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THE QUARTZ- AND NA/K GEOTHERMOMETERS.
II. RESULTS AND APPLICATION FOR MONITORING STUDIES

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ABSTRACT

Quartz equilibrium temperatures can be assessed with confidence for liquid enthalpy wet-steam wells by assuming boiling to be adiabatic. On the other hand, an uncertaintly is involved with respect to "excess" enthalpy wells because the boiling processes leading to the "excess enthalpy cannot be rigorously constrained. It appears that an open system model generally gives the most reliable results. Mixing of equilibrated geothermal waters of different temperatures leads to discrepancy between quartz and Na/K geothermometry temperatures, the discrepancy increasing with increasing temperature difference between the end-member components in the mixture. Time variations in quartz and Na/K temperatures for producing wells and discrepancy between the two geothermometers provide useful information on the response of exploited geothermal reservoirs to the production load, such as cold water recharge and partial re-equilibration in the depressurization zone around the producing wells.

1. INTRODUCTION

In a previous contribution (Arnórsson, 2000), new calibrations were proposed for the quartz- and the Na/K-geothermometers, based on evaluation of thermodynamic data on quartz solubility and on simultaneous equilibrium between low-albite, microcline and solution, respectively. These new calibrations were compared with earlier published calibrations. Even if the new thermodynamic calibrations of the quartz- and Na/K geothermometers are quite precise, various processes can cause discrepancy between quartz equilibrium and Na/K temperatures for hot spring and drillhole discharges and between the geothermometry temperatures and measured temperatures in wells at points of producing horizons. The main sources of discrepancy include: (1) Equilibrium between the respective minerals and solution is not closely approached for one or both of the geothermometry reactions, (2) the discharge is a mixture of two or more components of quite different temperatures and salinities, (3) partial re-equilibration occurs during cooling in upflow zones. Specifically, for wet-steam well discharges discrepancy in the geothermometry results may additionally be due to: (1) Partial re-equilibration in the depressurization zone around wells where cooling occurs by extensive boiling, (2) relatively rapid cold water recharge, which is brought about by long term production that has upset initial equilibrium conditions in producing aquifers, (3) injection of waste geothermal fluid and (4) uncertainty which is involved in calculating aquifer silica concentrations from analysis of silica in samples collected at the wellhead (see Arnórsson, 2000). The sources of discrepancy between quartz and Na/K geothermometry temperatures are briefly described in the present contribution and, in particular, those which relate to mixing and changes in the production characteristics of producing geothermal reservoirs that can be related to pressure drawdown and enhanced recharge.

2. RESULTS FOR SELETED NATURAL WATERS

Fig. 1 depicts the relationship between Na/K activity ratios and temperature for selected surface- and groundwaters. Surface waters and groundwaters below 100°C generally have lower Na/K ratios than those corresponding to equilibrium with low-albite and mirocline although some groundwaters with temperatures as low as 20°C are close to equilibrium. Stoichiometric, or near stoichiometric, rock dissolution is considered to control the Na/K ratios of surface waters and the majority of cold to warm groundwaters. Gradual change towards equilibrium between the water and the alkali feldspars have been considered to involve two kinds of reactions, dissolution of Na- and K-bearing primary rock forming minerals and precipitation of secondary albite and K-feldspar (Arnórsson, 1991). At low temperatures, and in particular in the case of surface waters, the dissolution reaction seems to control the aqueous Na/K ratios. With increasing temperature and residence time underground the relative importance of the precipitation reaction evidently increases. This could be due to increasing rate of precipitation in relation to the rate of Na and K release into solution by primary mineral dissolution. Waters above 100°C are generally quite close to simultaneous equilibrium with low-albite and microcline. Some waters seem, however, to have too high Na/K ratios for their aquifer temperature and others too low a ratio. In the case of wet-steam well discharges high ratios may be due to partial re-equilibration in the depressurization zone around wells where the water cools by extensive boiling. Low ratios may reflect higher temperatures at levels deeper than those penetrated by wells, or possibly non-equilibrium conditions with respect to the alkali-feldspars.

