

## The transport of oxygen isotopes in hydrothermal systems

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### 0. Abstract

As groundwater passes through porous rocks, exchange of oxygen between the fluid and the solid matrix causes a change in the oxygen isotope concentrations in both water and rock. If the rate at which the exchange takes place can be estimated (as a function of the isotope concentrations and temperature) then the time taken for a rock/water system to come to equilibrium with respect to isotope concentration might be calculated.

In this paper, the equation for isotope transport is derived using conservation laws, and a simple equation to describe the rate of isotope exchange is proposed. These are combined with the equations for fluid flow in a porous medium, to produce a general set of equations describing isotope transport in a hydrothermal system. These equations are solved numerically, using typical parameters, for the one-dimensional case.

Oxygen isotope data from the basement rocks underlying Kawerau Geothermal Field are modelled. The results indicate that the time taken for exchange of <sup>18</sup>O to present-day values is less than the postulated age of hydrothermal alteration in that field. This suggests that, although controlled by similar parameters, oxygen isotope exchange, in felsic rocks at least, is much faster than hydrothermal alteration. This conclusion is consistent with the petrographic observations from the Kawerau system as well as other geothermal fields.

### 1. Introduction

The question of the origin of water in geothermal systems puzzled geologists and geochemists for about 50 years after geothermal exploration first started in Italy. Before the advent of isotopic methods and their application to geothermics, it was not possible to draw a line between waters of meteoric and magmatic origins by means of conventional geochemical tools.

The systematic determination of the hydrogen and oxygen stable isotope ratios of water and steam from a number of geothermal fields by Craig (1963) proved the meteoric origin of geothermal waters beyond any doubt. This work was followed by a number of experiments culminating in the development of temperature-dependent mineral-water fractionation equations.

Subsequent oxygen isotope studies were concerned mainly with the estimation of "water-to-rock ratios" as a measure of the fluid throughflow responsible for the observed oxygen isotope compositions in geothermal and shallow hydrothermal systems. The estimates were made for given values of rock/mineral-water fractionation, i.e. for constant temperatures, using "closed" (Taylor, 1971) and "open" (Taylor, 1977) system models.

Since then, oxygen isotope data have been evaluated and modelled by a number of authors in various ways.

#### Notation

The oxygen isotope composition of a substance is reported in ‰ (per mille, or parts per thousand) delta (δ) values

$$\delta = (R_A/R_{std} - 1) \times 10^3$$

where  $R_A$  is the isotope mass ratio <sup>18</sup>O/<sup>16</sup>O of a sample and  $R_{std}$  is that same ratio in a standard, here taken to be Standard Mean Oceanic Water (SMOW). The delta value for SMOW is therefore  $\delta_{SMOW} = 0$ .

The oxygen isotopic fractionation between co-existing species A and B is a measure of the difference between the equilibrium δ values, δ<sub>A</sub> and δ<sub>B</sub>. It is reported as Δ<sub>A-B</sub>, defined by

$$\Delta_{A-B} = 10^3 \ln \alpha_{A-B}$$

where  $\alpha_{A-B} = (^{18}\text{O}/^{16}\text{O in A})/(^{18}\text{O}/^{16}\text{O in B}) = R_A/R_B$ .

To a very close approximation,

$$\Delta_{A-B} \approx \delta_A - \delta_B.$$

Experimental evidence indicates that, for a given mineral, the relationship between Δ and temperature is closely approximated by the formula

$$\Delta_{A-B} = a(10^6/T^2) - b$$

where T is the temperature in Kelvin, and a and b are mineral-dependent constants.

### 2. Previous work

Previous models of <sup>18</sup>O mass transfer between rocks and fluids fall into two categories:

- (a) instantaneous exchange models, and
- (b) those based on kinetic constraints.

The first category comprises the <sup>18</sup>O-exchange models of Taylor (1971, 1977), Spooner et al. (1977), Blattner (1981, 1985a) and Bowers & Taylor (1985). Basing his work on a simple <sup>18</sup>O mass balance equation, Taylor (1971, 1977) developed a "prototype" model for estimating the total amount of water involved in a meteoric-hydrothermal convective system. His "open system" model, allowing fresh water inflow, was subsequently modified by Blattner (1981, 1985a) to make it directly applicable to geothermal systems. Blattner's "mixed" model consists of batches of water passing into a fixed rock reservoir, coming to isotopic equilibrium and then passing out again; this provides an estimate of the cumulative throughput of water.

Spooner et al. (1977) were the first to attempt computer modelling of one-dimensional systems. Their model also takes into account linear thermal gradients and is easily adaptable to geothermal systems. Bowers & Taylor (1985) developed an integrated chemical and oxygen-isotope exchange model of the Mid-Ocean Ridge hot spring system. The results closely match the major-element chemistry and δ<sup>18</sup>O composition in spite of their "closed system" approach.

In all of the above models there is no time-scale involved with the isotope exchange. Although they may be described as instantaneous exchange models, there is in fact no estimate of the time taken for equilibrium to be achieved; this can only be done through the use of some kinetic constraints controlling the actual interchange reaction.

The kinetics constrained models already studied include the two-dimensional models of Norton & Taylor (1979), Parmentier (1981) and Cathles (1983). In these models, <sup>18</sup>O-exchange is described using measured mineral-water diffusion rates or calculated reaction rates. Norton & Taylor (1979) analysed the fossil geothermal

system associated with the Skaergaard intrusion, using numerical approximations of heat and mass transport, porosity and permeability; this permitted simulation of the thermal history and associated changes. They were able to make a close match between the calculated and measured  $\delta^{18}\text{O}$  values. Parmentier (1981) carried out numerical experiments on  $^{18}\text{O}$  depletion in igneous intrusion models cooling through groundwater convection.

Cathles (1983) modelled  $^{18}\text{O}$  variations in a hydrothermal system and compared the results with the Kuroko massive sulphide deposit. Kinetic constraints and formation permeability were considered, and the calculated whole rock  $\delta^{18}\text{O}$  anomalies at a time 50,000 years after intrusion show a pattern similar to that observed today. This is in contrast to a time of  $4 \times 10^5$  years indicated for the Skaergaard system; after that time fluid circulation was lost and  $\delta^{18}\text{O}$  wholerock values were "fossilized" (Norton & Taylor, 1979).

