THERMODYNAMIC PROPERTIES AND GEOCHEMISTRY
OF ISOTOPIC COMPOUNDS OF SELENIUM

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ABSTRACT

Using "normal vibration equations" and statistical mechanics, the isotopic vibrational frequencies and the partition function ratios for various Se^{76}- and Se^{82}-containing compounds have been calculated. The equilibrium constants for selenium isotope exchange reactions derived from these partition function ratios indicate that noticeable fractionation of selenium isotopes can be expected in the laboratory and in naturally occurring processes.

The Se^{82}/Se^{76} ratios for 16 natural samples have been compared mass spectrometrically. Variations of up to 1.5% found in this ratio are discussed.

A kinetic isotope effect of 1.5% found in a chemical reduction of selenite ion to elemental selenium is also discussed.

INTRODUCTION

It is well known that isotopes of the lighter elements differ in their chemical properties to the extent that significant fractionation of these isotopes occurs in laboratory and natural processes. This is explained theoretically by the dependence of many thermodynamic properties of molecules upon their vibrational frequencies which, in turn, depend upon the masses of the atoms in the molecule. Earlier theoretical studies of possible chemical exchange processes involving the isotopes of many of the lighter elements were made by Urey and Rittenberg (1), Urey and Greiff (2), and Urey (3). Equilibrium constants for isotope exchange reactions were predicted to differ from unity and many of these have been confirmed experimentally.

Because of the large number of isotopes for many of the heavier elements, the percentage mass difference between the lightest and heaviest isotope is often considerable and, therefore, chemical differences are to be expected in these isotopes. With this in mind, investigations of the selenium isotopes were carried out. Selenium, element 34, has six stable isotopes, 74, 76, 77, 78, 80, and 82, with abundances of approximately 1.0, 9.0, 7.5, 23.5, 50.0, and 9.0%. Although the percentage mass difference between Se^{74} and Se^{82} is about 10%, Se^{76} and Se^{82}, in which case the percentage mass difference is greater than 7%, were examined because of the more favorable abundance of Se^{76} over that of Se^{74}.

The examination of the isotopes of selenium was also prompted by the results which had been obtained from studies on sulphur isotope abundances. The variations of up to 5% initially found in the natural S^{34}/S^{32} ratio by Thode *et al.* (4) in 1949 have been widened to 8% by subsequent investigations. Here the percentage mass difference is about 6% and a theoretical study by Tudge and Thode (5) in 1950 predicted equilibrium constants significantly different from unity for exchange of S^{32} and S^{34} between sulphur-containing compounds. The studies on sulphur isotope abundances have proved most interesting because of the wide distribution and the many chemical forms and valence states in which sulphur exists in nature.

Since selenium is, to some extent, chemically similar to sulphur, one might expect to find some analogous fractionations of the selenium isotopes in nature. On the other

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hand, a study of the selenium isotopes might yield new and interesting information because of the physical differences between selenium and sulphur and their compounds. Therefore, the Se^{82}/Se^{76} ratio has been investigated both theoretically and experimentally to determine the extent to which it might be altered in natural and laboratory processes.

THEORY

Isotopic Equilibrium Exchange Reactions

Since the first application of statistical mechanics to the calculation of isotopic equilibrium exchange constants, Urey (3) and Bigeleisen and Mayer (6) have carried out further simplifications which make it possible to calculate these equilibrium constants, with the exception of the hydrogen isotopes, from a knowledge of the isotopic vibrational frequencies of the participating molecules.

A typical isotope exchange reaction can be written as

$$aA_1 + bB_2 \rightleftharpoons aA_2 + bB_1, \tag{1}$$

where A and B are molecules containing the element being exchanged and the subscripts 1 and 2 refer to the light and heavy isotopes respectively of this element.

