

16. GEOCHEMISTRY AND MINERALOGY OF IRON- AND TRACE-METAL-RICH MESSINIAN AND PLIOCENE MUDSTONES CORED ON THE SARDINIAN MARGIN: ODP LEG 107, TYRRHENIAN SEA (CENTRAL MEDITERRANEAN)¹

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ABSTRACT

Brightly colored mudstones within Messinian (late Miocene) and lower Pliocene successions were cored beneath the upper and lower slopes of the Sardinian continental margin of the Tyrrhenian Sea (Central Mediterranean). A total of 24 samples were analyzed for major and trace elements and 20 samples were studied by whole-rock X-ray diffraction. The colorful sediments studied include millimeter-thick limonitic laminations within coarser-grained clastic sedimentary rocks (Site 652) and local ferruginous zones near the top of the Messinian succession elsewhere (Site 653). The basal Pliocene metalliferous sediments comprise up to several tens of meters of colorful, mainly red, yellow, and brown, calcareous clays at the base of nannofossil-rich Pliocene deep-sea sediment successions (Sites 652, 653, 654).

Relative to average shale, the Messinian mudstones cored on the de Marchi seamount, the lowest rift fault block on the Sardinian margin (Site 656), are notably enriched in lead (Pb), zinc (Zn), and to a lesser extent, in copper (Cu) and nickel (Ni), and are associated with local clasts of sulfide ore. Messinian sediments higher on the Sardinian margin (Cornaglia Terrace, Site 653) are enriched in Zn and Pb. The basal Pliocene sediments, particularly at Site 653, are strongly enriched in iron (Fe), manganese (Mn), Pb and Zn, relative to the overlying Pliocene nannofossil oozes. This Fe and Mn enrichment is believed to have resulted from oxidation under hot arid conditions in the Messinian, followed by reworking of insoluble metal oxides during the Pliocene transgression that ensued. The Pb and Zn were apparently associated with sulfide ore, of either volcanic-hosted (?Mesozoic) Kuroko-type or (?Tertiary rift-related) sediment-hosted Mississippi-type. The Fe and Mn oxides and insoluble ore material were later reworked, leading to a marked Pb-Zn metal anomaly in ferruginous basal Pliocene sediments.

INTRODUCTION

Eye-catching, brightly colored, fine-grained sediments were cored in late Miocene and Pliocene successions on the Sardinian passive margin in the Tyrrhenian Sea (western Mediterranean) during Ocean Drilling Program (ODP) Leg 107 (Figs. 1 and 2). On the lower Sardinian margin, colorful Messinian sediments range from millimeter-thick red, yellow, and orange laminations in clastic and evaporitic sediments (Site 652), to ferruginous oxide segregations high in the Messinian succession elsewhere (Holes 653A and 653B). Reddish muds of presumed Messinian age also locally overlie the de Marchi seamount, the lowest rotated fault block of continental crust at the base of the rifted Sardinian margin. In addition, brownish and reddish nannofossil-rich clays were studied from the base of the Pliocene succession on both the upper and lower Sardinian margins (Sites 652, 653, 654).

The Tyrrhenian Sea began to form in late Miocene time by the rifting of Calabria from Sardinia and Corsica (Fig. 1). Rifting gave way to the emplacement of marginal and/or transitional ocean crust during Pliocene time, related to irregular spreading above a northwestward-dipping subduction zone (Kastens, Mascle, Auroux, et al., 1987; Kastens, Mascle, et al., 1988). Based on this study, one might argue that the main control of metal enrichment was paleoenvironmental change related to the Messinian salinity crisis (Hsü et al., 1978), combined with the tectonics of rifting and continental breakup.

ANALYTICAL PROCEDURE

A representative suite of brightly colored mudstones was analyzed for mineral content by whole-rock X-ray diffraction (Cu

K α radiation, Table 1). A total of 24 samples were selected for shore-based analysis for major and trace elements by X-ray fluorescence, using the method developed by Fitton and Dunlop (1985).

The near-basal Pliocene sediments are discussed in order of site occupation, and then compared with brightly colored Messinian sediments from two sites (Sites 652 and 656).

Basal Pliocene Sediments, Lower Sardinian Slope: Site 652

Five analyzed samples are composed of yellowish mottled, brown and brownish yellow, yellowish red, and dark gray muds of lower Pliocene age that occur within 14 m of the underlying Messinian succession (contact at 107-652R-6R, 20 cm). The overlying later Pliocene succession is made up of grayish, greenish, and olive-colored marly nannofossil oozes. By contrast, the underlying Messinian sediments mainly consist of turbiditic gypsum-bearing sandy and silty clay and calcareous mudstone (Fig. 2).

Mineralogy

Shipboard smear-slide analysis of the mudstone revealed clay with local calcite, subordinate planktonic foraminifers, and nannofossils, and minor accessory minerals, bioclasts, and micrite. Compositions corresponding to an estimated 25% of volcanic glass were reported in three smear slides from one core (107-652A-19R).

X-ray diffraction reveals abundant quartz, goethite, calcite, dolomite, illite, chlorite, halite, feldspar, and mixed-layer clays (Table 1). Samples lower in the succession contain generally greater abundances of quartz, goethite, and dolomite, while calcite is more abundant stratigraphically higher.

Geochemistry

All the samples are siliceous and aluminous, reflecting a dominantly terrigenous background and fine-grained sediment

¹ Kastens, K. A., Mascle, J., et al., 1990. *Proc. ODP, Sci. Results, 107*: College Station, TX (Ocean Drilling Program).

