

$^{87}\text{Sr}/^{86}\text{Sr}$  Isotope Evolution Trend of Groundwater Resources in the Hebei Plain, Northern China

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**Abstract:** In Hebei plain, the most important source of water supply is groundwater, which as system, can be divided into 7 aquifers. In this study, major ion hydrochemistry and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios data were analyzed in order to understand strontium isotope evolution mechanism of groundwater in the Hebei plain. Based on integrated analysis, it is considered that the radiogenic Sr in groundwater from quaternary sediments (Q<sub>4</sub>-Q<sub>1</sub>) comes from the weathering of silicate mineral rich in Na and Rb. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios increase systematically with the increasing age and depth of groundwater, and this reflects “the accumulative effect of time” to water-rock interaction. Although the low  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of groundwater is associated with the low content of Rb in the rocks, further research is required to reveal its evolution mechanism. [The Journal Of American Science. 2007;3(4):1-6]. (ISSN: 1545-1003).

**Keywords:**  $^{87}\text{Sr}/^{86}\text{Sr}$  Isotope; Evolution Trend; Hebei Plain; China

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### Introduction

As natural tracers of groundwater flow, Strontium isotopes have been extensively used (Bullen et al. 1996; Frost et al. 2002) due to its geochemical characteristics. During recharge, groundwater acquires Sr and as it moves along its flow path it interacts with Sr-bearing minerals within geologic units. Therefore the chemical evolution of groundwater is a function of a variety of factors that include residence time, initial water composition, and differences in the distribution and reactivity of individual minerals. According to Ma and Liu (1999), the strontium isotope composition of groundwater is affected by recharge water chemistry, host rock geochemistry and water-rock interaction (WRI) in groundwater systems, the residence time of groundwater in the aquifer and mixing of different groundwaters. Since WRI has an important control on strontium enrichment, strontium isotope ratios have been widely used for investigating the WRI occurring in groundwater systems (Oetting et al. 1996; Armstrong et al. 1998; Woods et al. 2000). In addition, strontium isotope ratios frequently serve as tracers for delineating recharge sources and mixing processes in groundwater system; representative studies including Lyons et al. (1995), Katz and Bullen (1995), Gosselin et al (2004), and Wang et al (2006).

For Hebei Plain, deep groundwater is the most important source of water supply in the region. In this study, twenty three groundwater samples were collected in Hebei Plain, and strontium isotopes and major ion hydrochemistry used to identify hydrochemical processes and water-rock interaction in water system. The differences of Sr isotope composition reflect regional geologic control on water flow in the Plain, and the distribution characteristics for Sr isotope in groundwater system were discussed.

### Regional Hydrogeology

The Hebei Plain is one part of the great North China Plain located in the eastern part of the People's Republic of China. Hebei plain covers an area of  $6.19 \times 10^4 \text{ km}^2$  (lat.  $36^{\circ}06' \text{N}$  -  $39^{\circ}35' \text{N}$ , long.  $114^{\circ}26' \text{E}$  -  $117^{\circ}50' \text{E}$ ) and is bordered on the north by the Yanshan Mountains, on the east by Bohai Sea, on the south by the yellow river and on the west by the Taihang Mountains. The plain has a relatively low and gentle topography of no more than 100 meters above sea level in some places and less than 50 meters in most sections. However, it has many depressions, totaling about  $1,000 \text{ km}^2$ . In the northern part of the plain there is a depression area, which lies between Baoding and Dagu. Some well-known depressions, such as the Baiyangdian, Wenanwa and Dawa, are located in this area.