The equilibrium constant for this exchange is given by

$$K = \frac{[Q_{A_2}/Q_{A_1}]^a}{[Q_{B_2}/Q_{B_1}]^b}, \tag{2}$$

where the Q's are the total partition functions of the molecules. Urey (3) and Bigeleisen and Mayer (6) showed that the equilibrium constant for isotopic exchange reactions could be expressed in terms of isotopic partition function ratios Q_2/Q_1 which depend only on the vibrational frequencies of the isotopic molecules. In the present work, the simplification of Bigeleisen and Mayer (6) was used in which the isotopic partition function ratio is given by

$$\frac{Q_2'}{Q_1'} = \frac{\sigma_1}{\sigma_2}\left[1 + \sum_i \left(\left(\frac{1}{2} - \frac{1}{u_{2i}}\right) + \frac{1}{e^{u_{2i}}-1}\right)\Delta_{u_i}\right], \tag{3}$$

where $u = hcw/kT$; "w" is the vibrational frequency in cm^{-1} units. The summation is over "i" fundamental vibrational frequencies of the molecule and an n-degenerate frequency is summed "n" times.

$\Delta_{ui} = u_{i1} - u_{2i}$ and is always positive. The σ's are the symmetry numbers of the molecule and σ_1/σ_2 is unity if the molecule contains only one atom of the element being exchanged or more than one atom occupying indistinguishable positions. The function $(1/2 - 1/u_2 + 1/(e^{u_2}-1))$ has been termed the free energy function $G(u)$ by Bigeleisen and Mayer (6) and has been tabulated for values of u from 0 to 25.

Using this theory, the partition function ratios were calculated for Se^{82}- and Se^{76}-containing compounds. In the absence of specific spectroscopic data for these isotopic molecules, the experimental frequencies available were assumed to apply to the molecule containing the most abundant species Se^{80}, and the frequencies of the Se^{76} and Se^{82} molecular species were calculated by means of "known vibration equations". These equations relate the fundamental vibrational frequencies of molecules to "force constants" and atomic weights on the assumption of a particular model of the molecule in question.

Kinetic Isotope Effects

Since the discovery by Urey and Washburn (7) that partially electrolyzed water is enriched in deuterium because protium is evolved faster at the cathode, it has been shown

that isotopic molecules of other light elements have different rates of reaction and that, in general, the molecule containing the lighter isotope reacts faster.

The ratio of rate constants for competing isotopic reactions, in principle, can be calculated from formulae given by Eyring (8) and Bigeleisen (9). Making only the assumptions inherent in the "theory of absolute reaction rates" of Eyring (8) and Evans and Polanyi (10), Bigeleisen obtains the following expression for the ratio of the reaction rates:

$$\frac{k_1}{k_2} = \frac{K_1}{K_2} S \frac{\nu_{1L}}{\nu_{2L}} \left[1 + \sum_i^{3n-6} G(u_i)\Delta u_i - \sum_i^{3n-7} G(u_i)^{\ddagger}\Delta u_i^{\ddagger} \right], \qquad [4]$$

where, as before, $G(u)$ is the Bigeleisen and Mayer (6) free energy function, $\ddagger$ refers to the transition state of the absolute reaction rate theory, 1 and 2 refer to the light and heavy molecules respectively, S is a statistical factor and depends on the symmetry numbers of the molecules and, finally, ν_L is the imaginary frequency along the reaction co-ordinates in the transition state. The factor ν_{1L}/ν_{2L} gives the ratio of the number of light and heavy molecules in transition state which decompose in unit time. K_1/K_2, the ratio of the transmission coefficients for the isotopic reaction, has been shown by Hirschfelder and Wigner (11) to be nearly unity above room temperature.

According to the theorem of Slater (12), developed for unimolecular reactions, the frequency factor ν_{1L}/ν_{2L} of equation [4] may be replaced by $(\mu_2^{\ddagger}/\mu_1^{\ddagger})^{1/2}$, where μ is the reduced mass across the bond being ruptured. This is based on the premise that only the motions of the two atoms across the ruptured bond are involved.

Bigeleisen and Wolfsberg (13) have suggested a reaction co-ordinate which tears the two decomposition fragments apart. Such a co-ordinate would lead to

$$\nu_{1L}/\nu_{2L} = \left(\frac{\mu_2^{\ddagger}}{\mu_1^{\ddagger}} \right)^{\frac{1}{2}},$$

where μ, the reduced mass across the ruptured bond, is evaluated by using the masses of the two fragments rather than the masses of the two atoms. The choice of the co-ordinate to use, the Slater co-ordinate or the co-ordinate that tears the two fragments apart, will probably depend on the reactions under consideration and the relative bond strengths of the molecules. The usefulness of equation [4] is also limited because of the lack of knowledge concerning the "transition state" and the inability to calculate the last term of the equation $\sum_i G(u_i)^{\ddagger}\Delta u_i^{\ddagger}$. Because of these difficulties, simplifying assumptions must be made in the calculation of kinetic isotope effects.

