

## The «Flysch Rosso» shales from the southern Apennines, Italy. 2. The origin of the colour

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**ABSTRACT.** — Mineralogical and geochemical studies were carried out on red and green shales from the «Flysch Rosso» sediments (southern Apennines, Italy) in order to investigate on the cause(s) of the colour variation.

The two chromatic types show compositional analogies and few differences are relevant, the main consisting in Fe content.

Although the statistical analyses evidenced a slightly significant difference in some chemical parameters indicative of the redox conditions at the water-sediment interface (U, Corg, FeO, V/Cr, U/Th), they, nevertheless, still indicate oxic environments both in red and in green shales. The difference in the organic carbon content is small and cannot be seen as the cause of the chromatic variation.

The origin of the red colour is ascribed mainly to the presence of hematite, which is ubiquitous in the red shales but in a very little amount in a few of the green ones.

Different hematite, feldspars, and kaolinite contents of red and green shales as well as geochemical considerations suggest a detrital hypothesis for Fe-hydroxides and a diagenetic one for the hematite.

**RIASSUNTO.** — Studi a carattere mineralogico e geochimico sono stati svolti sulle argilliti rosse e verdi dei sedimenti appartenenti alla formazione del «Flysch Rosso» (Appennino meridionale, Italia) al fine di comprendere le cause della loro variazione cromatica.

Le due varietà cromatiche delle argilliti esaminate mostrano una analoga composizione tranne alcune differenze, soprattutto per il contenuto del ferro.

Le analisi statistiche evidenziano una differenza, non molto significativa, dei valori di alcuni parametri chimici caratteristici delle condizioni redox all'interfaccia acqua-sedimento (U, Corg, FeO, V/Cr, U/Th); l'ambiente risulta essere ossidante sia per le argilliti rosse e verdi. La differenza del contenuto del carbonio organico è piccola e non può essere considerata la causa della variazione cromatica.

L'origine del colore rosso è principalmente ascrivibile all'ematite, che è sempre presente nelle argilliti rosse mentre è in modeste quantità solo in alcuni campioni delle argilliti verdi.

Differenti contenuti di ematite, feldspati e caolinite delle argilliti rosse e verdi così come le considerazioni geochimiche suggeriscono un'origine detritica per gli idrossidi di ferro ed una diagenetica per l'ematite.

**KEY WORDS:** *Shales, colour, mineralogy, geochemistry, Apennines*

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## INTRODUCTION

The origin of red and green colour in sediments is a very intriguing problem and has been the object of many investigations (see the review compiled by Taylor, 1982 and Mücke, 1994).

The earlier studies showed that the oxidation state of iron is the main cause of the red/green colour of rocks (Tomlison, 1916) and that high values of  $Fe^{3+}/Fe^{2+}$  ratio are characteristic of red beds and low values of green ones. Fine grained sediments may also experience variation in total iron and oxidation ratio because of diagenetical removal of  $Fe^{3+}$ , by aqueous reduction to  $Fe^{2+}$  and dissolution, from an initially all red sequence (e.g., Picard, 1965; Friend, 1966; Thompson, 1975). It is thought that in this process organic carbon may play an important role since it favours the more soluble reduced form of iron. Indeed a discrimination between chromatic types on the basis of  $C_{org} - Fe^{2+}/(Fe^{2+}+Fe^{3+})$  molar ratio has been suggested (Potter *et al.*, 1980). More recently it has also been hypothesised that the red-green colour transition is due to in situ oxidation - reduction of Fe within the crystal lattice of smectite (Lyle, 1983) and a continuous gradient of  $Fe^{2+}/Fe^{3+}$  has been documented in pelagic sediment (König *et al.* 1997). Most authors

believe that the staining pigment of red beds is submicronic and uniformly distributed hematite (see Einsele, 1992) and that it might be detrital in origin (see Boulvain, 1993, for references) as well as precipitated as a consequence of microbial activity (see Pr at *et al.*, 1998, and references therein).

