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Minerals "Straight Out of Water"

Earth is filled with a myriad of minerals and rocks that charm us with their beauty and diversity. They usually take the form of solids or mineral components dissolved in water.

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Prof. Agnieszka Gałuszka is an environmental geochemist and a biogeochemist. She studies the geochemistry of trace elements in waters, soils, plants, sediments, and rocks. Her interests focus on the elements found in environmental pollutants and the methods of analyzing the origin of elements in environmental samples.

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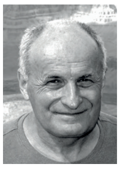

Prof. Zdzisław M. Migaszewski is a geochemist, a mineralogist, and a petrographer. He studies acid mine drainage (AMD) and its impact on the environment. He is an expert on the geochemistry of stable isotopes. He has authored new concepts of the genesis of dolomite rocks, rose-like calcites, and striped flint in the Holy Cross Mountains.

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The phrase *panta rhei*, attributed to Heraclitus, could be the motto of every geochemist. Environmental geochemistry is a little-known discipline of earth and environmental sciences that is quite often confused with environmental chemistry. It studies the distribution and circulation of the chemical elements and their isotopes in the environment. The essence of these topics is changeability – dynamic processes that cause the chemical elements to be found very rarely in the environment for prolonged periods in the form of the same chemical compound. Such changeability of the forms in which the chemical elements are found in nature is affected by physical, chemical, and biological factors. In the environment, each of them simultaneously affects many substances of various properties, which may interact with one another in different ways. This is why environmental geochemistry is so fascinating: it not only allows us to understand the laws of nature better but also poses considerable challenges for researchers, who must draw on findings from many disciplines or branches of science in their work. Studying geochemical processes and the phenomena they give rise to is a very interesting experience.

A natural factory of sulfuric(VI) acid

One of the processes taking place in nature that could be compared to a natural "factory" of sulfuric acid is the weathering of a mineral called pyrite, the most

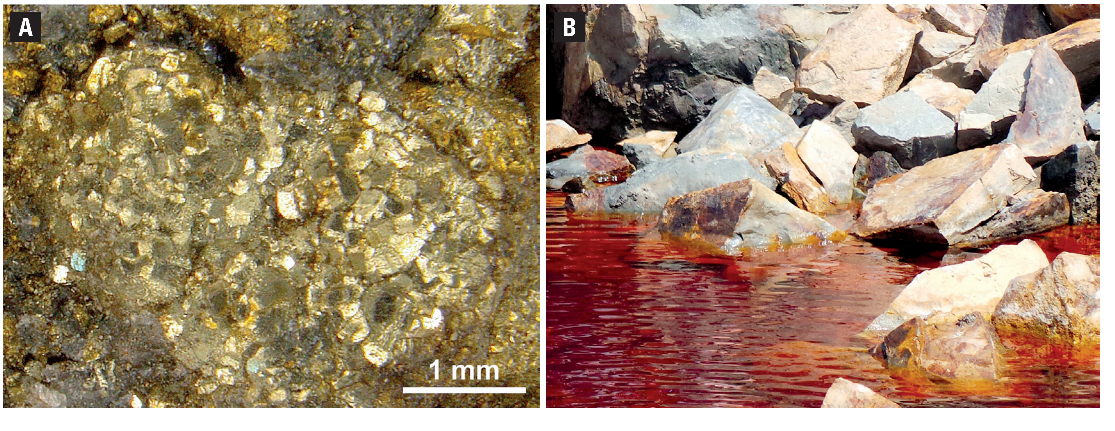

Fig. 1
Fine-grained pyrite (A) and a product of its weathering – acid mine drainage (B)

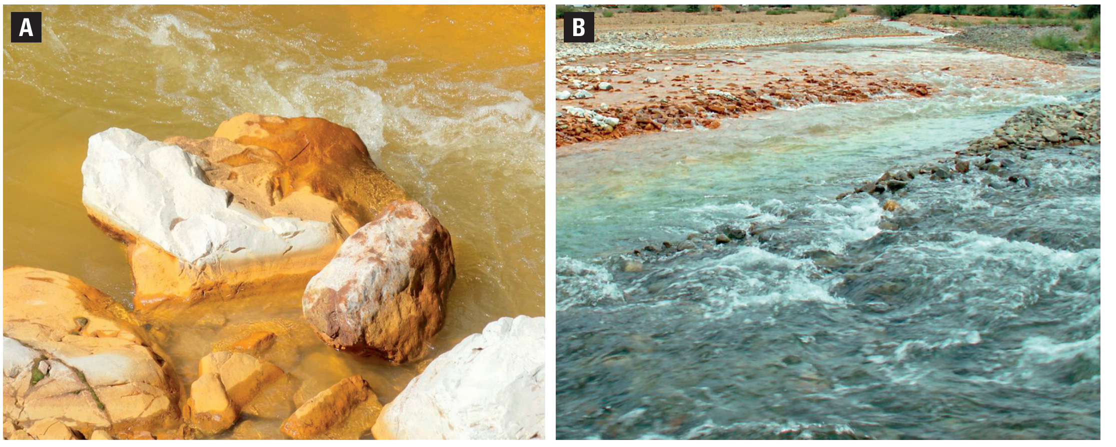

Fig. 2
Precipitates forming in an AMD stream (A) the confluence of streams with acidic and neutral pH (B)