Results of Theoretical Calculations

Table I summarizes the vibrational frequencies calculated for some Se^{76}- and Se^{82}-containing species. The spectroscopic data and the method of calculation used are found in Herzberg (14). Corrections for anharmonicity were taken into account.

Table II summarizes the fundamental vibrational frequencies that were calculated for Se^{82}- and Se^{76}-containing polyatomic molecules. References are given for the spectroscopic data and the normal vibrational force equations used in the calculations.

Table III summarizes the partition function ratios and the equilibrium constants for Se^{76}–Se^{82} exchange reactions. The method of tabulation is that used by Urey (15). The partition function ratios are listed in the first row under their respective compound at $0°$ C, $25°$ C, $100°$ C, and $250°$ C, while the equilibrium constants are contained in the main body of the table at the intersection of the pertaining row and column. An equilibrium constant greater than unity indicates that the heavier isotope will concentrate in the compound listed in the left column.

TABLE I

Diatomic molecular frequencies (cm^{-1})

	Molecule							
	PbSe	Ge^{74}Se	SnSe	C^{12}Se	Si^{28}Se	SeSe^{80}	Se$_2$	SeO^{16}
Frequency observed for Se^{80}-containing species (Herzberg)	276.6	404.4	329.8	1026.4	576.5	389.7	389.7	897.9
Frequency calculated for Se^{82}-containing species	274.2	403.0	327.3	1024.7	574.7	387.3	384.9	896.1
Frequency calculated for Se^{76}-containing species	281.8	410.5	334.9	1029.8	580.3	394.7	399.8	901.8

TABLE II

Polyatomic molecular frequencies (cm^{-1})
(The number in parentheses indicates the degeneracy of a frequency)

Molecule	w_1	w_2	w_3	w_4	w_5	w_6	Reference
H$_2$Se^{80}	2260	1074	2350				Observed (28)
H$_2$Se^{76}	2260.7	1074.4	2349.7				Calculated (29, 30)
H$_2$Se^{82}	2259.8	1073.8	2350.7				
Se^{80}O$_4^-$	834	875 (3)	416 (3)	339			Observed (31)
Se^{76}O$_4^-$	834	880.0 (3)	418.6 (3)	339			Calculated (32)
Se^{82}O$_4^-$	834	872.6 (3)	415.1 (3)	339			
Se^{80}F$_6$	708	662 (2)	787 (3)	461 (3)	405 (3)	245 (3)	Observed (33)
Se^{76}F$_6$	708	662 (2)	794.7 (3)	463.8 (3)	405 (3)	245 (3)	Calculated (34)
Se^{82}F$_6$	708	662 (2)	783.9 (3)	459.7 (3)	405 (3)	245 (3)	

EXPERIMENTAL

The Se^{82}/Se^{76} ratios of various samples were compared using selenium hexafluoride gas in a mass spectrometer.

Preparation of Samples

Selenium was extracted in its elemental form from natural samples by the hydrobromic acid – bromine technique as outlined by Noyes and Bray (16). The adaptations of this method to natural samples by Robinson et al. (17) and Williams and Lakin (18) were generally followed. The extracted selenium was then fluorinated to SeF$_6$ in a monel fluorine line. The prepared SeF$_6$ was handled in monel sample tubes to avoid contaminations.

Reduction of Selenite Ion to Elemental Selenium (Kinetic Isotope Effect Study)

Hydroxylamine hydrochloride was used to reduce sodium selenite to elemental selenium in dilute solution according to the reaction

$$2H^+ + 2NH_2OH + SeO_3^- \rightarrow Se\downarrow + N_2O\uparrow + 4H_2O .$$
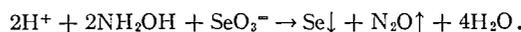
Five grams of sodium selenite were dissolved in 50 ml of water, and enough hydroxylamine hydrochloride ($\sim$0.04 g) in solution was added to slowly precipitate about 1% of the total selenium present. After 2 days, this precipitate was separated from the solution with a centrifuge. The remaining 99% of the selenium was then precipitated with excess hydroxylamine hydrochloride and separated. The Se^{82}/Se^{76} ratios for these two samples were then compared after fluorination to SeF$_6$.