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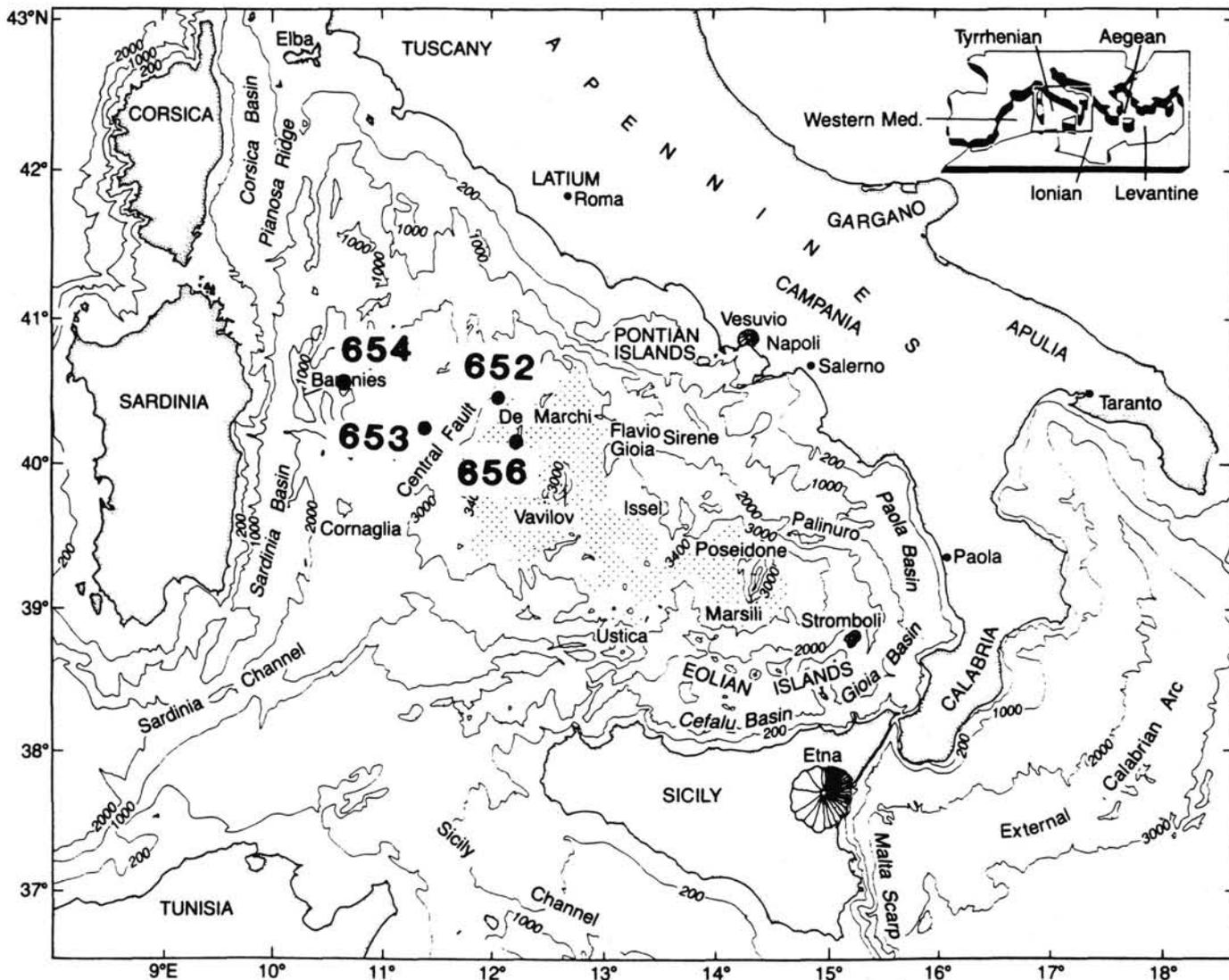


Figure 1. Bathymetric map showing locations of sites sampled in the Tyrrhenian Sea.

influx. Samples become progressively more aluminous upward, possibly reflecting increasing clay mineral and feldspar contents (Al_2O_3 , 7.11%–12.10%; Table 2). All the samples are ferruginous, especially lower in the interval (Fe_2O_3 ; 20.20%). MgO levels are constant, while K_2O fluctuates more widely, increasing upward, possibly correlating with the increased amount of illite detected by X-ray diffraction. All the samples are calcareous (CaO up to 49.06%). TiO_2 shows no systematic variation; levels are typical of shales and deep-sea clays generally (Turekian and Wedhepohl, 1961). MnO values are strongly enriched relative to deep-sea clays throughout, most notably lower in the analyzed interval (maximum 1.98%). P_2O_5 values show no systematic variation in any of the samples analyzed from the Tyrrhenian Sea.

The trace-element values lie in the range of average shale and are depleted relative to average deep-sea clay (e.g., Ni, Cu; Turekian and Wedhepohl, 1961). Barium (Ba) levels are high, corresponding to Fe_2O_3 content.

The mainly terrigenous-derived trace elements (chromium [Cr], zirconium [Zr], and rubidium [Rb]) typically are near average shale in composition (although Rb is 50% above the average shale value). Barium levels are closer to those of average shale (580 ppm) than deep-sea clay (2300 ppm). Copper values are typical of shale, except for one sample that is markedly en-

riched (212 ppm; Table 2). By contrast, levels of Zn and Pb are strongly enriched relative to average shale and deep-sea clay (Zn up to 470 ppm; Pb up to 420 ppm). Average Pb values are 22 ppm in shale and 60 ppm in deep-sea clay (Turekian and Wedhepohl, 1961).

Interpretation

The brightly colored basal Pliocene sediments overlying the Messinian evaporitic sediments are calcareous and clay-rich deep-sea sediments of near average shale composition. Shale, rather than oceanic clay, composition is consistent with rapid accumulation of these lower Pliocene sediments following transgression of the Messinian land surface to form a small ocean basin. On the other hand, these basal sediments are markedly enriched in Fe, Mn, Zn, and Pb. In theory, the Fe-Mn enrichment could be attributed to (1) slow condensed accumulation from seawater, (2) upward diagenetic mobilization from underlying reducing Messinian sediments, or (3) a detrital particulate origin. Alternatives are discussed in a later section.

