Ancient acid rains in Ediacaran – an alternative story for sulfate sedimentation

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Article

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Abstract

Vast deposits of anhydrite and magnesite widely distributed in Ediacaran strata of East Siberia near the Riphean unconformity. Anhydrite-rich rocks are not look like of evaporitic origin find mostly nodules and the layers of chicken-wire structure otherwise disseminated as tiny sulfate forms amongst the terrigenous rocks. Here we propose an alternative point of view for anhydrite appearance – the enrichment of Sulphur because of the slashing increase the content of sulfur in the Ediacaran atmosphere due to high volcanic activity. It is suggested that the ancient Earth's atmosphere could have also been influenced by powerful sulfuric acid rains that eroded the Precambrian dolomites causing their aggressive degradation. Chemical reactions with dolomite and sulfuric acid showed that in the early stages an unstable phase of bassanite occur which later stabilized as anhydrite after its heating as an analogue of aging. Aggressive acids have caused global process of dolomite karstification of the Siberian craton with appearance in Ediacaran strata in addition to the sulfate phases, including magnesite and sulphurous phases of pyrite and barite.

Introduction

Apparently, the Proterozoic epoch as a whole was characterized by an extensive accumulation of sulfate deposits. Extensive strata of anhydrite in the Precambrian are known in many regions of the world causing numerous disputes of its high content and unusual appearance with context of isotopic data ^{1,2,3,4,5,6,7}.

It is well known that the minerals of the sulfate group (anhydrite and gypsum) are the product of precipitation from an oversaturated salt solutions in salted basins, or in other words they have an evaporate origin⁸. Three crystalline Calcium-sulfate phases are known in the Nature: hydrated phases of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$), and crystalline anhydrite (CaSO_4) as the final phase and product of transformation for the first two. However, practical experiments on the deposition of anhydrite in the laboratory showed that anhydrite has restricted conditions for primary sedimentation comparing with the hydrated gypsum and bassanite^{9,10}. They also showed that the transition of hydrated sulfates to anhydrite requires long time and may not transform even after two years¹⁰.

The sulphate-bearing rocks of the Ediacaran of the Siberian platform have been studied. Rocks of mixed composition – multi-layer deposits of overlapping strata of a terrigenous-sulfate-carbonate sequence were drilled in deep wells at a depth of more than 2 kilometers. However, it is difficult to imagine how terrigenous rocks such as siltstones and sandstones could be deposited together with monomineralic anhydrite strata and actively mixed at the same time. One of these ways could be the ingress of clastic material into the carbonate basin – salted sabkha contaminated with clastic material. However, the sulfate layers and concretions in the form of separate nodules look isolated and were formed rather like high energy streams of solutions intruded in terrigenous sequences, subsequently acting as a cementing material for clastic rocks (Fig.1-2). The thickness of the sulphatic interlayers are generally more than 20-30 centimeters, but they can reach up to 1-2 meters. Their numerous quantities among the terrigenous rocks indicates that they cannot form as classic evaporitic sediments.

At the same time, the surface of the Riphean of the Siberian Platform at the point of unconformity on the border of the Ediacaran and Riphean is pitted and transformed by the processes resembling the karst with the active development of voids and cavities of dissolution, both hollow and filled in new minerals – quartz, dolomite, magnesite, anhydrite. Karst or signs of karst formation are revealed in almost every deep well of basin, which indicates a fairly largescale manifestation of it on a large territory - almost the entire territory of the Siberian platform. In addition, karst zones often develop inside the Riphean strata at a depth of several meters from the surface of the unconformity. They are often filled with anhydrite, which clearly is not the product of sedimentation, but have secondary origins.

Another important feature of the filling of the Ediacaran basins of the Siberian Platform is the appearance carbonate (more often), and terrigenous layers filled with magnesite (MgCO_3), having a regional distribution and developed over a distance of many hundreds of kilometers in the Nepsko-Botuobinskaya antecline¹¹. Also, in the strata of the Siberian platform there are talc findings with a stratiform occurrence and minor admixtures (1-2%) of pyrite, barite and celestine (only as traces). The general picture of deposited layers assumes the multiple stratification and change of the terrigenous (marine) sedimentation environments of chemogenic origin, primarily carbonate, which in turn often changes to a halogen one of sulfate composition in the absence of a chloride component.

