rainfall distribution in individual years. As such the mid-August minimum noticed in the normal summer monsoon rainfall has a climatological significance similar to that of the normal date of monsoon onset over Kerala around the beginning of June.

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Comparable role of copper in haemocyanins and oxide superconductors

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In this communication I draw attention to the comparable behaviour of Cu with respect to the reversible oxygen uptake in natural oxygen carriers, such as haemocyanins, and typical defect perovskites $YBa_2Cu_3O_{7-x}$. There are other similarities as well between the Cu sites in both groups of compounds.

THE active sites in Cu proteins and multi-copper oxidases perform a variety of biological functions, including oxygen transport, electron transfer and superoxide dismutation[1,2]. One such group of proteins, viz. haemocyanins, have binuclear Cu sites responsible for reversible oxygen uptake. Correspondingly, in multi-Cu oxidases such as laccases, the binuclear Cu sites are designated type 3. This form of Cu in haemocyanins and laccases is EPR-silent and is diamagnetic even to the very sensitive SQUID magnetometer. The Cu–Cu distances are less than 4 Å in both types and are antiferromagnetically coupled[3,4].

An important property of defect perovskite, $YBa_2Cu_3O_{7-x}$, is the reversible uptake of oxygen during thermal cycling between 350°C and 850°C; these compounds are, in fact, synthetic oxygen carriers. For values of x in the range 0.0 to 0.2, high-T_c (95 K) superconductivity is observed, but without dependence on the value of x. In the range of x between 0.2 and 0.6, composition-dependent low T_c (70 to 50 K) is noticed, while with $x > 0.6$ (or > 0.65), the samples are nonsuperconducting[5].

Goodenough[6] has argued that the redox reaction associated with oxygen intercalation/disintercalation in $YBa_2Cu_3O_{7-x}$ is related to the nature of Cu sites. The process is confined to the intercalating layer, with peroxide formation occurring between copper-bridging oxygens in contact with one another, if the oxidation exceeds $O_{6.5}$. Sarma *et al.*[7,8] did indicate the possible presence of peroxide-like species under certain conditions. Similar behaviour has been noted in the case of haemocyanins too. It has been shown earlier[2,9,10] that uptake of oxygen by deoxyhaemocyanin results in a peroxide bridge between the two Cu ions of a binuclear site. This oxygen uptake is also reversible, responsible for oxygen transport in molluscs and arthropods. It represents a well-studied example of a natural oxygen carrier.

The binuclear Cu sites in deoxyhaemocyanin are Cu^+, while in oxyhaemocyanin they are Cu^{2+} with a peroxide bridge. These sites are antiferromagnetically coupled[9,10], and function as cooperative two-electron donors/acceptors with a high redox potential[4]. The sites in haemocyanins and other Cu-bearing proteins, such as tyrosinase, are susceptible to bonding by CO as well. However, the type-3 binuclear Cu sites in laccases do not take up CO and may or may not have a bridging ligand.

From the vast amount of information available on 1,2,3 and other closely related systems, it appears that the Cu sites lying along the b axis, with linear coordination in $YBa_2Cu_3O_6$, and which on oxygen uptake finally transform to a coplanar configuration in $YBa_2Cu_3O_7$, can be regarded as synthetic analogues of the binuclear Cu sites of haemocyanins (antiferromagnetically coupled and with a bridging ligand). The dioxygen that is taken up would progressively be transformed to a peroxide ion, probably through an intermediate superoxide. Thus, as oxygen stoichiometry increases from $O_{6.4}$ to O_7, oxygen will intercalate along the b axis and will take part in the redox process.

Iwazumi *et al.*[11], through X-ray absorption near edge structure (XANES) measurements of Cu K-absorption

edge in these compounds, showed that Cu 1 sites are populated by Cu^{+} and Cu^{2+}, depending on oxygen deficiency.