Fig. 2 shows the relationship between aqueous silica concentrations and aquifer temperature for selected spring and drillhole discharges. Waters below 180°C are close to chalcedony saturation or somewhat supersaturated and, therefore, quartz supersaturated, a result that conforms with that of Arnórsson (1975). Waters above 180°C display considerable scatter around the quartz solubility curve. Some are supersaturated, others undersaturated. The data shown in Fig. 2 with tempreratures of less than 180°C are all from Iceland. Geothermal waters in other countries may attain equilibrium with quartz below 180°C.

The aquifer silica concentrations plotted in Fig. 2 for "excess" enthalpy wells are based on the open system model (see Arnórsson, 2000). Average and standard deviation from the equilibrium curve for the "excess" enthalpy data points is equivalent to 15 and 10°C, respectively, which is very similar to such numbers for well discharges with liquid enthalpy and temperature above 180°C. For the adiabatic model the scatter is greater (Fig. 3), average deviation being 25°C and standard deviation 15°C. The closed system model generally yields unrealistically low quartz equilibrium temperatures (Fig. 3) indicating that the process assumed by this model is not responsible for the "excess" enthalpy of the well discharges selected in the present study although it may contribute, at least in those cases where the quartz equilibrium temperature according to the other two models is higher than the measured aquifer temperature.

The average and standard deviations between Na/K geothermometry temperatures and measured aquifer temperatures are somewhat lower for liquid enthalpy wells (15° and 14°C, respectively) than for "excess" enthalpy wells (21° and 18°C). This is not to be expected since aqueous Na/K ratios and, therefore, Na/K-temperatures are independent of boiling processes between the undisturbed aquifer and wellhead. The observed difference in the statistical results for liquid enthalpy wells, on one hand, and "excess" enthalpy wells, on the other, could be due to the fact that the "excess" enthalpy wells selected for the present study have on average higher temperatures than the liquid enthalpy wells. With increasing temperature the error in estimated Na/K temperatures increases by all sources of error to the Na/K aqueous activity ratio in consequence to the shape of the Na/K geothermometry curve.

The average difference between the quartz equilibrium (open system model) and Na/K temperatures is about the same as that between the selected (measured) aquifer temperature and the respective geothermometry temperatures, indicating that aquifer temperature values derived from downhole measurements are not systematically in error.

3. EFFECTS OF MIXING

Isoenthalpic mixing of two or more water components, which are at equilibrium with quartz, does not cause the quartz equilibrium temperature to depart significantly (less than about 5°C) from the actual temperature of the mixed water, if the temperatures of the components in the mixture lie within 150° and 300°C (Fig. 4A). If, however, the temperature of the "coldest" water component is <150°C, or the temperature of the hottest component >300°C the quartz equilibrium temperature of the mixed water becomes significantly higher (by as much as 20°C) and lower (by as much as 25°C) than that of the mixture, respectively. The pH of dilute waters with temperatures below about 150°C may be sufficiently high for appreciable ionization of the dissolved silica and they may also have equilibrated with chalcedony rather than with quartz. Isoenthalpic mixing between such waters and waters with temperatures above about 200°C will cause quartz equilibrium temperatures of the mixed water to be higher than the actual temperature of the mixed water.

Isoenthalpic mixing of equilibrated waters of equal salinity causes the Na/K geothermometry temperature to become higher than the actual temperature of the mixed water, the difference increasing with increasing temperature difference between the end-member components in the mixture and reaching as much as 30°C (Fig. 4B). If the hot component has higher salinity, which is the case in most drilled geothermal systems, the Na/K temperature of the mixed water will be even higher in relation to the actual temperature of the mixed water and approach that of the hot component as its salinity increases relative to the cold water component, i.e. the mixing process can be regarded as dilution.

Mixing of waters of equal salinity in the range 100-250°C does not lead to significant discrepancy between the quartz and the Na/K geothermometry temperatures and particularly so, if the hot water component is <200°C (Fig. 4C). Yet, the geothermometers indicate temperatures, which are 10-20°C too high. With increasing temperature of the hot water component, the discrepancy between the two geothermometers increases, the quartz equilibrium temperature being lower, especially when the hot water component has higher salinity than the cold water component.