Results

The primary Riphean dolomite (98%) of Eastern Siberia with minor quartz admixture (about 2 %) was mixed with concentrated sulfuric acid (93.6%).

Chemical reaction in general form can be described as:

Experimentally, the obtained solution (after full interaction) was decanted after keeping it overnight and then the dry precipitate was studied by XRD method (Fig. 3). The XRD data after the reaction showed that the dolomite was almost completely dissolved and the final product of the reaction was bassanite (about 80%) and anhydrite (about 20%). Repeated XRD measurements after 6 months did not show any changes. However, the gradual heating of the sample in a muffle furnace showed the transformation of unstable bassanite into anhydrite (Table). We assume that bassanite, as it heats up, which can be equated with the ageing of the sample in geological time, completely turns into anhydrite as it evolves. At the same time, the content of silicon (quartz) in all samples were unchanged (Fig. 3).

Discussion

It is known that concentration of sulfate was not so high in Precambrian time causing its scarcity in seawater of the Paleoproterozoic and Neoproterozoic eras^{12,13,14,6}. Fakhrae and his coauthors have explained the appearance of Sulphur in significant concentrations by an input sulfate into the ocean as

result of weathering of sulphides on the land¹⁴. However, this way requires enormous fields of sulfide deposits and long time for weathering and dissolution with the following transportation towards the sea basins.

Thus, it is assumed that the source of sulfur for the deposition of sulfates in the Precambrian time could be in the form of sulfuric acid rains. They actually dissolved the dolomite causing the chemical disintegration and separation of Ca and Mg. This effect, for example, was proved by experiments in which the MgCO_3 content in the dolomite composition changed when it interacted with sulfuric acid¹⁵. Ca and Mg subsequently formed their new phases – calcium bound with the sulfate-ion to form bassanite, and magnesium returned as carbonate in the form of magnesite or the high-magnesium dolomite, which is also, had high distribution in Precambrian¹⁶. It is widely known that magnesite is often adjacent to anhydrite^{4,17} while the host rocks for both minerals are dolomite. The source of primary sulfur could be powerful volcanic events during the late Neoproterozoic and earlier in the Middle Proterozoic, which also contains multi-meter thicknesses of sulfate rocks around the world¹⁸.

As a consequence of industrialization and climate change, we are seeing frequent sulfuric acid rains in our modern era, causing the erosion of carbonates (marble statues, buildings, reefs etc.). However, the most extensive sulfuric acid rains as a geological process can be observed now on Venus, where this acid forms enormous clouds in the Venus atmosphere. McGouldrick with co-authors argued that the present atmosphere of Venus is saturated by clouds composed of a sulfuric acid/water solution creating acid rains/aerosols on the surface of planet. They also argued that the early Martian atmosphere was also sulfur-rich¹⁹. In addition to these, signs of sulfuric acid rains were observed on the surface of Mars in the form of the appearance of basanite on the planet's surface. It has been proven in veins of Gale crater in Martian surface where bassanite was formed by dehydration of gypsum and where it is an important mineral phase^{20,21} as well as the presence of jarosite (one more product of Sulphur activity and subsequent transformations) in Martian sediments²².

Volcanic activity provides the input of Sulphur in the atmosphere where it is mixed with atmospheric moisture and water and form acid clouds come in the form of rains or in the form of an aerosol. However, the difference comparing with ancient Earth is fact that neither the Venus nor the Mars have hydrosphere unlike the Earth where sea and lake water reservoirs could “extinguish” and sediment the products of the reaction of sulfuric acid rains turning and burying them in the form of precipitations as the sediments and rocks.

Simultaneously, this process caused a powerful aggressive karst formation on the dolomite surface in Precambrian lithosphere. These solutions eroded the Riphean dolomite rocks and formed the karstic processes causing the dissolution and distractions of carbonate rocks. The combination of aggressive sulfuric acid with alkaline carbonates led to their active dissolution of the Riphean dolomites and interaction with subsequent neutralization, with the formation of hydrated bassanite, magnesite, undissolved dolomite and water, as well as probably amorphous silica - SiO_2 .

