Oxygen-18 Composition of Oceanic Sulfate

Abstract. *Comparison of experimental data with analyses of oceanic sulfate indicates that oceanic sulfate is not in oxygen isotope equilibrium with ocean water. Preliminary experiments suggest that the turnover of sulfate in the sulfur cycle is too rapid to allow equilibrium to be established. If this is so, the sulfur cycle must exert a significant influence on the oxygen balance of the ocean-atmosphere system.*

The oxygen isotope method is proving to be one of the most useful tools for studying the reactions of oxygen-bearing minerals with one another and with water over a wide range of geological environments. Such studies often make it possible to define these environments with much greater precision than has hitherto been possible. Most of the major rock-forming mineral groups (carbonates, silicates, oxides) have been studied in detail. One group which has received almost no attention is the sulfate mineral group. My studies have revealed some interesting relationships regarding the sulfur cycle in the ocean-atmosphere system.

Early experimental studies by Teis (*1*) on the isotopic behavior of sulfates indicated that the exchange of oxygen between water and dissolved sulfate ion is extremely slow under oceanic conditions. I confirmed this general observation in a series of long-term experiments using O^{18}-enriched water and high-precision mass spectrometry. These data and those of Teis are shown in Fig. 1, where the log of the half-time of exchange (the time required for half of the sulfate oxygen atoms to exchange with water) in hours is plotted against the reciprocal of the absolute temperature. A centigrade temperature scale and a time scale in years are also shown. The rates are clearly *p*H-dependent, in agreement with experiments of Hoering and Kennedy (*2*), who found that exchange occurs through bisulfate ion and undissociated H_2SO_4. From *p*H 9 to *p*H 4 the HSO_4^-/SO_4^{--} ratio increases from about 10^{-6} to 10^{-2}. The lack of agreement between my data and those of Teis may not be real, as Teis did not specify the *p*H of his "neutral solution" (*3*).

Interpolating a line for oceanic *p*H of 8.2 and extrapolating to a mean ocean temperature of 4°C would indicate a half-time of exchange of ocean water with oceanic sulfate of about 50,000 years. To reach near isotopic equilibrium (97 percent exchange or 5 half-times) would take 250,000 years. The residence time of sulfur in the sea has been calculated to be about 21 million years (*4*), which would be equivalent to more than 80 half-times of exchange. Therefore, one would expect oceanic sulfate to be in isotopic equilibrium with ocean water.

To determine whether or not equilibrium exists in the ocean, it is first necessary to know the equilibrium isotopic fractionation factor between dissolved sulfate and water. In a series of experiments using the partial exchange technique described by Northrup and Clayton (*5*), I have been able to establish the fractionation factor temperature dependence for the anhydrite-water system and, to a less certain degree, for the dissolved sulfate-water system in the temperature range from 100° to 500°C. Figure 2 shows these data plotted as 1000 ln α versus $1/T^2$, where T is the absolute temperature in degrees Kelvin and α is the fractionation factor defined as:

$$\alpha = \frac{O^{18}/O^{16}\ \text{sulfate}}{O^{18}/O^{16}\ \text{water}}$$

In terms of the commonly used δO^{18} notation:

$$\alpha = \left(1 + \frac{\delta O^{18}\ \text{sulfate}}{1000}\right) \div \left(1 + \frac{\delta O^{18}\ \text{water}}{1000}\right)$$

where δO^{18} is the per mille difference of the O^{18}/O^{16} ratio from the O^{18}/O^{16} ratio of a standard (*6*). In the range of values discussed here, 1000 ln $\alpha \approx$ δO^{18} sulfate $-$ δO^{18} water. Hence, the 1000 ln α values in Fig. 2 closely approximate the δO^{18} difference between sulfate and water to be expected at equilibrium.

The general appearance of the anhydrite-water curve is similar to what has been found in other mineral systems (*7*). However, the slope of the curve is greater and therefore the fractionation effect larger than in any system reported previously.

