SYNOPSIS OF OXYGEN ISOTOPES IN GEOTHERMAL SOLIDS AND FLUIDS OF NEW ZEALAND
- THE NGAWHA PROBLEM

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ABSTRACT

Geothermal minerals serve as downhole probes of oxygen isotope compositions and thus of parameters of geothermal hydrology. "Deep" wells (2500 m) in New Zealand show no sign of $\delta^{18}O$ values 'bottoming out'. Ngawha differs from other systems both in the level and profile details of $\delta^{18}O$ values. The reservoir fluid at Ngawha may largely be of magmatic origin and Ngawha hydrogeology may or may not be suited for development of a high-throughput surface recharge system.

INTRODUCTION

Oxygen is a major component of common rocks (45 wt.%) and of hydrous solutions (90 wt.%), and the isotope ^{18}O is partitioned between solids and fluids in a predictable way, depending on temperature. One of two consequences that follow, is that geothermal precipitates (minerals) of drillcore provide a record, fixed in space, of temperature and isotope ratio of the fluid at the time of precipitation (Clayton et al. 1968, Blattner 1975, 1979; research logistics may appear easier in the case of <u>fossil</u> geothermal systems, where abundant outcrop can replace drillcore and cuttings, cf. Taylor and Forester 1979). A second consequence are shifts in the isotope composition of rocks and geothermal solutions, towards mutual equilibrium. Interacting rock and water of initially arbitary oxygen isotope compositions are setting up a potential for changes of their respective compositions (Isotope "shifting potential" P). Given masses or volumes of water and rock therefore have definite respective isotope "shifting capacities" C, beyond which they cannot exert a compositional influence (Blattner 1982). The same concepts apply to strontium, hydrogen, and other isotopes.

'HYDROLOGICAL AGE' AND EVOLUTION OF GEOTHERMAL SYSTEMS

Complex models of geothermal systems can be reduced to a basic 'mixed model' that nevertheless takes account of the 'open' nature of real systems, that is, of the input, circulation/isotope exchange, and discharge of waters in a relatively fixed rock framework. Individual batches of input or 'recharge' water are envisaged to circulate in, react with, and leave the reservoir rock, in sequence. This prototype of a model, first suggested by Taylor (1977) and developed in detail by Blattner (1980, 1981), provides considerable general insight into isotopic constraints on hydrological developments. Real geothermal systems can be treated as the sum of differing parts, with differing ages and rates of throughput, each handled in this basic manner. A central aspect of the 'mixed model' is the relationship it provides between the cumulative water-to-rock ratio (here W/R in units of the isotopic element exchanged) and relative isotope shifts of the reservoir rock and water. The ratio W/R offers a guide to the <u>hydrological age</u>, or maturity, of a system, whereas the isotope shifts can be measured directly.

If the isotope shifting potential P is defined as the difference between the initial (and coincidental) isotope relation between water and reservoir rock, $\delta_{Ri}-\delta_{Wi}$ (*) and the final isotopic difference that obtains under the conditions of the given geothermal system, $\delta_{rf}-\delta_{wf}$ (**), then we have

$$\sigma_R = P\,[(1 + W/Rn)^{-n} - 1] \qquad (1a)$$

where σ is an isotope shift $\delta_f-\delta_i$, in this case of the rock; n is the number of batches of water, w, that have passed through the system, so that W = nw, and allows to visualise a system with substantial recirculation and resistance to isotope exchange. Isotope shifts of idealised individual batches of water w must be clearly distinguished from shifts for the cumulative water throughput W, which cannot be sampled for analysis and matters only for purposes of material balance.

(*) δ stands for the usual $\delta^{18}O_{SMOW}$, in permille; i for initial, f for final.

(**) This corresponds to isotope equilibrium, if only the reacted portion of the rock is considered.

For the limit of infinitely small batch size W,

$$''_R = P\,(e^{-W/R} - 1). \qquad (1b)$$

Consider now the δD-$\delta^{18}O$ diagram in common use in geothermal hydrology, which gives the locus of surface waters and is amplified here by typical initial $\delta^{18}O$ values of rock as well as the equilibrium isotope differences for water and an average rock at 350°C (Fig. 1). We can see why oxygen isotope shifts σ_W of a water throughput W are usually positive; this must not become a dogma, however, since negative shifts may result, especially in lower temperature hydrology.