During an investigation regarding mineralogy and geochemistry of «Flyscht Rosso» sediments cropping out in the southern Apennines (Fiore *et al.*, companion paper), it was observed that green and red shales showed some chemical and mineralogical differences. So, in the present paper we discuss some geochemical and mineralogical data reported in the said paper to try to give pieces of information useful to evaluate the current models proposed and to interpret the red and green colours of shales from «Flyscht Rosso» formation.

## SOME REMARKS ON CHEMICAL AND MINERALOGICAL CHARACTERISTICS

As indicated in the previous paragraphs, the analytical data that will be discussed are reported in our previous paper. However, to have a comprehensive picture of the mineralogical and chemical compositions, we

TABLE 1

*Mineralogical composition (average values) of the green and red shales from the «Flyscht Rosso» formation.*

		Bulk					Clay fraction				
		$\Sigma$ Phy	Qtz	Fd	Chl	Hm	I/S	Ill	Ka	Chl	Qtz
Red	$\chi$	72	21	2	1	4	55	10	21	1	14
	$\sigma$	7	6	1	1	1	8	3	8	1	7
	n	15	15	15	15	15	15	15	15	15	15
Green	$\chi$	73	24	2	1	1	55	10	17	2	16
	$\sigma$	8	8	1	1	1	12	5	8	3	9
	n	24	24	24	24	24	24	24	24	24	24

$\Sigma$ Phy: sum of phyllosilicates; Qtz: quartz; Fd: feldspars; Chl: chlorite; Hm: hematite; I/S: interstratified illite- smectite; Ill: illite; Ka: kaolinite;  $\chi$  = mean value;  $\sigma$  = standard deviation; n = number of samples.

calculated their mean values and these are given in Table 1 and Table 2, respectively.

As concerns the mineralogy of the bulk rock and clay fraction (Table 1), the most evident difference existing between the green and the red shales is the content of hematite (bulk rock) and, to a lesser extent, that of kaolinite (clay size fraction). Hematite is ubiquitous in the red shales (up to 7%) whereas it occurs in very few green samples at trace level.

The chemical data (Table 2) reflect, obviously, the different hematite content of the green and red shales and the large difference between  $\text{Fe}_2\text{O}_3$  and FeO content. Also MnO content differs significantly. Moreover, the mean value of cobalt cannot be taken as relevant because of the large variations in its content from sample to sample, as evidenced by the high sigma-value.

Since the presence/absence of organic components may have a bearing on this subject, the content of organic carbon (TOC) has been also determined in 23 samples by LECO combustion infrared detection (detection limits: 0.003%C) including green and red terms. The results (Table 3) show that all the analysed samples contain organic C, even though at low concentration and that contents of the green shales are higher than those of the red ones.

The mean values of mineralogical and chemical data calculated for red and green shales have been compared by the Student *t*-test. The results of the statistical analysis are reported in Table 4. From the inspection of the results it emerges that the most significant differences regard  $\text{Fe}_2\text{O}_3$ , FeO and  $\text{SiO}_2$  contents, Rb concentration, V/Cr and  $\text{Fe}^{2+}/\text{Fe}^{2+}+\text{Fe}^{3+}$  values, and hematite and feldspars abundance all at high level of probability ( $p < 0.01$ ).

#### DISCUSSION AND CONCLUSIONS

Although the statistical analyses evidence a slightly significant difference in organic carbon content of the green and red shales, both fall in

the «red field» of the Potter's *et al.* diagram (fig. 1). Thus  $C_{\text{org}}$  cannot be considered an important factor in controlling the colour change in the studied shales. On the other hand a diagenetic removal of  $\text{Fe}^{3+}$  by reduction to  $\text{Fe}^{2+}$  should be monitored by manganese, an element mobile under similar redox potential (e.g., Turner *et al.*, 1981; Thomson *et al.*, 1993). In other words, green samples should contain lower amounts of Mn than the red one. We, however, actually found quite the opposite to be true.

