

## The isotopic and chemical composition of CO<sub>2</sub>-rich thermal waters in the Mont-Dore region (Massif-Central, France)

H. Pauwels and C. Fouillac

BRGM, Research Division, BP 6009, 45060 Orléans Cedex 2, France

F. Goff

Los Alamos National Laboratory, Earth and Environmental Sciences Division, Los Alamos, NM 87545, USA

and

F.-D. Vuataz

Centre of Hydrogeology, University of Neuchatel, 11, rue E. Argand, 2007 Neuchatel, Switzerland

**Abstract**—Chemical and isotope compositions of fluid samples, collected between 1974 and 1986 from 52 springs or shallow boreholes located in the Mont-Dore region (Massif Central, France), were examined. Some springs and wells were sampled several times during this period. The fluids emerge from Quaternary volcanic rocks or Paleozoic granite at temperatures between 4 and 62°C, and the origin of the H<sub>2</sub>O is meteoric. The waters can be classified into three groups: bicarbonate fluids, mixed bicarbonate-chloride fluids (with a mineralization up to 8 g/l), and acid-sulfate fluids. Only two fluids contain sufficient Cl<sup>-</sup> to be considered as 'mature' waters. Previous work has demonstrated that they all contain partly mantle-derived CO<sub>2</sub> gas, and that the CO<sub>2</sub>-rich gas phase and bicarbonate-chloride waters are separated at substantial depth.

Mineralized fluids circulate at depth and undergo several processes, such as cooling or dilution with recent freshwater, during their ascent to the surface. Therefore, the CO<sub>2</sub>-rich gas phase can be partly dissolved in the freshwater, or in deep fluids after their dilution. This process leads to the dissolution of surrounding rocks; such dissolution is discussed on the basis of major-element concentrations (Na, K, Ca, Mg), as well as the Sr 87/86 isotope ratio. Dissolution of S-bearing minerals has also been demonstrated. The presence of the CO<sub>2</sub>-rich gas phase also leads to isotope exchange between CO<sub>2</sub> and H<sub>2</sub>O. Some mineralized fluids are less affected by these processes than others, in which case they display the chemical and isotopic characteristics of the original deep fluids.

It was shown that the applicability of geothermometer calculations for these waters is hampered by several processes that modify the chemical composition. However, some geothermometers can be used for estimating the temperature of the deep fluids using the chemical composition of the less modified fluids. They indicate that fluids emerging from volcanic rocks in the Dordogne valley reach temperatures of around 100–130°C at depth, while the temperature of the fluid that issues from the granite at Saint-Nectaire is 160–175°C at depth.

### INTRODUCTION

The Massif Central in France is a vast area of Recent volcanism and tectonic activity, where CO<sub>2</sub>-rich mineral springs are common. A large amount of geological, geophysical, chemical and isotopic data has been collected, mainly for use in geothermal exploration. Geochemical study of the mineral and thermal springs began 20 years ago. The object of this paper is to synthesize the chemical and isotope data collected from 52 different points in the Mont-Dore volcanic complex (Mont-Dore and Sancy volcanoes) and surroundings. Comparisons are made between the relatively mineralized and dilute fluids. The chemical and isotopic compositions of fluids emerging from the volcanic rocks are also compared to those of fluids issuing from the granite, allowing a better understanding of the processes undergone by the fluids.

In other thermal or geothermal systems, equi-

librium between fluids and mineral assemblages has been widely demonstrated from the chemical composition of fluids (e.g., Giggenbach, 1981, 1988; Arnórsson *et al.*, 1983a; Michard, 1985). Equilibrium has also been assumed to explain the chemical composition of some cold waters (Grimaud *et al.*, 1990). However, some calculations carried out for fluids from the Mont-Dore region show that no equilibrium exists between most of the fluids and their host rocks at any temperature (Michard *et al.*, 1978, 1981). Therefore, a different explanation must be invoked for the chemical composition of these CO<sub>2</sub>-rich fluids. As discussed in this paper, mixing of fluids and water-rock reactions in the presence of CO<sub>2</sub> are the main processes that may change the chemical and isotopic composition of such fluids. The main purpose of this paper is to identify such processes in order to discuss the chemical and isotopic characteristics of the deep reservoir fluids.

This identification should help in determining the composition of which fluids should be used for estimating deep temperatures, using chemical and isotope geothermometers.

#### GEOLOGICAL ENVIRONMENT AND SAMPLING LOCATIONS

The Massif Central of France is formed by a basement consisting of granite and Hercynian metamorphic-rock, which according to Brousse (1984) is largely granitic, under the Mont-Dore volcanic complex. This basement was intruded by Late Tertiary and Quaternary volcanics that generally become younger from S to N. The petrology and volcanology of the region were studied and discussed by Brousse (1971, 1984), Brousse *et al.* (1989), Jung and Brousse (1962) and Lavina (1985). During the first period of volcanism in the Mont-Dore region (between 4.7 and 3.1 Ma) basalt flows were dominant. Renewed Mont-Dore volcanic activity began 2.5 Ma ago with the eruption of a large ash and pumice rhyolitic flow, which was responsible for the Haute-Dordogne caldera formation. During the post-caldera period, until 1.5 Ma, rhyolite, phonolite and basalt were formed. Between 1 Ma and 0.25 Ma, volcanic activity was focused on the E and S border of the caldera, with the formation of the Sancy volcano. This volcano consists mainly of trachy-andesite and basalt. The granite basement is exposed in the valleys outside the caldera and locally along the caldera walls.

Fluids from drill-holes and natural springs in the Mont-Dore region (Fig. 1) were sampled from 1974 to 1986. Seventeen springs and drill-holes were sampled along the Dordogne valley from the town of Le Mont-Dore to La Bourboule; 8 of these sites are located in the town of Le Mont-Dore. This valley closely follows the northeastern border fault of the caldera. Eighteen springs emerging S and E of the caldera were also sampled; 8 of these are located in the Chaudesfour River valley. Finally, this study also concerns 17 fluid samples from springs and shallow drill-holes at Saint-Nectaire, which emerge from the granite.

Chemical and isotopic data of samples collected before 1982 were obtained from the Analysis Department of BRGM, and have in part been reported earlier (Fouillac *et al.*, 1975; Baubron *et al.*, 1979; Bosch *et al.*, 1980; Michard *et al.*, 1981; Fouillac, 1983). Sampling and analytical techniques were described by Fouillac (1983). Samples collected in 1986 were analyzed by the Los Alamos National Laboratory (USA), and the analytical techniques are those described by Goff *et al.* (1985). Details of the analytical methods used by both laboratories are summarized in Table 1.

#### BASIC CHEMICAL AND ISOTOPIC DATA

The chemical and isotopic composition of the fluids discharging from natural springs or shallow drill-holes, is reported in Tables 2–5. Composition of the free gases discharged with such water is reported in

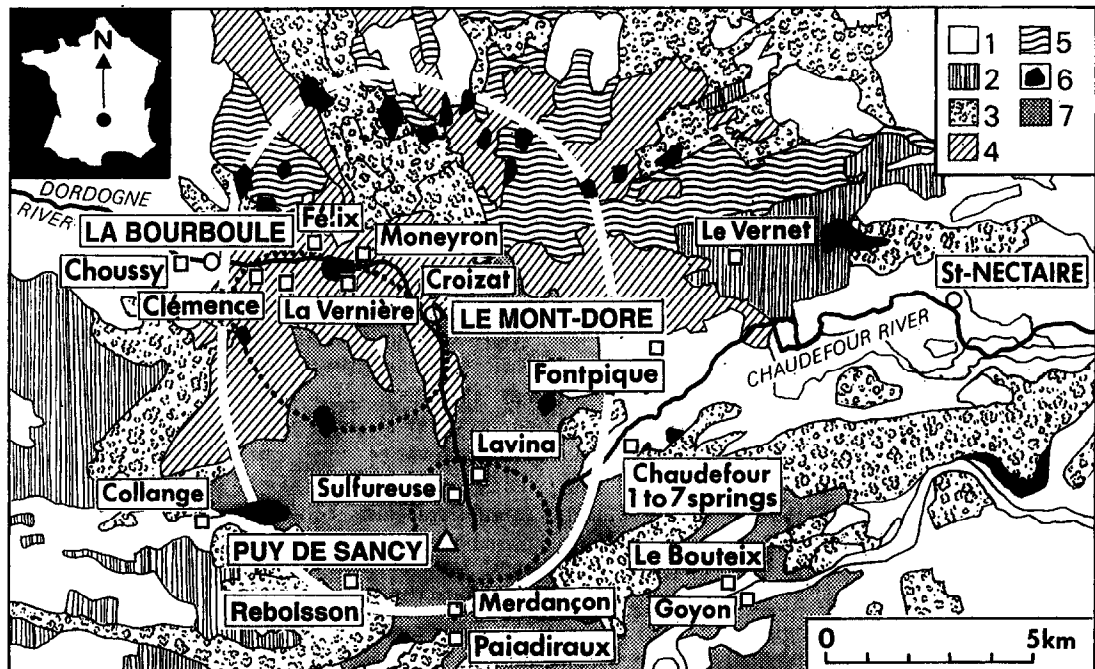


Fig. 1. Map of the study area showing CO<sub>2</sub> rich thermal springs and shallow boreholes. Chronologic map of the Mont-Dore (from Mossand *et al.*, 1982): 1) granite and gneiss basement; 2) ante-caldera basalts (6–3 Ma); 3) undifferentiated Mont-Dore basalt; 4) trachy-andesite, rhyolite, and pumice; 5) hawaiite and tephrite; 6) comendite, quartz trachyte, phonolite; 7) Sancy volcanism: trachy-andesite and pumice. Dotted lines indicate limits of the Haute-Dordogne caldera and outlines of the Sancy 'Structure'. White line indicates the outer limit for differentiated lavas of the central area.

Table 1. Details of analytical methods used by BRGM and Los Alamos Laboratories

|                         | Na, K, Ca, Mg, Li, Sr                    | Cl, SO <sub>4</sub>   | SiO <sub>2</sub>                     | Br                                            | B                                |
|-------------------------|------------------------------------------|-----------------------|--------------------------------------|-----------------------------------------------|----------------------------------|
| Method                  | • Atomic absorption<br>• ICP             | • ion chromatography  | • Atomic absorption                  | • Selective electrode<br>• ion chromatography | • colorimetry                    |
| RSD (%)                 | 5                                        | 5 to 10               | 5                                    | 5 to 15                                       | 5 to 10                          |
| Detection limit (mol/l) | 10 <sup>-7</sup> to 1.5 10 <sup>-5</sup> | 0.5 10 <sup>-5</sup>  | 1.5 10 <sup>-5</sup>                 | 10 <sup>-7</sup>                              | 10 <sup>-7</sup>                 |
|                         | δ <sup>18</sup> O (H <sub>2</sub> O)     | δD (H <sub>2</sub> O) | δ <sup>18</sup> O (SO <sub>4</sub> ) | δ <sup>34</sup> S(SO <sub>4</sub> )           | <sup>87</sup> / <sub>86</sub> Sr |
| Precision               | ± 0.1‰                                   | ± 0.8‰                | ± 0.3‰                               | ± 0.3‰                                        | ± 0.000030                       |

Table 2. Chemical composition of springs and well discharges used in this study: major and minor elements. All concentrations are in mol.l<sup>-1</sup>, except total alkalinity which is in meq.l<sup>-1</sup>

