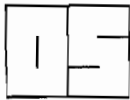


Chemical composition of waters from hot
springs at Lorino and Shaplino in Siberia,
Russia

Magnús Ólafsson

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CHEMICAL COMPOSITION OF WATERS FROM HOT SPRINGS AT LORINO AND SHAPLINO IN SIBERIA, RUSSIA

Introduction

In July of this year, the Chemical Division of Orkustofnun received water samples from hot springs in Siberia, sampled by Haukur Baldursson from the consulting engineering company of Afl og Orka ehf, Reykjavík, Iceland. Samples were collected at three hot springs, one in Lorino and two in Shaplino. The chemical laboratory provided equipment and containers for the sampling and the samples were partially treated in the field according to procedures of the laboratory.

Results of chemical analyses

Two of the samples, one from Lorino and one from Shaplino, were analyzed for all major elements and several trace metals, whereas only pH, carbonate, hydrogen sulfide and conductivity were analyzed in the second sample from Shaplino. The results of the chemical analyses are shown in Table 1. Included in the table are also the results of the analyses of a sample taken by Haukur Baldursson from the hot spring in Lorino in July 1998.

Evaluation of chemical data

The hot waters from Lorino, and especially Shaplino, have a high mineral concentration and are not feasible for direct use in heating systems. The salinity of the water in Lorino is 4.7‰ and 20.5‰ for the water in Shaplino and with any trace of oxygen the water will become extremely corrosive to iron and steel. Calculations show that free CO₂ is present in the water, indicating the possibility of carbonate corrosion for iron and steel as well.

The radioactivity of the water has been of some concern. In a previous report about the thermal water in Lorino radiation as high as 300 Bq/l has been reported, and there was a mention of health problems (cancer) related to this high radiation of the water. Therefore, the radioactivity from radon (Rn) was measured in the samples from last summer. The results are shown in Table 1, 170 Bq/l and 63 Bq/l for the samples from Lorino and Shaplino respectively. According to reference standards in the Scandinavian countries, the reference value of radium in drinking water is 100 Bq/l and it should under no circumstances be higher than 1000 Bq/l.

In order to evaluate the subsurface temperature of a geothermal system, based on the chemical composition of springs on the surface, one can apply the so-called chemical geothermometers. For low temperature waters these geothermometers are basically of two types: Those that are based on temperature dependent variations in the solubility of individual minerals (e.g. silica geothermometers) and those that are based on temperature dependent exchange reactions between different minerals (e.g. cation geothermometers). In Iceland a silica geothermometer based on equilibrium between the silica mineral chalcedony and water has been used extensively for low temperature geothermal water. However, the a silica geothermometer based a equilibrium between quartz and the water has often proven to be more realistic in waters rising from old bedrocks as is the case in Siberia. Calculations based on chalcedony and quartz reveal a subsurface temperature of 105° and 130°C, much higher than the measured temperature of the spring (58°C). For Shaplino the two geothermometers indicate a bit lower temperatures, 90° and 120°C respectfully, closer to the actual temperature of the spring (88°C). A cation geothermometer based on the Na/K ratio of the waters indicate a subsurface of 155°C in Lorino and 85°C in Shaplino. It is believed that the silica geothermometers are more reliable.

In order to further evaluate the equilibrium condition of the thermal water and its scaling potential, the so-called saturation index (SI) has been calculated at temperatures between 110 and 20°C for several hydrothermal minerals. The index gives information on whether a particular mineral is likely to precipitate or dissolve at a specific temperature, and it is usually represented as a value of $\log(Q/K)$ where Q is the ionic activity product and K is the solubility product. When $Q < K$, so that the saturation index is negative, the solution is undersaturated and the mineral will not precipitate. When $Q > K$, the water is said to be supersaturated, and scale (precipitate) may form. If $Q = K$ and $\log(Q/K) = 0$, the water is exactly saturated and in equilibrium with that mineral. If a group of minerals is close to equilibrium at one particular temperature one can assume that the water has equilibrated with this group of minerals and the temperature represents the temperature of the reservoir.

This kind of mineral equilibrium diagram has been constructed for the thermal water from Lorino and Shaplino based on seven different hydrothermal minerals. Figure 1 shows such a diagram for the thermal water from Lorino and Figure 2 shows a similar diagram for the water from Shaplino. During the model calculations, the saturation index was first calculated at the measured temperatures in the hot springs, 58°C for Lorino and 88°C for Shaplino. In the following calculations the saturation index was calculated to model cooling or heating of the water sample in a closed system. The results are shown on Figures 1 and 2. No clear indication is of the water being in equilibrium at any specific temperature between 20 and 120°C, although a slight indication of equilibrium may be seen at the temperature interval 80° to 120°C. The geothermometer calculations as well as the calculations of the saturation index indicate a subsurface temperature within the geothermal systems of Lorino and Shaplino of approximately 100°C. The poor equilibrium conditions of the waters from Lorino and Shaplino might be due to inflow or mixing of cold groundwater with the geothermal water.

