

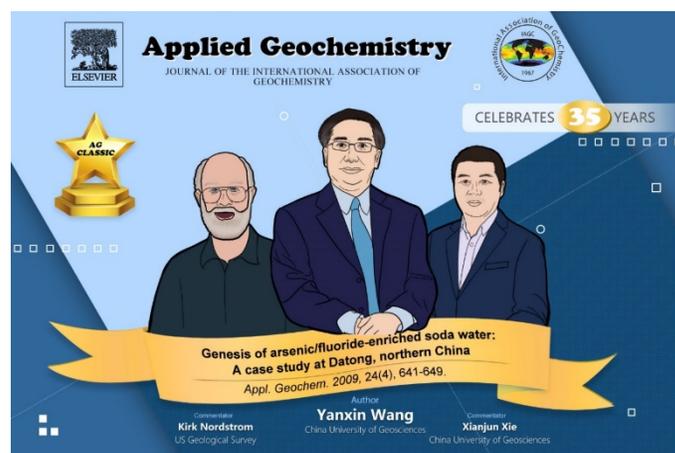
AG Classics

International Association of Geochemistry (IAGC)

Wang, Y., Shvartsev, S. L., & Su, C. (2009). Genesis of arsenic/fluoride-enriched soda water: a case study at Datong, northern China. *Applied Geochemistry*, 24(4), 641-649.

About AG Classics

The celebration of 35 years is a great moment to reflect on *Applied Geochemistry's* publication milestones, which often shaped their respective research areas. In our special program "AG Classics," we select and highlight those key publications. When possible, the journal will invite authors and a few commentators, who work in the same area and might have been influenced by the paper, to create a virtual panel discussion to present their perspectives on the evolution of the topic and identify the current frontiers, knowledge gaps, and research needs. We anticipate that this initiative will engage researchers all over the world with various backgrounds and eventually present valuable documentation of the journal's history and the discipline of geochemistry at large.



Q1. What was the opportunity to study the genesis of soda water when this paper was published in 2009?

Yanxin: Soda water is one of the four types of classification of natural waters proposed by Prof. Sulina, a Russian hydrogeochemist. However, both of the two previous major theoretical explanations could not fully unravel the genesis of soda waters: the first hypothesis indicated soda water as a result of silicate hydrolysis especially the dissolution of Na-feldspar cannot explain why Na is selectively enriched in the aqueous phase; while the second hypothesis proposed soda water formed via cation exchange cannot explain why HCO_3^- becomes the major anion in these waters. When Prof. Shvartsev and I conducted the research on high As and/or F groundwaters at Datong Basin, we found that most of these groundwaters are

This issue of *AG Classics* is a conversation with Yanxin Wang, Kirk Nordstrom, and Xianjun Xie. **Yanxin Wang** is lead author of the 2009 AG paper "Genesis of arsenic/fluoride-enriched soda water: a case study at Datong, northern China" and Professor and President, China University of Geosciences (Wuhan), and IAGC Fellow. **Kirk Nordstrom** is a Senior Scientist (Emeritus) at the US Geological Survey, IAGC Fellow, and GSA Birdsall-Dreiss Distinguished Lecturer. **Xianjun Xie** is a Professor at China University of Geosciences (Wuhan) and Associate Editor of *AG*.

soda waters, and thus we decided to collaborate on the research of the genesis of soda water.

In this paper, we proposed that the occurrence of soda water is the result of incongruent dissolution of aluminosilicates at one stage of their interaction with groundwater when the water is oversaturated with respect to calcite and evapotranspiration-related salt accumulation is not too strong. Such a model of soda water genesis has a universal environmental application and could be applied in similar regions worldwide.

Q2. Why and how did you initiate the collaboration with Professor Stepan L. Shvartsev of Russia?

Yanxin: I watched some former Soviet Union's films and read a lot of literary works of Russian writers such as Pushkin, Tolstoy, and Chekhov in the elementary and middle school, and was eager to have a chance to visit the vast terrain of Russia someday. Therefore, without any hesitation, I selected Russian as my second foreign language course when I studied at Nanjing University as an undergraduate student. Coincidentally, when I studied as a graduate student of Professor Zhaoli Shen at China University of Geosciences, he was the leading hydrogeochemist in China who obtained his *Kandidat* degree from Moscow Institute of Geology in 1960s. Thus, I read a lot of Russian professional literatures during my graduate period. When I went abroad for the first time in 1990, I went to Irkutsk and cooperated with Russian scholars to carry out geothermal research in the Baikal and Shanxi Rifted Systems. From then on, I have kept a long-term cooperation with Russian scholars and maintained close relationship with the Russian academia.

