it may have great durability and hence make possible the measurement of temperatures in past geological ages. In order that this thermometer shall be effective, it is necessary that living organisms lay down their shells in equilibrium with the sea, that the effects shall be preserved with time, that the oceans shall have a constant isotopic composition, and that a mass spectrometer of sufficient precision and reliability be constructed.

We have found that all these various difficulties can be overcome, though there is considerable error due to geographical variation of the isotopic composition of sea water in the present oceans and presumably this may have existed in the past. Using such a thermometer we have found that the temperatures of the Upper Cretaceous seas of the southeastern United States, England, and Denmark were remarkably constant at about 16° C. The organism used for most of this work has been *Belemnitella americana*, which has a particularly compact structure. The uniformity of this temperature may be due to the better circulation of water in the Upper Cretaceous seas, though the possibility of error due to variation in isotopic composition cannot be excluded.

Technical Papers

The Availability of Various Manganese Oxides to Plants

L. H. P. Jones and G. W. Leeper

School of Agriculture, University of Melbourne, Australia

Manganese deficiency of cereals is normally confined to soils of pH higher than 6.5, and to relatively few types in this range. The majority of neutral and alkaline soils can provide plants with ample manganese and most of these "healthy" soils contain large amounts of manganese (100 ppm or more) present as oxides which are insoluble in water but easily reducible (*5*). Such oxides may comprise many structural types of different degrees of oxidation, although they are conventionally referred to as manganese dioxide.

TABLE 1

X-ray structure	Preparation	Value of n in MnO_n	Response of Algerian oats	
			Rendelsham soil§	Yambuk soil‖
Manganous manganite	W* (*3*)	1.99	Cure	Cure
Pyrolusite 1	W (*1*)	1.97	Cure	Partial Cure
Pyrolusite 2	D† (*1*)	2.00	Nil	Nil
Manganite	W (*4*)	1.52	Cure	Cure
Hausmannite 1	W (*4*)	1.35	Nil	Nil
Hausmannite 2	D‡	1.35	Nil	Nil
Cryptomelane and γ-MnO_2	Ore	...	Nil	Nil

* W: Prepared in the wet way.

† D: Prepared in the dry way.

‡ Heat treatment of hausmannite prepared in the wet way.

§ The Rendelsham soil is a grey calcareous peat of pH 7.9 from South Australia.

‖ The Yambuk soil is a grey calcareous peat of pH 8.0 from Victoria.

We have compared several oxides, both natural and synthetic, for their ability to supply manganese to oats when mixed with soils on which oats had previously failed through manganese deficiency. The added manganese in all cases amounted to 90 ppm of the soils as a uniform mixture. The plants were grown in the open in glazed pots. As the figures show (Table 1), the effects ranged from zero to complete cure.

Only oxides prepared in the wet way were successful. Electron microscopy showed that all oxides prepared in the wet way had large specific surface. This in its turn implies a large area of contact of root with oxide, which seems to be needed for success. But failure of hausmannite shows that structural type is also important.

The oxides were also compared in the laboratory for their rate of releasing manganese to a weakly reducing solution. A solution of quinol in normal ammonium acetate as used earlier for soils (*5*: see also *2*, p. 20) failed different result (Table 2), giving a good correlation with pot tests.

TABLE 2

X-ray structure	Response of oats (see Table 1)	Ammonium acetate-quinol	Water-quinol
		%*	%*
Manganous manganite	+	94	57
Pyrolusite 1	+	100	33
Pyrolusite 2	−	87	14
Manganite	+	100	35
Hausmannite 1	−	91	8
Hausmannite 2	−	6	7
Cryptomelane and γ-MnO_2	−	78	14

* Manganese extracted, expressed as percentage of total amount from 10 mg oxide with 0.05% quinol solutions at pH 7. One hour contact.

The last experiment suggests that the combined effect of a reducing agent and a concentrated electrolyte is too drastic. Quinol alone, or in the presence of a dilute electrolyte, removes only those manganous ions that are loosely held by the crystal lattice after reduction. In the presence of concentrated ammonium ion, on the other hand, the manganous ions continuously leave the surface of the oxide, exposing a fresh surface to attack by the quinol. This argument in its turn suggests that in estimating the manganese in soil that is available to plants the reducing agent should be removed before an extraction with electrolyte. Preliminary work along these lines has given results that are correlated with the health of oats, as observed in pot tests. The earlier method of extracting with ammonium acetate accompanying quinol has failed to distinguish some of these soils.