Mass Spectrometry

In the normal electron bombardment of SeF$_6$, the most abundant ion species is SeF$_5^+$. Therefore, a 6-in. radius, 90° mass spectrometer was equipped with two collector slits for the simultaneous collection of Se^{76}F$_5^+$ and Se^{82}F$_5^+$ ions. The well-known null method of recording was used where a measured portion of the voltage produced by the one ion current is fed back inversely to cancel the voltage produced by the other ion current.

The sample handling system was of monel construction and entirely free of grease and mercury, which were found to produce contaminations. This system allowed two samples to be alternately introduced

TABLE III

Equilibrium constants for Se^{82}/Se^{76} exchange reactions

	$\dfrac{Se^{82}F_6}{Se^{76}F_6}$	$\dfrac{Se^{82}O_4^-}{Se^{76}O_4^-}$	$\dfrac{Se^{82}Se^{82}}{Se^{76}Se^{76}}$	$\dfrac{Se^{82}O}{Se^{76}O}$	$\dfrac{H_2Se^{82}}{H_2Se^{76}}$	$\dfrac{Se^{82}Se^{80}}{Se^{76}Se^{80}}$	$\dfrac{PbSe^{82}}{PbSe^{76}}$	$\dfrac{Se^{82-}}{Se^{76-}}$	T (°C)
$\dfrac{Q_2'}{Q_1'}$	1.059	1.044	1.012	1.009	1.005	1.006	1.005	1.000	0
	1.051	1.038	1.011	1.008	1.005	1.005	1.004	1.000	25
	1.034	1.023	1.007	1.005	1.003	1.003	1.003	1.000	100
	1.019	1.014	1.004	1.003	1.002	1.002	1.001	1.000	250
$\dfrac{Se^{82}F_6}{Se^{76}F_6}$	1.000	1.014	1.046	1.050	1.054	1.053	1.054	1.059	0
		1.013	1.040	1.043	1.046	1.046	1.043	1.051	25
		1.011	1.027	1.029	1.031	1.031	1.031	1.034	100
		1.005	1.015	1.016	1.017	1.017	1.018	1.019	250
$\dfrac{Se^{82}O_4^-}{Se^{76}O_4^-}$		1.000	1.032	1.035	1.039	1.038	1.039	1.044	0
			1.027	1.030	1.033	1.033	1.034	1.038	25
			1.016	1.018	1.020	1.020	1.020	1.023	100
			1.010	1.011	1.012	1.012	1.013	1.014	250
$\dfrac{Se^{82}Se^{82}}{Se^{76}Se^{76}}$			1.000	1.003	1.007	1.006	1.007	1.012	0
				1.003	1.006	1.006	1.007	1.011	25
				1.002	1.004	1.004	1.002	1.007	100
				1.001	1.002	1.002	1.001	1.004	250
$\dfrac{Se^{82}O}{Se^{76}O}$				1.000	1.004	1.003	1.004	1.009	0
					1.003	1.003	1.004	1.008	25
					1.002	1.002	1.002	1.005	100
					1.001	1.001	1.002	1.003	250
$\dfrac{H_2Se^{82}}{H_2Se^{76}}$					1.000	0.999	1.000	1.005	0
						1.000	1.001	1.005	25
						1.000	1.000	1.003	100
						1.000	1.001	1.002	250
$\dfrac{Se^{82}Se^{80}}{Se^{76}Se^{80}}$						1.000	1.001	1.006	0
							1.001	1.005	25
							1.000	1.003	100
							1.001	1.002	250
$\dfrac{PbSe^{82}}{PbSe^{76}}$							1.000	1.005	0
								1.004	25
								1.003	100
								1.001	250
$\dfrac{Se^{82-}}{Se^{76-}}$								1.000	0
									25
									100
									250

into the mass spectrometer under identical conditions. Usually, 5 minutes were required to switch these samples and in this operation, parts of the line used in common by both samples were evacuated and flamed. No difficulties with memory effects were experienced. Up to three continuous recordings of each sample were made in an hour. With this method of comparison, measurements of the ratio in two samples, within a single run, could be obtained with a standard deviation of ±0.0005. The same reproducibility could be obtained also for comparisons of the same samples on different days and for different chemical extractions from the same natural sample.

