Sedimentary recycling, provenance and paleoweathering from chemistry and mineralogy of Mesozoic continental redbed mudrocks, Peloritani mountains, southern Italy

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The Triassic to Lowermost Jurassic mudrocks from continental redbeds of the Longi-Taormina Unit (Calabria-Peloritani Arc; southern Italy) have been mineralogically, chemically and petrographically analyzed, in order to reveal their complex history, which record an important phase of the geological evolution of the Mediterranean area.

The Late Triassic corresponds with a low first-order sea level stand and a time of high continental emergence whereas the Early Jurassic was the time of the initiation of the first-order sea level rise in the mid-Mesozoic, generally marked by a transgressive trend.

The mineralogical assemblage, dominated by the occurrence of illite and illite/smectite mixed layers, coupled to the CIA index and to the A-CN-K plot, indicates post-depositional K-enrichments.

Palaeoweathering indices (CIW and PIA ratios) suggest that the source experienced intense weathering and that they likely record a recycling effect from their metasedimentary basement rocks. A recycling effect is also suggested by the distribution of Al_2O_3 , TiO_2 , and Zr. In the Zr/Sc vs. the Th/Sc plot the redbeds are not clustered along the primary compositional trend but fall along a trend involving zircon addition and thus sediment recycling. Recycling could significantly affect the weathering indices which likely monitor a cumulative effect including a first cycle of weathering at the source rocks. Weathering occurred under hot, episodically humid climate with a prolonged dry season. Wet-humid conditions favored the formation of stream channels that eroded the soil profiles, whereas the dry season promoted the sedimentation. The climate alternation in the Early Jurassic favored recycling.

An additional provenance terrane occurring in the basement, including metavolcanic rocks having mafic composition cannot be excluded, since the Eu anomaly is slightly higher than the PAAS value. Although the effects of recycling on REE distribution are uncertain, the Eu/Eu* should increase, as more feldspar is destroyed during weathering and diagenesis. This involves that the Eu/Eu* ratio could monitor a supply of low Eu/Eu* mafic detritus which compensate for the recycling effect by reducing Eu/Eu*. Eu released during the dissolution of feldspar could be retained by clay minerals contributing to minimize the recycling induced increase of the Eu-anomaly. This may involve that the recycling effect on the Eu-anomaly was minor and that the low Eu/Eu* mafic detritus supply was also minor. The subordinate importance of a mafic supply is confirmed also by other provenance proxies including the La-Th-Sc plot and the Cr/V and Y/Ni ratios.

The proportions of illitic layers in I/S mixed layers coupled with the illite crystallinity values, expressed as Kübler Index (KI), suggesting an estimated temperature experienced by the Longi Units in the range of 100–150°C. Starting from this range the diagenetic/tectonic evolution should correspond to a lithostatic/tectonic loading of about 4–5 km.

Keywords: mudrocks, paleoweathering, recycling, provenance, Mesozoic continental redbeds, southern Italy

INTRODUCTION

The chemical composition of sedimentary rocks is an important record of the geological evolution of the continental crust through time because some elements are quantitatively transported in the terrigenous fine fraction of

a sediment (Taylor and McLennan, 1985). Of these, the rare earth elements (REE), Th, and Sc are the most useful because their distribution is not affected by secondary processes. The REE pattern of fine-grained siliciclastic sediments and some elemental ratios, especially Eu/Eu*, are assumed to reflect the exposed crustal abundances in the source area (McLennan *et al.*, 1993; Mongelli, G. *et al.*, 1996; Fedo *et al.*, 1996; Hassan *et al.*, 1999; Bauluz *et al.*, 2000; Cullers, 2000; Condie *et al.*, 2001; Mongelli, 2004, among others). On the contrary, mobile elements

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Fig. 1. Geological sketch of the Peloritani Mountains. 1: Recent to Upper Pliocene dominantly clastic deposits; 2: Etna volcanics; 3: Lower Pliocene-Upper Tortonian mostly clastic deposits; 4: Floresta Calcarenes (a; Langhian) and variegated shales of the "Antisicilide Complex" (b; Paleogene-Cretaceous); 5: Stilo-Capo d'Orlando Formation (Lower Miocene), 6: Aspromonte and Mela Units (Pre-Triassic); 7: Mandanici Unit (Cretaceous-Paleozoic); 8: Ali Unit (Cretaceous-Upper Paleozoic); 9: Fondachelli Unit (Cretaceous-Paleozoic); 10: Longi-Taormina Unit sedimentary cover (Aquitania-Upper Triassic); 11: Longi-Taormina Unit basement (Paleozoic); Maghrebian Chain—12: Sicilide Units (Monte Soro and Troina-Tusa; Lower Miocene-Cretaceous); 13: External Units (Panormide and Imerese; Middle Miocene-Middle Triassic); 14: Stratigraphic contacts; 15: Tectonic contacts. Modified after de Capoa *et al.* (1997).

(such as Na and Ca) can be used to evaluate the degree of chemical weathering, characterizing paleoclimates in source regions at the time of deposition (Nesbitt and Young, 1982). Further the mineralogical features of fine-grained siliciclastic sediments proved to be a useful record of possible post-depositional changes, including diagenesis and incipient metamorphism (Chamley, 1995).

