shells and microforaminifera, or finely dispersed in the matrix of the rock.

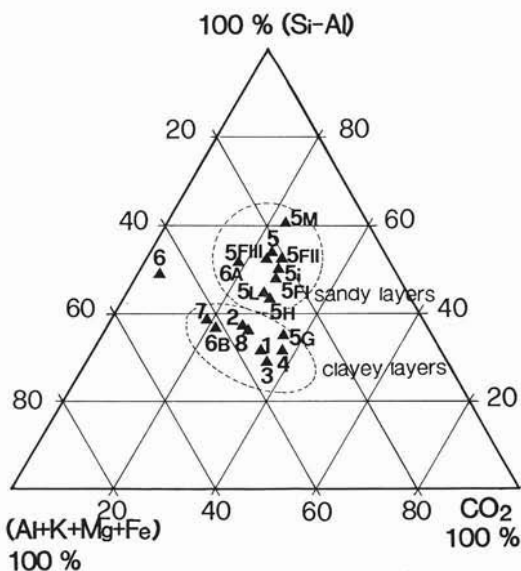


Fig. 4. — Distribution of samples according to their general chemistry.

In the whole rock, quartz and subordinate feldspars are present as detrital minerals; the clay minerals are illite, kaolinite, chlorite and/or montmorillonite. The fine clay fraction is essentially composed of montmorillonite, illite and kaolinite.

Geochemistry

An exhaustive definition of the geochemical parameters of the sequence is an

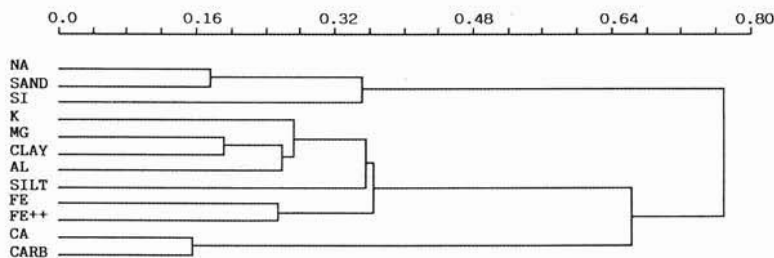


Fig. 5. — Dendrogram showing the relationships between the concentration of major elements and the grain-size of the rocks.

Mineralogy

Mineral identification was performed by XRD both on whole rock samples and fine clay fractions ($\varnothing < 0.5 \mu$) before and after removal of carbonates by 2% CH_3COOH .

essential tool for a better understanding of the geochemical processes that have been conditioning the behaviour of the elements in the Orte series.