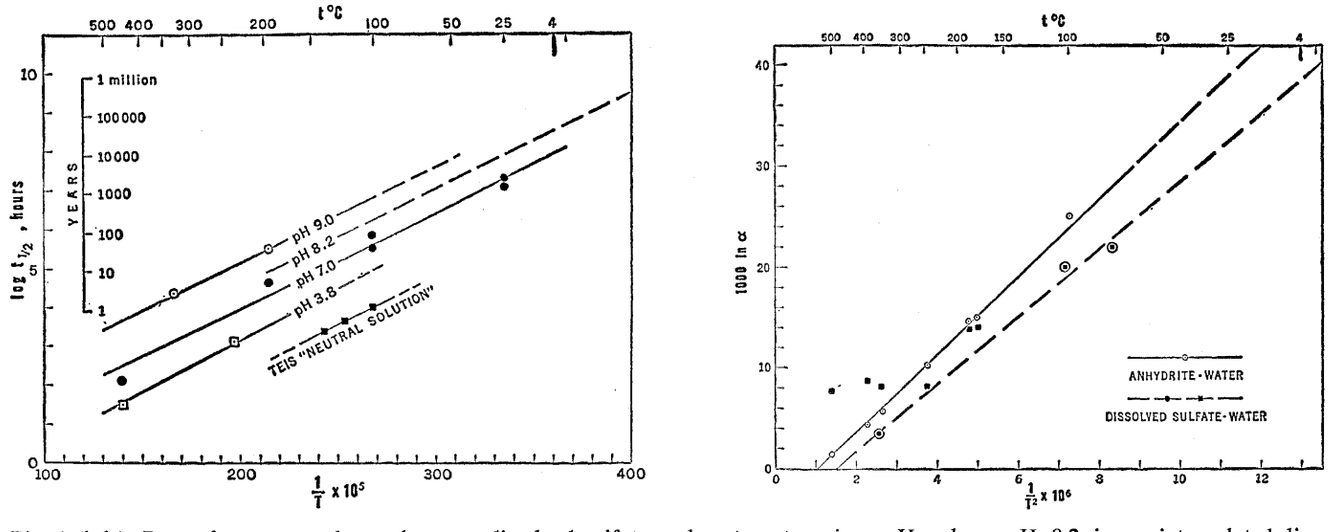

Fig. 1 (left). Rate of oxygen exchange between dissolved sulfate and water at various *p*H values; *p*H 8.2 is an interpolated line. Fig. 2 (right). Fractionation factor α as a function of temperature. The circled solid symbols are believed to be the most reliable values for dissolved sulfate-water exchange. (●) Experiments where predominant sulfur species is SO_4^{--}. (■) Experiments where predominant sulfur species is HSO_4^-.

The experimental data for the dissolved sulfate-water exchange are poorer than those obtained for the exchange between anhydrite and water. This is a result of basic experimental difficulties. In order to get measurable oxygen exchange at lower temperatures it is necessary to use a strong acid solution ($\sim 1N$ H_2SO_4), hence what is measured is the bisulfate ion–water fractionation. At higher temperatures the strong acid solution is too reactive and exchange takes place as the bomb is being cooled, making it impossible to "quench in" the equilibrium value for the bisulfate. Therefore, at higher temperatures a higher *p*H solution is used, in which the predominant sulfur species is the sulfate ion. Hence, the data for high- and low-temperature experiments are not comparable. For the purposes of discussion, however, a single dashed line has been drawn in Fig. 2 through what are considered the most reliable experimental points, on the assumption that if there is any difference in isotopic behavior between sulfate and bisulfate ions it is relatively small.

The data indicate that there is a fractionation between dissolved sulfate and anhydrite which might be as much as 6 per mille at 25°C. An experiment in which gypsum ($CaSO_4 \cdot 2H_2O$) was slowly precipitated from a saturated calcium sulfate solution yielded an apparent fractionation between dissolved sulfate and gypsum of about 2 per mille. This is in fair agreement with data from natural evaporation pans where gypsum in the sediment is about 3.6 per mille more positive than the dissolved sulfate in the associated brines (Table 1 and Fig. 3). It is not certain, however, whether these differences represent true equilibrium fractionation or a kinetic effect.

Extrapolating the dissolved sulfate curve in Fig. 2 to a mean ocean temperature of about 4°C, one would predict that oceanic sulfate should have a δO^{18} some 38 per mille more positive than ocean water. Our δO^{18} data on natural samples are expressed relative to standard mean ocean water (*6*). By definition, then, ocean water has a δO^{18} of 0 per mille and the expected value of oceanic sulfate would be 38 per mille. Analyses of seven ocean water sulfates from widely scattered localities (Table 1 and Fig. 3) are very consistent and average about 9.7 per mille. It does not seem reasonable that such a large discrepancy from the predicted isotopic equilibrium value could be due to uncertainty in the dissolved sulfate-water fractionation curve. Therefore, we must conclude that oceanic sulfate and ocean water are not in oxygen isotope equilibrium.