Lower Pliocene Sediments on the Cornaglia Terrace, Site 653

Four samples of metalliferous sediment were analyzed from Hole 653B, located on the Cornaglia Terrace on the mid-part of

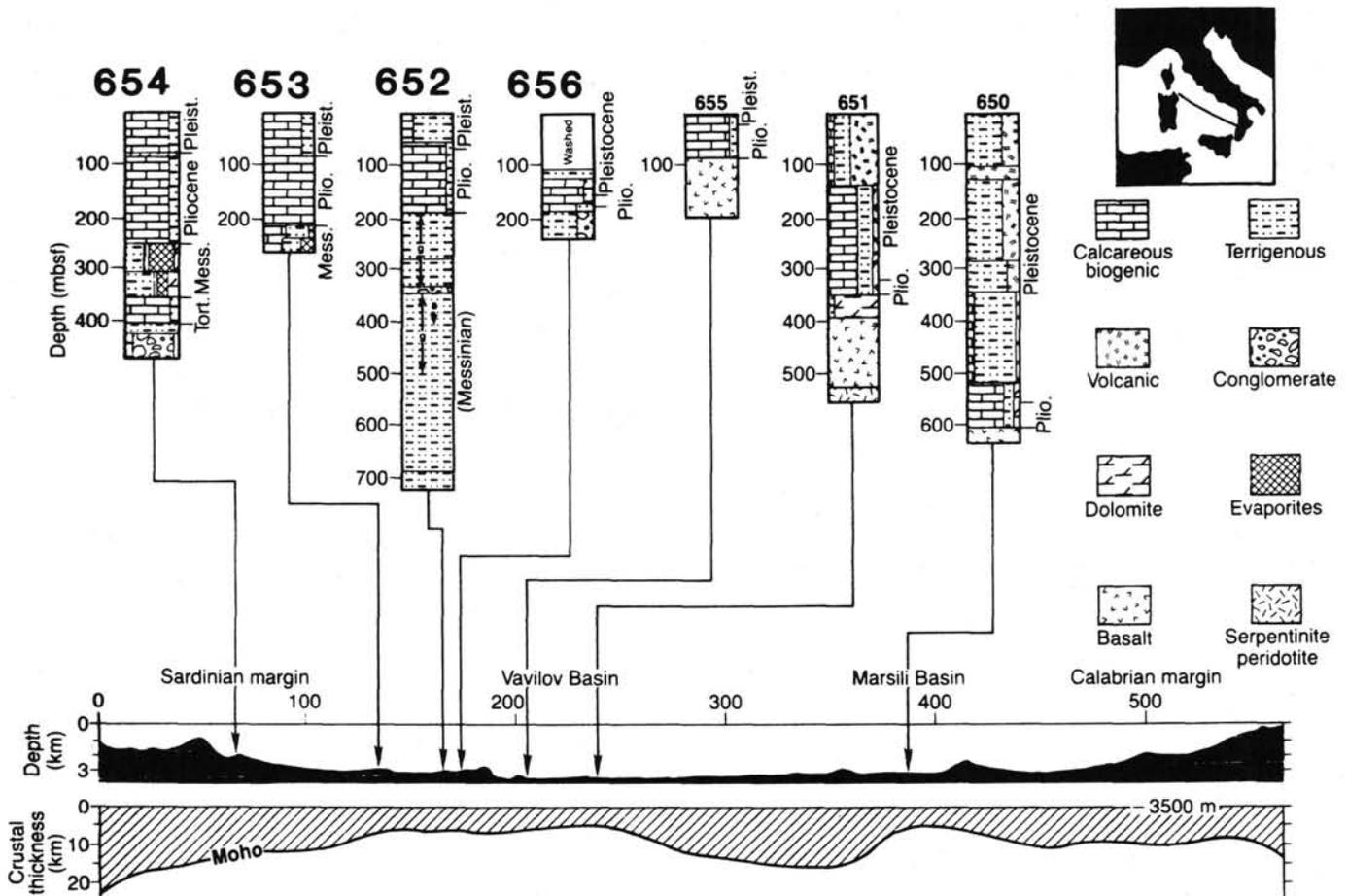


Figure 2. Simplified logs of the successions drilled during Leg 107 in the Tyrrhenian Sea. The sediments analyzed come from just above the Miocene/Pliocene boundary at Sites 652, 653, and 654. Colorful Messinian sediments also were analyzed from Sites 654 and 656.

Table 1. Summary of X-ray diffraction data¹ for analyzed samples.

Core, section, interval (cm)	Major component	Minor component	Trace component
107-650-2R-3, 50-51	Qtz	Cal Hal Feld	Ill Chl Anhyd
652-4R-5, 40-45	Cal Qtz	Ill Kaol	Chl Feld
6R-1, 40-42	Qtz	Ill Pyr Hal	Chl Dol Feld
64X-1, 23-24	Dol Qtz	Ill Chl	Feld Kaol
64X-1, 103-104	Qtz	Dol Pyr Chl	Ill Smect
653-7R-4, 29-31	Cal Qtz	Pyr Ill	Hal Chl Kaol Gyp Dol Feld
8R-1, 4-6	Cal Qtz	Ill	Chl Kaol Hal Feld
8R-1, 8-10	Cal Qtz	Ill	Pyr Chl Hal Kaol Smect
654-6R-4, 50-51	Cal	Qtz	Hal Kaol Chl Feld
6R-4, 142-144	Cal Qtz	Pyr Ill	Chl Kaol
38R-1, 126-132	Cal	Qtz Pyr	Ill
39R-2, 6-9	Dol Qtz	Pyr Hal	Gyp Ill Chl Feld Smect

¹(analyst, G. R. Angell)

Anhyd = anhydrite, Cal = calcite, Chl = chlorite, Dol = dolomite, Feld = feldspar, Gyp = gypsum, Hal = halite, Ill = illite, Kaol = kaolinite, Pyr = pyrite, Smect = smectite and mixed layer clays, and Qtz = quartz

the Sardinia passive margin (Figs. 1,2; Table 3). Three were from the Messinian interval and one from the overlying basal Pliocene interval. The Messinian sediments comprise yellow, olive gray, and red claystone. The Pliocene samples consist of reddish brown nannofossil ooze, located 6 m above the Messinian/Pliocene boundary (at the base of Core 107-653B-23X). The ba-

sal 12 m of the Pliocene sediments are stained yellow and orange and then grade into typical gray, greenish, and olive Pliocene nannofossil ooze.