|                                                 | Sampling date | Description | Temp (°C) | Field (pH) | Na (E-3) | K (E-3) | Ca (E-3) | Mg (E-3) | Alc (meq/l) | Cl (E-3) | SO <sub>4</sub> (E-3) | SiO <sub>2</sub> (E-5) | Li (E-5) | Sr (E-7) | Br (E-5) | B (E-5) |
|-------------------------------------------------|---------------|-------------|-----------|------------|----------|---------|----------|----------|-------------|----------|-----------------------|------------------------|----------|----------|----------|---------|
| <b>Dordogne Valley</b>                          |               |             |           |            |          |         |          |          |             |          |                       |                        |          |          |          |         |
| Mont-Dore Chazerat                              | Nov-74        | spring      | 41        | 5.93       | 14.3     | 1.37    | 2.15     | 1.39     | 16.0        | 6.47     | 0.42                  | 300                    | 20.0     | -        | -        | -       |
| Mont-Dore Madeleine                             | Nov-74        | spring      | 43.5      | 5.82       | 14.3     | 1.32    | 2.12     | 1.36     | 15.8        | 6.27     | 0.42                  | 305                    | 19.2     | -        | -        | -       |
| Mont-Dore Chanteurs                             | Nov-74        | spring      | 39.5      | 5.82       | 14.3     | 1.20    | 2.10     | 1.36     | 15.6        | 6.23     | 0.44                  | 307                    | 18.8     | -        | -        | -       |
|                                                 | Oct-79        |             | 44.2      | 6.18       | 14.7     | 1.08    | 2.05     | 1.46     | 15.0        | 5.70     | 0.37                  | 308                    | 17.0     | -        | -        | -       |
|                                                 | May-86        |             | 43.9      | 6.14       | 14.8     | 0.92    | 1.99     | 1.33     | 15.3        | 6.56     | 0.38                  | 271                    | 20.0     | 1.51     | 0.63     | 24.6    |
| Mont-Dore Ramond                                | Nov-74        | spring      | 39.5      | 5.84       | 14.3     | 1.23    | 2.07     | 1.34     | 15.6        | 6.15     | 0.43                  | 305                    | 19.0     | -        | -        | -       |
| Mont-Dore Pantheon                              | Nov-74        | spring      | 39.5      | 5.86       | 14.5     | 1.30    | 2.08     | 1.36     | 15.5        | 6.20     | 0.44                  | 305                    | 19.0     | -        | -        | -       |
| Mont-Dore Rigny                                 | Nov-74        | spring      | 43        | 6.21       | 14.5     | 1.23    | 2.11     | 1.34     | 15.8        | 6.31     | 0.42                  | 305                    | 19.4     | -        | -        | -       |
| Mont-Dore St Jean                               | Nov-74        | spring      | 40        | -          | 14.5     | 1.23    | 2.15     | 1.34     | 15.9        | 6.27     | 0.42                  | 307                    | 19.4     | -        | -        | -       |
|                                                 | Jun-78        |             | 42        | 5.90       | 14.2     | 1.09    | 2.03     | 1.29     | 15.5        | 6.30     | 0.38                  | 292                    | 19.0     | 1.43     | -        | -       |
|                                                 | Oct-79        |             | 40        | 6.18       | 14.7     | 1.08    | 2.05     | 1.46     | 15.0        | 5.70     | 0.37                  | 308                    | 17.0     | -        | -        | -       |
| Mont-Dore Cesar                                 | Nov-74        | spring      | 39        | 5.80       | 13.5     | 1.23    | 1.94     | 1.26     | 14.5        | 5.76     | 0.42                  | 290                    | 17.6     | -        | -        | -       |
| La Bourboule-Choussy                            | Nov-74        | well        | 53        | 6.50       | 74.0     | 2.55    | 0.96     | 0.31     | 27.4        | 49.5     | 1.14                  | 198                    | 66.4     | -        | -        | -       |
|                                                 | Oct-79        |             | 53.2      | 6.48       | 76.2     | 2.42    | 0.87     | 0.37     | 27.3        | 48.5     | 1.33                  | 191                    | 84.0     | -        | -        | -       |
|                                                 | May-86        |             | 54.8      | 6.47       | 73.4     | 2.19    | 0.82     | 0.31     | 26.8        | 48.2     | 1.28                  | 180                    | 96.4     | 3.69     | 4.50     | 107     |
| Clemence                                        | Oct-79        | spring      | 18.5      | 5.87       | 37.2     | 2.03    | 2.09     | 1.31     | 22.1        | 25.6     | 1.00                  | 170                    | 36.0     | -        | -        | -       |
|                                                 | May-86        |             | 18.5      | 5.82       | 37.3     | 2.66    | 2.00     | 1.11     | 17.1        | 24.8     | 1.00                  | 162                    | 43.0     | 2.86     | 2.88     | -       |
| La Vernière                                     | Oct-79        | spring      | 12.5      | 5.64       | 35.7     | 1.71    | 1.26     | 0.98     | 15.3        | 16.2     | 1.08                  | 175                    | 40.0     | -        | -        | -       |
|                                                 | May-86        |             | 11.9      | 6.10       | 35.3     | 2.08    | 1.24     | 0.86     | 22.2        | 17.2     | 1.14                  | 173                    | 47.1     | 1.38     | 1.75     | -       |
| Fenestre                                        | Nov-74        | spring      | 16        | -          | 4.80     | 0.34    | 0.16     | 0.15     | 3.0         | 2.33     | 0.38                  | 130                    | 6.70     | -        | -        | -       |
|                                                 | Oct-79        |             | 16        | 6.36       | 4.80     | 0.31    | 0.15     | 0.18     | 3.1         | 2.64     | 0.25                  | 125                    | 6.30     | -        | -        | -       |
| Felix                                           | Nov-74        | spring      | 30        | 6.02       | 61.5     | 2.32    | 2.84     | 1.93     | 28.2        | 44.8     | 2.00                  | 218                    | 85.0     | -        | -        | -       |
|                                                 | Oct-79        |             | 30.4      | 6.32       | 64.7     | 2.22    | 2.72     | 2.11     | 27.6        | 45.0     | -                     | 206                    | 79.0     | -        | -        | -       |
|                                                 | May-86        |             | 29.5      | 6.15       | 63.5     | 1.95    | 2.67     | 1.85     | 27.7        | 41.9     | 1.83                  | 213                    | 88.9     | 4.60     | 4.00     | 101     |
| Felix 2                                         | May-86        | spring      | 16.2      | 6.27       | 43.9     | 1.51    | 1.93     | 1.26     | 21.2        | 31.0     | 1.19                  | 172                    | 57.8     | 3.12     | 2.63     | 70.6    |
| Gabriel                                         | Nov-74        | spring      | 12        | 5.82       | 61.0     | 2.05    | 2.60     | 1.98     | 28.0        | 42.4     | 1.00                  | 192                    | 72.8     | -        | -        | -       |
| Croizat                                         | Nov-74        | well        | 37.3      | 6.81       | 112      | 3.77    | 3.78     | 1.10     | 34.2        | 87.5     | 2.66                  | 182                    | 192      | -        | -        | -       |
|                                                 | Oct-79        |             | 39        | 6.52       | 114      | 3.75    | 3.67     | 1.32     | 33.7        | 85.5     | 2.25                  | 173                    | 180      | -        | -        | -       |
|                                                 | Jun-78        |             | -         | 6.49       | 115      | 3.65    | 3.77     | 1.30     | 34.3        | 85.3     | 2.83                  | 167                    | 192      | -        | -        | -       |
|                                                 | May-86        |             | 39.1      | 6.56       | 108      | 3.54    | 3.57     | 1.14     | 34.2        | 84.8     | 2.76                  | 168                    | 198      | 9.38     | 7.38     | 183     |
| Moneyron                                        | Oct-79        | spring      | 15.5      | 5.86       | 66.9     | 1.75    | 2.39     | 1.25     | 14.8        | 58.0     | 0.92                  | 147                    | 89.0     | -        | -        | -       |
|                                                 | May-86        |             | 14.9      | 5.87       | 65.2     | 1.50    | 2.40     | 1.15     | 14.0        | 57.7     | 0.97                  | 135                    | 102.9    | 5.93     | 5.38     | 106     |
| <b>South and east of Haute-Dordogne caldera</b> |               |             |           |            |          |         |          |          |             |          |                       |                        |          |          |          |         |
| <b>Chaudefour Valley</b>                        |               |             |           |            |          |         |          |          |             |          |                       |                        |          |          |          |         |
| Chaudefour 1                                    | Oct-79        | spring      | 10.2      | 5.02       | 0.65     | 0.21    | 0.52     | 0.21     | 2.52        | 0.10     | 0.10                  | 170                    | 0.2      | 0.21     | -        | -       |
|                                                 | May-86        |             | 11        | 5.12       | 0.65     | 0.20    | 0.53     | 0.19     | 2.31        | 0.05     | 0.11                  | 150                    | -        | 0.24     | -        | -       |
| Chaudefour 2                                    | Nov-74        | spring      | 11.3      | 4.65       | 0.68     | 0.23    | 0.55     | 0.17     | 2.25        | -        | -                     | 155                    | -        | -        | 0.01     | 0.01    |
|                                                 | Oct-79        |             | 11.5      | 5.08       | 0.68     | 0.20    | 0.52     | 0.20     | 2.62        | 0.10     | 0.10                  | 160                    | 0.3      | -        | -        | -       |
|                                                 | May-86        |             | 11        | 5.04       | 0.67     | 0.20    | 0.53     | 0.20     | 2.42        | 0.05     | 0.11                  | 150                    | -        | -        | -        | -       |
| Chaudefour 3                                    | Oct-79        | spring      | 22.7      | 5.74       | 12.4     | 0.91    | 4.13     | 1.67     | 18.4        | 0.30     | 2.81                  | 203                    | 5.5      | 4.66     | 0.07     | -       |
|                                                 | May-86        |             | 22.3      | 6.00       | 12.6     | 0.92    | 4.17     | 1.50     | 19.3        | 0.28     | 2.74                  | 235                    | 5.9      | 4.66     | -        | 1.5     |
| Chaudefour 4                                    | Oct-79        | spring      | 23.5      | 5.62       | 10.4     | 0.80    | 3.55     | 1.44     | 16.1        | 0.30     | 2.29                  | 197                    | 4.9      | 4.02     | 0.05     | -       |
|                                                 | May-86        |             | 23.2      | 5.83       | 11.1     | 0.66    | 3.57     | 1.30     | 16.7        | 0.24     | 2.32                  | 222                    | 4.9      | 4.09     | -        | 1       |
| Chaudefour 5                                    | Nov-74        | spring      | 15.6      | 5.25       | 5.67     | 0.63    | 2.56     | 1.25     | 11.3        | -        | 1.02                  | 173                    | 2.7      | -        | -        | -       |
|                                                 | Oct-79        |             | 16        | 5.36       | 5.40     | 0.61    | 2.49     | 1.32     | 11.6        | 0.24     | 1.12                  | 182                    | 2.3      | 2.01     | 0.04     | -       |
|                                                 | May-86        |             | 15.3      | 5.56       | 5.80     | 0.66    | 2.55     | 1.15     | 12.0        | 0.18     | 1.21                  | 190                    | 2.1      | 2.03     | -        | 0.6     |
| Chaudefour 6b                                   | May-86        | spring      | 16.5      | 6.79       | 10.6     | 0.69    | 2.85     | 1.10     | -           | 0.26     | 2.00                  | 137                    | 4.5      | -        | -        | -       |
| Chaudefour 6                                    | Sep-82        | spring      | 7.6       | 5.20       | 0.39     | 0.10    | 0.44     | 0.24     | 1.51        | 0.52     | 0.44                  | 100                    | -        | 0.18     | -        | -       |
| Chaudefour 7                                    | Sep-82        | spring      | 9         | 5.01       | 0.63     | 0.22    | 0.68     | 0.41     | 3.14        | 0.72     | 0.32                  | 150                    | 0.3      | 0.25     | -        | -       |

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Table 2. *Continued*

|                   | Sampling date | Description | Temp (°C) | Field (pH) | Na (E-3) | K (E-3) | Ca (E-3) | Mg (E-3) | Alc (meq/l) | Cl (E-3) | SO <sub>4</sub> (E-3) | SiO <sub>2</sub> (E-5) | Li (E-5) | Sr (E-7) | Br (E-5) | B (E-5) |
|-------------------|---------------|-------------|-----------|------------|----------|---------|----------|----------|-------------|----------|-----------------------|------------------------|----------|----------|----------|---------|
| Sulfureuse        | Oct-79        | spring      | 4         | <4         | 0.86     | 0.14    | 0.79     | 0.52     | -           | 0.84     | 2.39                  | -                      | 1.0      | -        | -        | -       |
|                   | May-86        | spring      | 6.3       | 6.12       | 0.39     | 0.11    | 0.24     | 0.22     | -           | 0.042    | 0.68                  | 47.7                   | -        | 0.03     | -        | -       |
| Lavina Edembouche | Oct-79        | spring      | 4.2       | 3.39       | 0.19     | 0.09    | 0.45     | 0.29     | -           | 0.037    | 2.32                  | 58                     | -        | 0.13     | -        | -       |
| Goyon             | Oct-79        | spring      | 7         | 5.80       | 0.60     | 0.21    | 2.00     | 1.82     | 8.46        | 0.10     | 0.03                  | 110                    | 0.7      | 0.32     | -        | -       |
| Paiadiroux        | Oct-79        | spring      | 8.5       | 5.38       | 0.67     | 0.24    | 1.25     | 1.47     | 7.06        | 0.096    | -                     | 160                    | 0.3      | 0.22     | -        | -       |
| Merdançon         | Oct-79        | spring      | 7.5       | 5.28       | 0.96     | 0.32    | 1.21     | 0.93     | 5.43        | 0.081    | -                     | 127                    | 0.6      | 0.33     | -        | -       |
| Fontpique         | Oct-79        | spring      | 10.5      | 6.16       | 5.86     | 1.28    | 2.87     | 3.39     | 1.92        | 0.203    | 0.1                   | 170                    | 11.8     | 0.73     | 6.1      | -       |
| Le Vernet         | Oct-79        | spring      | 10        | 5.30       | 0.96     | 0.21    | 0.70     | 0.93     | 3.82        | 0.068    | 0.07                  | 127                    | 0.3      | -        | -        | -       |
| Le Bouteix        | Oct-79        | spring      | 8.5       | 5.86       | 0.51     | 0.11    | 0.78     | 0.84     | 3.70        | 0.56     | 0.28                  | 170                    | 0.3      | 0.33     | -        | -       |
| Collange          | Oct-79        | spring      | 12.2      | 7.20       | 7.91     | 1.13    | 2.53     | 4.23     | 24.3        | 0.21     | -                     | 167                    | 18.0     | 1.02     | 0.24     | -       |
| Reboisson         | Oct-79        | spring      | 11        | 5.62       | 7.96     | 1.12    | 1.03     | 1.73     | 16.5        | 0.41     | 0.05                  | 137                    | 13.0     | -        | -        | -       |
| Saint-Nectaire    |               |             |           |            |          |         |          |          |             |          |                       |                        |          |          |          |         |
| Drillhole #1      | May-86        | well        | 58.1      | 6.84       | 85.6     | 5.43    | 4.05     | 3.37     | 57.2        | 51.9     | 1.22                  | 225                    | 220      | 6.91     | 5.63     | 180     |
| Drillhole #2      | May-86        | well        | 62        | 6.91       | 84.3     | 5.43    | 3.50     | 3.30     | 55.9        | 47.0     | 1.18                  | 222                    | 215      | 5.90     | 5.38     | 184     |
| Drillhole #3      | May-86        | well        | 37.8      | 6.55       | 79.1     | 4.74    | 4.62     | 3.61     | 58.3        | 42.8     | 0.98                  | 182                    | 197      | 5.64     | 4.88     | 169     |
| Drillhole #B1     | Nov-81        | well        | 37        | 6.68       | 83.9     | 5.51    | 3.88     | 3.69     | 56.0        | 47.6     | 1.33                  | 218                    | 199      | 6.40     | -        | -       |
| Drillhole #A2     | Nov-81        | well        | 55        | 6.80       | 85.6     | 5.49    | 3.88     | 3.69     | 56.6        | 47.6     | 1.29                  | 228                    | 199      | 6.20     | -        | -       |
| Papon             | Nov-81        | spring      | 32        | 6.95       | 85.6     | 5.69    | 3.94     | 3.77     | 56.2        | 47.6     | 1.29                  | 221                    | 202      | -        | -        | -       |
| Pont              | Nov-81        | spring      | 15        | 6.28       | 77.4     | 5.13    | 4.38     | 4.04     | 56.5        | 47.6     | 1.21                  | 201                    | 196      | 6.70     | -        | -       |
| Parc              | Nov-81        | spring      | 20        | 6.37       | 80.0     | 5.44    | 4.11     | 3.70     | 55.6        | 50.7     | 1.33                  | 223                    | 197      | 6.70     | -        | -       |
| Boette            | Nov-74        | spring      | 34        | 6.52       | 82.0     | 5.50    | 4.74     | 4.07     | 56.2        | 47.3     | 0.94                  | 217                    | 198      | -        | -        | -       |
|                   | Sep-77        |             | 35        | 6.56       | 80.9     | 5.31    | 4.50     | 3.83     | 60.0        | 48.2     | 1.21                  | 210                    | 194      | 6.50     | -        | -       |
| Gros Bouillon     | Nov-74        | spring      | 36        | 6.11       | 76.0     | 5.05    | 4.71     | 3.99     | 55.8        | 41.8     | 0.88                  | 240                    | 177      | -        | -        | -       |
|                   | Sep-77        |             | 36        | 6.52       | 71.3     | 4.85    | 4.62     | 3.75     | -           | 44.0     | 1.02                  | 192                    | 169      | 6.05     | -        | -       |
| Bleue             | Nov-74        | spring      | 29.5      | 6.43       | 66.0     | 4.25    | 4.13     | 3.52     | 49.9        | 35.3     | 0.75                  | 220                    | 158      | -        | -        | -       |
| Mont Cornadore    | Nov-74        | spring      | 38.2      | 6.20       | 66.0     | 4.27    | 4.13     | 3.51     | 50.1        | 35.3     | 0.85                  | 232                    | 159      | -        | -        | -       |
|                   | Sep-77        |             | 38        | 6.54       | 63.1     | 3.90    | 4.08     | 3.33     | -           | 36.6     | 0.92                  | 183                    | 148      | 5.00     | -        | -       |
|                   | Jun-78        |             | 38        | 6.49       | 66.9     | 4.05    | 4.07     | 3.12     | 47.0        | 39.1     | 0.91                  | 180                    | 157      | 3.20     | -        | -       |
|                   | Nov-81        |             | 38        | 6.55       | 60.9     | 4.18    | 3.96     | 3.25     | 46.9        | 35.1     | 1.02                  | 188                    | 156      | 4.80     | -        | -       |
| Mandon            | Nov-74        | spring      | 28        | 6.10       | 59.0     | 4.07    | 3.43     | 2.99     | 43.9        | 31.1     | 0.60                  | 208                    | 143      | -        | -        | -       |
| Giraudon          | Nov-74        | spring      | 40        | 6.37       | 84.2     | 5.70    | 4.12     | 3.91     | 58.1        | 48.3     | 1.18                  | 252                    | 204      | -        | -        | -       |
|                   | Sep-77        |             | 40        | 6.58       | 84.8     | 5.54    | 4.11     | 3.87     | -           | 49.2     | 1.21                  | 237                    | 200      | 8.30     | -        | -       |
|                   | Nov-81        |             | 36        | 6.47       | 81.3     | 5.56    | 3.99     | 3.80     | 57.3        | 50.1     | 1.33                  | 221                    | 203      | 6.30     | -        | -       |
| Garçons           | Nov-81        | spring      | 33        | 6.47       | 58.7     | 3.95    | 3.83     | 3.14     | 44.8        | 35.1     | 0.94                  | 183                    | 147      | 4.60     | -        | -       |
| Simon             | Nov-81        | spring      | 27        | 6.38       | 58.7     | 3.92    | 4.31     | 3.07     | 45.4        | 35.1     | 0.92                  | 175                    | 146      | 5.90     | -        | -       |
| Desgranges        | Sep-77        | spring      | 9.5       | 6.96       | 0.48     | 0.20    | 0.34     | 0.30     | -           | 0.22     | 0.04                  | 62.9                   | -        | -        | -        | -       |