More importantly, the isotope shift of an individual water batch, current at a given time, σ_w, will gradually change as a geothermal system evolves. The change will not, however, be from the original water composition, perhaps on the meteoric water line, to the equilibrium point with reservoir rock at the prevailing temperature, but the reverse (arrows in Fig. 1). This is because, although every batch W may enter the system with a meteoric water composition, the first batch, by the time it is discharged, will have reacted with a previously completely unaltered rock at a small ratio W/R, and will be close to equilibrium with the unaltered rock. From that point in time the host, or reservoir, rock gets gradually shifted into equilibrium with the input water, and the discharged batches gradually work their way back to their point of origin, on the meteoric water line or elsewhere.

NEW ZEALAND GEOTHERMAL SYSTEMS

Oxygen isotope compositions of calcites of geothermal systems of New Zealand are compiled in Fig. 2, and listed in the Appendix. The calcites are in all cases of geothermal origin and, where doubtful, have been identified by X-ray diffraction. The crystals serve effectively as probes, fixed in space, of the oxygen isotope composition of the precipitating solutions and temperature. The source of the CO_3^{--} in the geothermal solutions is not well known, although $\delta^{13}C$ values of the calcites (e.g., Blattner 1979, 1980) suggests primary lithic carbonate sources. Fig. 2 shows $\delta^{18}O$-with-depth curves for calcite and also for the dilute hydrous solutions of each geothermal system. The dashed curves for solution are based on average measured downhole temperatures and published calcite-water oxygen isotope fractionations (Friedman and O'Neil, 1977. - In detail these fractionations are nominal, since analyses of water and calcite cannot be immediately compared).

Wairakei, Broadlands, Kawerau (WK, BR, KA)

For these fields the calcite $\delta^{18}O$ values indicate temperatures gradually increasing with depth, in many cases approaching a boiling point curve. Since measured downhole temperatures suggest no anomalies, the calcite values indicate reasonably steady $\delta^{18}O$ of solution with depth for each field (allowing for some loss of steam with decreasing pressure). In this way the three systems are clearly distinguished by the $\delta^{18}O$ of their secondary minerals and solutions, which increases in the order Wairakei → Broadlands → Kawerau. Actual measurement of discharged fluids shows a similar increase (Stewart, pers. com.). The reasonably tight organisation of the data implies that the calcite crystals from each area were precipitated from solutions of fairly constant $\delta^{18}O$ and temperature. Alternatively, if relatively stable conditions had prevailed long enough, older calcites of different isotope composition

