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RECORD 1974/21

ARSENIC IN SEDIMENTS ON THE CONTINENTAL SHELF OF SOUTHEAST AUSTRALIA

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During 1972, the Bureau of Mineral Resources collected grab samples on a grid pattern over the continental shelf of southeast Australia during a reconnaissance geological survey. About 200 sediment samples were collected between Sugarloaf Point and Cape Howe for sedimentological and geochemical study. The shelf surface is covered mainly by sand, but small patches of silty sand and clayey sand occur at depths of 60-120 m between Newcastle and Port Kembla. The sediments collected were analysed for $CaCO_3$, Sr, Sn, Cu, Pb, Zn, Ti, Co, Cd, As, Fe, Mn, Ni, C, and P_2O_5. All these data together with sample site and granulometric information have been analysed by means of Q and R mode factor analysis and will be reported in future publications. The arsenic values were obtained by atomic absorbtion analysis at the Australian Mineral Development Laboratories, Adelaide. The accuracy of the method is ± 10%. This report deals entirely with the distribution of arsenic in the shelf sediments. Its toxicity is well known (Angino et al., 1970), but its concentration and distribution in recent sediments is not well documented.

The maximum, minimum, and mean values of arsenic in the continental shelf sediments, together with a comparison with other data, are shown in Table 1. The distribution of arsenic in the sediments is shown in Figure 1. Sediments with low arsenic contents (less than 10 ppm) almost entirely occur close inshore, in well to medium sorted sands and gravels. Seawards, the arsenic content increases. South of Jervis Bay, the maximum arsenic content in the sediments is less than 50 ppm. North of Jervis Bay, and especially between Port Kembla and Newcastle, arsenic contents on the middle and outer shelf average between 50 and 100 ppm. In one place, southeast of Newcastle, 180 ppm of arsenic occurs in the sediment. Although arsenic forms only a small part of the sediment as a whole, it must obviously form a high proportion of some components.

Comparison of these data with those shown in Table 1 indicates that the arsenic contents in the shelf sediments are up to two orders of magnitude higher than those reported for the average shale, sandstone, and limestone (Turekian & Wedepohl, 1961). Similarly, the average value for crustal rocks (1.8 ppm) quoted by Mason (1966) is markedly lower than the shelf sediments. Tooms et al. (1969) report high arsenic contents (up to 188 ppm) in phosphorites, and Pilipchuk & Sevast'Yanov (1968) report high arsenic contents (18 ppm) in Black Sea sediments. Little is published on arsenic concentrations in sediments from other continental shelves of the world.

The main questions raised by the data from the southeast Australian shelf are the source of the arsenic, the reason for the increase in arsenic seawards, and the reason for the marked concentrations between Port Kembla and Newcastle.

Possible natural sources of arsenic in the sediments are normal sea water, sea water enriched in arsenic in solution derived by natural erosive processes, and arsenic contained in sediment deposited on the shelf. Artificial sources of arsenic are industrial and agricultural wastes, which again may be transported in solution and concentrated in the shelf sediments by organic or inorganic processes, or transported in solid form with sediment particles.

Sea water containing normal amounts of arsenic (2.6 ppb - Table 1) could be a source of metal enrichment in the sediments only if extreme inorganic or organic concentration occurred. Both processes would be aided by the fact that there has been little sedimentation on the outer continental shelf since the last sea level low (Davies, in prep.). While some inorganic mechanism aided by minimal sediment dilution is a possibility, it does not readily explain the distribution shown in Figure 1. Relict sediments occur on the outer continental shelf throughout the area studied, while high arsenic concentrations are only present locally. Organic concentration from sea water is also possible, but there is not a close relation between arsenic and organic carbon in the sediments. Table 2 shows that arsenic and organic carbon occur in different factors, and are therefore unlikely to be controlled by the same environmental parameters. Also, no significant statistical relation occurs between arsenic and organic carbon (= 0.09); this contrasts with the significant relation between arsenic and organic carbon found by Ruch et al. (1970) in Lake Michigan sediments.

Tooms et al. (1969) have shown that high arsenic concentrations occur in many phosphorites of the world. In the southeast Australian area, the P_2O_5 content of the sediments increases towards the edge of the shelf, and phosphate and arsenic appear therefore to be genetically correlated. However, R-mode factor analysis (Table 2) explaining 75% of the sample variance separates arsenic and phosphate into different factors, suggesting they are not related, and that they are likely to have been controlled by different parameters. Also the sample correlation coefficient for 78 outer shelf sediments of = 0.38 supports the hypothesis that the population correlation coefficient is 0.2 at the 95% confidence level, which indicates only a weak linear relation between arsenic and phosphate.

