GL03601

LETTER TO THE EDITOR

A systematic deviation from Na–K–Ca geothermometer below 75°C and above 10^{-4} atm P_{CO_2}

Abstract—If the temperature of ground water is below 75°C and the partial pressure of CO_2 in the aquifer is above 10^{-4} atm, a chemical steady-state between water and felsic rocks (rather than chemical equilibrium) may be maintained. The temperature of water in the aquifer may be estimated using a modified form of the Na–K–Ca geothermometer from,

$$\log K = \log \frac{Na^+}{K^+} + \tfrac{4}{3} \log \frac{\sqrt{Ca^{2+}}}{Na^+} - I,$$

where the departure of the steady-state from equilibrium, I, is a function of P_{CO_2}:

$$I = -1·36 - 0·253 \log P_{CO_2}.$$

CHEMICAL compositions of thermal waters vary linearly with the reciprocal of absolute temperature in many geothermal systems (FOURNIER and TRUESDELL, 1973). The variation has been interpreted by the authors as a chemical equilibration between water and Na-, K- and Ca-bearing minerals according to the van't Hoff equation. The mass-action laws of the complex equilibria lead to a generalized form

$$\log K = \log \frac{Na^+}{K^+} + \beta \log \frac{\sqrt{Ca^{2+}}}{Na^+}, \tag{1}$$

where K stands for an approximate equilibrium constant, the concentrations of ions are in mole/kg and β is a constant depending on the stoichiometry of the reactions between water and minerals. FOURNIER and TRUESDELL (1973) found that β is either $\tfrac{1}{3}$ or $\tfrac{4}{3}$ depending upon whether the water equilibrated above or below 100°C. The temperature change in $\log K$ for a range from 2 to 372°C inferred from the diagram in their paper is

$$\log K = -2·21 + 1·64(10^3/T), \tag{2}$$

where T is the absolute temperature in °K.

Not all ground waters are in chemical equilibrium with rocks. The two major causes of disequilibrium are fast percolation of water and a flux of an acidifying agent such as CO_2 into the aquifer. If the velocity of percolation and the flux of CO_2 are fast enough that the hydrolysis of minerals cannot bring the chemical composition of the water to equilibrium, a steady-state composition may be established (PAČES, 1973). In such a case the chemical composition of the water deviates from the equilibrium state expressed by the value of $\log K$. This is demonstrated by 20 samples of warm waters from felsic rocks (Fig. 1). No speculative selection of the samples was made except that they exhibit varied degrees of disequilibrium

with minerals of granitic rocks. The temperature of the water in the aquifer is known only in three instances indicated by the arrows in Fig. 1. Other data represent the temperature in the springs. The aquifer temperature in these cases probably cannot be estimated using the SiO_2 geothermometer (FOURNIER and ROWE, 1966; FOURNIER and TRUESDELL, 1970) because aluminosilicates rather then SiO_2 solid phases may control the concentration of silica in these low-temperature waters (PAČES, 1973). The unknown differences in the spring and aquifer temperatures are an important uncertainty in the following interpretation of the data. However, it is assumed in this letter that the temperature differences are probably not in excess of those represented by the three arrows in Fig. 1. The reason for the assumption is that the temperatures of all the springs are rather low and the discharges of the water are similar, in a range from 1 to 10 l/sec (discharge values are given in the caption of Fig. 1).
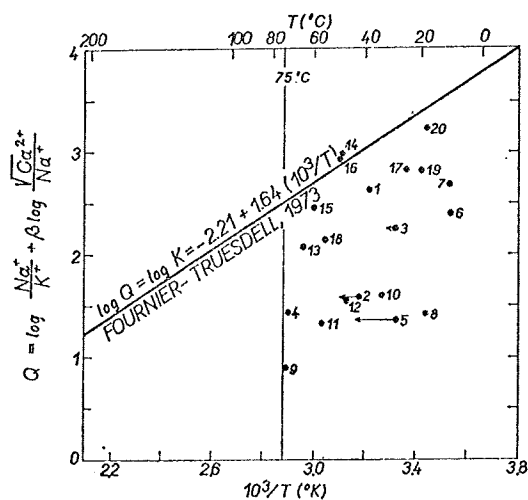

