The Isotopic Geochemistry of Water and Carbon in Geothermal Areas

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INTRODUCTION

From the geochemist's viewpoint the major problem associated with geothermal areas is the source of the volatiles — carbon, water, nitrogen, argon, etc. — emitted in these areas. More specifically, the problem is the proportion of these elements which is « juvenile », rising from the deep interior of the earth to contribute to the growth of the atmosphere and the ocean, compared to the proportion which is « recycled » or derived from material which has previously been at the earth's surface.

The pioneer work of JAGGAR, ALLEN, DAY, SHEPARD and others established the general proportions and characteristics of gases emanating from volcanic and hot spring areas. Water, carbon dioxide, nitrogen, argon, sulphur dioxide, and methane occur generally, often with lesser amounts of carbon monoxide, sulphur trioxide, hydrogen sulphide, chloride, fluoride, ammonia, and other compounds. All of these compounds have variously been considered as « juvenile », « magmatic », « recycled » or secondary, or, in some cases, as contamination either in the ascent of the lava, or in sampling. The occurrence of oxidized and reduced gases in the same sample is, of course, anomalous and has been ascribed to many factors. JAGGAR (1940) considered CO_2, SO_2, H_2, S_2, and CO as « truly magmatic » and H_2O, N_2, Cl_2, A, and SO_3 as « doubtful gases ». ALLEN and DAY (1935) concluded that CO_2, H_2, CH_4, N_2, A, and H_2S were original magmatic gases at Yellowstone Park. Ellis (1957) thinks it likely that N_2 is a primary magmatic gas, but that H_2 is doubtful. Many other statements could be quoted, but there is no general agreement in the literature, and no chemical criterion has yet been applied which is capable of actually defining the origin of any component.

It is very appropriate that the first conference on the application of the techniques of nuclear geology or isotopic geochemistry to the study of geothermal areas is being held here in Spoleto, because this type of research began in Italy with the work of Boato and Careri and their associates. The first application of mass spectrometric isotopic studies to geothermal areas was the study of argon isotope ratios in volcanic gases by Boato, Careri, Nencini, and Santangelo (1951) and Boato, Careri, and Santangelo (1952). They showed that the A^{40}/A^{36} ratio in Italian fumaroles and soffioni ranges up to twice as high as the ratio in atmospheric argon, reflecting the production of A^{40}, inside the earth, by radioactive decay of K^{40}. At the same time, Boato, Careri, and Volpi (1952) studied the deuterium concentration in steam and in hydrogen from the Larderello gases.

Elsewhere, Noetzlin (1952) studied the isotopic composition of volcanic sulphur samples as measured mass spectrometrically by Roth at the French AEC, and Craig (1953) measured carbon isotope variations in geothermal carbon dioxide, methane, and carbonate. Baertschi (1953) studied the O^{18}/O^{16} ratios in thermal waters, and pointed out that « juvenile » water should have about the same O^{18}/O^{16} ratio as the oxygen in silicate rocks. Noetzlin (1952) measured deuterium concentrations in springs from Auvergne, and Friedman (1953) measured deuterium in waters and gases collected by Craig in Yellowstone Park. In all these studies of thermal waters only one isotope was measured and no significant variations were observed. One exception to this was a fumarole condensate from Paricutin, analyzed for both D and O^{18} by Friedman, in which the deuterium content was similar to local water but the oxygen 18 content was enriched to about the same extent as in the silicate rocks of the area. By this time it was clear that only by studying *both* the deuterium and oxygen 18 content of thermal waters, and comparing these data with detailed studies of local meteoric water, could significant isotopic information be obtained. Therefore the present writer began a systematic study of isotopic variations in carbon, hydrogen, and oxygen in the Yellowstone Park geothermal area, together with a general study of deuterium and oxygen 18 variations in meteoric waters; with the collaboration of G. Boato and D. E. White this work was extended to the areas of Larderello, The Geysers, Lassen Park, and Steamboat Springs, and since then many other areas have been included (Craig, Boato, and White, 1956).

During the last decade a great deal of research has been done on the stable isotope geochemistry of the light elements; a general review of this work was given by Craig and Boato in 1955. The present status of our knowledge of the chemistry of thermal waters, and of magmatic, connate, and metamorphic waters has been discussed in detail by White (1957 a, b) and the chemistry of volcanic gases has been reviewed by White and Waring (1962). An excellent review of the problems of volcanology, and especially of the effects of ground water in volcanic areas, has been given by Williams (1954). From all of this work it has become evident that research on the isotopic variations in geothermal areas is important not only for the general study of the development of the earth's atmosphere, ocean, and crust, but that such techniques can make important contributions to the geological and geophysical studies of specific volcanic areas. In particular, we now have enough data to show that a systematic study of the isotopic geochemistry and geology of a geothermal or volcanic area should include all of the following:

1. Collection of gases, steam, and thermal waters in volcanic and hot spring areas, together with studies of field relationships, correlation with surface and sub-surface structure and lithology, temperature variations, regional heat flow and ground water circulation patterns, etc..

2. Analysis by mass spectrometric techniques of deuterium and oxygen 18 concentrations in thermal springs, geothermal steam, and associated meteoric and superficial ground waters.

3. Studies of carbon 13 and oxygen 18 variations in calcium carbonate surface and sub-surface deposits in thermal areas, together with similar measurements on dissolved bicarbonate and carbon dioxide gas.

4. Chemical analysis of gases in volcanic and hot spring areas, by mass spectrometry, gas chromatography, high-vacuum, and chemical methods.

5. Studies of isotopic relationships in volcanic gases such as C^{13}/C^{12} ratios in CH_4-CO_2; D/H in CH_4-H_2; A^{40}/A^{36} variations, sulphur isotope ratios, etc..

6. Chemical analysis of thermal and ground waters, and steam, for chloride, sulphate, etc. at all concentration levels.

7. Measurement of the radioactive isotopes carbon 14 and tritium in the gases, steam, and waters of thermal areas, in order to define rates of circulation, mixing, and addition of surface components.

At the present time the only geothermal region which can be considered to be studied systematically in the sense of all the seven criteria listed above is the Steamboat Springs, Nevada, area, and even here the data are not as complete as one could wish. About a dozen other geothermal areas have been studied in degrees ranging from the detail of Steamboat Springs down to a few isotopic analyses of thermal and meteoric waters. A synopsis of the work at Steamboat Springs carried out by the writer, D. E. White and F. Begemann is given elsewhere in this volume. The purpose of the present paper is to review briefly the isotopic geochemistry of hydrogen, oxygen, and carbon which is of importance for the study of geothermal areas, and to discuss some of the variations which have been observed in such areas together with the present interpretation of the results.

Isotopic variations in hydrogen and oxygen

Isotopic variations are expressed in delta units, defined as follows: if R is the isotopic ratio (D/H, O^{18}/O^{16}, C^{13}/C^{12}, etc.) in a sample, and R* is the ratio in some standard material, then:

$$R/R^* = 1 + \delta \quad .$$

The δ values are expressed in parts per thousand, or per mil (‰). The standard used for hydrogen and oxygen in natural waters is a standard mean ocean water, SMOW, defined by CRAIG (1961 b). The concentrations of the isotopic molecular species in this water, in molecules per 10^6 total water molecules, are approximately the following: $H_2O^{18} = 2000$, $H_2O^{17} = 420$, $HDO^{16} = 316$. All other molecular species except H_2O^{16} total less than one part per million. The measurement of H_2O^{17} is difficult and generally redundant, so that we shall discuss only the D and O^{18} variations.

We begin with the isotopic variations in oxygen, because the isotopic geochemistry of this element is much better known at present. The general picture of the O^{18}/O^{16} variations is given in fig. 1, which is a revised version of the drawing I sent to Dr. BOATO for presentation at the Varenna Conference on Nuclear Geology. In this drawing the δ values are given relative to SMOW which is the zero per mil reference line. The total variation of oxygen-18 in nature is about 100‰. The highest O^{18}/O^{16} ratios are found in the oxygen dissolved in sea water at intermediate depths, where the O^{18} is enriched relative to atmospheric oxygen by the preferential utilization of O^{16} for respiration. The lowest O^{18}/O^{16} ratios are found in high latitude precipitation because the oxygen-18 has been stripped from the atmospheric moisture at lower latitudes due to its preferential concentration in precipitation. This simply reflects the fact that H_2O^{18} has a significantly lower vapor pressure than H_2O^{16} so that the heavier species concentrates in the precipitation. Most of the high-latitude snow and ice has δ values no lighter than —40‰ but the snow at the South Pole has δ values as low as —53‰, the lowest values so far recorded (H. CRAIG, unpublished data).

