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Unexpected changes in the oxic/anoxic interface in the Black Sea

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THE Black Sea is the largest anoxic marine basin in the world today[1]. Below the layer of oxygenated surface water, hydrogen sulphide builds up to concentrations as high as 425 μM in the deep water down to a maximum depth of 2,200 m (ref. 2). The hydrographic regime is characterized by low-salinity surface water of river origin overlying high-salinity deep water of Mediterranean origin[1,3]. A steep pycnocline, centred at about 50 m is the primary physical barrier to mixing and is the origin of the stability of the anoxic (oxygen/hydrogen sulphide) interface. Here we report new observations, however, that indicate dramatic changes in the oceanographic characteristics of the anoxic interface of the Black Sea over decadal or shorter timescales. The anoxic, sulphide-containing interface has moved up in the water column since the last US cruises in 1969 and 1975. In addition, a suboxic zone overlays the sulphide-containing deep water. The expected overlap of oxygen and sulphide was not present. We believe that these observations result from horizontal mixing or flushing events that inject denser, saltier water into the relevant part of the water column. It is possible that man-made reduction in freshwater inflow into the Black Sea could cause these changes, although natural variability cannot be discounted.

The US-Turkish Oceanographic Expedition to the Black Sea consisted of five cruises on the RV *Knorr* from 15 April to 2 August 1988 (*Knorr* cruise 134, legs 8 to 12)[4]. One of the main goals was to study the anoxic interface in detail. The principal features of the anoxic interface were summarized by Caspers[1]. Oxygen was found to be depleted to zero concentration at depths of between 125 and 300 m. During the RV *Atlantis II* cruise in March and April 1969 the boundary between the oxygenated surface waters and the sulphide-containing deep waters was found to occur along a constant-density horizon. An overlap of oxygen and sulphide of a few metres was observed[2]. The isopycnal surface (potential density, $\sigma_\theta = 16.41$) of the oxygen zero boundary was dome-shaped and ranged from a depth of 115 m in the centre of the basin to about 275 m near the shelves[3,5]. The RV *Chain* visited the Black Sea in April 1975 and found hydrographic results that were nearly identical to those reported in 1969[6]. At that time the anoxic interface comprised a 20–30-m transition zone where oxygen and hydrogen sulphide coexisted at very low concentrations (<15 μM) (ref. 7). Russian scientists have frequently reported the coexistence of oxygen and hydrogen sulphide in a zone called the 'C layer' (see, for example, ref. 8).

Several studies in the early 1980s[8–12] reported that the upper boundary of the sulphide zone was rising. We have confirmed such observations with high-quality continuous data and we find that the first appearance of sulphide in the water column is higher by as much as 30 m relative to the previous US studies in 1969 and 1975. In addition, we have also observed a significant gap of 10–40 m between the layer of oxygen decrease to suboxic levels (less than 5 μM) and that of the first appearance of hydrogen sulphide. This gap was thicker in the centre of the Black Sea than near its boundaries.

During the 1988 RV *Knorr* cruises we studied the chemistry and microbiology of the interface zone in detail using a new pump-profiling system. This pump sampler was attached to a CTD (conductivity, temperature and depth instrument) and interfaced to an autoanalyser for detailed analyses of NO_3^-, NO_2^-, NH_4^+, Si, PO_4^{3-} and H_2S. The pump was stopped at specific depths to collect samples for manual analyses. The pump was lowered at a rate of 6–10 m min^{-1} and data were acquired every 3 s, giving a sampling rate of 2–3 data points per metre. Under calm conditions, features in the water column could be resolved to better than 2 m. Within less than an hour the detailed structure of the water column was characterized on a down cast and a discrete sampling strategy designed for the subsequent up cast.