McKibbin & Absar (1986) developed zero- and one-dimensional models for  $^{18}\text{O}$ -exchange in geothermal systems using the equations of isotope transport and rate of isotope exchange between fluid and rock. The time taken for  $^{18}\text{O}$ -exchange to present-day values in the Taupo Volcanic Zone geothermal fields was found to be much less than their postulated ages.

### 3. Equations for isotope transport in a porous medium

Since the isotope exchange and transport depends on the way fluid flows through the rock matrix as well as the reaction that takes place between them, the system of equations describing isotope transport must model both processes.

#### Fluid flow equations

The equations describing fluid flow in a porous medium are derived by using the principle of conservation of mass, momentum and energy (see Cheng, 1978, for example). For a single-phase fluid (water) moving in a non-deformable matrix, these equations are:

$$(\partial/\partial t)(\phi\rho) + \nabla \cdot (\rho\mathbf{u}) = 0 \quad (1)$$

$$\nabla p = \rho g - (\mu/K)\mathbf{u} \quad (2)$$

$$(\partial/\partial t)[\phi\rho cT + (1-\phi)\rho_r c_r T] + \nabla \cdot (\rho c T\mathbf{u}) = \nabla \cdot (k\nabla T) \quad (3)$$

Here  $p$  and  $T$  are the pressure and temperature at a point in the matrix;  $\mathbf{u}$ ,  $\rho$ ,  $\mu$  and  $c$  are respectively the Darcy velocity (volume flow rate per unit area), density, dynamic viscosity and specific heat of the fluid;  $\phi$ ,  $K$ ,  $\rho_r$  and  $c_r$  are the porosity, permeability, density and specific heat of the rock matrix, while  $k$  is the thermal conductivity of the saturated porous medium. The coordinate system has components  $(x, y, z)$ , where  $x$  and  $y$  are horizontal coordinates and  $z$  is vertically upward. The vector differentiating operator  $\nabla$  is defined by the equation  $\nabla \equiv (\partial/\partial x, \partial/\partial y, \partial/\partial z)$ .

The above equations are commonly used and their derivation will not be discussed further here. However, some simplifying assumptions can be made and these will be considered below.

#### Isotope transport equation

Of more interest here are the equations describing isotope transport and the rock/water interaction.

The principle of conservation of mass of  $^{18}\text{O}$  isotope is described by the equation

$$(\partial/\partial t)[\phi\rho v_w(^{18}\text{O}_w/O_w) + (1-\phi)\rho_r v_r(^{18}\text{O}_r/O_r)] + \nabla \cdot [\rho v_w(^{18}\text{O}_w/O_w)\mathbf{u}] = 0 \quad (4)$$

Here it is assumed that the major spatial transport of  $^{18}\text{O}$  is carried out by the moving fluid, and that the diffusion of isotope through the rock is negligible. Also, it is assumed that there are no sinks or sources of  $^{18}\text{O}$  within the matrix. In equation (4),  $v_w$  and  $v_r$  are the concentrations, by mass, of oxygen in the water and rock respectively, the fractions  $^{18}\text{O}_w/O_w$  and  $^{18}\text{O}_r/O_r$  are the ratios of the mass of  $^{18}\text{O}$  isotope and the mass of oxygen in the water and rock respectively, while the other parameters have been described above.

Since the fraction of  $^{18}\text{O}$  isotope in each mass  $\text{O}_w$  and  $\text{O}_r$  is small, the ratios  $^{18}\text{O}/\text{O} = ^{18}\text{O}/(^{16}\text{O} + ^{18}\text{O})$  can be written approximately as  $^{18}\text{O}/^{16}\text{O}$ . Equation (4) then becomes

$$(\partial/\partial t)[\phi\rho v_w(^{18}\text{O}_w/^{16}\text{O}_w) + (1-\phi)\rho_r v_r(^{18}\text{O}_r/^{16}\text{O}_r)] + \nabla \cdot [\rho v_w(^{18}\text{O}_w/^{16}\text{O}_w)\mathbf{u}] = 0$$

This equation is divided by the standard value  $(^{18}\text{O}/^{16}\text{O})_{\text{std}}$  defined for the oxygen isotope ratio. With the further assumption that  $v_w$ ,  $v_r$ ,  $\phi$  and  $\rho_r$  are stationary with respect to time (although the rock values may change spatially within the matrix), a multiple  $v_r$  of equation (1) is subtracted to yield the equation

$$(\partial/\partial t)[\phi\rho v_w[(^{18}\text{O}_w/^{16}\text{O}_w)/(^{18}\text{O}/^{16}\text{O})_{\text{std}} - 1] + (1-\phi)\rho_r v_r[(^{18}\text{O}_r/^{16}\text{O}_r)/(^{18}\text{O}/^{16}\text{O})_{\text{std}} - 1] + \nabla \cdot [\rho v_w[(^{18}\text{O}_w/^{16}\text{O}_w)/(^{18}\text{O}/^{16}\text{O})_{\text{std}} - 1]\mathbf{u}] = 0 \quad (5)$$

After multiplication by a factor  $10^3$  (i.e. 1000), equation (5) can be written

$$(\partial/\partial t)[\phi\rho v_w\delta_w + (1-\phi)\rho_r v_r\delta_r] + \nabla \cdot [\rho v_w\delta_w\mathbf{u}] = 0 \quad (6)$$

where

$$\delta = [(^{18}\text{O}/^{16}\text{O})/(^{18}\text{O}/^{16}\text{O})_{\text{std}} - 1] \times 10^3$$

is the delta value of  $^{18}\text{O}$  isotope in per mille (i.e. the fractional deviation of the  $^{18}\text{O}/^{16}\text{O}$  isotope ratio from the standard value in parts per thousand, or ‰).