Professor Shvartsev is a well-known hydrogeochemist in Russia, whose main contribution is to clarify the groundwater evolution in the biosphere and to interpret the genesis of natural waters from the perspective of water-rock interaction. He is the first and lead author of the *Hydrogeochemistry Volume (1982)* as one

of the six-volume *The Principles of Hydrogeology* series books published in 1980s, the second author and also the editor-in-chief is Professor E. V. Pinneker of the Siberian Branch of Russian Academy of Sciences (RAS), a correspondence academician of RAS. These six-volume publications marked the emergence of the "Siberian School" in the field of hydrogeology which inherited the academic idea of V. I. Vernadsky (Figure 2), and emphasizes a unifying, holistic concept and water-rock interaction research on groundwater in hydrosphere.

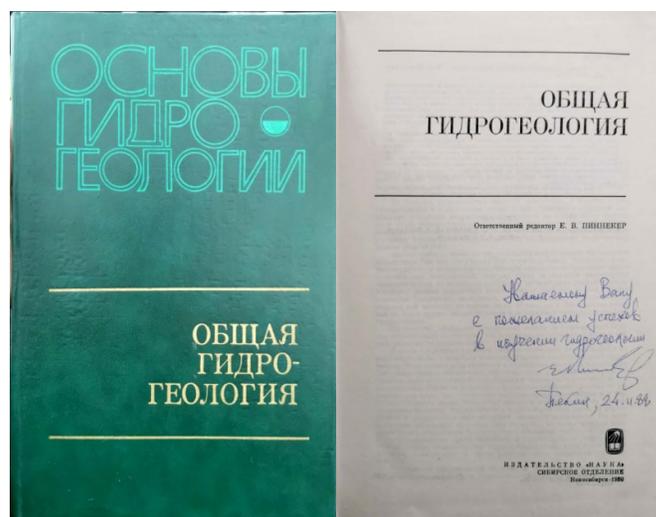


Figure 1. The cover of the first volume *General Hydrogeology* (1980) (left) of the six-volume *The Principles of Hydrogeology* series books, and the remarks by the editor-in-chief and Russian academician Professor Pinneker on the title page (right): "Dear Wang, I wish you success in hydrogeology studies, Beijing, 24 November 1988"

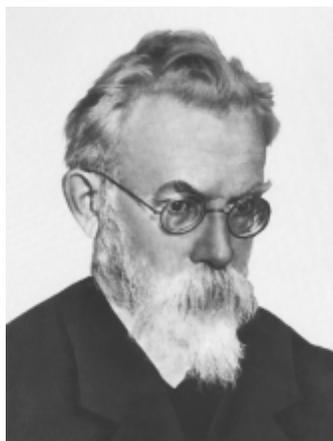


Figure 2. One of the founders of hydrogeochemistry, V. I. Vernadsky (1863-1945)

In November 1999, I invited Professor Shvartsev to give lectures in China (Figure 3-4). When our collaborated project was approved jointly by NSFC and RFBR in 2000, I invited Professor Shvartsev to China again and to participate in the International Conference on Hydrogeology and Environment sponsored by China University of Geosciences, Wuhan (Figure 5). After the conference, we carried out a field trip together. In the following years, we invited each other several times for lectures and joint field investigations, and our photographs were included in the book "70-Year History of the Department of Hydrogeology and Engineering Geology at Tomsk Polytechnic University" (Figure 6).