In line with this trend of thought, as the

TABLE 1
Chemical and grain size data of the samples

CAMP	NA	K	CA	MG	AL	SI	FE	FE+2	CU	PB	ZN	CO	CR	NI	CO	V	
1	59-2	18-1	10-0	17-1	55-1	17-0	36-1	20-1	33-0	24-0	93-0	25-2	13+1	85-0	14-0	75-0	
2	63-2	18-1	97-1	18-1	62-1	19-0	32-1	20-1	35-0	19-0	89-0	26-2	11+1	82-0	12-0	65-0	
3	49-2	18-1	11-0	19-1	62-1	17-0	31-1	19-1	32-0	23-0	90-0	16-2	13+1	72-0	13-0	77-0	
4	57-2	16-1	13-0	17-1	58-1	18-0	31-1	20-1	30-0	18-0	80-0	30-2	11+1	65-0	12-0	65-0	
5	11-1	15-1	97-1	92-2	40-1	24-0	19-1	58-2	12-0	19-0	48-0	20-2	65-0	42-0	14-0	31-0	
6	55-2	25-1	12-1	20-1	70-1	23-0	37-1	12-1	37-0	23-0	11+1	18-2	15+1	85-0	87-1	10+1	
7	52-2	16-1	12-0	18-1	58-1	17-0	30-1	16-1	27-0	23-0	86+0	18-2	10+1	62-0	12-0	66-0	
8	59-2	17-1	12-0	18-1	60-1	19-0	32-1	20-1	30-0	21-0	85+0	17-2	11+1	70-0	13-0	65-0	
5F1	11-1	12-1	81-1	66-2	48-1	21-0	15-1	40-2	90-1	18-0	49-0	12-2	56-0	29-0	17-0	39-0	
5F2	11-1	12-1	89-1	60-2	43-1	25-0	20-1	50-2	82-1	19-0	37-0	13-2	63-0	32-0	17-0	46-0	
5F3	10-1	13-1	88-1	75-2	49-1	25-0	16-1	50-2	12-0	16-0	49-0	11-2	64-0	35-0	15-0	42-0	
5G	41-2	12-1	14-0	13-1	53-1	18-0	34-1	93-2	25-0	16-0	61-0	22-2	79-0	66-0	16-0	12+1	
5H	81-2	13-1	97-1	12-1	57-1	22-0	21-1	81-2	23-0	18-0	37-0	12-2	92-0	35-0	16-0	65-0	
5I	99-2	11-1	10-0	80-2	48-1	24-0	18-1	98-2	12-0	17-0	55-0	90-3	62-0	41-0	14-0	43-0	
5L	47-2	13-1	79-1	12-1	54-1	21-0	22-1	12-1	27-0	22-0	67-0	13-2	96-0	76-0	19-0	72-0	
5M	10-1	11-1	11-0	74-2	44-1	34-0	17-1	11-1	11-0	21-0	54-0	80-3	61-0	43-0	14-0	39-0	
6A	88-2	16-1	60-1	80-2	52-1	23-0	24-1	92-2	14-0	22-0	52-0	75-3	78-0	61-0	15-0	67-0	
6B	42-2	17-1	69-1	10-1	59-1	19-0	62-1	32-1	29-0	21-0	83-0	80-3	13+1	74-0	15-0	12+1	
CAMP	MN	MN+2*	MN**	AS	MO	U	TH	RA	CAC03	SR	RB	TI	B	504	SAND	SILT	CLAY
1	65+1	32+1	43+1	70-1	35-2	31-1	88-1	70-8	27-0	34+1	16+1	28+2	73+0	17-2	01.1	67.2	31.6
2	75+1	37+1	44+1	70-1	40-2	36-1	83-1	84-8	24-0	34+1	16+1	28+2	65+0	23-2	01.5	71.9	26.6
3	80+1	33+1	44+1	70-1	35-2	34-1	10-0	79-8	27-0	48+1	18+1	27+2	87+0	11-2	00.2	69.8	29.9
4	80+1	36+1	44+1	60-1	35-2	32-1	73-1	69-8	30-0	42+1	15+1	24+2	60+0	84-3	01.3	75.0	23.7
5	50+1	26+1	31+1	65-1	45-2	25-1	56-1	70-8	21-0	33+1	11+1	15+2	26+0	11-1	72.7	15.8	10.1
6	25+1	50-0	50-0	13-0	37-1	42-1	13-0	79-8	29-1	11+1	28+1	42+2	12+1	74-2	09.1	44.5	46.3
7	55+1	38+1	42+1	65-1	75-2	26-1	78-1	70-8	33-0	41+1	15+1	25+2	66+0	16-2	03.9	62.4	33.6
8	67+1	39+1	48+1	70-1	40-2	23-1	10-0	85-8	23-0	29+1	14+1	30+2	60+0	13-2	03.2	72.6	24.2
5F1	50+1	25+1	41+1	30-1	25-2	19-1	50-1	58-8	21-0	28+1	93+0	15+2	24+0	19-3	82.4	12.5	05.1
5F2	60+1	29+1	45+1	23-1	31-2	22-1	50-1	65-8	24-0	29+1	83+0	16+2	36+0	26-3	78.6	14.1	07.3
5F3	53+1	26+1	41+1	29-1	35-2	16-1	55-1	62-8	22-0	29+1	10+1	18+2	48+0	31-3	76.7	17.0	06.3
5G	71+1	25+1	41+1	60-1	25-2	64-1	72-1	11-7	34-0	44+1	11+1	21+2	34+0	55-3	18.5	57.8	23.6
5H	49+1	23+1	36+1	51-1	32-2	32-1	76-1	93-8	24-0	30+1	12+1	25+2	60+0	43-3	33.3	53.3	13.3
5I	64+1	25+1	51+1	29-1	35-2	24-1	61-1	76-8	24-0	30+1	93+0	19+2	41+0	26-3	65.3	27.0	07.6
5L	45+1	23+1	41+1	81-1	41-2	78-1	38-1	72-8	22-0	31+1	13+1	27+2	44+0	17-3	09.7	74.1	16.2
5M	59+1	25+1	46+1	30-1	45-2	25-1	60-1	93-8	26-0	31+1	88+0	18+2	32+0	29-2	74.1	18.9	07.0
6A	35+1	12+1	20+1	66-1	30-2	29-1	63-1	86-8	15-0	29+1	12+1	21+2	52+0	12-1	55.3	32.6	12.1
6B	95+1	25+1	50+1	77-1	25-2	39-1	89-1	11-7	18-0	25+1	13+1	30+2	48+0	26-2	16.0	64.7	19.3