If it is further assumed that the rock matrix can be subdivided into blocks within each of which  $\phi$ ,  $\rho_r$  and  $v_r$  are constant, then equation (6) may be divided by  $(1-\phi)\rho_r v_r$  to give

$$(\partial/\partial t)[\Phi\delta_w + \delta_r] + (1/\phi)\nabla \cdot [\Phi\delta_w\mathbf{u}] = 0 \quad (7)$$

where

$$\Phi = [\phi\rho v_w / (1-\phi)\rho_r v_r] \quad (8)$$

is the "water-to-rock ratio", measured as the local ratio of mass of oxygen within the water to that in the rock within a given volume of the rock/water mixture.

#### Rock/water interaction

Theoretical and experimental evidence indicates that, for a rock/water mixture, a net  $^{18}\text{O}$  exchange will take place between the rock and the water while the difference in the rock and water  $\delta$  values,  $\delta_w - \delta_r$ , is different from an equilibrium value,  $A$ , which is closely approximated by the oxygen isotopic fractionation between the co-existing species. The value of  $A$  depends on the rock type and the temperature,  $T$ , of the mixture. For the typical rock type considered here, the dependence of  $A$  on  $T$  has been given as

$$\Delta(T) = 2.68 \times 10^6 / T^2 - 3.53 \quad (\text{Taylor, 1971})$$

$$\Delta(T) = 2.91 \times 10^6 / T^2 - 4.50 \quad (\text{Matsuhisa et al. 1979})$$

where  $T$  is measured in Kelvin (i.e. absolute temperature). The equation best estimating the greywacke-water fractionation may be written as

$$\Delta(T) = 2.74 \times 10^6 / T^2 - 1.53.$$

The simplest form of an equation which describes the rate at which such isotope exchange takes place is linear. Here it is proposed that a suitable equation is

$$\partial\delta_r/\partial t = -\kappa(\delta_r - \delta_w - \Delta) \quad (9)$$

i.e., while there is a contrast (compared with the equilibrium value) between the  $\delta$ -values of rock and water, there will be a change in the

$^{18}\text{O}$  concentration in the rock. The parameter  $\kappa$  is a rate constant for the reaction; further discussion of suitable values of  $\kappa$  will take place below.

It should be noted that equation (9) is only one of the simple forms that could be used. Others, for example, could be expressed in terms of the rate of change of  $\delta_r$ ,  $\delta_w$ , or of  $\delta_r - \delta_w$ . However, because the rock matrix is the stationary phase, it seems more intuitively satisfying to use the form given in (9).

The complete set of equations

Constitutive laws for the fluid phase describe how its properties depend on pressure and temperature. In the equations for fluid flow, (1) - (3), the main effects of density variation are in the buoyancy term  $\rho g$  in equation (2). Elsewhere, variation of the fluid density has negligible effect and can be neglected (this is known as the Boussinesq approximation). In a non-isothermal system, fluid viscosity varies, but in the relatively small temperature ranges considered here, the viscosity is assumed constant. A similar assumption is made about the fluid specific heat,  $c$ . Therefore, these values are written  $\rho = \rho_w$ ,  $\mu = \mu_w$ ,  $c = c_w$  in all terms except the buoyancy term of (2) where  $\rho = \rho_w [1 - \alpha(T - T_0)]$ . Here  $\rho_w$ ,  $\mu_w$ , and  $c_w$  are constants,  $\alpha$  is the coefficient of thermal expansion for the fluid and  $T_0$  is a reference temperature at which fluid properties are measured.

Any sub-block of rock to be considered is assumed to have constant matrix material properties, i.e. permeability  $K$ , specific heat  $c_r$  and thermal conductivity  $k$  are all assumed to be constants. Together with the other simplifying assumptions already made ( $\phi$ ,  $\rho_r$ ,  $v_r$ ,  $v_w$  are constants), the complete set of equations becomes

$$\nabla \cdot \mathbf{u} = 0 \quad (10)$$

$$\nabla p = \rho_w [1 - \alpha(T - T_0)] \mathbf{g} - (\mu_w/K) \mathbf{u} \quad (11)$$

$$\rho_m c_m \partial T / \partial t + \rho_w c_w \mathbf{u} \cdot \nabla T = k \nabla^2 T \quad (12)$$

$$(\partial / \partial t) [\Phi \delta_w + \delta_r] + (\Phi/\phi) \mathbf{u} \cdot \nabla \delta_w = 0 \quad (13)$$

$$\partial \delta_r / \partial t = -\kappa [\delta_r - \delta_w - \Delta(T)] \quad (14)$$

where  $\Delta(T) = 2.74 \times 10^6 / T^2 - 1.53$ .

Equations (12) and (13) are the result of further simplification using equation (10). The volumetric heat content for the rock/water mixture,  $\rho_m c_m = \phi \rho_w c_w + (1 - \phi) \rho_r c_r$ , is a constant.

The set of equations (10) - (14) comprise seven equations in the seven unknowns  $p$ ,  $T$ ,  $\delta_r$ ,  $\delta_w$  and the three components of  $\mathbf{u}$ . Clearly, a full solution to the complete set of equations and accompanying boundary and initial conditions would be very difficult. Simple configurations will clearly be more tractable. One, the zero-dimensional model ("lumped parameter" or "blob" model), was considered in detail in another paper (McKibbin & Absar, 1986). A one-dimensional model which describes fluid flow in a single coordinate direction through a rock matrix is the subject of closer study here. Both models are restricted to be at isothermal conditions.

#### 4. Solutions to the isotope transport equations

The zero-dimensional model

The simplest model is that constructed by supposing that there is no spatial variation in properties or parameters within the system. From a physical viewpoint this means that, apart from temperature and material properties being constant throughout the rock volume of interest, thorough mixing of the fluid is taking place. The rate of mixing is assumed to be much faster than that of oxygen isotope exchange, with the necessary consequence that there is no spatial variation of isotope concentrations in the water or the rock. While

such assumptions are certainly unrealistic, the overall averaging procedure should give a first approximation to the processes taking place.

This model was studied by McKibbin & Absar (1986), who considered not only the closed system case, where there is no fluid flow into or out of the aquifer, but also the case where there is a constant inflow of fresh meteoric water and a consequent outflow of the exchanged aquifer fluid. The solutions to the equations were found in analytic form.