Experimental Results

Table IV and Fig. 1 summarize the selenium isotope abundance data obtained for a variety of natural samples.

In view of the remarkable uniformity in the S^{32}/S^{34} ratio in meteorites of all types (15, 19, 20) and the considerable evidence that this ratio represents the primordial ratio of sulphur isotopes in terrestrial sulphur, it seemed reasonable in the first instance to assume that the selenium extracted from troilite in the Canyon Diablo meteorite represents the primordial ratio of the selenium isotopes. The Canyon Diablo meteorite sample was therefore used as a primary standard and a sample of selenium from Noranda was used as a secondary standard because of the small amount of meteoritic selenium available.

In Table IV and Fig. 1, δ_{82} is the enrichment of Se^{82} in $\permil$ defined by

$$\delta_{82} = \frac{Se^{82}/Se^{76} \text{ sample} - Se^{82}/Se^{76} \text{ meteoritic}}{Se^{82}/Se^{76} \text{ meteoritic}} \times 1000.$$

TABLE IV

Variations of the Se^{82}/Se^{76} ratio in natural samples

Sample No.	Location	Alleged type of deposit	δ_{82} (‰)
1	Canyon Diablo meteorite	Selenium in troilite	0.000
2	Noranda, Quebec	Hypothermal or magmatic hydrothermal massive sulphide	+0.5±0.5
3	Murdochville, Quebec	Hypothermal or magmatic hydrothermal massive sulphide	+1.0±0.5
4	Flin Flon, Manitoba	Hypothermal or magmatic hydrothermal massive sulphide	+0.5±0.5
5	Sudbury, Ontario	Molten magma or igneous origin	+0.5±0.5
6	Mt. Lyell, Australia	Mesothermal	−1.0±1.0
7	Mt. Wingen, N.S.W.	Selenium precipitated below a pyrite bed	−1.0±1.0
8	Beaverlodge Lake, Saskatchewan	Umangite ($Cu_2SeCuSe$) in hydrothermal pitchblende bearing sulphide vein	0.0±0.5
9	Beaverlodge Lake, Saskatchewan	Chalcomenite ($CuSeO_3.2H_2O$) in association with No. 8	+0.5±0.5
10	Unknown	Refined selenium, Phelps Dodge Refining Corp., New York	+0.5±0.5
11	Unknown	Refined selenium, American Smelting and Refining Co.	+0.5±0.1
12	Unknown	Commercial SeF_6, Allied Chemical and Dye Corp., Baton Rouge, Louisiana; selenium was purchased from Company in No. 11.	+0.5±0.5
13	Southwestern U.S.A., exact location unknown	*Astragalus bisulcatus* plant containing selenite and complex organic selenium compounds	+2.0±0.5
14	Southwestern U.S.A., exact location unknown	*Astragalus pattersoni* plant containing selenite and complex organic selenium compounds	−11.0±1.0
15	County Meath, Ireland	Soil sample containing selenite and complex organic selenium compounds	+4.0±0.5
16	Mt. Shirane, Japan	Elemental selenium in volcanic sulphur	−2.0±1.0

Table V summarizes the results obtained on three reductions of Na_2SeO_3 to elemental selenium at $3°$ C.

TABLE V

Fractionation in reduction
of sodium selenite
to elemental selenium

Run	R
1	1.014
2	1.016
3	1.016
Average	1.015±0.001

The isotope effect which occurred in the 1% reaction is expressed by

$$R = \frac{Se^{76}/Se^{82} \text{ reduced Se } (1\%)}{Se^{76}/Se^{82} \text{ remainder of solution } (99\%)}.$$