In the Alpine orogenic belts, developed along the central-western Mediterranean region from the Betic Cordilleras to Apenninic Chain, clastic sediments preserve informations of the Mesozoic Pangea supercontinent break-up, the Tethyan Ocean rifting and its closure during Tertiary orogenesis. The interpretations of the history of these sediments can be used to test paleogeographic and paleotectonic reconstructions during the key orogenic phases (Critelli, 1999) and can be of relevance for evaluating global changes (Perrone *et al.*, 2005). The continental rift-valley phase and the proto-oceanic phase of the Tethyan rifting in the western-central Mediterranean region occurred during the Late Triassic to Early Jurassic, and in many tectonic units of the Alpine orogenic belts, continental redbeds, which mark the base of the Meso-Cenozoic covers, are interpreted as deposited during the rift-valley phase. The domain of these redbeds was located around small mountain areas, from which alluvial depositional systems provided siliciclastic supply to neighbouring nascent continental sedimentary basins

formed during Triassic rifting. They reveal the erosion of metamorphosed Paleozoic successions extensively intruded by felsic plutonic rocks. Chemical weathering of such rocks under tropical, hot and episodically humid climate with a prolonged dry season allowed oxidation of iron and rubefaction of soils and sediments and caused illitization of silicate minerals and concentration of quartz in thick soil profiles. These soils were later denudated by fluvial erosion, producing relatively mature, quartz-rich red deposits (Perrone *et al.*, 2005).

In this paper we clear up the complex history of a set of redbed samples from a selected section of Upper Triassic to Lower Jurassic continental redbeds (Longi section, Peloritani Mountains), using geochemical and mineralogical tools. The history of these sediments, which include source area weathering, provenance, recycling and burial, record an important phase of the geological evolution of the Mediterranean area.

GEOLOGICAL AND STRATIGRAPHIC SETTINGS

The Calabria-Peloritani Arc represents an arcuate orogenic sector connecting the NW-SE-trending Southern Apennines with the E-W-trending Sicilian Maghrebids (Bonardi *et al.*, 2001 and references therein). It is made up both of units involving pre-Alpine crystalline basement and ophiolitic units, some of them evidencing HP/

Fig. 2. Geological sketch map of Longi area and location of the studied samples (VL1–VL19). Q: Breccie di versante, alluvial deposits, landslides (Holocene-Pleistocene); OMc: Stilo-Capo d'Orlando Formation (Middle-Upper Burdigalian); San Marco d'Alunzio Imbricate: Us = Platform and pelagic limestones (Liassic-Malm); Met = metapelites and metarenites (Palaeozoic); Uff = Sandy-pelitic turbidites (Aquitania); Mar: "Scaglia"-like marls and marly limestones (Upper Oligocene-Upper Cretaceous) and "Maiolica"-like limestones (Lower Cretaceous-Tithonian); Lm = marly limestones and marls (Middle Liassic); Ut = Neritic limestones and dolostones (Lower Liassic); Ve = continental redbeds (Pseudoverrucano-like conglomerates, sandstones and pelites; Lower Liassic-Upper Triassic). Line with triangles = Thrust and reverse fault; Line with squares = Overthrust. Modified after Lentini *et al.* (2000).

LT metamorphism and a pre-Miocene tectonism.

The Peloritani Mountains represent the southwestern extremity of the Calabria-Peloritani Arc and constitute an orogenic sector in which many tectonic units of the Alpine nappe stack are exposed. The Peloritani nappes have been piled as from early Miocene and thrust, during the Middle Miocene (Lentini and Vezzani, 1975) onto the nappes originated from the Maghrebien Flysch Basin, these latter made up of Upper Jurassic-middle Miocene sedimentary terrains and cropping out in the Nebrodi and Madonie Mountains. The tectonic boundary between Peloritani and Flysch Basin nappes is known as "Taormina line" (Scandone *et al.*, 1974).

Some Peloritani nappes (Fig. 1) consist only of pre-Alpine crystalline basement (Mela and Aspromonte Units), others include also a Meso-Cenozoic cover (Longi-Taormina, Fondachelli, Mandanici, Piraino and Ali Units). The Longi-Taormina Unit, cropping out along a WNW-

Fig. 3. Sedimentologic column of the continental redbeds (Verrucano Auct.) at the Longi section, Peloritani Mountains, Sicily. VL1 to VL19 mudrock samples used for mineralogical and geochemical analyses.

ESE oriented belt, 10 km wide and 70 km long, constitutes the lowermost nappe in the Peloritani nappe stack and is arranged in three imbricated subunits. It shows thick pre-Alpine crystalline basements and the most extensive and complete Mesozoic to Cenozoic sedimentary cover of the whole Calabria-Peloritani Arc. The basements of the three imbricates consist of low-grade metamorphics (phyllite, metarenite, metalimestone and metavolcanic rocks) of Paleozoic age (Messina *et al.*, 1996, among others), on which sedimentary successions, rest unconformably (Lentini, 1975; Lentini and Vezzani, 1975; Bonardi *et al.*, 1976). The redbeds forming the base of the successions, in particular, have variable thickness from few metres to over 200 metres.

The Longi Imbricate (Arnone *et al.*, 1978), cropping out on the Tyrrhenian versant of the Peloritani Mountains (Fig. 1) represents the largest subunit on the Longi-Taormina Nappe.

In the Longi Imbricate the continental redbeds are particularly thick (over 200 m), whereas they are few

metres in the other subunits. In particular, in the Longi section, cropping out immediately NW of the homonymous village (Fig. 2), Upper Triassic lenticular conglomerate and sandstone strata, representing fluvial channel-fill, interbedded with thin layers of red clays, are well exposed.

The measured stratigraphic section is about 60 m thick (Fig. 3). In the outcrop the contact between the metamorphic basements and the sedimentary successions is not visible, and many little faults are present, especially in transition to limestones. The fluvial deposits are characterized by sandstone and conglomerate beds, thick between 10 and 300 cm, interbedded with centimetrical layers of mudrocks; however the base of studied section shows some meters of covered clays. The sandstone beds are often lenticular in 5–10 meters, and normally the beds show an erosional base, very coarse or microconglomeratic; internally levels of pebbles (size 2–7 cm) are frequently present, as well as cross and curved laminae. In the medium of measured section an erosion of two meters is filled by planar thin beds. Even if the correlation with other outcrops is not possible, the studied section can be interpreted as a portion of braided river, a very little outcrop (likely in landslide) near Longi village shows a thin sequence of mudrocks with thin planar and parallel sandstone beds, interpreted as floodplain deposits.