The data shown in fig. 1 are taken from many sources in the literature and I shall not have time to discuss all of this work. The data on silicate rocks are taken from the work of SILVERMAN, BAERTSCHI, EPSTEIN, CLAYTON, and TAYLOR; the data on waters and limestones is from my own research. The point marked PDB at + 30‰ under the heading « carbonates » in the diagram is approximately the value of the PDB Chicago carbonate standard which is used by many workers as the reference standard for oxygen isotope ratios in carbonates; some other workers use the SMOW standard, so that care has to be taken to notice which standard is used. The PDB standard is generally used for paleotemperature research. The value of + 30‰ relative

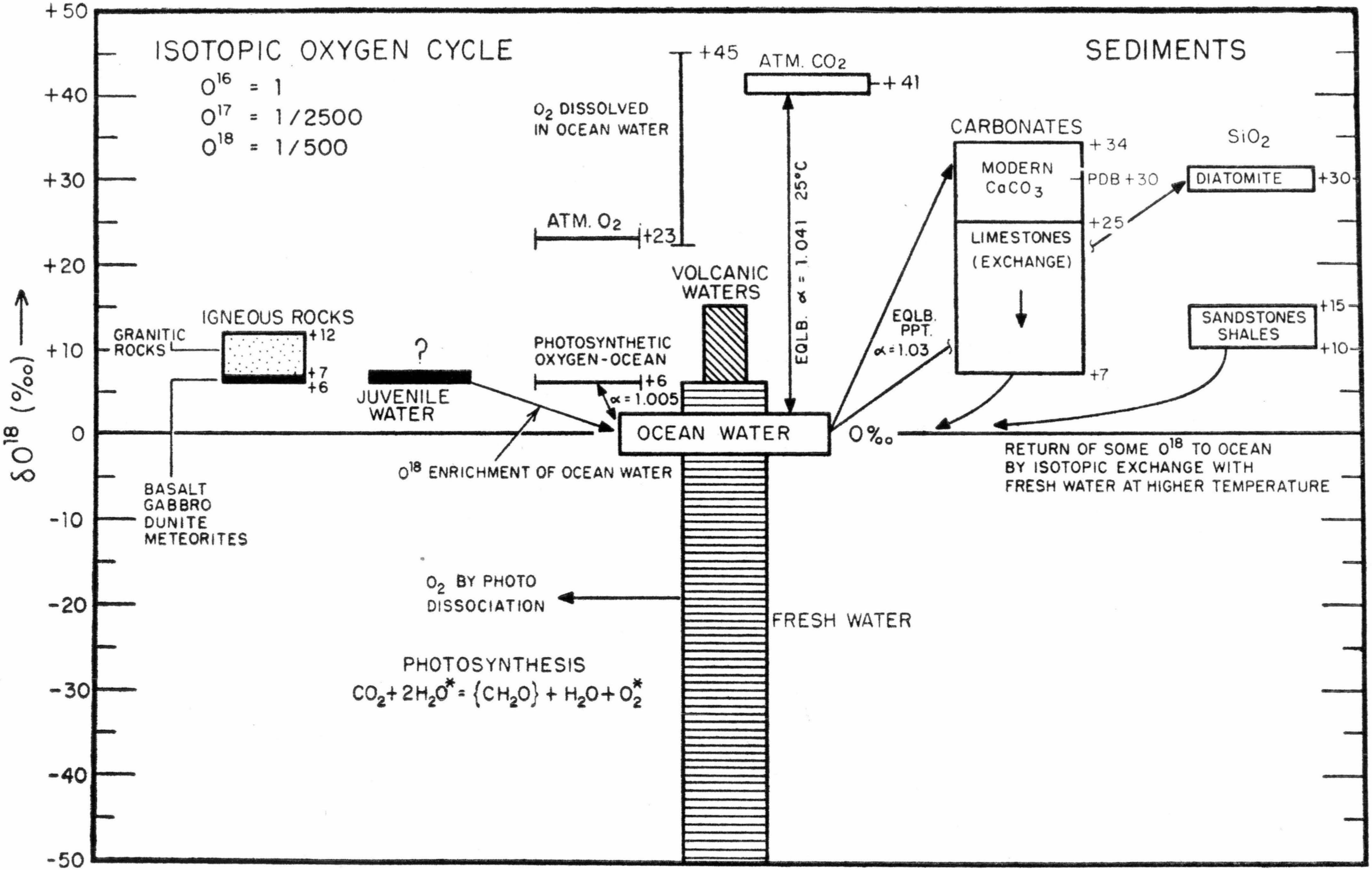

FIGURE 1. — *The oxygen isotope geochemical cycle. Isotopic variations in per mil, relative to standard mean ocean water (SMOW).*

to SMOW is only approximate as the precise intercalibration of these standards is beset by experimental difficulties and there may be an error of 1 or 2‰ in the value shown.

In the present context of research on geothermal phenomena, I want to discuss only the relationships of the rocks to the ocean water. In the first place, we note that the basic and ultrabasic igneous rocks, and the meteorites, show a very narrow range of variation with δ values of about + 6 to + 7‰. Now we know from both theory and experimental data that the fractionation factors for isotopic exchange approach unity at high temperatures, so that the isotopic species are simply distributed statistically between compounds with no preferential enrichments. The temperatures at which the fractionation effects vanish, i.e. become experimentally undetectable, can be calculated for perfect gases, but have to be measured for exchange involving solids or liquids. In the case of water exchange with carbonate and quartz, CLAYTON has shown that the isotopic fractionation essentially vanishes at temperatures of about 1000°C, and we can be sure that at temperatures in the upper mantle of the earth, there will be little or no isotopic fractionation between water and silicates. Therefore we can say that « juvenile » water, meaning water which is assumed to be coming from below the crust due to the general degassing of the mantle, will have a delta value of about + 7‰, representing high temperature equilibration with the large mass of silicates from which it separated. This value is shown in the diagram for juvenile water; the question mark refers to the question of whether, in fact, any such water is actually coming from the mantle at all at present.

Of course we should recognize that what we may call « magmatic » water, i.e. water coming from a magma in the crust, may be somewhat different in composition, and such water might be juvenile, in the sense defined above, or might simply be what I call « recycled » water, i.e. water from the earth's surface which has become involved in anatexis or magma formation. But juvenile water, in the sense of water coming from the mantle, should have the composition shown *when it comes into the crust*. After it leaves the mantle it may exchange with silicates or carbonates at lower temperatures, or undergo a variety of processes so that in fact we may never see water coming to the earth's surface with an isotope ratio which has remained completely unchanged since the water left the mantle. In other words, when we talk of juvenile material, we have to refer to material transferred from the mantle into the general complex of the earth's crust, ocean, and atmosphere, all three of which are exchanging material with each other over geological time.

In general the heavier isotope oxygen 18 concentrates in silicates and carbonates relative to water, so that water exchanging with rocks at temperatures where appreciable isotopic fractionation can exist will be somewhat depleted in oxygen 18 relative to the rock. For example, water boiling off from a granitic magma at say 700°C might have a δ value of $+ 11‰$ if the granite has a mean δ value of $+ 12‰$, and this would be true whether the water was originally juvenile water from the mantle, or simply meteoric or ocean water involved in anatexis. We would call such water « magmatic water », or in volcanic areas we might use « volcanic » water, and we could not distinguish whether such water was originally « juvenile » or « recycled » because the original oxygen isotope composition has been wiped out by exchange with the silicates. Such exchange can also take place at sub-magmatic temperatures of course. BAERTSCHI (1953) observed appreciable isotopic exchange of oxygen between water and calcite, adularia, oligoclase, quartz, and diatoms, at 100°C in times of a few weeks for the calcite and feldspars and of 100 days for quartz. In these experiments, involving exchange with finely powdered minerals, no exchange was observed at room temperature over times of three months. Both BAERTSCHI and CLAYTON have observed that the exchange with calcium carbonate takes place much more readily than the exchange with silicates, as would be expected. The experimental data on fractionation between water and various minerals have been discussed most recently by CLAYTON (1963) (*).

(*) The centigrade temperatures shown in CLAYTON's fig. 2 are in error at 700°C so that the absolute temperature should be used for quartz-water data. CLAYTON's equations for both quartz and calcite exchange with water are of the form $\ln \alpha = aT^{-2} + b$, where b is 0.00256 in both cases. The experimental constant b includes the fractionation factor between CO_2 and water at 25°C among other things, and it may be that $b = 0$ and that there

The principal oxygen isotopic interaction between the crust and the ocean is the exchange between limestone and water, which is shown in the box of « carbonates » in fig. 1. The carbonate precipitated from the ocean at present has δ approximately $+30‰$, reflecting the equilibrium fractionation factor of about 1.03 between calcium carbonate and water; the range of modern marine carbonate is about 9‰ as shown in the diagram. (Heaviest values, about $+4‰$, are found in benthonic foraminifera, lightest values occur in corals and shells of some echinoderms). Paleotemperature research has shown that well preserved fossils from the Mesozoic and late Paleozoic have preserved their isotopic composition and that it is not much different from present day values. However, most old limestones show very much lower δ values, ranging down to about $+7‰$ relative to SMOW, as shown in fig. 1, and such values are found even in late Tertiary formations. This depletion of O^{18} is evidently due to exchange with water. Exchange with ground water derived from precipitation will remove O^{18} from the limestone because the water is depleted in O^{18} relative to ocean water, so that even at normal temperatures the carbonate will become lighter. At higher temperatures of course, the fractionation factor is smaller, so that

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is an error in the estimated fractionation factor, which is in fact very poorly known. This is based on the fact that the experimentally determined ln α for calcite vs. water from 0-1000°C over the entire range of measurements is a linear function of T^{-2}, which is a behaviour characteristic of fractionation factors in the high temperature limit as the fractionation vanishes. However, in the present context, the purpose is only to point out that in calculating temperatures or fractionation factors from CLAYTON's equations for carbonates with δ values given in terms of the PDB standard, the same data must be used to convert to the absolute factors relative to water as were used in CLAYTON's equations, so that uncertainties in the term *b* cancel out. The algorithm of conversion is somewhat complicated but the result is that for any carbonate sample, (δ vs. SMOW) = 1.0306 (δ vs. PDB) + 30.6, with the δ values in per mil. The conversion of CLAYTON's carbonate-water fractionation equation to the PDB scale gives:

$$\ln(1 + \delta_c) - \ln(1 + \delta_w) = 2730\ T^{-2} - 0.03270$$

where δ_c is δO^{18} of the carbonate on the PDB scale, and δ_w is δO^{18} of the water on the SMOW scale. The slope is of course the same in both equations.

exchange with meteoric water or even with connate water of approximately the oxygen isotopic composition of sea water will cause considerable depletion of oxygen-18 in the rock. Thus some of the O^{18}removed from the sea by the precipitation of carbonate is returned to the sea after the carbonate becomes a continental limestone and undergoes isotopic exchange with water. To some extent, though not with the same facility, a similar cycle affects the siliceous sediments.

The result is that it is difficult to estimate what change, if any, has been occurring in the mean oxygen isotopic composition of sea water with time. It seems likely that at least since the Cretaceous there has been a net progressive depletion in O^{18} in the sea due to carbonate and silica deposition in the deep sea, which effectively removes material from the exchange cycle with the continents and probably outweighs the effect of any addition of juvenile water and magmatic water to the sea. However, no quantitative statements can be made until paleotemperature research is extended to some material such as marine phosphatic shells, so that by studying both phosphates and unexchanged carbonate fossils the effect of temperature variations on the isotopic fractionation can be removed and the isotopic composition of the ancient ocean can be deciphered.