Figure 3. By the invitation of Professor Yanxin Wang (second row, first from the right), Professor Shvartsev (third row, third

from the right) visited China in 1999. The photo was taken with Professor Zhaoli Shen (front row on the right) and his group after a lecture at China University of Geosciences, Beijing. The photograph was included in the book Progress in Hydrogeochemical Research

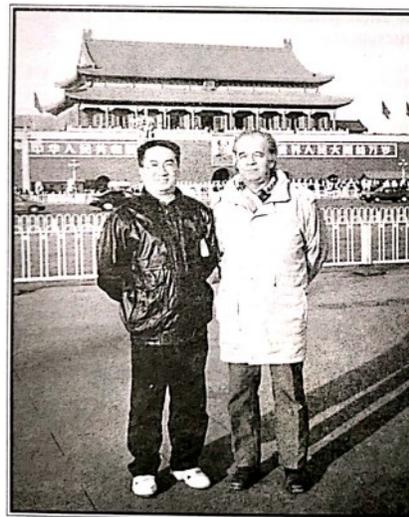


Figure 4. Professor Yanxin Wang (left) and Professor Shvartsev (right) visiting Tian'anmen Square, Beijing, in 1999



Figure 5. In 2000, Professor Shvartsev (second row, fifth from left) and his wife (second row, fourth from left) were invited by Professor Yanxin Wang (second row, third from left) to attend the International Conference on Hydrogeology and Environment hosted in China University of Geosciences, Wuhan.



Figure 6. The cover of the book “70-Year History of the Department of Hydrogeology and Engineering Geology at Tomsk Polytechnic University”

Q3. Is there any interesting story behind this article? Why did you choose to publish in Applied Geochemistry?

Yanxin: I clearly remember when we went to the field trip together with graduate students at Datong Basin, Shanxi, China in a freezing cold winter, the working conditions in the rural areas were harsh at that time. I really admire Professor Shvartsev's optimism and generosity, and he was very fond of Chinese cuisine. He insisted on speaking English with me although he was not very good at it, and only spoke Russian when he could not express himself well in English. Despite being a well-known expert and more than 30 years older than me, he was quite humble and approachable and turned the tough field work into a pleasant journey of scientific exploration. When the hydrochemical data were available, we analyzed the data together, and by 2006 we decided to use the hydrogeochemical data set obtained from 2004-2005 field campaigns to write this paper together with my former graduate student Dr. Chunli Su. It took us two years to revise it over and over

again, and the paper was finally published online at AG at the end of 2008. There were two reasons for choosing to publish on AG: Firstly, the journal is professional in the hydrogeochemistry field, and secondly, the peer reviewing of the journal is of high quality with the contribution of strictly selected reviewers.

Q4. What position and career stage were you in at the time of the publication of the paper? Does this article have a further implication for your follow-up research?

Yanxin: I was just granted a project for Distinguished Young Scholars of National Science Foundation of China in 2004 which focused on the genesis of high arsenic groundwater. After that, I was granted a project for the "Environmental Hydrogeology" Innovative Research Group of NSFC in 2015, still focusing on geogenic contaminated groundwaters (GCGs), with expanded research targets covering arsenic, fluoride and iodine in groundwater, and expanded case study areas in the Yellow River basins and the Haihe River basins to the Yangtze River basins.

To a certain extent, this paper has laid the foundation of our understanding for the genesis of GCGs. Since then, we have further carried out interdisciplinary systematic research on GCGs by integrating approaches of trace element and non-traditional isotope geochemistry, sedimentology, and geomicrobiology. The importance of hydrogeological conditions (including meteorological conditions) and water-rock interaction for groundwater chemistry emphasized in this paper has always been the focus of attention in our follow-up researches.

By 2020, we propose four basic genetic types of GCGs: leaching-enrichment type, burial-dissolution type, compaction-release type, and evaporation-concentration type. This theoretical framework of four basic types for the first time unifies the theories concerning the genesis of different types of GCGs, which

have been supported by worldwide multidisciplinary evidences of hydrodynamics, hydrochemistry, isotope geochemistry and numerical simulation, and has thus significantly improved our understanding and capability of predicting their spatial and temporal distribution, which provides theoretical and technological support for sustainable safe supply of drinking water.

Q5. Would you like to share some viewpoints about international research collaborations? And messages to young scholars in the field?

Yanxin: I think we should always strengthen rather than weaken international research collaboration. Without opening up to the outside world and international cooperation, there cannot be great successes in China like today. Under the current stressful international circumstance along with the pandemic, great importance must be attached than ever to international cooperation, especially the cooperation with Russia. However, there is very few researchers proficient in Russian among the young generations of Chinese scholars, we should send more young scholars to Russia for study and cooperation. I have three suggestions for young scholars: (1) read more literature, not only the recent publications, but also the classic ones, which could help understand the history and development of your discipline; (2) to consciously seek the opportunity for collaborating with the first-class international institutions or scholars like Professor Shvartsev; (3) be sure to overcome the language barrier as early as possible.