The Hubei plain lies in the temperate zone, with a continental monsoon climate. It is windy in the springs, hot and rainy in summers, and cold and dry in winters. The annual mean air temperature of the plain is  $12^{\circ}\text{C}$  to  $13^{\circ}\text{C}$ ; with the annual average rainfall of 400-800mm. The annual mean water surface evaporation is 1100-1800mm. The groundwater system of Hebei Plain is mainly from quaternary aquifers which can be divided into 7 groups, depending on the various depths as follows: (1) aquifer ( $Q_4$ ), 20-50m deep; (2) aquifer ( $Q_3$ ), 100-150m deep; (3) aquifer ( $Q_2$ ), 200-300m deep; (4) aquifer ( $Q_1$ ), 350-500m deep; (5) aquifer (N), 500-1000m deep; (6) aquifer (E), 1000-4000m deep; (7) aquifer (C and Z), also called "the old buried-ills groundwater", and up to 4000m deep.

### Materials and Methods

**Sampling:** A total of 23 groundwater samples from the wells were collected over the Hebei plain. These wells are either active municipal wells, domestic or agricultural wells equipped with sub-mersible pumps or windmills that penetrate different lithological units. The groundwater sampling locations are identified by the inventory numbers as shown in table 1. Just prior to sampling, the wells were pumped until at least three casing volumes were drawn away. At each location, samples filtered through  $0.45 \mu\text{m}$  membranes were obtained in three new 350 ml low-density polyethylene bottles well rinsed with deionised water before sampling. One of these three samples for the determination of metallic elements, was acidified with  $\text{HNO}_3$  until its pH was around 1.0; sufficient to stabilize trace metals. The second and third samples were unacidified and collected for the anions and strontium analyses respectively.

**Test method:** Temperature and pH values of the samples were determined in situ using portable Hanna pH meter which had been calibrated before use. Alkalinity was measured on the sampling day using the Gran titration method. Major anions and cations were determined using ion chromatography and ICP-AES with the precision of 0.01 mg/L. Strontium concentration measurements and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio analyses were completed at Yichang Institute of Geology and Mineral Resources. Dissolved  $\text{Sr}^{2+}$  was determined using a standard flame atomic absorption method. Strontium was isolated from each sample solution using conventional anion exchange chromatography (Dowex AG50- X8 resin). Strontium isotope ratios were measured on a Finnigan MAT 261 Thermal Ionisation Mass Spectrometer. Following internal normalization, results were corrected for fractionation against a monitored value of the NBS 987 standard of  $0.710221 \pm 0.000015$  ( $2\sigma$ ,  $n = 8$ ).

Table 1. Hydrochemical Properties, Major Ions and Strontium Isotope Composition of Water Samples from Hebei Plain (in mg/L except pH and  $^{87}\text{Sr}/^{86}\text{Sr}$ )

No.	Depth (m)	pH	$\text{HCO}_3^-$	$\text{SO}_4^{2-}$	$\text{Cl}^-$	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{K}^+\text{+Na}^+$	$\text{Sr}^{2+}$	$^{87}\text{Sr}/^{86}\text{Sr}$
Hb02	1600-1700	7.05	204.65	95.43	2236.57	105.36	15.28	1875.39	6.87	0.70864
Hb03	241.5-280	6.62	471.56	21.09	372.23	5.11	3.59	452.93	0.24	0.71220
Hb04	380	6.53	412.62	93.95	292.46	9.20	9.01	394.20	0.29	0.71268
Hb05	680	6.82	471.56	89.10	638.10	11.24	7.16	660.83	0.30	0.71077
Hb06	1150-1599	7.01	176.84	91.93	2539.11	95.05	13.45	1764.68	6.34	0.71075
Hb07	400	7.04	412.62	94.28	345.64	6.13	6.61	440.63	0.24	0.71340
Hb08	400	6.82	412.62	70.32	110.78	3.07	1.79	276.28	0.05	0.71393
Hb09	370	6.91	324.20	52.35	400.08	9.20	8.40	400.08	0.21	0.71409
Hb10	350	6.93	294.73	101.92	664.69	25.55	22.18	565.05	0.82	0.71288
Hb11	>300	6.84	442.09	84.92	141.80	3.07	3.00	315.33	0.08	0.71319
Hb12	>300	7.52	442.09	86.79	137.37	6.13	8.43	298.18	0.24	0.71234
Hb13	360	7.52	265.25	47.89	159.53	5.11	5.41	228.60	0.09	0.71324
Hb14	360	7.55	265.25	45.77	66.47	4.09	1.77	170.63	0.17	0.71527
Hb15	350	7.06	147.36	55.52	132.94	5.11	1.76	173.03	0.10	0.71221
Hb16	500	6.51	501.04	8.50	447.56	8.18	5.98	502.83	0.28	0.71251
Hb17	380	6.52	235.78	43.32	93.06	3.07	2.39	176.03	0.09	0.71452
Hb18	2571-2694	7.05	1098.22	24.36	3024.21	284.26	30.25	2145.89	7.04	0.71114
Hb19	370	6.58	206.31	84.68	177.25	7.15	3.56	237.35	0.20	0.71260
Hb20	300	6.59	176.84	60.42	110.78	5.11	1.76	172.03	0.20	0.71251
Hb21	1100	7.03	1178.91	21.95	3500.69	295.37	33.55	2525.68	11.36	0.70902
HB27	240	7.03	383.14	136.12	48.74	62.34	1.08	182.20	0.36	0.71153
Hb28	350	7.01	147.36	78.19	101.92	26.57	11.84	115.45	1.17	0.71156
Hb29	370	7.05	442.09	1.63	159.53	3.07	3.00	284.48	0.14	0.70912