Table 4. The total dissolved solids content of these fluids varies from about 200 mg/l, for the less mineralized ones, to almost 8000 mg/l. The chemical composition of the fluids can be shown diagrammatically in terms of the major anions  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  (Fig. 2). The fluids can be classified into 3 groups: bicarbonate waters, mixed bicarbonate-chloride waters, and sulfate waters, but only 2 fluids belong to the last group, i.e., the Sulfureuse and Edembouche-Lavina springs, which are characterized by pH values below 4 and thus are called acid-sulfate waters. The more mineralized fluids from Saint-Nectaire and the Dordogne valley belong to the mixed bicarbonate-chloride waters group. Dilute fluids from the Chaudefour valley and other locations are bicarbonate waters. The composition of some fluids, such as those from Fontpique, Le Bouteix and Chaudefour 6 and 7, is intermediate between those of bicarbonate and mixed bicarbonate-chloride waters. All the fluids with a high  $\text{HCO}_3^-$  concentration have similar physico-chemical features, i.e. Na is always the major cation and free, almost pure,  $\text{CO}_2$  gas is present. Giggenbach (1991) proposed to classify waters along the  $\text{Cl}^-$ - $\text{HCO}_3^-$  axis into 2 groups, i.e. the mature

waters (with a relatively high  $\text{Cl}^-$  content) and the peripheral waters. Croizat and Moneynon fluids from the Dordogne Valley are the only fluids belonging to the mature-waters group. Anion composition of the La Bourboule-Choussy fluid is close to that of the mature group (Fig. 2).

The  $^3\text{He}/^4\text{He}$  ratios were determined by Matthews *et al.* (1987); the corresponding R/Ra, where R and Ra are respectively the sample and atmospheric  $^3\text{He}/^4\text{He}$  ratios, range from 0.3 at Saint-Nectaire to 5.5 in the Chaudefour valley. In the fluids from the well of Choussy, the maximum R/Ra is 2.8. The authors concluded that there was a significant component of mantle helium in the gas phase. They also demonstrated from  $^{13}\text{C}$  values that range from  $-4.2$  to  $-6.1\text{‰}$  and  $\text{C}/^3\text{He}$  ratios ( $5 \times 10^8$  to  $1.4 \times 10^{12}$ ), that part of the  $\text{CO}_2$  in the fluids of the Massif Central is mantle-derived and that mantle-derived gas components are removed from their deep sources at great depths. Calculations performed by the same authors suggest that a  $\text{CO}_2$ -rich gas phase and  $\text{HCO}_3^-$ -dominated water are separated at a substantial depth, probably several kilometers. The bicarbonate waters are acidic, but their pH is always above 5. The

Table 3. Isotope composition of springs and well discharges in this study

|                                          | Sampling date | D(H <sub>2</sub> O) (‰) | O <sup>18</sup> (H <sub>2</sub> O) (‰) | <sup>34</sup> S(SO <sub>4</sub> ) (‰) | O <sup>18</sup> (SO <sub>4</sub> ) (‰) | Tritium U.T. | <sup>87</sup> Sr/ <sup>86</sup> Sr |
|------------------------------------------|---------------|-------------------------|----------------------------------------|---------------------------------------|----------------------------------------|--------------|------------------------------------|
| Dordogne Valley                          |               |                         |                                        |                                       |                                        |              |                                    |
| Mont-Dore Chazerat                       | Nov-74        | -61.1                   | -9.60                                  | —                                     | —                                      | —            | —                                  |
| Mont-Dore Madeleine                      | Nov-74        | -60.8                   | -9.60                                  | —                                     | —                                      | —            | —                                  |
| Mont-Dore Chanteurs                      | Nov-74        | -61.0                   | -9.80                                  | —                                     | —                                      | —            | —                                  |
|                                          | Oct-79        | -62.4                   | -9.20                                  | 15.6                                  | 8.1                                    | 13           | —                                  |
|                                          | May-86        | -62.2                   | -9.35                                  | —                                     | —                                      | —            | 0.70652                            |
|                                          | Nov-74        | -61.0                   | -9.40                                  | —                                     | —                                      | —            | —                                  |
| Mont-Dore Ramond                         | Nov-74        | -61.2                   | -9.70                                  | —                                     | —                                      | —            | —                                  |
| Mont-Dore Pantheon                       | Nov-74        | -61.0                   | -10.10                                 | —                                     | —                                      | —            | —                                  |
| Mont-Dore Rigny                          | Nov-74        | -60.6                   | -9.40                                  | —                                     | —                                      | —            | —                                  |
| Mont-Dore St Jean                        | Jun-78        | -61.3                   | -9.40                                  | —                                     | —                                      | —            | —                                  |
|                                          | Oct-79        | -62.3                   | -9.50                                  | 16.3                                  | —                                      | 8            | —                                  |
|                                          | Nov-74        | -60.9                   | -10.00                                 | —                                     | —                                      | —            | —                                  |
|                                          | Nov-74        | -60.2                   | -9.00                                  | —                                     | —                                      | —            | —                                  |
| Mont-Dore Cesar                          | Oct-79        | -61.2                   | -9.00                                  | 12.7                                  | —                                      | <1           | —                                  |
| La Bourboule-Choussy                     | May-86        | -61.5                   | -9.09                                  | —                                     | 4.3                                    | —            | 0.710639                           |
|                                          | Oct-79        | -60.4                   | -9.10                                  | 8                                     | —                                      | 3            | —                                  |
|                                          | May-86        | -59.9                   | -9.06                                  | —                                     | 1.1                                    | —            | 0.707106                           |
|                                          | Oct-79        | -61.7                   | -9.00                                  | 9.3                                   | —                                      | <1           | —                                  |
| La Vernière                              | May-86        | -63.0                   | -9.28                                  | —                                     | 1.1                                    | —            | —                                  |
|                                          | Nov-74        | -57.2                   | -9.10                                  | —                                     | —                                      | —            | —                                  |
| Fenestre                                 | Oct-79        | -58.3                   | -8.60                                  | 4.7                                   | —                                      | 33           | —                                  |
|                                          | Nov-74        | -61.7                   | -10.00                                 | —                                     | —                                      | —            | —                                  |
| Felix                                    | Oct-79        | -63.2                   | -9.40                                  | 7.7                                   | 2.3                                    | 3            | —                                  |
|                                          | May-86        | -64.9                   | -9.34                                  | —                                     | —                                      | —            | 0.707003                           |
|                                          | May-86        | -62.1                   | -9.12                                  | —                                     | —                                      | —            | —                                  |
|                                          | Nov-74        | -61.2                   | -9.50                                  | —                                     | —                                      | —            | —                                  |
| Gabriel                                  | Nov-74        | -60.8                   | -9.40                                  | —                                     | —                                      | —            | —                                  |
| Croizat                                  | Jun-78        | -61.4                   | -9.05                                  | —                                     | —                                      | —            | —                                  |
|                                          | Oct-79        | -61.8                   | -8.90                                  | 11.7                                  | 3                                      | 6            | —                                  |
|                                          | May-86        | -62.7                   | -8.99                                  | —                                     | —                                      | —            | 0.707826                           |
|                                          | Oct-79        | -61.1                   | -8.90                                  | 10                                    | 3.3                                    | 2            | —                                  |
| Moneyron                                 | May-86        | -62.4                   | -8.89                                  | —                                     | —                                      | —            | 0.708243                           |
| South and east of Haute-Dordogne caldera |               |                         |                                        |                                       |                                        |              |                                    |
| Chaudefour Valley                        |               |                         |                                        |                                       |                                        |              |                                    |
| Chaudefour 1                             | Oct-79        | -61.0                   | -9.50                                  | 6.2                                   | —                                      | 50           | —                                  |
|                                          | May-86        | -61.9                   | -9.65                                  | —                                     | —                                      | 33           | —                                  |
| Chaudefour 2                             | Nov-74        | -60.3                   | -9.70                                  | —                                     | —                                      | —            | —                                  |
|                                          | Oct-79        | -61.6                   | -9.20                                  | 7.8                                   | —                                      | 48           | —                                  |
| Chaudefour 3                             | Oct-79        | -61.1                   | -9.80                                  | 14.4                                  | —                                      | 6            | —                                  |
|                                          | May-86        | -65.9                   | -10.04                                 | —                                     | 7.7                                    | 0.29         | 0.704912                           |
| Chaudefour 4                             | Oct-79        | -61.1                   | -9.70                                  | 14.8                                  | —                                      | 3            | —                                  |
| Chaudefour 5                             | Nov-74        | -60.1                   | -10.20                                 | —                                     | —                                      | —            | —                                  |
|                                          | Oct-79        | -61.1                   | -9.70                                  | 19.6                                  | —                                      | 6            | —                                  |
|                                          | May-86        | -65.1                   | -9.50                                  | —                                     | 7.8                                    | —            | 0.704822                           |
| Chaudefour 6b                            | May-86        | —                       | —                                      | —                                     | 11.4                                   | —            | —                                  |
| Sulfureuse                               | Oct-79        | -61.2                   | -9.40                                  | 13.2                                  | —                                      | 21           | —                                  |
|                                          | May-86        | -60.9                   | -9.01                                  | 10.8                                  | 13.6                                   | 1.63         | 0.704408                           |
| Lavina Edembouche                        | Oct-79        | -59.5                   | -8.80                                  | —                                     | -2.8                                   | —            | 0.704419                           |
| Goyon                                    | Oct-79        | -59.5                   | -9.50                                  | 7.2                                   | —                                      | 19           | —                                  |
| Païadiroux                               | Oct-79        | -59.5                   | -9.30                                  | 4.5                                   | —                                      | 8            | —                                  |
| Merdançon                                | Oct-79        | -58.8                   | -9.30                                  | 8.9                                   | —                                      | 23           | —                                  |
| Fontpique                                | Oct-79        | -61.6                   | -9.80                                  | 14.8                                  | —                                      | 4            | —                                  |
| Le Vernet                                | Oct-79        | -59.9                   | -9.10                                  | —                                     | —                                      | <1           | —                                  |
| Le Bouteix                               | Oct-79        | -61.0                   | -9.20                                  | 3.2                                   | —                                      | 6            | —                                  |
| Collange                                 | Oct-79        | -59.2                   | -9.30                                  | —                                     | —                                      | 4            | —                                  |
| Reboisson                                | Oct-79        | -62.0                   | -9.80                                  | 15                                    | —                                      | 13           | —                                  |
| Saint-Nectaire                           |               |                         |                                        |                                       |                                        |              |                                    |
| Drillhole #1                             | Apr-84        | -60.3                   | -8.50                                  | —                                     | —                                      | —            | —                                  |
|                                          | May-86        | -60.3                   | -8.44                                  | 16.1                                  | 3.6                                    | 0.04         | —                                  |
| Drillhole #2                             | May-86        | -61.2                   | -8.43                                  | 16.1                                  | 3.3                                    | —            | 0.714062                           |
| Drillhole #3                             | May-86        | -63.0                   | -8.37                                  | 18                                    | 5.2                                    | 0.11         | 0.714226                           |
| Drillhole #B1                            | Nov-81        | -61.2                   | -8.80                                  | 13.7                                  | —                                      | —            | —                                  |
| Drillhole #A2                            | Nov-81        | -61.2                   | -8.90                                  | 13.7                                  | —                                      | —            | —                                  |
| Papon                                    | Nov-81        | -59.0                   | -9.00                                  | —                                     | —                                      | —            | —                                  |
| Parc                                     | Nov-81        | -60.2                   | -8.80                                  | —                                     | —                                      | —            | —                                  |

