Pleistocene Sea Levels possibly indicated by Buried Black Sediments in the Black Sea

MODERN surface sediments containing H_2S are often coloured black by fine grained, iron monosulphide minerals such as mackinawite, $Fe_{1+x}S$, and greigite, Fe_3S_4. The black monosulphides are thermodynamically unstable, under H_2S-rich sedimentary conditions, relative to the disulphide pyrite, FeS_2[1,2], which is not a black pigmenting agent. As a result, the black colour normally disappears with depth during diagenetic transformation to pyrite[2,3]. In some situations, however, such as in older buried layers of the deep water sediments of the Black Sea, the black monosulphides persist.

Volkov[4] has shown that the black sediment of the Black Sea, when compared with the more common lighter grey sediment, is characterized by low concentrations of pyrite, lower total reduced sulphur, high concentrations of iron monosulphides, and very low dissolved H_2S in associated pore waters. He has suggested that this black sediment results from limited bacterial sulphate reduction during early diagenesis with insufficient hydrogen sulphide formed to enable complete transformation of black "FeS" to FeS_2. Recent analyses confirm these conclusions (see Table 1). Methods of determination of each constituent have been described previously[2]. Note that the total "reactive" iron content (pyrite iron plus HCl-(soluble iron) does not consistently differ between grey, pyritic sediment and black sediment. Thus the decrease in total reduced sulphur in the black layers must have been caused by a lower original production of H_2S by bacteria.

Limited H_2S production in anaerobic sediments and bottom waters is related primarily to (1) a low concentration of bacterially metabolizable organic matter, or (2) a low concentration of dissolved sulphate. Because the black layers of the Black Sea sediment are not distinctly different in organic carbon content from interbedded grey layers (see Table 1), barring such speculative factors as trace metal bacterial poisoning, the lowered H_2S production during deposition of the black layers must have been caused by a low concentration of dissolved sulphate in the overlying water. In a low sulphate situation, diffusion of sulphate into sediments may be too slow to provide enough sulphur for the complete diagenetic transformation of iron monosulphides to pyrite.

Table 1. MEASURED PARAMETERS FOR A CORE (1464-K) OF BLACK SEA SEDIMENT

Sampling depth range	Colour	Per cent sulphur as— $FeS + Fe_3S_4$	FeS_2	"Reactive" iron (per cent)	Organic carbon (per cent)
152–155 cm	Black	0·58	0·30	6·13	0·56
157–159	Black	0·74	0·22	7·10	0·58
162–164	Black	0·75	0·31	6·47	0·60
166–168	Grey	0·01	1·99	6·42	0·59
172–175	Grey	0·01	1·59	6·27	0·77
181–185	Grey	0·01	1·40	5·19	0·77
239–241	Grey	0·01	1·82	6·31	0·52
247–249	Black	0·33	0·30	5·18	0·59
259–262	Black	0·44	0·20	5·89	0·49
270–272	Black	0·58	0·44	5·76	0·71
279–281	Grey	0·01	2·52	7·06	0·59
284–287	Black	0·45	0·16	5·95	0·60
297–299	Grey	0·01	1·68	6·11	0·58
305–307	Black	0·67	0·30	6·46	0·68
329–331	Black	0·46	0·26	6·35	0·63
341–343	Grey	0·02	1·75	6·34	0·62
347–349	Black	0·39	0·46	6·75	0·73
362–364	Grey	0·02	1·56	5·60	0·87

The core was taken at 43·0° N, 35·5° E, water depth 2,179 m. Percentages are based on $CaCO_3$-free acid soluble iron-free, dry weight. "Reactive" iron refers to the sum of pyrite iron and that soluble during boiling for 1 min in 12 N HCl.

Present day Black Sea water, which contains about 18 mmoles/l. dissolved sulphate, represents a mixture of fresh water derived from inflowing rivers with a high proportion of seawater derived from the Sea of Marmara by way of the Bosporus. The sulphate is derived almost entirely from seawater, which contains about 28 mmoles/l. as compared with the rivers, which contain, on average, only 0·35 mmoles/l.[6]. Because of the high contribution of seawater sulphate, black FeS minerals in the present deep water sediments are completely converted to pyrite[5], resulting in grey sediment which is similar to the buried grey layers described in Table 1. During the Pleistocene, when the worldwide sea level was sufficiently lowered below the Bosporus so that seawater inflow was excluded from the Black Sea, the constant influx of river water could have flushed out pre-existing sea salts, eventually resulting in a brackish or fresh bottom water low in dissolved sulphate. During these periods of maximum sea level lowering the black layers may have been deposited. Whenever the sea level rose high enough for seawater to spill over the Bosporus sill, an influx of sulphate to the deep water would occur and black iron sulphides formed at at the same time could be completely converted to pyrite resulting in grey sediment. Thus it is possible that sediment sections containing many black layers record periods of glacial maxima. (The simultaneous change in sea level and appearance of each black layer would not be expected because of complications arising from the interaction of seawater and freshwater in the Bosporus and from time lags from rates of mixing of the two water types within the Black Sea itself.)

This suggestion must await detailed comparison of the age, thickness and frequency of black layers in undisturbed sections of deep Black Sea sediments with other indicators of Pleistocene sea level change. Preliminary examination of cores from the Black Sea deep basin suggests that the black layers are confined to an overall depth range of approximately the same age span as the last major glaciation. In addition, Markov *et al.*[7] state that during the last major glaciation, the shallow waters of the Black Sea, as inferred from faunal evidence, were very dilute with salinities of less than 5 parts per thousand, which corresponds to less than 4 mmoles/l. dissolved sulphate. At certain times, the deep water was probably similarly dilute which enabled formation of the black layers.

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Photosensitized Oxidation of Ammonia by Singlet Oxygen in Aqueous Solution and in Seawater

THE various forms of inorganic nitrogen in seawater undergo complex transformations involving a variety of biological, chemical and photochemical processes which are important for protein synthesis and which determine the development of the marine ecosystem[1].

But the process involving nitrification of ammonia to nitrite and nitrate by chemical mechanisms is still not clearly understood.

Swallow[2] has recently shown that short lived chemical species such as hydrated electrons can play an important part in seawater processes. Singlet oxygen is another