In fig. 2 the deuterium and oxygen-18 variation in meteoric waters are shown as per mil deviations from SMOW. The data represent lakes, rivers, and precipitation from all over the world (Craig, 1961 a); samples from the South Pole mentioned above would extend the data down to δ values of $-53‰$ for O^{18} and about $-410‰$ for D. Waters which fall significantly off the solid straight line are waters from closed basins or other areas where evaporation has strongly affected the isotopic composition; one example of this effect is the series of points on the dashed line at the high enrichment end of the data which represents samples of the Nile River and East African lakes where the evaporation rate is very high. The isotopic effect of the evaporation of natural waters is not simply due to the loss of vapor in isotopic equilibrium with the water body, but reflects a much more complicated effect of exchange with atmospheric vapor and an approach to an isotopic stationary state (Craig, Gordon, and Horibe, 1963). For our present discussion, however, we are interested principally in the deuterium- oxygen-18 correlation shown by normal meteoric waters, in which the δ values are linearly correlated with a slope of 8, as shown in the diagram. This correlation, which is due to the relationship of the vapor pressures of HDO and H_2O^{18} over the temperature range of precipitation, provides an isotopic label for meteoric waters over the entire world, so that the ground water supplied to geothermal areas is marked by this characteristic relationship.

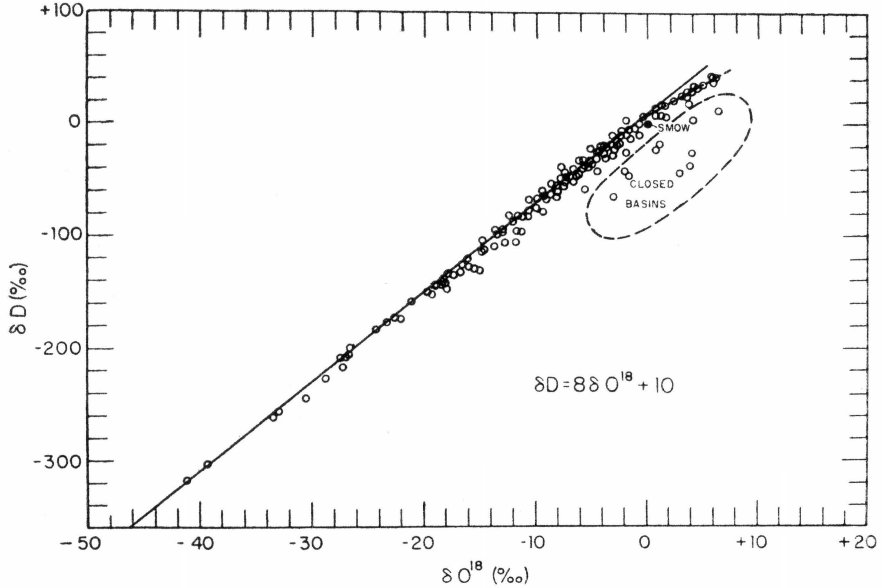

FIGURE 2. — *Isotopic variations in meteoric waters, in per mil variations relative to SMOW.*

Aside from the variations in natural waters, the isotopic geochemistry of hydrogen is rather poorly known. BOATO (1954) has shown that the water in the carbonaceous chondritic meteorites is quite similar to terrestrial water, δD values ranging from + 270‰ to — 154‰. (BOATO's data, converted to the SMOW scale and corrected for a slight calibration error in the deuterium standard, are given by (δvs. SMOW) = 0.867 δ_B — 40.8, where δ_B refers to the data given by BOATO, and the values are in per mil).

This at least gives us some assurance that there is no reason to expect juvenile water to be very greatly different from the water we see at the surface of the earth. As shown by BOATO, CARERI, and VOLPI (1952) the hydrogen gas emerging at Larderello has an isotopic composition consistent with a high-temperature equilibrium with the steam, though it is not stated whether methane hydrogen is included in the hydrogen they analyzed. FRIEDMAN (1953) found a similar effect in Yellowstone gases, after an approximate correction for the methane hydrogen.

The isotopic composition of atmospheric hydrogen has been studied by BEGEMANN and FRIEDMAN (1959); their values, approximately converted to the SMOW scale, indicate a range of δD from $-200‰$ to $+25‰$ relative to SMOW. The hydrogen is thus quite similar to meteoric water and is almost certainly derived from a photodissociation of water vapor in the atmosphere. The deuterium concentration is roughly correlated with the tritium content of the hydrogen, so that BEGEMANN and FRIEDMAN postulated that the data represent mixtures of free atmospheric hydrogen with locally produced industrial hydrogen; under such conditions, the highest values of deuterium concentration are most representative of the actual hydrogen which occurs in the high atmosphere. Hydrogen is continually escaping from the earth and there is probably isotopic fractionation with preferential loss of H and retention of D, but the magnitude of the effect is very difficult to assess as the species H, D, H_2, and HD are all involved, and if the escape is controlled by molecular diffusion in the high atmosphere the ratio of the isotopic diffusion coefficients, and thus the effective fractionation factor, is a funtion of the composition of the atmosphere (i.e. of its mean molecular weight). A quantitative evaluation of these effects, such as was attempted by MIYAKE and MATSUO (1962), is simply not possible at present. (The latter authors have in fact assumed fractionation factors for the supply of juvenile water, the escape process from the earth, and between liquid water and vapor, which simply have no relation to reality).

About all one can say about the escape process is that there has probably been a progressive enrichment of deuterium in the ocean with time, due to preferential escape of H, relative to D, from the earth. On this basis we might assume that juvenile water should have a lower deuterium concentration than present day ocean water, because the continual preferential removal of H has enriched the oceans in D relative to the supply from the mantle. Even here, however, we have to bear in mind that there may have been an initial supply of water on the earth's surface which differed considerably in isotopic composition from water incorporated in the interior of the earth.

The deuterium concentration in water in volcanic rocks has been studied by Friedman and Smith (1958) and Kokubu, Mayeda, and Urey (1961). Friedman and Smith found that water in obsidians from five localities varied from approximately $\delta D = -80$ to -150‰ (approximate values relative to SMOW), with no dependence on the quite large differences in meteoric water in these areas. Water in associated perlites did show such a dependence and was assumed to be secondary. Kokubu et al found a range from -25 to -160‰ in volcanic rocks, with no correlation with water content. Other data on hydrogen in rocks have been given by Godfrey (1962) and by Friedman, Smith, Levin, and Moore (1964). The latter authors found that the deuterium content varied inversely with total water content of biotite and hornblende in glassy rhyolites. In general, the range of D/H in volcanic rocks is quite large, and no convincing evidence, except possibly that of Friedman and Smith seems to have been obtained for any specific composition of possible magmatic hydrogen.

Kokubu, Mayeda, and Urey (1961) also analyzed water in liquid inclusions in Japanese basalts. These highly dilute waters, containing a few ppm of chloride, had previously been studied chemically by Iwasaki, Kokubu, and Katsura (1956) and Kokubu, Watanabe, and Ide (1957), who concluded that they were residual magmatic waters. δD of these waters ranged from -33 to -60‰, and Kokubu, Mayeda, and Urey concluded they represented juvenile waters. However, these authors also determined the O^{18} content of these waters (their Table 2, the heading is concealed). Although they did not note the fact, the isotopic composition of these waters falls on the line of meteoric waters shown in fig. 2, and it must be concluded that they are simply rain waters, as would be expected from the very low salinity. The isotopic composition of these waters matches that of Japanese rain, as shown in the paper of Kokubu et al..

ISOTOPIC VARIATIONS IN GEOTHERMAL WATERS

The origin of water in geothermal areas is of great interest, bearing as it does on the problem of the rate of growth of the oceans. All studies of this problem rest on assumptions as to the amount of «juvenile» water issuing from volcanoes and hot springs, and the various theories of constant ocean volume, rapid initial growth of the ocean, roughly constant rate of growth through time, and significant increase since the Cretaceous, require greatly different amounts of juvenile water. It is often assumed that superheated steam and associated CO_2 are of primary magmatic origin. Thus ALLEN and DAY (1935) computed the amount of magmatic water in Yellowstone Park hot springs by calculating the proportion of superheated steam required to raise ground water to the observed spring temperatures. They concluded that more than 13% of the discharging waters is of juvenile origin, as discussed by DAY (1939). Similar calculations have been made for other volcanic regions and much higher figures have been estimated for water directly associated with volcanoes. But until the advent of mass spectrometric work on the isotopes of water, no method of actually making quantitative measurements on the proportion of juvenile to meteoric water had been proposed.

The present approach to the problem of the origin of geothermal waters is indicated in fig. 3. It is assumed that *juvenile* water in *sensu stricto*, i.e. water ascending to the crust of the earth from the mantle, has a uniform, albeit unknown, D/H ratio. (At least it can certainly be assumed that the isotopic composition of such water is completely independent of the isotopic composition of rain on the overlying earth's surface). For the purposes of the figure, I have assumed δD of juvenile water to be $-20‰$; the specific number assigned is not important for the argument. Then in any geothermal area we should except to find varying mixtures of the local rain water and this juvenile water, and, e.g., contours on the diagram for mixtures of rain water from various areas with juvenile water, containing 20 and 40 per cent of the latter are shown. That is, the mixtures should all trend from the local rain water composition to the composition of juvenile water. The O^{18} content of the juvenile water is taken to be that of basic rocks, as discussed in the previous section, but a range of composition is shown to indicate, as discussed above, that the water may vary somewhat due to interactions with more acidic rocks or to exchange at lower temperatures in the crust, prior to reaching the surface.