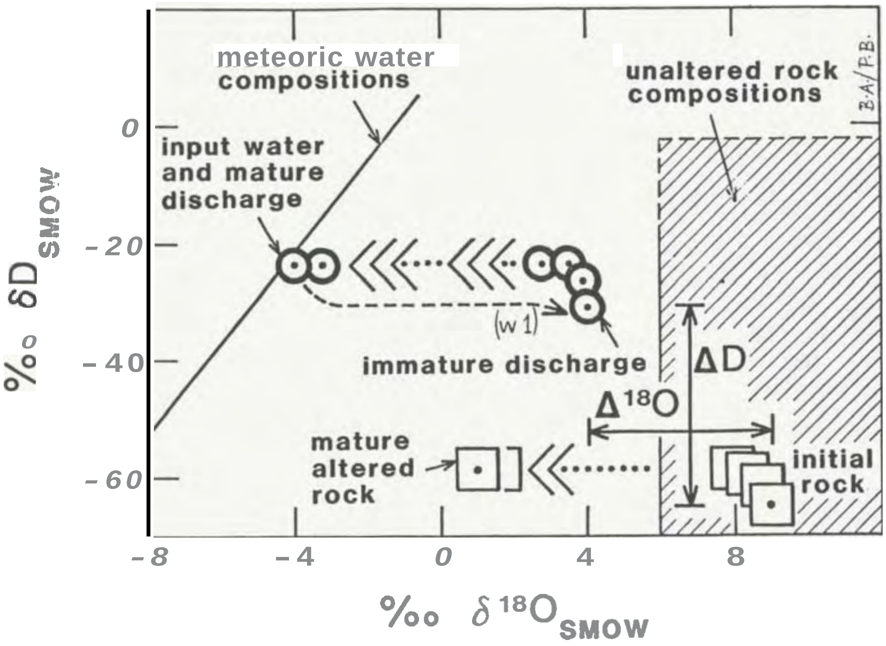

Fig. 1. Plot of δD vs $\delta^{18}O$, showing the evolution of a geothermal system, starting from mutually coincidental compositions of water and rock. All normal rocks lie in the marked field, reaching up to 30‰ $\delta^{18}O$ (sediments). The δD 'matures' more quickly because of the excess of hydrogen in water relative to rock (L-shaped track). "w1" shows the path of the first batch of water while equilibrating in the reservoir. Δ's are approximate equilibrium fractionations for 350°C. δD estimates from Taylor (1979).

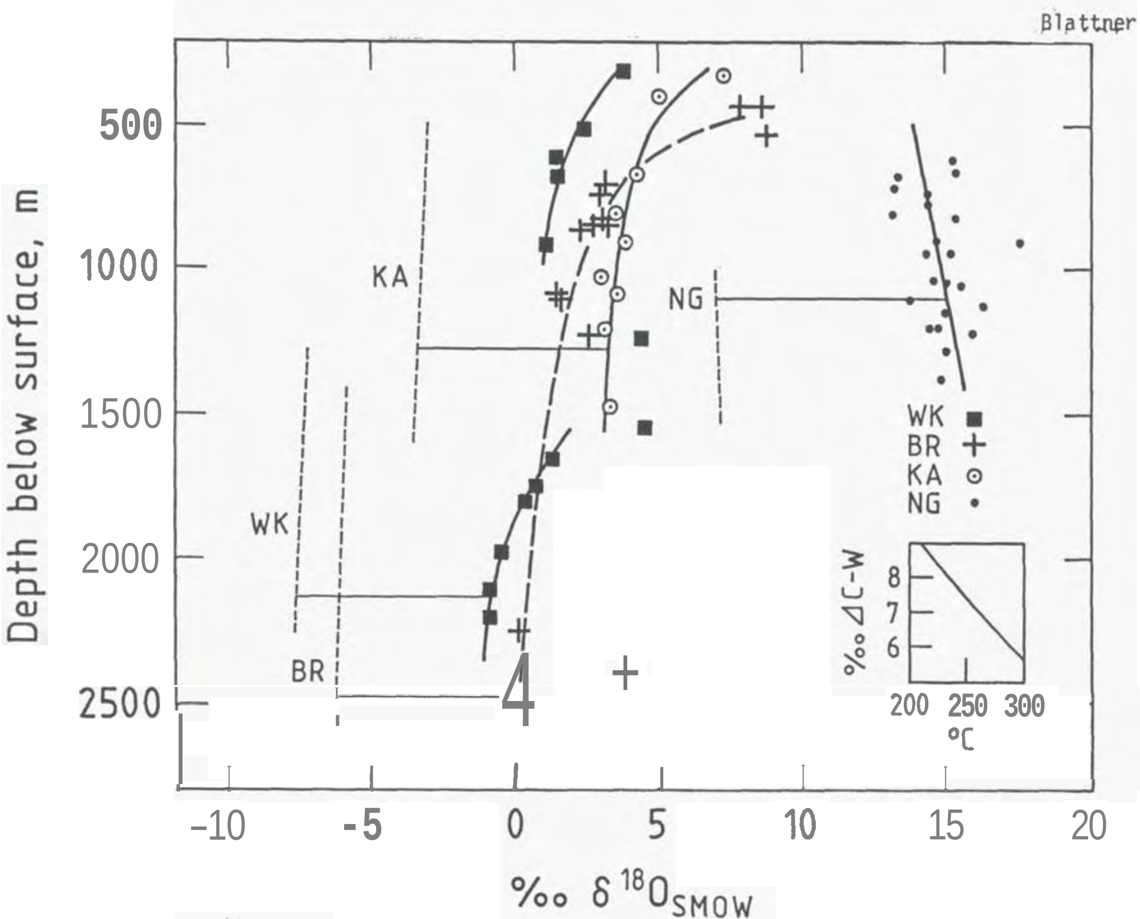

Fig. 2. Synopsis of $\delta^{18}O$ values for downhole calcite; Wairakei, Broadlands, Kawerau, Ngawha. Dashed lines are inferred values for solution, and inset shows Δ (Calcite-H_2O) with temperature.

could have exchanged isotopes to yield the present values. Data of Giletti et al. (1978) indicate that for this a period of at least about 10,000 years would be required, insofar as feldspar and calcite have similar diffusion properties.