Mineralogy

Smear slides of the Messinian sediments in the two cores examined on board ship (107-653B-27X and 28X) revealed clay, quartz, dolomite, limonite, gypsum, anhydrite, opaque oxide grains, accessory minerals, localized nannofossils, and planktonic foraminifers. The Pliocene sediment comprises abundant clay, nannofossils, planktonic foraminifers, quartz, minor mica, radiolarians, limonite, gypsum, and opaque mineral grains.

X-ray diffraction of a Messinian sample (Table 1) revealed quartz, gypsum, feldspar, and illite, with minor chlorite and kaolinite. By contrast, a Pliocene sample is composed of quartz hematite, goethite, gypsum, and minor illite, chlorite, feldspar, and kaolinite. This sample also contains small white particles within a reddish matrix. The two sediment types were analyzed separately. The reddish background sediment matrix is made up of quartz, hematite, chlorite, and minor illite, feldspar, and kaolinite, while only gypsum and quartz were detected in the pale material (Table 1).

Chemistry

The Messinian and Pliocene sediments are similarly aluminous and siliceous, reflecting a constant terrigenous influx during both late Miocene and early Pliocene. The high alumina- and magnesian-rich nature of one sample corresponds to an

abundance of feldspar and illite detected by X-ray diffraction. The samples are all ferruginous and reach 53.26% Fe₂O₃ in the upper of the Messinian samples analyzed (Table 3). CaO values are low in the Messinian sediments (maximum 7.42%), but much higher in the Pliocene (36.47%), reflecting calcareous microfossil content. Levels of K₂O are lower than in the Messinian sediments. MnO values are also low in the Messinian sediments, similar, or lower than, average shale (0.085%; Turekian and Wedhepohl, 1961). By contrast, the Pliocene sediments are very enriched in MnO relative to deep-sea clay, as noted at Site 652.

Of the trace elements, all are within the ranges of average shale, with the exception of strong enrichment in Zn (372 ppm) and Pb (756 ppm) in the lower Pliocene sample.

Interpretation

Lithogenous influx to the Messinian sediments studied was continentally derived. Petrology and sedimentary structures suggest that the Messinian intervals of Holes 533A and 533B accumulated in a sabhka setting (Kastens, Mascle, Auroux, et al., 1987). The pronounced Fe enrichment reflects strong oxidation. In modern evaporitic areas (Shearman, 1982), as around the desert shores of the Great Salt Lake, Utah, limonitic sediments are precipitated from springs where very saline and more normal salinity groundwaters mix (Hardie et al., 1978; McKenzie et al., 1980). Such springs could be the source of the strong iron oxide enrichment in the Messinian sediments analyzed. Extremely low MnO levels then possibly reflect iron oxide precipitation following evaporation of reducing ?sulfide-rich groundwaters. By contrast, the Pliocene sediments are similar to terrigenous shale, apart from, once again, a striking enrichment in MnO, Zn, and Pb (see below).

Messinian and Pliocene Sediments on the Upper Sardinian Margin: Site 654

Three samples of brightly colored mudstones were analyzed from the lower Pliocene interval of the upper Sardinian margin (Figs. 1 and 2). The Messinian sample comprises greenish silty clay. The two lower Pliocene samples consist of olive to olive brown burrowed nannofossil ooze.

Smear slides of the Messinian sediment (107-654-28R) reveal clay, feldspar, quartz, micrite, gypsum, dolomite, and minor accessory minerals. The Pliocene sediments are composed of nannofossils, planktonic foraminifers, clay, quartz, dolomite, sulfide minerals, traces of volcanic glass, and accessory minerals.

X-ray diffraction of the Messinian sediment confirms the presence of calcite, quartz, and minor dolomite, illite, kaolinite, chlorite, and halite. The Pliocene sediments are made up of calcite and quartz, with subordinate kaolinite and feldspar and minor amounts of illite, chlorite, feldspar, dolomite, and halite (Table 1).

Major- and trace-element chemistry (Table 4) shows that the Messinian sample is again effectively terrigenous clay. However, levels of Zn (353 ppm) and Pb (130 ppm) are well above average shale values (95 ppm and 20 ppm, respectively; Turekian and Wedhepohl, 1961). The most notable feature of the lower Pliocene sediment is its strong enrichment in Fe₂O₃ (up to 14.96%), MnO (up to 2.25%), and Zn and Pb (up to 1196 ppm and 1041 ppm, respectively).

Interpretation

The Pb and Zn enrichment at Site 654 occurs in the Messinian as well as the Pliocene intervals; possible explanations are discussed later.

Messinian Sediments on the Continental de Marchi Seamount, Lower Sardinian Margin: Site 656

Eight more samples of colorful sediments were analyzed from the unfossiliferous basal (inferred Messinian) interval of

Holes 656A and 656B, the site of a tilted rift fault block at the base of the lower Sardinian margin near the Vavilov Basin (Fig. 1). Dredging (Heezen et al., 1971; Colantoni et al., 1961) and submersible study (Genesseeux et al., 1986) farther southeast on the steeper east flank revealed Paleozoic and Mesozoic sedimentary and low-grade metamorphic rocks (Sartori et al., 1987).