## Results and Discussion

**Strontium and major ion chemistry:** The positive correlation between  $[\text{Sr}^{2+}]$  and  $[\text{Cl}^-]$  in groundwater samples indicates that subsequent evaporation causes the increase in  $[\text{Cl}^-]$  and an approximately proportionate increase in  $[\text{Sr}^{2+}]$  (Fig.1). However, the  $[\text{Sr}^{2+}]/[\text{Cl}^-]$  ratio of each groundwater sample is significantly higher than that of seawater (Fig.2), and this is particularly noticeable at the dilute end of the spectrum. Since there are no chloride-bearing minerals in the plain, dissolved  $\text{Cl}^-$  is thought of to be conservative and controlled only by evapo-transpiration. Therefore, the  $[\text{Sr}^{2+}]/[\text{Cl}^-]$  ratio reflects an excess of  $[\text{Sr}^{2+}]$  in the groundwater. The  $[\text{Sr}^{2+}]/[\text{Na}^+]$  ratio of the most dilute groundwater samples show no obvious correlation with increasing  $[\text{Cl}^-]$  (Fig.3). Because  $\text{Sr}^{2+}$  can be derived from weathering of carbonate, sulphate and silicate minerals, and since  $\text{Na}^+$  predominantly comes from silicates; variations in the  $[\text{Sr}^{2+}]/[\text{Na}^+]$  ratio may be indicative of the relative importance of these reactions in determining solute compositions. This low  $[\text{Sr}^{2+}]/[\text{Na}^+]$  tends to be associated with Na-silicate minerals, whereas high  $[\text{Sr}^{2+}]/[\text{Na}^+]$  are associated with carbonate dissolution.

**Strontium and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio:** The relation between  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $[\text{Sr}^{2+}]$  is shown in Fig.4, and the groundwater samples can be divided into three groups:

(1) Middle  $\text{Sr}^{2+}$ , high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio groundwater (group I). This group of groundwater can also be divided into two types based on the difference of strontium concentration. The groundwater samples with high  $\text{Sr}^{2+}$  (type A) mostly distribute in piedmont area, which is the recharge area of the plain groundwater

system. Lateral recharge is an important recharge source to above groundwater (type A), and the recharge water possibly flows across the metamorphic rocks regions and igneous rocks region with high Rb content. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of groundwater samples with low  $\text{Sr}^{2+}$  (type B) are related to the water's age. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios show a systematic increase with the increasing age and depth of groundwater, and this reflects "the accumulative effect of time" to water-rock interaction.

(2) Low  $\text{Sr}^{2+}$ , high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio groundwater (group II). This group of groundwater is distributed in the center of Hebei Plain. The low  $\text{Sr}^{2+}$  is relative to the rocks with low Sr content, and the high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is relative to the groundwater with old age.