A conversation with Kirk Nordstrom, commentator

Q1. How do researchers understand the genesis of soda water before the paper published in 2009? And what is the significance of this paper in the field of hydrogeochemistry?

Kirk: The understanding of the processes leading to soda water formation in the U.S., or what we refer to as Na-HCO₃ water, gradually developed over several decades as more wells and deeper wells were drilled, and obtained groundwater samples from along dominant flow lines within the same aquifer, and the analytical chemistry of water improved. In the latter half of the 19th century, data from Europe and North America mention the occurrence of carbonated groundwaters with occasionally elevated arsenic and fluoride concentrations (e.g. F.W. Clarke, 1908, *The Data of Geochemistry*, p. 149). By the 1940s, USGS researchers identified that aquifers in the Atlantic Coastal Plain typically evolved from dilute Ca-HCO₃ waters in recharge areas to Na-HCO₃ waters in down-gradient, discharge areas, a process often called “freshening.” Fluoride was often highly elevated in these Na-HCO₃ waters. The change in major cation concentrations were recognized as cation exchange, chiefly Ca-Na exchange, as freshwater flowed through marine sediments with substantial exchange capacity. Additional CO₂ from organic matter in the sediments contributed to the bicarbonate alkalinity and promoted calcite precipitation, removing more calcium from solution. These processes have now been modeled and can simulate the observed chemical evolution, thus corroborating the initial interpretations. Another type of recognized Na-HCO₃ water has a somewhat different origin. Substantial amounts of CO₂ occasionally arise from depth caused by geothermal activity or degradation of a large reservoir of organic matter (e.g. oil or coal deposits). Elevated CO₂ increases the weathering rate of plagioclase feldspars, especially sodic-rich feldspars, to form Na-HCO₃ water, like Prof. Wang’s interpretation for Datong Basin. There is little or no cation exchange, but the resultant calcite precipitation, soda water formation, high pH, and high fluoride and sometimes high arsenic is the same as found in the U.S. Atlantic Coastal Plain.

The importance of Prof. Wang's paper is that the Datong basin is not like Atlantic Coastal Plain aquifers in the U.S. The shallow sedimentary aquifers in Datong are recent (Quaternary) and generally flat-lying as they are filling in a rift zone, the climate is arid to semi-arid, the potentiometric surface is flatter, and evaporation and soil salinization play a greater role. His group have successfully applied water analyses to interpret the effect of these processes on the genesis of elevated arsenic and fluoride in a part of China where the population that is suffering from the toxic consequences of these elements.

Q2. Could you tell us about your impressions of Professor Wang and Professor Shvartsev?

Kirk: Unfortunately, I have had only a few very brief opportunities to meet Prof. Shvartsev at WRI meetings, but his reputation is well known in the field of aqueous geochemistry. I was certainly aware of his contributions well before I met him for the first time. I knew nothing about Prof. Wang before my first trip to China in 2006 for the IAGC meeting in Beijing. Following the meeting, he had invited me to join with Dr. Oleg Chudaev and his wife Valentina on a field trip to Wudalianchi World Heritage Park in very northern China. For me, it was an extraordinary opportunity to visit Harbin, Wudalianchi, and the Hydrogeological Institute of Heilongjiang. On several return visits to China I spent time in Wuhan giving lectures and meeting with Prof. Wang and his students and post-docs. I was quite impressed with his students and his keen interest in education and giving students the opportunity to interact with scientists from the West. To my pleasant surprise, I discovered Yanxin to be well-read in classical (non-scientific) literature, especially philosophy. It is rare to meet someone in the sciences or engineering fields who is equally versed in the broader picture of why we do what we do. Whenever I go back to Wuhan, I reread the Tao Te Ching in case he decides to test me on it again.

Q3. Would you like to talk about the contributions of former Soviet scholars and Chinese scholars to the field of hydrogeochemistry, respectively?

Kirk: Perhaps this is a good moment to mention that Russian geochemists had a hand in introducing me, indirectly, to the field of geochemistry. I was a chemistry major as a university undergraduate with no particular affinity for any aspect of chemistry. Early in my junior year I was browsing through some books in the chemistry section of the library and 3 books caught my attention – Fersman's "Geochemistry," Vernadsky's "Geochemistry," and Garrels and Christ's "Solutions, Minerals, and Equilibria." For the first time I realized there was a field of geochemistry and that this is the field I wanted to study.