The existence of a possible change in the redox potential in the red-green colour transition is suggested by the difference in the mean values of U,  $C_{\text{org}}$ , FeO, V/Cr, U/Th. In fig. 2 it appears that some differences exist between red and green shales. Except for one sample, green shales display positive correlation between U/Th and V/Cr ratios and they have higher values of the above ratios when compared with the red shales. Therefore, although these element concentrations and elemental ratios suggest differences in the degree of oxidation, they still nevertheless indicate oxic environments both in red and in green shales.

As previously said, one of the hypotheses suggested to explain the red-green colour transition is an in situ oxidation-reduction of iron present within the crystal lattice of smectite (Lyle, 1983). Since in the studied shales smectite (as component of I/S mixed layers) represents the most abundant phyllosilicate, we checked this hypothesis by correlating the amount of phyllosilicates (Phy) to their iron content ( $\text{Fe}_2\text{O}_3(\text{Phy})$ ). As previously said (Fiore *et al.*, companion paper), this may be estimated by subtracting hematite content from the total iron content, that is  $(\text{Fe}_2\text{O}_3(\text{Phy})) = (\text{Fe}_2\text{O}_3(\text{total})) - (\text{Fe}_2\text{O}_3(\text{hematite}))$  and a positive correlation exists between amount of phyllosilicates (Phy) and their iron content. Such a correlation involves also the green samples with high contents of smectite rich I-S mixed layers and very low contents of FeO. This implies that all the clay minerals, including smectite-rich phase – the most

TABLE 2

*Chemical composition (average values) of the green and red shales from the «Flysch Rosso» formation.*

		SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub> tot	FeO	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	C <sub>org</sub>	LOI
Red	$\chi$	59.73	0.79	16.53	9.05	0.66	8.35	0.06	1.65	0.67	0.75	1.53	0.10	0.05	9.17
	$\sigma$	3.00	0.07	1.49	1.01	0.39	1.06	0.07	0.52	0.35	0.39	0.23	0.05	0.02	2.37
	<i>n</i>	15	15	15	15	14	14	15	15	15	15	15	15	9	15
Green	$\chi$	64.17	0.73	15.73	6.30	1.44	4.82	0.20	1.56	0.52	0.74	1.35	0.07	0.09	8.77
	$\sigma$	3.56	0.10	1.97	1.29	0.95	1.31	0.44	0.25	0.24	0.32	0.30	0.02	0.06	1.67
	<i>n</i>	24	24	24	24	22	24	24	24	24	24	24	24	15	24
		Ba	Ni	Cr	V	Rb	Sr	Y	Zr	Nb	Sc	Co	Th	U	
Red	$\chi$	161.82	79.07	96.60	113.07	89.00	98.60	28.87	18.87	17.27	5.78	20.00	10.29	3.13	
	$\sigma$	56.05	19.15	9.94	19.63	7.80	29.83	5.95	7.05	2.76	0.26	6.28	1.03	2.45	
	<i>n</i>	11	15	15	15	15	15	15	15	15	8	8	7	7	
Green	$\chi$	153.39	110.71	90.00	118.04	78.58	90.04	24.83	15.25	16.71	5.60	55.38	9.87	1.93	
	$\sigma$	29.54	89.34	12.42	18.42	13.14	18.90	6.77	9.64	3.44	0.47	44.01	1.08	1.14	
	<i>n</i>	24	24	24	24	24	24	24	24	24	5	5	6	6	
		La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Red	$\chi$	37.28	81.32	8.99	32.74	6.95	1.48	6.17	0.99	4.77	1.06	2.61	0.40	2.45	0.39
	$\sigma$	5.40	12.75	1.34	5.08	1.49	0.35	1.69	0.25	1.19	0.26	0.60	0.10	0.56	0.09
	<i>n</i>	11	11	11	11	11	11	11	11	11	11	11	11	11	11
Green	$\chi$	36.49	81.40	9.05	33.11	7.17	1.53	6.22	1.08	4.71	1.06	2.60	0.42	2.41	0.38
	$\sigma$	5.58	10.64	1.12	5.48	1.62	0.41	1.91	0.27	1.19	0.26	0.47	0.04	0.41	0.04
	<i>n</i>	10	10	10	10	10	10	10	10	10	10	10	10	10	10

Major elements as percent oxides and trace elements as ppm;  $\chi$  = mean value;  $\sigma$  = standard deviation; *n* = number of samples.

