

Abyssal Cretaceous Varicolored Clays of the Northern Apennines of Italy: mineralogical, geochemical and paleontological insights

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Supplementary Materials

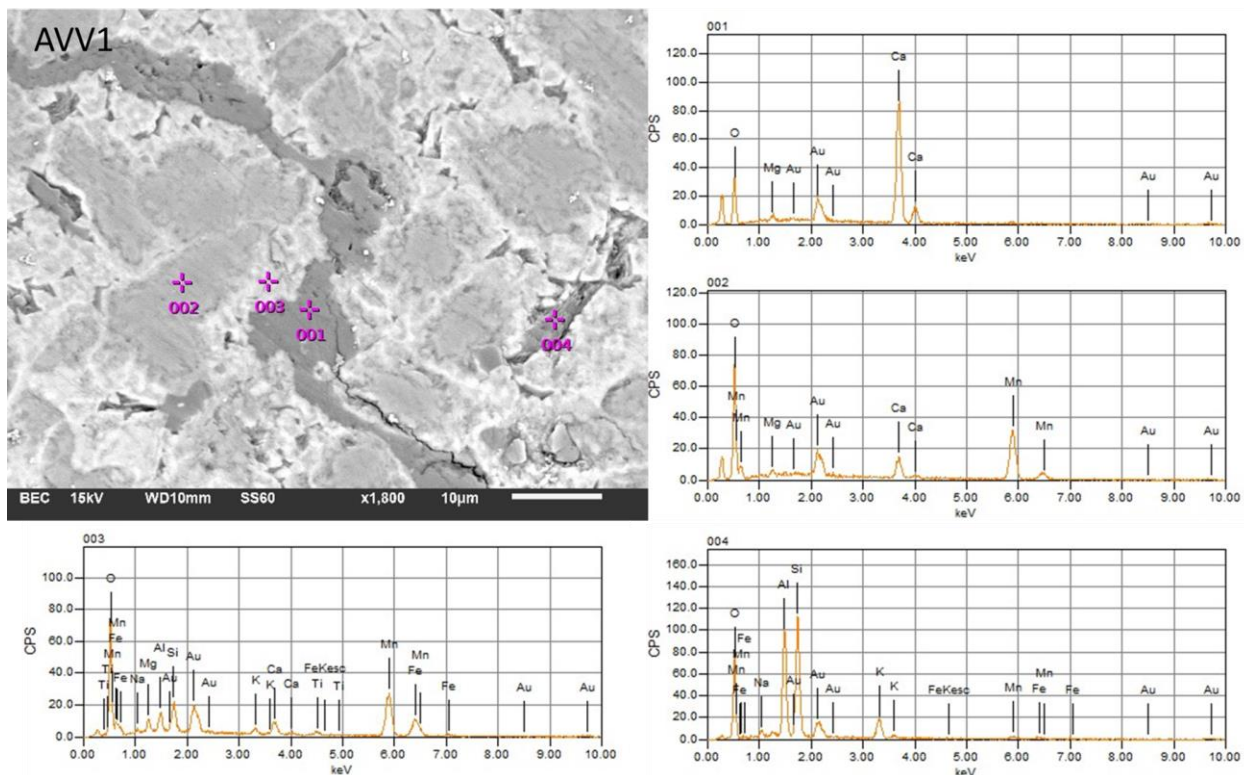
Table 15. Major and trace elements composition of AVV concretions from XRF measurements. L.O.I. is Loss on Ignition.