SAMPLING AND METHODS

Nineteen mudrock samples, interbedded in the quartzarenite and conglomerate strata, were collected along the Longi section. The mineralogy of clay fractions ($<2\ \mu\text{m}$) has been obtained by XRD using a Siemens D5000 ($\text{CuK}\alpha$ radiation, graphite secondary monochromator, sample spinner). In order to distinguish chlorite from kaolinite, the samples have been heated to 550°C for one hour. The heating causes that the intensity of the chlorite 001 reflection increases greatly and shifts to about 6.3 to $6.4^\circ 2\theta$ whereas kaolinite becomes amorphous to X-ray and its diffraction pattern disappears (Moore and Reynolds, 1997).

In order to determine the degree of post-sedimentary processes possibly affecting the samples analysed in the present study and the range of temperature they experienced, the most widely XRD-based illite “crystallinity” technique (Merriman and Peacor, 1999) was used. The most widely adopted method for measuring $10\text{-}\text{\AA}$ peak profile is still the one first used by Kübler (1967); the Kübler Index (KI) measured the width of the $10\text{-}\text{\AA}$ peak at half-height above the background (FWHM). Illite “crystallinity” values (IC), expressed as Kübler Index (KI), and % of illitic layers in I/S mixed layers were measured in the pelite samples as indicators of diagenesis and low-grade metamorphism (Pollastro, 1993) and to estimate

tectonic loading (stress) experienced by the Early Jurassic continental redbeds.

The illite crystallinity index, expressed as Kübler Index (KI), was measured on both air-dried and ethylene-glycol solvated slides; ethylene-glycol (EG) treatment was carried out on some samples to corroborate the identification of smectite and/or illite-smectite mixed-layers. Our IC measurements (y) were transformed into C.I.S. values (x) according to the equation $y = 1.8957x + 0.0104$ ($R^2 = 0.9817$), obtained in laboratory using the international standards of Warr and Rice (1994).

Elemental analyses for major and some trace elements (Nb, Zr, Y, Sr, Rb, Ba, Ni, Co, Cr, V) concentrations were obtained by X-ray fluorescence spectrometry (Philips PW 1480) on pressed powder disks. X-ray counts were converted into concentrations by a computer program based on the matrix correction method according to Franzini *et al.* (1972, 1975) and Leoni and Saitta (1976). Average errors for trace elements are less than $\pm 5\%$ except for those elements at 10 ppm and lower ($\pm 5\text{--}10\%$).

Total loss on ignition (L.O.I.) was determined, after heating the samples for three hours, at 900°C .

Instrumental Neutron Activation Analysis (INAA) at the Activation Laboratories (Ancaster, Canada) was used to determine the abundance of the rare earth elements (La, Ce, Nd, Sm, Eu, Tb, Yb and Lu) and Sc, Zn, Cs, Th, and U. Average errors for trace elements are less than $\pm 5\%$ except for those elements at 10 ppm and lower ($\pm 5\text{--}10\%$). The estimated precision and accuracy for trace element determinations are better than 5%, except for those elements having a concentration of 10 ppm and lower (10–15%).

MINERALOGY

The samples are mainly composed of clay minerals (illite, illite/smectite mixed layers and negligible amounts of kaolinite and chlorite), quartz, hematite and negligible amounts of feldspars. The $<2\ \mu\text{m}$ grain-size fraction is composed by illite prevailing on illite/smectite mixed layers and negligible amounts of kaolinite and chlorite.

The Kübler Index (KI) values for the samples studied, range between 0.66° and $0.72^\circ \Delta 2\theta$, even if there are little difference, the mean illite crystallinity value for the pelitic sediments of the stratigraphic section studied is $0.70^\circ \Delta 2\theta$ ($\pm 0.1^\circ \Delta 2\theta$) whereas the modal illite crystallinity value is $0.69^\circ \Delta 2\theta$, typical values of a high diagenetic zone (Merriman and Frey, 1999).

The percent of illitic layers in I/S mixed layers estimated following Moore and Reynolds (1997) suggestions, is in the range of 70–90% ($R > 1$ ordering, Reickeweite number). The high ordering of the mixed layers and the high % of illitic layer in I/S mixed layers are also consistent with high diagenetic conditions.