Depth of geothermal cycle

In the case of WK, BR, and KA it is obvious that the major part of the water throughput is of meteoric origin: Since the reservoir rocks are of normal volcanic and sedimentary origins, there would otherwise be nothing to reduce the $\delta^{18}O$ of the water to less than about 0‰ (equilibrium with rocks 27‰ at ≳250°C). If substantially deeper wells were available (5 km?) one might expect a gradual turning back, with decreasing permeability, of the $\delta^{18}O$ with depth curves, to normal values ≳5‰ for solution and solids. The permeability boundary would probably be irregular, and we may actually see in the deep well BR15 a similar but lateral boundary of the system.

Stages of evolution of Wairakei and Kawerau

The oxygen isotope shifts of current water throughput of the WK and KA systems according to measurements of Stewart (1978, and pers. com.) is shown in Fig. 3. It is seen that the suggested recharge water of KA has a higher initial $\delta^{18}O$ value than that of WK and that, in addition, the positive shift for KA is almost twice that for WK. Both these factors may contribute to the considerable difference between the geothermal calcites of the two systems. Based on equations (1) (because of the constant isotope difference Δ under the terms of the 'mixed model', between the water being discharged at any given time and the shifted isotope composition of the reservoir rock at this same time) the cumulative water-to-rock ratio can be expressed in terms of the measured isotope shift σ_W of current throughput as follows,

$$W/R = n[(P/\sigma_W)^{1/n} - 1] \underset{n\to\infty}{=} -\ln {}^{\sigma_W}/P \qquad (2)$$

For an estimate of W/R, the 'hydrological age' of a geothermal system, the current σ_W as given in Fig. 3 is obviously of use only when measured against the oxygen isotope shifting potential, P.

How do the P values for WK and KA compare? In both fields the reservoir is made up of the same two rock types, 'axial' greywacke basement with $\delta^{18}O \approx 12$‰, and volcanic cover rocks with $\delta^{18}O \approx 8$‰. If the depth of both systems were 6 km, Wairakei would have a higher proportion of volcanic host rock, perhaps up to twice as much as Kawerau's ca. 30 percent (if the volcanics are weighted doubly on account of the greywacke's

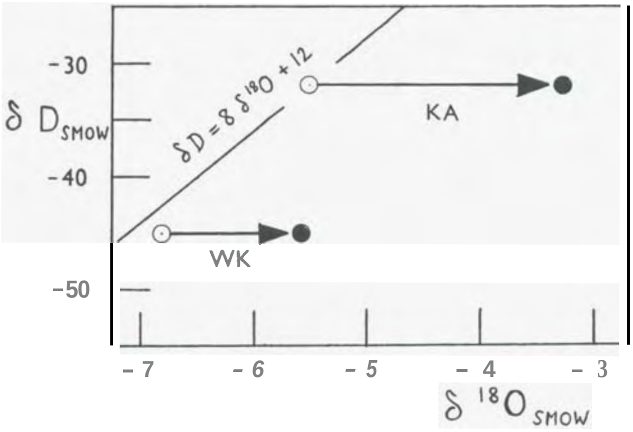

Fig. 3. Oxygen isotope shift σ_w between assumed surface recharge and current discharge at Kawerau and Wairakei (M.K. Stewart 1978 and pers. comm.).

poorer permeability). Table 1 shows the make-up of resulting estimates of $P = \delta_{ri} - \delta_{wi} - \Delta$, and estimates of W/R. It is seen that P is insensitive to possible geological differences, but would be sensitive to any uncertainty in the exact source of surface recharge. With that limitation, the 'mixed model' approximation suggests the pre-drilling Wairakei system to have reached a significantly more mature stage than Kawerau (Fig. 4). There is, however, no obvious reason (in possible contrast to the case of Ngawha) against substantial and continuous recharge taking place in the Kawerau as well as the Wairakei system.