Table 1. δO^{18} of natural sulfates.

Location	δO^{18} SO_4	δO^{18} gypsum	δO^{18} water
	Oceanic sulfate		
Florida	9.6		0.8
Bahamas, British West Indies	9.7		.2
Gulf of Mexico	10.1		.5
British Honduras	9.3		.4
Persian Gulf	9.7		.4
Pacific Ocean			
Ventura, California	9.5		.2
San Francisco, California	9.5		.2
	Marine evaporating pans		
Qatar, Persian Gulf	9.7	14.0	4.0
Bonaire, British West Indies	9.9	13.7	1.4
	9.5		1.1
	10.9	13.5	0.5
	Nonmarine sulfates		
Salt Flat, West Texas	14.9		9.8
Radium Hot Springs, New Mexico	4.8		–9.5
Deep Springs Lake, California	15.7		–9.9

In considering what factors might prevent the establishment of isotopic equilibrium of oceanic sulfate, the one that first comes to mind is the turnover of sulfate in the sulfur cycle in nature. The two principal elements of the cycle are the bacterial reduction of sulfate to sulfur and sulfide and the oxidation of sulfur and sulfide to sulfate by inorganic or biological means.

A group of experiments on bacterial sulfate reduction using *Desulfovibrio desulfuricans* at 26°C indicate that the bacteria preferentially metabolize O^{16} according to the relationship

$$\delta - \delta_o = 1000(\alpha^* - 1) \ln f \qquad (1)$$

where δ_o is the δO^{18} of the original sulfate, δ is the δO^{18} of the sulfate when the fraction of sulfate remaining is f, and α^* the kinetic fractionation factor for this process. I found $1000(\alpha^* - 1)$ to be −4.6 per mille. This factor probably varies according to experimental conditions, but it seems reasonable to assume that it will always be negative and that residual sulfate in solution will be-

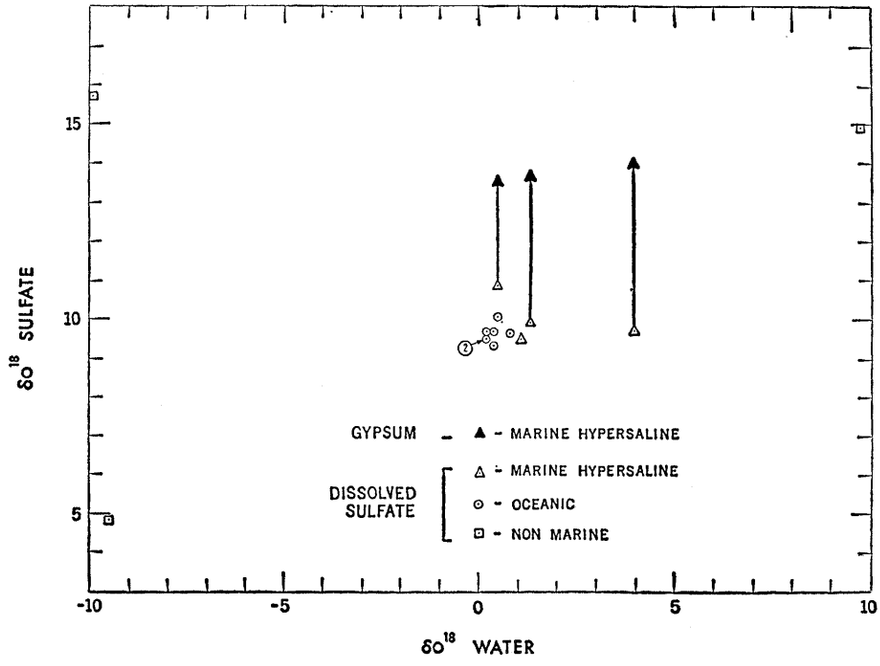

Fig. 3. Variations in δO^{18} of dissolved sulfate compared to the δO^{18} of the water from various natural waters. Locations of samples are given in Table 1.

come progressively more positive as reduction proceeds. Since oceanic sulfate is more negative than the predicted equilibrium value we cannot call on bacterial reduction as the primary controlling factor for its isotopic composition.