It should be noted that this diagram applies specifically to the problem of *juvenile* water, and not to magmatic water in general,

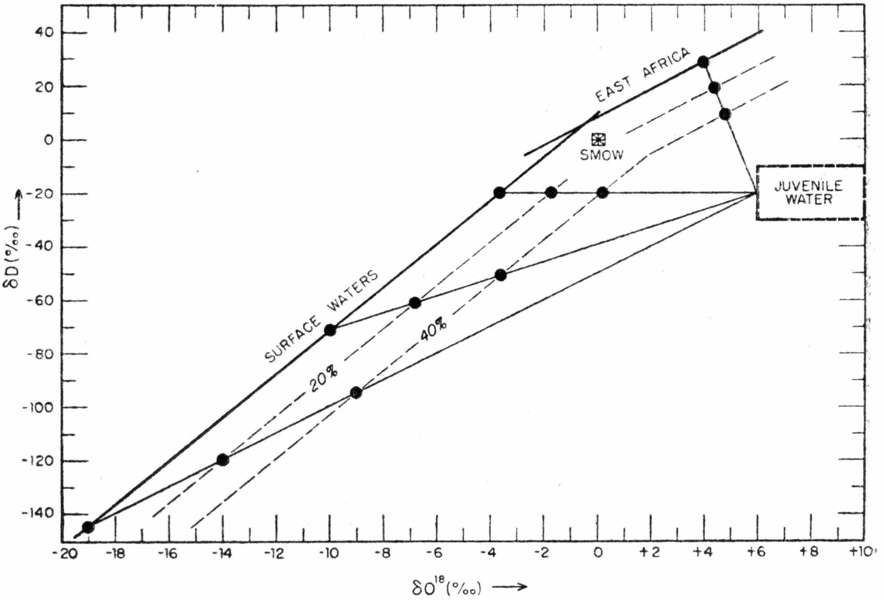

FIGURE 3. — *Isotopic pattern expected in geothermal areas for mixtures of meteoric waters with juvenile water of a constant deuterium concentration. Lines of constant proportions (20 and 40 percent) of juvenile water are also shown. The deuterium content of juvenile water assumed here is arbitrary.*

which may include *recycled* water from the earth's surface and might have any isotopic composition depending upon its history. Fig. 3 shows what we should expect to see if waters in geothermal areas are simply mixtures of local rain water and juvenile water. It will be seen that the identification of juvenile additions to thermal waters thus depends on the fortunate fact that the meteorological cycle produces a well-defined isotopic relationship in meteoric waters which definitely tags them as meteoric. Thus we want to examine the isotopic composition of volcanic water from many different areas of quite different local meteoric water, to look for evidence of the convergence indicated in fig. 3.

In fig. 4 the isotopic data are shown for some of the better known geothermal areas of the world. The area marked « Niland » is the new Salton Sea geothermal area in S. California where the very high salinity geothermal brines have recently been discovered; the other areas are, I am sure, familiar to all of you.

The data plotted in fig. 4 represent only those volcanic waters which occur as steam, or as the characteristically neutral pH or slightly alkaline hot springs, that is with pH in the general range of 5 to 9, and most often from 6 to 8. The so-called acidic type springs of low pH have been excluded from the diagram in order to show the pattern of these nearly neutral, high chloride waters or steam samples which occur in these areas. The pattern of the isotopic variations is seen at once. The deuterium concentration is constant and equal to that of the local meteoric waters of the area, and the oxygen 18 concentration shows the characteristic enrichment which we have come to refer to as the « oxygen shift », meaning the shift of the isotopic composition toward an O^{18}/O^{16} ratio higher than that of the local meteoric water. In these areas, the oxygen shift varies from essentially zero at New Zealand, to 14‰ in the Salton Sea area, the highest shift so far observed.

It should be noted that the steam and the chloride water, which I have attempted to distinguish in the diagram, show the same phenomenon in these areas. This is not true of all geothermal steam, but is true of the very high pressure, high temperature steam which is found in areas where geothermal power has been developed.

There are only two ways I known of by which such a pattern might be produced. The first is liquid-vapor isotopic fractionation. It is known that at 220°C, the fractionation of deuterium between liquid water and steam vanishes and the two phases at equilibrium have the same isotopic composition. Above this temperature the fractionation pattern found at lower temperature is reversed, and the steam contains *more* deuterium than the liquid phase; the fractionation factor goes through a minimum and then gradually approaches unity as the critical point of water is approached. However, at this « crossover » temperature of 220°C it seems there is still appreciable oxygen isotope fractionation, with the heavy isotope concentrating in the liquid phase. Thus it would be possible to boil off steam at 220°C, and to enrich meteoric waters in oxygen 18 while keeping the D/H ratio constant. This seems manifestly impossible as a cause for the observed pattern in fig. 4. The temperature to which these waters have been subjected has certainly not been a uniform 220° in every area, or even within a single area. Moreover, in some cases we are observing a steam phase, and sometimes a supercritical water phase, so that a very complicated mechanism would be required to produce this pattern by liquid-vapor fractionation. It seems clear that such mechanisms can be eliminated from consideration as a cause of the major variations.

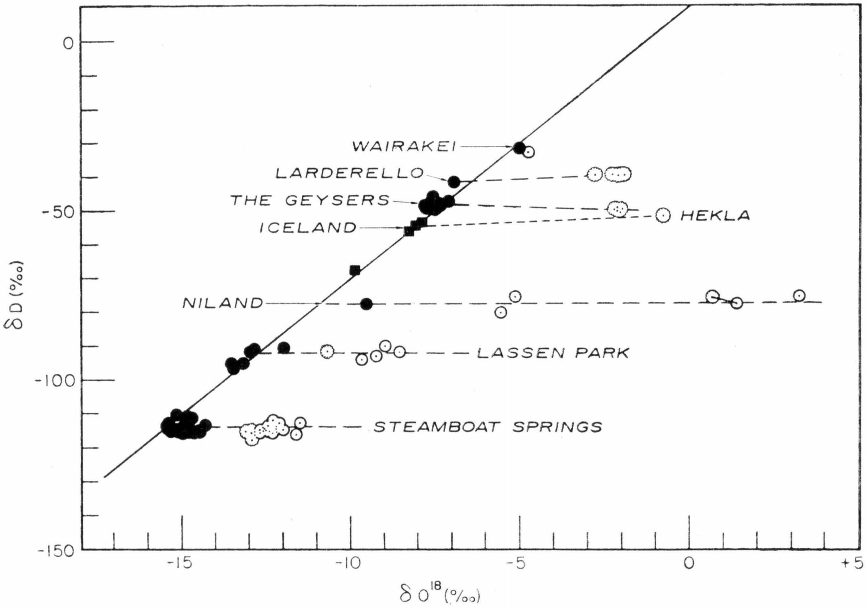

FIGURE 4. — *Observed isotopic variations in near-neutral chloride type geothermal waters and in geothermal steam in geothermal areas. Solid points are the local meteoric waters, or slightly heated near-surface ground waters. Open circles are hot springs or geothermal water, crinkled circles are high temperature, high pressure, geothermal steam.*

By far the most simple explanation of the oxygen shift is that it is due to isotopic exchange with carbonates and silicates in the rock matrix through which these waters have moved. That is, meteoric waters descending and reascending in geothermal areas exchange their oxygen with the surrounding rocks, and the isotopic composition of the water is shifted toward that of the rocks because of the high temperatures at which the exchange takes place. (At high temperatures the oxygen fractionation factor between water and minerals is smaller than the actual difference between pristine meteoric water and the rock, so that the isotopic exchange results in the water becoming higher in oxygen 18). There is a corresponding depletion in oxygen 18 of the rock, but this will not be as large because of the large amount of oxygen in the rock, relative to the water phase. On the other hand, there is very little hydrogen in a rock compared to the large amount in the water, so that the hydrogen isotope ratio in the water is hardly affected in the process of oxygen exchange.

In most of the areas shown in fig. 4 silicates predominate in the geological column and the exchange of oxygen is not large. However, in the Salton Sea (Niland) area, the geothermal brine occurs in Tertiary clastics containing much fine grained calcite and dolomite, and the oxygen shift is much higher, reflecting the much greater ease of exchange. In cores from this area Clayton has found that the carbonates show a well-marked « reverse » oxygen shift in the direction toward the isotopic composition of the water.

What about the evidence for juvenile water? As far as one can see from these areas, there is none. Of course, we could not exclude the possibility that juvenile water has precisely the D/H ratio of the meteoric water in one particular area shown in the figure, so that *one* (but only one) of the lines connecting the springs leads directly to juvenile water. Thus, for example, we could say that the geothermal steam of the Geysers contains 38 per cent of juvenile water. In that case the other areas contain none (except possibly Hekla in Iceland), and this will be true whatever area we choose. It seems hardly likely that geologists would all agree on *which* area contains the juvenile water, at the expense of all the others. Nevertheless, we can never exclude the possibility that all of the oceans have grown from one single tiny spring on a neglected hillside somewhere.

Of course we cannot say that there is not one or two per cent or so of juvenile water in these springs, because the convergence effect on the diagram would be too small to see. There is, after all, a fine structure to the diagram which is due to minor liquid-vapor fractionation effects, so that a very small amount of juvenile water, a few percent, might well be masked. But it seems difficult to believe that there could be more than five per cent in any of these areas (except for the possible one which has provided the oceans).

As far as magmatic water is concerned, we should recognize that the distinction between an exchange between meteoric water and rock, and the presence of magmatic water, breaks down as the water gets closer and closer to the magma, so that some of the effect observed might well be due to a slight addition of « recycled » meteoric water which could actually have gotten into the magma and emerged again with unchanged hydrogen isotopic composition.

