

supercoiled¹².

Probably the greatest argument against the existence of free underwinding in eukaryotic cells is the very large levels of topoisomerase I activity usually found, which might be expected rapidly to relax to equilibrium any such region. But while nucleosome-topoisomerase associations have been isolated from nuclei^{13,14}, there exist no data on the possible sub-nuclear location of this enzyme. It might therefore be premature to conclude that eukaryotic DNA could not become stressed, perhaps transiently.

Acquisition of torsional stress by selected parts of the genome may be important for two main reasons. By this means free energy can be released into the DNA in an available manner, which could be used to drive structural transitions and/or promote transcription. Several examples of supercoil-driven DNA perturbation are known, such as cruciforms¹⁵⁻¹⁷ and Z structure^{18,19}, and it remains entirely possible that such structural polymorphism is important for gene function. Particularly

intriguing in this respect are the recent observations by Larsen and Weintraub²⁰, of nuclease-hypersensitive domains of chick globin gene DNA in supercoiled, but not relaxed, plasmid clones, in positions corresponding to those activated in chromatin. The coupling of supercoiling free energy and transcription has a clear precedent in the prokaryotes. Open complex formation is expected to be stimulated by negative supercoiling, and bacterial promoters exhibit differential sensitivity of promoter strength upon template underwinding²¹. Indeed, the role of supercoiling in the control of prokaryotic gene expression appears to be gaining more and more importance. Whilst the available data for the eukaryotes must still be regarded as preliminary, it is tempting to suppose that similar topological gene control may be important, and further developments in this area are eagerly awaited. □

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Atmospheric chemistry

The oceans and the global sulphur budget

from Suzanne Turner and Peter Liss

GASEOUS sulphur compounds, such as sulphur dioxide (SO₂), dimethyl sulphide (DMS), carbonyl sulphide (COS), carbon disulphide (CS₂) and hydrogen sulphide (H₂S), are thought to be important in two main aspects of atmospheric chemistry. First, they affect the acidity of rain directly; SO₂ forms sulphurous and sulphuric acids, and COS produces a solution of the weak acids H₂S and H₂CO₃. Several other sulphur gases (DMS, for example) are also readily oxidized in air to SO₂, and so further contribute to rainwater acidity. Second, these compounds are reactive in the atmosphere and susceptible to attack by hydroxyl radicals, although the rate of reaction varies between the various compounds¹. Ultimately, their oxidation leads to the production of sulphate aerosol particles, especially in the stratosphere, where they play an important part in controlling the radiation balance and hence the climate of the Earth^{2,3}.

In order to assess quantitatively the role of sulphur gases in these two processes, their global budgets must be understood, that is, the various sources and sinks of the gases must be properly quantified. Such budgeting is made complicated by the perturbation of the natural cycles that results from human activity. For example, about 65 × 10¹²g of sulphur, mostly as SO₂, are injected into the atmosphere each year from the burning of fossil fuels and the roasting of metal sulphides ores. This is a rather substantial amount relative to the

total natural sources of sulphur to the atmosphere of approximately 80 × 10¹²g per year.

An important term in all global sulphur budgets is the flux of gaseous sulphur across the sea surface. Early budgets always had to invoke a substantial flux of volatile sulphur from the oceans into the atmosphere to achieve balance, and the form of the sulphur was generally assumed to be H₂S. However, except in very shallow coastal waters overlying reducing sediments, the existence of H₂S near the sea surface is most unlikely because it is rapidly oxidized to sulphate in oxygenated waters.

In the last few years it has become possible to determine directly several natural sulphur gases in surface seawater, at concentrations of less than 1 part per 10⁹ by volume, using gas chromatographic separation and a flame photometric detector. By this approach, it has been shown that relatively high concentrations of DMS are present in oceanic surface waters⁴, and this is related to the productivity of marine algae. The concentration in the atmosphere is, however, considerably lower and the residence time is only about 1 day, owing to the high reactivity of the compound. Applying model calculations, a sea-to-air flux of about 40 × 10¹²g per year has been proposed⁴. DMS therefore can account for about 50 per cent of natural emissions. Clearly the oceans are a significant source of atmospheric sulphur.

Results for COS have shown that it is the most abundant sulphur-containing gas in the atmosphere (512 parts per 10¹² by volume; ref.5). There is little difference between Northern and Southern Hemisphere values⁵, suggesting that the sources of COS are distributed uniformly; that is, due to slow interhemispheric mixing, a higher concentration in the north could indicate industrial sources. Several sources of COS have been proposed including biomass burning, volcanoes, salt marshes and the combustion of fossil fuels, but the importance of these sources is not yet certain. Hydrolysis of COS in the ocean⁶ and reaction with hydroxyl radicals in the atmosphere² have been proposed as sinks. The residence time of COS in the atmosphere has been determined by modelling, but as knowledge of the sinks of the gas is limited, estimates vary from 160 days (ref.2) to 4-7 years (ref.6).

Recent measurements of COS in oceanic surface waters, in fact, indicate that seawater is almost certainly a source, rather than a sink, of the gas for the atmosphere^{7,8}. If hydrolysis is significant in removing COS and production is low, surface waters should be undersaturated with respect to the atmosphere. Conversely, if production is high, supersaturation of the surface seawater will occur. Ferek and Andreae⁹ recently published findings for the degree of saturation in ocean waters. Averaging the results for coastal, open-ocean and productive waters, they derive a supersaturation value of about 2. A positive correlation between COS and DMS concentrations was found, suggesting that the presence of COS may also be related to algal productivity. The authors calculate a flux of COS from the oceans to the atmosphere of 0.46 × 10¹²g of sulphur per year. Although this is significantly less than the emission of DMS from the oceans, it shows again that seawater is a considerable source of volatile sulphur to the atmosphere.

In the future it will be necessary to ascertain how the degree of supersaturation of DMS and COS in the oceans varies both spatially and temporally, as well as to identify other sulphur gases which may contribute to the air-sea transfer of this element. □

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