TABLE 3

Total organic carbon for the green and red shales from the «Flysch Rosso» formation.

Sample	Colour	C <sub>org</sub> (%)
CC18	Green	0.03
CC20	Green	0.04
CC21	Green	0.10
CM22	Green	0.06
CM24	Green	0.10
CM26	Green	0.09
CM27	Green	0.08
CM28	Green	0.12
CM30	Green	0.09
CM32	Green	0.08
CM33	Green	0.11
CC11	Red	0.01
CC15	Red	0.03
CC19	Red	0.03
CC24	Red	0.04
CM16	Red	0.06
CM19	Red	0.07
CM23	Red	0.06
CM29	Red	0.09
CM31	Red	0.06

$\bar{x}$  = mean value;  $\sigma$  = standard deviation;  $n$  = number of samples;  $t$  = value of Student  $t$ -test for unpaired values;  $p$  = probability (null hypothesis).

abundant one – should have a very high Fe-oxidation ratio in green and red shales. In addition, the mean values of the iron content of the green and red shales after the subtraction of the hematite iron content are, for all practicable measures, indistinguishable ( $t = 0.602$ ;  $p = 0.553$ ). Thus Lyle's hypothesis, in the studied case, seems not to be viable.

Hematite is ubiquitous in the reddish shales (up to 7 % in weight) but it occurs only in 4 of the 24 greenish samples, and in a very small amount (1%) (Table 1). Therefore it is the presence of this mineral, which has high pigmenting power (e.g., Thompson, 1975; Torrent and Schwertmann, 1987; Einsele, 1992), rather than the oxidation state of iron that controls the red or green colour of the shales.

Hematite might have a detrital origin or might be authigenic. SEM observations showed the presence of both shapeless grains and well crystallised platelets (fig. 3a-c).

A detrital derivation from the residual red soils originated by weathering of carbonates of

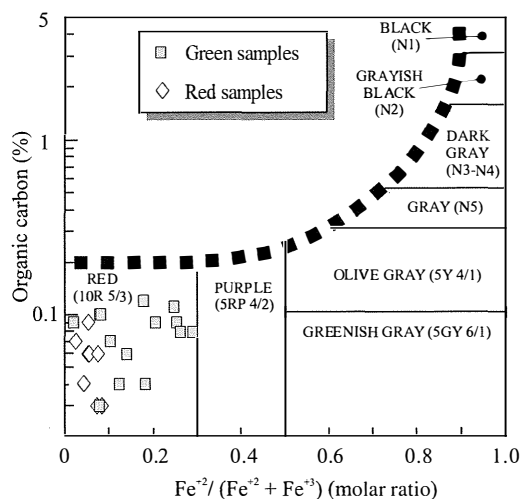


Fig. 1 – Content of organic carbon vs.  $Fe^{2+}/Fe^{2+}+Fe^{3+}$  molar ratio (after Potter *et al.*, 1980) of the «Flysch Rosso» shales. The studied samples plot in the «red» field of the diagram irrespective of their colour.

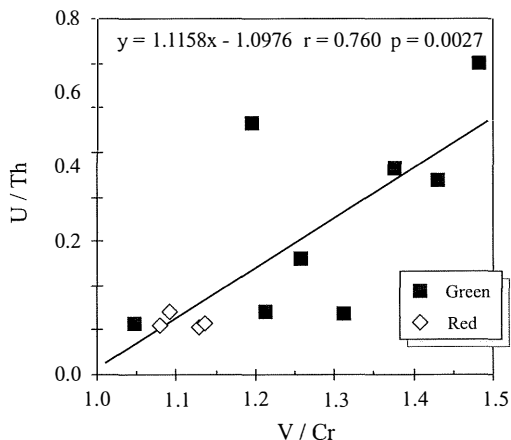


Fig. 2 – A plot of U/Th ratio vs. V/Cr ratio of the «Flysch Rosso» shales. The limited range of variation in reddish shales and the wider variation in the greenish ones, especially for the U/Th content, is apparent.