		AVV1	AVV2	AVV3	AVV4	AVV5	AVV6	AVV7	BAI4
SiO ₂	(%)	6.55	6.15	1.36	1.52	0.34	4.4	13.74	4.61
Al ₂ O ₃	(%)	2.31	2.27	0.6	0.63	0.2	1.79	3.99	1.45
Fe ₂ O ₃	(%)	17.41	18.33	1.15	1	0.94	6.37	8.24	0.45
MnO	(%)	39.51	32.53	0.9	0.23	0.6	47.63	32.53	245 (ppm Mn)
MgO	(%)	2.29	3.38	0.45	0.54	0.38	1.97	2.56	0.31
CaO	(%)	5.68	4.69	59.58	54.97	58.09	5.09	8.48	0.95
Na ₂ O	(%)	0.24	0.14	0.08	0.05	0.05	0.25	0.27	0.16
K ₂ O	(%)	0.37	0.25	0.03	0.03	0	0.19	0.37	0.18
TiO ₂	(%)	0.09	0.07	0.04	0.04	0.02	0.04	0.09	-
P ₂ O ₅	(%)	0.21	0.18	0.02	0.02	0.02	0.06	0.1	83 (ppm P)
L.O.I.	(%)	26.09	32.92	35.76	40.89	39.36	31.93	29.68	1.03
Trace elements (ppm)									
F	(ppm)	udl	udl	udl	udl	udl		udl	
S	(ppm)	480	312	106	208	108	379	1162	28.69 (wt.% SO ₃)
Cl	(ppm)	83	80	76	69	76	138	64	296
Sc	(ppm)	10	udl	udl	udl	udl		11	
V	(ppm)	53	27	11	11	9		38	
Cr	(ppm)	udl	udl	udl	udl	udl		udl	
Co	(ppm)	40	15	udl	udl	udl	134	62	
Ni	(ppm)	64	28	udl	udl	udl	157	80	
Cu	(ppm)	62	10	udl	udl	udl		28	
Zn	(ppm)	196	67	15	33	7	120	97	
Ga	(ppm)	udl	udl	udl	udl	udl		udl	
As	(ppm)	11	udl	udl	udl	udl		udl	
Rb	(ppm)	15	12	3	2	1		16	
Sr	(ppm)	1400	66	479	650	591	261	330	0.165 (wt.% SrO)
Y	(ppm)	24	26	51	24	29		27	
Zr	(ppm)	11	16	udl	udl	udl		17	
Nb	(ppm)	udl	udl	udl	udl	udl		udl	
Mo	(ppm)	udl	udl	udl	udl	udl		udl	
Cd	(ppm)	34	27	7	6	9		21	
Sn	(ppm)	udl	udl	udl	udl	udl		udl	
Sb	(ppm)	udl	udl	udl	udl	udl		udl	
Cs	(ppm)	udl	udl	udl	udl	udl		udl	
Ba	(ppm)	227	74	11	14	13	1881	5733	61.94 (wt.% BaO)
Pb	(ppm)	39	13	5	3	2	55	22	
La	(ppm)	34	34	46	42	28		26	
Ce	(ppm)	udl	udl	73	58	41		udl	
Nd	(ppm)	udl	udl	45	37	25		udl	
Th	(ppm)	udl	4	2	udl	udl		2	
U	(ppm)	udl	udl	udl	udl	udl		udl	

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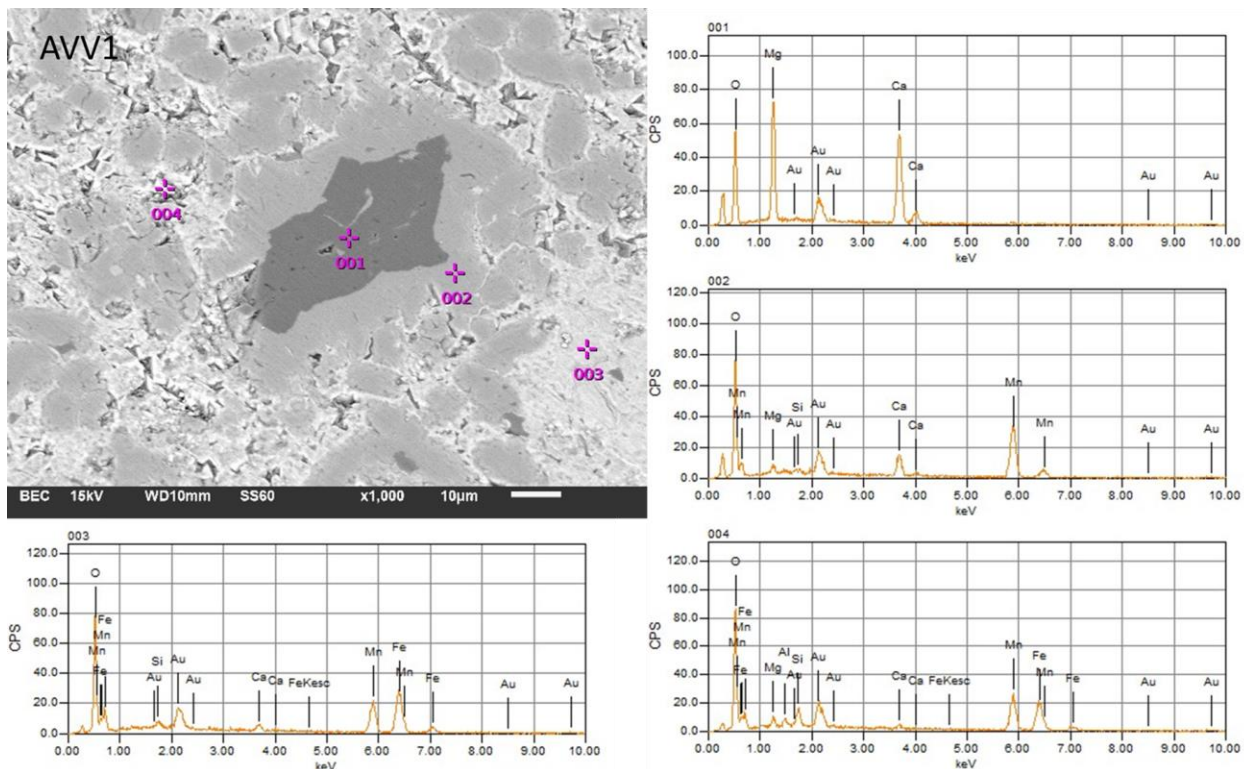