Na, K, Ca, Mg, Al, Si, Fe, Fe²⁺, CaCO₃, SO₄, in %; Ra in $\mu\text{Ci/g}$ and other elements in ppm (the second figure is the power of 10); Sand, Silt, and Clay in %; Mn = total Mn; Mn²⁺ = soluble reduced Mn; Mn²⁺ = total soluble Mn.

main objective of the actual research is to unravel the elements migration connected with the environmental redox conditions, information on the partition between residual, authigenic and adsorbed elements were sought through monitoring the abundance of several major, minor and trace elements in the whole rock as well as in the different grain-size fractions.

Whole rock

The major constituents of the samples are shown in table 1 and the correlations between chemical and lithological compositions are displayed in the triangular diagram of fig. 4, characterized by two clusters of points, the first one representing samples n. 1, 2, 3, 4, 7, 8, 5G and 6B (clayey-silt) and the second one samples n. 5, 5F1, 5F2, 5F3, 5I, 5L, 5M and 6A (silty-sand

and sandy-silt). The chemical parameters have been selected in order to show the consistency of the chemistry with the lithology

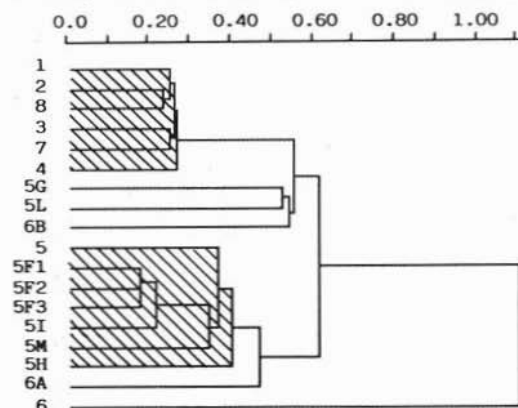


Fig. 6. — Dendrogram showing the clustering of samples according to their grain-size and major elements composition (see text).

($r = -0.76$) and K ($r = -0.52$). Such a behaviour can be attributed to the presence of Na-bearing feldspars in the sand fraction, as it was shown by XRD.

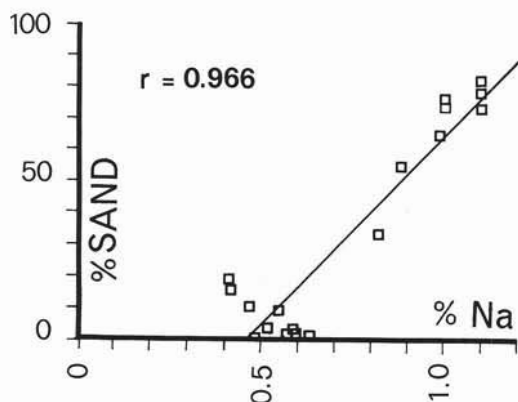


Fig. 7. — Na-sand correlation.

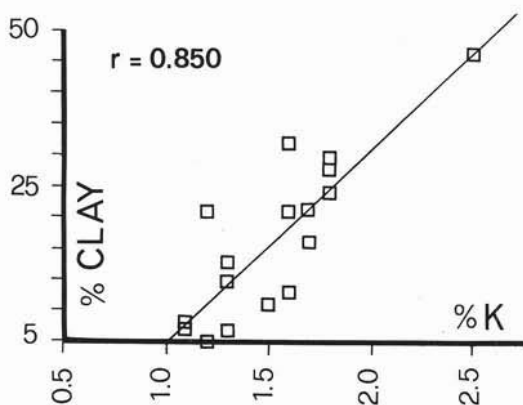


Fig. 8. — K-clay correlation.