δ Se^{82} in ‰	METEORIC SELENIUM	MASSIVE SULPHIDE ORES	ELEMENTAL SELENIUM BELOW PYRITE	PITCHBLENDE CONTAINING SULPHIDE VEIN	OTHER ORES	VOLCANIC ELEMENTAL SELENIUM	PLANT MATERIALS	SOIL
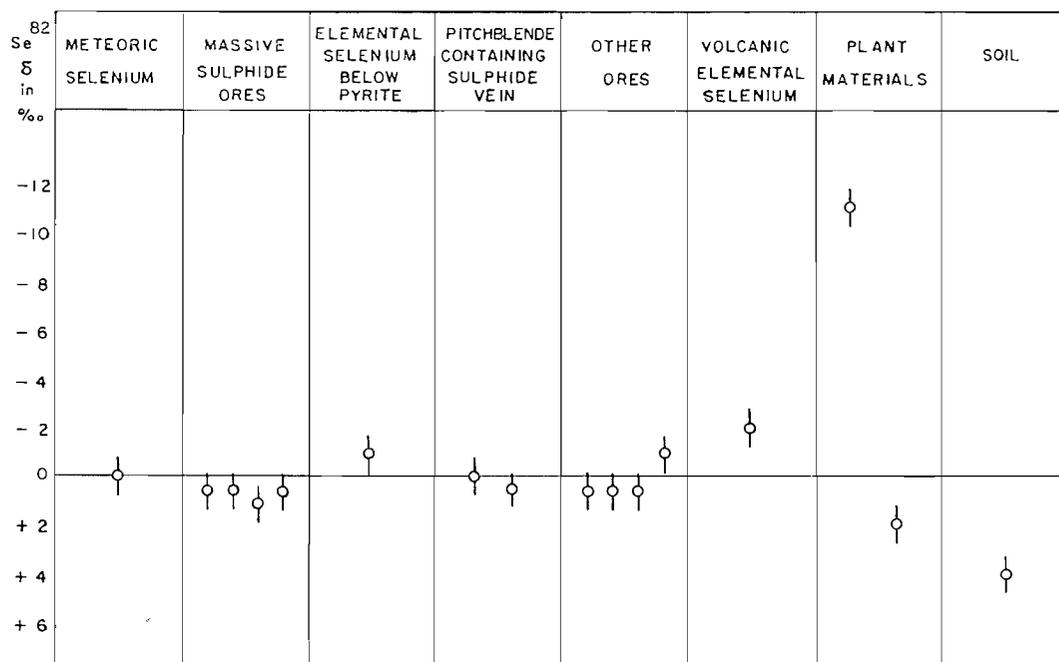
FIG. 1. Variations in the Se^{82}/Se^{76} ratio found for natural samples.

DISCUSSION AND CONCLUSIONS

Isotope Distribution in Nature

It is obvious from the theoretical study (Table III) that Se^{76} and Se^{82} differ in their chemical properties to the extent that isotope fractionations of up to 6% are predicted for Se^{76}–Se^{82} equilibrium exchange processes, provided that mechanisms are available for such exchanges.

Table IV and Fig. 1 show that the Se^{82}/Se^{76} ratio in the natural samples examined varied by 1.5%. The selenium samples from plant materials and soil show the largest variations to both sides of the meteoritic value, whereas selenium in massive sulphide ores shows little or no deviation from the meteoritic selenium value.

It is interesting to compare these selenium isotope results with similar results obtained in sulphur isotope studies.

There is an indication that the selenium extracted from massive sulphide ores is slightly enriched in the heavy isotope Se^{82} ($\delta_{82} = +0.5$‰). The effect in the case of sulphur is more pronounced. For example, samples of Sudbury igneous ore have been found enriched by 0.5 and 2.5‰ in Se^{82} and S^{34} respectively, the meteoritic values being taken as standard in each case (21).

The Se^{82}/Se^{76} ratio for volcanic elemental selenium from Mt. Shirane, Japan, is, of course, not indicative of the average value of the selenium in this volcano, since selenium is also present in other compounds. Since the theoretical study indicates that fractionation of selenium isotopes is possible between such compounds in volcanic gases, the depletion of Se^{82} ($\delta_{82} = -2$‰) found would indicate that such a fractionation occurred in this volcanic sample. Elemental sulphur from the same location is also depleted in the heavy isotope S^{34} ($\delta_{34} = -5$‰) (Sakai et al. 22).

