APPENDIX C

Experimental Procedures For Radiocarbon Dating

The radiocarbon dating requires determination of the residual ^{14}C content in the sample. This value is then translated into an age that is an estimate of time elapsed since the given sample was removed from the environment in which it was in equilibrium with respect to ^{14}C. The following steps are involved in the procedure:

C.1 Pre-treatment of the sample.

C.2 Preparation of sample for ^{14}C activity measurement.

C.3 Estimation of the residual ^{14}C activity.

C.4 Age determination.

C.1 Sample pre-treatment

Some degree of post depositional alteration of sample often occurs in nature. The purpose of pre-treatment is to isolate a fraction that is most likely to have remained unaltered. For lake mud, in the case of this study, it usually involved dilute acid wash to remove secondary carbonate material. Subsequently the sample was washed repeatedly with distilled water and dried.

C.2 Preparation of sample for counting

Following chemical reactions are involved:

C.2.1 Carbon dioxide preparation. This involved the use of a specially prepared vacuum line. For organic samples, CO_2 was released by combustion in a flow of oxygen. For carbonate samples, the CO_2 was released by treatment of powdered sample with H_3PO_4.

Once the CO_2 gas was obtained, the next step involved its chemical and physical purification. The following sequence was followed, as described in Gupta and Polach (1985),

- KI/I_2 solution for oxidation/decomposition of phosphorus, nitrogen and sulphur.
- Solution of 0.1N $AgNO_3$ for the precipitation of chlorides and other halides and acidic vapours.
- Solution of $K_2Cr_2O_7/H_2SO_4$ for final oxidation of traces of CO and trapping of SO_3.
- Silica gel to trap the moisture.

Carbonate samples are relatively clean. The CO_2 from their acid hydrolysis was dried by passing through two dry ice/alcohol or acetone cooled traps. The purified CO_2 was frozen and then expanded in glass bottles.

C.2.2 Acetylene synthesis: This was accomplished in two steps. The first step involved reaction of sample CO_2 with molten Li, inside a reaction vessel, to form lithium carbide. In the second step, lithium carbide was hydrolysed to yield C_2H_2.

C.2.3 Benzene synthesis: The C_2H_2 was trimerised to C_6H_6 by letting the frozen C_2H_2 sublime slowly onto an activated vanadium catalyst in an evacuated column. Complete conversion of the C_2H_2 gas into benzene took ~8 hours. To recover the benzene subsequently, the column was heated at 110°C and benzene collected under vacuum in a liquid nitrogen cooled trap. The frozen benzene was aerated, allowed to melt at room temperature, transferred to a storage vial and refrigerated.

C.3 Measurement of activity

The activity of sample carbon, converted into benzene, was measured using liquid scintillation counter (LKB Wallace 1220 Quantulus). The counter had photomultiplier tubes which sensed light signals produced by decay of ^{14}C in benzene. As such ^{14}C decay will not produce light. Hence, organic scintillators were dissolved in the sample prior to counting. The sample was counted for about 2500 min.

C.4 Age determination

Having measured the residual radiocarbon activity of a sample, the ^{14}C age was estimated by relating the measured residual activity (A_{SN}), to the original equilibrium ^{14}C activity of the reservoir (A_{ON}), that supplied the sample. The relationship based on radioactive decay equation is given as

$$A_{SN} = A_{ON} \exp(-\lambda t)$$

where t = years elapsed since the sample was removed from the equilibrium condition in the ^{14}C reservoir.

λ = decay constant of $^{14}C = 0.693/t_{1/2}$.

$t_{1/2}$ = half life of $^{14}C = 5730 \pm 40$ years.

The reservoir activity is supposed to be represented by a wood grown before 1890 AD, and hence unaffected by fossil or bomb produced CO_2. The Primary Modern Reference Standard (A_{ON}) for radiocarbon dating is a 1950 batch of oxalic acid from the U.S. National Bureau of standards. 95% activity of the primary reference standard corresponds to activity of wood grown in AD 1890. In the PRL radiocarbon laboratory, a specially prepared batch of sucrose, pre-calibrated with primary oxalic acid standard, was used as a standard for modern ^{14}C activity comparison.

For details of standard procedures involved in checking efficiency of counting, statistical monitoring and age calculations, reference is made to Gupta and Polach (1985).

Results of ^{14}C dating of Nal Sarovar samples are given in Tables 3.2 and 3.3.