Table 1. Major, trace element and ratios distribution in Redbeds samples

Sample No.	VL1	VL2	VL3	VL4	VL5	VL6	VL7	VL8	VL9	VL10	VL11	VL12	VL13	VL14	VL15	VL16	VL17	VL18	VL19
<i>Oxides (wt. %)</i>																			
SiO ₂	65.86	72.05	61.19	70.15	64.79	61.48	63.4	63.55	70.43	60.21	66.83	61.26	59.70	59.80	62.73	66.81	67.97	65.09	66.23
TiO ₂	0.62	0.66	0.59	0.74	0.71	0.66	0.78	0.79	0.74	0.83	0.70	0.81	0.82	0.84	0.82	0.79	0.68	0.78	0.78
Al ₂ O ₃	16.3	14.23	18.05	15.38	16.48	17.24	16.98	17.43	14.53	19.36	16.69	18.88	19.46	19.58	18.41	16.50	14.77	17.71	17.85
Fe ₂ O ₃	6.01	3.76	7.47	4.26	6.86	7.28	6.91	7.47	5.80	8.11	7.06	8.13	8.12	7.91	6.60	6.48	5.58	3.66	2.93
MnO	0.20	0.11	0.03	0.01	0.14	0.19	0.06	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.06	0.01	0.04	0.02	0.05
MgO	1.68	1.55	1.83	1.23	1.65	1.84	1.64	1.60	1.10	1.68	1.21	1.38	1.47	1.45	1.43	1.20	1.89	1.53	1.70
CaO	0.20	0.13	0.22	0.13	0.15	0.37	0.18	0.22	0.15	0.21	0.12	0.08	0.17	0.11	0.26	0.21	0.89	0.22	0.38
Na ₂ O	0.18	0.15	0.14	0.19	0.21	0.16	0.19	0.18	0.22	0.21	0.15	0.15	0.17	0.16	0.20	0.15	0.15	0.17	0.20
K ₂ O	4.37	4.04	4.48	3.95	4.53	4.49	4.62	4.54	3.32	4.90	3.84	4.49	4.76	5.00	4.16	3.68	3.92	4.80	4.73
P ₂ O ₅	0.06	0.03	0.03	0.05	0.05	0.04	0.07	0.07	0.07	0.09	0.07	0.05	0.07	0.05	0.04	0.04	0.02	0.02	0.03
LOI	4.51	3.28	5.96	3.89	4.44	6.26	5.17	4.13	3.62	4.37	3.29	4.75	5.25	5.07	5.29	4.11	4.09	5.01	5.13
Total	99.99	99.99	99.99	99.98	100.01	100.01	100.00	100.00	100.00	99.99	99.98	100.00	100.01	99.99	100.00	99.98	100.00	99.01	100.01
<i>Trace elements (ppm)</i>																			
Sc	15.8	9.7	19.3	12.5	13.7	17.0	14.4	13.6	12.0	16.4	11.7	15.4	16.3	17.6	14.6	13.4	10.1	14.2	13.6
V	100	81	127	110	106	112	111	113	98	126	104	128	136	132	130	125	99	112	110
Cr	60	75	75	73	68	73	79	73	62	84	60	81	83	85	78	70	57	75	83
Co	22	12	27	10	18	23	19	20	15	19	16	20	20	24	20	17	14	15	12
Ni	37	25	42	25	36	55	34	38	26	39	25	32	39	43	41	32	29	30	31
Zn	97	59	98	62	76	110	80	100	80	90	77	74	75	99	64	80	51	96	66
Rb	146	131	181	142	166	188	178	187	142	216	147	190	206	228	185	153	158	225	232
Sr	91	79	94	157	105	113	150	125	108	157	110	138	157	163	111	111	100	99	93
Y	40	34	37	37	38	74	40	36	41	41	31	39	40	43	41	41	31	38	38
Zr	236	284	174	342	270	205	269	235	339	215	226	250	228	218	242	339	285	260	223
Nb	16	12	18	16	19	19	21	20	16	22	17	21	22	23	22	18	16	19	19
Cs	15	13	28	13	17	24	19	23	16	27	17	23	23	23	16	13	13	18	18
Ba	367	400	483	466	517	602	586	564	439	1395	541	671	729	634	655	500	471	893	579
La	42.2	37.7	37.3	47.5	42.7	50.1	45.3	41.1	47.6	44.2	37.6	45.5	46.5	47.8	46.8	48.8	39.9	43.1	43.1
Ce	79	79	82	86	82	85	89	82	89	86	68	84	89	92	90	93	72	80	82
Nd	36	33	33	39	30	50	36	29	39	33	29	26	42	34	34	38	26	31	30
Sm	8.1	6.1	8.8	7.5	7.6	16.2	7.2	6.8	7.7	8.2	5.9	6.7	7.4	7.5	7.0	7.5	6.3	6.3	6.3
Eu	1.9	1.4	2.0	1.5	1.8	4.2	1.5	1.4	1.7	1.9	1.3	1.6	1.6	1.6	1.6	1.6	1.3	1.4	1.4
Tb	1.0	0.9	1.1	0.8	1.0	2.2	0.6	0.8	0.9	1.1	0.7	0.8	1.0	0.9	0.9	0.8	0.8	0.8	0.9
Yb	3.7	3.4	3.8	3.5	3.8	5.7	3.7	3.4	3.8	3.7	3.0	3.7	3.8	3.8	3.6	3.8	3.2	3.5	3.5
Lu	0.55	0.53	0.56	0.53	0.59	0.85	0.55	0.58	0.56	0.58	0.45	0.55	0.56	0.55	0.54	0.56	0.49	0.53	0.54
Hf	5.9	6.7	4.9	7.6	6.4	5.4	6.3	5.6	7.8	5.5	5.3	6.2	5.8	5.6	5.8	8.1	7.1	6.4	5.8
Th	10.7	10.1	12.7	12.1	11.4	12.1	12.0	11.4	12.4	12.5	10.0	12.3	12.3	12.6	11.1	12.5	9.8	12.2	11.1
U	2.1	2.3	3.7	3.0	2.8	2.7	3.2	2.5	2.6	2.8	2.4	2.6	2.4	2.3	2.0	2.5	1.9	2.3	3.4
<i>Ratios</i>																			
CIW	96.9	97.4	97.4	97.2	97.1	96.0	97.1	97.0	96.7	97.1	97.8	98.3	97.7	98.1	96.7	97.1	91.3	97.2	95.8
CIA	68.9	67.9	70.6	69.9	68.5	69.0	68.7	69.5	71.8	70.1	72.3	71.9	71.1	70.5	72.1	72.5	66.2	69.9	68.5
PIA	94.8	95.4	95.7	95.5	95.0	93.5	95.1	95.0	94.8	95.3	96.7	97.4	96.3	96.9	95.0	95.6	86.1	95.5	93.0
(La/Yb) _{ch}	7.71	7.49	6.63	9.17	7.59	5.94	8.28	8.17	8.46	8.07	8.47	8.31	8.27	8.50	8.78	8.68	8.43	8.32	8.32
Eu/Eu*	0.77	0.72	0.74	0.68	0.76	0.83	0.75	0.68	0.73	0.74	0.73	0.79	0.69	0.71	0.74	0.73	0.67	0.72	0.70

Fig. 4. Major element compositional ranges normalized to the PAAS.

Fig. 5. Trace element compositional ranges normalized to the PAAS. Outlayer samples showing anomalous Y (VL6) and Ba (VL10) contents are shown separately.