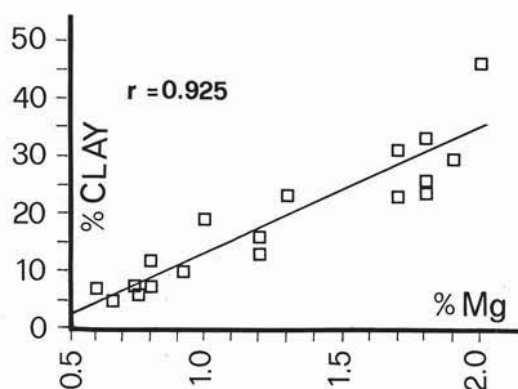


Fig. 9. — Mg-clay correlation.

TABLE 4

Manganese content (ppm) in treated and untreated samples referred to certain different particle sizes

SAMPLES	UNTREATED SAMPLES				SAMPLES TREATED WITH ACETIC ACID			
	W.R.	20-2 μ	20-5 μ	<0.5 μ	W.R.	20-2 μ	20-5 μ	<0.5 μ
1	650	890	240	130	450	800	200	60
2	750	960	340	150	470	880	280	80
3	800	570	270	160	360	500	330	160
4	800	880	450	190	430	820	220	160
5	500	540	470	290	340	480	n.d.	160
6	250	440	330	120	260	380	270	50
7	550	730	210	120	320	660	180	72
8	675	930	610	210	430	550	510	170
5 F I	504	388	347	73	95	273	265	155
5 F II	630	689	654	327	191	534	574	321
5 F III	548	302	229	110	112	226	179	79
5 G	581	364	48	30	97	103	59	30
5 H	476	198	73	30	133	177	89	30
5 I	689	356	325	116	180	390	332	85
5 L	496	197	73	35	147	174	112	30
5 M	621	455	387	280	173	320	335	243
6 A	337	417	244	106	167	268	242	71
6 B	927	800	196	108	356	264	407	331

TABLE 5

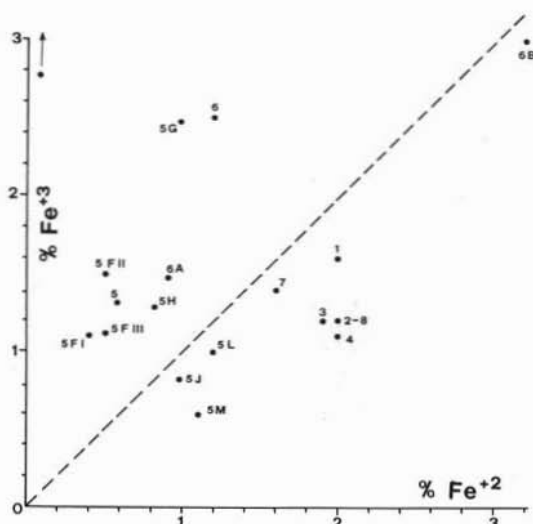
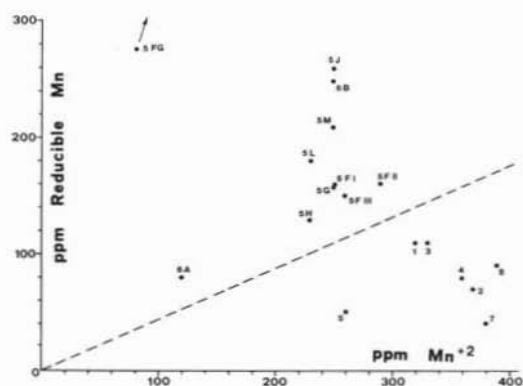
Rubidium content (ppm) in treated and untreated samples referred to certain different particle sizes

SAMPLES	UNTREATED SAMPLES				SAMPLES TREATED WITH ACETIC ACID			
	W.R.	20-2 μ	20-5 μ	<0.5 μ	W.R.	20-2 μ	20-5 μ	<0.5 μ
1	164	151	229	234	214	191	259	330
2	160	141	236	244	205	163	303	287
3	180	170	262	266	231	189	260	345
4	147	108	258	281	196	123	294	312
5	115	172	211	211	133	192	n.d.	269
6	278	193	307	316	275	197	328	224
7	153	102	268	271	210	131	290	311
8	138	99	230	274	194	79	256	302
5 F I	93	189	221	308	109	155	193	241
5 F II	83	158	206	259	109	135	179	190
5 F III	101	185	232	270	118	172	199	279
5 G	114	149	265	237	159	161	248	239
5 H	121	163	234	273	136	165	223	235
5 I	93	168	233	254	116	160	195	226
5 L	133	162	253	276	161	146	219	219
5 M	88	174	227	254	104	146	196	205
6 A	123	152	270	293	134	135	267	275
6 B	134	161	258	285	177	170	249	226