Table 1. Cumulative W/R from σ_w and P for Kawerau and Wairakei geothermal systems

	σ_w	ass'd % volcanics	δ_{ri}	δ_{wi}	Δ_{350^oC}	P	$-\ln(\sigma_w/P)$
KA	2.2	30	10.8	-5.5	5	11.3	1.6
WK	1.2	30	10.8	-6.8	5	12.6	2.4
	1.2	60	9.6	-6.8	5	11.4	2.3

NGAWHA

Ngawha differs from the other geothermal systems discussed in that it occurs like the others in greywacke basement, but has an impermeable covering layer of ca. 500 m of carbonaceous sediment (Browne et al. 1981). A natural discharge larger than the existing one, carefully estimated at 2 ℓ/sec by Giggenbach and Lyon (1977), could be inhibited by the presence of this cover sequence. The difference in $\delta^{18}O$ of calcite from Ngawha and other deep reservoirs is shown dramatically in Fig. 2. Significant calcite does not normally occur in Northland greywacke and, as the calcite of the volcanic covers of WK, BR, and KA, the calcite of Ngawha basement may safely be considered of geothermal origin. Together with estimated reservoir temperatures the calcite-$\delta^{18}O$ of ca. 14 $^o/oo$ (one of the highest values for secondary minerals from any geothermal system) indicates a deep water composition of ca. 7 $^o/oo$, in approximate isotopic equilibrium with the original greywacke (Blattner and Bunting 1980).

Increase of $\delta^{18}O$ with depth

New results, summarised in Fig. 5, strongly suggest an increase of $\delta^{18}O$ of secondary calcite with depth in wells NG2 and 5 and, at a higher average $\delta^{18}O$, in NG4. In NG4 the trend is confirmed by four analyses of secondary quartz. This reversed trend for Ngawha, which would be difficult to pick up from downhole water sampling, could signify either (I.) a decrease in temperature by about 30°C between 700 and 1300 m depth (i.e. substantially more than suggested by Grant 1981 for post-exploration NG4 from well performance), or (II.) an increase of about 1 $^o/oo$ in the $\delta^{18}O$ of solution at constant temperature over the same depth range. Both possibilities are the opposite of common geothermal situations, and each of the two variables could be 'normalised' only at the cost of even greater abnormality in the other.

Possibility II (δ_{H_2O}) could relate to the lower boundary of a surface recharge system, where W/R begins to decrease. In that sense the 'fresh water recharge' of Ngawha might appear limited to a lateral intrusion at the base of the cover sequence. One would expect this intrusion to have a cooling effect, so that the low $\delta^{18}O$ of calcite near the base of the cover (where the sedimentary carbonate could be an additional reason for raised $\delta^{18}O$ values) requires a still greater drop in the $\delta^{18}O$ of water, on account of larger Δ. An upwards decrease in $\delta^{18}O$ of 1 or 2 $^o/oo$ could represent only minor dilution of an upwelling fluid of 7 $^o/oo$ by the regional meteoric water of ca. -5 $^o/oo$!

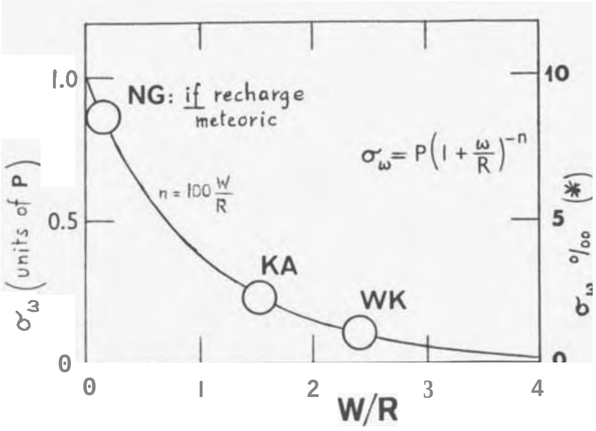

Fig. 4. Evolution of a 'mixed model' geothermal system, revised from Blattner (1981). W and R are in units of oxygen content. * The right hand scale applies if δ_{wi} = 0 and P = 10 $^o/oo$.