The one-dimensional model

For an isothermal aquifer, with no thermally-driven convection, it is likely that fluid flow in it would be able to be described as one-dimensional, at least within local blocks. Here, a one-dimensional uniform flow with a constant velocity is assumed to be flowing through an aquifer of thickness  $L$ . The direction of the flow is arbitrary. The only adjustment to be made is to the pressure distribution if the flow is not horizontal. Since the object is to model a vertical upflow in the Kawerau Geothermal Field, it will be assumed that the flow has only one component, in the vertical direction. Therefore  $\mathbf{u} = (0, 0, w)$  where  $w$  is a constant,  $p = p(z)$  and the delta values  $\delta_r$  and  $\delta_w$  may be functions of  $z$  and  $t$  i.e.  $\delta_r(z, t)$ ,  $\delta_w(z, t)$ . The appropriate equations are, from (10) - (14) with  $T = \text{constant}$ ,

$$w = - (K/\mu_w) (dp/dz + \rho_w g) \quad (15)$$

$$(\partial / \partial t) [\Phi \delta_w + \delta_r] + (\Phi/\phi) w \partial \delta_w / \partial z = 0 \quad (16)$$

$$\partial \delta_r / \partial t = -\kappa (\delta_r - \delta_w - \Delta) \quad (17)$$

If it is assumed that, initially, the  $\delta$  values of the rock and the water are  $\delta_{ri}$  and  $\delta_{wi}$  respectively, and that, at  $t = 0$ , "fresh" water with  $\delta_w = \delta_{wi}$  begins flowing in at  $z = 0$  and out at  $z = L$ , then the boundary conditions are

$$\delta_r(z, 0) = \delta_{ri}, \quad \delta_w(z, 0) = \delta_{wi} \quad \text{for } 0 < z < L$$

$$\text{and } \delta_w(0, t) = \delta_{wi}.$$

Equation (15) merely indicates that a (constant) pressure gradient in excess of the hydrostatic gradient must exist to drive the flow. Note that, even though the flow is constant, the isotope concentrations vary both spatially and with time.

It is most useful to non-dimensionalise the independent variables according to

$$Z = z/L, \quad \tau = t/(\phi L/w).$$

Then the limits of the portion of the aquifer considered are at  $Z = 0$  and  $Z = 1$ , and a unit time  $\tau = 1$  corresponds to the time taken for a fluid particle to travel the thickness of the aquifer (the interstitial velocity is  $u/\phi$ ). With the new coordinates, the equations and the boundary conditions become:

$$(\partial / \partial \tau) [\Phi \delta_w + \delta_r] + \Phi \partial \delta_w / \partial Z = 0 \quad (18)$$

$$\partial \delta_r / \partial \tau = -C (\delta_r - \delta_w - \Delta)$$

$$\text{with } \delta_r(Z, 0) = \delta_{ri}, \quad \delta_w(Z, 0) = \delta_{wi} \quad \text{for } 0 < Z < 1$$

$$\text{and } \delta_w(0, \tau) = \delta_{wi}.$$

The parameter  $C$ , defined by

$$C = \kappa (\phi L/w),$$

is best interpreted as the ratio of two times: one is  $t_v = \phi L/w$  which is

the replacement time for the fluid, and which equals the time taken for a fluid particle to travel the thickness of the aquifer, and the other is  $t_r = 1/K$  which is the reaction rate time for the isotopic exchange. Then  $C = t_v/t_r$ .

A finite-difference formulation of equations (18) and the associated boundary conditions was solved numerically.

## 5. Modelling of oxygen isotope data from the Kawerau Geothermal Field

The Kawerau Geothermal Field is ideal for testing the one-dimensional oxygen-isotope exchange model. The fluid flow in the field can be approximated by a uniform upflow (Grant *et al.*, 1982). Borehole KA-21, in the northeastern part of the field (see Figure 1) produces abundantly from the geywacke basement, and a major upflow zone is indicated around this and bore KA-27 (Nairn,

1982). Also, the lowest reported  $\delta^{18}\text{O}$  values for the geywacke are from this zone (Absar & Blattner, 1985).

The distribution of the  $\delta^{18}\text{O}$  values in the basement rock is shown in Figure 2. In general, relatively low values of  $\delta^{18}\text{O}$  3 to 5‰ are confined to the northern and presently producing part of the field. The present study is restricted to an estimated  $1\text{ km}^2$  volume of the basement extending to a depth of 2 km below ground level (1 km below the greywacke surface) with boreholes KA-21 and KA-27 in the centre. The temperature in the basement is assumed to be  $280^\circ\text{C}$  with liquid water flowing. The fractionation at that temperature is calculated to be  $A = 7.43$ . The initial rock composition has been reliably estimated as 11‰ (Absar & Blattner, 1985). The  $^{18}\text{O}$  composition of the meteoric water is  $-5.7\text{‰}$  (Stewart, 1980).

It is further assumed that, before the beginning of flow, the rock and water are in isotopic equilibrium, ie that  $\delta_{ri} = 11\text{‰}$  and  $\delta_{wi} = 3.57\text{‰}$ . The water subsequently flowing into the aquifer from  $Z = 0$  is supposed to be meteoric water with  $\delta_{w1} = -5.7\text{‰}$ .

Another important parameter to be estimated is the velocity of the water. Reasonable values may be calculated if either the natural discharge of the deep aquifer or the pressure gradient and vertical permeability are reliably known. Studt (1958) estimated the natural discharge to be about  $9\text{ ls}^{-1}$ . If the minimum field area is taken to be  $6\text{ km}^2$ , this gives an average vertical flow rate per unit area (Darcy velocity) of  $1.5 \times 10^{-9}\text{ ms}^{-1}$ . Donaldson *et al.* (1981) presented a reservoir pressure-depth profile for the Kawerau Field; this is shown here in Figure 3. From the excess pressure gradient, Grant *et al.* (1982) estimated the vertical permeability as 1 millidarcy. Taking their values of  $dp/dz = 85.2\text{ bar/km}$  and  $K = 10^{-15}\text{ m}^2$ , a velocity of  $3\text{ to }6 \times 10^{-10}\text{ ms}^{-1}$  is calculated. Petrographic observations suggest that permeability was much higher in the past as indicated by the presence of adularia in the presently impermeable basement rocks encountered by wells KA-22, 25 and 31 (Absar & Blattner, 1985). Assuming a permeability of 10 md, ten times higher than that estimated by Grant *et al.* (1982), a velocity of  $3 \times 10^{-9}\text{ ms}^{-1}$  is calculated. This is equivalent to a total discharge of  $20\text{ ls}^{-1}$ , which is between the values suggested by Studt (1958) and Thompson (1962).

