Geochemical characterization and grain size analysis of Late Eocene volcaniclastic horizons in the northeastern Apennines

Stephanie Fisk
Pomona College Department of Geology, Claremont, California 91711
Faculty Sponsor: Donald Zenger, Pomona College

INTRODUCTION

The continuous sequence of Tertiary pelagic limestones and marls in the northeastern Apennines contains a variety of biozones, magnetic polarity zones and geochemical anomalies which have been tightly correlated in the past in order to accurately calibrate the Late Eocene-Oligocene boundary (Montanari and others, 1988). In addition, volcanic ash horizons interbedded in the sequence contain biotite which can be chemically analyzed in order to further calibrate the time scale.

Within the Middle to Late Eocene portion of the Tertiary sequence lies the colorful Scaglia Variegata formation, good exposures of which are found at Massignano and Contessa, near Gubbio. The Scaglia Variegata sequence at Contessa Valley is 80 m thick (Montanari and others, 1988). The upper (Priabonian) Scaglia Variegata is characterized by pink marly limestone which grades upward to gray marly limestone at the boundary between the Scalia Variegata and the Oligocene Scaglia Cinerea. Volcaniclastic clay layers are interbedded within the upper 6 m of Scaglia Variegata at Contessa and the upper 4m at Massignano (Figure 1). The close proximity of the volcaniclastic layers to each other (generally within <1 meter) provides the potential to precisely correlate the upper Variegata section with different locations in the Umbria-Marche Apennines.

The generally clay-rich, air-fall volcaniclastic layers found in this sequence contain biotite, feldspar, quartz, apatite, and zircon. The unaltered condition of the biotite flakes permits the chemical analysis of the biotite using an electron probe microanalysis. Grain size analysis of the insoluble constituents is being done in an attempt to determine their provenance, suspected to be associated with Alpine and/or western Apennine orogenesis (Montanari, 1988). This work is still in progress.