GEOCHEMISTRY

The elemental concentrations are given in Table 1. The elemental distributions normalized to PAAS are shown in Figs. 4 and 5. REE plots normalized to chondrite (Taylor and McLennan, 1985) are reported in Fig. 7, with the PAAS (Taylor and McLennan, 1985) shown for comparison.

The inter-elemental relationships have been evaluated using R-mode factor analysis. The factors were extracted by Principal Component Analysis (PCA) using the Statistica ® package. This operation was performed on the standardized correlation matrix, thus weighting all the variables equally, and allowing us to convert the principal component vectors into factors. The factor loadings arranged as in Table 2 form the factor matrix. The communalities provide an index of the efficiency of the proposed set of factors (Davis, 1986) and the magnitude of the communalities here calculated suggests that most of the original variance is still accounted for our set of factors. Three factors explain 91.2% of the total variance associated with the chemical database (major and selected trace elements) of the analyzed samples.

Major elements

The redbeds are characterized by narrow compositional changes for Si, Ti, Al, Fe, Mg and K which have concentrations close to those of PAAS (Fig. 4). Ca, Na, and P are strongly depleted relatively to PAAS and Ca shows a high variability in concentration ranging from 0.10 to 0.89 wt %. Mn shows the highest relative dispersion in abundance, ranging from 0.01 to 0.20 wt % and the element is, in most of the samples, well below the PAAS value (0.11 wt %). The Mn depletion may be due to a sum of effects likely including source-area composition and redox chemistry of the element promoting Mn solubility as Mn^{2+} under surface conditions.

Al_2O_3 , Fe_2O_3 , and K_2O have high positive weights in the first factor obtained (53.2% of the total variance) whereas SiO_2 has a high negative weight. In pelites Al_2O_3 monitors clays (Crichton and Condie, 1993) and this factor may thus account for the competition between mica-like clay minerals and quartz. In the second factor (22.7% of the total variance) TiO_2 and MnO and TiO_2 and MgO have negative weights whereas MnO and MgO have a positive weight. This factor could account for the competition between cations in the structure of chlorite and possibly also in the structure of 2:1 clay minerals (illite, smectite).

Large ion lithophile trace elements (LILE): Rb, Cs, Ba, Sr

Sr, similarly to Ca, is depleted relatively to PAAS. Rb, Ba, and Cs, similarly to K, have abundances close to those of PAAS (Fig. 5). Sample VL 10 has the highest Ba content (1395 ppm) well above the PAAS content (650 ppm). Furthermore Rb and Cs, which behave similarly to K, have high positive weights in the first factor suggesting that these elements are mostly controlled by the mica-like clay minerals.

High field strength trace elements (HFSE): Y, Zr, Nb, Hf, REE, Th, U

HFSE have concentrations very similar to those of PAAS, although the intermediate rare earth elements (MREE) are enriched relative to the standard shale (Fig. 5).

The chondrite normalized REE patterns (Fig. 6) have a PAAS-like shape characterized by LREE/HREE fractionation (average $(La/Yb)_{ch} = 8.08 \pm 0.76$) and negative Eu-anomaly (average $Eu/Eu^* = 0.73 \pm 0.04$). The average $(La/Yb)_{ch}$ ratio is lower than the $(La/Yb)_{ch}$ of PAAS (9.2), whereas the Eu-anomaly is higher ($Eu/Eu^*_{PAAS} = 0.66$). Within this suite of samples VL6 is an

Table 2. *R-mode Factor analysis: weights of the variables in the extracted factors. Variables having weight less than 0.600 are omitted.*

	F1	F2	F3
SiO ₂	-0.96		
TiO ₂		-0.83	
Al ₂ O ₃	0.90		
Fe ₂ O ₃	0.65		
MnO		0.81	
MgO		0.61	
K ₂ O	0.77		
Sc	0.91		
V	0.79		
Cr	0.68		
Co	0.76		
Ni	0.82		
Zn	0.65		
Rb	0.76		
Cs	0.87		
Zr	-0.71		
Hf	-0.67		
Nb	0.85		
Th	0.64		
La			0.84
Eu		0.69	
Yb			0.61
Y			0.61
Var. %	53.2	22.7	15.3

outlier having very low (La/Yb)_{ch} (5.94) and low Eu-anomaly (Eu/Eu* = 0.83) also coupled to the highest Y concentration.

In the first factor obtained by factor analysis Zr and Hf have negative weights, like silica, whereas Th and Nb have positive weights. Zr and Hf in sediments are controlled by zircon, and due to a combination of resistance to weathering and high specific gravity, this mineral suffers a sorting related fractionation which, in turn, means that Zr and Hf are most affected by gravitative fractionation (e.g., Taylor and McLennan, 1985). In the contrast Th and Nb, which in clastic sediments are usually hosted by resistate minerals (apatite and Ti-oxides) which follow the fate of the clay-sized component, are not seriously affected by sorting-related fractionation.

Eu has significant positive weights in the second factor. It is well known that Eu, due to its different redox chemistry, and differently from the remaining REE's, is concentrated in plagioclase. The weight of the element in this factor may thus indicate that most of the Eu released during plagioclase dissolution could have been trapped by clay minerals by adsorption phenomena, as a mechanism which has proposed, on the basis of mass balance considerations, for fine grained sediments (Mongelli, G. *et al.*, 1996).

Fig. 6. Rare earth element compositional ranges, chondrite-normalized (Taylor and McLennan, 1985). The plot of the Post Archean Australian Shales is shown for comparison. Sample VL6, showing higher content in MREE and HREE is shown separately.

La, Yb, and Y, which behave like HREE, have positive weights in the third factor (15.3% of the total variance). The lack of correlation with Al₂O₃, is consistent with the observation that in pelites these elements are generally housed in accessory phases (e.g., Slack and Stevens, 1994; Mongelli, G. *et al.*, 1996). We infer that these elements occur in the sediment mostly as resistate phases, supporting the idea they efficiently record the provenance (e.g., McLennan *et al.*, 1993; Cullers, 1994; Girty *et al.*, 1996; Hassan *et al.*, 1999; Bauluz *et al.*, 2000).