The second element of the cycle, the oxidation of reduced sulfur, was examined in two series of experiments. In the first series a solution of sulfate-free Na_2S was placed under an oxygen atmosphere in a closed system. As the oxygen was consumed the δO^{18} of the remaining O_2 was measured. The results showed that O^{16} is preferentially incorporated in the oxidized sulfur compound in solution following a relationship similar to that of the bacterial reduction experiments (Eq. 1). In this case δ_0 is the δO^{18} of the original oxygen while δ is the δO^{18} of the oxygen when the fraction of oxygen remaining is f. I calculated $1000(\alpha^* - 1)$ to be -8.7 per mille. Since the residual oxygen becomes more positive, the oxygen used for sulfide oxidation must concentrate O^{16} by about 8.7 per mille. In the experiment the oxidation product was predominantly sulfite rather than sulfate. In a separate set of experiments with enriched O^{18} tracers, sulfide oxidation appeared to be a two-step process:

$$S^{--} + H_2O + O_2 \rightarrow SO_3^{--} \quad (2)$$

$$SO_3^{--} + \tfrac{1}{2}\, O_2 \rightarrow SO_4^{--} \quad (3)$$

The first step was rapid but the second step was rather slow in experiments using pure components. Junge and Ryan (*8*) have shown, however, that catalytic amounts of Fe, Co, Mn, or Cu can increase the rate of the second reaction (Eq. 3) as much as a hundred fold.

A further complication is introduced by the experimental observation that sulfite undergoes isotopic exchange with water more rapidly than sulfate by a factor of as much as 10^5. In nature, therefore, the isotopic composition of sulfate produced by oxidation will be affected by the rate at which sulfite exchanges with water competing with the rate at which sulfite is oxidized to sulfate. Sorting out these effects will be difficult. However, to arrive at some rough idea as to what actually takes place in nature a second series of experiments was performed with the apparatus shown in Fig. 4. Hydrogen sulfide was allowed to diffuse slowly through a column of fine argillaceous sediment into a chamber containing sulfate-free artificial sea water of known

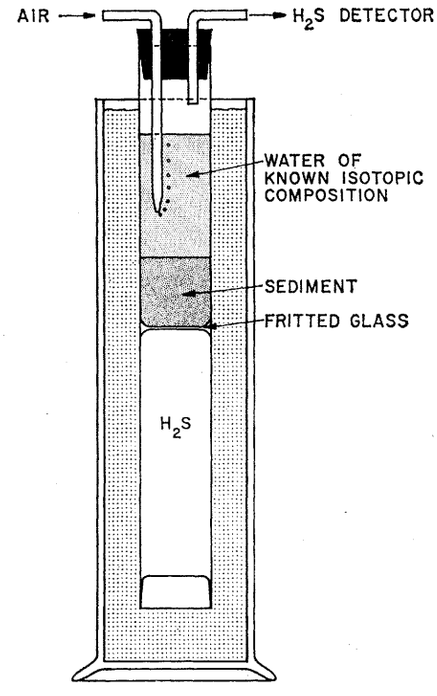

Fig. 4. Apparatus for oxidizing sulfide under simulated natural conditions.

isotopic composition. The water was kept oxidized by slowly bubbling air through the chamber. The air was prehumidified by passing it through a gas-washing bottle containing fresh water of the same isotopic composition as that in the chamber.

Initially the H_2S was absorbed in the sediment by the formation of black sulfides and the movement of H_2S could easily be traced by the migration of the black zone. During this time no sulfate formed in the chamber. The black zone moved to within a few millimeters of the sediment surface and stopped, after which sulfate began to be detected in the chamber water. The flow of H_2S was allowed to continue until the concentration of sulfate was sufficient for analysis. During this time the gas evolved from the chamber showed no detectable H_2S in $AgNO_3$ solution. No sulfite was found in the chamber water.