Once the velocity is estimated, the replacement time for the fluid, ie the travel time through the reservoir of thickness  $L$  and porosity  $\phi$ , may be calculated as

$$t_v = \phi L/w.$$

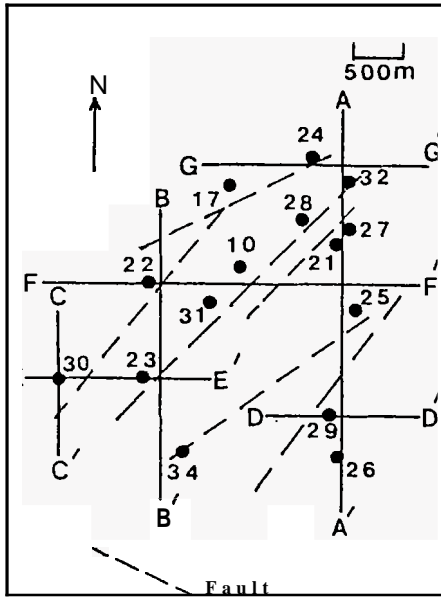


Fig. 1: Bore location map of Kawerau Geothermal Field. Drillholes shown have intersected the greywacke/argillite basement.

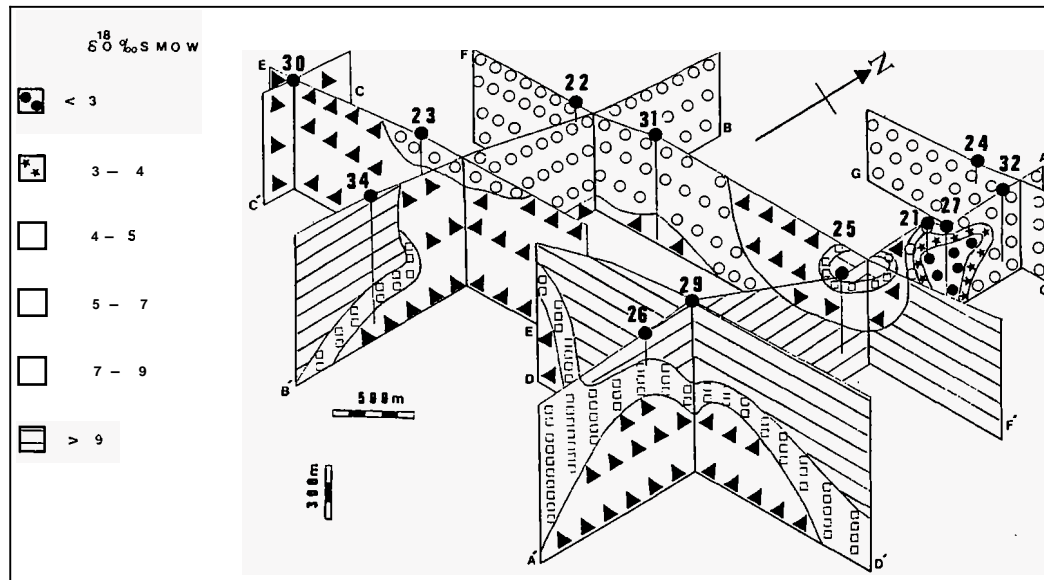


Fig. 2: Distribution of  $\delta^{18}\text{O}$  values in the greywacke/argillite basement underlying the Kawerau Geothermal Field; section-lines are shown in Fig. 1.

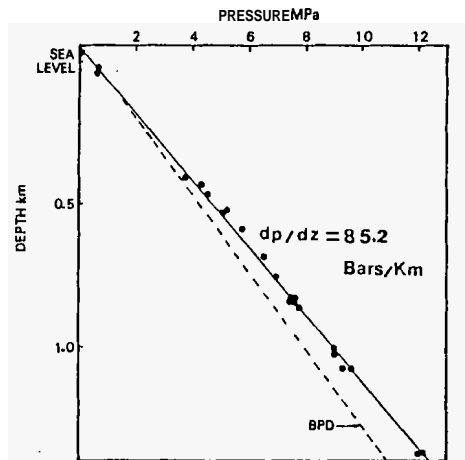


Fig. 3: Reservoir pressure-depth profile in the Kawerau Geothermal Field (after Donaldson *et al.*, 1982).

The porosity in the basement rocks is relatively small; an average value of 0.07, as determined experimentally (Whiteford & Lumb, 1975) is used. The thickness of the reservoir considered here is 1 km. With an assumed velocity of  $3 \times 10^{-9} \text{ ms}^{-1}$ , a replacement time of  $t_r = 750$  years is calculated. For the range of velocity values as discussed above, replacement times of up to 3750 years may be calculated. There is no reason for preferring one value over any other. The important point is that the major conclusions be qualitatively unaffected by altering the choice.

For modelling the oxygen isotope exchange in a system and obtaining reliable results, a close approximation of the constant  $C$  is necessary. As might be intuitively expected, large values of  $C$  ( $C > 1$ ) produce results that correspond closely to those from an instantaneous exchange model. Estimation of  $C$  is aided by knowledge of present-day values of  $\delta_r$  and  $\delta_w$ . That these values are reliably known for the Kawerau Field is one of several reasons for choosing that field to test the one-dimensional model presented here.

The  $\delta_r$  values average around 4.8‰ in the northern part of the field (Absar & Blattner, 1985). The average  $\delta_w$  value from downhole samples is -3.4‰ (Stewart, 1980). The value of  $C$  used in the calculations is adjusted until the best match is found between the calculated and physical values of  $\delta_r$  and  $\delta_w$ . For the Kawerau case, no comparable values were found for  $C < 0.2$  or  $C > 0.5$ . The best match was found for  $C = 0.35$ ; the results given below were obtained by using that value. The rate constant,  $K$ , for the isotope exchange can be calculated from the estimated  $C$  value: it is of the order of  $10^{-12} \text{ s}^{-1}$ .