Transition trace elements (TE): Sc, V, Cr, Co, Ni, Zn

The concentrations of Sc, V, and Zn, are close to those of PAAS, whereas Cr, Co, and Ni have abundances generally slightly lower than those of PAAS.

All the transition metals appear to covary in the first factor with Al₂O₃, Fe₂O₃, and K₂O, suggesting these trace elements are mostly hosted by mica-like clay minerals.

DISCUSSION

The chemical composition of clastic sediments depends on several factors including source-area composition, palaeoweathering, sorting, and in some cases, burial history. Thus in using terrigenous sediment to monitor provenance one is faced with the nontrivial problem to evaluate and minimize the effects of the other factors.

Source-area weathering

The most widely used chemical index to determine the degree of source-area weathering is the Chemical Index of Alteration (CIA) proposed by Nesbitt and Young (1982). This index, which works correctly when Ca, Na, and K decrease as the intensity of weathering increases (e.g., Duzgoren-Aydin *et al.*, 2002), can be calculated

Fig. 7. a) Ternary A-CN-K plot. Legend: Gr, granite; Ms, muscovite; Ill, illite; Ka, kaolinite; Ch, chlorite; Gi, gibbsite; Sm, smectite. The samples fall close to the A-K join along a trend indicating K addition during diagenesis. b) A-C-N plot. The samples fall close to the A apex suggesting intense weathering at the source. See text for more details.

using molecular proportion:

$$\text{CIA} = [\text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O})] \times 100$$

where CaO* is the amount of CaO incorporated in the silicate fraction only. In general, CIA values in Phanerozoic shales ranging from 70 to 75 reflect muscovite, illite and smectite compositions, and indicate a moderately weathered source, whereas CIA values close to 100 are due to more intense weathering which produces residual clays enriched in kaolinite and Al oxi-hydroxides.

The CIA values of analyzed redbeds are very low (66–73, average = 69.9 ± 1.7) and in the A-CN-K triangular diagram the samples plot in a tight group on the A-K join, and close to the muscovite point (Fig. 7a), suggestive of K-enrichment during diagenesis, according to the mineralogical investigation. Since the CIA index is not sensitive to the weathering degree when K reintroduction occurs in the system, as in the present case, alternative indices can be used to monitor paleo-weathering at the source. Harnois (1988) proposed the CIW index (Chemical Index of Weathering) which is not sensitive to post-depositional K-enrichments and, similar to the CIA, is a molecular immobile/mobile ratio based on the assumption that Al remains in the system and accumulates in the residue while Ca and Na are leached away:

$$\text{CIW} = [\text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O})] \times 100$$

where CaO* is the amount of CaO incorporated in the silicate fraction only. Phanerozoic shales have CIW values close to 85 and higher values are indicative of intense weathering. The redbeds, with the exception of the sample VL17, show very uniform CIW values (95–98, average = 97.1 ± 0.65) and in the A-C-N diagram form a tight array close to the A apex (Fig. 7b) suggestive of intense weathering in steady-state conditions where ma-

terial removal rate matches the production of mineralogically uniform weathering products generated in the upper zone of soil development. Sample VL17 has a slightly lower CIW index (91) suggestive of less intense weathering at the source.

The degree of the chemical weathering can also be estimated using the Plagioclase Index of Alteration (Fedo *et al.*, 1995); in molecular proportions:

$$\text{PIA} = [(\text{Al}_2\text{O}_3 - \text{K}_2\text{O}) / (\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} - \text{K}_2\text{O})] \times 100$$

where CaO* is the CaO residing only in the silicate fraction. Unweathered plagioclase has PIA value of 50 whereas the PAAS has PIA value of 79. The redbeds, with the exception of the sample VL17 (PIA = 86), show very high PIA values (93–97, average = 95.3 ± 1.08) indicating that most of the plagioclase has been converted to clay minerals. This, in turn, accords with data obtained using the CIW index, and indicates intense weathering at the source area.

Although the REE are quantitatively transferred from the source to the sediment (e.g., McLennan *et al.*, 1993), intense weathering produces LREE/HREE fractionation (e.g., Mongelli, 1998), possibly due to preferential HREE retention in solution (e.g., Cantrell and Byrne, 1987). For instance carbonate complexes show an increase in stability with increasing atomic number and a preferential retention of HREE in solution as carbonate ions may cause an increase in the $(\text{La}/\text{Yb})_{\text{ch}}$ and slight alkaline conditions may also favour a preferential LREE retention via adsorption onto particle surfaces (Sholkovitz, 1995). This in shales and mudstones may be recognized by both higher values of the $(\text{La}/\text{Yb})_{\text{ch}}$ ratio relatively to the $(\text{La}/\text{Yb})_{\text{ch}}$ of the PAAS and the UCC and significant correlations between this ratio and the weathering indices (Mongelli, 2004). In this case the $(\text{La}/\text{Yb})_{\text{ch}}$ index (average = 8.08 ± 0.76) is lower than the $(\text{La}/\text{Yb})_{\text{ch}}$ of the PAAS (9.2) and it

Fig. 8. Ternary $10\text{Al}_2\text{O}_3$ - 200TiO_2 -Zr plot showing possible sorting effects. See text for more details.

is not correlated with the weathering indices ($\text{CIW}-(\text{La}/\text{Yb})_{\text{ch}}$, $r = 0.06$; $\text{PIA}-(\text{La}/\text{Yb})_{\text{ch}}$, $r = 0.09$).