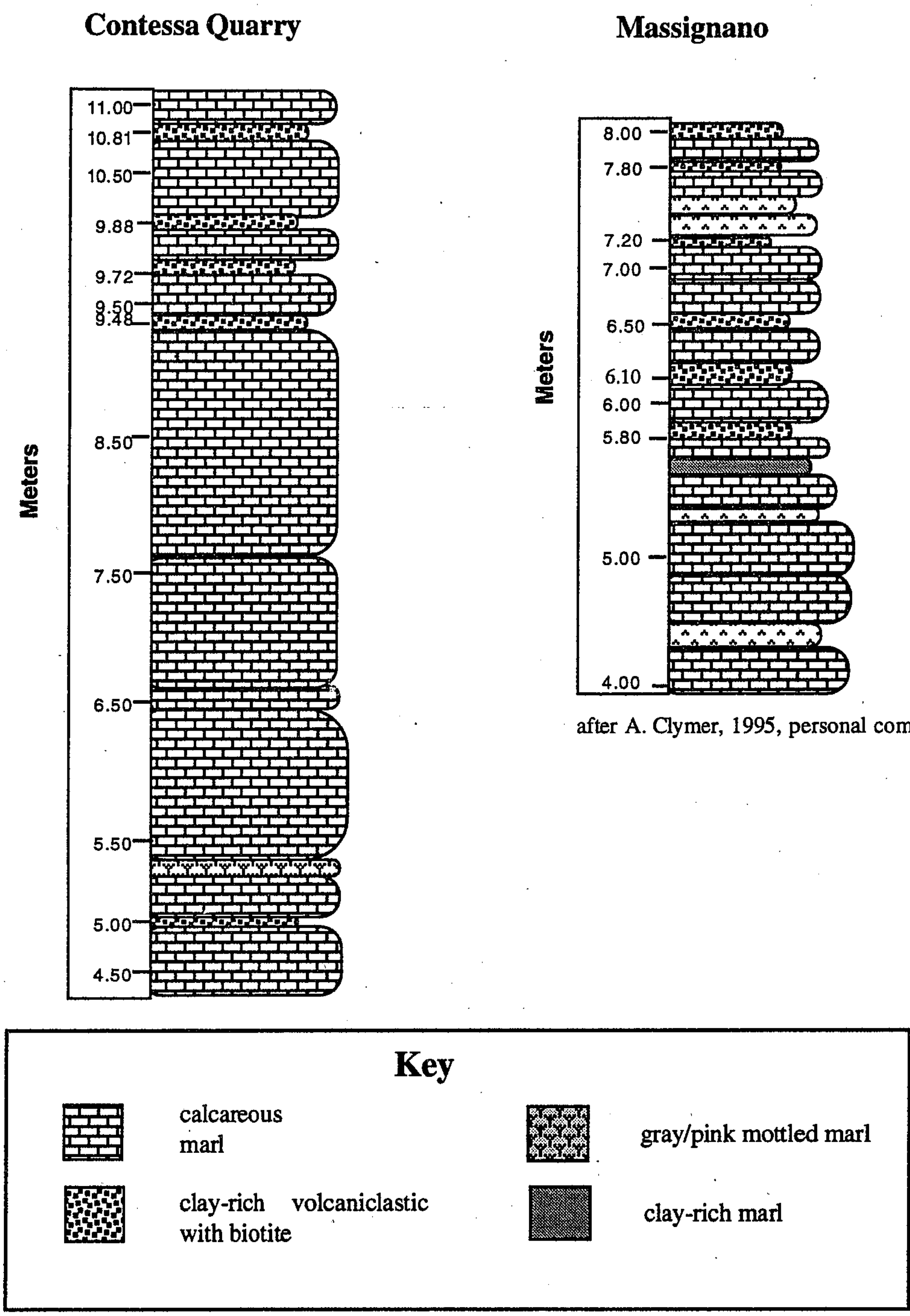
PREVIOUS WORK

Much work has been done to compile a bio-, magneto-, and chemostratigraphic record of the region, but little detailed information about the Apennine volcaniclastic layers exists in the literature. Montanari (1988) analyzed fifteen samples from formations spanning approximately 30 million years of the Tertiary sequence from the Late Eocene to Late Miocene. Geochemical characterization of the biotite was done for correlation of the samples with other volcaniclastic horizons in the region, as well as to test the reliability of the biotites as geochronometers. Earlier radioisotopic dating of some biotite near the Eocene-Oligocene boundary resulted in dates which deviated from a time scale constructed using precise data from the Contessa section (Montanari and others, 1988). A comparison of Mg-Fe ratios by Montanari showed that some of the volcanic layers contained bimodal biotite populations possibly resulting from the mixing of volcanic materials at the time of eruption. The lack of turbidites and synsedimentary slumps in the northeastern Apennines implies a stable depositional environment, precluding the possibility that the biotite would have commingled during sedimentation.

METHODS

Samples of the volcanic ash layers were collected from the upper Scaglia Variegata at Massignano and at a working quarry at Contessa. Samples containing biotite to be analyzed with an electron microprobe were first wet sieved and then biotite was extracted using a Franz magnetic separator. The biotite grains were then mounted in round metal microprobe mounts with epoxy, polished, and carbon coated. The samples were analyzed in a CAMEBAX model Cameca electron microprobe at UCLA. Operating conditions were a voltage of 15 keV, sample currents of 9nA, beamsize of approximately 6.0 μm (large beam size used to avoid volatilization), and counting periods of 10 s (F. Kyte, 1996, oral communication). At least two and up to four points were analyzed for each grain, and from three to twelve grains per sample were analyzed, depending on the number of testable grains present in the mount. The

Figure 1: Stratigraphic Sections



after A. Clymer, 1995, personal communication biotite was analyzed for Mg, Al, Si, Ca, Ti, Cr, Mn, Fe, and Ni. Analyses totals average 93.6%, those less than 91.9% being discarded.

The other insoluble minerals used in the grain-size study were extracted by dissolving the surrounding carbonate using 20% hydrochloric acid. The sieve analysis was conducted using a standard sieve set with a 1/2 phi interval; fractions greater than 2 phi were eliminated because they contained undissolved marl aggregates.

GEOCHEMICAL CHARACTERIZATION

The results of the microprobe analyses of biotite from each sample are reported in Table 1. Biotite varies notably in its magnesium-iron ratio (Brownlow, 1979), and this ratio has been used to here to characterize the biotite. Comparisons between other elements, especially aluminum and silicon, may also be useful in characterizing the biotite, but magnesium-iron ratios have been used in order to facilitate comparison with work done by Montassari.