(3) High  $[\text{Sr}^{2+}]$ , low  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio groundwater (group III). The host lithology for this type of water is limestone of Ordovician age since the high Sr content and low  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of these waters is a direct reflection of those characteristics in the limestone. The high Sr content for this water is due to high temperature, which increased the solubility of Sr. however, it is difficult to explain the low  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in these samples.

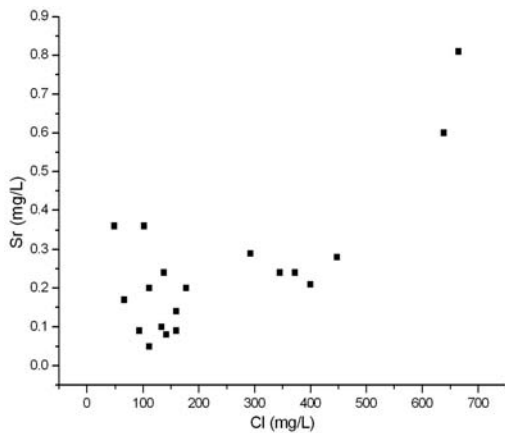


Figure 1. Relationship between  $\text{Cl}^-$  and  $\text{Sr}^{2+}$

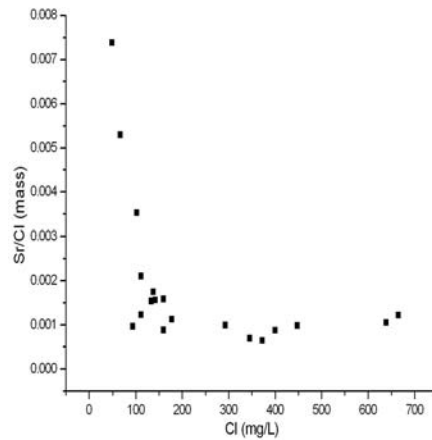


Figure 2. Relationship between  $\text{Cl}^-$  and  $[\text{Sr}^{2+}]/[\text{Cl}^-]$

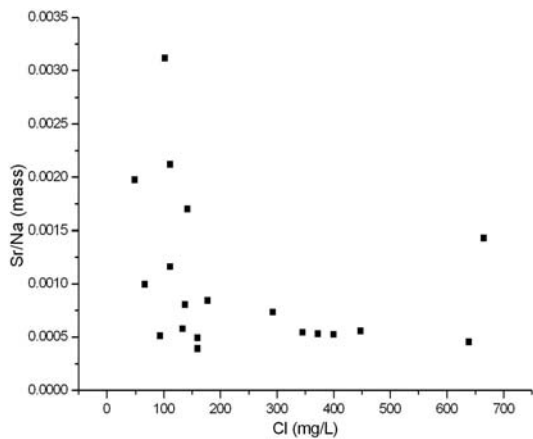


Figure 3. Relationship between  $\text{Cl}^-$  and  $[\text{Sr}^{2+}]/[\text{Na}^+]$

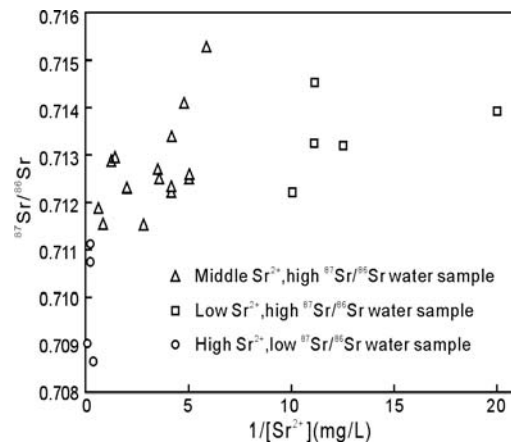


Figure 4. Relationship between  $[\text{Sr}^{2+}]$  and  $^{87}\text{Sr}/^{86}\text{Sr}$