The potential temperature (θ) in the central part of the western basin of the Black Sea (station BS3-2; 32° E, 42°50′ N; 5 June 1988)[13] decreased from high surface values of >17 °C, reflecting seasonal warming, to a minimum of 6.95 °C at 45 m, then increasing to 8.58 °C at 100 m and to 8.9 °C at 2,050 m (Fig. 1*a*). Station 1445 of the 1969 *Atlantis II* Black Sea cruise[2] (31°27′ E, 43°08′ N; 1 April 1969) was in close proximity to our station BS3-2 and

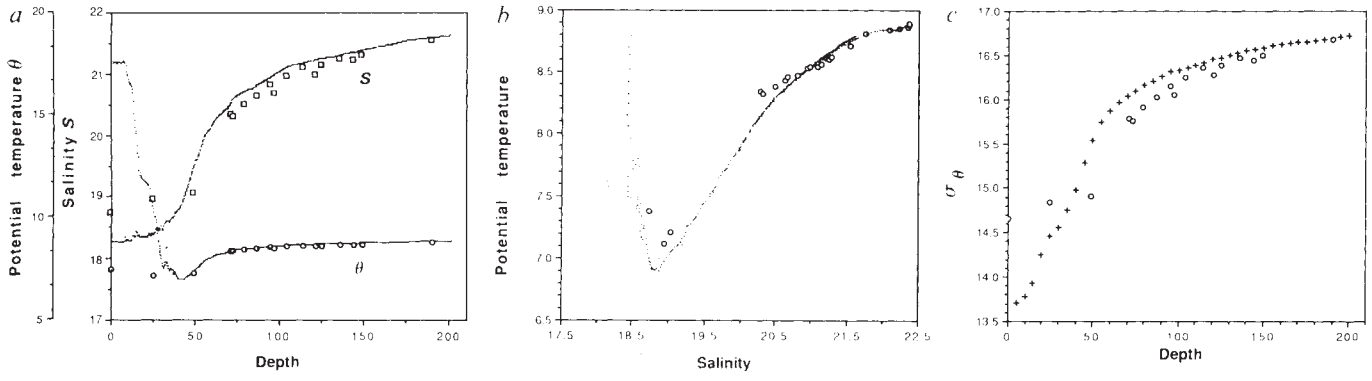


FIG. 1 Potential temperature, salinity and density in the Black Sea. Open symbols are from station 1445 of the March 1969 *Atlantis II* Black Sea cruise. Closed symbols are from station BS3–2 of cruise 3 of the US–Turkish expedition (June, 1988). *a*, Potential temperature (θ) and salinity (S) plotted against water depth to 200 m, calculated from SeaBird CTD data with the assistance of G. White and M. Relander. *b*, Potential temperature against salinity for the entire water column. *c*, Potential density (σ_θ) against water depth to 200 m.

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is used for comparison. The 1969 and 1988 data agree well in the range from 50 m and 100 m and below 200 m. From 100 m to 200 m the 1988 temperature is about 0.1 °C warmer. The surface temperatures are quite different because the cruises were made at different times of the year.

The salinity in 1988 increased from 18.33‰ at the surface to 21.09‰ at 100 m (Fig. 1*a*) and then to 22.33‰ at 2,050 m. The 1969 data are sparse above 70 m, but the salinity was definitely higher by at least 0.1‰ in 1988 over the 50–200 m depth range[2].

The change in hydrographic properties can also be seen by comparing plots of the potential temperature versus salinity (θ–S) (Fig. 1*b*). There is clearly a departure toward higher salinities at a given potential temperature for salinities greater than 21.00‰. The net result is that the potential density (σ_θ) was higher from 50 m to 200 m by up to 0.3 in 1988. This corresponds to an upward shift of the isopycnal surfaces in this depth interval by as much as 20 m. In 1969 the θ–S diagram was linear across the anoxic interface from 50 to ~400 m. In 1988 the θ–S data were linear from about 45 m to 70 m, and there was a small degree of curvature through the anoxic interface region. Since 1969 (and 1975) there has been a small but significant change in the hydrographic and density structure of the anoxic interface region (50–200 m) at this location in the Black Sea.