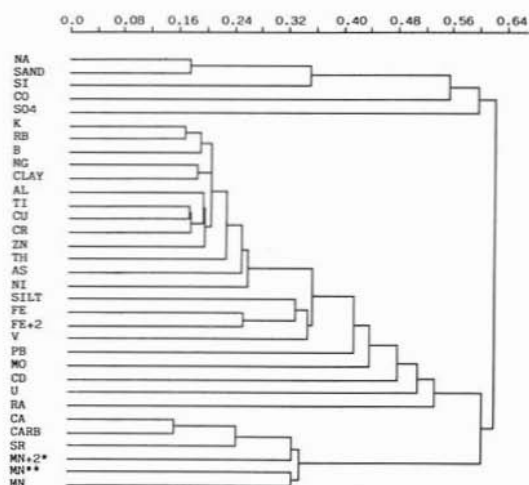
TABLE 6

Zinc content (ppm) in treated and untreated samples referred to certain different particle sizes

SAMPLES	UNTREATED SAMPLES				SAMPLES TREATED WITH ACETIC ACID			
	W.R.	20-2 μ	20-5 μ	<0.5 μ	W.R.	20-2 μ	20-5 μ	<0.5 μ
1	90	86	75	57	228	157	107	92
2	99	101	130	82	206	119	239	93
3	99	83	110	111	179	115	223	164
4	91	89	175	129	177	121	150	168
5	51	118	181	120	128	172	n.d.	186
6	123	83	158	82	194	103	182	49
7	89	60	126	73	181	93	150	100
8	67	78	152	109	153	45	143	100
5 F I	37	145	266	337	34	119	216	204
5 F II	30	119	234	198	32	111	197	110
5 F III	41	117	235	224	39	122	170	169
5 G	42	69	91	65	51	69	104	73
5 H	55	75	157	143	52	87	133	83
5 I	39	126	253	206	39	87	173	146
5 L	67	68	96	93	57	56	53	66
5 M	35	132	215	205	34	97	182	126
6 A	47	77	140	98	35	60	173	90
6 B	63	89	109	92	66	66	131	101

Fig. 10. — Fe^{+2} - Fe^{+3} correlation.Fig. 11. — Mn^{+2} -Reducible Mn correlation.

- Potassium is positively correlated with clay ($r = 0.85$; fig. 8), Mg ($r = 0.75$), Fe^{2+} ($r = 0.50$), Fe_{tot} ($r = 0.58$) and Al ($r = 0.79$). This seems to support the assumption that this element is connected with clay minerals, illite and also chlorite. On the contrary, it appears to be negatively correlated with the sandy fraction ($r = -0.63$), probably due to both the low content and the irregular distribution of feldspars in this fraction.
- Calcium is essentially related to carbonates ($r = 0.81$) whereas no correlation is shown with Mg ($r = 0.10$).
- Magnesium shows a highly positive correlation with clay ($r = 0.93$; fig. 9), silt

Fig. 12. — Dendrogram showing the relationships among all the measured parameters. $\text{MN} + 2^*$ = soluble reduced Mn; MN^{**} = total soluble Mn; MN = total Mn.

($r = 0.80$) and Al ($r = 0.84$) but a negative correlation with sand ($r = -0.91$) and Si ($r = -0.65$).

- Aluminum is essentially associated with clay minerals (the correlation coefficient between Al and clay fraction is $r = 0.86$), as it also emerges from the above mentioned correlations.
- Total iron shows quite a high positive correlation with reduced iron ($r = 0.86$). However their correlations with K, Al, and Mg, assumed to be characteristic elements of the clay fraction, are significant but not as high as the correlations among these three elements. This observation is enhanced by the presence of iron not only in clay minerals but also in sulphides, oxides, and hydroxides. In sample n. 5FG, for example, the Fe excess is undoubtedly related to iron hydro- and/or oxides, as determined by XRD.