I have had the great honor of knowing personally, for nearly 40 years, Boris Ryzhenko of the Vernadsky Institute. His scholarly contributions with Stanislav Kraynov, Igor Khodakovsky, and many others are legendary. I first met Dr. Kraynov and Dr. Ryzhenko in 1982 at a meeting on Geochemistry of Natural Waters in Rostov-on-Don. Of course, I had no idea at the time that Kraynov, Ryzhenko, and Shvets were to become authors of the most important book in Russian hydrogeochemistry, "Geochemistry of Groundwater," published in 2nd edition in 2012. Dr. Khodakovsky was also one of the best geochemical thermodynamicists I have ever met. Every time I met him, he had some new ideas about how to compile and evaluate thermodynamic data for mineral reactions. In many ways he was ahead of his time in this important field of water-rock interactions. I gradually learned of Igor's contributions to other areas such as cosmochemistry. I was amazed at his energy and relentless pursuit of his scientific interests. The other outstanding Russian hydrogeochemist whom I know is Dr. Oleg Chudaev. He contributed greatly to improving the facilities at the Far Eastern Geological Institute in Vladivostok and made many contributions in groundwater geochemistry, especially thermal water geochemistry. The Kuriles Islands were one of his field

laboratories where he continued a long-standing Russian tradition of interpreting water-rock interactions at high temperatures in this remote island-arc of active volcanoes.

Among Chinese scholars, it was through meeting and getting to know Prof. Wang that I had the opportunity to meet scholars at CUG Beijing, Chinese Academy of Sciences Beijing, and Nanjing University. I had met the well-known hydrogeochemist Prof. Yan Zheng when she was still teaching at Queens College before she accepted a position in Environmental Science and Engineering at South University of Science and Technology (SUSTech) in Shenzhen. Her perspectives on Western and Eastern science and engineering, especially her knowledge of arsenic geochemistry brings considerable strength to SUSTech. My only regret is that I did not have more time to meet with these famous academicians and their students. The breadth and depth of Chinese scholarship in hydrogeochemistry has exploded from the end of the last millennium into this one. It is an extremely important research area, especially in China where rapid exploitation of groundwater resources has led to deleterious consequences for many residents because of water quality contaminants such as arsenic and fluorine as well as loss of long-term groundwater supply.

Q4: Do you have any interesting stories and experiences to share about international collaborations?

Kirk: Sure. My first international collaboration was on the International Stripa Project, roughly 1980-1990. The hydrogeochemical group involved researchers from Canada, Germany, France, Sweden, Switzerland, the UK, and the USA. The purpose of the project was to test the properties of a deep granite as a possible repository for high-level radioactive waste. The site was a recently abandoned iron ore mine in central Sweden which was renovated for numerous physical, chemical, and engineering tests.

When I joined this group and attended my first meeting at IAEA in Vienna (1982), I learned that chloride concentrations were unexpectedly high (up to 700 mg/L) in the deep groundwaters with no obvious source of the halogen. The running hypotheses were modern seawater intrusion, ancient seawater intrusion, dissolution of evaporite beds, and leakage from fluid inclusions in the granite. I quickly responded that fluid inclusions were highly unlikely, and I could easily prove that because I knew the USGS had equipment to crush crystalline rock and leach the fluid inclusions from them for analysis. All I needed to do was to compare the Br/Cl ratio of the leached fluid inclusions with the ratio from groundwater analyses. I proceeded with the project and I had a student helping with the analyses who brought the first Br/Cl sample results to me. The ratio was distinctly different from seawater and identical to the groundwater ratio. I told her to go back and do ten more samples. More results confirmed the initial finding. Suddenly, against my intuition, fluid inclusion leakage became a viable hypothesis. Furthermore, there were no known evaporite beds in the vicinity of the granite. The other group members were mostly isotope hydrologists and did not seem to appreciate the abundance of fluid inclusions in granites and their high salinity. I even enlisted Werner Giggenbach who happened to attend our meetings because he had accepted a temporary position at IAEA at that time. He tried to convince me that these were just normal low-temperature groundwaters. I badgered him enough that he submitted our groundwater analyses to his geothermal mineral equilibria program to prove to me that the major ions do not indicate high-temperature reactions. Within 2 minutes, this famous geothermal chemist completely changed his mind and agreed with me. He then tried to explain the import of his calculations to the rest of the group, but they did not seem to appreciate what he was saying. For me, it was a whole new and unexpected line of research from which new ideas were born. It also demonstrated how

the solutes in a groundwater could be of a completely different age (many millions of years) than the water itself (hundreds to thousands of years), a fact not often appreciated by hydrogeologists. That whole experience was one I never forgot.