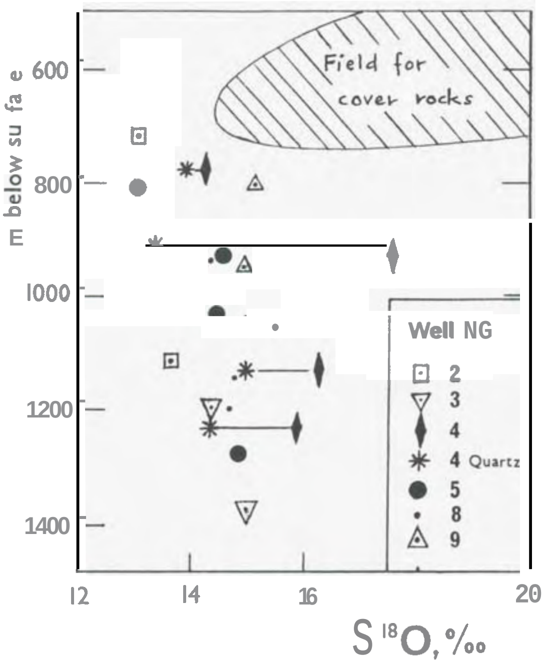

Fig. 5. Secondary calcite from below cover sequence, Ngawha (see App.). In spite of many irregularities a positive trend of $\delta^{18}O$ with depth is evident. The following holes show good correlations individually: NG2, 3 and 5. In the case of NG4 results on vein quartz have been included (✳) and seem to confirm the trend. The most negative values occur near the cover-basement interface and the most negative values for given depths occur in wells NG2, 3, and 5.

Transition from magmatic output to surface recharge?

In view of Northland meteoric water values of $\delta^{18}O \simeq 5$‰, an original reservoir rock with $\delta^{18}O \simeq 13$‰, and in view of $P \simeq 12$, the lack of an O-isotope shift $\gtrsim 1$‰ of the rock demonstrates that only a small cumulative W/R ratio can have been achieved at Ngawha. In fact, meteoric recharge water would have to carry a shift of ca. 12/00, about equal to P, so that we would be at a very early stage of a system's lifetime. This cannot be explained away by lack of equilibration of water and rock, since the secondary calcite is close to equilibrium with the rock, and samples from a 970 m deep production zone in NG9 have recently provided the corresponding values for H_2O near 6‰ $\delta^{18}O$ (Sheppard, 1982); thus a surface recharge would have equilibrated.

Since geothermal systems start up only when a heat source is provided, and since heat sources are usually cooling magma, the initial output of fluid of a developing system must contain a magmatic contribution. Whether it will soon begin to include reacted surface water as well, depends on whether the required hydrology is geologically possible. If Ngawha's small known discharge was irrelevant in the sense that we cannot claim control over all discharge over a large area, a higher rate of meteoric water throughput would ensure a more rapid 'evolutionary drop' of δ-values. McNabb and Macdonald (1982) postulate an outflow of 52 kg/sec of hot water on the basis of an energy balance; although equally young in terms of W/R, their system would be 26 times younger in terms of actual elapsed time, than a system with 2 ℓ/sec surface output.

Hydrogen isotopes could do much to refine our understanding of systems with large σ_W, whereas strontium isotopes could do the same for more mature systems, on account of the relative shifting capacities of rock in respect to isotopes of the three elements H, O and Sr (Blattner 1981). However, even with respect to oxygen we are only at the beginning of detailed study.

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REFERENCES

Browne PRL *et al* 1981 The Ngawha Geothermal Area. New Zealand DSIR Geothermal Report No 7. Wellington 178 pp.

Blattner P 1975 (Broadlands) Am J Sci 275 785-800.

Blattner 1979 (Kawerau) DSIR Unpubl Geothermal Circ PB-101 16 pp.

Blattner P 1981 Combined stable isotope trajectories for water-rock interaction. Proc NZ Geothermal Workshop, Auckland 75-80.

Blattner P 1982 (Oxygen isotope shifting capacity of rock) In: Symposium 'Isotope Studies of Hydrologic processes. Northern Illimois Univ Press 9-14.

Blattner P and Bunting DG 1980 (Ngawha) DSIR Unpubl Geothermal Circ PB/DGB-102 24 pp.