Further information about the iron distribution can be obtained from table 3 where the iron content is shown for different grain-size fractions both from acetic acid leached and untreated samples. For the whole rock data the higher iron percentages in the leached samples are due to the dissolution of no iron bearing carbonates, whereas no

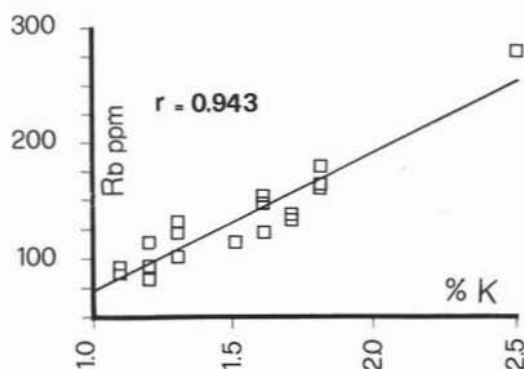


Fig. 13. — K-Rb correlation.

significant differences appear for iron distribution in the fractions.

Oxidation state of iron and manganese

The post-depositional variations of the redox potential can be conveniently studied by two suitable parameters, the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio, and the ratio between Mn^{2+} and that fraction of manganese, found in reducible conditions (Mn^{3+} , Mn^{4+}) (hereinafter: Mn^{4+}). Accordingly, the total content of reduced and oxidized forms leads to meaningful results when different samples of similar mineralogical composition are compared.

It is further accepted that the values of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Mn}^{2+}/\text{Mn}^{4+}$ ratios depend upon: 1) the composition of the primary minerals, 11) the possible variation of the ratios within some of the primary minerals due to the change of the Eh conditions, and 111) the presence of new, secondary minerals formed during the post-depositional evolution of the rock.

Iron

In fig. 10 a plot of total Fe^{2+} versus total Fe^{3+} is presented (referred to the whole rock). The samples of the clayey-silt layers show a high $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio, in good accord with the assumption that a postdepositional oxidation is hard to occur for the low permeability and buffering capacity of clayey-silt materials.

In sands and silty-sands the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios are lower than those of the previous group: this is partially due to the free cir-

culatation of oxygenated water, possibly leading to the partial oxidation of the pre-existing Fe^{2+} , and to the formation of iron oxides and/or hydroxides. Nevertheless, in some sands or silts the oxidation of iron is not so evident, their $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios being similar to those shown by the clayey-silts. Despite its lower permeability, sample n. 5G exhibits a low $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio, but a very high total iron content; it is a very thin (2-4 cm) silty layer, underlying an iron oxide hard-ground ($\text{Fe}_{\text{tot}} \approx 30\%$). In fact it has not been possible to pick-up a sample with no contamination from the hardground.

Manganese

Although manganese has an affinity with carbonates, as exemplified by the correlation coefficient ($r = 0.61$), this affinity is also valid for other minerals in which it can be present in different oxidation forms. From table 4, where the distribution of manganese in different grain-size fractions is shown, the whole rock values for the acetic acid leached and the untreated samples confirm that part of manganese is contained in the carbonate fraction. On the other hand the higher Mn content in the 20-2 μ fraction is explained if manganese is assumed to be also present as finely dispersed oxides enriched in such fraction.

As far as the oxidation state of manganese is concerned, (referred to the easily soluble fraction), the results are presented in fig. 11 where the clayey-silt samples exhibit the

TABLE 7

Boron content (ppm) in treated and untreated samples referred to certain different particle sizes

SAMPLES	UNTREATED SAMPLES				SAMPLES TREATED WITH ACETIC ACID			
	W.R.	20-2 μ	20-5 μ	<0.5 μ	W.R.	20-2 μ	20-5 μ	<0.5 μ
1	73	50	152	97	100	78	173	170
2	68	82	102	120	95	70	110	178
3	87	80	100	92	103	58	115	175
4	60	36	75	92	100	50	100	95
5	26	50	73	168	44	65	132	175
6	118	60	104	160	115	80	70	137
7	66	34	140	160	87	48	177	227
8	60	36	66	90	73	44	78	173
5 F I	24	60	105	125	39	95	81	n.d.
5 F II	36	68	70	n.d.	44	70	87	118
5 F III	48	183	82	n.d.	66	154	113	138
5 G	34	70	134	160	70	76	124	115
5 H	60	68	100	n.d.	68	53	82	87
5 I	41	68	106	n.d.	60	63	138	113
5 L	44	100	93	104	70	82	148	124
5 M	32	46	138	n.d.	34	36	104	103
6 A	52	68	140	104	60	58	110	138
6 B	48	60	118	120	60	53	124	90