All these compounds were actively washed off by water-acid currents flowing down from the mountains and highland forms of Precambrian relief forming the deposits saturated with bassanite. Aggressive acid solutions fall into the relic sedimentary basins of shallow seas and lakes of the Ediacaran time and was buried with different types of other sediments - terrigenous (clayey and sandy-silty), carbonate and others, intensely mixed with them. Bassanite, as unstable mineral over time serves as a precursor phase for its further conversion to the gypsum and anhydrite. Thus, peculiar sulfate-terrigenous sequences were formed creating bizarre structural shapes of sulfate rocks. At the same time, magnesium sulfate, as an easily soluble compound in water, was actively carried by the waters also into sedimentary depressions, where it was also deposited together with terrigenous sediments and formed extensive magnesite mixtures, and later got buried together with terrigenous and carbonate rocks (Fig. 4).

Hence, anhydrite as a mineral phase of rocks can be formed not as a process of evaporate sedimentation. Acid rains can cause the currents of dissolved carbonates and returned to bassanite suspension further flowing down in the Ediacaran depression of the Siberian platform. However, huge fields of anhydrite and magnesite fields are known in not only the Neoproterozoic, but also are generally characteristic of the Precambrian²³. Giant strata-bound magnesite deposits are known and have occurred predominantly in Precambrian strata^{4,17}. Many of them explained as results of hydrothermal activity formed by the replacement of parental limestones^{24,25}. For example, the world's largest strata-bound magnesite deposit belt of 2.1 Ga Dashiqiao Formation in China, which was not formed as a result of hydrothermal origins¹⁸. The same feature characterized for Brazilian magnesite ore deposits where magnesite shows textural characteristics related to original sedimentary structures²⁶.

Thus, we suppose that the Neoproterozoic era was the epoch of extensive sulfuric acid rains that can cause catastrophic geological events of all ancient spheres of the Earth where anhydrite-rich strata could be the result of chemical neutralization after sulphuric acid rains. However, epochs of acid rain could be distributed in Mesoproterozoic time and PostCambrian on the boundaries of geological periods supported by other catastrophic events²⁷. Moreover, such rains could play crucial role in vast distribution of other unusual ancient events explaining for example high silicon compounds that could have been involved in the same story and form huge talc fields²⁸ as well as also explain the abnormal appearance in Precambrian of sulfides (the problem of "heavy pyrite")^{3,29,30} and barite^{31,32,33}.

Method

XRD-patterns were recorded using Rigaku Ultima IV X-ray diffractometer in Bragg–Brentano geometry, with a Cu anode, performed a qualitative characterization of the minerals. The X-ray tube voltage of 40 kV, the current of 30 mA, and a power of 1.2 kW. Whole rock samples were scanned from 5 to 60° 2θ at a scanning speed 1° per minute with a step of 0.02°. XRD-patterns were analyzed employing the program Siroquant, using the database ICDD-PDF2.

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Declarations

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Tables

Phase	Stage	Quartz	Dolomite	Bassanite	Anhydrite	Sum
Dolomite	Clean	1,5	98,5	-	-	100
Bassanite	After treatment H_2SO_4	1,5	1	79.5	18	100
Anhydrite	Aging = heating 500C	1,5	-	-	98,5	100

Table. Content of quartz, dolomite and sulphate minerals before and after treatment in sulfuric acid.

Figures

Figure 1

Anhydrite nodules (A) and layer of chicken-wire anhydrite (B) in terrigenous Ediacaran rocks of Siberian craton; features of karstification (C) near the unconformity between Riphean dolomites and Ediacaran terrigenous rocks.

Figure 2

Anhydrite nodules submerged in clastic rock (A) and disseminated anhydrite in dolomite-magnesite matrix (B). Photos made in thin section under cross-polarized light.

Figure 3

XRD-patterns via the dolomite transformation into anhydrite when interacting with sulfuric acid (D – dolomite, A – anhydrite, B – bassanite, Q - quartz).

Figure 4

A simplified schematic of the anhydrite formation on the Earth surface in Ediacaran time.