4. RE-EQUILIBRATION UPON COOLING IN UPFLOW ZONES

Field data indicate that surface waters and non-thermal and slightly thermal groundwaters possess Na/K ratios similar to those of the host rock, corresponding roughly to Na/K geothermometry temperatures of 200-400°C for basaltic to silicic volcanics. With progressive water-rock interaction towards equilibrium the waters gradually approach equilibrium at the temperature of the water. In extreme cases this may be at temperatures as low as 10-20°C (Fig. 1).

When applied to thermal spring discharges, the Na/K geothermometer sometimes indicates higher temperatures than the quartz (or chalcedony) geothermometers, but in the case of dilute waters it is often the other way around. Higher Na/K temperatures, as compared to quartz equilibrium temperatures, may result from: (1) Lack of mineral-solution equilibration at depth, (2) mixing with colder water in the upflow, (3) slower re-equilibration for the Na/K geothermometer and (4) enhanced primary mineral dissolution as a consequence of mixing. If the geothermal water has not attained equilibrium at depth, the Na/K geothermometer tends to indicate a higher temperature than the quartz geothermometer. Mixing and associated enhanced primary mineral dissolution, which tends to occur, if the mixing prevents boiling (Arnórsson, 1985), also causes Na/K temperatures to be higher than those of quartz.

The Na/K geothermometer is generally considered to respond more slowly to cooling than the quartz geothermometer. However, as already pointed out, the Na/K temperature of boiling hot springs and well discharges is often significantly lower than the quartz equilibrium temperature. Changes in aqueous Na/K ratios, as geothermal waters cool and react towards equilibrium with alkali feldspars, are considered to be affected by the water salinity. Aqueous Na/Al (and K/Al) ratios increase with increasing water salinity. Equilibrated water at 250°C and with 200 ppm K has a K/Al molal ratio of >200. Even if re-equilibration was rapidly reached for such water during cooling for the individual feldspars by removing most of the Al from solution, both Na and K concentrations would be little affected and so would Na/K ratios. This is, on the other hand, not the case with dilute waters, which may have K/Al molal ratios as low as 5.

5. MONITORING STUDIES

With increased utilization of geothermal resources, the emphasis of applying chemical geothermometers has shifted to some extent, from exploration to monitoring studies. The purpose of monitoring studies is to evaluate the response of exploited geothermal reservoirs to the production load. Pressure drawdown in producing aquifers enhances recharge, often of cold water, and in the case of boiling or near boiling reservoirs, the pressure downdown leads to cooling of the aquifer fluid through extensive boiling. The geothermometers tend to respond to changes in temperature, whether caused by cold recharge or extensive boiling. For this reason precise evaluation of both quartz and Na/K temperatures is important to evaluate the response of geothermal reservoirs to the production load. This requires well documented sampling conditions, accurate analysis of Si, Na and K and, in the case of relatively saline waters (ionic strength >0.1) above 300°C, calculation of Na/K ion activity ratios with the aid of an aqueous speciation program. In order to be able to estimate quartz equilibrium temperatures with maximum accuracy, samples from wet-steam wells with "exces" enthalpy should be collected at elevated pressures (≥10 bars vapour pressure).

Monitoring results for two wells in the Krafla field, Iceland, which have been extracted from Gudmundsson and Arnórsson (2000) are depicted in Figs. 5 and 6. It is seen that in well 9 Cl concentrations have remained constant whereas they have decreased substantially in the water discharged from well 21 (Fig. 5). Decreasing Cl is indicative of enhanced colder water recharge in response to the production load. For well 9 both quartz equilibrium and Na/K temperatures have decreaed with time. Yet, the Na/K geothermometry temperature stayed fairly constant up to 1986 after which it has fallen significantly. The decrease in the geothermometry temperatures for well 9 cannot be explained by colder water recharge unless the recharging water has a similar Cl content as the initial aquifer water. There may be several causes for this decline as well as for the difference between the two geothermometers as explained below.