TABLE 8

Titanium content (ppm) in treated and untreated samples referred to certain different particle sizes

SAMPLES	UNTREATED SAMPLES				SAMPLES TREATED WITH ACETIC ACID			
	W.R.	20.2 μ	20.5 μ	<0.5 μ	W.R.	20.2 μ	20.5 μ	<0.5 μ
1	2800	4687	6423	3704	4995	4409	6390	3931
2	2816	3559	6371	3580	4970	3646	6252	3503
3	2716	5165	6398	3822	5392	4778	5632	3567
4	2453	2495	5495	3438	4958	2531	6116	3166
5	1531	5634	6433	3742	3207	5631	n.d.	3579
6	4230	6426	8037	3379	5406	5687	7393	3171
7	2506	2825	6300	3526	5040	2605	5515	3197
8	2965	3131	5757	3905	4912	1081	5113	3132
5 F I	1518	6073	5471	2824	2221	4669	5320	3424
5 F II	1593	6390	5682	3450	2444	4614	5333	3891
5 F III	1801	5784	5908	3664	2717	4771	5674	3612
5 G	2120	4370	5583	3682	4510	4546	5590	3595
5 H	2498	5482	5578	3755	3990	4656	6080	3028
5 I	1857	5687	5696	3570	2962	5546	6282	3854
5 L	2718	5246	5811	4112	4434	4252	6923	4021
5 M	1784	5875	6704	3380	3045	5229	5889	3317
6 A	2101	5307	6490	3098	2988	4163	6456	3276
6 B	3000	5030	6085	3746	4565	4700	6797	4331

TABLE 9

Strontium content (ppm) in treated and untreated samples referred to certain different particle sizes

SAMPLES	UNTREATED SAMPLES				SAMPLES TREATED WITH ACETIC ACID			
	W.R.	20.2 μ	20.5 μ	<0.5 μ	W.R.	20.2 μ	20.5 μ	<0.5 μ
1	341	171	247	85	154	159	270	77
2	339	238	219	101	136	222	272	117
3	476	120	334	186	182	118	189	219
4	423	400	235	127	108	406	348	127
5	326	70	71	58	101	74	n.d.	82
6	115	63	79	42	72	57	83	12
7	407	341	124	96	100	367	130	90
8	290	331	355	177	145	307	323	186
5 F I	277	82	106	132	69	73	99	113
5 F II	288	68	96	102	71	68	100	95
5 F III	287	73	98	98	68	71	83	83
5 G	445	157	79	64	59	65	93	64
5 H	296	68	64	69	61	68	74	55
5 I	300	64	73	60	64	63	75	90
5 L	311	62	76	78	60	59	68	53
5 M	312	75	91	86	59	70	79	68
6 A	288	60	73	64	63	66	77	49
6 B	249	64	90	68	68	61	96	77

highest ratio between Mn^{2+} and reducible manganese, in agreement with the observations made on the Fe^{2+}/Fe^{3+} ratios. The sandy, silty-sandy and silty samples show however more scattered and lower ratios. Sample n. 5 (sand) has a Mn^{2+} content similar to that averaged by the other sands, but a much lower content of reducible manganese; this means that the amount of oxidized manganese compounds in this levels is low, as specific pH-Eh conditions may have only allowed the oxidation of iron (GARRELS and CHRIST, 1965).

Trace elements

Their contents and their correlation coefficients are shown in table 1 and table 2 respectively.

