Mechanism of anomalous manifestations $\delta^{13}$C CO$_2$ underground water on Tashkent geodynamic range

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Abstract. The results of long-term isotope and gas measurements of various groundwater sources in the Tashkent artesian basin are presented. In addition to areal studies, the results of regime observations of selected wells at the Tashkent geodynamic test site are also presented to identify prognostic features as a precursor to strong earthquakes. The first results were obtained related to the manifestation of the Nazarbek earthquake on December 11, 1980, with a magnitude of 5.3, a source depth of 10 km. On the basis of this earthquake, the behavior of isotopic and gas precursors at the Ulugbek well, Tashkent geodynamic test site, was analyzed. A quantitative analysis was made of the anomalous manifestation of the gas and isotopic composition of groundwater in the Ulugbek borehole during the preparation and execution of the Nazarbek earthquake. Determination of CO$_2$ release from rock samples recovered from deep wells of the landfill made it possible to quantify the ratio of "background" CO$_2$ mixing from carbonate decomposition to anomalous. Judging by the obtained ratio, the rocks during the preparation of the earthquake should emit 2 times more carbon dioxide than the background CO$_2$. This was confirmed by observations of the CO$_2$ content in the well, when an increase in its relative concentration of 250% was recorded. The analysis of the $\delta^{13}$C time series, obtained as a result of long-term regime observations of the carbon isotopic composition of CO$_2$ in the groundwater of the Tashkent geodynamic test site, made it possible to identify significant anomalies in the carbon content.

1. Introduction

The analysis of the time series $\delta^{13}$C, obtained as a result of long-term monitoring of the carbon isotopic composition of CO$_2$ in the groundwater of the Tashkent geodynamic test site, made it possible to identify significant anomalies in the carbon content. In a number of cases, a synchronous change in the $\delta^{13}$C value is observed for all tested water points. In search of possible reasons for the occurrence of these anomalies, we were led to consider the variation of $\delta^{13}$C in connection with the seismic activity of the test site. As can be seen from Fig. 2, in the variations in the carbon isotopic composition in the groundwater of the observed wells, the time of occurrence of earthquakes is preceded by periods of CO$_2$ heavier carbon $^{13}$C. The duration of the manifestation of the $\delta^{13}$C anomaly can be considered as the period of preparation and occurrence of earthquakes. For example, during the Nazarbek earthquake (M = 5.3; H = 10 km; 12/11/1980) the duration of the anomaly was 250-280 days (9-10 months) before the event.

With the heavier CO$_2$ of groundwater in terms of carbon-13 in the periods preceding the earthquake, there is a general increase in the percentage of CO$_2$ (Fig. 2) in the gas composition in the
same water. This phenomenon can be associated with the processes of earthquake preparation (cracking, elastic deformation, changes in PT factors, acoustic and ultrasonic vibrations, etc.), which, most likely, contribute to the release of carbon dioxide from carbon-containing rocks, some change in hydrochemical processes in the system gas - water - rock, due to microinclusions of water-bearing rocks and, possibly, inflow along the fault from the depths.

2. Materials and methods

The results of hydrogeochemical studies on the problem of searching for precursors of strong earthquakes, which in recent years are a necessary part of the plans for scientific research in many countries of the world, carried out in seismically active zones, have been published in a number of monographic works and articles [1-13]. The study of the nature of hydrogeoseismological anomalies, the development of the foundations of the mechanism of formation of various classes of hydrogeochemical precursors and the identification of the most reliable and informative criteria that could be precursors of strong earthquakes are the main directions of our long-term research in the laboratory of Hydrogeoseismology of the Institute of Seismology of the Academy of Sciences of the Republic of Uzbekistan.

During the preparation of earthquakes, rocks experience significant elastic deformations, which, spreading into the environment, affect the course of physicochemical and hydrogeodynamic processes, which are expressed in fluctuations in the level, flow rate, chemical, gas and isotopic composition of groundwater. The latter, being a dynamic system, are sensitive to the influence of factors external to it, including deep ones.