The Na-K temperature for well 9 has remained lower than the quartz equilibrium temperature throughout the production history of the well. This cannot be explained by mixing. Three explanations are offered to explain this and the decline with time in the geothermometry temperatures. One is partial re-equilibration in the depressurization zone around the well, where extensive boiling occurs, and that the Na/K geothermometer responds faster. The second explanation assumes that the well is recharged by colder water from shallower level and that quartz re-equilibrates faster than the Na/K geothermometer as this shallow water descends and gains heat by contact with the reservoir rock. The third explanation also assumes colder recharge and that the recharging water has relatively low Na/K temperature relative to the quartz temperature, as is the case with many boiling hot springs (Arnórsson, 1985), and as this water descends and gains heat it does not react significantly with the rock.

Initially, the quartz equilibrium and Na/K temperatures for well 21 were about the same (Fig. 6) but around 1987-88 both fell considerably. Thereafter they have remained about constant, the Na/K temperature being about 240°C and the quartz equilibrium temperature 10-20°C higher. Prior to 1987 the temperature of the producing aquifer was 260-265°C. The rapid decline in the geothermometry temperatures during 1987-88 is considered to be due to incursion of shallow, relatively cold water into the producing aquifer. The discrepancy between the results of the two geothermometers since 1988 can be explained by cases 2 and 3 given for well 9 above. The steady decline in Cl in the water from this well indicates progressively increasing recharge of colder water into the producing aquifer. Prior to 1987 the recharging colder water appears to have equilibrated thermally and chemically with the aquifer rock. This is, however, not the case since 1988 after the sudden decline in the geothermometry temperatures.

6. DISCUSSION AND CONCLUSIONS

Most drilled geothermal systems are hosted in fractured volcanic rocks, which are heterogeneous with respect to both porosity and permeability, i.e. their permeability is anisotropic. For this reason, it is inevitable that water discharged from a well, even if it has intersected only one permeable horizon, will be a mixture of many components that have originated in different parts of the system and travelled different distances from their sources to the point of well inflow. Mixing of equilibrated waters may lead to discrepancy between quartz and Na/K geothermometry temperatures, if the different components have very different temperatures (>100°C), the Na/K temperature always becoming higher. Mixing of hot equilibrated and cold non-equilibrated waters has the same effect. If rapid recharge of partially equilibrated water occurs from shallow levels into producing aquifers of wet-steam wells, the Na/K temperature may become lower than the quartz equilibrium temperature. Relatively rapid re-equilibration of descending shallow water with respect to quartz, as compared with the alkali-feldspars, has the same effect.

Even if waters are mixed, Na/K and quartz equilibrium temperatures may be similar. Yet, such waters have geothermometry temperatures which depart from their actual temperature, the geothermometry temperatures being higher.

In conjunction with circulation losses during drilling and temperature logging during thermal recovery of wells, quartz and Na/K geothermometry is very useful for locating levels of producing horizons in wet-steam wells. Differences between these geothermometers are further useful for recognizing contributions to well discharges from aquifers of significantly different temperatures. Finally, quartz and Na/K geothermometry provides useful information about recharge into geothermal reservoirs, particularly when combined with results on Cl.

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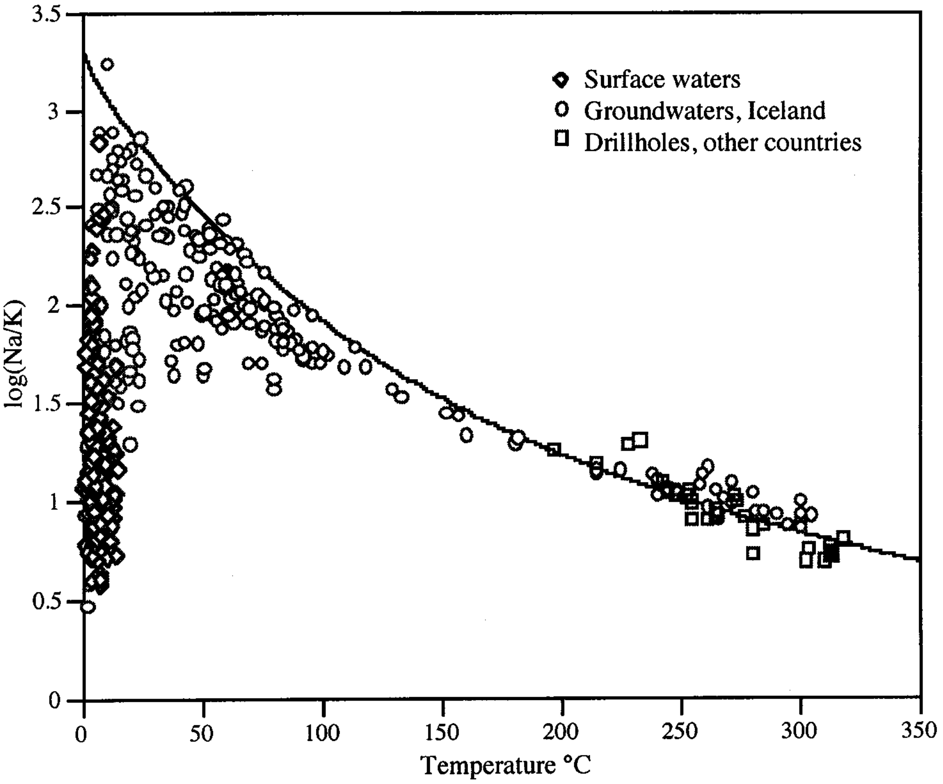

