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SEMI-ANNUAL TECHNICAL REPORT

Leona M. Libby

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13. ABSTRACT

The research program in Historical Climatology has the general purpose to show feasibility of determining global climate in the past, by determining past trends in surface temperature of the earth. The method being studied involves measuring past temperatures using isotope "thermometers" in bio-organic data bases. For example, isotope ratios in tree rings being formed are expected to change if the temperature changes so that tree rings formed long ago may exhibit different ratios than those being formed today. Lower limits on the temperature co-efficients have been computed, and compared favorably with experimental coefficients. New measurements of these coefficients have been undertaken. Feasibility of measurement of the isotope ratio by neutron activation for oxygen is under study, as an independent check on measurement by mass spectroscopy.

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SUMMARY

The research program in Historical Climatology has the general purpose to show feasibility of determining global climate in the past, by determining past trends in surface temperature of the earth. The method being studied involves measuring past temperatures using isotope "thermometers" in bio-organic data bases. For example, isotope ratios in tree rings being formed are expected to change if the temperature changes so that tree rings formed long ago may exhibit different ratios than those being formed today. Lower limits on the temperature coefficients have been computed, and compared favorably with experimental coefficients. New measurements of these coefficients have been undertaken. Feasibility of measurement of the isotope ratio by neutron activation for oxygen is under study, as an independent check on measurement by mass spectroscopy.

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SEMI-ANNUAL TECHNICAL REPORT
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The research program in Historical Climatology has the general purpose to show feasibility of determining the global climate in the past, determining past trends in surface temperature of the earth. The method being studied involves measuring past temperatures using "isotope thermometers," which may be understood in the following way. When bio-organic material is formed, such as cellulose, in trees, the isotope ratios of elements in the bio-organic material may differ from those in the inorganic material from which the living organism was formed and, if so, the difference depends on the local temperature. For example, the stable isotope ratios of O^{18}/O^{16}, C^{13}/C^{12} and D/H in cellulose may differ as a function of the radius of the ring or age of the tree, indicating that from time to time in the life of the tree, the climate varied.

Two important tree ring sequences are available to us for exploring the method: one a chronological sequence of Bristlecone pines assembled at the Tree Ring Laboratory, University of Arizona, and the other a sequence of European oak trees assembled in the Radio Carbon Laboratory at UCLA.

As a first step in initiating this research, computation was made of the magnitude of effect to be expected, that is, the temperature coefficients of isotope ratios of oxygen, hydrogen, and carbon were computed in cellulose assuming that it is manufactured at equilibrium with water, carbon dioxide, and oxygen in the surroundings. If instead, manufacture does not occur in an equilibrium process, then the true temperature coefficients should be larger than those computed for equilibrium. Thus from this calculation we should obtain lower limits of the effects to be expected. The report of these calculations, entitled "Multiple Thermometry in Paleo Climate and Historic Climate," by Leona Libby, January 1972, has been accepted for publication in the Journal of Geophysical Research and has been sent to the printer.

The temperature coefficient for C^{13}/C^{12} in cellulose was computed to be 0.36 parts per thousand per degree C for equilibrium formation. It is in agreement with an experimental value measured in the laboratory for water plants by Degans, et.al. (E. T. Degans, R. R. Guillard, W. M. Sackett, and J. A. Hellebust, "Metabolic Fractionation of Carbon Isotopes in Marine Plankton," Deep Sea Research, <u>No. 15</u>, pp. 1-9 (1968).

That for D/H was computed to be 2.4 parts per thousand per degree C. Shortly after completion of the calculation, data from which an experimental value for D/H in peat could be estimated was published by W. E. Schiegl, "Deuterium Content of Peat as a Paleo-Climate Recorder," Science <u>175</u>, pp. 512-513 (1972), amounting to 3.0 parts per thousand per °C, compatible with the calculated value.

With the help of Lewis Pandolfi, a graduate student in the Chemistry Department of UCLA, an experiment to determine the temperature coefficients in water plants has been undertaken. In an outdoor pond of 800 liters volume, a water plant was grown and its new growth was harvested at constant temperature 9°C during December 1971 and January 1972. Dried of external moisture, the plant material was freeze dried in a vacuum system, then pyrolysed, and finally the residual charcoal was burned in a supply of external oxygen. All fractions of H_2O and CO_2 so obtained were collected and samples of them sent to Teledyne Isotopes, Inc., Westwood, New Jersey, C/O Dr. George Kincaid, for isotope analysis of oxygen, carbon and hydrogen by mass spectrograph.

A second crop of new growth was obtained at 13°C, and also a crop of algae. These plant materials have been treated similarly, and the resulting CO_2 and H_2O is packaged and will be sent to Kincaid as soon as he is ready for them. We are now heating the pond at a rate of about 1/2 degree per day and will stabilize the water temperature at about 22° and grow a new crop of plants.

Together with Dr. Rainer Berger of UCLA, we have similarly treated Bristlecone Pine wood grown approximately 1000 years and 500 years ago, and the resulting CO_2 and H_2O samples have been sent to Kincaid.

A second part of this research interests itself in the possibility of determining isotope ratios by neutron activation, as an alternative to mass spectroscopy. In the latter method, before the isotope ratio can be measured, many chemical reactions are involved in any one of which isotope fractionation might occur. Thus using an alternate method for determination of the ratio would be important as a check on the method of mass spectroscopy.

To this end, determination of the ratio O^{18}/O^{16} is being explored by measuring the activities

$$O^{18}(n,\gamma)O^{18}(200\mathrm{KeV}\gamma)$$

$$O^{16}(n,p)N^{16}(6.1\mathrm{MeV}\gamma)$$

induced by neutrons, the first by slow neutrons and the second by neutrons of more than 10 MeV. If the thermal neutron flux in a reactor were equal to that above 10 MeV, the activities A produced in oxygen of normal isotopic abundance would have the ratios,

$$\frac{A(O^{16})}{A(O^{18})} = 2 \times 10^5$$

To determine this ratio accurately, it is best to have its magnitude ~ 1. We have achieved this by irradiating in a reactor which has a very high fast neutron flux relative to that in graphite moderated reactors. In particular, this is true of the Gulf General Atomic TRIGA reactor. In irradiations of wood and water in this reactor, both these activities have been observed at about equal intensities.

Now we have acquired several heavy water samples with concentrations of O^{18} up to 40%. Our next step will be to measure the concentrations of O^{18} as accurately as possible, probably to somewhat better than 1% with the present equipment, and with the GGA TRIGA reactor. After that has been done, we expect to be in a position to design optimal counting equipment for counting both activities at Megacycle rates so that the ratio O^{18}/O^{16} can be determined with good statistical accuracy in a reasonable time.