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## 8. Mineralogy and geochemistry

### 8.1 Methods

The following techniques were used for the mineralogical and geochemical studies:

- a X-Ray diffraction. The samples were dried at room temperature. A homogeneous, representative part was ground and sieved to < 270 mesh ASTM (0.053 mm) and then used for the mineralogical study of the whole sample. Another part was used for extraction of the clay fraction. The equipment used was a Philips PW 1710 diffractometer with automatic slit (Department of Mineralogy and Petrology, University of Granada, Spain). The reflecting factors calculated for this equipment and its instrumental conditions on the basis of the data by Schultz (1964) and Barahona (1974) were: powder diffractograms (phyllosilicates, 0.09; quartz, 1.43; calcite, 1.05; feldspars, 1.03), oriented aggregate diffractograms (illite, 1; smectites, 2.80; chlorite, kaolinite, 2.75). The estimated error of the quantitative analysis is 5%.
- b X-Ray fluorescence, neutron activation, inductively coupled plasma and atomic absorption spectrometry. These techniques were used for analyses of major and minor elements and rare-earth elements (REE) at the X-Ray Assay Laboratories in Ontario (Canada).

### 8.2 Results and the anoxic interval of deposition

The mineralogical results are shown in Figure 4, 5, 6 and 19. Table 3 and 4 show the data obtained from the chemical analyses.

The black shale levels in the Valdorbia section are located in the MS Formation, mainly in the upper part of Tenuicostatum Zone. In their description the stratigraphical intervals (s.i.) are those shown on Figure 20, related to the microfacies types. The black shale facies is mineralogically defined by an illite-smectite-quartz-feldspar major association and low contents of calcite and kaolinite. This is particularly characteristic of samples VD-359,8 to VD-375,8 (Fig. 19), especially the 369-359,2 stratigraphic interval.

The illite-smectite association, and to a lesser extent the kaolinite, should be interpreted as an indication of the detrital character of this facies. The same applies to the abundance of quartz and feldspars, the high values of the detrital index ( $D = 0.70-0.90$ ) (Chamley 1989) and the  $Ce/Ce^*$  ratio (0.85-1) (Courtois & Hoffert 1979).

The mineralogical associations of the layers lying above and below the most typical black shale facies are similar. The main difference is in the greater abundance of smectite in the samples from the top of 391,8-369 s.i. in comparison to 204,6-190 s.i. (Fig. 20). We believe this indicates that the anoxic episode is perceptible in Tenuicostatum Zone, at least from level VD-382 up. On the other hand, black shale type facies ceased to be deposited from the beginning of 204,6-190 s.i. (Fig. 20).

From the geochemical point of view, the anoxic facies of Valdorbia is characterized by important anomalies in Ba, V, Cr, Ni, Co, Cu, Zn, As, Sb, and Pb (Tab. 3, Fig. 20). In addition they present higher contents of U (Tab. 3), REE (168-104 ppm in samples VD-368,5 and VD-371 respectively), MnO (up to 0.25%) and TiO<sub>2</sub> (0.41% to 0.86%). This geochemical facies therefore compares closely with that of Gavshin (1991) for Jurass-