These facts suggest that the arsenic content of the shelf sediments is not a function of a mineralogic characteristic, like phosphate. Also, the fact that arsenic does not occur within any factor (Table 2) related to mineralogic or depositional variables supports the conclusion that arsenic in the shelf sediments is not a part of an inherent sedimentary characteristic. The arsenic is likely therefore to be entering the system from an external source.

Natural erosion of rock and soil in the hinterland may conceivably be a source of arsenic. However, the major rock types contain very little arsenic. Brown & Swaine (1964) and Swaine (pers.comm.) report only small arsenic concentrations in the coals of the Sydney Basin (3 ppm). This is small compared with coals from other parts of the world. Swaine (1955) also reports arsenic concentrations of 1-50 ppm in soils of various countries. If one assumes similar levels for Australian soils, the arsenic will likely be derived from underlying rocks, and from pesticides and fertilizers used in agriculture. Ammonium sulphate (114 ppm), phosphates (100 ppm) and super phosphates (hundreds of ppm) contain arsenic in various proportions (Swaine, 1962). Much of this will remain in the soil because the pH of the system renders it insoluble. It is therefore unlikely to reach the ocean unless it moves attached to other particles. As mentioned above, however, very little sedimentation is occurring on the continental shelf. An agricultural source for the arsenic seems also to be precluded by its distribution (Fig. 1): the maximum arsenic concentrations occur offshore from areas of major urban and industrial development, and not offshore from the agricultural areas. This points to an external source of arsenic linked to the major industrial centres; i.e., the arsenic may be a pollutant which is being discharged on the continental shelf either as a result of industrial activities or as some by-product of urban development. For example, Angino et al. (1970) report increasing concentrations of arsenic in the Kansas River due to pollution by detergents used in household washing.

At this stage it is not possible to pinpoint the source of arsenic in the continental shelf sediments, but if arsenic compounds were discharged into sea water (pH = 8) then the arsenic would very quickly be converted into reactive forms. This, plus its ability to change valency in the course of redistribution, make it one of the most mobile elements in the sediment/sea-water system. Some researchers suggest that arsenic migrates in the colloidal form, adsorbed on metal complexes (Bostrom & Valdes, 1969; Pilipchuk & Sevast'Yanov, 1968; Sevast'Yanov, 1967), thus explaining why arsenic is commonly richer in sediments farthest away from coastal areas. R-mode factor analyses of the Australian sediments show a factor (Table 2 - factor 5) whose major components are manganese and arsenic (the correlation coefficient of r = 0.68 is highly significant). It is suggested therefore that on the continental shelf of southeast Australia, arsenic is being transported adsorbed on colloidal manganese compounds which are being deposited in the deeper, quieter waters of the outer continental shelf, while in shallow waters, arsenic-carrying colloids are likely to remain in suspension because of greater water agitation.

It is concluded from the above presented work that arsenic is enriched in the surface sediments of the continental shelf of southeast Australia, particularly between Port Kembla and Newcastle, where concentrations of 50-100 ppm are common. The arsenic may be derived from the hinterland by natural erosion, or from urban and industrial effluent. Complexing of arsenic with colloidal manganese compounds results in its deposition in the quieter areas of the middle to outer shelf. Whether the high arsenic values are due to modern urban/industrial effluents, or are in some way related to natural concentration mechanisms coupled with non-sedimentation, could be resolved by a series of sediment cores in the areas of high arsenic concentration. This has not yet been undertaken, however.

