

### SESSION III

## I. THEORY AND INTERPRETATION OF ISOTOPE EFFECTS

### (C) Isotope effects of various important isotopes

**Sur la conversion d'oxygène en CO<sub>2</sub>, en vue du dosage isotopique de O**—H. HERING *et al.*, *Centre d'Etudes Nucléaires de Saclay, France*

*Question:* What are the reasons for converting oxygen to carbon dioxide for isotopic analysis? Could not oxygen be analysed directly? How many analyses can be done with a single charge of carbon? D. SAMUEL, *Weizmann Institute of Science, Israel*

*Answer:* Isotopic analysis on O<sub>2</sub> seems to be used to an increasing extent, but at Saclay CO<sub>2</sub> continues to be used in mass-spectrometry for the following reasons: first, corrosion of filament and other parts of the source is less than with O<sub>2</sub>; secondly, CO<sub>2</sub> is easily equilibrated with H<sub>2</sub>O whereas complete conversion of H<sub>2</sub>O into O<sub>2</sub> is difficult to achieve; thirdly, most natural carbonates give off CO<sub>2</sub> when heated; and, fourthly, the conversion of O<sub>2</sub> into CO<sub>2</sub> is not difficult and produces no appreciable change in isotopic composition if it is brought near enough to completion.

In reply to your second question, if, for example, 1.5 g of graphite were put into the boat and the process continued until 0.5 g was left over, 1.8 l. (N.T.P.) of O<sub>2</sub> would be converted into CO<sub>2</sub>. If the oxygen samples amounted to 5 ml (N.T.P.), 360 successive samples would be converted.  
HERING

*Comment:* It is comparatively easy to use CO<sub>2</sub> and thus the δ<sup>18</sup>O measurements are more precise. There are many reasons for this, such as the relative inertness of CO<sub>2</sub>, the apparent ease with which 44 and 46 peaks can be more satisfactorily focused on most dual-collector, high-precision instruments, the ability of CO<sub>2</sub> to form positive ions, *etc.* M. LEROY JENSEN, *Yale University, U.S.A.*

*Comment:* The reasons why CO<sub>2</sub> is used so extensively for mass-spectrometry are mainly historical and, with modern machines, the possibility of using oxygen should be explored. We do many such analyses and, at least as far as oxidation of the filament is concerned, we have not found that the filament is burnt out unreasonably quickly. D. SAMUEL, *Weizmann Institute of Science, Israel*

*Comment:* The use of a δ<sup>18</sup>O standard was not absolutely necessary in this case. The United States Bureau of Standards will provide suitable standards to anyone who is doing isotopic research. By using these standards,

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each research worker's results can be compared with those obtained by others who use the same standards. In  $\delta^{34}\text{S}$  work, for example, all research workers (with the exception of the Soviet scientists, who, we hope, might also follow this suggestion) have been using Cañon Diablo troilite as a standard since 1963; they assume that it has an absolute  $^{32}\text{S}/^{34}\text{S}$  ratio of 22.220, which is equivalent to zero per mil. M. LEROY JENSEN, *Yale University, U.S.A.*

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*Question:* We have found quite large isotope effects in the conversion of enriched  $^{18}\text{O}$  to  $\text{CO}_2$ . Have you considered investigating these effects more thoroughly? D. SAMUEL, *Weizmann Institute of Science, Israel*

*Answer:* The isotope effect is large (*cf. Table 2*). It is therefore very important to achieve an almost complete conversion of  $\text{O}_2$  into  $\text{CO}_2$ , and that is one of the reasons for working at about  $900^\circ$ . HERING

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### Carbon Isotope Effects in the Pyrolytic Decomposition of Manganoous Oxalate—P. E. YANKWICH and P. D. ZAVITSANOS, *University of Illinois, U.S.A.*

*Question:* In our paper† on approximation procedures Stern and I reported that, with the gamma-bar method, we have found it necessary for simple bond rupture to use an average frequency considerably larger than the frequency which one would usually associate with the broken bond. Might not a frequency larger than  $1600\text{ cm}^{-1}$  result in larger values of  $\Delta_c$  in your calculations? M. WOLFSBERG, *Brookhaven National Laboratory, U.S.A.*

*Answer:* A frequency somewhat larger than  $2000\text{ cm}^{-1}$  would yield a  $\Delta_c$  value in reasonable correspondence with at least C—O bond stretching force constants, though not C=O. However, this agreement is achieved at the expense of a reasonable value for TIF, which is taken, in this case, as the  $1/T^2 = 0$  intercept of a plot of  $L(k_2/k_3)$  versus  $1/T^2$ . The values of TIF which would be obtained for  $\omega \simeq 2000\text{ cm}^{-1}$  are significantly smaller than unity and, for a reaction model of the type employed by us, automatically suspect. We identify TIF (or, at least,  $L[\text{TIF}]$ ) with the intercept mentioned. In other words we assume that the temperatures employed in these experiments can justifiably be called "high", that is, that a linear extrapolation of a  $1/T^2$  plot is valid. YANKWICH

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### Large-scale Bacteriogenic Fractionation of Sulphur Isotopes—M. L. JENSEN and N. NAKAI, *Yale University, U.S.A. and Nagoya University, Japan*

† These proceedings, *Pure Appl. Chem.* **8**, 225 (1964).