Continued overleaf

Table 3. (Continued)

|                | Sampling date | D(H <sub>2</sub> O) (‰) | O <sup>18</sup> (H <sub>2</sub> O) (‰) | <sup>34</sup> S(SO <sub>4</sub> ) (‰) | O <sup>18</sup> (SO <sub>4</sub> ) (‰) | Tritium U.T. | <sup>87</sup> Sr/ <sup>86</sup> Sr |
|----------------|---------------|-------------------------|----------------------------------------|---------------------------------------|----------------------------------------|--------------|------------------------------------|
| Boette         | Nov-74        | -59.2                   | -9.80                                  | —                                     | —                                      | —            | —                                  |
|                | Sep-77        | -60.3                   | -9.00                                  | 16                                    | —                                      | <1           | —                                  |
| Gros Bouillon  | Nov-74        | -59.7                   | -8.80                                  | —                                     | —                                      | —            | —                                  |
|                | Sep-77        | -60.2                   | -8.90                                  | 17                                    | —                                      | <1           | —                                  |
| Bleue          | Nov-74        | -59.6                   | -8.90                                  | —                                     | —                                      | —            | —                                  |
| Mont Cornadore | Nov-74        | -58.7                   | -8.80                                  | —                                     | —                                      | —            | —                                  |
|                | Sep-77        | -59.3                   | -8.80                                  | 15.3                                  | —                                      | <1           | —                                  |
|                | Jun-78        | -59.0                   | -8.85                                  | —                                     | —                                      | —            | —                                  |
|                | Nov-81        | -59.3                   | -8.80                                  | 15.3                                  | 6.4                                    | —            | —                                  |
| Mandon         | Nov-74        | -58.0                   | -9.00                                  | —                                     | —                                      | —            | —                                  |
| Giraudon       | Nov-74        | -59.7                   | -9.20                                  | —                                     | —                                      | —            | —                                  |
|                | Sep-77        | -60.2                   | -8.80                                  | 15.6                                  | —                                      | 5            | —                                  |
|                | Nov-81        | -59.9                   | -8.90                                  | —                                     | —                                      | —            | —                                  |
| Garçons        | Nov-81        | -58.6                   | -8.40                                  | 13.5                                  | —                                      | —            | —                                  |
| Simon          | Nov-81        | -59.5                   | -8.60                                  | —                                     | —                                      | <1           | —                                  |
| Desgranges     | Sep-77        | -61.9                   | -9.00                                  | 6.4                                   | —                                      | 73           | —                                  |

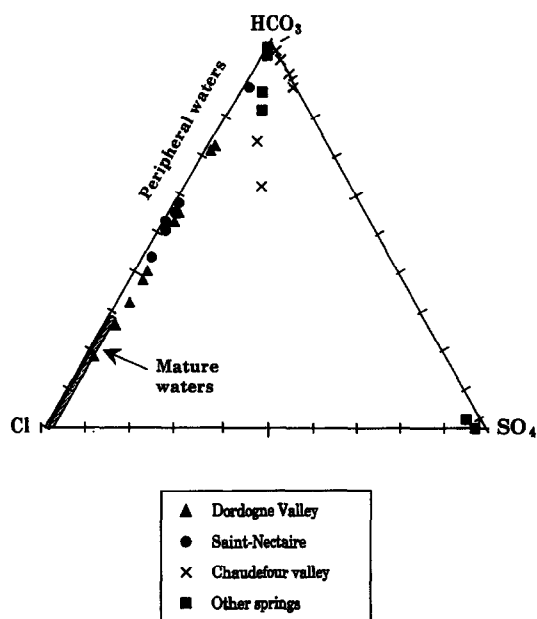


Fig. 2. Plot of the relative molecular proportions of  $\text{Cl}^-$ ,  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$  for the spring and well discharges discussed in this paper. The designations 'mature' and 'peripheral' waters are from Giggenbach (1991).

Table 4. Chemical composition of gases from the area studied

|                              | CO <sub>2</sub> (%) | N <sub>2</sub> (%) | Ar (ppm) | He (ppm) |
|------------------------------|---------------------|--------------------|----------|----------|
| Saint-Nectaire Gros Bouillon | 94.6                | 4.7                | 0.15     | -        |
| Giraudon                     | 98.8                | 0.8                | 70       | -        |
| Boette                       | 99.6                | 0.2                | ≤50      | -        |
| Desgranges                   | -                   | -                  | 11,000   | -        |
| Cornadore                    | 99.5                | 0.2                | ≤50      | -        |
| Chaudesfour                  | 99.3                | -                  | -        | 5.9      |

pH of the mixed bicarbonate-chloride waters ranges from 5.8 to 7.

Fluids from some (20 of the 52) of these locations have been collected up to 4 times between 1974 and 1986. The chemical composition of fluids from all sampling points, except the Sulfureuse spring, has remained relatively constant. Variation in chloride concentrations of the less saline chloride-bicarbonate waters did not exceed 8% and was less than 3% for the more saline waters. However, variations with time of the stable isotope composition, i.e. in  $\delta\text{D}$  and  $\delta^{18}\text{O}$ , of these waters was observed.

#### PROBABLE MIXING TRENDS

The different fluids from the Saint-Nectaire area and the Dordogne and Chaudesfour valleys, display large variations in their total dissolved solid contents. Therefore, the chemical composition in each of these 3 areas could partly be related to dilution of a mineralized fluid by freshwater. Such a process would explain at least the behavior of 'conservative' components such as Cl and Br. The presence of tritium of thermonuclear origin in most of the samples (Table 3) suggests that during their rise to the surface, the mineralized fluids were diluted by freshwater that had been recently recharged. Generally, the tritium content of these fluids decreases as the salinity increases. The tritium content of the more dilute fluids in springs S and E of the Haute-Dordogne caldera is high, indicating that these samples contain a large proportion of recent freshwater. Nevertheless, no linear correlation was found between tritium content and  $\text{Cl}^-$  concentration, as is illustrated in Fig. 3 for the Chaudesfour and Dordogne valley fluids. The chemical composition of the fluids from each area investigated, thus cannot result from a simple mixing process between 2 endmembers only, i.e. an old mineralized

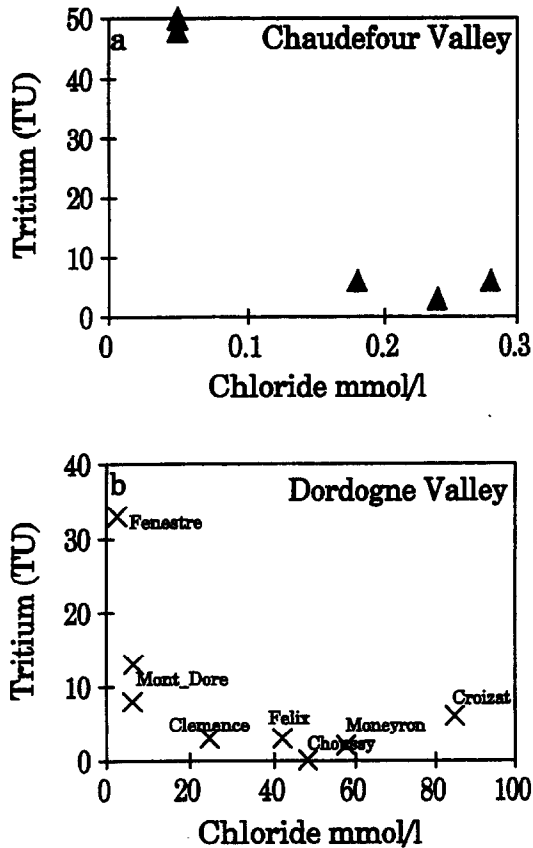


Fig. 3. Plot of tritium content vs. chloride; (a) Chaudefour valley; (b) Dordogne valley.

component and recent freshwater, but several end-members (dilute or mineralized) must be involved in the mixing process. It is also inferred that each of these areas had its own chemical signature of the fluids at depth, prior to dilution with recent freshwater. For example, despite its relatively high  $\text{Cl}^-$  concentration, the tritium content of the Croizat well sample is higher than that of the La Bourboule-Choussy well sample, which may suggest that these 2 fluids are derived from 2 deep fluids with a different composition.

#### ORIGIN OF THE WATER

Deuterium and  $^{18}\text{O}$  isotope contents of water are indicators of the origin of a fluid, and in some cases of

the degree of water-rock interaction, and of boiling and mixing processes. All available  $^{18}\text{O}$  and D data from the studied area plot close to the local meteoric water line, or LMWL (Fig. 4), whose equation (Fouillac *et al.*, 1991) is:

$$\delta D = 8 \delta^{18}\text{O} + 13.1$$

This indicates that all the thermal waters are of a local meteoric origin. Some waters collected in Mont-Dore town and from springs emerging S and E of the caldera plot on the left of the LMWL, which can be explained by isotope exchange between  $\text{H}_2\text{O}$  and  $\text{CO}_2$  (Fouillac *et al.*, 1991). The same explanation has been proposed for other  $\text{CO}_2$ -rich aquifer systems (Fritz and Frape, 1982; Vuataz and Goff, 1986). In addition, Matthews *et al.* (1987) studied fluids of a similar chemical and isotopic composition from the southern Massif Central. They concluded from the  $^{18}\text{O}$  composition of  $\text{CO}_2$  gas and  $\text{H}_2\text{O}$ , and from the  $^{13}\text{C}/^{12}\text{C}$  fractionation between  $\text{CO}_2$  and  $\text{HCO}_3^-$ , that a low-temperature equilibration of  $^{18}\text{O}$  between  $\text{CO}_2$  and  $\text{H}_2\text{O}$  took place. Their results support the idea of isotope exchange between  $\text{H}_2\text{O}$  and  $\text{CO}_2$  in the mineralized fluids of the area investigated.

Only the fluids from the Saint-Nectaire area plot significantly (about 1‰) to the right of the LMWL (Fig. 5a). These fluids may have undergone some isotope exchange with silicate rocks (Craig, 1963); specifically, the mineralized end-member of the Saint-Nectaire fluids may have undergone such a process and, could have been diluted by groundwater whose isotopic composition lies on the LMWL, during flow towards the surface. However, according to the  $\delta D$  vs. Cl diagram (Fig. 5b), it appears that a two-step mixing process may be involved. Fluids sampled from the drill-holes plot on a line that could result from mixing between a mineralized endmember and a fluid with lower  $\delta D$  and  $\text{Cl}^-$  contents. The tritium content of the fluid from drill-hole #3, the least mineralized of the drill-hole fluids, is higher than that of the fluid from drill-hole #1, which is the most mineralized. Therefore, the less mineralized endmember involved in the mixing should be the younger one, and its  $\delta D$  can be very negative if its  $\text{Cl}^-$  content is relatively low. From this observation, it seems a reasonable assumption that the deep (oldest) fluid must be the more mineralized endmember. According to the same  $\delta D$  vs. Cl diagram, the first mixing must be followed by

Table 5. Strontium isotope ratios measured in rock samples

| Sample | Description                              | Rb (ppm) | Sr (ppm) | $^{87}\text{Sr}/^{86}\text{Sr}$ |
|--------|------------------------------------------|----------|----------|---------------------------------|
| F86-25 | Two-mica granodiorite (Saint-Nectaire)   | 205      | 300      | 0.722282                        |
| F86-29 | Muscovite granite (Choussy)              | 280      | 160      | 0.733804                        |
| F86-31 | Crystal. xenolith, Intracaldera          | 195      | 50       | 0.706572                        |
|        | Rhyolitic ignimbrite (la Bourboule)      |          |          |                                 |
| F86-33 | Biotite-bearing basanite (Mont-Dore)     | 45       | 715      | 0.703844                        |
| F86-36 | Hornblende trachyandesite (Puy de Sancy) | 86       | 900      | 0.704215                        |
| F86-37 | Biotite phonolite, pre-Caldera (Croizat) | 185      | 490      | 0.703980                        |

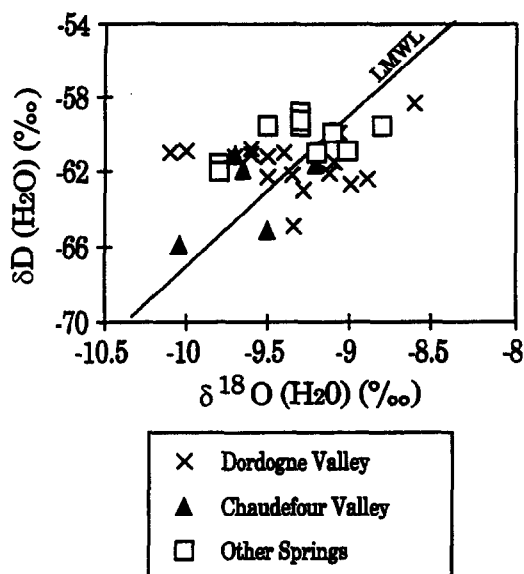


Fig. 4. Plot of  $\delta D(H_2O)$  vs.  $\delta^{18}O(H_2O)$  for some fluids discussed in this paper. LMWL: local meteoric water line.