Long-term regime observations made it possible to identify significant anomalies in the $^{13}$C content (carbon CO$_2$ becomes heavier to $-6 \div -8 \%$), which correlated with the manifested seismicity. Therefore, it became necessary to explain the nature of carbon dioxide, which participated in the formation of the precursor anomaly. For this purpose, the isotopic composition of carbon in the carbonate system CO$_2$ (gas) – CO$_2$ (plant) – HCO$_3^-$ – CO$_3^{2-}$ of the groundwater of the landfill was studied.

CO$_2$ is contained in groundwater in the following forms:

1. In the form of free (spontaneous) CO$_2$, which is released in the form of bubbles at normal atmospheric pressure.
2. In the form of dissolved carbon dioxide, which remains dissolved in water after being brought to atmospheric P and T conditions, as well as the chemically bound state of HCO$_3^-$ and CO$_2$.
3. CO$_2$ released from carbonates under certain P-T conditions (CaCO$_3$ → CaO + CO$_2$).

All these types of CO$_2$ make up a single carbonate system.

To differentiate by the isotopic composition of each of the CO$_2$ components and to find the main culprit responsible for the formation of anomalies, an experiment was set up to study the $\delta^{13}$C of each of the CO$_2$ components separately.

Phased studies of the isotopic composition of carbon in the gas - water - rock system were mainly carried out in the wells of the Tashkent geodynamic test site. Table 1 shows the $\delta^{13}$C values measured in CO$_2$ dissolved gas, bicarbonate ion and recovered from the rocks of various water points.

The distribution of carbon over these three states has a significant shift in isotopic composition (Figure 1). Judging by these data, it can be assumed that if the change in the isotopic composition proceeds to the left side of the system, then the $\delta^{13}$C CO$_2$ becomes heavier in terms of carbon-13, and in the opposite direction - to its lightening.

According to the theoretical calculations of S.I. Golyshov et al. [14] "... most carbonates at low temperatures are heavier in C than carbon dioxide". In the works of E. Uzdowski, M. Hoefs [15, 16], J. Sharan [17], J. Vogel, P.M. Groth, V.G. Moka [18], S.T. Reitmain, B.B. Hanshaw [19] and E.M. Galimov [20], the same tendency can also be traced. Indeed, as can be seen from the histograms, our studies also confirm that, under the condition of equilibrium, carbonate is heavier than its solution in relation to carbon-13.
\[ \text{CO}_2 - \text{HCO}_3^- = 8\%_\text{o}; \]
\[ \text{CaCO}_3 - \text{HCO}_3^- = 4\%_\text{o}; \]
\[ \text{CaCO}_3 - \text{CO}_2 = 12\%_\text{o}. \]

Many researchers believe that in a seismically quiet period, the reaction in the carbonate system proceeds to the right side, i.e. in the pores and cracks of rocks, carbonates are mainly formed, leading to the cementation of cracks and pores in the rocks, making it difficult for the dissolution and degassing of \( \text{CO}_2 \) from other sources of carbon dioxide. In this case, the observed value for \( \delta^{13}\text{C} \) in this period (called background) corresponds to the value of \( \delta^{13}\text{C} \) for free gas \( \text{CO}_2 \) in groundwater.

![Figure 1. Histogram of distribution of \( \delta^{13}\text{C} \) values of three states in the underground Tashkent geodynamic test site.](image)

**Table 1.** Isotopic composition of carbon in the gas-water-rock system in the underground waters of the Tashkent geodynamic test site.