### Conclusion

$^{87}\text{Sr}/^{86}\text{Sr}$  compositions of Hebei Plain groundwater samples are higher than the values of seawater ( $0.709073 \pm 0.000003$ ). These data all reflect groundwater interactions with marine carbonates and/or silicate minerals with slightly higher  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios than the carbonates. These  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios therefore provide compelling evidence that weathering of old silicate minerals (which have high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios) in a sedimentary environment is an important source of major ions (especially  $\text{Na}^+$  and  $\text{HCO}_3^-$ ) and dissolved silica in this groundwater system. However, no explanation is available for waters with low  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios; hence further research is needed to reveal the formation mechanism of these waters. Above all, there are three possible sources of  $[\text{Sr}^{2+}]$  to groundwater in the Hebei Plain:

- (1)  $[\text{Sr}^{2+}]$  delivered via atmospheric aerosols dissolved in rainfall;
- (2)  $[\text{Sr}^{2+}]$  derived from dry fallout associated with salts, carbonates and silicates from outside the plain; and
- (3)  $[\text{Sr}^{2+}]$  released from minerals during weathering within the soil zone or aquifer. These processes are believed to have occurred at the initial stage of groundwater chemical evolution.

### Acknowledgements

This research work was financially supported by National Science Foundation of China (NSFC-40602030, 40572140), the Research Award Program for Outstanding Young Teachers of China University of Geosciences (Wuhan) (CUGQNL0608), and China Geological Survey (CGS-200320150002).

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**Received:** 9/3/2007

### References

1. Armstrong SC, Sturchio NC, Hendry MJ. Strontium isotopic evidence on the chemical evolution of pore waters in the Milk River Aquifer, Alberta, Canada. *Applied Geochemistry*. 1998; 13: 463-475.
2. Bullen TD, Krabbenhoft DP, Kendall C. Kinetic and mineralogic controls on the evolution of groundwater chemistry and  $^{87}\text{Sr}/^{86}\text{Sr}$  in a sandy silicate aquifer, northern Wisconsin, USA. *Geochim. Cosmochim. Acta*. 1996; 60: 1807-1822.
3. Frost CD, Pearson BN, Ogle KM. Sr isotope tracing of aquifer interactions in an area of accelerating coal-bed methane production. *Geology*. 2002; 30: 923-926.
4. Gosselin DC, Harvey FE, Frost C. Strontium isotope geochemistry of groundwater in the central part of the Dakota (Great Plains) aquifer, USA. *Applied Geochemistry*. 2004; 19: 359-377.
5. Katz BG, Bullen TD. The combined use of  $^{87}\text{Sr}/^{86}\text{Sr}$  and carbon and water isotopes to study the hydrochemical interaction between groundwater and lakewater in mantled karst. *Geochim. Cosmochim. Acta*. 1996;60 (24): 5075-5087.
6. Lyons WB, Tyler SW, Gaudette HE. The use of strontium isotopes in determining groundwater mixing and brine fingering in a playa spring zone, Lake Tyrrell, Australia. *Journal of Hydrology*. 1995 ; 167: 225-239.
7. Ma Y, Liu C. Using strontium isotopes to trace nutrient element circulation and hydrochemical evolution within an ecosystem. *Advance in Earth Sciences*. 1999;14 (4): 377-382. (In Chinese with English abstract).
8. Oetting GC, Banner JL, Sharp JM. Regional controls on the geochemical evolution of saline

10. groundwaters in the Edwards aquifer, central Texas. *Journal of Hydrology*. 1996; 18: 251-283.
11. Wang YX, Guo QH, Su CL. Strontium isotope characterization and major ion geochemistry of karst water flow, Shentou, northern China. *Journal of Hydrology*. 2006; 328: 592-603.
12. Woods TL, Fullagar PD, Spruill RK. Strontium isotopes and major elements as tracers of ground water evolution: examples from the upper Castle Hayne Aquifer of North Carolina. *Ground Water*. 2000; 38 (5): 762-771.