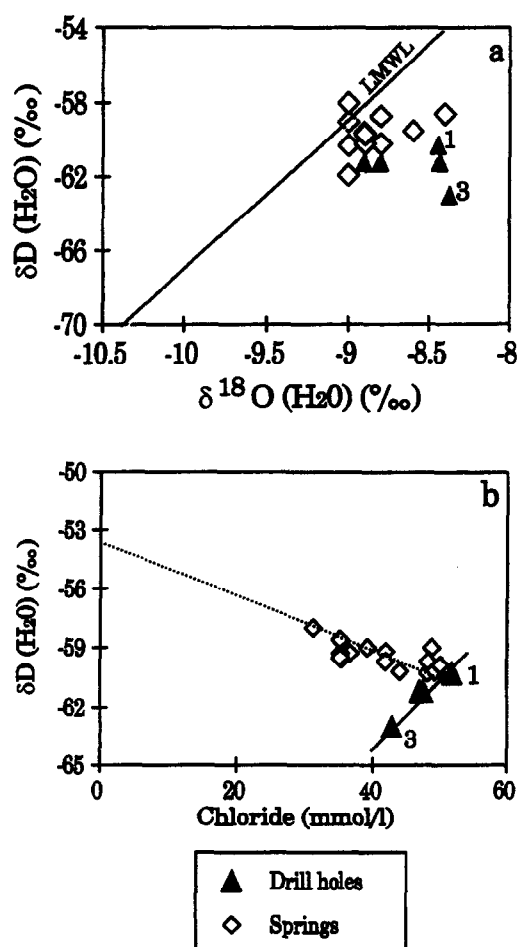


Fig. 5. Isotopic composition of the Saint-Nectaire fluids. (a) Plot of  $\delta D(H_2O)$  vs.  $\delta^{18}O(H_2O)$  (b) Plot of  $\delta D(H_2O)$  values vs. chloride concentrations. LMWL: local meteoric water line.

rather strong dilution with groundwater, which results in the composition of the spring waters. It appears that the deuterium isotope ratio of this dilute endmember is close to  $-54\%$ . On the other hand, the  $\delta D$  value for the very dilute Desgranges spring water is around  $-62\%$ . The freshwater feeding the Desgranges spring is thus different from that emerging from the other springs. With a  $\delta D$  value for the dilute endmember around  $-54\%$ , the  $\delta^{18}O$  composition of the spring waters should depart more significantly from that predicted by the LMWL than is actually observed in the  $\delta D$  vs.  $\delta^{18}O$  diagram (Fig. 5a): these fluids would plot along a line that would connect the  $\delta D$  value for the fluid from drillhole #1 to the point on the LMWL where  $\delta D = -54\%$ . Once again, isotope exchange between  $H_2O$  and  $CO_2$  must be invoked to explain the observed isotope composition. In any case, fluid from drill-hole #1 must be the most representative sample for the  $Cl^-$  content and isotope composition of the deep fluid of Saint-Nectaire.

A change in the  $\delta D$  values of fluids with time is observed, although there is no significant change in  $Cl^-$  content. Data are presented for the Dordogne valley on a  $\delta D$  vs.  $Cl^-$  diagram (Fig. 6a). The  $\delta D$  value for each fluid decreases with time except that for the Clemence spring water. Chloride variations are too small to explain this observation by a change in the mixing proportions between a deep mineralized fluid and shallow groundwater: the  $\delta D$  of the latter would be too negative for this hypothesis to hold. This phenomenon seems to represent a change in the isotopic composition of the water, which could imply a strong variation in the isotopic composition of the shallow endmember. Nevertheless, the gradual change of  $\delta D$  to more negative values from 1974 to 1986 remains unexplained although fluctuations are expected with time because of annual climatic changes (e.g. the hydrologic cycle). However, because no regular decrease in the  $\delta D$  value of the deep mineralized fluid can be seen, this gradual change might be an analytical artifact, because only few data are available.

Data scattering in the  $\delta D$  vs.  $Cl^-$  diagram (Fig. 6a) may be due to the variations in the chemical composition of the deep fluid along the Dordogne valley. This scattering also reflects in part the presence of several dilute endmembers. Croizat, Moneyron and Felix are located close to each other, and their  $\delta D$  values decrease with decreasing  $Cl^-$  content, while at Choussy, Clemence and Fenestre, located to the W of the first 3, the  $\delta D$  values increase as  $Cl^-$  contents decrease. The mineralized fluids giving rise to the first group of waters are thus diluted by a fluid with a low  $\delta D$  value during their rise to the surface, but the second group of waters results from dilution with freshwater enriched in D relative to the mineralized fluids. This implies that the dilution waters must have different recharge levels.

Selected  $\delta D$  and  $\delta^{18}O$  data of the Dordogne valley are plotted in Fig. 6b. If the  $\delta D$  variations in these

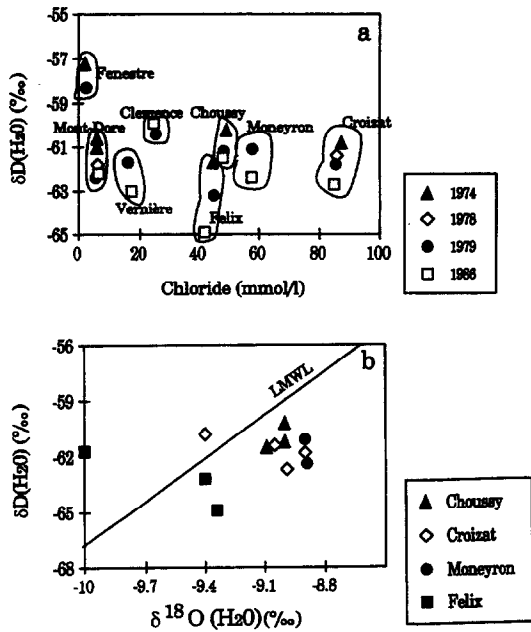


Fig. 6. Isotopic composition of selected fluids from the Dordogne valley: variability with time. (a)  $\delta D(H_2O)$  values vs. chloride concentration. (b)  $\delta D(H_2O)$  vs.  $\delta^{18}O(H_2O)$  values.

waters are due to changes in the dilute endmember isotopic composition, the data in this figure should plot along a line parallel to the LMWL, but there is no such correlation between  $\delta D$  and  $\delta^{18}O$ , especially in the case of Croizat and Felix. Isotope exchange between  $CO_2$  and  $H_2O$  has to be invoked again to explain the  $\delta^{18}O$  variations in these fluids. If no significant  $^{18}O$  shift relative to the LMWL can be seen for most of the waters in this study, this may be due to a subsequent isotope exchange between  $CO_2$  and  $H_2O$ , but it does not exclude an exchange between the fluid and silicate rock. Nevertheless, samples collected in wells such as drill-hole #1 at Saint-Nectaire, or that at Choussy, should not have undergone significant isotope exchange because such an exchange occurs at a low temperature, meaning that the  $\delta^{18}O$  shift from the LMWL is limited. This could suggest that large volumes of water have circulated through the hydrologic system, i.e. that the water/rock ratio must be very large.

#### CHEMICAL GEOTHERMOMETERS

Chemical composition can be used to determine processes affecting the fluids during their rise to the surface. These processes include: dissolution, precipitation of minerals and cation-exchange. For example, temperature changes during the rise of the fluids affect mineral solubilities favoring such reactions. This is further shown by ascending  $CO_2$ -rich fluids, which become more acid when cooled (Fouillac, 1983) and thus increase mineral dissolution. On the other hand, if gas and aqueous phases are separated at depth, as

suggested by Matthews *et al.* (1987), 2 processes may occur: the escaping  $CO_2$  may be dissolved in the freshwater, or the  $CO_2$  solubilization may be increased by the dilution of mineralized fluids. In either case, solubilization of  $CO_2$  leads to mineral dissolution.

A diagram based on relative Na–K–Mg contents has been proposed by Giggenbach (1988), to check on the degree with which equilibrium in the waters is attained with respect to surrounding minerals. Such diagrams have been used successfully in many studies (Hedenquist *et al.*, 1990; Ueda *et al.*, 1991), and are very helpful for interpreting the processes affecting rising fluids. They involve a ‘full equilibrium line’ that verifies the equilibrium with respect to the adularia-muscovite-chlorite association. In the present case, we cannot assume that the fluids should have equilibrated with this mineral assemblage at depth. Furthermore, Michard (1990) showed that Giggenbach’s assumptions cannot be applied to fluids from granitic areas. Therefore, chemical data for all samples collected are simply presented in Mg/Na vs. Na/K and Ca/Na vs. Na/K diagrams. (Figs 7 and 8). The chemical composition of the basalt (Lavina, 1985) is plotted as well, but no data were available on the chemical composition of Saint-Nectaire granite. However, since major elements are used in these diagrams, the known dissolution trend for another granite may be substituted for the Saint-Nectaire granite. We used the chemical composition of the Margeride granite (Beaucaire and Michard, 1982) in Figs 7 and 8. Numerous studies have been carried out on water–rock interactions, in particular on basalt–water and granite–water reactions (Ellis and Mahon, 1964, 1967; Seyfried and Bischoff 1977; Beaucaire and Michard, 1982; Savage, 1986; Gislason and Eugster, 1987; Pauwels *et al.*, 1992). According to their results, rocks should not dissolve congruently, and dissolution behavior depends on several parameters, including temperature, crystallinity, pH, mineralogical composition of the rocks, chemical composition of both fluids and initial rocks, and the water–rock ratio. Because these parameters are variable and because various chemical reactions may take place (precipitation of secondary phases, cation exchange), dissolution trends cannot be predicted and have not been plotted in the diagrams. The most dilute fluids plot in the upper left of the diagrams, as do the basalt and the granite which represent their isochemical dissolution. They are not evolved fluids and are considered as ‘immature’ waters (Giggenbach, 1988). The most mineralized fluids, which are more evolved, plot in the lower right of the diagrams.

The trend observed in the figures clearly indicates that the chemical composition of most fluids that circulate through the Mont-Dore volcanic area, is changed by mineral dissolution during their ascent toward the surface. Such a change leads to gains of K, Ca and Mg relative to Na. The most mineralized fluids of the Dordogne valley, such as those of Croizat, Moneyron and Choussy that have the highest Na/K

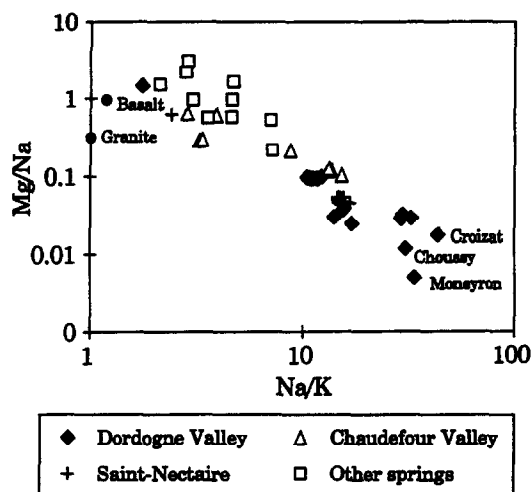


Fig. 7. Mg/Na molar ratio vs. Na/K molar ratio of Mont-Dore massif area fluids, and of basalt (Lavina, 1985) and granite (Beucaire and Michard, 1982).

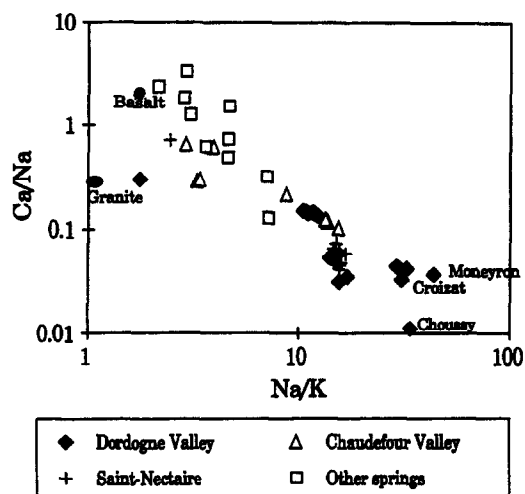


Fig. 8. Ca/Na molar ratio vs. Na/K molar ratio of Mont-Dore massif area fluids, and of basalt (Lavina, 1985) and granite (Beucaire and Michard, 1982).

and lowest Mg/Na ratios, seem to be least changed chemically. On the other hand, cation ratios of fluids from Saint-Nectaire are very constant irrespective of  $\text{Cl}^-$  content. They are identical in samples collected from drill-holes and springs. Therefore, it seems that the late dilution of fluids by freshwater does not induce a significant supply of cations by mineral dissolution.

Calculations were carried out using chemical geothermometers to estimate the temperatures of some of these fluids (Fouillac *et al.*, 1975; Bosch *et al.*, 1980), but the results are strongly related to the geothermometer that was used and on the particular fluid because of processes affecting rising fluids. The authors were unable to estimate the temperature of the fluids at depth. Nevertheless, as shown in Fig. 7, the chemical composition of fluids with low Mg/Na and

high Na/K ratios, can be used to estimate the temperature of deep fluids using Na/K and  $\text{Mg/K}^2$  geothermometers. Na/K temperatures for Moneyron fluids, using equations from Truesdell (1976) and Arnórsson *et al.* (1983b), are around 110°C (Table 8). Using the same equations, the temperature of the Choussy and Croizat fluids at depth should be 130 to 135°C. The temperatures calculated for the other fluids of the Dordogne valley are higher, but must have been overestimated because of K-leaching. Na/K temperatures of Saint-Nectaire fluids vary around 200°C using Truesdell's equations, but Michard (1990) established from chemical data on fluids circulating exclusively in granite areas, a relation between Na/K ratio and temperature that gives 175°C (Table 9). This would imply that the deep fluid at Saint-Nectaire is warmer than that in the Dordogne valley. The Mg/Na vs. Na/K diagram shows that the chemical composition of fluids emerging in the Chaudefour valley and in other dilute springs S and E of the caldera, is too distant from that of 'mature' waters to provide reliable temperatures.

The processes affecting the chemical composition of the fluids cause an underestimate for the temperature calculated with the  $\text{Mg/K}^2$  geothermometer (Giggenbach, 1988). Results for the most mineralized fluids of the Dordogne valley using this geothermometer, i.e. 124, 121 and 97°C for Choussy, Croizat and Moneyron, respectively, agree with the Na/K temperatures. This would confirm a temperature of 100 to 130°C for the deep fluids. Thermodynamic calculations performed by Michard *et al.* (1981) on the Choussy fluid confirm this temperature estimate. The agreement between Na/K and  $\text{Mg/K}^2$  temperatures also confirms that these 3 fluids are derived from deep fluids that are relatively unchanged chemically. The  $\text{Mg/K}^2$  temperature of Saint-Nectaire fluids is close to 120°C, which is rather low compared to the Na/K temperature, but Michard (1990) showed that this formula cannot be applied to fluids from granite areas.