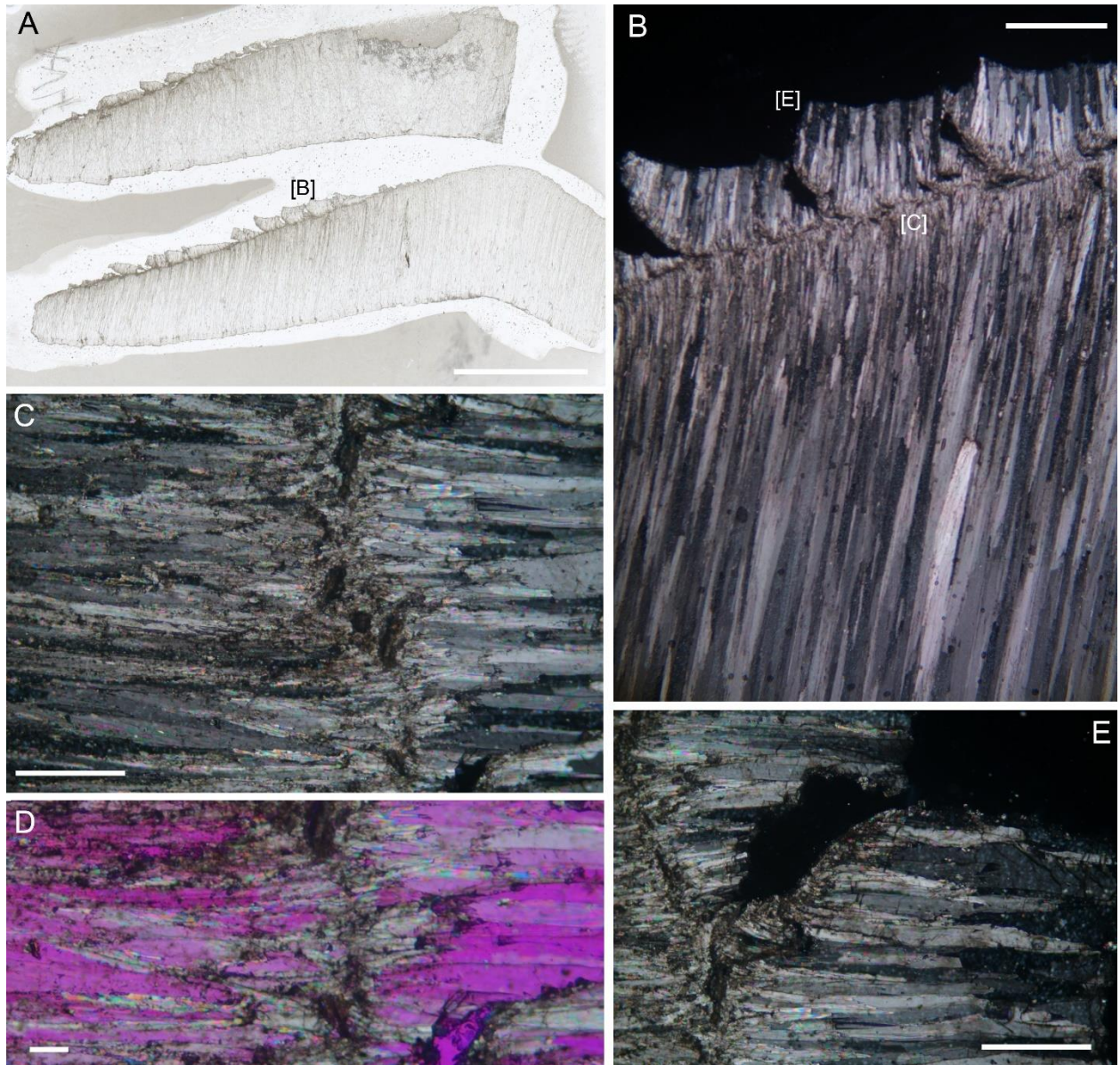
c)