Figure 1. Na/K activity ratios in selected natural waters. The curve represents simultaneous equilibrium between low-albite, microcline and solution according to equation (7) in Arnórsson (2000).

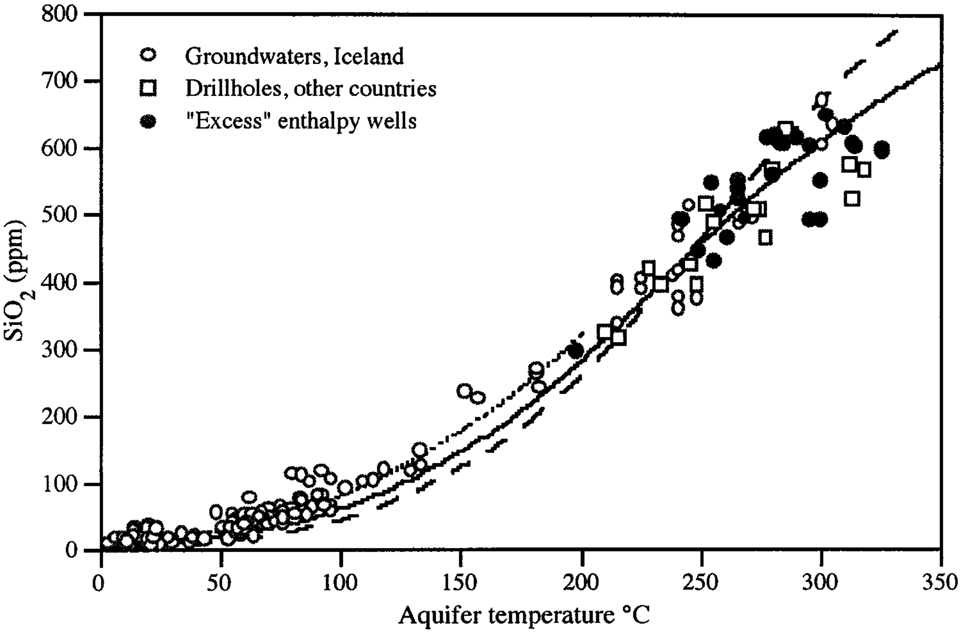

Figure 2. The state of quartz saturation in selected drillhole discharges. Solid and broken curves: Quartz solubility according to Arnórsson (2000) and Fournier and Potter (1982), respectively. Dotted curve: Chalcedony solubility (Fournier, 1977)