The sample from Beaverlodge Lake, Saskatchewan, which contains umangite (Cu_2Se-CuSe) and chalcomenite ($CuSeO_3.2H_2O$) (samples 8 and 9, Table IV), is considered to

have been derived from primary sulphide ore as the selenide and subsequently partially oxidized (Robinson (23)). The results found show that little or no fractionation of the selenium isotopes occurred in this natural oxidation process.

The variations found in the Se^{82}/Se^{76} ratio for selenium extracted from plant material and soils indicate large isotope effects which have occurred probably in oxidation and reduction processes in biological systems. It is now fairly well established that the major portion of sulphur isotope fractionation in biological systems occurs in the bacterial reduction of sulphate (Thode *et al.* (24, 25)). In addition to reducing sulphates, anaerobic bacteria are known to reduce selenates and selenites as well, and these might provide a mechanism for fractionation of the selenium isotopes.

Equilibrium Isotope Effects

The fractionations in the Se^{82}/Se^{76} ratio is not expected to be as high as that found in the S^{34}/S^{32} ratio for two reasons:

(1) From statistical mechanics, the partition function ratios are lower, e.g., for $S^{34}O_4^=/S^{32}O_4^=$, $Q_2'/Q_1' = 1.088$ at 25° C; while for $Se^{82}O_4^=/Se^{76}O_4^=$, $Q_2'/Q_1' = 1.038$ at 25° C.

(2) The potential for oxidizing elemental selenium to the $+6$ valence state is quite high ($Se \rightarrow H_2SeO_4$ -1.89 volts) in comparison to that of sulphur ($S \rightarrow H_2SO_4$ -0.58 volts). For this reason, sulphates are abundant in nature, while selenates are rarely found. Since isotope effects are higher in equilibrium exchanges if a greater valence change is involved (See Table III), the above fact further lowers the natural isotope fractionation expected with selenium in comparison to sulphur.

Kinetic Isotope Effects

It has been found in studies of kinetic isotope effects in the bacterial reduction of sulphate that, while the fractionation varies with the metabolic rate, the maximum value obtained at low metabolic rates approaches that obtained in a direct chemical reduction (Harrison and Thode (25, 26)). For this reason, the isotope effect found in the reduction of selenite is of importance. The results (Table V) indicate a kinetic isotope effect of $(R-1)\times 100 = 1.5\%$ in the chemical reduction of selenite to elemental selenium.

The question may arise about whether this is a true kinetic effect in which case $R = k_1/k_2$ for

$$Se^{76}O_3^- \xrightarrow{k_1} Se^{76}$$

$$Se^{82}O_3^- \xrightarrow{k_2} Se^{82}$$
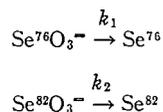
or whether some isotopic exchange of selenium has also occurred between the reactant and the product in the course of the experiment. Such an exchange would result in a gradual increase of $(R-1)$ since the equilibrium isotope constant for the exchange

$$Se^{76}O_3^- + Se^{82} \rightleftharpoons Se^{82}O_3^- + Se^{76}$$
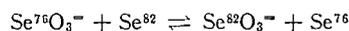
would be considerably larger than 1.015. In this connection, Haissinsky and Pappas (27) observed with tracer experiments that amorphous selenium exchanges with its ions in a $5.5 N$ HCl solution 0.1 M with respect to SeO_2. The rate was found to increase with acid concentration approaching 40% in 1 hour at $10 N$ HCl. Since this exchange was found to take place only at high acid concentrations, it would seem that a true kinetic isotope effect was observed in the almost neutral dilute solutions of the present work.

The kinetic isotope effect for the reduction of selenite to elemental selenium could be calculated using the equation of Bigeleisen (9) if the isotopic vibrational frequencies were known for the selenite ion and the activated complex. The former is currently being

calculated, while the latter is unknown. The analogous reduction of sulphates indicated that the rate-controlling step is the initial S—O bond breakage. If the rate-controlling step in the reduction of selenites is assumed to be the initial Se—O bond breakage, a simple calculation can be made by considering a Se—O diatomic model whose bond is completely broken in the activated complex. With this model, k_1/k_2 from the Bigeleisen equation is found to be 1.015 and 1.014 at 0° C and 25° C respectively. In view of the simple model assumed, the close agreement with the experimental value indicates only that the result is of the order expected.

ACKNOWLEDGMENTS

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