The chemical composition of fluids with low Ca/Na and high Na/K ratios is expected to be used for estimating the temperature of deep fluids using geothermometers that involve Ca (Fig. 8). Nevertheless, temperatures calculated by Fouillac *et al.* (1984) using Na-K-Ca (Fournier and Truesdell, 1973) and Na-K-Ca-Mg (Fournier and Potter, 1979) geothermometers gave very different values from those obtained using the Na/K and  $\text{Mg/K}^2$  geothermometers. The behavior of Ca would depend rather on  $\text{CO}_2$  pressure and Giggenbach (1988) thus proposed a K/Ca geobarometer. More recently, the theoretical investigation of Chiodini *et al.* (1991) of chemical geothermometry at different  $\text{CO}_2$  pressures, validates the use of Na/K and  $\text{Mg/K}^2$  geothermometers for estimation of the deep temperature. It actually indicates that the Na/K and  $\text{Mg/K}^2$  ratios are relevant temperature indicators, whereas cation ratios involving calcium are  $\text{PCO}_2$  indicators.

Silica geothermometers are affected by both dis-

solution and dilution. The  $\text{SiO}_2$  content of water can also be rapidly equilibrated by mineral precipitation; this effect has been observed in many fields to be faster than similar changes for many other geothermometers, (Edmiston and Benoit, 1984; Pauwels *et al.*, 1993), and the dissolved  $\text{SiO}_2$  concentration can be used to provide evidence for water-rock interaction temperatures of a rising fluid before its discharge (Giggenbach *et al.*, 1994). At depth, the  $\text{SiO}_2$  concentration should reach equilibrium with either quartz or chalcedony, but the identification of the mineralogical phase which is in equilibrium with the fluid, is problematic. In a basalt environment, Arnórsson (1975) showed that fluids are always in equilibrium with quartz above  $180^\circ\text{C}$ , whereas below  $110^\circ\text{C}$ , they are in equilibrium with chalcedony; between these 2 temperatures, either phase can be in equilibrium. In granite areas, Michard (1990) considered that the change of mineralogical phase in equilibrium with fluids is at around  $100^\circ\text{C}$ . Both chalcedony and quartz geothermometers were thus used to calculate the temperature of Dordogne valley fluids from  $\text{SiO}_2$  concentrations (Table 6). Results of calculations for the Croizat, Moneyron and Choussy fluids were from  $98$  to  $115^\circ\text{C}$ , according to the chalcedony geothermometer and from  $126$  to  $142^\circ\text{C}$  according to the quartz geothermometer. From these results, there is no clear evidence of the phase with which the fluids are at equilibrium at depth. Nevertheless, the presence of tritium in the Croizat fluid suggests an underestimate of the  $\text{SiO}_2$ -geothermometer temperature through dilution, which would suggest an equilibration of deep fluids with chalcedony rather than with quartz. For the diluted fluids of the Dordogne valley the calculations gave higher temperatures, indicating that  $\text{SiO}_2$  concentrations show far greater change due to

late dissolution of minerals than by the dilution of fluids. The quartz geothermometer was used to evaluate the temperature of the Saint-Nectaire fluids (Table 7). The result is  $154^\circ\text{C}$  for drill-hole #1 fluid, the most representative of the deep fluids in this area. This  $\text{SiO}_2$  temperature is lower than the Na/K temperature; it may be too low due to partial reequilibration during the rise of the fluid and is, therefore, a lower limit of the temperature. Quartz temperatures for the other drill-holes and springs are lower because of fluid dilution. However, the  $\text{SiO}_2$  concentration of spring waters should be still lower if dilution by freshwater were the only process operating. Therefore, the  $\text{SiO}_2$  concentration of these fluids must have been changed by dissolution of minerals that probably took place after the mixing with freshwater, probably to a lesser extent in Saint-Nectaire than in the Dordogne valley.

Geothermometers based on Li contents have been proposed in the literature. They can be applied to those fluids that are the most representative of deep fluids with respect to the other cations. The Na/Li geothermometers (Fouillac and Michard, 1981; Kharaka and Mariner, 1989) give temperatures higher than those estimated using other geothermometers. Lithium is usually present as a trace element in minerals, and relationships between the Na/Li ratio and temperature can vary with the nature of the Li-bearing secondary minerals. Therefore, this geothermometer can be inconsistent in some areas, and is therefore not used in this study.

The Mg/Li geothermometer (Kharaka and Mariner, 1989) was developed for formation waters with much higher salinities than the present ones. It can also be used for low-temperature reservoirs, because of the relatively rapid exchange of Li and Mg with clay

Table 6. Temperatures of fluids in Dordogne Valley calculated using chemical and isotope geothermometers. Equations for most geothermometers are found in Fournier (1981) (1) Chalcedony geothermometers; (2) Quartz geothermometer; (3) Na/K equation of Truesdell (1976); (4) Na/K equation of Arnórsson *et al.* (1983b); (5) Mg/Li equation of Kharaka and Mariner (1989); (6) Mg/K<sup>2</sup> equation of Giggenbach (1988); (7)  $^{18}\text{O}$  isotope geothermometer of Mizutani and Rafter (1969b)

|                      | $\text{SiO}_2$ (1) | $\text{SiO}_2$ (2) | Na/K (3) | Na/K (4) | Mg/Li (5) | Mg/K <sup>2</sup> (6) | $^{18}\text{O}_{(\text{SO}_4)}$ (7) |
|----------------------|--------------------|--------------------|----------|----------|-----------|-----------------------|-------------------------------------|
| Dordogne Valley      |                    |                    |          |          |           |                       |                                     |
| Mont-Dore Chazerat   | 151                | 173                | 247      | 251      | 88        | 92                    | -                                   |
| Mont-Dore Madeleine  | 152                | 174                | 242      | 246      | 87        | 91                    | -                                   |
| Mont-Dore Chanteurs  | 143                | 166                | 194      | 201      | 89        | 83                    | 92                                  |
| Mont-Dore Ramond     | 152                | 174                | 233      | 237      | 87        | 90                    | -                                   |
| Mont-Dore Pantheon   | 152                | 174                | 238      | 242      | 87        | 91                    | -                                   |
| Mont-Dore Rigny      | 152                | 174                | 231      | 236      | 88        | 90                    | -                                   |
| Mont-Dore St Jean    | 151                | 173                | 215      | 220      | 83        | 86                    | -                                   |
| Mont-Dore Cesar      | 148                | 171                | 240      | 244      | 86        | 91                    | -                                   |
| La Bourboule-Choussy | 115                | 142                | 124      | 135      | 151       | 125                   | 132                                 |
| Clemence             | 109                | 136                | 209      | 216      | 112       | 114                   | 176                                 |
| La Vernière          | 113                | 139                | 188      | 195      | 119       | 110                   | 172                                 |
| Fenestre             | 94                 | 122                | 198      | 205      | 85        | 80                    | -                                   |
| Felix                | 127                | 151                | 127      | 137      | 126       | 98                    | 154                                 |
| Felix 2              | 112                | 139                | 136      | 146      | 119       | 96                    | -                                   |
| Gabriel              | 120                | 145                | 134      | 144      | 119       | 98                    | -                                   |
| Croizat              | 111                | 138                | 132      | 142      | 158       | 121                   | 149                                 |
| Moneyron             | 98                 | 126                | 105      | 116      | 139       | 97                    | 147                                 |

Table 7. Temperatures of fluids emerging at Saint-Nectaire calculated with chemical and isotope geothermometers

|                | SiO <sub>2</sub> (1) | Na/K (2) | Na/K (3) | Mg/Li (4) | Mg/K <sup>2</sup> (5) | <sup>18</sup> O <sub>(SO<sub>4</sub>)</sub> (6) |
|----------------|----------------------|----------|----------|-----------|-----------------------|-------------------------------------------------|
| Saint-Nectaire |                      |          |          |           |                       |                                                 |
| Drill hole #1  | 155                  | 196      | 174      | 146       | 119                   | 149                                             |
| Drill hole #2  | 154                  | 198      | 175      | 146       | 119                   | 153                                             |
| Drill hole #3  | 142                  | 190      | 170      | 141       | 113                   | 130                                             |
| Drill hole #B1 | 153                  | 200      | 176      | 141       | 118                   | —                                               |
| Drill hole #A2 | 156                  | 197      | 175      | 141       | 117                   | —                                               |
| Papon          | 154                  | 201      | 177      | 142       | 118                   | —                                               |
| Pont           | 148                  | 201      | 177      | 139       | 114                   | —                                               |
| Parc           | 154                  | 204      | 179      | 141       | 117                   | —                                               |
| Boette         | 151                  | 200      | 176      | 140       | 116                   | —                                               |
| Gros Bouillon  | 145                  | 204      | 179      | 136       | 114                   | —                                               |
| Bleue          | 153                  | 198      | 175      | 135       | 111                   | —                                               |
| Mont Cornadore | 144                  | 205      | 180      | 135       | 111                   | 113                                             |
| Mandon         | 150                  | 205      | 180      | 134       | 112                   | —                                               |
| Giraudon       | 154                  | 204      | 179      | 142       | 117                   | —                                               |
| Garçons        | 143                  | 203      | 178      | 134       | 110                   | —                                               |
| Simon          | 140                  | 202      | 178      | 134       | 110                   | —                                               |
| Degranges      | 89                   | 577      | 377      | —         | 64                    | —                                               |

(1) Quartz geothermometers, (2) Na/K equation of Truesdell (1976); (3) Na/K equation of Michard (1990); (4) Mg/Li equation of Kharaka and Mariner (1989); (5) Mg/K<sub>2</sub> equation of Giggenbach (1988); (6) <sup>18</sup>O isotope of Mizutani and Rafter (1969b).

minerals (Kharaka and Mariner, 1989), and plausible results have been obtained for it (Land and Macpherson, 1992; Pauwels *et al.*, 1993). When applied to the Moneyron, Choussy and Croizat fluids (Table 6), this geothermometer indicates temperatures between 130 and 160°C, which are slightly higher than those estimated using Na/K and Mg/K<sup>2</sup> geothermometers. The Mg/Li temperature reaches 146°C for the sample from drill-hole #1 of Saint-Nectaire (Table 7). In that case, the calculated Mg/Li temperature provides a lower limit for the source temperature, because of the rapid re-equilibration of the Mg/Li geothermometer during cooling of the fluids. To our knowledge, the Mg/Li geothermometer has not been tested to estimate the temperature of thermal waters in similar cases and these results must be considered with caution.

#### SULFATE CONTENTS AND SULFATE ISOTOPE GEOTHERMOMETER

In the most mineralized fluids of the Dordogne valley and of Saint-Nectaire, the SO<sub>4</sub> concentrations are far lower than those of Cl<sup>-</sup>. The fluids plot along the Cl<sup>-</sup> – HCO<sub>3</sub><sup>-</sup> axis of the (Cl, HCO<sub>3</sub>, SO<sub>4</sub>) diagram (Fig. 2). However, SO<sub>4</sub> content relative to Cl<sup>-</sup> content is even more important in the fluids from the Chaudefour valley and other springs emerging S and E of the Haute-Dordogne caldera. In both water types, the SO<sub>4</sub> concentration is of the same order of magnitude. The large variations in δ<sup>34</sup>S<sub>(SO<sub>4</sub>)</sub> values from +4.7‰ to +19.6‰ suggest the existence of several sulfur sources. Only few δ<sup>18</sup>O<sub>(SO<sub>4</sub>)</sub> data are available, but large variations are observed (+1.1‰ to +13.6‰) sulfur.

The Lavina-Edembouche and Sulfureuse springs are both acid-sulfate waters, the latter also containing some dissolved sulfides. Ancient fumarole deposits have been observed in different parts of the massif (see Lavina, 1985, for a compilation), that contain SO<sub>4</sub> minerals such as alunite, and S minerals such as pyrite and chalcopyrite, whose dissolution and oxidation provide acid SO<sub>4</sub> fluids, as documented from many sulfide mines. The δ<sup>34</sup>S value for SO<sub>4</sub> of the acidic Sulfureuse spring water is positive (+10.8‰), whereas the δ<sup>34</sup>S in the dissolved sulfide is –14.2‰. The S-isotope ratios in this spring could be explained by a bacterial reduction of SO<sub>4</sub> which involves an enrichment in <sup>34</sup>S of the remaining SO<sub>4</sub> (Mizutani and Rafter, 1969a). Nevertheless, the sulfur cannot be supplied by the dissolution of sulfide minerals only. Sulfate derived from sulfide oxidation would have a similar δ<sup>34</sup>S<sub>(SO<sub>4</sub>)</sub> value to that of the sulfide under acid conditions (Taylor *et al.*, 1984), and a lower one than for sulfide for some types of bacterial oxidation (Nissenbaum and Rafter, 1967). Moreover, according to the δ<sup>18</sup>O<sub>(H<sub>2</sub>O)</sub> value (–9.01‰), oxidation of sulfide, even in a highly aerated environment, should produce a SO<sub>4</sub> with a lower δ<sup>18</sup>O<sub>(SO<sub>4</sub>)</sub> value than the one determined (+13.6‰) (Taylor *et al.*, 1984; Van Everdingen and Krouse, 1985). Therefore, if sulfide is not supplied by reduction of SO<sub>4</sub>, sulfur in this fluid must be derived from at least two sources. In the Chaudefour valley, the fluids also vary in SO<sub>4</sub> isotope composition. The δ<sup>34</sup>S<sub>(SO<sub>4</sub>)</sub> value for the most mineralized fluid (Chaudefour 3) is +14.4‰, but in other, more dilute, fluids this value varies from +6.2‰ to +19.6‰. In this volcanic area, the SO<sub>4</sub>-isotope composition of the deep fluids is affected by dissolution or oxidation of S-bearing minerals (sulfates, sulfides) of different origins. These data on bicarbo-

nate and acid-sulfate waters illustrate that the sulfur in the subsurface has multiple sources.