The sediments analyzed comprise reddish, brown, and gray metal-rich silty claystones. The samples in Hole 656A come from a core (107-656A-9R) that contains pebbles of siltstone, sandstone, dolomitic marl, dolomite, red chert, silicified micritic limestone, altered greenstone, crystalline sulfides, tremolite-rich metagabbro, metasedimentary rocks, and numerous red mudstone intraclasts. Clasts of crystalline massive sulfide are also present (?galena, pyrite, and chalcopyrite). Samples from Hole 656B (107-656B-6R and -8R) are associated with calcareous sandy mud, dolomitic sandstone, mudstone and (slumped) nannofossil-rich calcareous ooze, limonitic mud, and sandstone (Kastens, Mascle, Auroux, et al., 1987).

Mineralogy

Smear slides reveal clay, quartz, limonite and/or hematite, calcite, dolomite, mica, clay, feldspar, and micrite. Accessory minerals include possible zeolites, volcanic glass, gypsum, pyroxene, and sphene.

X-ray diffraction (Table 1) of samples from Hole 656A reveals abundant quartz, with subordinate dolomite, hematite, calcite, and minor anhydrite, kaolinite, chlorite, feldspar, and halite. In Sample 107-656A-9R-2, 138–139 cm (Table 1), red and gray mottles were analyzed separately. The red patch contains quartz, dolomite, hematite, goethite, and minor feldspar, kaolinite, chlorite and illite, while the adjacent gray patch contains dolomite, chlorite, illite, and traces of mixed-layer clays only. Similarly, gray, red, and white mottles were again analyzed separately in another sample (107-656A-9R-3, 77–79 cm; Table 1). Distinct differences again exist. The red patch contains quartz, dolomite, hematite, goethite, kaolinite, illite, feldspar, and mixed-layer clays, in approximately decreasing abundance. The gray patch is similar but also contains detectable chlorite. By contrast, the white patch contains only chlorite and quartz. One other sample (107-656A-9R-6, 105–107 cm) was found to contain quartz, dolomite, and kaolinite. Hard, white mineral grains in this sample were analyzed separately and identified as magnesite.

Chemistry

Like the Messinian sediments discussed earlier, a continental source is indicated. Several samples are extremely ferruginous (up to 30.50%), reflecting the high hematite and goethite contents, as detected by X-ray diffraction. The mudstones are only moderately calcareous (CaO 4.13%–14.44%). K₂O varies within a narrow range (1.68%–2.65%). MnO values are greatly above normal shale values (0.38%–1.27%; Table 5).

Of the trace elements, Ba reaches values higher than most of the other Messinian and Pliocene sediments analyzed (up to 606 ppm). Chromium and zirconium contents are constant. All the samples are strongly enriched in Pb (up to 1040 ppm), Zn (up to 438 ppm), and to a lesser extent, also enriched in Cu (up to 154 ppm) and Ni (up to 130 ppm) relative to average shale. The sample showing the most marked enrichments is from the core containing pebbles of a wide range of meta-igneous and sedimentary rocks and massive sulfides.

Interpretation

These unfossiliferous sediments of presumed Messinian age accumulated, probably as small clastic wedges, on the west flank of the last rotated rift fault block at the base of the lower Sardinian margin. An evaporitic Messinian paleoenvironment is reflected by occurrence of detrital magnesite, dolomite, anhydrite, and gypsum. Enrichment in Mn, and to a lesser extent of

Table 2. Major- and trace-element compositions of metalliferous sediments from Site 652 on the lower Sardinian margin.¹

Core, section, interval (cm)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	MnO	P ₂ O ₅	TOT	LOI	V	Ba	Sc	La	Nd	Ce	Cr	Ni	Cu	Zn	Pb	Th	Rb	Sr	Y	Zr	Nb	
107-652A-																														
19R-4, 3	35.04	12.09	14.98	3.74	29.41	1.82	0.52	0.44	0.75	0.11	98.92	28.1	178	147	2	11	21	44	70	104	35	251	213	12	70	930	16	116	10	
19R-5, 76	36.15	11.76	10.85	2.97	33.18	1.53	0.75	0.56	1.20	0.22	99.21	25.5	247	138	5	18	27	52	89	68	35	228	166	8	81	1122	22	105	13	
19R-6, 125	24.92	8.02	9.83	2.10	49.08	0.96	0.18	0.35	1.54	0.24	97.25	31.7	211	98	—	2	22	47	62	68	212	278	420	5	58	1608	23	76	8	
20R-3, 143	27.20	8.49	18.45	2.62	37.88	1.05	0.30	0.40	1.98	0.28	98.69	28.0	467	103	—	8	25	52	66	63	36	468	182	4	55	1192	18	89	9	
20R-5, 70	22.98	7.11	20.07	2.19	42.86	0.79	0.15	0.32	1.72	0.26	98.47	29.7	405	101	—	—	12	29	60	72	40	430	155	1	50	1295	16	74	7	

Note: Major elements in weight percent oxide; trace elements in parts per million; LOI = Loss on ignition.
¹(analysts: D. James and G. R. Angell)

Table 3. Major- and trace-element compositions of metalliferous sediments analyzed from the Messinian and overlying basin intervals on the lower Sardinian margin.¹

Core, section, interval (cm)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	MnO	P ₂ O ₅	TOT	LOI	V	Ba	Sc	La	Nd	Ce	Cr	Ni	Cu	Zn	Pb	Th	Rb	Sr	Y	Zr	Nb	
107-653A-																														
23R-3, 86	33.25	10.89	10.80	2.98	36.47	1.39	0.61	0.52	1.38	0.24	98.57	26.8	215	128	3	21	28	68	76	78	53	372	755	13	75	1203	20	92	11	
27R-4, 26	34.26	11.53	43.28	1.98	1.55	1.32	2.09	0.51	0.02	0.13	96.70	6.6	101	392	—	15	6	47	100	36	25	50	82	1	98	1596	16	64	10	
28R-1, 40	49.07	15.76	11.38	8.65	5.20	1.50	2.87	0.69	0.25	0.15	95.57	15.6	126	240	8	38	26	54	113	46	10	80	11	10	132	186	23	115	14	
28R-1, 75	38.30	12.44	24.44	3.29	7.41	1.36	2.21	0.54	0.08	0.15	90.25	11.4	106	264	3	31	14	40	96	35	39	56	10	6	103	201	17	89	10	