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d)





30 **Figure 2S. Petrographic thin section of diagenetic calcite veins (AVV4). A)** Overview of the thin section in plane-polarized light (PPL); **B)** surface detail of the sample under cross-polarized light (CPL); **C,D,E)** clay pockets in between calcite fibers (**C,E** under CPL; **D** under CPL with gypsum plate). Letters in square brackets correspond to panels position. Scale bars are: **A)** 1cm; **B)** 1mm; **C)** 200 μm ; **D)** 50 μm ; **E)** 300 μm . Compare with Fig. 10.

Table 2S. Carbon and oxygen stable isotope data from the analyzed concretions, veins and associated wall rocks.

Subunit	Coordinates	Description	Name	CO ₂	
				δ ¹⁸ O ??	δ ¹³ C (VPDB)
C	44°30'42"N 10°37'16"E	diagenetic calcite vein	ET-F	-7,32	1,77
C	44°30'42"N 10°37'16"E	diagenetic calcite vein	2020 Fa	-7,00	0,85
C	44°30'42"N 10°37'16"E	diagenetic calcite vein	F2 2020	-6,19	2,22
C	44°30'42"N 10°37'16"E	diagenetic calcite vein	F2 2020	-7,05	2,48
C	44°30'42"N 10°37'16"E	diagenetic calcite vein_WR	2020 Fa_WR	-3,60	1,39
C	44°30'42"N 10°37'16"E	diagenetic calcite vein_WR	2020 Fa_WR	-3,17	1,42
A	Undefined	tabular concretion (Mn rich carbonate)	ET4	0,70	-9,02
A	Undefined	tabular concretion (Mn rich carbonate)	ET4	0,69	-9,10
A	Undefined	tabular concretion (Mn rich carbonate)	ET4	0,22	-9,05
A	Undefined	fossil trace (Mn rich carbonate)	ET1	1,16	-5,01
A	Undefined	fossil trace (Mn rich carbonate)	ET1	0,34	-4,94
	Undefined	barite-rich concretion	BAI4	-3,25	1,92
C (in tectonic contact with B)	44°30'36"N 10°37'31"E	tectonic calcite vein	Etm_M1a	-4,10	0,17
C (in tectonic contact with B)	44°30'36"N 10°37'31"E	tectonic calcite vein	Etm_M1a	-3,31	0,26
C (in tectonic contact with B)	44°30'36"N 10°37'31"E	tectonic calcite vein	Etm_M1a	-4,22	0,15
C (in tectonic contact with B)	44°30'36"N 10°37'31"E	tectonic calcite vein	Etm_M2a	-3,02	1,22
C (in tectonic contact with B)	44°30'36"N 10°37'31"E	tectonic calcite vein	Etm_M2a	-3,42	1,21
C (in tectonic contact with B)	44°30'35"N 10°37'31"E	tectonic calcite vein	Etm_L	-3,98	0,28
C (in tectonic contact with B)	44°30'35"N 10°37'31"E	tectonic calcite vein	Etm_L	-3,13	0,40
C (in tectonic contact with B)	44°30'35"N 10°37'31"E	tectonic calcite vein	Etm_F1	-4,96	1,25
C (in tectonic contact with B)	44°30'35"N 10°37'31"E	tectonic calcite vein	Etm_F1	-6,12	1,10
C (in tectonic contact with B)	44°30'35"N 10°37'31"E	tectonic calcite vein	Etm_F1	-6,38	1,21
C (in tectonic contact with B)	44°30'35"N 10°37'31"E	tectonic calcite vein	Etm_F1	-4,37	1,76
C (in tectonic contact with B)	44°30'35"N 10°37'31"E	tectonic vein_WR	Etm_F1_WR	-6,94	1,05
C (in tectonic contact with B)	44°30'35"N 10°37'31"E	tectonic vein_WR	Etm_F1_WR	-5,71	1,02
C (in tectonic contact with B)	44°30'36"N 10°37'31"E	tectonic vein_WR	Etm_M1a_WR	-3,76	-0,15
C (in tectonic contact with B)	44°30'36"N 10°37'31"E	tectonic vein_WR	Etm_M1a_WR	-4,15	-0,12
C (in tectonic contact with B)	44°30'36"N 10°37'31"E	tectonic vein_WR	Etm_M2a_WR	-4,20	1,33
C (in tectonic contact with B)	44°30'36"N 10°37'31"E	tectonic vein_WR	Etm_M2a_WR	-4,16	1,23
C (in tectonic contact with B)	44°30'35"N 10°37'31"E	tectonic calcite vein	Etm_L_WR	-2,77	-0,06
C (in tectonic contact with B)	44°30'35"N 10°37'31"E	tectonic calcite vein	Etm_L_WR	-1,73	0,40

Table 3S. Organic matter decomposition zones according to Hesse and Schacht, 2011.