The isotopic composition of the sulfate made in this experiment can be expressed as follows:

$$\delta SO_4 = X(\delta_w + \epsilon_w) + (1 - X)(\delta_a + \epsilon_a) \quad (4)$$

where

$\delta SO_4 = \delta O^{18}$ of the sulfate;

$\delta_w = \delta O^{18}$ of the water oxygen;

$\delta_a = \delta O^{18}$ of the oxygen in the air;

$\epsilon_w = 1000(\alpha_w^* - 1)$, where α_w^* is the kinetic fractionation factor for the incorporation of water oxygen in sulfate;

$\epsilon_a = 1000(\alpha_a^* - 1)$, where α_a^* is the kinetic fractionation factor for the incorporation of air oxygen in the sulfate; and

X = the fraction of oxygen contributed by the water.

Because of the relatively large volume of water and constant supply of air, δ_w and δ_a did not change as a consequence of the formation of sulfate.

By using any two waters of different isotopic composition in the chamber, other factors being constant, it is possible to calculate X from values of δ_w and δSO_4. Three different experiments were run using δ_w values of 34.0, 20.0, and -4.7 per mille. The three calculations of X were 0.76, 0.64, and 0.65, with a mean of 0.68.

If 0.68 is taken as the fraction of water oxygen used, then the fraction of air oxygen used must be 0.32. Substituting these values in Eq. 2 and using $\delta_a = 23.0$ per mille yields as an average equation for the three experiments:

$$0.68\epsilon_w + 0.32\epsilon_a = -2.8 \quad (5)$$

Taking $\epsilon_a = -8.7$ from the earlier experiments, the value for ϵ_w would be 0.0 per mille, suggesting no fractionation in the incorporation of water oxygen.

Assuming for the purpose of discussion that the fractionation effects are relatively insensitive to temperature, it is possible to make a calculation of the δO^{18} of sulfate produced under oceanic conditions by use of Eq. 4.

Taking $\delta_w = 0.0$, $\epsilon_w = 0.0$, $\delta_a = 23.0$, $\epsilon_a = -8.7$, and $X = 0.68$, sulfate produced by oxidation of sulfide should have a δO^{18} of 4.6 per mille. The source of the sulfide in the ocean sulfur cycle is the bacterial reduction of sulfate, for which an experimental kinetic fractionation of -4.6 was found. Under steady-state conditions the δO^{18} of oceanic sulfate would be the algebraic difference of the two fractionations, or about 9.2 per mille. The net isotopic effect for oxidation under oceanic conditions can also be estimated graphically by plotting δSO_4 versus δ_w for the three experiments and from the curve connecting these points finding the value for δSO_4 that corresponds to a δ_w of 0. The value determined by this method is 5.2 per mille, giving a predicted δO^{18} of oceanic sulfate of 9.8 per mille. Both of these estimations compare very well with measured values for oceanic sulfate of 9.7 per mille.

This close agreement cannot be taken too seriously because in addition to

the crude nature of the experiments we are ignoring the fact that the isotopic composition of dissolved oxygen in the ocean is altered by biological activity (*9*). Also, some sulfur and sulfide oxidation occurs by biological means in the ocean and inorganically on the continents and in the atmosphere under nonoceanic conditions.

However, the results are encouraging enough to consider as a working hypothesis that the reduction of sulfate and oxidation of sulfides (and probably sulfur) exert the primary control on the oxygen isotope composition of oceanic sulfate.

Should further research confirm this hypothesis, then there are some very important geochemical implications. The total oxygen tied up as sulfate in the oceans is about 2.6×10^{15} metric tons (*4*). Inorganic isotopic equilibrium between this sulfate and ocean water ought to be established in a period of about 250,000 years. If oxidation-reduction turnover of the sulfate is responsible for preventing the establishment of isotopic equilibrium, then approximately 7.8×10^{14} metric tons of elemental oxygen (30 percent of the sulfate oxygen) passes through the sulfur cycle over a time period certainly less than 250,000 years and probably less than 50,000 years. This represents more than half the oxygen found in the present atmosphere and suggests that the sulfur cycle could be one of the important factors regulating the oxygen balance in the ocean-atmosphere system.