Note: Major elements in weight percent oxide; trace elements in parts per million; LOI = Loss on ignition.
¹(analysts: D. James and G. R. Angell)

Table 4. Major- and trace-element compositions of metalliferous sediments analyzed from the Messinian and basal Pliocene intervals of Site 654 on the upper Sardinian margin.¹

Core, section, interval (cm)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	MnO	P ₂ O ₅	TOT	LOI	V	Ba	Sc	La	Nd	Ce	Cr	Ni	Cu	Zn	Pb	Th	Rb	Sr	Y	Zr	Nb	
107-654A-																														
26R-5, 16	21.97	7.11	13.76	2.03	48.89	0.95	0.30	0.32	2.24	0.31	97.89	31.3	30	125	—	—	15	40	54	72	58	1196	848	9	53	1523	18	76	7	
26R-5, 5	23.16	7.98	14.98	2.58	45.10	0.99	0.31	0.36	2.00	0.29	97.80	30.1	46	70	—	3	19	44	70	93	73	611	1041	12	56	1531	19	88	8	
28R-3, 37	42.55	13.47	5.35	6.86	26.64	1.32	1.87	0.60	0.25	0.16	99.11	23.7	13	625	14	27	32	63	111	75	42	352	130	9	112	468	23	104	12	

Note: Major elements in weight percent oxide; trace elements in parts per million; LOI = Loss on ignition.
¹(analysts: D. James and G. R. Angell)

Table 5. Major- and trace-element compositions of metalliferous sediments analyzed from the inferred Messinian interval at Holes 656A and 656B on the lower Sardinian margin.¹

Core, section, interval (cm)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	MnO	P ₂ O ₅	TOT	LOI	V	Ba	Sc	La	Nd	Ce	Cr	Ni	Cu	Zn	Pb	Th	Rb	Sr	Y	Zr	Nb	
107-656A-																														
4R-6, 31	49.75	16.20	10.03	6.39	11.47	1.34	2.65	0.72	0.37	0.27	99.23	17.2	264	381	14	42	30	80	129	76	27	126	36	13	133	218	24	134	16	
4R-6, 54	52.79	14.26	5.77	7.15	14.43	1.11	2.16	0.65	0.43	0.17	98.97	19.5	118	608	9	30	26	68	108	55	75	218	18	13	115	166	24	155	14	
4R-6, 74	55.27	13.86	14.17	3.24	6.74	1.59	2.52	0.62	0.53	0.20	98.78	11.0	175	631	7	30	24	48	113	59	92	243	137	11	121	173	20	135	13	
7R-1, 18	49.30	13.61	15.11	6.10	9.46	1.14	2.21	0.61	1.26	0.19	99.04	16.5	184	496	13	35	24	64	121	70	71	288	107	11	112	133	22	125	13	
107-656B-																														
9R-1, 14	49.91	14.95	8.75	8.49	11.94	1.21	2.33	0.68	0.78	0.17	99.25	18.9	146	277	19	33	28	68	117	64	42	310	68	12	126	148	24	128	14	
9R-2, 38	44.57	12.87	25.07	5.26	6.20	1.19	2.19	0.58	0.68	0.25	98.89	13.3	232	455	8	35	19	59	106	63	111	462	337	11	101	135	20	110	11	
9R-3, 77	47.39	13.25	20.61	6.24	6.54	1.18	2.12	0.59	0.60	0.24	98.80	13.7	220	521	6	32	24	63	114	84	189	289	405	15	103	132	19	118	12	
9R-6, 105	41.20	11.59	30.49	5.17	4.12	1.75	1.68	0.52	1.12	0.27	97.95	11.7	238	276	1	29	12	63	92	130	154	438	1040	18	71	116	15	97	10	

Note: Major elements in weight percent oxide; trace elements in parts per million; LOI = Loss on ignition.
¹(analysts: D. James and G. R. Angell)

Table 6. Major- and trace-element compositions of mainly metalliferous sediments from within the Messinian succession at Site 652 on the lower Sardinian margin.¹

Core, section, interval (cm)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	MnO	P ₂ O ₅	TOT	LOI	V	Ba	Sc	La	Nd	Ce	Cr	Ni	Cu	Zn	Pb	Th	Rb	Sr	Y	Zr	Nb	
107-652A-																														
58X-3, 63	55.12	16.88	7.8	6.34	7.70	1.35	2.97	0.79	0.12	0.19	99.32	14.0	118	163	12	28	29	62	111	59	19	74	14	12	132	121	25	144	16	
58X-4, 42	55.98	17.08	12.97	3.72	3.84	1.30	3.03	0.78	0.04	0.17	98.95	10.1	135	237	9	37	24	64	126	66	42	89	17	12	136	165	22	144	15	
59X-1, 130	56.40	17.08	9.93	4.93	5.58	1.14	2.86	0.79	0.09	0.19	99.03	11.7	129	287	11	32	24	61	119	61	21	69	13	11	134	143	25	150	17	
59X-1, 136	60.11	18.22	7.38	4.42	3.95	1.26	3.20	0.84	0.06	0.18	99.64	10.2	133	205	12	32	26	61	123	61	6	76	12	14	145	130	25	159	17	

Note: Major elements in weight percent oxide; trace elements in parts per million; LOI = Loss on ignition.
¹(analysts: D. James and G. R. Angell)

Fe, in a continental setting points to strongly oxidizing conditions. The enrichment in base metals (Pb, Zn, Cu, and Ni) is associated with angular clasts of possible meta-ophiolitic rocks, and, notably, also clasts of massive sulfide ore. Base metal deposits within the basement are thus a possible source of this metal enrichment.