The "cure" referred to in these tables was obtained in the first year after application. Some oxides revert in some soils to a less active form in later years; the results of work on the conditions of this reversion are being prepared for publication elsewhere.

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The Distribution of S^{34} in Nature and the Sulfur Cycle[1]

A. Szabo,[2] A. Tudge, J. Macnamara, and H. G. Thode

McMaster University, Hamilton, Ontario, Canada

Relatively large variations in the abundances of the sulfur isotopes in natural sources have been reported from this laboratory (*1, 2*). Also, A. Trafimov (*3*) reported some indication of these variations. In our work, sulfates in general were found to be enriched in the heavy isotopes of sulfur as compared to hydrogen sulfide and other sources of sulfur (see Fig. 1). The results suggested that sea water sulfate, the source of many sulfate deposits, would also be enriched and that the large reservoir of sulfur in the sea might provide a base level from which the isotopic content of other sulfur sources might be reckoned. The results of four sea water sulfate samples investigated to date are given in Table 1. From Fig. 1 it can be seen that the sea water sulfates are enriched in these heavy isotopes in comparison to other sources of sulfur and that the isotopic ratios obtained are remarkably constant for the three different oceans. The high precision abundance data does show, however, some significant difference between Pacific and Atlantic.

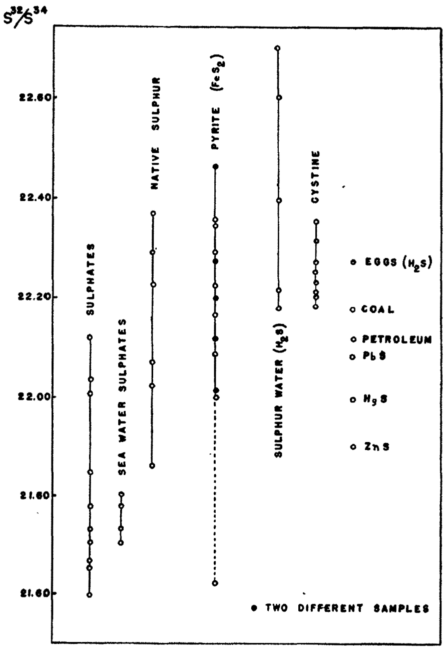

Fig. 1. Distribution of S^{34} in nature.

Previous results reported from this laboratory showed that sulfate and hydrogen sulfide present together in ground water samples, contained markedly different isotopic abundances. The sulfate samples were in every case enriched in S^{34} as compared to H_2S. This result and the fact that sea water sulfate samples are also enriched by about the same factor suggest isotope fractionation in the conversion of sulfate to hydrogen sulfide in nature.

The partition function ratios for isotopic substances involving sulfur have been calculated by the well-known methods of statistical mechanics. For example: $\frac{QS^{34}O_4^-}{QS^{32}O_4^-}$ and $\frac{QH_2S^{34}}{QH_2S^{32}}$ turn out to be 1.088 and 1.015 respectively where Q is the partition function of the isotopic molecule in question. These calculations indicate that in the conversion of SO_4^- to H_2S, perhaps by action of sulfur bacteria, the isotopes of sulfur will be fractionated, favoring S^{34} and S^{36} in the sulfate ion by a factor of the

TABLE 1

Isotopic Constitution of Sulfur from Sulfate in Sea Water

Sample No.	Location	180° Mass spectrometer* S^{32}/S^{34} ratio
1	Halifax Harbor (Atlantic Ocean)	21.70 ± 0.02
2	Resolute Bay Cornwallis Island (Arctic Ocean)	21.73 ± 0.02
3	Straits of Juan de Fuca Victoria, B.C. (Pacific Ocean)	21.78 ± 0.02
4	Pacific Naval Laboratory #27 Depth 200 yd	21.80 ± 0.01
	Average	21.75 ± 0.02

* Each sample is ratioed to Park City, Utah, having S^{32}/S^{34} equal to 22.12.

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