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Geochemistry of Groundwater from a typical hard rock terrain*

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The concentration of the dissolved chemical species, [Y], is the only definitely known parameter in natural waters. From this, the geochemist tries to understand the processes, [A], assuming an initial content of the corresponding species, [X], within all the possible sources:

$[Y] = [A] \cdot [X]$

[A] and [X] form matrices and to solve for the elements, $a_j i$, within [A], there is no simple method. Therefore, several statistical models are built to understand the process/processes that bring about the observed chemical character [Y], of the natural waters.

The most simple models are based on the following equations:

$$H_2O \rightleftharpoons H^- + OH^+$$

$$K_{H_2O} = 10^{-14} \qquad \cdots 1$$

$$H_2O + CO_2 \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

$$K_{HCO_3^-} = 1 \cdot 3 \times 10^{-6} \qquad \cdots 2$$

$$a_{H^+} = \sqrt{P_{CO_2} \quad K_{HCO_3}} \qquad \cdots 3$$

The hydrogen ion concentration, $[H^+]$, controlled by the partial pressure of carbon dioxide in soils and the pH, acts on the rock materials to produce clays and in this process several cations are released. It would depend on the ambient conditions for the cations to exist in the dissolved aqueous phase.

The Vedavati River Basin is an area of 24,200 sq km lying within Lat. 13°05′: 15°44′N and Long. 75°43′: 77°23′E. Peninsular Gneisses, Dharwar group of formations and later granites occur in the area. It is a typical drought prone hard rock area in Peninsular India. During the groundwater assessment studies, taken up in the Vedavati River Basin by the Central Groundwater Board, 5600 water samples from various sources were analysed and the results were examined in order to understand the various processes bringing about the chemical character of the waters. A team of officers including geologists, hydrologists and chemists in addition to several others were involved. Some of the salient features of this study are given below:

1. Based on the quality of the water, two distinct populations can be separated within the open wells as;

   A—Domestic wells and

   B—Irrigation wells.

   Usually the domestic wells in the villages are more polluted and have a higher salinity. More than 90% of the irrigation wells have a total dissolved salt content of less than 1600 ppm whereas the corresponding figure for the domestic wells is 70%.

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*Summary of a talk delivered at the Geological Society of India on 30th October 1981.

2. The salinity in the waters increases after monsoon rather than decrease as an effect of dilution from rain water. This could be because the rising water table in the post-monsoon period dissolves more saline matter from the soils.
3. No statistically valid correlations could be found betwen the water quality and lithology, depth or discharge from a well, even when they were considered sub-basin-wise within the Vedavati River Basin. In order to avoid spurious values only the chemical analytical results from borehole waters were correlated for the above purpose. This shows that the quality is not directly related to any simple or single factor.
4. The frequency histograms of the dissolved ions showed a skewed distribution. Only fluoride has an apparently normal distribution. If the plotting is done using their log values, normal distribution pattern is obtained. This fact, viz. the log normal distribution is very important for any statistical studies on the analytical data. Based on the log normal distribution the mean value of magnesium in the Vedavati Basin works out to 42 ppm whereas the raw data gives the value of 62 ppm which would not be correct.
5. The dispersal of fluoride in groundwaters is determined not by the amount of fluoride bearing minerals in the bulk rock. Bulk rock analysis of 8 samples gave the fluorides of 410 ppm to 1300 ppm. The waters in the nearby wells have 0.9 ppm-4 ppm of fluoride. But there was no significant correlation.

   Soil samples were collected and leachates using 1/4N acetic acid were obtained at 48 hours and 72 hours duration. A high correlation was observed between the fluoride content in the leachates and in the nearby tank waters. This clearly shows that the soil layer has an important role in determining the fluoride content in groundwater.

   In such a case, the tank catchment draining large areas should obviously have more fluoride in the tank water. This was in fact found to be so and in quite a few villages, the fluoride in the tank water was higher than in the groundwaters. There is also a scope for CaF_2 to precipitate if there is a higher calcium content in the soils.
6. The relationship between the flood discharge and the chemical quality of water was studied at two stream gauging sites within the Vedavati River Basin. It was usually found that an increase in discharge is accompanied by a dilution in the salinity. However, this relationship does not hold during the first floods following a long dry spell. The initial storms flush out more salts from the soils. In the lower reaches of the Vedavati Basin, the flood discharges and the quality of water are more complicated in their relationship because of the additional components of applied irrigation return waters, municipal sewage from nearby towns etc.
7. The rock-water interactions were studied carrying out the chemical analysis of the water samples at the site of collection itself as far as was possible. The silica content in the aqueous phase was found to be much less than what one would expect from the stoichiometric proportions of the reactions. The Na^+/Ca^{2+} and Na^+/Mg^{2+} ratios are higher in the groundwater than in the rocks. The Ca^{2+}/Mg^{2+} ratio is about the same in the waters that are draining both gneisses and schists even though the Ca^{2+}/Mg^{2+} is higher in gneisses than in schists (Figure 1).