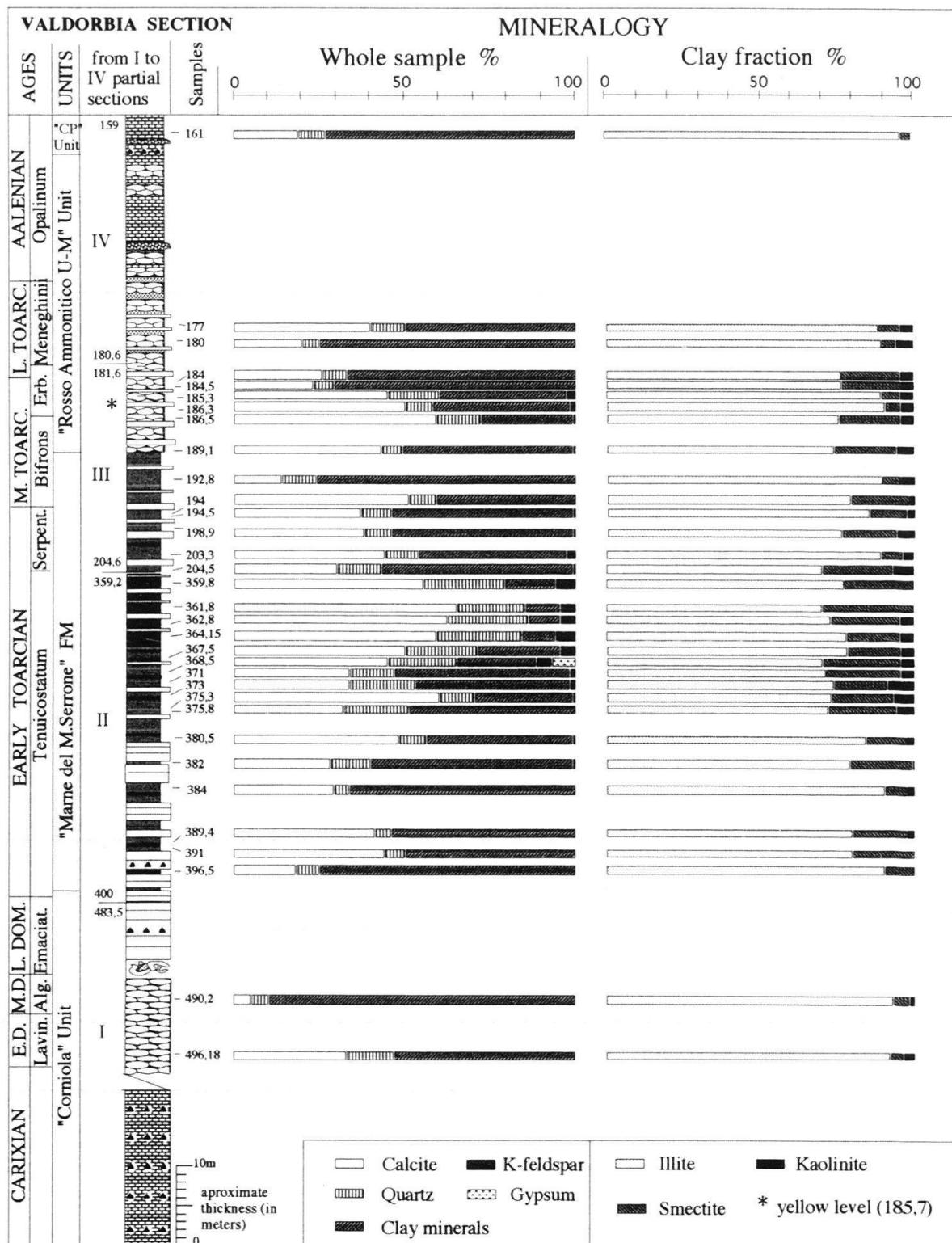


Fig. 19. Mineralogy of the studied samples.

sic black shales. This geochemical anomaly is also detected, although less strongly, down to the underlying VD-382 level.

In view of the mineralogical and geochemical data, we may conclude that the anoxic facies in the Valdorbia section begins within 391,8-369 s.i. (sample VD-382) and includes the interval up to the top of 369-359,2 s.i. (at least up to the sample VD-361,8). The degree of anoxia was not uniform, reaching maximum values in levels VD-364,15 and VD-362,8, where the organic contribution (carbonate content) is lowest. Therefore, since analysis in the field is not always sufficient, the geochemical anomalies described above are a valid chemical-stratigraphic criterion by which to delimit the anoxic levels in the Toarcian of the Apennines (central Italy). Similar anomalies have been described by Ortega-Huertas et al. (1993) for correlatable stratigraphic levels in the Pozzale and Pale Vallone sections.

The mineralogical and geochemical data indicate that these facies were deposited (Fig. 21) in a pelagic environment, in which restricted palaeogeographical subenvironments developed. It seems likely possible that the presence of physiographically subdivided environment encouraged the existence of calm subenvironments in which confined conditions formed with restricted water circulation. This agrees with the positive anomaly in B (Tab. 4), detected in the black shale samples in comparison with the other levels at Valdorbia. According to this model maximum restriction of circulation would have occurred in levels VD-364,15 and VD-362,8. Maximum anoxia conditions also occurred in these levels, according to other mineralogical and geochemical criteria mentioned above. This model also agrees with the values found for the La/Lu ratio (9.90 to 12), which are typical of pelagic environments, as indicated by Ronov et al. (1967). The ternary diagram of V-Cr-Ni, which are elements usually associated with a detrital origin, can be used to study the possible variations in input from the source area. Comparison of the V/Cr ratio in the Valdorbia (1.70), Pozzale (1.69), Monte Serrone (1.51) and Pale Vallone (1.49) sections indicates that the MS Formation as a whole was deposited under the influence of a homogeneous source area.

## 9. Discussion and conclusions

### 9.1 The Lower Toarcian anoxic event

The occurrence of black shales in the Valdorbia Section has been discussed by Baudin et al. (1990), Nocchi et al. (1991) and by Bartolini et al. (1992). These authors consider the laminated, pyrite-rich black sediments as evidence of the extension of the Early Toarcian anoxic event, widespread in the North European Jurassic shelves to the Umbria-Marche basin.

Geochemical, Total Organic Carbon content, micropaleontological data (see Fig. 9 and 5 in Bartolini et al. 1992) and trace fossils show that anoxia reaches the maximum in the upper part of the *Tenuicostatum* Zone, between 369 m and 360 m, with a peak around 364 m. However, the positive geochemical anomalies have revealed that the seafloor was poorly oxygenated in the older part of the *Tenuicostatum* Zone as well, at least from the 382 m level (Tab. 4). These data confirm that the abundance of small *Eoguttulina*'s is indicative of a restricted and poorly ventilated environment but these forms become slightly less able to tolerate adverse bottom conditions than *Paralingulina gr. tenera* when the anoxia increases.