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References and Notes

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3. A rough estimate of the maximum analytical uncertainty in my determinations would be about 25 percent, while the discrepancy with Teis is almost two orders of magnitude. Without more complete information on the experimental and analytical techniques used by Teis it is not possible to speculate on the source of this discrepancy. I find my two experiments at 25°C to be particularly persuasive in that one ran for a little more than a year (8930 hours) while the other ran for a little less than 2 years (16,600 hours), and they both yielded essentially the same rate. It should be noted that my *p*H measurements were all made at room temperature.
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6. $\delta O^{18} = \left(\frac{O^{18}/O^{16} \text{ sample}}{O^{18}/O^{16} \text{ standard}} - 1 \right) \times 1000.$
The standard used in this report is the O^{18}/O^{16} ratio of standard mean ocean water (SMOW) as defined by Craig. Sulfates were run on carbon dioxide gas produced by carbon combustion of barium sulfate, with an adaptation of the technique described by R. N. Clayton and S. Epstein [*J. Geol.* **66**, 352 (1958)].
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Living Relative of the Microfossil Kakabekia

Abstract. *A living, ammonia-obligate, umbellate form, similar to the Precambrian microfossil* Kakabekia umbellata *Barghoorn, has been isolated from two soil specimens collected at Harlech, Wales. This organism is amenable to culture on agar and in broth. The two soil specimens are similar in that they differ from a typical clay loam in high content of carbon, hydrogen, and organic nitrogen and low levels of sodium, potassium, and titanium. In all other constituents, such as calcium, magnesium, and iron, they are quite dissimilar.* Kakabekia*-like forms can be grown in glucose-ammonia media with the latter as the sole source of nitrogen, but they can also be grown on peptone and silicate in glucose-free media. Ammonia is necessary, and growth is always slow without glucose. The fission process was not observed, but the enlargement and differentiation of a preumbellate structure into its "mature" form, followed by disintegration (senescence) of this stage, was seen. An ontogeny is proposed in which the stalk and basal bulb of the complete umbellate structure are assumed to be part of the reproductive apparatus.*

During an investigation of biological behavior in exotic and harsh environments, the ammonia-tolerant microflora in soils of different origins was studied. Ammonia tolerance is remarkably widespread (*1*), but even more remarkable was the appearance, in soil specimens from Wales, of a small microorganism exceptional for its complex structural differentiation. This form did not fall into ordinary categories such as bacteria, algae, and so forth, and its affinities remained totally obscure until *Kakabekia umbellata* Barghoorn (a Precambrian microfossil) was described by Barghoorn and Tyler (*2*).

This fossil was found in a chert deposit about 2×10^9 years of age in the Gunflint range of southern Ontario. Deposition at this site was apparently associated with a change, in the microhabitat at least, from reducing to oxidizing conditions. Barghoorn and Tyler noted that the affinities of *K. umbellata* could not readily be assigned ". . . to a living counterpart, provided any exists." When petrographic sections containing *Kakabekia* were compared with the living microorganism from Welsh soil, cultured under ammonia, the two organisms were found to be similar in size and structural detail (*3*). Within the respective morphological ranges of fossil and living populations, there were individuals that were essentially identical. At points of closest correspondence, the following description fits both forms: an umbellate form 5 to 10 μ in diameter with a centrally attached stalk, about 5 to 15 μ long, that has a terminal swelling or enlargement. The umbrella or crown is more or less polygonal and heavily rimmed, with five

Table 1. Chemical composition of soil samples tested for *Kakabekia*-like forms. Organic constituents were analyzed by combustion; the principal inorganic, calculated as oxides, by spectrography; and the trace inorganic, by spectrography. Strontium, zinc, and molybdenum were not detected.

Constituent (mg/g dry wt.)	Soil H-1 Harlech (castle wall)	Soil H-2 Harlech (courtyard)	Soil T-1 Tarrytown (orchard)
Organic			
C	106.1	46.0	24.8
H	15.3	6.7	5.5
N	9.2	9.2	5.0
Principal inorganic			
SiO_2	766.	779.	797.
Fe_2O_3	11.4	71.5	42.9
Al_2O_3	5.7	3.8	3.8
K_2O	4.8	9.6	24.0
CaO	1.4	56.0	14.0
TiO_2	1.1	2.9	4.3
MnO	1.0	2.6	1.0
P_2O_5	0.9	1.8	1.8
MgO	.7	6.8	6.8
Na_2O	.4	1.3	7.8
Trace inorganic			
Ba	0.10	0.20	0.20
Rb	.10	.20	.30
Cr	.08	.08	.08
Cu	.02	.80	.20
Ni	.02	.08	.04
B	.01	.03	.03
Zr	.00	.03	.20
V	.00	.08	.10
Pb	.00	.10	.04