Metalliferous-Looking Laminations in the Messinian Lower Sardinian Margin Succession: Site 652

There was discussion among the shipboard scientists about the possible origin of orange and reddish colored laminations within mainly terrigenous and evaporitic (sabkha and/or lacustrine) thick successions of Messinian age, which had been cored on the lower Sardinian margin at Site 652 (Figs. 1 and 2). Three intervals, at 27, 10, and 20 m thick, respectively, contain sporadic, thin, colorful laminations within an overall 84-m-thick interval of the Messinian succession. Four samples were analyzed from two cores (107-652A-58R and -59R) (Table 6); these were composed of millimeter-thick red, yellow, and orange limonite partings within grayish and greenish dolomitic and/or gypsiferous fine-grained sandstone.

Mineralogy

Smear slides of the red bands reveal clay, limonite, and accessory opaque minerals, minor calcite, and traces of quartz.

X-ray diffraction of the stratigraphically lowest samples (Core 107-652A-59R) reveals quartz, with minor dolomite, chlorite, illite, and trace amounts of feldspar, kaolinite, and halite (Table 1). Red and gray claystone is finely interlaminated in Sample 107-652A-59R-1, 135–136 cm (Table 1). The red lamination contains quartz and dolomite, with minor anhydrite and hematite, and trace amounts of kaolinite, chlorite, and feldspar. By contrast, the adjacent gray lamination contains quartz and dolomite, with subordinate chlorite, illite, and trace amounts of kaolinite, feldspar, and anhydrite. The red lamination is richer in hematite and anhydrite and contains no detectable illite relative to the gray lamination. A sample higher in the succession (Core 107-652A-58R) contains quartz, dolomite, subordinate chlorite, illite, feldspar, and minor halite, kaolinite, and mixed-layer clays.

Geochemistry

All samples are nearly equally siliceous and aluminous and contain similar contents of K_2O , TiO_2 , P_2O_5 , and MgO (Table 6). Despite the bright red color, levels of Fe_2O_3 are only slightly enriched relative to average shale composition (4.72%; Turekian and Wedhepohl, 1961). Fe_2O_3 in one sample reaches 12.97% (Core 107-652A-58R, Table 6).

The trace elements confirm a lithogenous composition, with no values departing far from normal shale compositions.

Interpretation

Red laminae are interbedded with gypsiferous and dolomitic clastic sediments that some believe to have accumulated on a coastal floodplain, or in a lake, marine embayment, or saline sea (Robertson et al., this volume). Possible origins of the red layers are (1) accumulation of wind blown dust, (2) desiccation of rainwater ponds on a floodplain, (3) precipitation from groundwater below the water table, or (4) subaqueous deposition. The undisturbed nature of the fine lamination is consistent with a primary, rather than diagenetic, origin for this red sediment. The low MnO content indicates these sediments were originally depleted in Mn and/or Mn was removed during diagenesis. The fine laminations do not confirm any evidence of erosion (e.g., scouring) or desiccation (e.g., mud cracking) and the author favors a quiet water-laid origin.

Aeolian influx may be the most plausible explanation for the rare, fine, orange laminations. In this scenario, silt and highly

oxidized clays were introduced by desert dust storms, and then settled onto the basin floor. Similar deposits coat modern Middle East sabkhas after dust storms, for example. Aluminosilicates were possibly wind-suspended to a greater extent than calcite, owing to lower density and/or smaller grain size. An alternative, less favored, explanation is that compositional differences existed in the source areas and that this resulted in the accumulation of occasional red layers.

DISCUSSION

Taking all the Messinian and Pliocene sediments into account, mineralogy and geochemistry show that compositionally similar continental basement rocks supplied all the sites. Major and trace-element compositions do not obviously discriminate among the different basement terrains identified by petrographic study of the coarser interbedded clastic sediments (e.g., conglomerates and breccias). On the upper Sardinian margin (Site 654), provenance was apparently mainly from Paleozoic low-grade metamorphic siliceous basement and carbonate platform rocks, as those now exposed in Sardinia and Corsica (Sartori et al., 1987; Robertson et al., this volume). By contrast, provenance at Site 652 on the lower Sardinian margin was mainly from Tertiary calcareous sedimentary rocks similar to those now exposed in the southern Apennines and Sicily (Sartori et al., this volume). Furthermore, the breccias that accumulated on the flanks of the de Marchi seamount on the lower Sardinian margin at Holes 656A and 656B were derived from local metamorphosed ophiolite-type rocks and deep-sea sedimentary rocks somewhat similar to outcrops in the Mesozoic Piedmont zone of the mainland to the north (Lemoine, 1980).

Based on coring at Site 132 (Leg 13) in the Tyrrhenian Sea (Fig. 1), Chamley et al. (1976) noted that clay minerals in the Messinian succession are dominated by well-crystallized smectite and chlorite, with both minerals attributed to an evaporitic genesis. Evaporitic sediments were not analyzed in this study and the clay mineral assemblage identified (illite, chlorite, kaolinite, and minor mixed-layer clays) is similar to that of the overlying Pliocene interval (see Chamley et al., this volume). From the Pliocene at Site 132, Chamley et al. (1978) recorded mainly illite, smectite, attapulgite, and kaolinite. Based on limited data from Site 132 (Leg 13), Nesteroff (1973; see also Zemmel and Cook, 1973) earlier noted similar clay mineral assemblages in both the Messinian and Pliocene. Nesteroff also commented on the presence of hematite in the basal Pliocene sediments above the evaporites and suggested derivation from subaerial outcrops soon after Pliocene flooding; he believed that the isolated occurrence of phillipsite was diagenetic. Today's Italian rivers supply mainly mica (illite) and minor chlorite (Quakernaat, 1968). Smectite and mixed-layer clays in the Messinian and Pliocene intervals are attributed to a volcanogenic influx, mainly as volcanic ash and volcanoclastic turbidites.

A striking feature noted in this study is the strong enrichment in Pb, Zn, and to a lesser extent, in Cu and Ni, within the ferruginous mudstones associated with "meta-ophiolitic" and other rock clasts at Site 656. Enrichment of Zn and Ni was also detected in the Messinian sediments of Site 653, also on the lower Sardinian margin.