Starting with the Stripa experience and seeing the recurrence in both national and international projects, I found that there is a serious divide between scientists and engineers in how they perceive environmental problems and their solution. This divide is somewhat broken down in environmental science and engineering departments which are much more common than they used to be. Science seeks to understand the driving phenomena behind the physical-chemical world whereas engineering seeks to solve environmental problems and not waste time trying to fully understand them. The best solutions to environmental problems are reached when scientists and engineers work side by side, properly respecting each other's knowledge and skills, to protect and improve our environmental quality. In the few instances where I have seen such cooperation, the best results were produced.

A conversation with Prof. Xianjun Xie, commentator

Q1. Do you still remember the circumstances the first time you read this article?

Xianjun: I was also conducting research on high arsenic groundwater at Datong Basin when the first time I read this article. At that time, despite a huge amount of international researches on the mechanisms of arsenic mobilization, there was still controversy about the genesis of high arsenic groundwater. This article not only gives us a comprehensive understanding for the genesis of soda water, but also provides new insights for geochemical constraints on the enrichment of As and/or F in groundwater since most of the high As and/or F groundwaters are soda waters.

Q2. How did the knowledge learned from this article shape your professional career afterwards, e.g., Do you hold the momentum to continue working on arsenic contamination problem?

Xianjun: This article discusses the genesis of soda waters and its significant control on As and F enrichment in the aquifer system, which greatly strengthens my conviction on continuing the research about the occurrence and mobilization of arsenic in the groundwater. So far our group is still conducting related researches at Datong Basin, and has already established one in situ monitoring site and one remediation demonstration site there. Now I have been granted three projects focused on high arsenic groundwater by National Science Foundation of China, and my research interests expand to the genesis of geogenic contaminated groundwaters, including the mobilization mechanisms and remediation technologies for high arsenic, fluoride, and iodine groundwaters.

Q3. Do you have any suggestions for the young geologists based on your field work in decades?

Xianjun: As a geologist, we are responsible for preserving the samples as they are and obtaining the reliable data as far as possible besides just analyzing them. Only by maintaining the geological environment of aquifer system can we reflect the real geogenic issues in the groundwater and make our research more meaningful.

Q4. Are you still recommending this article to the students in your research group?

Xianjun: Yes, it is a very classic paper. I always recommend the students to read this article and learn how to discuss the evolution of water chemistry when doing their researches. This article not only offers the basic theoretical knowledge and data analysis methods, but also provides the logical thinking mode for considering such problems in the hydrogeochemistry field. In addition, when I teach the course Groundwater Pollution and Prevention, I often use this article to

explain how to link the hydrochemical evolution process with the environmental behavior of geogenic components in the groundwater. It is a really great reading material to help the students grasp the highlights of this course, and learn how to apply the theoretical knowledge to the practical problems in the field.

Q5. Could you briefly summarize and envision the hot research topics on the groundwater contamination and remediation in the near future, as well as describe your personal research interests related to it?

Xianjun: In terms of groundwater contamination and remediation, I think there are three hot research topics: (1) remediation mechanisms, (2) remediation materials, and (3) application scenarios. As far as high-arsenic groundwater is concerned, a large number of studies have reported that sulfhydrylation and methylation are important processes in the arsenic biogeochemical cycling. The analysis of related arsenic forms and in situ rapid detection techniques are current difficulties and challenges. Thus, the in situ groundwater remediation technology based on different arsenic forms and mechanisms would be a research hotspot in the near future. In addition, contam-

inant is not usually existed alone in the real environment. For instance, high arsenic, fluoride, iodine, and/or ammonium are found to co-exist in one geological environment. The research on new remediation materials and technologies for co-existing contaminants for different application scenarios would also be another hot research direction.

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Genesis of arsenic/fluoride-enriched soda water: A case study at Datong, northern China

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