In comparison with the subtle changes in the water-column hydrographic and density structure, the changes in the oxygen, sulphide and nutrient distributions have been more pronounced. The new data show that dissolved oxygen is high in the surface water with a photosynthetically produced maximum at 10 m (Fig. 2*a*). Oxygen concentration decreases rapidly, to values of less than 5 μM at a depth of 55 m. In 1969 the measured oxygen concentration did not decrease to zero until about 125 m depth. Sulphide first appeared at about 95 m and increased almost linearly with depth (Fig. 2*a*). Repeat casts indicated that the uncertainty in this depth was about 5 m. This first appearance of sulphide occurred close to the density surface of $\sigma_\theta = 16.32$. In 1969 sulphide first appeared at 125 m, corresponding to the density surface of $\sigma_\theta = 16.39$. Thus sulphide appears to have shoaled slightly relative to the water-column density structure.

A prominent new feature in the anoxic interface is a suboxic zone that exists from 55 m to 95 m at station BS3-2. This zone is characterized by oxygen concentrations less than 5 μM, with no discernible gradients. This suboxic zone was found at all stations occupied during the 1988 expedition and was unexpected, because most recent literature[3,14,15] reported the coexistence of O_2 and H_2S; the vertical extent of this coexistence was reported to be as large as 90–100 ml (ref. 15) and appeared to vary laterally and seasonally[8]. There is one earlier report of a suboxic zone but it appeared to be limited to an isolated eddy experiencing unusually intense vertical mixing[16].

Ammonia content (Fig. 2*b*) increased rapidly and linearly with depth below 80 m. The gradient relative to depth for ammonia in 1988 was similar to that in 1969[2], but was shifted upward by about 50 m in the recent data.

The 1988 phosphate profile (Fig. 2*c*) is intriguing because it shows a maximum at 55 m, decreasing to a minimum at 70 m, and then increasing rapidly to a large maximum at 95 m, coincident with the first appearance of sulphide. Similar profiles were found at most offshore stations. Examination of the 1969 data suggests that two PO_4^{3-} maxima were present but could not always be identified unambiguously because of the coarse sampling resolution[14]. The spline fit of the total 1969 data set used by Shaffer[17] showed that they were probably present. The upper PO_4^{3-} maximum is probably due to release from decomposing organic matter during aerobic respiration[14]. The deeper PO_4^{3-} maximum probably results from reductive dissolution of solid Mn and Fe oxides, which release adsorbed PO_4^{3-} (ref. 17). Both PO_4^{3-} maxima appear to have risen in the water column by about 50 m relative to 1969.

The changes in the salinity and density structure may reflect horizontal mixing or flushing events that inject new water into the pycnocline. Several authors have proposed that the pycnocline is most probably influenced by lateral ventilation rather than by one-dimensional vertical transport (see, for example, ref. 18). The shallow temperature minimum bounded by the 8 °C isotherms is called the cold intermediate layer (CIL). At station BS3-2 the CIL is between 25 and 55 m. Tolmazin[19] has summarized the evidence (for example, ref. 20) to suggest that the water in the CIL originates in the Northwestern Shelf (NWS) region of the Black Sea. Here, the coldest temperatures and low river runoff in winter result in the formation of dense water which descends the slope and spreads across the rest of the Black Sea on a timescale of about one year. Ovchinnikov and Popov[21] have recently proposed the alternative view that the water in the CIL originates at the centres of the cyclonic gyres.

