The electric charge of mineral surfaces changes in flowing water

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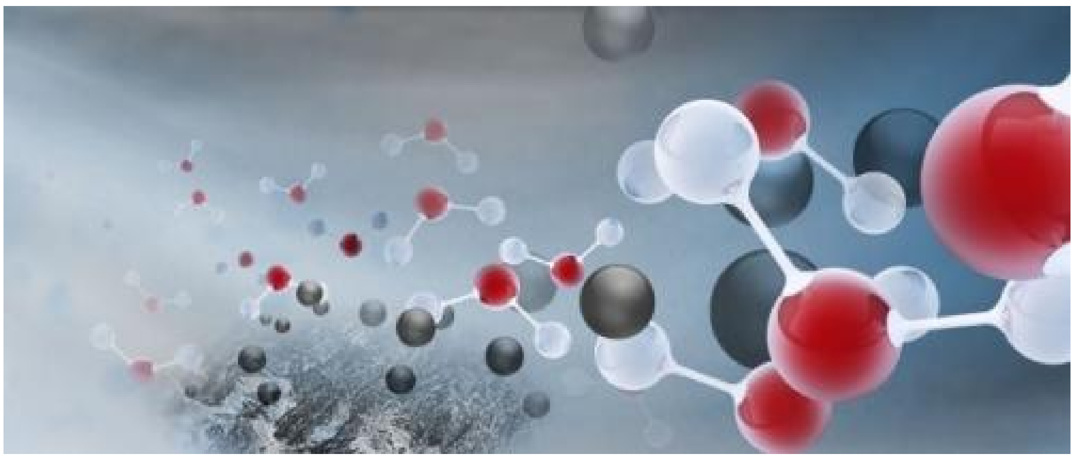

A flowing river: If water - consisting of oxygen, represented here by the red balls, and hydrogen, represented here by the white balls - moves over a mineral surface, ions (symbolised by the grey balls) are released from the surface. Both the ions and water acquire a charge. This discovery could affect our understanding of many chemical processes, such as the weathering of rock. Credit: MPI for Polymer Research

(Phys.org) —When water flows over glass or rock, the chemical changes that occur are more profound than had been previously assumed. Using a sophisticated spectroscopic method, a team from the Mainz-based Max Planck Institute for Polymer Research and the University of Namur in Belgium has discovered that the electric charge of mineral surfaces changes radically under a flow of water, as many ions are preferentially dissolved from the material. The type of mineral involved and the acidity or alkalinity of the flowing water determine whether and how strongly the surface is positively or negatively charged. However, the change in the charge can be so radical that it corresponds to a 100-fold change in the acid concentration. The change in the surface charge is directly linked to electrical activity and consequently changes the energy of the surface and its reactivity. This recent discovery could therefore have consequences for understanding numerous chemical processes in nature and in industry.

In chemistry, surfaces often play key roles – certainly when reactions on solid materials are involved. Changes to the charge of mineral surfaces in flowing water were previously an unknown phenomenon, which affects the properties of surfaces and thus their chemical behaviour – almost across the board in nature and science: when raindrops run down a window pane, when streams and rivers leach away their beds, when cliffs are eroded or when dissolved reactants converge at a solid catalyst.

While the importance of the new findings cannot yet be accurately assessed, the implications could be enormous: Most of the land surface consists of minerals whose surfaces are constantly, or at least frequently, washed over by flowing water, be it in the form of rivers, streams or precipitation. The reactivity of minerals in flowing water changes in accordance with the charge of their surface, and, depending on the surface, they also dissolve faster or slower. Hence, the findings of the team headed by the Max Planck researchers could be relevant for soil erosion and rock weathering. The weathering of rock also plays a role in the long-term development of carbon dioxide concentration in the atmosphere because carbon dioxide is absorbed during this process

The surface charge is relevant in the case of erosion and weathering

"As a result of our findings on elementary dissolution processes of minerals, it will be necessary to review established geological theories and to investigate the effect of the change in the surface charge on processes such as erosion and weathering," explains Mischa Bonn, Director at the Max Planck Institute for Polymer Research. Many models for rock weathering are often based on experimental studies in static water.

Mischa Bonn and his team induced water with varying levels of acidity and alkalinity to flow over calcium fluoride. Negatively charged fluoride ions have a preference for releasing themselves from the surface, whereas the positive calcium ions remain in the solid. The charge acquired by the surface depends on whether it has a positive or negative charge in static water and on how strong this charge is. After all, as scientists have already known for a long time, a mineral surface acquires a charge if it is dampened with static water because some ions dissolve better than others. The charge depends on whether the water is acidic or alkaline. When the researchers began their experiment with calcium fluoride in slightly alkaline water in which the surface had only a slight negative charge, they were able to reverse the polarity of the surface through the water flow.

The team also studied silicon dioxide, the main component of rocks and quartz glass, under flowing water. Its surface has a negative charge in neutral and alkaline water. However, if the water is moving, the negative charge is reduced, as negatively charged ions move away from the silicic acid. In neutral water, the surface sheds charge particularly well. If acidic water flows over the mineral, silicic acid molecules are once again released, but do not contain any charge. The surface charge therefore does not change.

Aligned water molecules indicate surface charge

The study conducted by the researchers in Mainz was only possible because Mischa Bonn and his team have a proven means of studying the surface charge under water: sum frequency generation spectroscopy. This allows the researchers to focus two differently coloured laser pulses onto the interface between the water and the mineral. The overlapping laser beams interact particularly well with the water molecules at the surface if the molecules are accurately aligned there and not simply whirling wildly around one another as they usually do in liquid water. This is precisely the case with charged surfaces, as water molecules have a negative and a positive end and always align themselves according to the principle of attraction and repulsion to the neighbouring charge. If the overlapping laser pulses meet on the surface at the aligned molecules, they generate a characteristic signal. The more molecules are aligned at the surface, the stronger the signal is, and consequently the stronger the surface charge.

"Our method provides information about the alignment that is brought about by the electric charge," says Mischa Bonn. "We can therefore determine the charge directly 'on site' and interpret what is happening at the surface." This is precisely where other experiments were lacking – the charge could not be measured directly at the mineral surface.

Now, however, he and his team have discovered the electric clue that flowing water leaves almost everywhere in the world. And because both the flowing water and the surface of a material acquire a charge, every river apparently also has a flow in both senses of the word.

More information: Dan Lis, Ellen H. G. Backus, Johannes Hunger, Sapun H. Parekh und Mischa Bonn. "Liquid flow along a solid surface reversibly alters interfacial chemistry." *Science*, 6 June 2014; DOI: 10.1126/science.1253793

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