The amounts of magnesium and iron in the samples, presented as MgO and FeO, range between 9.40% to 12.68% and 13.69% to 21.36%, respectively. Mg/Fe ratios range between a maximum of 0.73 to a minimum of 0.45, with the exception of sample M 7.8 with a ratio of 1.13 (Table 2).

The presence of bimodal biotite populations is evident in several samples, though too few grains were analyzed in most cases to verify this statistically. Because the biotites were not geochronologically dated the presence of bimodal populations is not so critical. Nevertheless, samples CQ 5.00, CQ 9.48, CQ 10.81, and M 7.8 may have bimodal biotite populations based on grains with Mg/Fe ratios which vary significantly (>0.1) from the Mg/Fe ratios of the mean biotites in the sample. Further microprobe analyses are necessary to verify this possibility.

Table 1: Electron probe microanalytical results

Sample	SiO_2	MgO	Na_2O	Al_2O_3	FeO*	MnO	Cr_2O_3	K_2O	CaO	TiO_2
M 5.8	36.17	11.63	0.47	14.87	17.99	0.15	0.02	8.39	0.05	3.49
M 6.1	35.31	9.68	0.47	15.86	21.36	0.20	0.03	7.85	0.04	3.42
M 6.5	36.35	11.13	0.51	14.66	19.05	0.17	0.04	8.12	0.09	3.47
M 7.2	35.78	10.07	0.50	15.55	19.86	0.15	0.04	8.05	0.06	3.45
M 7.8	37.35	15.03	0.65	14.59	13.69	0.22	0.03	8.22	0.03	3.34
M 8.0	35.52	9.40	0.48	15.71	21.03	0.19	0.04	8.41	0.02	3.63
CQ 5.0	36.20	12.68	0.46	14.34	17.05	0.13	0.02	8.40	0.05	3.96
CQ 9.48	36.22	12.20	0.50	14.62	18.06	0.15	0.02	8.15	0.08	3.60
CQ 9.72	36.11	11.07	0.46	14.91	19.73	0.18	0.02	7.86	0.07	3.51
CQ 9.88	35.93	10.95	0.48	14.83	19.64	0.17	0.02	7.92	0.11	3.44
CQ 10.81	35.42	10.10	0.46	15.44	20.54	0.17	0.04	7.38	0.43	3.39

* Total iron as FeO

STRATIGRAPHIC CORRELATION

Correlating the volcaniclastic layers at Massignano with those at Contessa is not altogether straightforward. It appears that some of the volcanic horizons found at Massignano have either not been found or do not exist at Contessa. Biotite from M 7.80, M 7.20, and CQ 5.00 are not similar to any other biotite analyzed (Table 2). Sample CQ 10.81 may not be heterogeneous but is characterized by a mean Mg/Fe ratio of 0.46, similar to that of 0.45 for M 8.00, which is expected from their similar stratigraphic positions (Figure 1) in the Scaglia Variegata. Biotite from levels 5.80 at Massignano and 9.48 at Contessa have chemistries which are similar to each other. Even though its composition is similar to that of CQ 10.81, level M 6.10 cannot be correlated with the former because of its stratigraphic position below M 6.50, which correlates well with two levels which lie beneath CQ 10.81. The Mg/Fe ratio of biotite at M 6.50 compares well with two samples at Contessa quarry, CQ 9.88 and CQ 9.72; closer study of other chemical characteristics of these biotites may further distinguish them; interpretation is still in progress.

Table 2: MgO/FeO ratios

Section and Level	Microprobe Sample Number	Mean MgO/FeO
M 5.80	B 1	0.65 ± 0.05
M 6.10	A 11/A 12	0.46 ± 0.01
M 6.50	B 4	0.58 ± 0.04
M 7.20	B 5	0.51 ± 0.04
M 7.80	B 7/B 8	1.13 ± 0.04
M 8.00	B 10	0.45 ± 0.01
CQ 5.00	A 1	0.73 ± 0.04
CQ 9.48	A 4	0.69 ± 0.04
CQ 9.72	A 6	0.56 ± 0.03
CQ 9.88	A 8	0.57 ± 0.03
CQ 10.81	A 10	0.46 ± 0.01

REFERENCES CITED

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