Clayton RN and Steiner A 1975 (Wairakei) Geochim Cosmochim Acta 39 1179-1186.

Clayton RN Muffler LJP White DE 1968 (Salton Sea) Am J Sci 266 968-979.

Friedman I and O'Neil JR 1977 (Compilation of stable isotope fractionation factors) US Geol Survey Prof Paper 440-KK.

Giletti BJ Semet MP Yund RA 1978 Studies in diffusion-I11 (O in feldspars) Geochim Cosmochim Acta 42 45-57.

Grant MA 1981 Ngawha Geothermal Hudrology In: Browne *et al* (1981) pp 60-86.

McNabb A and Macdonald WJP 1982 An energy balance model for the Ngawha Geothermal Field NZ J Sci 25 167-173.

Sheppard DS 1982 Unpubl Note on NG9 tests Chem Div DSIR (T.N. 82/1)

Stewart MK 1978 (Wairakei) In: NZ DSIR Bull 220 113-119.

Taylor HP Jr 1977 Water/rock interactions and the origin of H_2O in granitic batholiths J Geol Soc Lond 13% 509-558.

Taylor HP 1979 (Review) In: Geochemistry of hydrothermal ore deposits 2nd edn 236-277 Wiley NY

Taylor HP and Forester RW 1979 (Skaergaard) J Petrol 20 355-419.

Giggenbach WF and Lyon GL 1973 (Ngawha) DSIR Unpubl. Geothermal Circ. CD 30/555/7 WFG.

P.T.O.

APPENDIX: $\delta^{18}O$ values of downhole geothermal calcite of New Zealand geothermal fields, deepest available samples (cf. Fig. 2).

No.	Depth (m)	$\delta^{18}O_{SMOW}$† ($^o/oo$)
WAIRAKEI		
WK 121		
168033-2	1238	4.4
3	1453	3.3
4	1540	4.5
5	1643	1.4
6	1755	0.9
7	1809	0.3
8	1981	0.5
9	2108	-0.9
10	2201	-0.9

Fig. 2 also contains a few data from Tauhara (WK225), WK221 and WK224 of Clayton and Steiner (1975 no ref. value).

No.	Depth (m)	$\delta^{18}O_{SMOW}$† ($^o/oo$)
BROADLANDS		
BR 1		
*	1235	2.5
BR 7		
*	429	8.5
*	431	7.8
*	528	8.7
*	708	3.1
*	748	3.0
*	834	3.0
*	841	3.1
*	850	2.7
*	865-867	2.2
BR 13		
*	850	3.5
*	905	2.2
*	957	2.7
BR 15		
168040-1	2243	0.1
2	2426	3.7
BR 34		
168046-3	2590	-0.1

*These samples from Blattner (1975), adjusted to present reference values.

No.	Depth (m)	$\delta^{18}O_{SMOW}$ ($^o/oo$)
KAWERAU		
KA 21*		
168019-1	310	7.2
4	605	4.7
5	652	4.2
6	710	4.2
7	772	3.4
8	837	4.0
9	900	3.7
10	1022	3.0
11	1086	3.5
KA 24*		
168007-3	392	5.0
5	515	4.2
6	635	3.9
7	801	3.5
10	875	4.1
11	940	4.2
8	1129	3.1
9	1195	3.1
KA 27		
168031-1	1455	3.3

*KA 21 and 24 from Blattner (1979).

No.	Depth (m)	$\delta^{18}O_{SMOW}$ ($^o/oo$)
NGAHWA		
NG 2		
8006-3	711	13.1
1	1109	13.7
NG 3		
8056-4	1200	14.4
5	1375	15.0
NG 4		
8056-6	770	14.3
7	905	17.6
8002-23	1125	16.3
8056-8	1225	15.9
NG 5		
8056-9	801	13.1
8006-4	1026	14.5
6	1277	14.9
8002-14	922	14.6
NG 8		
8061-3	935	14.4
4	1035	15.0
5	1050	15.5
6	1140	14.8
7	1195	14.7
NG 9		
8056-1	805	15.2
2	940	15.1

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† Reference K-1 = 3.05 $^o/oo$, K-2 = 3.25 $^o/oo$ SMOW, (-26.85 $^o/oo$ PDB) (cf. Blattner and Hulston, 1978).