common of sulfides with the chemical formula FeS_2. In addition to pyrite, these chemical reactions also involve water, oxygen or iron (in its +3 oxidation state) as well as autotrophic, acidophilic, and thermophilic microorganisms. The latter, thanks to sulfur and iron oxidation in pyrite, gain the energy needed to synthesize simple organic compounds from inorganic substrates in a process called chemosynthesis.

Pyrite weathering leads to the production of water whose pH is acidic (usually in the range between 2

Fig. 3
Hydrobasaluminite precipitate forming in water flowing from a closed mine shaft, Paradise Portal, United States. Photographs A–D show consecutive closeups

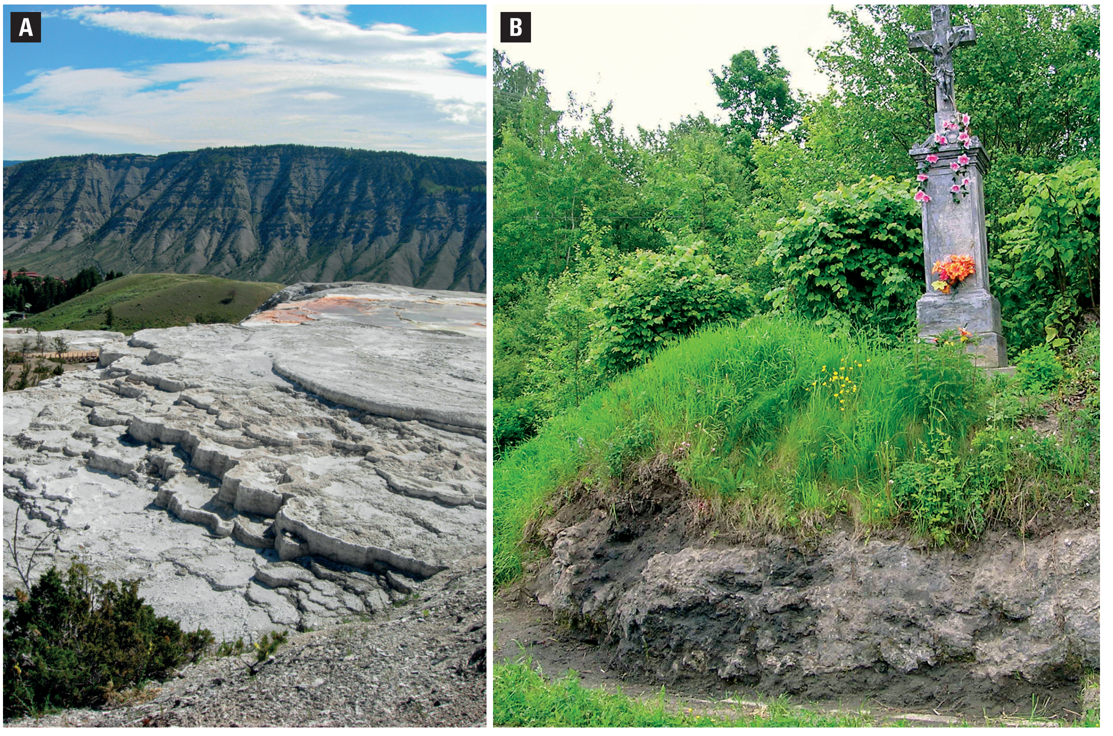

Fig. 4
Travertine terraces in the section Mammoth Hot Springs in the Yellowstone National Park in the United States; (A) Travertine outcrop in Cząstków in the Holy Cross Mountains (B)

and 4). Because many chemical compounds dissolve in water of such pH, aside from its low pH it is characterized by very high concentrations of ions, especially iron and sulfate ions. Such water is referred to as acid mine drainage (AMD) in view of its unusual properties and the places where it can be predominantly found (mining and post-mining areas). Another characteristic feature of AMD is its red, yellow, or orange color. Similar colors are found in the sediments at the bottom of streams and on the pebbles through which AMD waters flow. They come from iron minerals, such as the pale yellow mineral called schwertmannite with the chemical formula $Fe_8O_8(OH)_{5,5}(SO_4)_{1,25}$, the red-brown ferrihydrite $Fe^{3+}{}_5O_6[OH]_3\,3H_2O$, the yellow-brown goethite α-FeO(OH), or the red-brown hematite α-Fe_2O_3. Large accumulations of pyrite are associated with polymetallic deposits, so AMD waters are found chiefly in areas where metal ores are mined as well as in hard and brown coal mines.