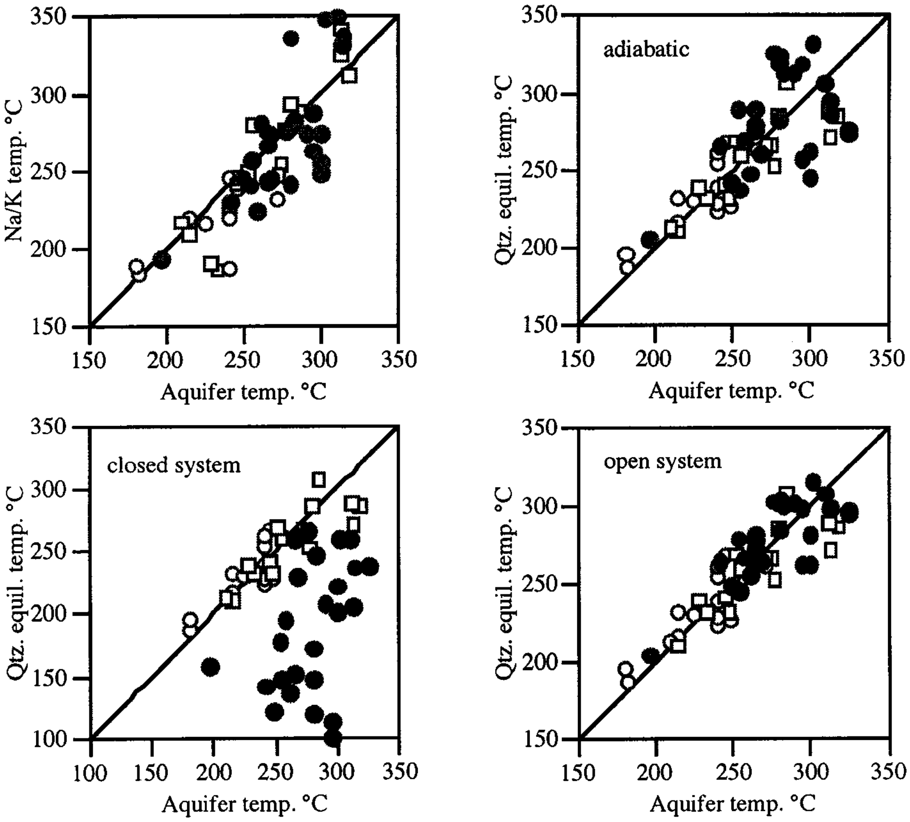

Figure 3. Relationship between aquifer temperature and Na/K and quartz equilibrium temperatures. The three models (adiabatic, closed and open) of Arnórsson (2000) were used to calculate aquifer silica concentrations and sunsequently quartz equilibrium temperatures. Circles and squares: Drillholes in Iceland and in other countries, respectively with liquid enthalpy. Dots: "excess" enthalpy wells.