Fig. 1. Na–K–Ca geothermometer for natural waters (FOURNIER and TRUESDELL, 1973) and 20 samples of ground water with varied P_{CO_2} from granitic rocks. Sources of chemical analysis: (1) Borský massif, Czechoslovakia: unpublished analysis courtesy of J. Skořepa, (2) Pravřídlo (discharge 3·5 l/sec), Teplice: ČADEK et al., 1968 (3) HG-1 (9·5 l/sec), Jáchymov: LABOUTKA and PAČES, 1966 (4) Vřídlo II (1·7 l/sec; discharge of group 35 l/sec), Karlovy Vary: MACHÁČEK and ŠULCEK, 1965 (5) Ln-1 (1·4 l/sec), Louny: KOLÁŘOVÁ, 1963 (6) BJ 2, Konstantinovy Lázně: PAČES, 1970 (7) BJ 14, Konstantinovy Lázně: PAČES, 1970 (8) Císařský spring (discharge of group 9 l/sec), Hájek: AMBROŽ et al., 1961 (9) Mammoth (0·25 l/sec, discharge of group 47 l/sec), Yellowstone Park; (10) Keene Wonder (1·9 l/sec), California; (11) Big Horn (795 l/sec), Wyoming; (12) Lýsuhóll (2·5 l/sec), Iceland; all cited by WHITE et al., 1963 (p.F 54) (13) Grovers hot spring, California; (14) Bowers Mansion (3 l/sec), Nevada; (15) Walley hot spring, Nevada; (16) California hot spring 1214, California; (17) Mayors, spring 1219, California; (18) Scovern, spring 1299, California; (19) Calpine, spring 1563, California; (20) Arnold spring, California; all cited by FETH et al., 1964 (p.I 54).

Let us express the steady-state chemical composition of water by $\log Q$, whose value is equal to the right-hand side of equation (1) providing that an equilibrium state is not assumed. Now, the deviation of a water sample from the equilibrium composition can be expressed by the disequilibrium index

$$I = \log Q - \log K \qquad (3)$$

or, after substituting equation (2) and the definition of $\log Q$ into (1),

$$I = \log \frac{Na^+}{K^+} + \beta \log \frac{\sqrt{Ca^{2+}}}{Na^+} + 2 \cdot 21 - 1 \cdot 64(10^3/T). \qquad (4)$$

The values of I for the 20 samples vary from $+0 \cdot 1$, which approximately indicates an equilibrium state, to $-2 \cdot 02$, indicating the largest deviation.

It has been found that the values correlate best with $\log P_{CO_2}$ of water ($r = -0 \cdot 777$), the partial pressure of CO_2 being either measured if larger than 1 atm or calculated using the equation

$$- \log P_{CO_2} = pH - \log HCO_3^- + 7 \cdot 689 + 4 \cdot 22 \times 10^{-3}t + 3 \cdot 54 \times 10^{-5}t^2,$$

where HCO_3^- is the activity of bicarbonate in the water and t is temperature of the water in °C.

The linear regression between $\log P_{CO_2}$ and I is apparent in Fig. 2 where the least square fit gives the line

$$I = -1 \cdot 36 - 0 \cdot 253 \log P_{CO_2}. \qquad (5)$$

The linear regression of I with other physicochemical parameters is less obvious, e.g. I vs pH gives $r = 0 \cdot 618$, I vs log Ca^{2+} gives $r = -0 \cdot 402$. The correlation coefficient for 20 samples at the confidence level $p = 0 \cdot 01$ is $0 \cdot 561$. Hence the linear regression with $\log P_{CO_2}$ is highly probable.

The functional relationships reflect the competition between the hydrolysis of feldspars and the dissociation of carbonic acid whose concentration is controlled by the flux of CO_2 into the aquifer.

These observations indicate that the Na–K–Ca geothermometer should be applied with caution if P_{CO_2} in equilibrium with water is more than 10^{-4} atm and

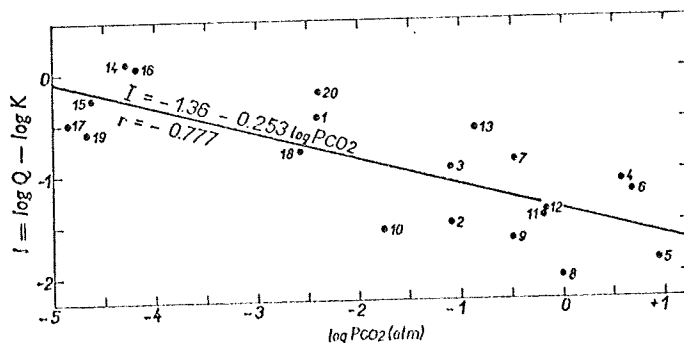Fig. 2. Disequilibrium index I, equation (4), vs log P_{CO_2} in the aquifer.

the temperature in the aquifer is less than 75°C. In granitic terrains, where P_{CO_2} is high, the approximate temperature in the aquifer may be estimated from the diagram presented by FOURNIER and TRUESDELL (1973) and replotted in Fig. 1 if a correction is made for a steady state

$$\log K = \log \frac{Na^+}{K^+} + \tfrac{4}{3} \log \frac{\sqrt{Ca^{2+}}}{Na^+} - I,$$

where I is read out from Fig. 2.

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