Geochemical barriers

Geochemical phenomena that are particularly interesting, even to non-experts, take place during a sudden change of the physicochemical properties, which leads to the precipitation of elements in the form of different chemical compounds. In such cases, which are called "geochemical barriers" by geochemists, observers actually are witnesses of the formation of minerals. The presence of geochemical barriers is responsible for the formation of numerous deposits of minerals that are currently being harnessed. Geochemical barriers may be caused by various factors, including physicochemical and mechanical factors, the presence of living organisms, and also human activity, such as liming of soil. Geochemical barriers may result from the simultaneous occurrence of several factors, in which case they are known as complex barriers.

Interesting phenomena may be observed when AMD mixes with surface waters whose pH is alkaline or neutral or when it flows through rocks containing minerals whose dissolution neutralizes the acidic pH (such as calcite $CaCO_3$ or dolomite $CaMg[CO_3]_2$). We can then observe the intensive precipitation of various oxides, hydroxides, and salts.

One of the most interesting examples of geochemical barriers we have observed was in the western part of the San Juan Mountains in Colorado in the United States. Near a mountain pass called Ophir Pass, at 3,245 meters above sea level, there is a closed mine called Paradise Portal. The water that flows out of the mine has a pH of around 5.0–5.5 and is enriched in aluminum ions and sulfate ions. When seen from afar, the Paradise Portal looks like a small cave with something like a bride's veil or an icefall coming out of it. Those were the first associations that sprang to our minds back in August 2005, when we first visited that site together with Dr. Paul Lamothe and Dr. James Crock from the US Geological Service to study AMD in the southwestern part of Colorado. As we neared the closed mine shaft, we could see more and more clearly that what appeared to be snow was in fact sediment that had precipitated out of the mine water that came into contact with rainwater and surface waters outside the mine shaft. Before we explain what that sediment actually was, we should identify the rocks on the ground – they were propylitically altered tuffs, or rocks formed from volcanic ashes that contain aluminosilicate minerals. Another mineral found in those rocks is pyrite. Water flowing out of the shaft is a source of aluminum, which precipitates in the form of hydrated hydroxysulfate – a mineral called hydrobasaluminite with the formula $Al_4[(OH)_{10}|SO_4] \cdot 15\text{–}36H_2O$. One factor that causes the formation of this mineral is the increase in the pH of AMD as a result of its mixing with surface waters. As stated before, the pH of AMD is usually between 2 and 4, while the precipitation of hydrobasaluminite starts at a pH of around 5.

A sudden change in temperature or pressure may cause a geochemical barrier involving the formation of travertine from thermal waters saturated with calcium carbonate. Travertine is a sedimentary rock made above all of calcium carbonate ($CaCO_3$ in the form of aragonite or calcite minerals). The most beautiful examples of this rock are found in the Yellowstone National Park, but also in many places in Poland, such as Cząstków outside Nowa Słupia in the Holy Cross Mountains. A similar process takes place when hard water is boiled, leading to the buildup of limescale inside the kettle. Once hot water saturated with silicon dioxide flows onto the surface of the Earth, siliceous sinter will form in the conditions of lowered pressure and temperature.

Water, as the best natural solvent, carries compounds that result from the dissolution of minerals and rocks. Sometimes the concentration of ions in water is so high (for example in AMD) that it does not resemble the chemical substance expressed by the formula H_2O almost in any respect. The increase in pH and the diffusion of oxygen from the air lead to the precipitation of aluminum and iron minerals from such a solution once it becomes mixed with neutral or alkaline waters. When water comes in contact with deeper layers of the Earth's crust, it heats up, whereas speedy cooling and a change of pressure after the hot waters flow onto the surface of the Earth lead to the formation of travertine or siliceous sinter. The phenomena described in this article cause a change in the mobility of the elements included in the newly-formed minerals and accompanying elements that may undergo adsorption or create substitutions in the crystal structure of minerals.

Photos by **Agnieszka Gałuszka, Zdzisław M. Migaszewski**

Further reading:

Migaszewski Z.M., Gałuszka A., *Geochemia środowiska* [Geochemistry of the Environment]. Warsaw 2016.

Migaszewski Z.M., Gałuszka A., *Pierwiastki ziem rzadkich w kwaśnych wodach kopalnianych – zarys problematyki* [Rare Earth Elements in Acid Mine Drainage – An Outline of the Issues]. *Przegląd Geologiczny* 2019, 67 (2).

Migaszewski Z.M., Gałuszka A., *Podstawy geochemii środowiska* [Foundations of Geochemistry of the Environment]. Warsaw 2007.