The  $\delta^{34}\text{S}_{(\text{SO}_4)}$  generally varies from +13 to +18‰, in the fluids from Saint-Nectaire, and in a relatively dilute fluid (e.g. Desgranges spring) it is +6.4‰. Nevertheless,  $\text{SO}_4$  isotope values of the Saint-Nectaire fluids correlate with the  $\text{SO}_4$  content:  $\delta^{34}\text{S}_{(\text{SO}_4)}$  values plotted against the  $\text{Cl}/\text{SO}_4$  ratio show a positive correlation (Fig. 9a). A straight line on this type of diagram suggests two  $\text{SO}_4$  sources, which can be provided by either the mixing of two  $\text{SO}_4$  containing fluids, or the dissolution of a S-bearing mineral into a S-containing fluid. The figure shows that the  $\delta^{34}\text{S}$  of the minerals dissolved by fluids during their ascent in this granite area should be around +5‰. This may be induced by the circulation of the cooled fluid through an area rich in  $\text{SO}_4$  minerals, because the solubility of such minerals (e.g. anhydrite) increases with decreasing temperature. The dissolved  $\text{SO}_4$  with the isotopically heaviest S ( $\delta^{34}\text{S}_{(\text{SO}_4)}$  of +18‰ and a  $\delta^{18}\text{O}_{(\text{SO}_4)}$  of +5.2‰) is in the fluid from drill-hole #3, and could represent the isotopic composition of the deep mineralized fluid. The isotope composition of this fluid may then be used to estimate the temperature of the deep fluid using the  $^{18}\text{O}$  isotope geothermometer for  $\text{SO}_4\text{--H}_2\text{O}$  (Mizutani and Rafter, 1969b). Calculations indicate a temperature of 130°C, i.e. lower than the temperatures estimated using chemical geothermometers. This result cannot be explained by a rapid isotope exchange between  $\text{H}_2\text{O}$  and  $\text{SO}_4$  during the ascent and cooling of the fluid. According to the kinetic data of Lloyd (1968) and Chiba and Sakaï (1985), several thousand of years are required for isotopic equilibrium to be attained between  $\text{H}_2\text{O}$  and  $\text{SO}_4$  in this temperature range. Assuming a  $\delta^{18}\text{O}_{(\text{SO}_4)}$  of the deep fluid equal to that found in drill-hole #3, i.e. +5.2‰, the  $\delta^{18}\text{O}(\text{H}_2\text{O})$  should be around -5‰ for the isotope geothermometer to yield a temperature equal to that obtained by the Na/K geothermometer. This value is rather high compared to the actual one (-8.37‰), and as isotope exchange between  $\text{H}_2\text{O}$  and  $\text{CO}_2$  occurs only at a low temperature in shallow conditions, we have to conclude that the  $\delta^{18}\text{O}_{(\text{SO}_4)}$  of the deep fluid is lower than that found in drill-hole #3. Therefore, when cooling during its ascent from the deep reservoir to the level of sampling, the deep fluid is likely to have dissolved sulfates with a high  $\delta^{18}\text{O}_{(\text{SO}_4)}$  value. At the same time, the  $\delta^{34}\text{S}_{(\text{SO}_4)}$  value inherited from the deep fluid would also have been changed, meaning that the value found cannot be considered to be that of the deep fluid.

The plot of isotope composition of the Dordogne valley fluids vs. the  $\text{Cl}/\text{SO}_4$  ratio is more scattered than that of the Saint-Nectaire fluids (Fig. 9b). At equilibrium between water and a  $\text{SO}_4$  mineral at a given temperature, the  $\text{SO}_4$  concentration decreases with increasing Cl concentration (Michard, 1985). The scattering may thus be partly explained by variations of the total dissolved solids content of the deep mineralized fluids. Nevertheless, as observed in the

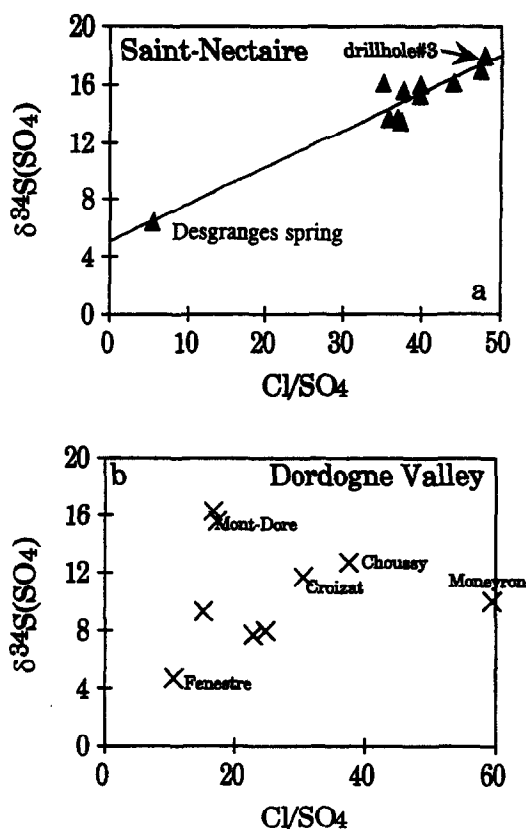


Fig. 9. The  $\delta^{34}\text{S}$  values of dissolved sulfates from Saint-Nectaire (a) and Dordogne valley (b) fluids plotted against chloride/sulfate ratio.

case of bicarbonate and acid-sulfate waters, several S-minerals with low or high  $\delta^{34}\text{S}$  values must be dissolved by deep fluids during their rise. The  $\delta^{34}\text{S}_{(\text{SO}_4)}$  and  $\delta^{18}\text{O}_{(\text{SO}_4)}$  values of the fluids show a positive correlation with each other (Fig. 10): the sources of  $\text{SO}_4$  with low or high  $\delta^{34}\text{S}_{(\text{SO}_4)}$  also show low or high  $\delta^{18}\text{O}_{(\text{SO}_4)}$  respectively. Calculations using the  $^{18}\text{O}$  isotope geothermometer, made on the most mineralized fluids of the Dordogne valley (Croizat, Moneymon and Choussy), indicate a temperature between 132 and 150°C, which is slightly higher than the temperature calculated using chemical geothermometers. Therefore, these fluids were supplied with sulfates with a low  $\delta^{18}\text{O}_{(\text{SO}_4)}$ , and thus also with a low  $\delta^{34}\text{S}_{(\text{SO}_4)}$ . Therefore, we cannot presently determine the sulfate-isotope composition of the deep fluid, which should have a  $\delta^{34}\text{S}_{(\text{SO}_4)}$  value higher than that of the Moneymon or Croizat fluids (+12‰).

#### STRONTIUM ISOTOPE COMPOSITION

The  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratio of the Mont-Dore fluids discussed in this paper varies from 0.704408 to 0.714226, depending on where they emerge (Fig. 11). Analyses of the  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratio on 6 rock samples are given in Table 5, together with their Rb

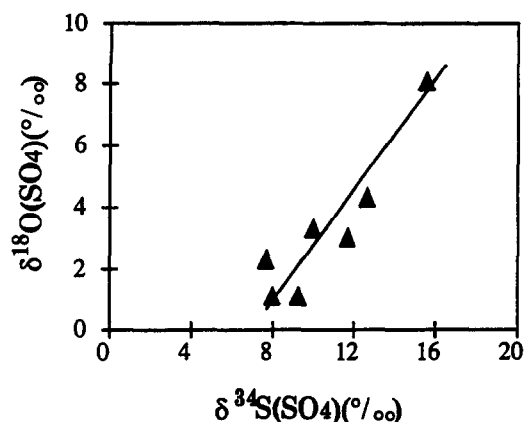


Fig. 10. Plot of  $\delta^{18}\text{O}(\text{SO}_4)$  vs.  $\delta^{34}\text{S}(\text{SO}_4)$  values for the Dordogne valley area fluids.

and Sr concentrations. Strontium isotopes have been used as tracers to show equilibrium between granite and water (Stettler and Allègre, 1978), between fluids and their host rocks in a geothermal system (Vuataz *et al.*, 1988; Goff *et al.*, 1991), and between water and a particular mineral (Kay and Darbyshire, 1986; McNutt *et al.*, 1984). The fluids collected at Saint-Nectaire have the highest  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (0.714062 and 0.714226). Isotope ratios of granite samples collected near Choussy (at La Bourboule) and at Saint-Nectaire reach 0.733804 and 0.722282, respectively, far higher than the ratios for the fluid samples. This indicates that no equilibrium was reached between these 2 phases, and that the Sr isotope value was obtained either through mixing, or from equilibrium being reached between fluids and particular granite minerals.

As discussed above, the dissolution of minerals changes the chemical composition of fluids in a volcanic area. During such reactions Sr is leached from the rock, leading to Sr concentrations that can equal those of the more saline fluids from Saint-Nectaire or the Dordogne valley. The Sr-isotope compositions of these dilute fluids are less radiogenic ( $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of Sulfureuse and Chaudefour 3 are 0.704408 and 0.704912; Fig. 11) than those of the more saline fluids. Strontium is provided during the dissolution of basalt and other volcanic rocks, which combine high Sr contents (715 and 900 ppm in basalt and trachyandesite, respectively) with low Sr-isotope ratios ( $^{87}\text{Sr}/^{86}\text{Sr}$  ratios 0.703844 and 0.704215, respectively; Table 5).

The Sr-isotope ratios of the fluids from the Dordogne valley are intermediate, varying from 0.706520 at Mont-Dore to 0.710639 at Choussy, the other values falling in the 0.707–0.708 range. According to cation concentrations, the Moneyron, Croizat and Choussy fluids are among the least changed during ascent, and late Sr leaching should be limited. These fluids should therefore have a Sr isotope ratio very close to that of their deep component. Never-

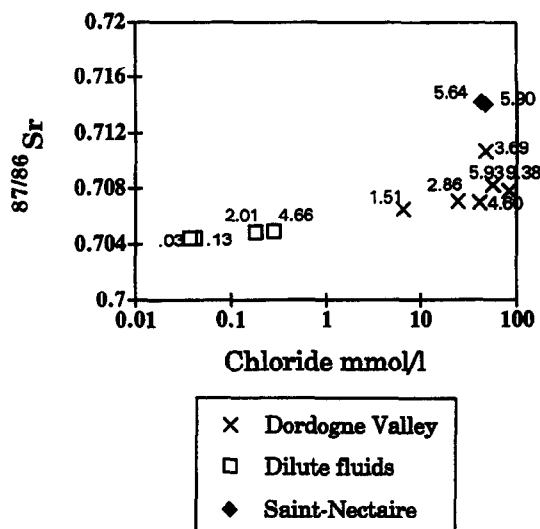


Fig. 11.  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of some Mont-Dore area fluids vs. chloride content. Numbers on the graph represent the strontium content in  $10^{-7}$  mol/l.

theless, variations in the Sr isotope ratio are likely to exist in the fluids at depth because the ratios in fluids vary from 0.707826 to 0.710639. At Choussy (La Bourboule), where granite is exposed, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the deep fluid should be higher than that of the deep fluid giving rise to the Moneyron or Croizat fluids. Differences already expected in deep-fluid composition are confirmed by Sr-isotope compositions.  $^{87}\text{Sr}/^{86}\text{Sr}$  should depend on the path of the fluid, through either granite or volcanic rock. Dissolution of volcanic host rock induces a decrease in isotopic Sr, which is the reason why the Clemence and Felix fluids have lower  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios. In the fluids of Mont-Dore, where the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is 0.70652, the proportion of volcanic Sr must be important.

## CONCLUSIONS

$\text{CO}_2$ -rich waters collected in the Mont-Dore region show large variations in their chemical composition. Mineralized fluids can be assumed to be in equilibrium at depth, where they obtain part of their chemical and isotope content, this content is changed during their ascent to the surface. The factors that affect the composition vary from one area to another, and include: 1) dilution by meteoric waters; 2) isotope exchange between  $\text{CO}_2$  and  $\text{H}_2\text{O}$ ; 3) leaching of cations (K, Mg, Ca, Sr) and  $\text{SiO}_2$  by dissolution of the host rock in the presence of  $\text{CO}_2$ ; 4) dissolution of S-bearing minerals, including those located in ancient fumarole deposits (dissolution and oxidation of sulfide minerals are also possible); 5) re-equilibration of  $\text{SiO}_2$ ; 6) solubilization of  $\text{CO}_2$  gas in the diluting water or after mixing. Our work established that the Moneyron, Croizat and Choussy waters, i.e. the most mineralized fluids, are likely to be closest to the deep

fluids in the Dordogne valley in chemical and isotope composition. From consideration of the composition of these 3 mineralized fluids, variations in the chemical and isotope composition exist at depth. These include variations in the total salinity of the fluids and the Sr-isotope composition, indicating that these waters originate from different deep fluids. The other fluids of the Dordogne valley result from strongly disturbed deep fluids. In the Saint-Nectaire area, the fluids collected from drill-hole #1 are the most representative of conditions at depth. Nevertheless, some characteristics of the deep fluids, such as the isotope composition of their  $\text{SO}_4$  content, could not be determined. The less mineralized fluids obtain most of their chemical and isotopic character by dissolution at shallow levels of the host rock, e.g. the Mont-Dore and Chaudesfour-valley fluids, and other fluids emerging S and E of the paleo-Caldera, and the chemical composition of their deep component could not be estimated.

Although deep fluids in volcanic (Dordogne valley) and granitic (Saint-Nectaire) areas have similar mineralization characteristics, some differences have been identified. These include differences in the  $\delta^{18}\text{O}_{(\text{H}_2\text{O})}$  composition, which in the case of Saint-Nectaire suggests that isotope exchange occurs between  $\text{H}_2\text{O}$  and silicate rock to a larger extent. Differences are also found in the Sr isotope composition, as a higher  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is found in the Saint-Nectaire fluid than in the Dordogne Valley fluids because of circulation through the granite. Finally, differences in cation concentrations cause different element ratios in the granitic and volcanic-rock areas, because these fluids reach different temperatures at depth and circulate through different geological environments, thus reaching equilibrium with different mineral assemblages.