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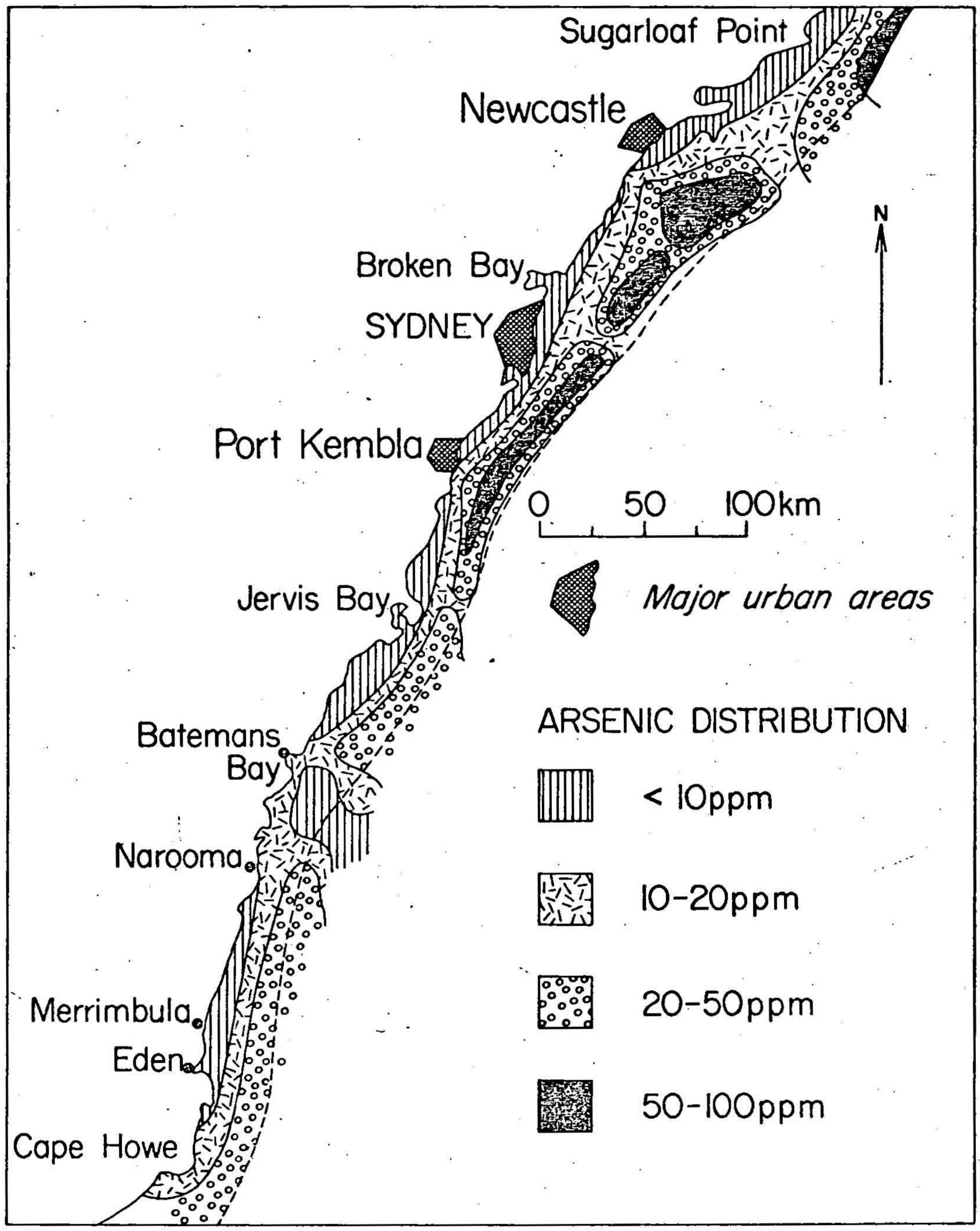

Fig. 1: Arsenic distribution on the Continental Shelf of southeast Australia.

SE AUSTRALIA - CONTINENTAL SHELF - Minimum -	2 ppm	
Maximum -	180 ppm	
Mean -	18 ppm	
AVERAGE SHALE	1.3 ppm	Turekian & Wedepohl (1961)
AVERAGE SANDSTONE	1.0 ppm	
AVERAGE LIMESTONE	1.0 ppm	
CRUSTAL ROCKS	1.8 ppm	Mason (1966)
SEA WATER	2.6 ppb	Turekian (1968)
PHOSPHORITES OF WORLDWIDE DISTRIBUTION	0.4-188 ppm	Tooms et al. (1969)
UNCONSOLIDATED SEDIMENTS - LAKE MICHIGAN	5-30 ppm	Ruch et al. (1970)
BLACK SEA SEDIMENTS	18 ppm	Pilipchuk and Sevast'Yanov (1968)

Table 1. Arsenic contents of surface sediments of the continental shelf of southeast Australia compared with those of sea water and various other sedimentary rocks.

VARIABLE	FACTOR 1	FACTOR 2	FACTOR 3	FACTOR 4	FACTOR 5	FACTOR 6
$CaCO_3$			– –			
P_2O_5	– – –					
Sn		+ + +				
Cu	– –					
Pb						– –
Zn	– – –					
Mn					– – –	
Ni	–				– –	
Fe	– –				–	
Co						+
Cd			– –			
As					– – –	
$C^{Org.}$				– –		
Ti	–					
St.Dev.			– –			+
Mean		+ + +				
Gravel		+ + +				
Sand		– –	+			
Mud				– – –		
Depth			– –			

Table 2. Varimax-rotated factor matrix for sediments occurring on the middle and outer continental shelf, southeast Australia. Only positive and negative factor loadings greater than 0.4 are presented.

Key to Factor Matrix

+ + + – – – Factor loadings greater than 0.8.
+ + – – Factor loadings between 0.6-0.8.
+ – Factor loadings between 0.4-0.6.