Owing to the large number of parameters here considered, the dendrogram appears the most appropriate representation (see fig. 12). The following considerations can be made, bearing in mind that correlations are possible, simply because of the relative abundance, in each sample, of minerals containing different elements.

a) Rb, As, Cu, Zn, B, Ti, Cr, Ni and Th seem to be associated with the clay fraction. Rubidium, in accord with its geochemical behaviour, is strictly associated with potassium ($r = 0.94$, see fig. 13). From table 5, where the Rb contents for different grain-size fraction is reported, it appears that this element is mainly concentrated by adsorption in the fine clay fraction. Arsenic,

copper, and zinc in sedimentary rocks are mainly related to iron oxides and clay minerals (when they are adsorbed), organic matter and sulphides (ONISHI, 1969; WEDEPHOL, 1972, 1974). In the Orte suite they are chiefly related to the clay fraction ($r = 0.83$ for As, $r = 0.89$ for Cu, and $r = 0.91$ for Zn), as it can be seen from the distribution of Zn for different grain-size fractions of table 6. The distribution of boron within the different grain-size fractions (table 7) confirms that this element is strongly enriched by adsorption by the fine fractions (VILLUMSEN and NIELSEN, 1976). The enrichment of Ti (tab. 8) in the fine fractions ($\phi < 2 \mu$) ties well with the results of the cluster analysis, in agreement with the known capability of Ti to be accepted in the structure of many clay minerals. Ni and Cr are strictly correlated ($r = 0.86$); in the dendrogram they fall distant from iron, which is also present in secondary minerals, devoid of Ni and Cr. The association of Th with the clay fraction is in agreement with its capability to be adsorbed by clay minerals (ROGERS and ADAMS, 1969).

b) According to its geochemical behaviour, vanadium shows a good correlation with Fe^{3+} , since it is associated with iron minerals such as oxides and hydroxides. Nevertheless it is worth noting that, although the clayey-silt and the sandy-silt samples average a very similar Fe^{3+} content, the first group shows a higher vanadium content,

probably due to adsorption of vanadium in clay minerals.

c) Strontium is essentially correlated with carbonates ($r = 0.70$), but it is also contained in the not-carbonate fraction (table 9). It appears enriched in the 20-2 μ and 2-0.5 μ fractions, referred to the acetic acid leached samples. The Sr content of the fine silt and clay fractions from sandy samples is lower with respect to the same fractions from clayey samples.

For other trace elements only a few significant correlations can schematically be made, as follows:

1. Co is negatively correlated with clay and elements enriched in clay.
2. Pb is positively correlated with clay and elements enriched in clay.
3. Cd shows a positive correlation with clay, Mg and Cu, and a negative one with Si and sand.
4. Mo shows a negative correlation with carbonates, where it shows a positive correlation with clay.
5. U is negatively correlated with Na. Its positive correlation with V agrees with its general geochemical behaviour.
6. Ra only shows positive correlations with Fe and V.

Conclusions

From the lithological point of view, in agreement with the results of a geologic and paleogeographic study carried out by FARABEGOLI (1984), the sandy materials of the Orte series can be classified as sands, silty-sands or sandy-silts, whereas the clayey layers correspond to clayey-silts or silty-clays.

These rocks, as far as the mineralogy, are

mainly composed of illite and kaolinite associated with chlorite and some montmorillonite. Detrital minerals are present as quartz and subordinate feldspars. The carbonate content is quite high and it is due to calcite (aragonite is present only in sample 6A) as well as shell fragments or microfossiles.

The distribution of major elements is coherent with the lithological and mineralogical characteristics of the rocks and the behaviour of trace elements is related to: clay minerals (Rb, B, Ti, Cu, Cr, Zn, As, Ni, and Th), carbonates (Mn and Sr), and iron minerals (V).

The Fe^{2+}/Fe^{3+} ratio is generally lower in the sands and sandy-silts, than in the clayey-silts, as the circulation of the oxidizing agent is easier in the more permeable rocks, where iron can be precipitated as more or less hydrated oxides. Some exceptions of this may be explained by the variability of the Fe^{2+}/Fe^{3+} ratio in the detrital and syngenetic minerals, that can be able to hide the variations of the same ratio due to redox processes occurring after the deposition.

A confirmation of this is supplied by the state of oxidation of manganese: in the samples n. 5i and 5M (sands) the ratio between reducible and divalent manganese is high, whereas the reduced iron is prevailing over the oxidized. In this case it can be assumed that the Eh value was high enough to oxidate manganese and, therefore, iron; nevertheless, it is possible that iron oxidation did not occur, as iron is strictly bound in detrital mineral structures.

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