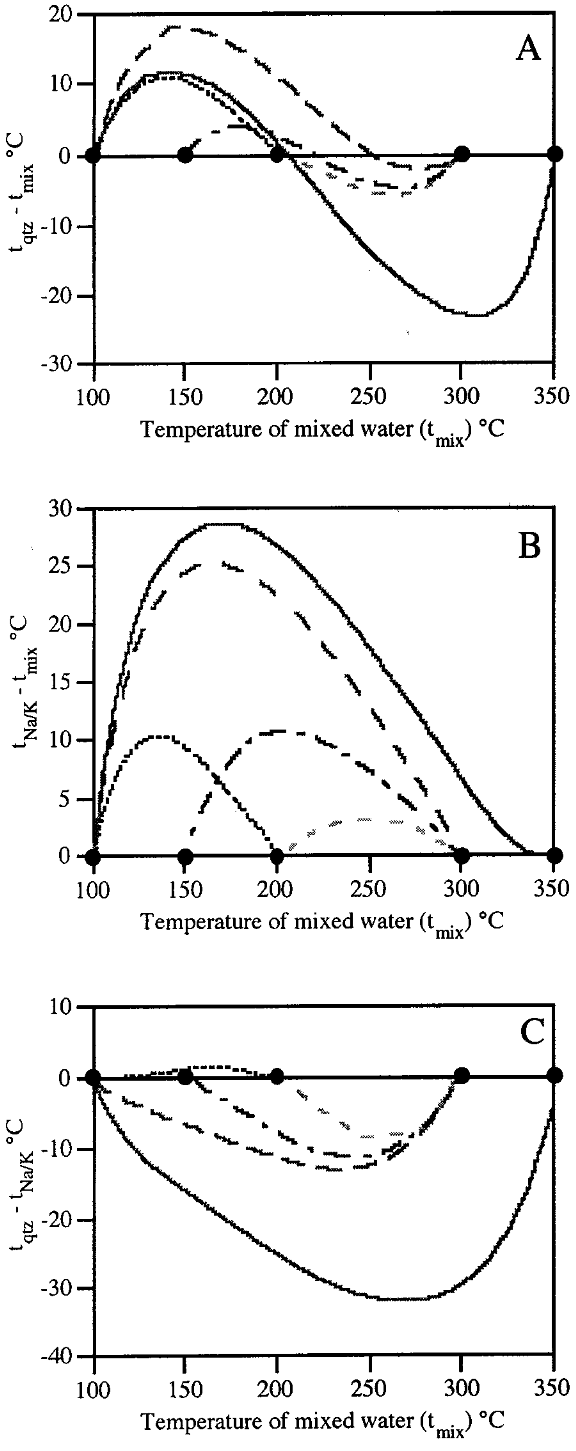

Figure 4. The difference between Na/K, quartz and actual temperatures of variably mixed waters initially at equilibrium with quartz and low-albite and microcline. End-member components in the mixed waters are shown by dots.

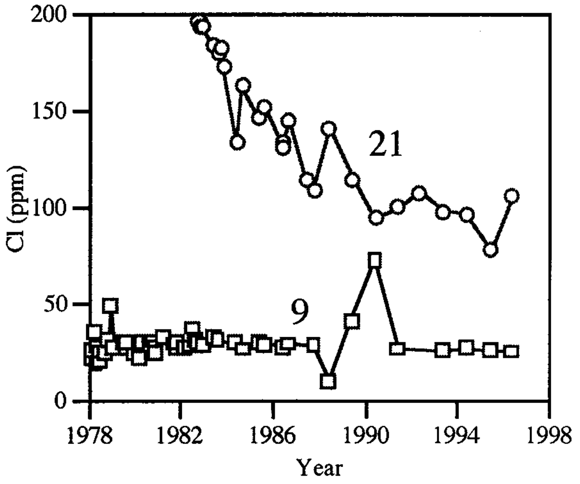

Figure 5. Variations in Cl concentrations with time in water at 10 bars abs. vapour pressure discharged from wells 9 and 21 at Krafla, Iceland.

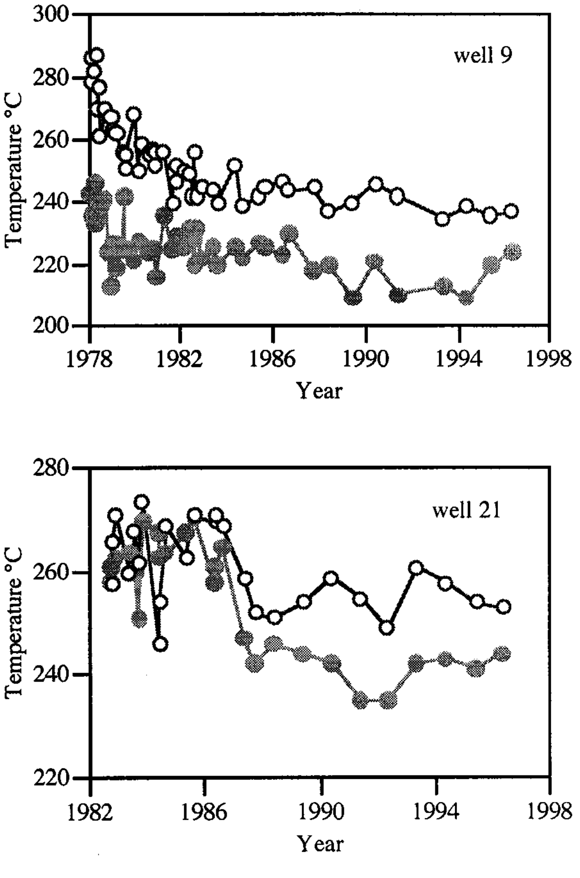

Figure 6. Quartz equilibrium (circles) and Na-K (dots) temperatures for 2 wells in the Krafla field, Iceland.