Regardless of the origin of the water in the CIL, its production rate and density must be closely linked to long-term variations in the freshwater and heat budgets of the Black Sea. When very dense water forms, the flow overshoots the traditional lower boundary of the CIL. Natural interannual or decadal variations in climate and river runoff can produce horizontal temperature and salinity (that is, density) waves in this shallow intermediate

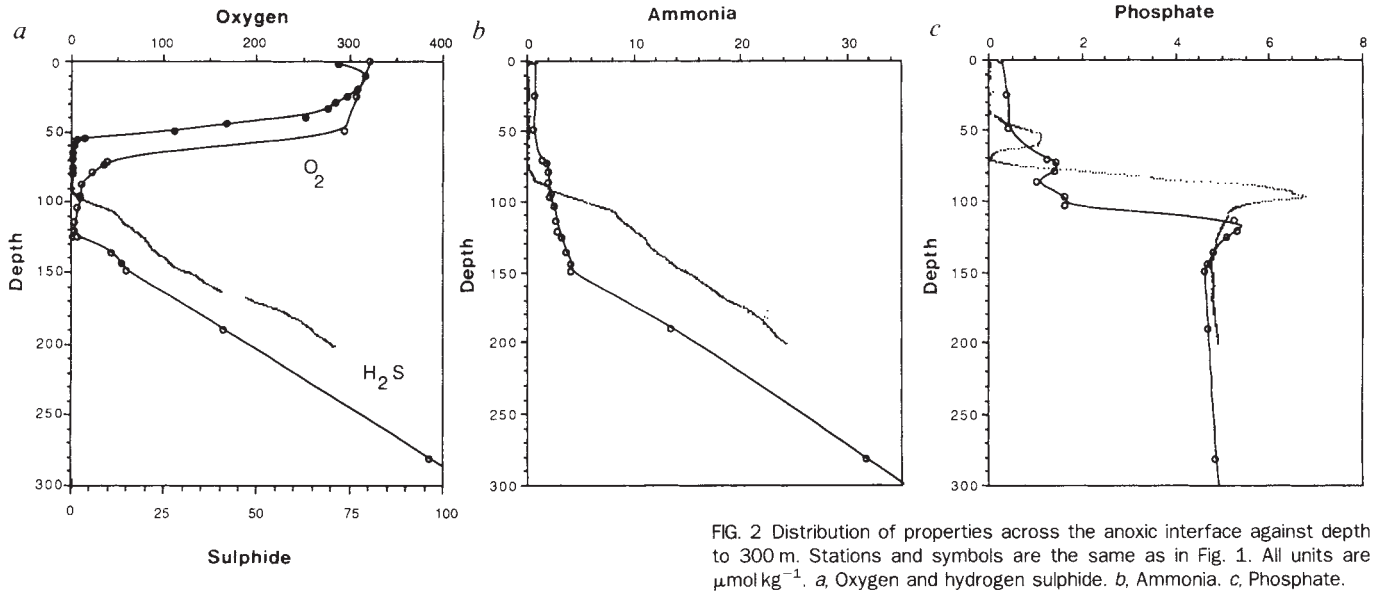


FIG. 2 Distribution of properties across the anoxic interface against depth to 300 m. Stations and symbols are the same as in Fig. 1. All units are μmol kg^{-1}. *a*, Oxygen and hydrogen sulphide. *b*, Ammonia. *c*, Phosphate.

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layer. Superimposed on these natural variations is the man-made reduction in the freshwater runoff from Soviet rivers entering the NWS region of the Black Sea. Tolmazin[19,22] reported that river flow of the Dnieper and Dniester had already been reduced by 50% in 1981. The total freshwater input from all rivers had been reduced by about 15%. Reduction in river input will also result in increased Mediterranean sea-water input through the Bosphorus[23]. Substantial reduction in freshwater influx should cause changes in the salinity structure of the upper layer of the Black Sea. The extreme case of no river input would eventually result in a Mediterranean-style circulation for the Black Sea.

Our data clearly show that the salinity and density in the depth range 50–200 m was high in 1988 relative to historical values. It is possible that a reduction in the freshwater inflow is resulting in the formation of intermediate waters that have higher salinities and densities than in the past. The data set is not complete enough, however, to allow us to distinguish man-made effects from possible natural variations.