The results are shown in Table 1 and are presented graphically in Figures 4 to 7. Figure 4 shows the delta values for the rock and water at various times up to  $\tau = 1$ . It is seen that as the 'front' of meteoric water advances up the aquifer, ahead of it the water and rock are in isotopic equilibrium and no change occurs there as the old water is moving out of the system. Behind the 'front' the rock begins to move towards a new equilibrium with the fresh water. For  $\tau > 1$ , the original water has been flushed from the aquifer (Figure 5) and the system slowly approaches a new equilibrium which asymptotically is

$$\delta_w(Z, \infty) = \delta_{w1}, \quad \delta_r(Z, \infty) = \delta_{w1} + A.$$

Figures 6 and 7 show how the delta values at several fixed points in the aquifer vary with time.

## 6. Discussion

The kinetics constrained models proposed by earlier authors describe  $^{18}\text{O}$ -exchange in hydrothermal systems, i.e. in 'fossil' equivalents of present-day geothermal systems. In such models, only the calculated and measured  $\delta_r$  values can be compared as the geothermal fluid circulation has been lost. The model presented here, although also applicable to hydrothermal systems associated with shallow igneous intrusions, has been developed specifically for describing rock-water  $^{18}\text{O}$ -exchange in geothermal fields and for determining the evolution of rock and water  $^{18}\text{O}$  compositions to their Present-day values. In this respect, this model is the first of its kind.

The results indicate that the time taken for the evolution of the Kawerau system to its present  $^{18}\text{O}$  composition is of the order of 2 to  $8 \times 10^4$  years, with an average of  $4 \times 10^4$  years. The variation is due to the range of assumed fluid velocity values with a consequent range of fluid replacement times,  $t_r$ . Studies of hydrothermal alteration of rocks at Kawerau have provided almost conclusive evidence that the inception of geothermal activity there occurred before the eruption of the Matahina Ignimbrite,  $2 \times 10^5$  years ago (Browne, 1979; Absar & Blattner, 1985). The time required for oxygen isotope exchange to reach present-day values is therefore an order of magnitude less than that indicated by the alteration (assuming geothermal activity at a constant rate), although one might assume that the two processes proceed side by side, as suggested by O'Neil & Taylor (1967).

This discrepancy could be resolved in the light of some observations on the relative rates of  $^{18}\text{O}$ -exchange and hydrothermal alteration or cation-exchange. Large  $^{18}\text{O}$  shifts have been noticed in samples that are little altered mineralogically at Kawerau and Broadlands (Absar, 1985), Wairakei (Clayton & Steiner, 1975), Rotokawa (Blattner, 1985b) and Waitapu (Hedenquist, 1983). Similar instances have been reported from geothermal and hydrothermal systems outside New Zealand. This suggests that  $^{18}\text{O}$ -exchange is faster than the cation-exchange and, consequently, a substantial  $^{18}\text{O}$  shift may precede hydrothermal alteration. This is clearly indicated by similar  $^{18}\text{O}$  values of the variably altered greywacke basement as seen in drillholes KA-22, 27 and 32 (see Figure 2). Such observations also rule out the possibility of commensurate  $^{18}\text{O}$ -exchange and alteration, i.e. alteration also being  $4 \times 10^4$  years old, which may be possible if the geothermal activity and alteration were episodic. Feldspars have the fastest rate of  $^{18}\text{O}$  exchange and attain equilibrium with water even under laboratory conditions (O'Neil & Taylor, 1967). Rocks consisting of  $> 50\%$  feldspars therefore should be expected to show  $^{18}\text{O}$  depletion long before the appearance of conspicuous alteration phases.

The possibility that the age calculated from  $^{18}\text{O}$ -exchange is far too low should also be considered. This is possible when very low permeabilities, say  $< 1 \text{ md}$ , giving rise to a total discharge of  $< 1 \text{ ls}^{-1}$ , are considered. Such values are unrealistic and preclude the existence of a geothermal system. Effective recirculation would also tend to increase the apparent age of isotope exchange because the process will slow down if the pre-shifted water keeps coming in contact with the rock. Recirculation is a distinct possibility in geothermal systems. However, the extent of  $^{18}\text{O}$ -shift in the rock and water suggest that it plays only a minor role. The calculated age of  $^{18}\text{O}$ -exchange at Kawerau may at most be 20% higher, i.e. about  $5 \times 10^4$  years if it is assumed that some pre-shifted water enters the reservoir in addition to the meteoric water. This calculated time for the  $^{18}\text{O}$ -exchange is comparable to that calculated by Cathles (1983) for the massive sulphide deposition in the Hokuroku Basin of Japan.

## Acknowledgements

The authors thank C. Houston, P.R.L. Browne and G. Scott for their contribution to this work by way of technical assistance and helpful discussion and comments.

Table 1: Variation of  $\delta_r$  and  $\delta_w$  values with time at several points in the aquifer ( $C = 0.35$ ,  $\Phi = 0.07$ ).

Time in $\tau$ units	$\delta_{\text{rock}}$			Later		
	Z = 0.1	0.5	1	Z = 0.1	0.5	1
0	11	11	11	3.57	3.57	3.57
1	9.27	10.79	11	-3.15	2.01	3.47
3	6.46	9.72	10.79	-4.10	0.65	2.92
6	4.08	7.94	10.14	-4.90	-1.16	1.92
9	2.90	6.29	9.18	-5.30	-2.58	0.74
12	2.31	4.94	8.06	-5.50	-3.62	-0.47
15	2.02	3.91	6.90	-5.60	-4.35	-1.60
18	1.87	3.17	5.82	-5.65	-4.84	-2.58
21	1.80	2.66	4.88	-5.67	-5.16	-3.38