| № | name of water points | № well | \( \delta^{13}\text{C}, \%_\text{o} \) |
|---|---------------------|--------|-----------------------------------|
| 1 | Galaba              | 3      | \( -18.0 \) \( -8.3 \)          |
| 2 | Buyuk ipak yuli     | 6      | \( -12.5 \) \( -9.2 \)          |
| 3 | Ulugbek             | 7      | \( -16.0 \) \( -11.7 \)         |
| 4 | Tashminsvu          | 1      | \( -13.2 \) \( -7.7 \)          |
| 5 | Fozilov             | 16a    | \( -12.0 \) \( -7.6 \)          |
| 6 | Fozilov             | 7T     | \( -15.4 \) \( -8.5 \)          |
| 7 | DVS                 | 5      | \( -14.3 \) \( -8.0 \)          |
| 8 | Gazalkent           | 5T     | \( -20.8 \) \( -14.0 \) \( -6.3; -8.7; -9.9 \) |
| 9 | Chinobad            | 9      | \( -16.2 \) \( -3.2 \)          |
| 10| TashGRES            | 13     | \( -15.7 \) \( -4.9 \)          |
| 11| Tekstilkombinat     | 11     | \( -19.2 \) \( -3.6 \)          |
| 12| Epicentral          | 12     | \( -16.0 \) \( -6.3; -8.7; -9.9 \) |
| 13| Nazarbek            | 1TN    | \( -20.6 \) \( -12.9 \) \( -5.0; -2.0 \) |

* - 48 measurements along the entire section of the well.
3. Results

The abnormal change in $\delta^{13}C$ corresponds to a heavier isotopic composition. An attempt at a quantitative analysis of the possible causes leading to abnormal changes in the concentration and isotopic composition of CO$_2$, separation of carbonates (CaCO$_3$), was carried out using data from well No. 7 (Figure 2). The background CO$_2$ concentration for this well is 5 vol.%, and $\delta^{13}C = -19$ ‰. The volume of the sample obtained from 5 liters of water was 100 ml. The results of chromatographic analysis (5 vol.% CO$_2$) show that 1 ml of carbon dioxide is extracted from 1 liter of well water. For an anomalous case, when the CO$_2$ concentration in the samples from the same well reaches about 12 vol.%, i.e. 2-2.5 times more than the background, respectively, 2-2.5 ml of CO$_2$ per 1 liter of water.

When analyzing, the most interesting is the calculation of the possibility of the water-bearing rock, i.e. how much CO$_2$ can be released when it decomposes? According to our experimental data, 1 g of rock sampled from the studied aquifer (Cenomanian), at 100% yield, emits 0.28 ml of CO$_2$ and, accordingly, from 1 cm$^3$ of rock ($\rho = 2.5$ g/cm$^3$) 0.71 cm$^3$ CO$_2$.

Research shows that the water-bearing rocks of the Tashkent artesian basin contain $1 \cdot 10^{-3}$ cm$^3$ CO$_2$ in 1 cm$^3$ of water, i.e. the same amount of CO$_2$ from 10 cm$^3$ of water-bearing rocks (at 10% porosity). Assuming rock is the main source of CO$_2$ in groundwater, only 14 g out of 1000 g of rock (i.e. 1.4%) should be decomposed while maintaining the background CO$_2$ concentration. However, under natural conditions, the source of CO$_2$ in groundwater is not only rock, but also other components, which reduces the ratio of rock participation in maintaining the background CO$_2$ concentration.

![Figure 2](image_url)

**Figure 2.** Variations in the content of CO$_2$ and isotopic composition of hydrocarbon in the water of well № 7 Tashkent geodynamic test site. The vertical line corresponds to the moment of the Nazarbek earthquake on December 11, 1980.

During the periods of earthquake preparation, an increase in CO$_2$ concentration was observed by 2-2.5 times relative to the background value. To provide such a quantity of dissolved CO$_2$ in groundwater, it is necessary to decompose about 30 g from 1000 g of rock, i.e. 3%.
4. Conclusions

Obviously, the precursor anomalies are the result of the mixing of carbon dioxide in the aquifer and CO$_2$ from the decomposition of carbonates. Determination of CO$_2$ release from rock samples extracted from deep wells of the landfill made it possible to quantitatively estimate the ratio of mixing of CO$_2$ "background" with isotopic composition $\delta^{13}C = -19\%$ and CO$_2$ from decomposition of carbonates with $\delta^{13}C = -4\%$ for anomaly $\delta^{13}C = 8\pm10\%$ as 1:2. Judging by the obtained ratio, the rocks during the preparation of the earthquake should emit 2 times more carbon dioxide than the background CO$_2$. This was confirmed by observations of the CO$_2$ content in the well, when an increase in its relative concentration of 250% was recorded.

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