Research Advances

The Source of Groundwater Recharge Based on Entropy Theory in the Arid Areas of North China

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Objective

Any natural system is constantly exchanging material, energy and information with the environment, and all these processes follow the basic law of thermodynamics, with no exception of groundwater recharge and discharge process. On the basis of the principle of the first law of thermodynamics, the reverse geochemical simulation method is widely used in the study of groundwater recharge, runoff and drainage process. However, some studies only consider the material conservation in the process, but ignore the probability of the transformation. The second law of thermodynamics specifies the direction of development and points out that any isolated system tends to develop in the direction of increasing entropy which can not occur in the opposite way. Introducing the entropy theory to the study of recharge and discharge relationship of the groundwater can make the process not only meet the conservation law but also meet the entropy theory which point out the direction of material transformation.

Methods

The material composition of the fluid itself and all kinds of material carried are related to the progress of supply, runoff and discharge. Ion concentration and isotopes in liquid must satisfy the second law of thermodynamics ($S \geq 0$) in the motor process. So Information entropy can be used to test the path, initial conditions and boundary conditions of the groundwater flow. Isotope, temperature, ion, conductance, fluorescence, pigment, microorganism, virus and bacteria can be used as information entropy in the fluid, which not only carries some characteristics of water source area, but also contains information about the interaction between water and rocks, isotopic exchange and dissolution. For a groundwater recharge and discharge progress with a preliminary initial boundary condition, once the recharge and discharge zones are determined, the entropy (S) of a single supply source to groundwater in the runoff process must meet the relationship: $\triangle S \geq 0$. If $\triangle S \leq 0$, it demonstrates that there must be another recharge flow. The emergence of negative entropy has become an important criterion to determine the groundwater recharge process and its boundary conditions.

Results

During the process of reverse geochemical modeling, plagioclase, dolomite, calcite, feldspar, illite, chlorite and gypsum are generally chosen as "possible mineral phase", while K, Na, Ca, Mg, C and S are chosen as constrained variables. However, in the application of the model, some researcheres did not identify the applicable conditions of underground water, and they contribute the change of Ca^{2+}, Mg^{2+} concentration to dissolution or precipitation of calcite, dolomite or gypsum rock. These views are to a certain extent not in accordance with the second law of thermodynamics. On the one hand, studies lasting for 200 years show that the dolomite is formed under high temperature condition, the temperature of dolomite inclusions in the Erdos Basin is about 104–368°C, and there is no scientific certification that the dolomite can be directly precipitated from natural water. On the other hand, $\delta^{13}C_{PDB}$ of CO_2 in the atmosphere is between −8% and −7%. If the calcite ($CaCO_3$) or dolomite (MgCa

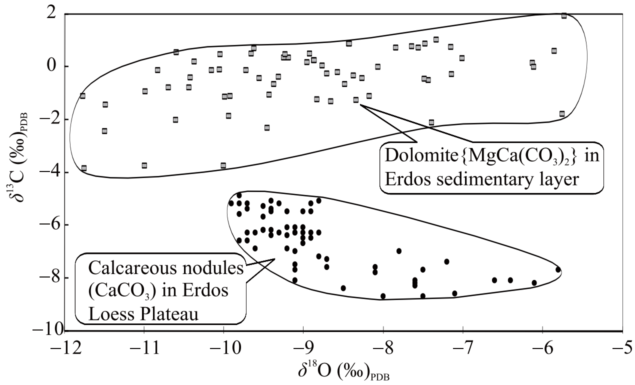

Fig. 1. Relationship between $\delta^{13}C$-$\delta^{18}O$ of dolomite and calcium in the Ordos Basin.

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$(CO_3)_2$) is dissolved by CO_2 from the atmosphere generating Ca^{2+}, Mg^{2+}, HCO_3^-, carbon isotope in CO_2 should have inevitable equilibrium fractionation, and the reformation dolomite should be depleted in ^{13}C. However, the truth is not so. CO_2 can also be derived from the deep strata. The CO_2 from the deep strata is enriched in $\delta^{13}C_{PDB}$ (−2% to 2% CO_2). If the calcite or dolomite is dissolved by CO_2 from the deep strata, generating Ca^{2+}, CO_3^{2-} then regenerated calcite, the regenerated calcite should be enriched in ^{13}C. Figure 1 indicates that the ^{13}C in calcite is obviously influenced by the precipitation, however. Although the inverse geochemical modeling method accords with the first law of thermodynamics, dolomite and ^{13}C values do not meet the second law of thermodynamics. Thus, the recharge and discharge relationship inferred from the dolomite diagenesis under normal temperature and the source of ^{13}C of calcite and dolomite is not consistent with the actual situation. The emergence of negative entropy indicates that the groundwater system in the Ordos Basin is not closed, and that there is external water supply to groundwater. The decrease of Mg^{2+} in the water is caused by the mixing of the low Mg^{2+} external water.

Conclusion

According to the second law of thermodynamics, reverse geochemical simulation on the groundwater recharge which is based on the first law of thermodynamics has been further constrained to meet the entropy and the first law of thermodynamics.

Acknowledgement

This work is granted by the National Natural Science Fund of China (Grant no. 51578212).