Increased production of water to the shallow intermediate layers could be viewed as analogous to the mixing or flushing events that occur in other anoxic basins, such as Saanich Inlet[24–26] and the Baltic Sea[27]. These flushing events produce suboxic zones similar to the one recently observed in the Black Sea. Flushing is thought to displace anoxic water upward in the water column. The sulphide in this displaced water then reacts with oxygen to form an oxygen-depleted layer[28]. Any remaining oxygen is then consumed by aerobic respiration, thus producing a suboxic layer.

Additional chemical and microbiological results will need to be considered for a complete description of the changes in the oxic/anoxic interface. The flushing-event hypothesis is attractive, however, because it can simultaneously explain the changes in salinity, density and concentration of oxygen, sulphide and nutrients. □

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Static amorphization of anorthite at 300 K and comparison with diaplectic glass

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DIAPLECTIC glass, which is produced without fusion, is characteristic of meteorite impact sites in feldspar- and quartz-rich sites on the Earth and Moon; it has also been produced in laboratory shock experiments[1–3]. Its presence in nature is thus considered to be strong evidence of exposure to a high-pressure shock wave generated by impact. The formation of such glasses has been universally interpreted in terms of the brief, high-temperature and high-pressure conditions characteristic of shock loading. Here we report that crystalline anorthite ($CaAl_2Si_2O_8$) becomes amorphous at static pressures of between 22 and 28 GPa at 300 K. The amorphization is associated with a pressure-induced increase in the coordination of silicon and aluminium by oxygen, from fourfold to five- and sixfold. The increase in coordination appears as the sample vitrifies at pressure; on decompression, the coordination reverts to fourfold. The vitrification is spatially heterogeneous, and may be crystallographically controlled. The formation of glass from crystalline material under static conditions at 300 K indicates that the high strain rates and temperatures associated with shock compression are not required for the creation of glasses without fusion.

The starting material used in this study is 'transitional' anorthite from Miyake-zima, Japan, and is identical to the sample material used in previous shock experiments[4]. Single crystals of this material, each about 15 μm in thickness, were statically compressed in a Mao-Bell-type diamond cell; pressures were determined using ruby fluorescence[5]. A 16:3:1 mixture of methanol, ethanol and water was used as a pressure-transmitting medium, as this mix is hydrostatic to pressures of 15 GPa (ref. 6). At higher pressures, the samples were sufficiently small that the pressure gradients across them did not exceed 1 GPa. In particular, samples never bridged the gap between the diamond anvils. Pressures were increased over about 10 minutes, and the samples were then held at each pressure for approximately 18 hours, which is about 11 orders of magnitude longer than the corresponding periods in shock experiments. High-pressure infrared spectra were measured using a technique described elsewhere[7], and indices of refraction were measured by the oil-immersion technique at ambient conditions.

Figure 1*a* shows a single crystal of anorthite before compression. The sample is optically anisotropic, with a birefrigence of 0.013, in accord with the typical value for such crystals[8]. Samples compressed to 15 GPa exhibit no evidence for vitrification, nor any departure from single-crystal characteristics. After compression to 22 GPa, however, two optically isotropic bands appear in the sample (Fig. 1*b*). Each of these is about 20 μm wide, and they have a separation of about 40 μm. The birefringence of the crystalline material is indistinguishable (to within 20%) from that of the starting material. After compression to 28 GPa, the sample is optically isotropic, with a birefringence of less than 0.002 (Fig. 1*c*). Thus, crystalline anorthite is transformed to a glassy state merely by static compression to pressures exceeding 25 (±3) GPa, at ambient temperature.

The index of refraction of a quenched isotropic sample of anorthite glass is 1.62 (±0.02), significantly higher than the mean value of 1.58 observed for both anorthite crystal and shock-produced anorthite glass[9]. Thus, it seems that the amount of time over which a sample is compressed, and possibly the post-shock thermal regime, may profoundly affect the degree of densification within pressure-amorphized silicates. Comparisons between glasses formed by shocks of different duration might not, therefore, yield reliable estimates of peak shock pressures.

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