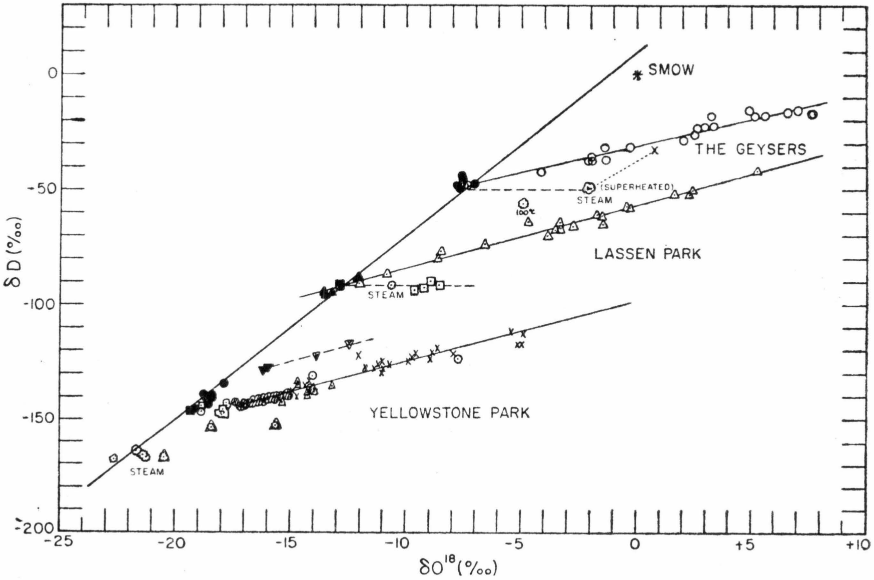

FIGURE 5. — *Isotopic patterns observed in acid type hot springs, compared with near-neutral waters and different types of steam. Solid points are local meteoric waters.*

In fig. 5 the data from two of the areas of fig. 4, and from Yellowstone Park are shown for all waters analyzed in these areas. The analyses of acidic type hot springs from The Geysers (open circles) and from Lassen Park (open triangles) are shown in addition to the waters already discussed. For Yellowstone, both the acid type waters (shown with x's) and the near-neutral chloride waters (circles and squares) are shown, as well as mixtures of these two types (triangles). This diagram is much more complicated, and I do not have time to explain all of the details shown. I want to concentrate here on the acid springs.

These acidic springs also show a well pronounced pattern in these areas (which has also been seen in several other areas now), consisting of essentially parallel lines with a slope of about 3. Again there is no indication of any convergence toward a single juvenile water. This parallelism is an effect due to high temperature evaporation at temperatures of about 70-90°C. The slope observed is not that expected if steam is being removed in isotopic equilibrium with the water, but in fact it has been shown that below the boiling point evaporation of water is characterized by a kinetic isotope effect and the equilibrium slope is not attained (CRAIG, GORDON, and HORIBE, 1963). I have been able to duplicate the slopes seen in the figure in the laboratory, simply by evaporating waters at the temperatures of these springs. So this effect is simply one of evaporation, acting on purely meteoric waters (since the lines extend from the local meteoric waters) heated by conduction and in some cases by slight addition of chloride water and steam.

The acidity of these springs must simply be due to superficial oxidation of H_2S near the earth's surface where oxygen is available. Early workers in hot spring areas had generally felt that the acid springs were the closest to magmatic water samples, but more recently WHITE at Steamboat Springs had already concluded from chemical, thermal and discharge evidence that the acid springs were only a superficial manifestation in geothermal areas.

A major part of the program during the most recent phases of this research has been the emphasis on studies of volcanic steam and its isotopic relationship to local meteoric and thermal waters. Studies have been made of the steam at Hekla Volcano, Iceland; the Njorowa gorge in Naivasha, Kenya; Carupano, Venezuela; Larderello, Italy; The Geysers, California; and St. Lucia in the West Indies; all areas where steam is the principal thermal manifestation, and at Wairakei, New Zealand, where the average bore discharge from the geothermal wells consists of a mixture of about 75% water and 25% steam by weight, as measured at one atmosphere pressure.

Two general types of steam, characterized by isotopic composition, have been found. In all the steam areas just mentioned, the steam shows an oxygen isotope shift, with no hydrogen isotope shift, relative to local meteoric waters; the oxygen 18 enrichment, relative to local meteoric water ranging from 3‰ down to no shift at all at Wairakei, New Zealand. Detailed collections were made in New Zealand in 1961 by myself and BANWELL and the bore discharge over a wide area has been found to be remarkably constant in isotopic composition. This certainly represents a reservoir of water derived directly from the local meteoric water, with no change in isotopic composition, probably reflecting a very short circulation time, and absence of isotopic exchange with rocks. In other areas, the shift of oxygen isotope ratio reflects exchange with silicates and carbonates.

The geothermal fluid at Wairakei is unique in showing no exchange effects at all. S. H. WILSON had concluded on the basis of chemical evidence that this was magmatic steam, but the isotopic data show clearly that the geothermal water is simply derived from rapidly circulating meteoric water.

The oxygen shift phenomenon is remarkably general in areas of true geothermal steam activity, and is the same as the relation observed with near-neutral chloride type thermal waters in areas of high ground water circulation. The steam in these areas is simply the reflection of the lower supply of ground water, and of tapping a reservoir at depths where steam can exist.

The second type of natural steam is that observed at Yellowstone Park and Steamboat Springs, and other areas of high ground water circulation. The isotopic relationships in the steam in such areas show that the steam is in isotopic equilibrium with the thermal water and simply boils off the hot water table. For example, we have collected steam from inside the throats of geysers, just after eruption when the level drops, and this steam shows the same effect as observed in the fumaroles in these areas. Several points for such samples of low temperature, low pressure, steam from geysers and fumaroles are shown in fig. 5 for Yellowstone, where all the steam samples are of this type, and one such point is shown for The Geysers. These steam samples display the isotopic composition expected for isotopic liquid-vapor equilibrium at the temperature at which they form.

The steam in the souffrieres of St. Lucia does not follow either pattern, in that it seems to show a hydrogen shift as well as an oxygen shift. This is the only case of such an effect observed to date, and the reason is not yet understood. Studies in this area are continuing.

This concludes the discussion of the hydrogen and oxygen isotopes, although a few specific notes on certain geothermal areas are appended to this paper, summarizing the status of the work in these areas.

CARBON ISOTOPE STUDIES

The approach to the characterization of volcanic carbon has been studied in two ways: (1) comparison of the C^{13}/C^{12} ratio of CO_2 and of total carbon in volcanic gases and waters with the carbon of limestones, organic matter, atmospheric carbon, etc., and (2) comparison of the C^{13}/C^{12} ratio in CO_2 and associated CH_4 as an indication of whether isotopic equilibrium has been obtained at some temperature or whether perhaps the two gases are derived from different sources and never equilibrated. One of the most important aspects of the carbon problem is the comparison of the isotopic relations in volcanic areas of widely different character and geologic environment, i.e. areas with and without limestones and/or shales in the local geologic column, terrestrial and oceanic areas, etc.

Fig. 6 summarizes the variations in the C^{13}/C^{12} ratio in different natural materials. These variations are in per mil relative to the Chicago PDB standard, which has about the composition of average limestone. For our purposes, it is important to note that organic carbon and material derived from organisms, such as the organic matter in shales, is quite low in C^{13} relative to the inorganic carbon present as carbonate in limestones and in the bicarbonate in the sea. An approximate mean value for the C^{13} content of carbon in the crust of the earth can be obtained by averaging the carbon in shales and limestones, using the relative proportions of these rocks in the geological column (CRAIG, 1953). This gives a value of about $-12‰$, which is probably good to about $\pm 3‰$. This is a value quite different from what may be called the active « mixed reservoir » at the earth's surface, from which this carbon has been derived. The « mixed reservoir » consists of the carbon in the sea and the atmospheric CO_2, together with the marine and terrestrial biosphere; the mean δ value of this reservoir is about —3 or —4%, depending on how such items as soil humus are weighted.

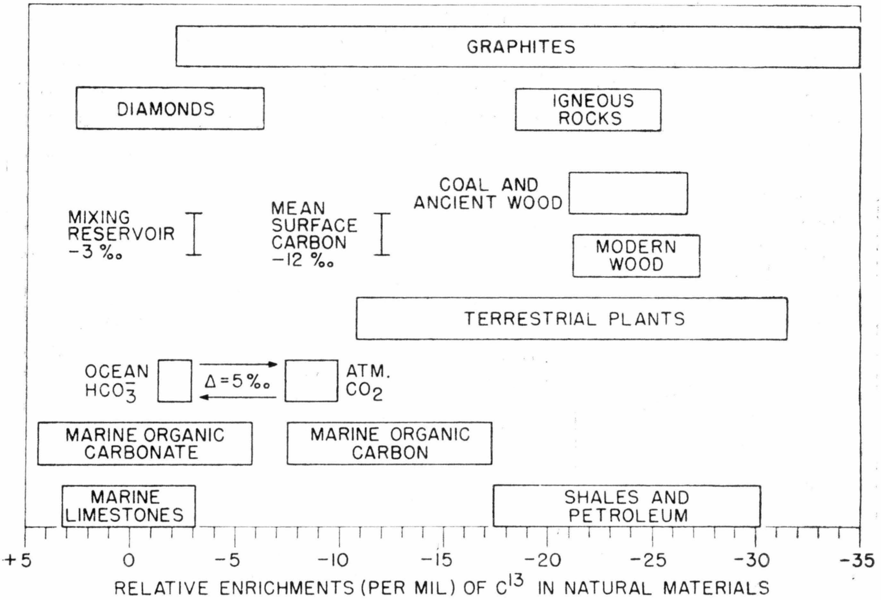

FIGURE 6. — *Carbon isotope ratios in different natural materials, shown as δ values relative to the Chicago PDB standard.* Data from CRAIG (1953).

In fig. 7, the major carbon reservoirs are displayed. The mean carbon removed from the mixed reservoir over geological time is about 8‰ lower in C^{13} than the carbon in the mixed reservoir itself, reflecting the net effect of the biological and inorganic fractionation in the withdrawal process. Because of this difference, the carbon isotope ratio in sediments should have been changing with time unless there is a steady state input of carbon of about the same isotopic composition as the material withdrawn from the mixed reservoir.