TABLE 4

Statistical comparison (Student *t*-test, unpaired values) of mean values of selected elements, elemental ratios and minerals in red and green shales from the «Flysch Rosso» formation. Differences with low level of probability ( $p > 0.05$ ) were considered statistically not significant and are not reported. Values of  $p$  lower than 0.01 are considered strongly indicative of a difference between two mean values.

	Green			Red			<i>t</i>	<i>p</i>
	$\chi$	s	<i>n</i>	$\chi$	$\sigma$	<i>n</i>		
SiO <sub>2</sub>	64.17	3.56	24	59.73	3.00	15	4.017	0.0003
TiO <sub>2</sub>	0.73	0.10	24	0.79	0.07	15	2.283	0.0283
P <sub>2</sub> O <sub>5</sub>	0.07	0.02	24	0.10	0.05	15	2.084	0.0442
Fe <sub>2</sub> O <sub>3</sub> (total)	6.30	1.29	24	9.05	1.01	15	6.990	0.0001
Fe <sub>2</sub> O <sub>3</sub>	4.82	1.31	22	8.35	1.06	14	8.456	0.0001
FeO	1.44	0.95	22	0.655	0.39	14	2.974	0.0066
C <sub>org</sub>	0.093	0.06	15	0.05	0.02	9	2.000	0.0580
La	34.97	5.16	14	39.34	4.19	9	2.126	0.0455
Th	9.62	1.05	8	10.84	0.34	5	2.473	0.0309
Rb	78.53	13.16	24	89.03	7.88	15	2.787	0.0083
Fe <sup>2+</sup> /(Fe <sup>2+</sup> +Fe <sup>3+</sup> )	0.17	0.09	16	0.05	0.02	10	4.130	0.0004
Al/Ti	19.20	1.22	24	18.44	0.85	15	2.136	0.0393
V/Cr	1.32	0.14	24	1.17	0.11	15	3.493	0.0013
U/Th	0.35	0.22	8	0.12	0.01	5	2.301	0.0419
Hematite	1.00	0.01	4	3.73	1.44	15	3.723	0.0017
Feldspars	1.70	0.88	23	2.47	1.19	15	2.304	0.0017

the Apulian Platform (see companion paper for geological details) and its concentration in the red shales is ruled out since other signatures such as enrichment of immobile elements (i.e., Al, Ti, Cr, Zr, Sc) are lacking. Statistical comparison of mean values shows in fact that differences in concentrations of immobile elements in greenish and reddish shales are negligible.

A diagenetic origin by dehydration of Fe-hydroxides precursor (e.g., Mücke and Agthe, 1988; Mücke, 1994) might be suggested. Under this hypothesis, Fe-hydroxides in the studied shales might derive from *i*) weathering of source rock(s) and transferred into the sedimentation basin as mineral coating, and concentration in small lens and layers by gravity settling; *ii*) precipitation from sea water after the oxidation of iron within the ocean flooring sediments; or *iii*) precipitation from

pore water when the migrating upward Fe<sup>2+</sup> reached the suitable redox conditions in a sedimentary unit.

Statistical comparison of mineralogical and chemical data reveals some interesting relationships that allow the formulation of a reliable hypothesis. In hematite-bearing samples there exists a positive correlation between hematite and feldspars ( $r = 0.628$ ;  $p = 0.003$ ), and there is also a difference in abundance of Rb in red and green shales ( $t = 2.787$ ;  $p = 0.0083$ ). The high statistical difference of rubidium concentrations in the two chromatic types and the higher content of this element in the reddish shales are not fortuitous, since a linear correlation exists between Rb and Fe<sub>2</sub>O<sub>3</sub> ( $r = 0.524$ ;  $l.d.p. = 0.001$ ) and between Rb and K<sub>2</sub>O ( $r = 0.902$ ;  $p << 0.0001$ ). The statistical difference in the potassium content of reddish and greenish