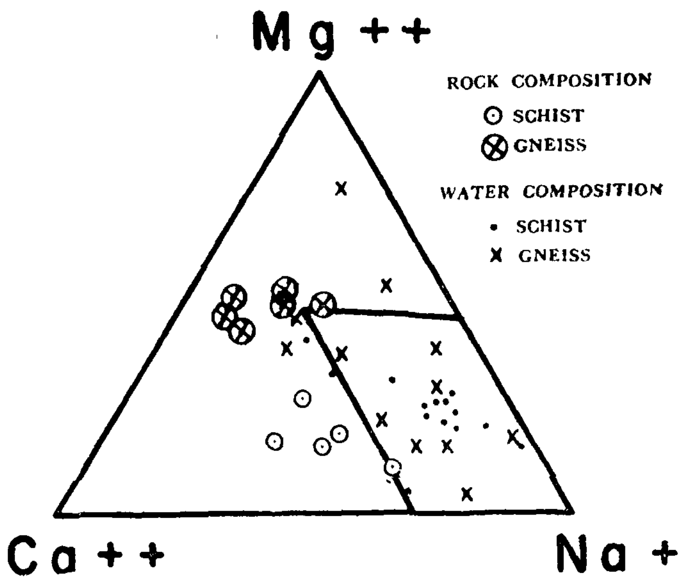

Figure 1.

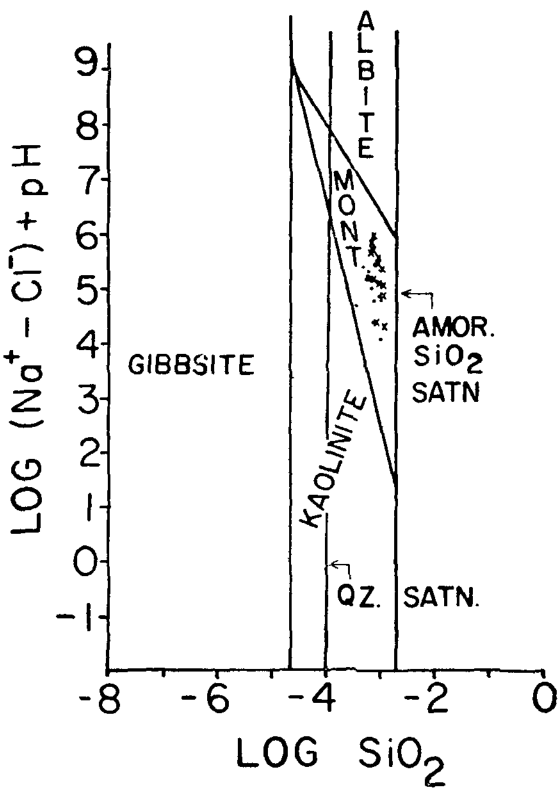

Figure 2. Water from schist (.), Gneiss (×)

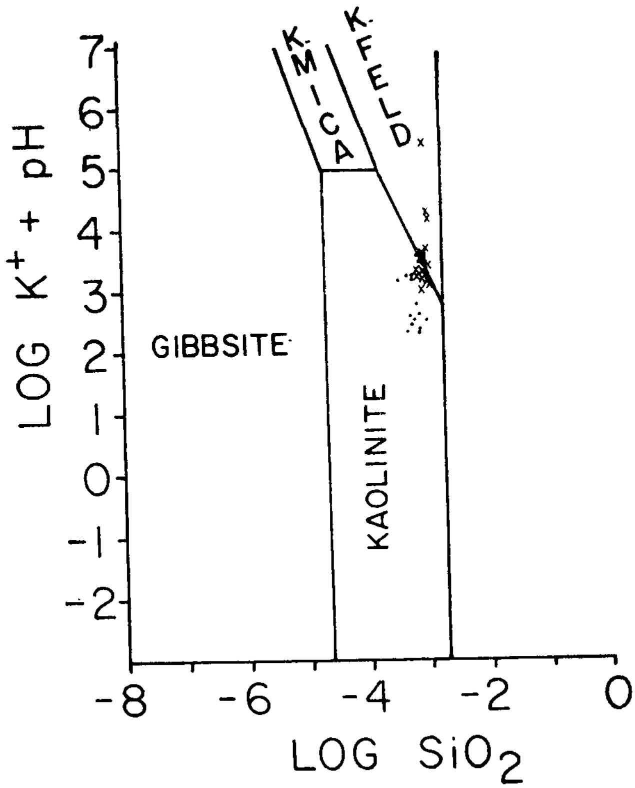

Figure 3. Water from schist (.), Gneiss (×).

8. The phase-diagrams were plotted using log (Na^+–Cl^-) + pH *vs* log SiO_2 and log K^+ + pH *vs* log SiO_2 bringing out the following important relations (Figures 2 and 3). The sodium silicate minerals are in equilibrium with montmorillonite. The K-silicate minerals show a distinction between those from gneisses and schists. The K-silicate minerals from gneisses fall on the boundary between K-feldspar and kaolinite fields and those from schists are in equilibrium with kaolinite.

9. The groundwater temperatures varied between 24°C and 31°C, the higher temperature being obtained towards the discharge end of the basin.

From the above facts it is more than clear that the prognosis of the water quality is not very easy and the available models are unable to adequately predict the water quality in a given area. Whether any teleological effects are also operative is an aspect to be investigated by the groundwater geochemists, beyond time-space-causation phenomena.