At least back to the late Precambrian, there is no indication of a trend in the isotopic composition of carbon in sediments (CRAIG, 1954). This evidence is not as firm as we would like it to be, because (*a*) the time span is only about a third of geological time, (*b*) the carbon in shales has been fractionated relative to its original source in marine organisms, and (*c*) the carbon in limestones may have been affected by the solutions which caused the oxygen isotope exchange in these rocks noted earlier. However, at least one can say there is no sign of an age effect, and we can ask what material looks like a source of juvenile carbon which might be entering the mixed reservoir to provide a steady state supply.

Of course the steady mass and steady isotopic state for the mixed reservoir require an input of juvenile carbon with $\delta =$ about —12‰, or else a simple recycling of average crustal carbon. Curiously enough, however, the carbon isotope ratios in two possible sources of juvenile carbon are quite different. As shown in fig. 7, the carbon in diamonds is about —3‰, while the carbon in igneous rocks is about —25‰. The latter carbon is actually the small amount of non-carbonate carbon found in basalts (CRAIG, 1953), and we might surmise that this is simply organic carbon from humic acids left behind by ground water or picked up by the flowing lava, except for one thing. The isotopic composition of this carbon is the same as that found for normal chondritic meteorites by BOATO (1954), and thus it may be primary. The origin of this carbon in basalts, found in amounts of a few hundredths of a percent of the rock, is one of the outstanding problems in isotope geochemistry and badly needs further study. If this carbon is real-

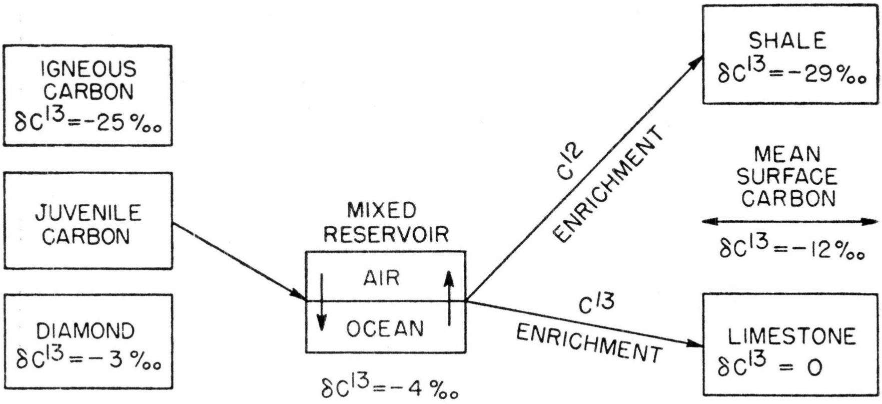

FIGURE 7. — *A model of the carbon isotope cycle and possible types of input carbon from the mantle.*

ly inorganic in origin, the difference between such carbon and the carbon in diamonds is a major puzzle.

Another place to look for juvenile or magmatic carbon is in the gases, and the data I have obtained on this type of carbon are shown in fig. 8. This figure shows only the carbon in CO_2, dissolved bicarbonate, and calcium carbonate precipitating from the waters.

A generalization which can be made from the geologic data on the areas studied is that the carbon emerging in areas where limestone is present in the column looks isotopically like the carbon in limestone itself. (The isotopic ranges of limestones and diamonds are also shown in the figure for comparison). The two major areas where this is seen are Yellowstone Park, and the rather minor thermal features at Tivoli, near Rome.

The characteristic pattern in such areas, for temperatures of carbonate precipitation below about 120° is that the C^{13} is enriched in the order: carbonate, dissolved bicarbonate, CO_2. At higher temperatures the fractionation reverses so that the carbonate has less C^{13} than the dissolved HCO_3^-, and about the same content as the CO_2. A rather crude justification can be made for this from theoretical considerations; at least it was predicted by UREY before being observed. In any case the effect can be seen in the difference between the «neoteric» (a word I invented for recent superficial precipitation in thermal areas) carbonate and the carbonate found in deep cores at Yellowstone Park, shown in fig. 8. The O^{18} difference between the core carbonates and the hot spring water at Yellowstone show that the carbonate precipitation at Yellowstone took place at about 200°C. Similarly, the range of C^{13} variation at Steamboat Springs in the carbonates shown in fig. 8 are correlated with temperatures of precipitation. In both these areas the dissolved bicarbonate gives the best mean value for the C^{13} content of the emerging carbon.

At Steamboat Springs, no limestone is known to occur in the geothermal area, and unless it is concealed under a large thrust fault somewhere at depth WHITE has been forced to conclude it is absent from the section. Similarly at Lassen Park and at The Geysers, there is no evidence for any significant amount of limestone anywhere in the local section. Time is not available here for me to review the geological details of these areas, but they are easily found in the literature, and McNITT, who has recently been restudying the area around The Geysers in detail has been unable to find any evidence for a significant amount of limestone. Interestingly enough, in these three areas, the carbon 13 content of the carbon is trending around —8 to —11‰, rather close to the value required for juvenile carbon in a steady state crustal model. Of course we do not have nearly enough data, but as more geothermal areas are studied we will surely begin to understand this situation a good deal better.

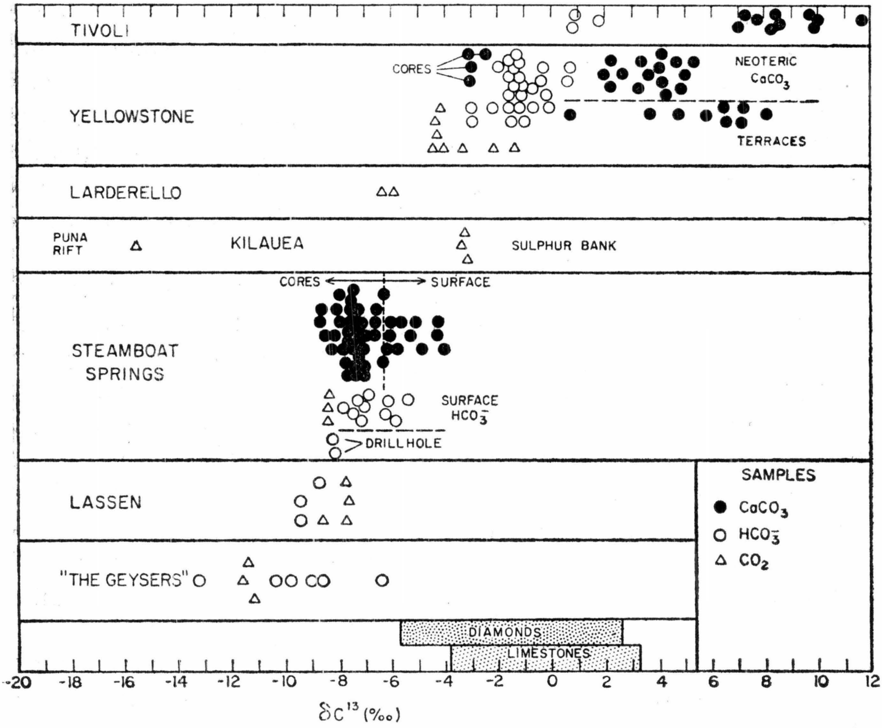

FIGURE 8. — *Carbon 13 variations in CO_2, bicarbonate and calcium carbonate in thermal areas.*

HULSTON and MCCABE (1962) have studied the carbon at Wairakei and find it is similar to the carbon at Yellowstone Park in isotopic composition. The CO_2 emerging at Wairakei contains a small amount of radiocarbon, indicating a relatively short circulation time with some carbon derived from carbon in ground water which contains some activity (FERGUSSON and KNOX, 1959). In contrast, the CO_2 emerging at The Geysers, Steamboat Springs, and the Salton Sea area is completely dead. The observable activity at Wairakei is probably correlated with the relatively shorter circulation time indicated by the lack of an oxygen shift in the geothermal water.

NAUGHTON and TERADA (1954) collected CO_2 from the Sulfur Bank fumarole on Hawaii which was analyzed mass spectrometrically by NIER. The data cannot be exactly correlated with δ values vs. PDB, but the results were very similar to the data shown in fig. 8 for Sulfur Bank, which are analyses on other samples which NAUGHTON collected and I analyzed. NAUGHTON and TERADA also gave data on gas collected from a 1950 Mauna Loa lava flow in an evacuated metal tube while the lava was still at a temperature of about 700°C. The CO_2 δ value of this gas was about $-26‰$, which is very close to the values described above for carbon in Hawaiian lava flows. A sample of the lava heated in vacuum by NAUGHTON and TERADA gave off CO_2 with a δ value which would be about $-20‰$ on the PDB scale. WASSERBURG, MAZOR and ZARTMAN (1963) obtained δ values of -18 and $-24‰$ on CO_2 from a hole drilled into molten lava on Hawaii. These samples were collected by trapping at liquid air temperature, and the values may be somewhat affected by fractionation effects in collection. In any case, one sees that CO_2 collected from the lavas themselves agrees generally with the carbon actually found in basalts, with respect to isotopic composition. However, this carbon is quite different from that found in fumaroles nearby. The explanation of these data must be intimately connected with the problem of the carbon in the rocks and its origin, as discussed earlier.

Carbon also occurs in volcanic and hot spring gases as methane. The CH_4 at Yellowstone was studied by CRAIG (1953); samples varied widely from -10 to $-28.4‰$. It is now known that the high C^{13} values obtained are incorrect and were due to incomplete separation of the very much larger amount of CO_2 during flow through liquid nitrogen cooled traps. BOATO and I have measured other samples from this area and find that the value for Diamond Spring, given previously as $-10‰$ should actually be $-30‰$. We have also analyzed methane from The Geysers, and found a range in three springs of from -29 to $-29.5‰$. Methane from Larderello analyzes $-24.8‰$; which may be compared with CO_2 from the same gases shown in fig. 8. Thus the newer data show that the methane in all these areas is generally light, ranging from about —25 to —30‰. Geothermal methane data given by Hulston and McCabe (1962) and by Wasserburg et al (1963) show similar values, much lower in C^{13} than associated CO_2.