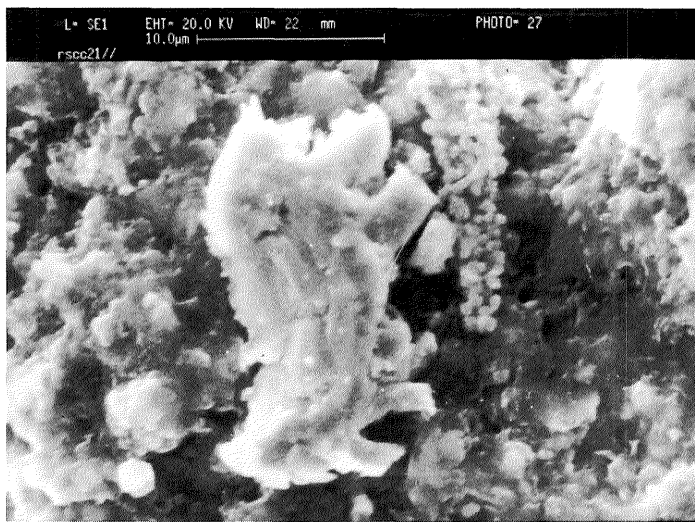
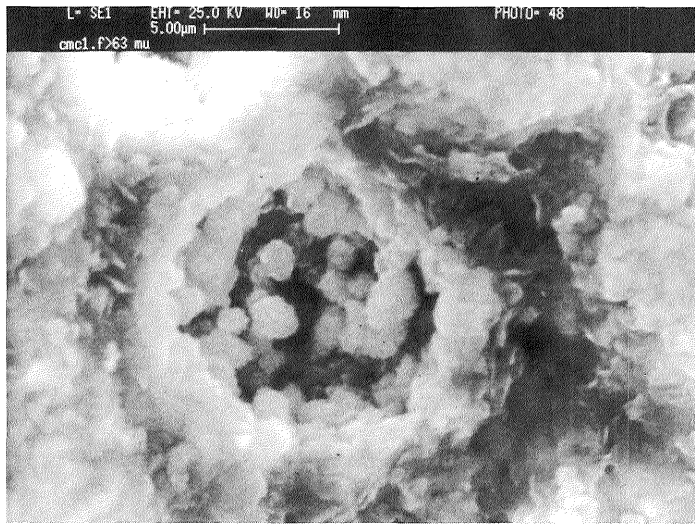


Fig. 3 – SEM micrographs of some Fe-grains (likely hematite) occurred in the «Flysch Rosso» shales.

shales, however, is not high ( $t = 1.952$ ;  $p = 0.0586$ ) most probably because the influence of feldspars on the potassium content is masked by that of the more abundant illite, which quantitatively does not vary from reddish to greenish shales. Since the principal carriers of rubidium are illite and feldspars, as evidenced by the linear correlation ( $r = 0.629$ ,  $p < 0.0001$ ; and  $r = 0.518$ ,  $p = 0.0007$ , respectively), the precursor of hematite might well have the same origin.

It should be stated, however, that the hypothesis of a detrital origin of Fe-hydroxides does not imply that the red and the green shales derived from two lithologically different areas because, had this been the case, there would have been a much more marked difference both in the chemical and the mineralogical compositions. It is most likely that the colour of the shales reflects different degrees of weathering of the same source area. Under this hypothesis, the higher content of kaolinite in red shales is suggestive of more intense alteration.

Other hypotheses regarding the derivation of Fe-hydroxides may well be equally valid and these include seawater precipitation, oxidation-reduction due to organic matter, and precipitation due to biological activity. Yet, even though they may have well played a concomitant role, they cannot explain by themselves the observed mineralogical and chemical differences. For these reasons, we are inclined to the hypothesis of a detrital origin of Fe hydroxides and their diagenetic transformation into hematite.

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