What about the other two Cu ions in the 1,2,3 system? Being Cu^{2+} even in $YBa_2Cu_3O_6$, these ions (a pair) may be considered equivalent to the type-3 Cu present in laccases (antiferromagnetically coupled but without a bridging ligand). Though there is some evidence by extended absorption fine structure (EXAFS) and XANES at Y edge for a partial occupancy of the oxygen sites in the Y plane[12], such a result is excluded by diffraction studies.

EXAFS work on haemocyanin active Cu sites bears out some similarity between these structural units and those of $YBa_2Cu_3O_{7-x}$ (refs. 5,9). Comparison of the Cu-Cu distances in haemocyanins and these compounds[9,13] shows that, in oxyhaemocyanins, it is 3.67 Å; upon deoxygenation it decreases to 3.39 Å. On the other hand, Cu 1–Cu 1 distance in the O_7 compound is 3.885 Å, and decreases only slightly to 3.857 Å in the O_6 compound, indicating structural rigidity in the perovskite.

Turning to the spectral information in $YBa_2Cu_3O_{7-x}$, bands are noted[14] at 309 and 335 cm^{-1}. In oxyhaemocyanins drawn from different sources, shoulders are seen at these positions[10]. A special feature of oxyhaemocyanins is the appearance of a band at 1075 cm^{-1}, assigned to the singlet–triplet transition of the peroxide-bridged binuclear Cu^{2+} unit. Arguments for the possible presence of peroxide-like species in 1,2,3 when x is close to zero were already alluded to[6–8]. Raman studies by Czerwosz *et al.*[15] in $YBa_2Cu_3O_{7-x}$ and related compounds (where Ba is partially substituted by Ca or Sr) revealed a significant band at 1100 cm^{-1}. Is this one due to the above feature in oxyhaemocyanins? On the other hand this could also be due to a superoxide. In KO_2 it is seen at 1145 cm^{-1} and in BaO_2 at 1061 cm^{-1}. The 1100 cm^{-1} band could be due to the attachment of a superoxide ion to Cu^{+} as an asymmetrical mononuclear complex[16].

In conclusion, it may be seen from the above discussion that the active copper sites in $YBa_2Cu_3O_{7-x}$ do resemble the binuclear, antiferromagnetically coupled and EPR-silent Cu sites in haemocyanins in several features. Up to an oxygen stoichiometry of $O_{6.4}$, only oxide ions are present. On uptake of additional oxygen, i.e. in the range $O_{6.4}$ to $O_{6.8}$, where T_c is composition-dependent, another chemical species in the lattice, like a superoxide ion, would make its presence felt. Further oxidation to O_7 would lead to a peroxide species, with T_c becoming composition-independent. In the overall process of oxidation, the binuclear Cu^{+} sites along the b axis are progressively converted to binuclear Cu^{2+} sites with a superoxide or a peroxide bridge. Experimental work on the uptake of Co (or NO) by $YBa_2Cu_3O_{7-x}$, where x is in the range 0.0 to 0.6, could shed additional light on the unique behaviour of Cu 1 sites in such defect perovskites.

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A parsimonious model for prediction of monsoon rainfall in India

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Recently Gowariker *et al.* have used multiple and power regression involving 15 independent variables for long-range forecasting of monsoon rainfall in India. They have also argued that, when most of the independent variables are 'favourable', almost invariably the monsoon rainfall is normal. In this note we formalize this approach using a parsimonious logistic regression model. The probability of a normal rainfall can be assessed in most cases using only five of the 15 variables. Of these, three are related to temperature and two to wind. This gives us correct results for 36 (out of 38) years, including the exceptional year 1957, when all but one independent variables were unfavourable and yet rainfall was normal.

Of late, successful prediction of monsoon rainfall in India by meteorologists has attracted considerable attention. In a recent paper Gowariker *et al.*[1] explained their approach to long-range forecasting. Gopinathan and Shastri[2] expressed reservations about the model used by Gowariker *et al.* This model is

$$R = c_0 + \sum_{i=1}^{15} c_i x_i^{p_i},$$