The lack of evidence of intense paleoweathering at the source depicted by the LREE/HREE fractionation is inconsistent with the results obtained using the weathering indices (CIW and PIA). Both CIW and PIA indices are strongly controlled by the amount of plagioclase in the rock, and their paucity in the redbeds could be also record a recycling effect which may especially involve the siliciclastic metasediments of the basement.

Sorting and recycling

It is well known that transport and deposition of clastic sediments involves mechanical sorting. Its effect on the chemical composition of terrigenous sediments is important and may affect the distribution of paleoweathering and provenance proxies (Bauluz *et al.*, 2000; Le Pera *et al.*, 2000). The distribution of the chemical components within a suite is mainly determined by the mechanical properties of the host minerals. The process basically fractionates Al_2O_3 (clay minerals) from SiO_2 (quartz and feldspars). Sorting also fractionates TiO_2 , mostly present in clay minerals and Ti-oxides, from Zr, present in zircon, and sorted with quartz. However, the variable content of inert elements in mudstone is mostly due to the weathering degree, which affects parent rocks. Ternary plots based on Al_2O_3 , TiO_2 , and Zr eliminate the weathering effects and may illustrate the presence of sorting-related fractionations which are recognizable by simple mixing trends on a ternary Al_2O_3 - TiO_2 -Zr diagram (Garcia *et al.*, 1991). In our case a mixing trend, mostly characterized by changes in the $\text{Al}_2\text{O}_3/\text{Zr}$ ratio, which could be due to a recycling effect, is clearly envisaged

Fig. 9. Th/Sc vs. Zr/Sc plot. Samples depart from the compositional trend indicating zircon addition suggestive of a recycling effect.

(Fig. 8). Zircon, and thus Zr enrichment during sorting, can also be evaluated when the Zr/Sc ratio, a useful index of sediment recycling (e.g., Hassan *et al.*, 2000), is plotted against the Th/Sc ratio, an indicator of chemical differentiation (McLennan *et al.*, 1993). The redbeds are not clustered along the primary compositional trend but fall along a trend involving zircon addition (Fig. 9) and thus sediment recycling, consistent with the Al_2O_3 - TiO_2 -Zr diagram. In addition recycling could significantly affect the weathering indices which likely monitor a cumulative effect including a first cycle of weathering at the source which produced the siliciclastic metasediments of the basement.

It is interesting to observe that the Late Triassic-Earliest Jurassic was the time of rifting between Gondwana and Laurasia; initiation of ocean basin formations, rifts and microplates in the western Tethys region and rapid northward drift of the Cimmerian continent, by active seafloor spreading within the Neotethys Ocean (Sengör, 1984), occurred during this time. In the early-late Jurassic time the carbonate sedimentation predominated along all Neotethyan margins (Dercourt *et al.*, 1993; Fourcade *et al.*, 1996); shallow platform grainstones to argillaceous deeper-water carbonates accumulated on the passive margin shelves of the western Neotethys. In the Calabrian-Peloritani Arc indeed the mudstones evolve from continental-transitional redbeds to slope and deep-marine carbonate/clastic sequences (Zuffa *et al.*, 1980).

The late Triassic (Norian supersequence) corresponds with a low first-order sea level stand and a time of high continental emergence; the Early Jurassic (Pliensbachian-Toarcian supersequence) was the time of the initiation of the first-order sea level rise in the mid-Mesozoic (Golonka, 2000, 2002). The Early Jurassic was generally

Fig. 10. La-Th-Sc plot. The redbeds fall in a region close to the PAAS point that rules out mafic supply.

marked by a transgressive trend that would continue throughout the entire Jurassic. The transition from icehouse to greenhouse conditions continued in this time (Frakes *et al.*, 1992); greenhouse conditions prevailed with a warm, humid environment, and moderate temperatures into high latitudes, generally arid continental interiors, and no evidence of significant continental glaciation (Golonka, 2000, 2002).

The chemical weathering of such rocks under hot, episodically humid climate with a prolonged dry season, would produce illitization of silicate minerals, oxidation of iron and concentration of quartz in thick soil profiles, that were later denudated by fluvial erosion, producing relatively mature, quartz-rich red deposits. Moreover, palaeocurrent analysis clearly indicates that terrigenous clastics derived from rapid erosion of reliefs located to the N, NW and W of the present-day outcrops of the Calabria-Peloritani Arc realms.

The wet-humid conditions favored the formation of stream channels that eroded the soil profiles, whereas the dry season favoured the sedimentation; successively a new wet-humid conditions causes the erosion of the sediments formed before. The alternation in the early Jurassic time of these two different climatic conditions favoured the recycling process affecting the studied sediments as showed in the Al_2O_3 -Zr-TiO₂ and Th/Sc vs. Zr/Sc diagrams.

Provenance

It is generally accepted that among trace elements HFSE, especially REE and Th, and some transition elements, including Sc and Cr, are useful to constrain the

Fig. 11. Cr/V vs. Y/Ni diagram. Curve model mixing between granite and ultramafic end-members. Ultramafic sources have very low Y/Ni and high Cr/V ratio. The samples have Y/Ni and Cr/V ratios which exclude mafic supply.

average provenance composition (e.g., Taylor and McLennan, 1985; Fedo *et al.*, 1996; Cullers and Berendsen, 1998). In our case, although we may assume that the metasediments of the Paleozoic basement were a first order source we have to test if other lithologies occurring in the basement, including mafic metavolcanic, represented an additional provenance terrane to the redbeds.