The most common scaling material to be expected from low temperature water are calcite, magnesium silicates, oxides (if oxygen is present) and sulfides (if hydrogen sulfide is present). The equilibrium calculations discussed above demonstrate which minerals are likely to precipitate, or form a scaling product, during the utilisation of the water. Hydrogen sulfide is not present in the samples from Lorino nor Shaplino, indicating that

ironsulfides will not form. Iron oxides are likely to form if oxygen comes into contact with the water, but most likely as a corrosion product. The model calculations demonstrate that the water from Lorino is slightly supersaturated (oversaturated) with respect to calcite (calcium carbonate) at the temperature of the spring (58°C). However, due to the low supersaturation it is unlikely that a calcite scale will form. Subsequent cooling of the water in a closed system will then lower the saturation index. On the other hand, heating of the sample in a closed system will increase the saturation index, and a calcite scale might form. Model calculations of the water sample from Shaplino show that it is undersaturated with respect to calcite at all temperatures (20° to 120°C) when cooled or heated in a closed system.

Conclusions

The main conclusions of the present study are:

- The hot waters from Lorino, and especially Shaplino, are highly mineralized and are not feasible for direct use in heating systems. However, scaling products are not likely to form during utilization of the water.
- Measurements show that radioactivity of the water is 170 Bq/l and 63 Bq/l for the samples from Lorino and Shaplino respectively making the water even suitable for drinking with regard to radioactivity.
- Calculations based on the chalcedony geothermometer indicate a temperature of approximately 105° to 110°C in an underlying geothermal system at Lorino, which is almost two times higher than the measured temperature of the spring (58°C). For Shaplino the silica geothermometer indicates a bit lower temperature, 90° to 95°C, much closer to the actual temperature of the spring (88°C).

Table 2. Chemical composition of water from Siberia (mg/l).

| Place | Lorino Spring I | Shaplino Spring II | Shaplino Spring III | Lorino Spring |
|---|--------------------|-----------------------|------------------------|------------------|
| Date | 2001.07.13 | 2001.07 | 2001.07.20 | 1998.07.08 |
| Time (local) | 10:00 | 15:00 | 16:00 | 16:30 |
| Sample # | 2001-2001 | 20012002 | 2001-2003 | 1998-2001 |
| Temperature (°C) | 58 | 88 | 43.5 | 58 |
| pH/°C ¹⁾ | 7.3 / 27.7 | 8.1 / 22.8 | 7.0 / 22.7 | 7.3 / 23 |
| Conductivity (µS/25°C) | 7540 | 25900 | 25600 | 7050 |
| Carbonate (CO ₂ (t)) ¹⁾ | 51.1 | 1.35 | 2.7 | 58.1 |
| Hydrogen sulfide (H ₂ S) ¹⁾ | <0,03 | <0,03 | <0,03 | <0.03 |
| Boron (B) | 1,57 | 0,96 | - | 1.6 |
| Silica (SiO ₂) | 94,4 | 75,9 | - | 97.2 |
| Lithium (Li) | 3.60 | 2.38 | - | - |
| Sodium (Na) | 1331 | 4414 | - | 1293 |
| Potassium (K) | 87.4 | 114 | - | 85.4 |
| Magnesium (Mg) | 0.96 | 0.80 | - | 0.96 |
| Calcium (Ca) | 320 | 2427 | - | 318 |
| Strontium (Sr) | 7.96 | 40.5 | - | - |
| Barium (Ba) | 0.442 | 1.150 | - | - |
| Fluoride (F) | 3.36 | 3.79 | - | 3.14 |
| Chloride (Cl) | 2650 | 11370 | - | 2635 |
| Sulfate (SO ₄) | 54.5 | 193 | - | 77.3 |
| Aluminum (Al) | 0.0044 | 0.0166 | - | 0.002 |
| Manganese (Mn) | 0.103 | 0.102 | - | 0.099 |
| Iron (Fe) | 0.0125 | 0.0848 | - | 0.025 |
| Zinc (Zn) | 0.011 | 0.054 | - | - |
| Cadmium (Cd) | 0.00003 | 0,00009 | - | - |
| Lead (Pb) | 0.00022 | 0.00135 | - | - |
| Total dissolved solids (TDS) | 4790 | 20080 | - | 4790 |
| Radon (Rn) | 170 | 63 | - | - |

