

CO₂ rich springs of the Far East Russia. Composition and Origin

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Introduction

CO₂-rich cold springs are widespread in the Far East Russia. The measured temperatures vary from 5°C up to 10°C. In most cases dissolved oxygen (DO) is close to 0%, which means that the system is isolated from the atmosphere. pH values are in the range of 5.22-6.3. They are mainly of the Ca-Mg-HCO₃ type with high amount of CO₂. Content of elements depends on residence time, type of bedrocks and dissolved CO₂ gas. Over 90% of the cationic species occur as free ion and less than 10% as ion-pairs with HCO₃. Waters of springs are over-saturated with the clay minerals (smectite, illite, kaolinite), low temperature zeolites (heulandites, mordenite, clinoptilolite), and dolomite. Using tritium isotope study we previously showed the young age of these ground waters and the hydrogen and oxygen isotopic ratio suggested meteoric origin. Yet, the origin of CO₂ remained uncertain and is a subject of the present study.

Results and Conclusion

In studied springs dissolved CO₂ ranged from 94% to 99% and the maximum calculated CO₂ partial pressure is 1.7 bar. We hypothesized that the carbon was of magmatic origin. Geological data and young volcanic activities in some areas of location springs support this hypothesis. δ¹³C and ³He/⁴He data also suggests magmatic origin (up to 70%) for the CO₂ in Primorye (Maritime region of the Russia) springs [1,2]. δ¹³C for most studies springs ranged from -4.19‰ to -8.19‰. These values are too high for the CO₂ to have an organic source and too low to be carbon of limestone. They are, however, close to magmatic carbon, but it is difficult to assert that this, because some processes cause fractionation of these carbon isotopes. To solve the problem we selected an alternative method to identify carbon source. The ratio of carbon to mantle helium (C/³He) had been used by others in similar situation. [3]. Using this method mantle carbon and atmosphere carbon had ratios of about 2*10⁷ - 2*10⁹ and 10¹², respectively. The studied springs had a value close to 2*10⁹, suggesting that most of the carbon in the studied CO₂-rich waters has magmatic origin. Similar deep origin of CO₂ in spring waters had been previously shown in other springs around the world, for example in the Malki CO₂-rich cold springs in Kamchatka [2], in Wudalianchi springs in N-E China [2] and in the springs of San-Andreas fault in California. [4].

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Structure and surface reactivity of Al-, Si- and organic matter-rich naturally occurring ferrihydrite

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Ferrihydrite is a poorly crystalline iron oxide nanomineral (2-7 nm) found in a variety of natural surface environments. Its occurrence is documented at near-neutral pH conditions in a variety of redox-active environments, such as soils and sediments, as well as freshwater and marine settings. As a result of its high surface area and its chemical reactivity, it is an important environmental sorbent, and plays an essential role in the geochemical cycling of pollutant (in)organic species. Under natural aqueous conditions, ferrihydrite precipitates in the presence of several inorganic species such as aluminum, silica, phosphate, etc., or in the presence of organic matter (OM). These impurities can affect the domain size, composition, and molecular-level structure of ferrihydrite, thus modifying fundamental properties that are directly correlated with solid-phase stability and surface reactivity. In this study we have characterized a series of ferrihydrite samples of variable Al, Si, and OM content by laboratory (TEM, chemical extractions, electrophoresis) and synchrotron-based techniques (high energy x-ray total scattering and pair distribution function analysis, scanning transmission x-ray microscopy) in order to place constraints on their short- and intermediate-range structure, their composition, their surface chemistry and association with organic matter. A significant decrease in crystallinity occurred with increasing impurity content. We attribute these changes primarily to the presence of strong binding ligands such as silica and organic matter, both of which are known to affect Fe polymerization and poison particle growth. It is expected that the presence of these ligands at the ferrihydrite surface will alter significantly its surface composition and reactivity in the environment.