A minor supply from mafic metavolcanic rocks cannot be excluded since the Eu anomaly, which is retained as the more conservative provenance proxy (e.g., McLennan *et al.*, 1993; Mongelli *et al.*, 1998; Cullers, 2000), is slightly higher (average $\text{Eu}/\text{Eu}^* = 0.73 \pm 0.04$) than the PAAS value ($\text{Eu}/\text{Eu}^* = 0.66$). It is important to observe that, although the precise effects of recycling on REE distribution are uncertain, it could be expected that Eu/Eu^* should increase, as more feldspar is destroyed in a second weathering cycle (Hassan *et al.*, 1999). On this basis we may state that the average Eu/Eu^* of the redbeds, slightly higher than that of the PAAS, could likely monitor supply of low Eu/Eu^* mafic detritus which compensated for the recycling effect by reducing Eu/Eu^* . In our case, however, the results of the Principal Component Analysis, as previously stated, suggest that most of the Eu released during the dissolution of feldspar should be retained by clay minerals thus minimizing the recycling-induced increase of the Eu-anomaly. This may imply that the recycling effect on the Eu-anomaly was minor and, in turn, that the low Eu/Eu^* mafic detritus supply was also minor although not negligible.

The limited importance of a mafic supply is confirmed also by other provenance proxies including the La-Th-Sc plot and the Cr/V and Y/Ni ratios. The La-Th-Sc plot has been used to discriminate sediments from felsic sources

to progressively more mafic sources (Bhatia and Crook, 1986; Cullers, 1994). The redbeds fall in a region close to the PAAS point (Fig. 10) that clearly rules out a predominantly mafic source; a significant mafic-ultramafic supply is excluded also on the basis of the mixing curve between granite and a mafic-ultramafic end-member (Fig. 11) in the Y/Ni vs. Cr/V diagram.

Burial history

The reaction in which smectite is a reactant and illite a product, recognized to occur over a predictable range of depth in mudstones, is here used as a comparative “geothermometer” jointly with the illite crystallinity value (IC), expressed as Kübler Index (KI). Usually, the smectite-to-illite reaction concerns the diagenetic range, whereas the illite “crystallinity” improvement and the mica polytype 2M₁ percentage variation mainly applies to the early stages of metamorphism, i.e., very low (anchizone) and low (epizone) grades (Chamley, 1995).

In estimating temperatures from clay minerals evolution in the Longi succession, the basin maturity chart, showing correlation of reaction progress in the smectite-I/S-illite series and IC with temperature, proposed by Merriman and Frey (1999) was adopted, since it refers to a large variety of geological settings and is therefore more representative of the evolution of such minerals through time. So by integrating data relative to the percentage of illitic layers in I/S mixed layers with illite crystallinity values, expressed as Kübler Index (KI), the temperature experienced by the Longi Units following the Basin Maturity Chart (BMC) of Merriman and Frey (1999), can be estimated as in the range of 100–150°C.

Starting from the temperature estimates by clay-minerals-based geothermometers and considering an average geothermal gradient of 20/30°C (Mongelli, F. *et al.*, 1996), a diagenetic/tectonic evolution corresponding to about 4–5 km of lithostatic/tectonic loading can be hypothesized for the Longi succession.

CONCLUSIONS

Geochemistry and mineralogy of Mesozoic continental redbeds from the typical Longi stratigraphic section of the Peloritani Mountains suggest a complex history. The redbeds have concentrations very similar to those of the PAAS for Si, Ti, Al, Fe, Mg, K, Rb, Ba, Cs, HFSE, and transition metals whereas Ca, Na, P, and Sr are strongly depleted.

The mineralogical assemblage, dominated by the occurrence of illite and illite/smectite mixed layers, coupled to the CIA index and to the A-CN-K plot, indicates that post-depositional K-enrichments affected the bulk composition of the rock. CIW and PIA indices suggest that weathering at the source was intense and occurred in

steady-state conditions. Since CIW and PIA indices are strongly controlled by the amount of plagioclase in the rock, their paucity in the redbeds likely record a recycling effect which may especially involve the siliciclastic metasedimentary basement rocks.

The distribution of Al₂O₃, TiO₂, and Zr and the values of the Zr/Sc and Th/Sc ratios further support this idea. In the Zr/Sc vs. the Th/Sc plot the redbeds are not clustered along the primary compositional trend but fall along a trend involving zircon addition and thus sediment recycling. Zr addition may also account for the observed low (La/Yb)_{ch} ratio of the redbeds. In addition, recycling could significantly affect the weathering indices which likely monitor a cumulative effect including a first cycle of weathering at the source which produced the siliciclastic metasediments of the basement. During Early Jurassic weathering likely occurred under hot, episodically humid climate with a prolonged dry season. The wet-humid conditions promoted erosion whereas the dry season favored the sedimentation. Thus, climate alternation favored the recycling process affecting the studied sediments as showed in the Al₂O₃-Zr-TiO₂ and Th/Sc vs. Zr/Sc diagrams.

Although we may assume that the metasediments of the Paleozoic basement were a first order source lithologies an additional provenance terrane occurring in the basement, including metavolcanic rocks of mafic composition cannot be excluded, since the Eu anomaly, which is retained as the more conservative provenance proxy, is slightly higher than the PAAS value.

Although the precise effects of recycling on REE distribution are uncertain, the Eu/Eu* should increase, as more feldspar is destroyed in a second weathering cycle which, in turn, involves that the Eu/Eu* ratio of the redbeds could monitor a supply of low Eu/Eu* mafic detritus which compensate for the recycling effect by reducing Eu/Eu*. Statistical analysis (PCA) however suggests that most of the Eu released during the dissolution of feldspar should be retained by clay minerals thus contributing to minimize the recycling induced increase of the Eu-anomaly. This may involve that the recycling effect on the Eu-anomaly was minor and that the low Eu/Eu* mafic detritus supply was also minor. The limited importance of a mafic supply is confirmed also by other provenance proxies including the La-Th-Sc plot and the Cr/V and Y/Ni ratios.

Finally, the estimated temperature experienced by the Longi Units, obtained by coupling data relative to the percentage of illitic layers in I/S mixed layers with the illite crystallinity values, expressed as Kübler Index (KI), is in the range of 100–150°C. Starting from the temperature estimates by clay-minerals-based geothermometers the diagenetic/tectonic evolution should correspond to a lithostatic/tectonic loading of about 4–5 km.

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