Isotopic equilibrium might be established between CO_2 and CH_4 via the chemical reaction

$$CH_4 + 2H_2O = CO_2 + 4H_2$$

if the kinetics of the reaction are such that appreciable exchange can occur at the temperatures involved. The isotopic fractionation factors for exchange between methane and CO_2 were calculated by Craig (1953). Above 300°C, the fractionation factor goes exponentially to unity vs. T^{-2}, and the data, extrapolated above 600°K from the general calculation, are represented by

$$1000 \ln \alpha = 6.736 \left(\frac{1000}{T}\right)^2$$

where T is absolute temperature, and $\alpha = R_{CO_2}/R_{CH_4}$ and R is C^{13}/C^{12}. This equation is obeyed closely at 600°K but the relation is non-linear at lower temperatures. Calculated data at lower temperatures are given by Craig (1953).

Equilibrium temperatures calculated for the CO_2 data in fig. 8 vs. the associated CH_4 data given above, give isotopic temperatures of 200°C for Yellowstone, 320°C at Larderello, and 340°C at The Geysers. These are characteristic of the kind of temperatures found by this method and are certainly reasonable as temperatures at which the kinetics of the chemical exchange reaction might be quenched so that the isotopic composition is frozen in.

However it should be noted that the isotopic composition of the CH_4 is quite characteristic of organic carbon (*cf.* fig 6) and thus the « reasonable » temperature may be completely fortuitous. We may simply be dealing in these areas with methane derived from organic matter, associated with the CO_2 but never having undergone any significant isotopic exchange with the CO_2. Further data on this matter can be obtained from a study of the kinetics of the reaction and the possible catalytic effects of substances in the rocks through which such gases travel.

Craig, Bainbridge, and Bien (in preparation) have shown that the CO_2 emerging at The Geysers and at Steamboat Springs contains no measureable radiocarbon. The radiocarbon content of the groundwater which enters these geothermal systems is reduced by addition of dead carbon from a magmatic or a limestone source, and also by the radioactive decay of C^{14}. These authors have presented a model for the decrease of the activity as a function of time, in which any proportions of hydrodynamic or « pipeline » flow through an aquifer and mixing in a general thermal water reservoir can be combined; this model is shown schematically in fig. 9. In the equation shown in this figure, R and R_o are the C^{14}/C^{12} ratios in the emerging hot spring CO_2 and in the carbon in the original groundwater entering the system respectively, and C and C_o are the carbon concentrations in the emerging and entering water (it is assumed that the bulk of the carbon is carried by the dissolved

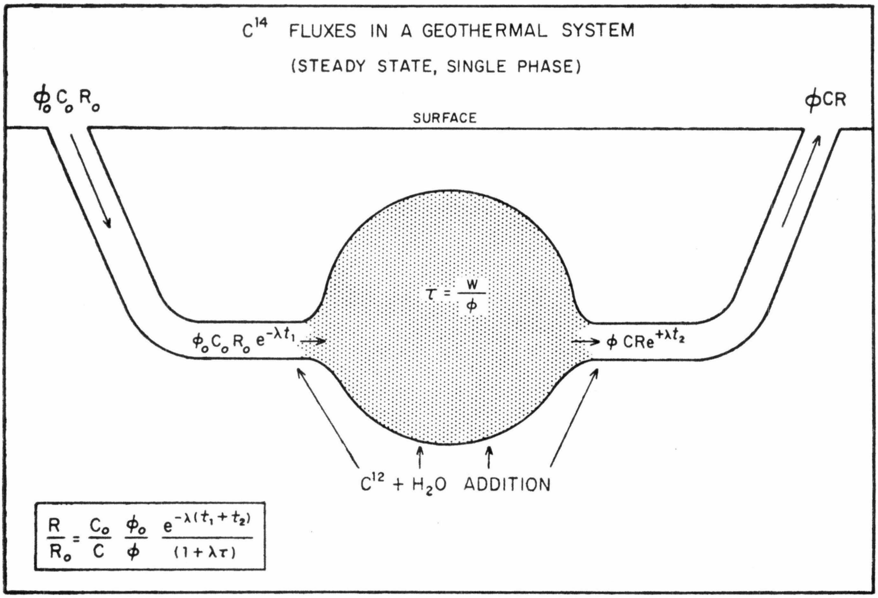

Figure 9. — *A model for the decrease of radiocarbon activity in thermal waters and gases, relative to entering ground water. Symbols are described in the text.*

bicarbonate). Thus C_o/C is the fraction of surface carbon in the mixture. Φ and Φ_o are the flowrates of water from and into the system, and the ratio of these flowrates is about unity, since the isotopic data on water show that no significant amount of magmatic water is added to the meteoric water. λ is the radioactive decay constant, and τ is the mean lifetime of water in the mixed reservoir, which may or may not actually exist.

With $\tau = 0$, the effects are only those of « pipeline » flow and addition of dead carbon at depth. The parameter t, where $t = t_1 + t_2$, is the total time elapsed in such flow into (t_1) and out of (t_2) the system, and in this case t is the mean flow time through the geothermal system. With $t = 0$, the aquifer transport is very fast, and all the effects are due to time spent in a mixed thermal water reservoir plus the addition of dead carbon into the reservoir. With both t and $\tau = 0$, the effect is one of dilution only. Since some estimates can be made of the value of Φ, as has been done by WHITE at Steamboat Springs by measuring the chloride water flow from the thermal system, the model allows rather quantitative estimates of time spent underground as a function of estimated size of the mixed thermal reservoir (which can be zero).

Samples collected in these two areas have shown radiocarbon activities of less than 0.54% of modern activity, using a three standard deviation upper limit. This shows there is no contamination in the collection procedure. In the work on these samples it was found that the coal standard in use at the Chicago and La Jolla radiocarbon laboratories actually contained 0.86% of the activity of modern wood. Tar from the La Brea tar pits, now used as a standard at La Jolla, is similar to the geothermal gas samples and contains no detectable activity. A small amount of activity in the standard does not affect most types of radiocarbon dating, but is most important when looking for very small traces of activity in geothermal systems.

We have since found that CO_2 emerging from the old CO_2 wells in the former commercially used CO_2 gas field near Niland, California (in the Salton Sea geothermal area) is completely dead. We plan to obtain a large amount of carbonate from this gas for a radiocarbon standard for geothermal work, and hope to be able to supply samples of this to other laboratories working on this problem.

SPECIFIC AREAS INVESTIGATED

A few comments on some specific areas investigated are here appended in order to show the type of work which has been done. Space and time are not sufficient for a large amount of detail and only brief summaries are given. In areas such as Steamboat Springs, where no limestone source of carbon is known, the emerging carbon, minus the fraction of carbon which is entering the system in ground water, is stated to be « probably magmatic » as we know of no other source, and the δ C^{13} values do not resemble limestone but are closer to what may be magmatic or juvenile carbon. However, it should be noted that of course no definite evidence of the magmatic origin is yet available, and further study may modify such statements.

Much of this work has been done in collaboration with various investigators who have worked in the specific areas: with D. WHITE at Steamboat Springs and in other areas, and also with F. BEGEMANN who has done tritium analyses on the waters from Steamboat and other areas and done much thinking on models for the tritium activity; with G. BODVARSSON who provided the Iceland samples; with C. J. BANWELL and T. A. RAFTER in New Zealand; with G. R. ROBSON of the Volcanological Research Department in Trinidad, B.W.I.; with Dr. A. O. THOMPSON of the Mines and Geological Department in Kenya and many others. I am very grateful for the samples, knowledge, and assistance they have provided. Professor BOATO collected some of the early samples and arranged for samples from Larderello; he has maintained an active interest in this work and has provided invaluable discussion and comments throughout all this research. I regret the fact that he has gone back to pure physics but the development of Professor TONGIORGI's very active research group at Pisa will insure the continuing development of this type of research in Italy.

Steamboat Springs, Nevada

This work has been done in collaboration with D. WHITE of the USGS. Some one hundred water and steam samples have been analyzed for deuterium and oxygen 18 concentration. About 50 samples have been analyzed for dissolved bicarbonate concentration and carbon 13 content. Some 50 samples of surface and vein deposit carbonate have been analyzed for carbon 13 and oxygen 18 variation. Gas samples have been analyzed for carbon 13 and carbon 14 content, and chloride and pH measurements have been made on the water samples. Detailed chemical analyses of the waters have been made by the USGS. This is typical of the coverage and analytical data for other major areas discussed below.

Seasonal variations of these parameters, over several years, have been studied in the thermal waters, ground waters, of the surrounding areas, and streams and lakes. The thermal waters show the « oxygen isotope shift » relative to local meteoric waters. The work has shown that at least 95% of the thermal water in this area is of meteoric origin, and possibly all of it is meteoric. The source water feeding the hot springs has been characterized and the supply areas and structures feeding the geothermal reservoir have been indicated. A kinetic isotope effect in the high evaporation of the local lake and Steamboat Creek causes a seasonal fluctuation in the isotopic composition of this water, which provides a natural isotope tracer for this particular water.

About 80% of the carbon in the springs is probably of magmatic origin; the isotopic composition is similar to that observed in other areas where no limestone is known to occur in the area and quite different from that at Yellowstone Park and other limestone areas, where the hot spring carbon is similar to limestone carbon. The carbon and oxygen isotope variations in surface and vein carbonates reflect temperatures of deposition, and have provided a thermometer for these deposits up to about 200°C. The observed temperatures from these measurements reflect the local geothermal gradient.

The water and carbon supplied from the surface to the geothermal reservoir at depth spend at least 30,000 years underground; possibly 300,000 years or more, if a mixing reservoir model is applicable, rather that a pipeline flow model. The surface carbon is diluted about five-fold with dead carbon of probable magmatic origin. A small amount of surface water containing tritium is added to the old thermal water as it emerges near the surface.

Yellowstone Park, Wyoming.