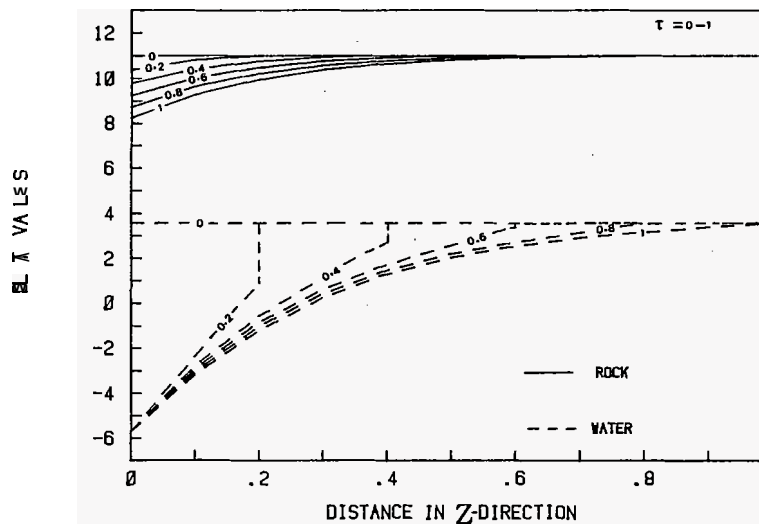


Fig. 4: Calculated delta values for the rock and water at various dimensionless times  $\tau$ ,  $0 \leq \tau \leq 1$ ; the curves are for  $\tau$  values of 0, 0.2, 0.4, 0.6, 0.8 and 1.0. Note the front of shifted water advancing through the rock.

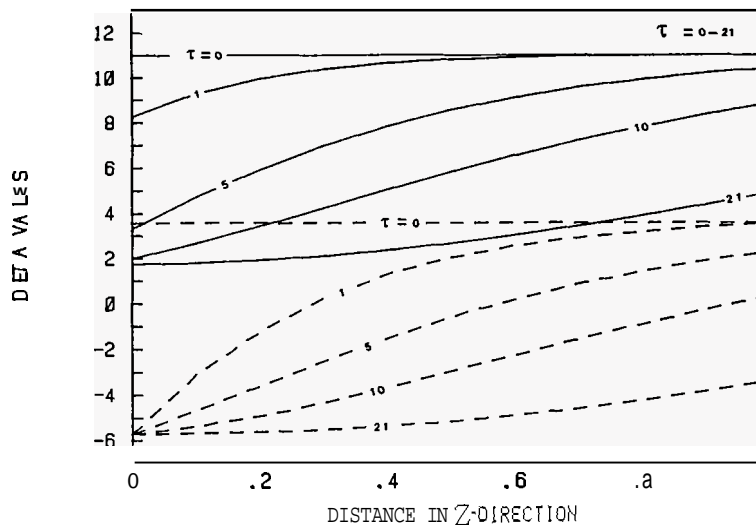


Fig. 5: Calculated delta values for the rock and water at various dimensionless times  $\tau > 1$ . Curves for  $\tau = 0$  and  $\tau = 1$  are also given for comparison. Delta values at  $Z = 1$  and  $\tau = 21$  are present-day values.

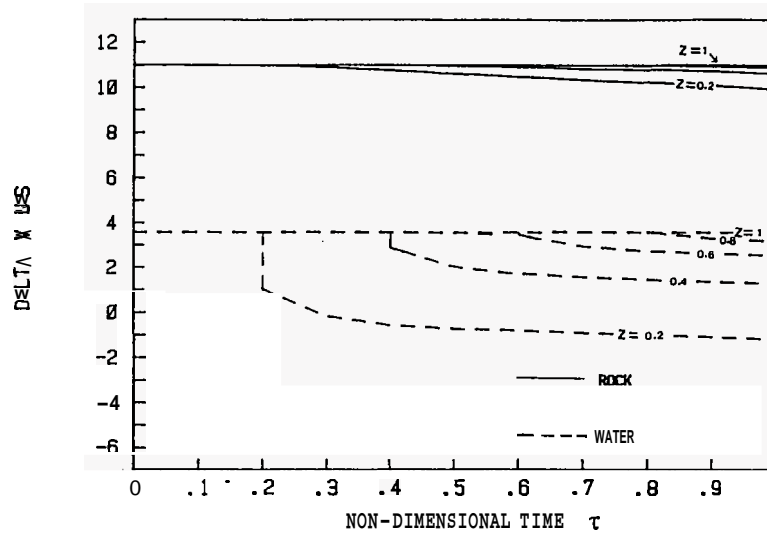


Fig. 6: Variation of delta values for  $0 \leq \tau \leq 1$  at several fixed levels  $Z$  in the aquifer. Note that the water shows a large positive shift whereas the rock values show a relatively small negative shift. This is a characteristic feature of geothermal systems at the time of their inception.

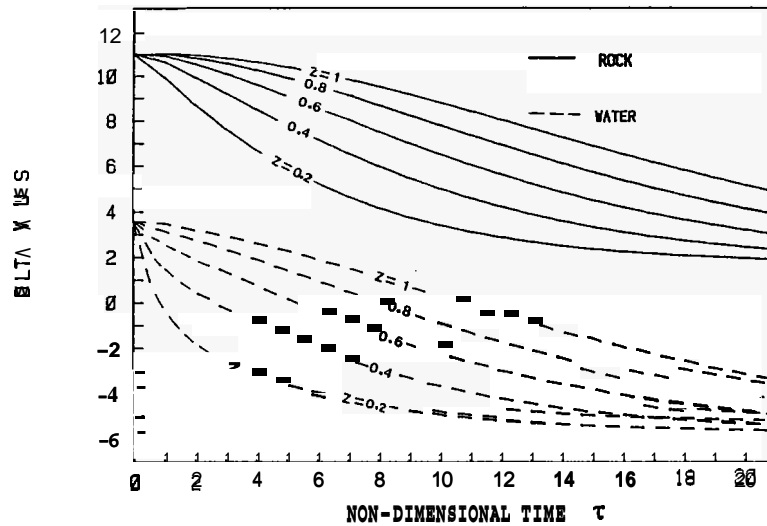


Fig. 7: Variation of delta values at times to  $\tau = 21$  at several fixed levels  $Z$  in the aquifer. At  $\tau = 21$ , the curves show the present-day vertical distribution of  $\delta_r$  and  $\delta_w$  in the greywacke basement. The system is seen approaching an equilibrium defined by  $\delta_r = 1.73$  and  $\delta_w = -5.7\%$ . Calculated present-day values (when  $\tau = 21$ ) at  $Z = 0.2$  are  $1.9$  and  $-5.6\%$  respectively.



