In this issue

Holes in solid state chemistry

The general assumption that the anions in solids play a passive role as a structural matrix is examined by Jean Rouxel (**page 31**). Such a view is appropriate only when the sp electron bands lie very low compared to valence electron energy levels of the cations. When the situation is altered as, for example, in transition metal chalcogenides by either elevation of the sp band energies of the anions (by moving down the periodic table) or changing the orbital energies of the cations (by moving towards right in the periods of the transition elements), the d levels can indeed be made to penetrate into the sp energy bands. This leads d–sp redox reactions and fascinating structural and electronic phenomena.

$NbSe_3$ is an example of the d–sp redox reactions which lead to formation of charge density waves via structural effects. Formation of layered dichalcogenides with left side transition elements (eg. ZrS_2) and pyrites and marcasites with right side transition elements (eg. MnS_2) are consequences of electron transfer from sp to d bands and consequent variation in interanionic distances. sp bands can be positioned deliberately which can control the properties of the resulting materials. Thus by changing the chalcogen from S to Te one observes TiS_2, $TiSe_2$ and $TiTe_2$ behave respectively as a semi-conductor, a semimetal and a metal. De-populating antibonding sp states by introducing low energy d states leads ultimately to complete anion polymerization as it happens in IrTe. Anion–anion distances are also found to vary linearly as a function of electron transfer from the sp level.

Control over the sp–d energies can open soft chemical (chime douce) routes to perform redox reactions, for example, Cu^+ can be intercalated into $CuCr_2S_4$ or Na^+ ions intercalated into $CrSe_2$. It is also possible to see why de-intercalation of Cu^+ is possible in $CuTi_2S_4$ (a cation mixed valence system) while it is not so in $CuCr_2S_4$ (which is a anionic mixed valence system) using the above concepts. The d–sp redox reactions are also responsible for formation of non-stoichiometric compounds like $V_{0.78}PS_3$ and $Ti_{0.5}PS_3$. Creation of holes in anionic sublattices and stabilization of unusual structures such as those of $Si_{0.25}CrS_2$ and $P_{0.2}VS_2$ are similarly understood from relative positioning of d and sp bands and electron donation from Si and P.

K. J. Rao

Climatic see-saw in Southern India: Unravelling the alternating moist and arid epochs during the last 40,000 years

In a multi-institutional, multi-disciplinary study involving rather close cooperation between ecologists, physicists and paleobotanists reported on **page 60** of this issue, R. Sukumar and colleagues describe how the climate of the Nilgiris fluctuated rather dramatically between moist and arid epochs during the last forty thousand years.

The starting point of this analysis is the collection of peat samples from the walls of 2–3 meters deep pits dug in the valleys or basins at suitable locations in the Nilgiris. Peat is formed by regular deposition of plant material over thousands of years; the deeper portions therefore correspond to older epochs. Using radiocarbon dating, based on the amount of ^{14}C, it was possible to determine the age of the plant material at various depths, and the peat samples were found to span a period from about four hundred years to forty thousand years before present (40 kyr BP).

The naturally occurring carbon also contains the isotope ^{13}C in a small amount. This is 'fixed' during photosynthesis by different types of plants to a different extent. Dicots and temperate grasses (C3 plants) have a lower proportion of ^{13}C in them compared to tropical grasses and sedges (C4 plants). By estimating the proportion of ^{13}C at different depths in the peat samples, it is possible to estimate the relative proportions of C3 and C4 plants at different periods in the past. It is known that the C3 plants mainly prefer regions of high moisture while the C4 plants dominate at low moisture regimes. The proportion of ^{13}C at different depths thus allows us to infer the moist/dry status of the climate during different periods in the past.

Using these techniques, Sukumar and co-workers have confirmed their earlier findings – an arid period from 2 kyr BP to about 5 kyr BP, which was a sharp change from a moist climate which had peaked around 9 kyr BP. The new results presented in the article describe how the moist phase of C3 dominance at 9 kyr BP was replaced with high C4 dominance at 16 kyr BP – again a sharp change to relatively arid conditions. There was a gradual return of moist conditions up to 28 kyr BP, and again a shift to aridity to 40 kyr BP. The authors also point out how the climatic changes in the Nilgiris (and in the southern Indian tropics) seem to have been in tune with the global climatic change – a significant finding in view of the anticipated global warming scenario.

N. V. Joshi

Fighting an invisible enemy

Viruses, bacteria and more complex pathogenic organisms have evolved sophisticated and remarkably efficient mechanisms to evade immune surveillance, making vaccine development a hazardous and risky enterprise. Managers of biomedical science, therefore, have a difficult task of deciding whether to back strategies for prevention or rely on approaches towards new therapeutics.

In the heady days, following the introduction of antibiotics it seemed that cures for every infectious disease would be found. But, the growing spread of drug-resistant microorganisms suggests that we have barely skimmed the surface of biological deviousness. Microorganisms have learnt to destroy, evade and expel almost all classes of therapeutics, displaying an incredible chemical virtuosity. The growing threat of drug-resistant malaria and tuberculosis, coupled with the difficulty in stemming the tide of AIDS, suggests that major efforts at vaccine development may indeed be the need of the future.

The prevention of infectious disease is the primary goal of public health strategists. While improved sanitation, safe water supply and better living standards for the vast majority of the populace are undoubtedly desirable, effective vaccines are, clearly, a most important component in the public health armamentarium. The amazing success of Edward Jenner's vaccine and its later variants, has successfully eradicated smallpox; the only apparent case of total victory against a pathogen. Other visible successes have been Pasteur's 19th-century rabies vaccine and the more recent Salk–Sabin vaccines against polio. Despite the great promise of vaccines in prevention of disease and the enormous effort invested in vaccine development, there have been few major victories in the war against microbial pathogens. In the dying years of the 20th century looking to the future is an increasingly popular exercise. V. Ramalingaswami **(page 18)** takes a broad view of what lies ahead focussing on four selected diseases of particular importance in India – malaria, AIDS, cholera and rabies.

The pharmaceutical companies, many of which even dictate the course of biomedical research in major academic institutions in the West, malaria, rabies and cholera are hardly high on the agenda, with vaccine research being accorded a low priority. The striking exception is, of course, AIDS which is favoured by a powerful and vocal lobby in the United States. Tuberculosis research now rides piggyback on the AIDS bandwagon. The burden of developing vaccines against infectious disease must necessarily be borne by governments, particularly in the less developed parts of the world. The Colombian effort towards a malaria vaccine is an example of what can be achieved in an environment less than conducive to scientific research. However, what must be emphasized is that in vaccine research (as in the case of pharmaceuticals), it is easier to achieve laboratory success that to come out triumphantly after a prolonged classical trial.

The war against infectious disease requires a high level of scientific commitment and perseverance, consistent and enlightened governmental support and a clear recognition of the scientific hurdles that lie ahead. In India, unfortunately, many of the publicly-funded, visible vaccine projects aimed at birth control and leprosy appear to be slowly fading. Ramalingaswami's call for new thrusts in vaccine development must of course, be viewed in the light of past experience. Irrespective of the means chosen to fight disease, one sobering conclusion is clear; the invisible microbial enemies are formidable in their abilities to take evasive actions.

P. Balaram