Bacteria	Diagenesis		Thickness	Organic Matter Decomposition Zones	
aerobic bacteria and facultative aerobes at the bottom.	oxic diagenesis	early diagenesis	from a few mm to hundreds of m Absent in stagnant or euxinic basins.	(1) the oxidation zone (OZ) Dissolved O ₂ from sea water trapped in the sediment. Microbial degradation of organic molecules (e.g. hydrocarbon chains and carboxyl groups, ...) and conversion of smaller molecules (e.g. acetate, lactate, propionate, isobutyrate) to CO ₂ . Aerobic bacteria consume O ₂ , locally and temporary inducing oxygen depletion, especially with high sedimentation rates and low water diffusion. Brownish/yellowish sediment color. Biological remnants preservation is a function of their residence time in this zone.	positive electrochemical potential
aerobic (at the top) and dysaerobic bacteria, Nitrate reducers	suboxic diagenesis		a few cm	(2) the nitrate-reduction zone (NR) O ₂ < 0.5 cm ³ /10 ³ cm ³ H ₂ O. Benthic macroorganisms disappear from the sediment. Nitrates produced in the OZ reach a maximum concentration at the top of the NR and goes to zero at the bottom. Nitrate thus trace both oxic and suboxic diagenesis. Oxides and hydroxides of manganese and iron are reduced and become soluble thus serving as important sources of oxidant (electron acceptor) in addition to the nitrate of the pore water. Manganese is reduced nearly simultaneously with nitrate and Mn ²⁺ either diffuses to the bottom seawater or is reoxidized. Iron reduction starts after manganese reduction at greater depth, at the boundary with the SR zone. Both manganese and iron reduction are hydrogen-ion consuming reactions, increasing the pH, and allowing the possible precipitation of early diagenetic carbonates in concretions.	
Sulphate reducers. The sulphate-reducing bacterium <i>Desulfovibrio desulfuricans</i> is the dominant species. Small organic molecules (lactic acid, four-carbon dicarboxylic acids) are produced by fermenting bacteria and then oxidized by sulphate reducers. This symbiosis is a prerequisite for the SR process.	anoxic diagenesis		from a few cm to a few m	(3) the sulphate-reduction (SR) zone In the upper SR zone, 1/3 of the organic-matter is oxidized to reduce iron and 2/3 to reduce sulphate. Hydrogen sulfide is produced by sulphate reduction. Reduction of Fe ³⁺ continues producing Fe ²⁺ and inducing instantaneously precipitation of metastable FeS, keeping dissolved sulfide concentrations low (<5 mM). FeS is later converted to pyrite. In iron-poor marine carbonate oozes, the process will lead to elevated sulfide levels and produce sour gases. The SR zone is considerably thicker than the NR zone because dissolved sulphate is about 3 orders of magnitude more abundant (27 mM) than nitrate in oceanic bottom waters.	negative electrochemical potential
carbonate reducers and methanogenic bacteria (e.g. <i>Methanothermobacter thermautotrophicus</i>)				(4) the carbonate-reduction (or methane-generation) zone (CR) Previous oxidation steps mainly produce carbonic acid, its dissociated species bicarbonate, HCO ₃ ⁻ , or carbonate, CO ₃ ²⁻ . Below the SR zone, carbonate becomes the main oxidants for further organic-matter oxidation by methanogenic bacteria producing methane. H ₂ produced by other organic matter degradation processes is used by bacteria to reduce HCO ₃ ⁻ and CO ₃ ²⁻ . Oxidation inhibits the buildup of CH ₄ by upward diffusion to any substantial levels in the SR zone.	
fermenters				(5) the fermentation zone Bacterial fermentation reactions of organic compounds produce oxygen that is used to oxidize other organic matter, simultaneously yielding CO ₂ and CH ₄ .	
Only a few thermophilic bacterial populations.			intermediate diagenesis	(6) the thermocatalytic decarboxylation zone At temperatures above 75 °C, bacterial activity ceases and thermocatalytic reactions start. Abiogenic thermocatalytic reactions induce decarboxylation (CO ₂ removal) of organic acids generating aggressive acidic pore waters that may dissolve carbonates and feldspars, leading to secondary porosity in sandstones.	