The processes affecting the deep fluids, commonly prevent the use of chemical or isotope geothermometers. Nevertheless, Na/K,  $\text{Mg}/\text{K}^2$  and  $\text{SiO}_2$  geothermometers can be applied to the relatively little changed fluids of the Dordogne valley, giving temperature estimates for these fluids from 100 to  $130^\circ\text{C}$ . The Na/K and  $\text{SiO}_2$  geothermometers also indicate that the temperature of deep Saint-Nectaire fluid may reach  $160\text{--}175^\circ\text{C}$ . The  $\text{Mg}/\text{K}^2$  estimate does not agree with the results from other geothermometers because it is unsuitable for waters circulating through granite. At present, there is no available information concerning the depth at which the calculated temperatures occur. Our work also indicates that a Mg/Li geothermometer gives, for these  $\text{CO}_2$ -rich fluids, slightly different results ( $\pm 30^\circ\text{C}$ ) than those obtained using the Na/K geothermometer. In the case of Saint-Nectaire, the difference can account for the high re-equilibration rate with decreasing temperature. However, in this type of water, the Na/K geothermometer should give more reliable results than cation geothermometers that include calcium, because of the presence of  $\text{CO}_2$  gas.

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## REFERENCES

- Arnórsson S. (1975) Application of the silica geothermometer in low temperature hydrothermal areas in Iceland. *Amer. J. Sci.* **275**, 763–784.
- Arnórsson S., Gunnlaugsson E. and Svarvarsson H. (1983a) The chemistry of geothermal waters in Iceland. II. Mineral equilibria and independent variables controlling water compositions. *Geochim. Cosmochim. Acta* **47**, 547–566.
- Arnórsson S., Gunnlaugsson E. and Svarvarsson H. (1983b) The chemistry of geothermal waters in Iceland. III. Chemical geothermometry in geothermal investigation. *Geochim. Cosmochim. Acta* **47**, 567–577.
- Baubron J.-C., Bosch B., Degranges P., Leleu M., Marce A., Rissler J.-J. and Sarcia C. (1979) Recherches géochimiques sur les eaux thermales de la bordure Ouest de Limagne. *Bull. Minéral.* **102**, 676–683.
- Beaucaire C. and Michard G. (1982) Origin of dissolved minor elements (Li, Rb, Sr, Ba) in superficial waters in a granitic area. *Geochem. Jour.* **16**, 247–258.
- Bosch B., Degranges P., Fouillac C., Leleu M. and Sarcia C. (1980). Geochemistry of thermal water in the Mont-Dore area. Proc. 2<sup>nd</sup> Int. Semin. Results E.E.C. Geotherm. Energy Res., 360–369.
- Brousse R. (1971). Magmatologie du volcanisme néogène du Massif central. Symp. Jean Jung, Plein Air Service, Clermont-Ferrand, 377–478.
- Brousse R. (1984) Comblement de la fosse volcanotectonique et socle du massif du Mont-Dore. Programme GPF1, thème 9, Document BRGM no. 81, pp. 9–21.
- Brousse R., Tempier P., Rançon J. P., Veyret-Mekdjian Y. (1989) Notice explicative, carte géol. France (1/50000), feuille Bourg-Lastic (716) Orleans BRGM, 78p. Carte géologique par Brousse R. and Tempier P. (1981).
- Chiba H. and Sakaï H. (1985) Oxygen isotope exchange ratio between dissolved sulfate and water at hydrothermal temperatures. *Geochim. Cosmochim. Acta* **49**, 998–1000.
- Chiodini G., Cioni R., Guidi M. and Marini L. (1991) Chemical geothermometry and geobarometry in hydrothermal aqueous solutions: A theoretical investigation based on mineral-solution equilibrium model. *Geochim. Cosmochim. Acta* **55**, 2709–2727.
- Craig H. (1963). The isotopic geochemistry of water and carbon in geothermal areas. Nuclear Geology in Geothermal areas (ed. E. Tongiorgi), Pisa Italy, Consiglio Nazionale delle Ricerche, Laboratorio de Geologia Nucleare, 17–53.
- Edmiston R. C. and Benoit W. R. (1984) Characteristics of Basin and Range geothermal systems with fluid temperatures of  $150^\circ\text{C}$  to  $200^\circ\text{C}$ . *Geotherm. Res. Council Trans.* **8**, 417–424.
- Ellis A. J. and Mahon W. A. J. (1964) Natural hydrothermal systems and experimental hot-water-rock interactions (part I). *Geochim. Cosmochim. Acta* **31**, 1323–1357.
- Ellis A. J. and Mahon W. A. J. (1967) Natural hydrothermal systems and experimental hot-water-rock interactions (part II). *Geochim. Cosmochim. Acta* **31**, 519–538.
- Fouillac C. (1983) Chemical geothermometry in  $\text{CO}_2$ -rich thermal waters. Example of the French Massif Central. *Geothermics* **12**, 149–160.
- Fouillac C. and Michard G. (1981) Sodium–lithium ratio in

- water applied to geothermometry of geothermal reservoirs. *Geothermics* **10**, 55–70.
- Fouillac C., Caillex P., Michard G. and Merlivat L. (1975). Premières études de sources thermales du Massif Central français au point de vue géothermique. 2<sup>nd</sup> Symposium on Development and Utilization of Geothermal Resources, San Francisco, 721–729.
- Fouillac C., Fouillac A. M. and Vuataz F. D. (1984). Les sources thermales de la région de Sancy: nouvelles données et synthèse géothermométrique. Rapport GPF, thème 9, Doc BRGM no.81-9, 53–64.
- Fouillac C., Fouillac A.-M. and Chery L. (1991). Isotopic studies of deep and surface waters in the French Massif Central. In: *Proc. Intern. Symp. Isot. Techn. Water Resour. Developm.* IAEA, Vienna, Austria, 646–648.
- Fournier R. O. (1981). Application of water geochemistry to geothermal exploration and reservoir engineering. In *Geothermal Systems: Principles and Case Histories* (ed. L. Rybach and L. J. P. Muffler), pp 109–143. Wiley.
- Fournier R. O. and Potter R. W. M. (1979) A magnesium correction for the Na–K–Ca geothermometer. *Geochim. Cosmochim. Acta* **43**, 1543–1550.
- Fournier R. O. and Truesdell A. M. (1973) An empirical Na–K–Ca geothermometer for natural waters. *Geochim. Cosmochim. Acta* **43**, 1543–1550.
- Fritz P. and Frapé S. K. (1982). Comments on the  $^{18}\text{O}$ ,  $^2\text{H}$ , and the chemical composition of saline groundwaters in the Canadian Shield. In *Isotope Studies of Hydrologic processes* (ed. E. C. Perry), Northern Illinois University Press, De Kalb, 57–63.
- Giggenbach W. F. (1981) Geothermal mineral equilibria. *Geochim. Cosmochim. Acta* **45**, 393–410.
- Giggenbach W. F. (1988) Geothermal solute equilibria: Derivation of Na–K–Ca–Mg geothermometers. *Geochim. Cosmochim. Acta* **48**, 2693–2711.
- Giggenbach W. F. (1991). Chemical techniques in geothermal exploration. In *Application of Geochemistry in Geothermal Reservoir Development* (Co-ordinator D'Amore, F.), UNITAR/UNDP Centre on Small Energy Resources, Rome, pp. 119–144.
- Giggenbach W. F., Sheppard D. S., Robinson B. W., Stewart M. K. and Lyon G. L. (1994) Geochemical structure and position of the Waiotapu geothermal field, New Zealand. *Geothermics* **23**, 599–644.
- Gislason S. R. and Eugster H. (1987) Meteoric water-basalt interactions I: A laboratory study. *Geochim. Cosmochim. Acta* **51**, 2827–2840.
- Goff F., Gardner J., Vidale R. and Charles R. (1985) Geochemistry and isotopes of fluids from sulphur springs, Valles Caldera, New Mexico. *J. Volcanol. Geotherm. Res.* **23**, 273–297.
- Goff F., Wollenberg H. A., Brookins D. C. and Kistler R. W. (1991) A Sr-isotopic comparison between thermal waters, rocks, and hydrothermal calcites, Long Valley caldera, California. *J. Volcanol. Geotherm. Res.* **48**, 265–281.
- Grimaud D., Beaucaire C. and Michard G. (1990) Modelling of the evolution of ground waters in a granite system at low temperature: the Stripa ground waters, Sweden. *Appl. Geochem.* **5**, 515–525.
- Hedenquist J. H., Goff F., Phillips F. M., Elmore D. and Stewart M. K. (1990) Groundwater dilution and residence times, and constraints on chloride source, in Mokai geothermal system, New Zealand, from chemical, stable isotope, tritium and  $^{36}\text{Cl}$  data. *Jour. Geophys. Res.* **95**(B12), 19365–19375.
- Jung J. and Brousse R. (1962). Les provinces volcaniques néogènes et quaternaires de la France. Bull. Serv. Carte Géol. Fr. 158 (267), 61 pp.
- Kay R. L. F. and Darbyshire D. P. F. (1986). A strontium isotope study of groundwater–rock interaction in the Carnmenellis granite. *Proc. 5th Intern. Symp. Water–Rock Interaction*, 379–381.
- Kharaka Y. K. and Mariner R. H. (1989). Chemical geothermometers and their application to formation waters from sedimentary basins. In: *Thermal History of Sedimentary Basins* (eds. N. D. Naeser and T. McCulloch), pp 99–117. Springer Verlag, New York.
- Land L. S. and Macpherson G. L. (1992) Geothermometry from brine analysis; lessons from Gulf Coast USA. *Appl. Geochem.* **7**, 333–340.
- Lavina P. (1985). Le volcan du Sancy et le 'Massif Adventif'; étude volcanologique et structurale. PhD. dissertation, Université de Clermont Ferrand II, 220 pp.
- Lloyd R. M. (1968) Oxygen isotope behavior in the sulfate water system. *J. Geophys. Res.* **73**, 6099–6110.
- Matthews A., Fouillac C., Hill R., O'Nions R. K. and Oxburgh E. R. (1987) Mantle-derived volatiles in continental crust: the Massif Central of France. *Earth Planet. Sci. Lett.* **85**, 117–128.
- McNutt R. H., Frapé S. K. and Fritz P. (1984) Strontium isotope composition of some brines from the Precambrian Shield of Canada. *Isotope Geoscience* **2**, 205–215.
- Michard G. (1985) Equilibre entre minéraux et solutions géothermales. *Bull. Mineral.* **108**, 29–44.
- Michard G. (1990) Behavior of major elements and some trace elements (Li, Rb, Cs, Sr, Fe, Mn, W, F) in deep hot waters from granitic areas. *Chem. Geol.* **89**, 117–134.
- Michard G., Fouillac C., Evrard M. and Lambret B. (1978) Acquisition des ions alcalino-terreux par les eaux thermales carbogazeuses. *Earth. Planet. Sci. Lett.* **41**, 170–174.
- Michard G., Fouillac C., Grimaud D. and Denis J. (1981) Une méthode globale d'estimation des températures des réservoirs alimentant les sources thermales. Exemple du Massif Central Français. *Geochim. Cosmochim. Acta* **45**, 1199–1207.
- Mizutani Y. and Rafter T. A. (1969a) Oxygen isotopic composition of Sulphates—Part 4 Bacterial fractionation of oxygen isotopes in the reduction of sulphate and in the oxidation of sulphur. *New Zealand J. Sci.* **12**, 60–68.
- Mizutani Y. and Rafter T. A. (1969b) Oxygen isotopic composition of Sulphates III Oxygen isotopic fractionation in the bisulphate ion-water system. *New Zealand J. Sci.* **12**, 54–59.
- Mossand Ph., Cantagrel J. M., Vincent P. M. (1982). La Caldéra de Haute-Dordogne: âge et limites (Massif des Monts-Dore, France). *Bull. Soc. Géol. France*, **7**, t. XXIV, 727–738.
- Nissenbaum A. and Rafter T. A. (1967) Sulphur isotopes in altered pyrite concretions from Israel. *J. Sediment. Petrol.* **37**, 961–962.
- Pauwels H., Fouillac Ch. and Criaud A. (1992) Water–rock interactions during experiments within the geothermal Hot Dry Rock borehole GPK1, Soultz-sous-Forêts, Alsace, France. *Applied Geochem.* **7**, 243–255.
- Pauwels H., Fouillac Ch. and Fouillac A. M. (1993) Chemistry and isotopes of deep geothermal saline fluids in the Upper Rhine Graben: Origin of compounds and water–rock interactions. *Geochim. Cosmochim. Acta* **57**, 2737–2749.
- Savage D. (1986) Granite–water interactions at 100°C, 50 MPa: an experimental study. *Chem. Geol.* **54**, 81–95.
- Seyfried W. and Bischoff J. L. (1977) Hydrothermal transport of heavy metals by seawater: the role of seawater/basalt ratio. *Earth. Planet. Sci. Lett.* **34**, 71–77.
- Stettler A. and Allègre C. J. (1978)  $^{87}\text{Rb}$ – $^{87}\text{Sr}$  studies of waters in a geothermal area: the Cantal, France. *Earth Planet. Sci. Lett.* **38**, 364–372.
- Taylor B. E., Wheeler M. C. and Nordstrom D. K. (1984) Isotope composition of sulphate in acid mine drainage as measure of bacterial oxidation. *Nature* **308**, 538–541.
- Truesdell A. H. (1976) Geochemical techniques in exploration. Summary of section III. *Proc. Sec. United Nations Symp. Develop. Use Geotherm. Res.* **1**, 53–78.
- Ueda A., Kubota Y., Katoh H., Hatakeyama K. and Matsubaya O. (1991) Geochemical characteristics of the

- Sumikawa geothermal system, northeast Japan. *Geochem. Jour.* **25**, 223–244.
- Van Everdingen R. O. and Krouse (1985) Isotope composition of sulphates generated by bacterial and biological oxidation. *Nature* **315**, 395–396.
- Vuataz F.-D. and Goff F. (1986) Isotope geochemistry of thermal and nonthermal waters in the Valles caldera, Jemez Mountains, Northern New Mexico. *J. Geophys. Res.* **91**(B2), 1835–1853.
- Vuataz F.-D., Goff F., Fouillac C. and Calvez J.-Y. (1988) A strontium isotope study of the VC-1 core hole and associated hydrothermal fluids and rocks from Valles caldera, Jemez Mountains, New Mexico. *J. Geophys. Res.* **93**(B6), 6059–6067.