## References

- Absar, A. (1985) Oxygen isotope exchange in relation to hydrothermal alteration of rocks. *Proc. of the 7th New Zealand Geothermal Workshop*, p. 167-169. University of Auckland, 1985.
- Absar, A. and P. Blattner (1985) Successive hydrothermal events, as indicated by oxygen isotope composition and petrography of greywacke basement rocks, Kawerau Geothermal Field, NZ. *Proc. of the 7th New Zealand Geothermal Workshop*, p. 115-122. University of Auckland, 1985.
- Blattner, P. (1981) Combined stable isotope trajectories for water-rock interaction. *Proc. of the New Zealand Geothermal Workshop*, p. 75-80. University of Auckland, 1981.
- Blattner, P. (1985a) Isotope shift data and the natural evolution of geothermal systems. *Chem. Geol.* **49**, p. 187-203.
- Blattner, P. (1985b) Greywacke basement Rotokawa: evidence for  $^{18}\text{O}$  composition and high fluid throughput. Open File Report MS/5/1 • PB. Institute of Nuclear Sciences, DSIR, New Zealand.
- Bowers, T. S. and H. P. Taylor (1985) An integrated chemical and stable isotope model of the origin of Mid-Ocean Ridge hot spring systems. *J. Geophys. Res.* **90**, No. B14, p. 12583-12606.
- Browne, P.R.L. (1979) Minimum age of the Kawerau Geothermal Field, North Island, NZ. *J. Volcanol. Geotherm. Res.* **6**, p. 213-215.
- Cathles, L. M. (1983) An analysis of the hydrothermal system responsible for massive sulphide deposition in the Hokuroku Basin of Japan. *Econ. Geol. Monograph* **5**, p. 439-487.
- Cheng, P. (1978) Heat transfer in geothermal systems. *Adv. Heat Transfer* **14**, p. 1-105.
- Clayton, R.N. and A. Steiner (1975) Oxygen isotope studies of the geothermal system at Wairakei, NZ. *Geochim. Cosmochim. Acta* **39**, p. 1179-1186.
- Craig, H. (1963) The isotope geochemistry of water and carbon in geothermal areas. In Tongiorgi, E. (ed) *Nuclear Geology on Geothermal Areas*. Spoleto, Pisa, 1963, p. 17-53.
- Donaldson, I.G., M.A. Grant and P.F. Bixley (1981) Non-static reservoirs: the natural state of the geothermal reservoir. 56th Ann. Fall Tech. Conf. SPE-AIME, paper SPE 10314.
- Grant, M.A., I.G. Donaldson and P.F. Bixley (1982) *Geothermal Reservoir Engineering*. Academic Press, Inc., NY, USA.
- Hedenquist, J.W. (1983) Waiotapu, New Zealand: The geochemical evolution and mineralisation of an active hydrothermal system. Ph. D. thesis. University of Auckland.
- Matsuhisa, Y. et al. (1979) Oxygen isotopic fractionation in the system quartz • albite • anorthite • water. *Geochim. Cosmochim. Acta* **43**, p. 1131-1140.
- McKibbin, R. and A. Absar (1986) Modelling the transport of oxygen isotopes in hydrothermal systems. *Proceedings of the Groundwater Chemistry Workshop, 18-20 August, 1986*. Technical Publication no. 41. Auckland Regional Water Board, ARA, Auckland, NZ. (To be published.)
- Naim, I.A. (1982) Geology of Kawerau Geothermal Field: results of drilling, 1977-1982. Geothermal Circular IAN-4. DSIR, Wellington, NZ.
- Norton, D. and H. P. Taylor (1979) Quantitative simulation of the hydrothermal systems of crystallizing magmas on the basis of transport theory and oxygen isotope data: an analysis of the Skaergaard intrusion. *J. Petrol.* **20**, p. 421-486.
- O'Neil, J.R. and H.P. Taylor (1967) The oxygen isotope and cation exchange chemistry of feldspars. *American Mineralogist* **52**, p. 1414-1437.
- Parmentier, E. M. (1981) Numerical experiments on  $^{18}\text{O}$  depletions in igneous intrusions cooling by groundwater convection. *J. Geophys. Res.* **86**, p. 7131-7144.
- Spooner, E. T. C. et al. (1977) Hydration,  $^{18}\text{O}$  enrichment and oxidation during ocean floor hydrothermal metamorphism of ophiolitic metabasic rocks from E. Liguria, Italy. *Geochim. Cosmochim. Acta* **41**, p. 857-871.
- Stewart, M.K. (1980) Stable isotopes in waters from the Kawerau geothermal area and surroundings. In Stewart, M.K. (ed): *Composition of well discharges at Kawerau*. Geothermal Circular MKS-6, DSS-2. DSIR, Wellington, NZ.
- Studt, F.E. (1958) Geophysical reconnaissance at Kawerau, New Zealand. *N.Z. J. Geol. Geophys.* **1**, p. 219-246.
- Taylor, H. P. (1971) Oxygen isotope evidence for large-scale interaction between meteoric groundwaters and Tertiary granodiorite intrusions, Western Cascade Range, Oregon. *J. Geophys. Res.* **76**, p. 7855-7874.
- Taylor, H. P. (1977) Water-rock interaction and the origin of  $\text{H}_2\text{O}$  in granitic batholiths. *J. Geol. Soc. Lond.* **133**, p. 509-558.
- Thompson, G.E.K. (1962) Report on the natural heat survey of Onepu Springs and surrounding area. March-April 1962. In *Report for Tasman Pulp and Paper Co. Ltd. on Geothermal Survey at Kawerau 1962*. DSIR, Wellington, NZ.
- Whiteford, C.M. and J.T. Lumb (1975) *A catalogue of physical properties of rock, vol. 3: Listing by rock types*. Geophysics Division., DSIR, Wellington, NZ.

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