The basal Pliocene sediments analyzed at Sites 652, 653, and 654, on both the upper and lower Sardinian margins, also are enriched in Fe, Mn, Pb, and Zn relative to the overlying Pliocene nannofossil oozes. However, other heavy metals (Cu, Ni) exhibit only typical shale values. Selective enrichments in metals might in theory relate to (1) slow selective precipitation from seawater, (2) upward mobilization of metals from lower in the succession, (3) hydrothermal influx, (4) coeval aeolian derivation, or (5) a detrital source. Taken together, the absence of cor-

responding enrichments in other metals (Cu, Ni), the paleontological data (Kastens, Mascle, Auroux, et al., 1987), and sedimentary structures provide no evidence that this metal enrichment resulted from slow accumulation from seawater. The underlying Messinian sediments do not include large volumes of organic-rich sediments that, conceivably, could have dissolved metals before upward mobilization during diagenesis. Pb and Zn hydrothermal ores are common in Tuscany in regions of modern and Late Tertiary hydrothermal activity (e.g., near Pisa, just south of the modern Lardarello hydrothermal field). However, no evidence exists of any contemporaneous hydrothermal activity in the vicinity of the Pliocene Leg 107 sites. Consequently, detrital influx of the trace metals (Pb, Zn) is the preferred explanation of the metal enrichment, although syndepositional aeolian influx cannot be ruled out.

In this explanatory model, the land surface is considered to have been strongly oxidized during the Messinian time of lowered sea level. Under arid conditions, iron and manganese oxides coated rock and sediment surfaces (i.e., including desert varnish). When the seas flooded at the close of the Messinian, this oxidized material was readily suspended and reworked by currents into the basal clay- and nannofossil-rich deep-sea sediments. A plausible source of Pb and Zn enrichment is the basement terrane that supplied the sulfide mineral clasts cored at Site 656 on the lower Sardinian margin. Metals may have been eroded from an exposed rift fault-block in Messinian time; this material may have then been widely disseminated in the basin during the terminal Miocene transgression. Oxide influx later ceased after transgression was complete, and any remaining metal content was diluted with normal pelagic sedimentation.

Despite the spatial association with presumed meta-ophiolitic rock clasts, Pb and Zn enrichment is not characteristic of massive sulfide ore bodies within ophiolites (e.g., Troodos, Cyprus; e.g., Oudin and Constantinou, 1984); Pb and Zn enrichment is more suggestive of Kuroko-type deposits associated with volcanic arcs and subduction. For example, black sulfide ore from a type locality in Japan contains 1.41% Cu, 9.4% Pb, and 1.87% Zn (Oshima et al., 1974; reviewed in Mitchell and Garson, 1981). Were the "meta-ophiolitic" rocks cored at Site 656 derived from the deformed, deeply dissected roots of a volcanic arc related to subduction of the Mesozoic Tethys ocean? A problem, however, is that Kuroko ores are normally interstratified with thick successions of intermediate to acid composition volcanic and tuffaceous sediments, but these types of sediments were not cored at Site 656.

Alternatively, the association of massive sulfide ore and "meta-ophiolitic" clasts might be coincidental. The ore clasts could instead be derived from sediment-hosted Pb and Zn mineral deposits (i.e., Mississippi-type), possibly, for example, similar to the Carboniferous Pb and Zn deposits (reviewed by Maynard, 1983). Lead- and Zn-rich solutions might have migrated from deep in the continental crust up faults related to rifting of the Tyrrhenian Sea, followed by subaerial exposure during end-Miocene crustal thinning and continental breakup. It may conceivably be significant that the sulfide clasts cored on de Marchi seamount come from the last tilted rift fault-block nearest inferred oceanic crust in the Vavilov Basin (Fig. 1). Thus, lead- and Zn-rich mineralization may possibly have exploited the thinned continent-ocean boundary area. Insufficient data exist to decide between possible Kuroko vs. sediment Pb- and Zn-hosted origins. In either case the Pb and Zn anomaly in the basal Pliocene sediments may be explained in terms of erosion of base metal ore deposits exposed on the Messinian land surface.

CONCLUSIONS

1. Variably metal-enriched sediments occur as local laminations and segregations within Messinian successions of the lower

Sardinian margin at Sites 652 and 653 (respectively). Abundant metalliferous mudstones are also associated with "meta-ophiolitic" rock clasts at Site 656A on the Gortani Ridge on the lower Sardinian margin.

2. The basal Pliocene sediments cored on both the upper and lower Sardinian margin at Sites 652 and 654 and Holes 653A and 653B comprise reddish and brownish clays up to several tens of meters thick that contrast with the overlying green and gray nannofossil oozes.

3. X-ray diffraction, combined with major- and trace-element analyses, shows that all the sediments were derived from compositionally similar continental basement terrains. At Site 656, on the lower Sardinian margin, reddish mudstones associated with the "meta-ophiolitic" rock clasts are strongly enriched in Fe, Mn, Pb, Zn, and, to a lesser extent, in Cu and Ni. Messinian sediments higher on the Sardinian margin at Site 653 are also detectably enriched with Pb and Zn.

4. The basal Pliocene sediments are strongly enriched in Fe, Mn, Pb, and Zn relative to the overlying Pliocene nannofossil oozes. In the model proposed, Fe and Mn were oxidized on the Messinian land surface and later reworked into the sea during the Pliocene transgression.

5. The source of the lead and zinc enrichment may be base metal deposits. Possible sources include Mesozoic volcanic-hosted, Kuroko-type, or ?Tertiary Mississippi-type ore deposits. In this scenario, the ores were exposed on tilted rift blocks near the continent/ocean boundary and eroded on the Messinian land surface. The insoluble heavy metal oxides were transported later into the basal deep-sea Pliocene sediments during the transgression that followed Messinian desiccation.

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