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*Question:* Do your analyses confirm the earlier data of Thode and his colleagues indicating that the apparent time of origin of fractionation was about 800 million years ago? Secondly, does fractionation occur in higher plants which, for example, also reduce sulphate to the level of sulphide? Have any experiments been done in this regard with isolated enzyme systems? S. ARONOFF, *Iowa State University, U.S.A.*

*Answer:* The results of  $\delta^{34}\text{S}$  measurements on many hundreds of Pre-Cambrian sulphides indicate sulphur isotopic variations extending to 2000 million years ago. In addition, thousands of  $\delta^{34}\text{S}$  measurements on Phanerozoic sulphides show no correlation with time. I believe that sulphate-reducing bacteria have existed on the earth for probably more than 2500 million years.

Very cursory work and analyses carried out initially by Thode and subsequently by Kaplan show that sulphate reduction in plants is not accompanied by sulphur isotopic fractionation. Now that enzymes are being isolated in sufficient quantities, more detailed isotopic studies should be made. JENSEN

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*Question:* Does reverse fractionation occur in bacteria which oxidize sulphide or sulphur to sulphate? S. ARONOFF, *Iowa State University, U.S.A.*

*Answer:* Yes. But we believe that these processes of bacterial reduction and oxidation are unidirectional, rather than equilibrium reactions, and that the oxidized sulphur products are therefore also enriched in the lighter isotope. JENSEN

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*Question:* With regard to the biogenic origin of sulphide ores, those ores represent the end-product of considerable oxidation of organic carbon. Are the amounts of organic carbon required to produce such quantities of hydrogen sulphide compatible with the geological findings? P. D. KLEIN, *Argonne National Laboratory, U.S.A.*

*Answer:* There has been, of course, during biogeologic time, considerable oxidation of organic matter by bacteria, but I know of no biogenic sulphide deposits where all the original organic material has been consumed. In fact one gets the impression that the organisms were, so to speak, very frugal. Modern marine shales may contain more than 5 per cent organic matter, and even ancient marine shales still contain a small percentage. JENSEN

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**Variations in the Ratio  $^{48}\text{Ca}/(\text{total Ca})$  in the Natural Environment—**J. T. CORLESS and J. J. WINCHESTER, *University of Rhode Island, U.S.A.*

*Question:* With regard to the possibly erroneous analysis of the human tooth

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(sample 19), is there any indication that there is a normal distribution in fractionation effects within a population? In other words, is it possible that the known individual differences in enzymes are reflected in different rates or equilibrium values of fractionation? S. ARONOFF, *Iowa State University, U.S.A.*

*Answer:* I think the assumption implied in your question is reasonable. I should be quite surprised if all individuals in a population had teeth which exhibited the same relative abundance of  $^{48}\text{Ca}$ . I am just beginning an investigation to determine whether there might not be variations within a single tooth. Such variations might occur due to the varying rate of calcium replacement in different areas of the tooth, *e.g.*, enamel, dentine, *etc.* CORLESS

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*Question:* With regard to the wide variation in the figures concerning teeth, could the fact that one figure is doubtful be due to a difference in age of the individual, *i.e.*, could the first or second dentition have been involved? H. AEBI, *Berne University, Switzerland*

*Answer:* While the existence of an age effect in teeth is an interesting idea, I do not feel we can attribute the very large negative  $\delta$  value of sample 19 to any natural phenomenon until the sample has been re-determined. At present I am more inclined to doubt the accuracy of the analysis. However, I do feel that an investigation of the possible existence of an age effect in teeth and bones might prove fruitful. CORLESS

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*Question:* Both the passage of cations such as  $\text{Ca}^{2+}$  through biological membranes and the deposition of  $\text{Ca}^{2+}$  salts in shell and bone appear to require complexing with organic polyanions. In your oral presentation you suggested diffusion through membranes as one source of the fractionation. Have any studies been undertaken as yet, to your knowledge, with model systems in which  $\text{Ca}^{2+}$  diffuses or is actively transported through a polyanionic lattice? P. GROSS, *Brown University, U.S.A.*

*Answer:* As far as I know, no theoretical or experimental study has been made of the diffusion of the isotopes of calcium through a polyanionic lattice. At the moment we are considering carrying out laboratory experiments designed to produce fractionation. CORLESS

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*Comment:* It is important to determine whether the observed effects are single-stage or multi-stage fractionation factors. In principle they could be either, but are more likely to be multi-stage factors. J. BIGELEISEN, *Brookhaven National Laboratory, U.S.A.*

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*Reply:* As soon as we began to accumulate data and were able to form some idea of the magnitude of the fractionation, we suspected that multi-stage mechanisms might be operative in the case of calcium. At present, however, we have no concrete evidence of the relative importance of single-stage or multi-stage mechanisms. Detailed studies of local systems are just now being undertaken with a view to ascertaining which types of mechanisms may be important. As stated in the paper, it appears that "bio-mechanisms" are operative in this case. CORLESS