¹⁾ : Measured 2001.07.25

- : Not analyzed

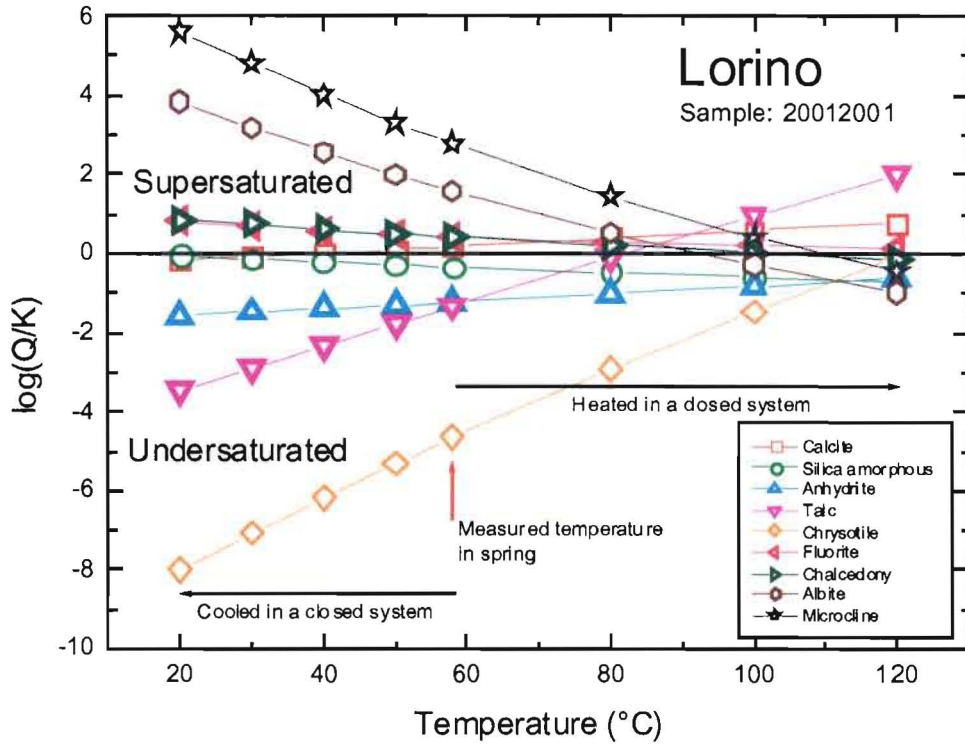


Figure 1. Calculated saturation index of several minerals at selected temperatures for the water sample from Lorino.

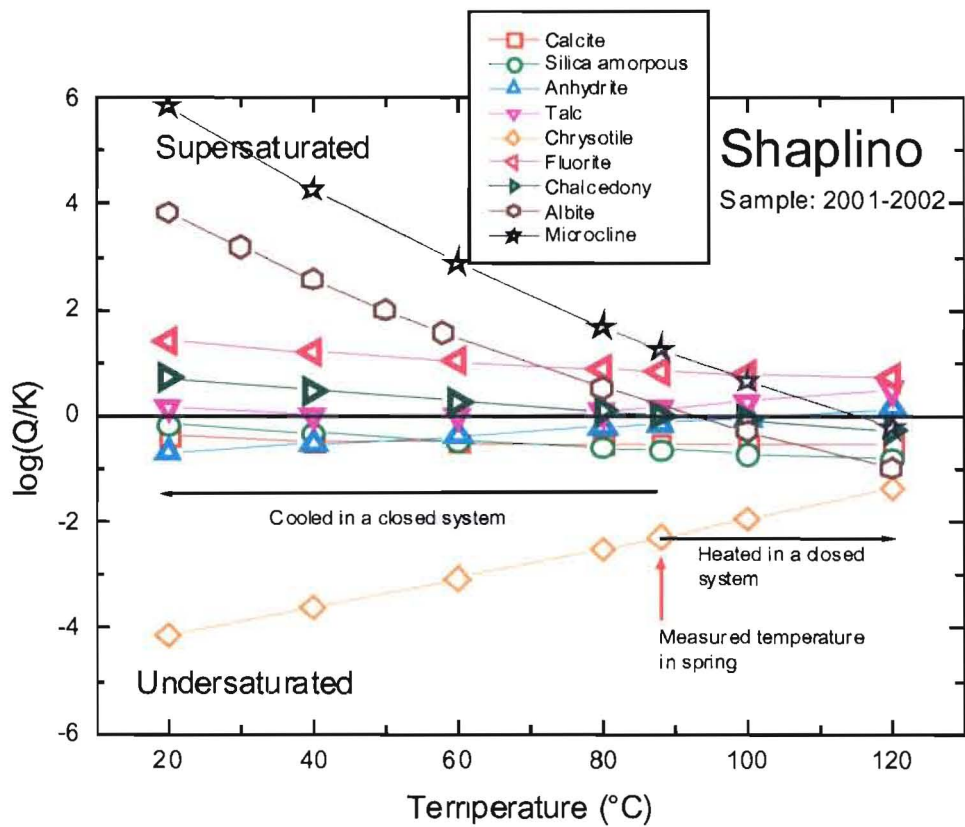


Figure 2. Calculated saturation index of several minerals at selected temperatures for the water sample from Shapliino.