Studies similar in scope and type to those described for Steamboat Springs have been completed. In this area, the carbon is principally derived from limestone, or has exchanged with limestone to such an extent as to make another source unrecognizable. At least 95% of the water is of direct meteoric origin. The « oxygen shift » effect is similar to that of Steamboat Springs, and characterizes the near-neutral chloride water, as well as the mixed chloride-sulphate waters of Norris Basin. The oxygen shift increases progressively in going from the carbonate-rich waters of Mammoth, south to the Upper Basin.

In this area, acid hot springs occur, and are principally derived from superficial evaporation of the ground waters and chloride water table, with oxidation of H_2S to sulphuric acid. Any volcanic water present must be principally confined to the large body of near-neutral hot chloride water showing the oxygen shift.

Carbonates show the same isotopic phenomena as at Steamboat Springs, but old surface carbonates, deposited before the present cycle, have been deposited at lower temperatures. Methane gas in this area contains much less carbon 13 than associated carbon dioxide, a phenomenon also observed at The Geysers and Lassen Park in California. The isotopic difference is that predicted for isotopic equilibrium at reasonable temperatures, but may also reflect an organic origin of the methane and non-equilibrium conditions.

The geothermal steam in this area is entirely derived by boiling off from the surface of the thermal water table below, and is markedly different, in the isotopic relation to the thermal water, from steam in true geothermal areas.

Lassen Park and The Geysers, California.

Similar studies, with emphasis on the geothermal steam at The Geysers, have been made. The chloride type thermal water, displaying the oxygen isotope shift, does not occur in these areas, except at Morgan Springs, south of Lassen Park. However, the geothermal steam at The Geysers shows an entirely similar phenomenon. Condensation of the steam produces water with an isotopic composition similar to acid springs resulting from evaporation of surface waters, because of the special relations between the isotope effects and compositions of these waters. This effect is more pronounced at The Geysers than at Lassen, and can be distinguished by measurement of chloride contents of the various types of waters, because of the very low chloride concentration of the steam.

Carbon in the carbon dioxide has an isotopic composition similar to that at Steamboat Springs, quite different from the limestone type carbon at Yellowstone Park; however, the carbon in the methane is similar to that in the Yellowstone methane. The carbon dioxide at The Geysers contains no measurable radiocarbon, but the steam does contain some tritium, showing that there is an incorporation of a small amount of recent water near the surface.

Iceland.

The isotopic data show that the warm thermal waters at Reykjavik are entirely of meteoric origin, and no oxygen shift at all is observed. These waters are derived from snow in the interior of the island, and not from waters along the coast. However, the steam at Hekla Volcano, and the thermal waters of the Hengill-Olfus volcanic area on the south coast, do show the oxygen shift, and display variations similar to those of the areas described above.

Other Areas.

Other geothermal areas studied include the Wairakei and Geyser Valley areas in New Zealand, St. Lucia island in the British West Indies, the Carupano thermal area in Venezuela, various thermal areas in East Africa, Hawaii, the Tivoli and Larderello areas in Italy, and various areas of thermal activity in California, including especially areas of high salinity thermal water.

The Tivoli area in Italy is notable for the fact that carbonate precipitating from the thermal springs has the highest concentration of carbon 13 of any natural material. This effect seems to be due to derivation from limestone, loss of CO_2 by evaporation, and precipitation at low temperatures. The hot springs in the New Zealand areas show the same isotope effects as those at The Geysers and Lassen Park. Carbonates in the steam wells at Wairakei seem to reflect temperatures of precipitation and are of great interest in tracing the geothermal history of the region; this study has just begun. The high salinity thermal springs of California have isotopic compositions similar to oilwell brines in California, Texas, and Louisiana, and probably have a similar origin.

CONCLUSION

In concluding this lengthy presentation, I want only to emphasize the tremendous amount of knowledge about geothermal areas available through nuclear geological studies of stable and radioactive isotopes, coupled with chemical and geological studies. This knowledge is not only that concerned with the ultimate origin of geothermal emanations, the oceans, the atmosphere, and the crust of the earth, but also knowledge vitally important for the immediate practical work of developing geothermal fields for energy production. Information on sources of water and gas, and on the recharge areas and flow rates of water entering these geothermal systems is of great importance for such development and for the prediction and study of useful lifetimes of production areas.

It is therefore of great importance that this first Spoleto conference on Nuclear Geology has dealt with this rapidly developing science of geothermal studies. Professor TONGIORGI is to be congratulated for organizing such a succesful conference on this timely subject.

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REFERENCES

ALLEN E. T., DAY A. L. 1935. Hot springs of the Yellowstone National Park. *Carnegie Inst. Washington Pub.* 466.

BAERTSCHI P. 1953. Über die relativen unterschiede im H_2O^{18}-gehalt naturlicher wasser. *Helv. Chim. Acta.* 36:1352.

BEGEMANN F., FRIEDMAN I. 1959. Tritium and deuterium content of atmospheric hydrogen. *Zeits. Naturforschung.* 14:1024.

BOATO G. 1954. The isotopic composition of hydrogen and carbon in the carbonaceous chondrites. *Geochim. Cosmochim. Acta.* 6:209.

BOATO G., CARERI G., NENCINI G., SANTANGELO M. 1951. Sulla composizione isotopica dell'argon nei gas naturali. *Ann. Geofis. (Roma).* 4:111.

BOATO G., CARERI G., SANTANGELO M. 1952. Argon isotopes in natural gases. *Nuovo Cimento.* 9:44.

BOATO G., CARERI G., VOLPI G. G. 1952. Hydrogen isotopes in steam wells. *Nuovo Cimento.* 9:539.

CLAYTON R. N. 1963. High-temperature isotope thermometry. *Nuclear Geophysics,* National Academy of Sciences - National Research Council Publication 1075.

CRAIG H. 1953. The geochemistry of the stable carbon isotopes. *Geochim. Cosmochim. Acta.* 3:53.

CRAIG H. 1954. Geochemical implications of the isotopic composition of carbon in ancient rocks. *Geochim. Cosmochim. Acta.* 6:186.

CRAIG H. 1961 a. Isotopic variations in meteoric waters. *Science.* 133:1702.

CRAIG H. 1961 b. Standard for reporting concentrations of deuterium and oxygen-18 in natural waters. *Science.* 133:1833.

CRAIG H., BOATO G. 1955. Isotopes. *Ann. Rev. Phys. Chem.* 6:403.

CRAIG H., BOATO G., WHITE D. E. 1956. Isotopic geochemistry of thermal waters. *Proc. Second Conf. on Nuclear Processes in Geologic Settings. Nat. Acad. Sci.-Nat. Res. Council Pub.* 400:29.

CRAIG H., GORDON L., HORIBE Y. 1963. Isotopic exchange effects in the evaporation of water 1. Low-temperature experimental results. *J. Geophys. Res.* 68:5079.

DAY A. L. 1939. The hot-spring problem. *Bull. Geol. Soc. Am.* 50:317.

ELLIS A. J. 1957. Chemical equilibrium in magmatic gases. *Am. J. Sci.* 255:416.

FERGUSSON G. J., KNOX F. B. 1959. The possibilities of natural radiocarbon as a ground water tracer in thermal areas. *N. Zealand J. Sci.* 2:431.

FRIEDMAN I. 1953. Deuterium content of natural water and other substances. *Geochim. Cosmochim. Acta.* 4:89.

FRIEDMAN I., SMITH R. L. 1958. The deuterium content of water in some volcanic glasses. *Geochim. Cosmochim. Acta.* 15:218.

FRIEDMAN I., SMITH R. L., LEVIN B., MOORE A. 1964. The water and deuterium content of phenocrysts from rhyolitic lavas. Isotopic and Cosmic Chemistry (H. C. Urey volume), ed. by H. Craig, S. L. Miller, G. J. Wasserburg, (North Holland) Chapter 15.

GODFREY J. 1962. The deuterium content of hydrous minerals from the East-Central Sierra Nevada and Yosemite National Park. *Geochim. Cosmochim. Acta.* 26:1215.

Hulston J. R., McCabe W. J. 1962. Mass spectrometer measurements in the thermal areas of New Zealand. *Geochim. Cosmochim. Acta.* 26:383, 399.

Iwasaki I., Kokubu N., Katsura T. 1956. Geochemical investigations of volcanoes in Japan. 32. Residual magmatic waters in cavities of trachyandesitic basalt in Imari District, Saga prefecture. *Japan. Bull. Chem. Soc.*: 379.

Jaggar T. A. 1940. Magmatic gases. *Am. J. Sci.* 238:314.

Kokubu N., Mayeda T., Urey H. C. 1961. Deuterium content of minerals, rocks and liquid inclusions from rocks. *Geochim. Cosmochim. Acta.* 21:247.

Kokubu N., Watanabe S., Ide Y. 1957. Liquid inclusions in the amygdaloidal cavities of olivine-basalt from Imazu, Hukuoka City. *Japan. Mem. Fac. Sci. Kyushu Univ. C, Chem.* 2:151.

Miyake Y., Matsuo S. 1962. A note on the deuterium content in the atmosphere and the hydrosphere. *Papers Met. and Geophysics.* 13:245.

Naughton J. J., Terada K. 1954. Effect of eruption of Hawaiian volcanoes on the composition and carbon isotope content of associated volcanic and fumarolic gases. *Science.* 120:580.

Noetzlin J. 1952. La mesure des rapports isotopiques et ses applications possibles à la volcanologie. *Bull. Volcanol.* 12:115.

Wasserburg G. J., Mazor E., Zartman R. E. 1963. Isotopic and chemical composition of some terrestrial natural gases. Earth Science and Meteoritics (F. G. Houtermans volume), ed. by J. Geiss and E. D. Goldberg (North Holland) Chapter 12.

White D. E. 1957 a. Thermal waters of volcanic origin. *Bull. Geol. Soc. Am.* 68:1637.

White D. E. 1957 b. Magmatic, connate, and metamorphic waters. *Ibid.* 1659.

White D. E., Waring G. A. 1962. Volcanic emanations. Data of Geochemistry, Chapter K, *U. S. Geol. Survey Prof. Paper.* 440-K.

Williams H. 1954. Problems and progress in volcanology. *Quart. J. Geol. Soc.* 311.