

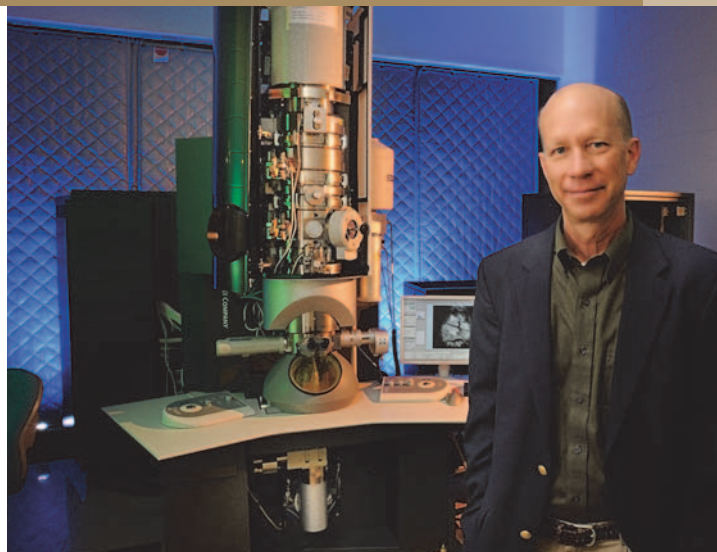
STANDING BACK AND LOOKING AT THE FOREST: A PERSPECTIVE ON SURFACES AND INTERFACES, THE UBIQUITOUS STUFF OF NEARLY ALL THINGS

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Happy 50th issue of *Elements*! Of the 49 issues that have come before, only one has included the word “surface” or “interface” in its title. However, *every* issue of this magazine has dealt with surface and interface phenomena either explicitly or implicitly, because these processes cannot be avoided even in the vacuum of deep space (due to the presence of intergalactic particles). Now, Christine Putnis and Encarnación Ruiz-Agudo bring us this *Elements* issue, in which the mineral–water interface plays the key role. Seems simple enough, unless you care to consider the trillions of square kilometers of this kind of interface on this mineral–water planet (Fig. 1). Perhaps that explains why a recent issue of *Geochemical Perspectives* on this theme, written by Gordon Brown and Georges Calas and entitled “Mineral-Aqueous Solution Interfaces and Their Impact on the Environment,” is 210 pages long with over 700 references. Yet, Brown and Calas use a Sir Winston Churchill quote to help them express the idea that perhaps their magnum opus (and it is that!) is “the end of the beginning” for this field of study. If that is so, this issue of *Elements* is an excellent start to the first day of the rest of the life of this central field of research on how nature works.

It has always been known that surfaces and interfaces present great challenges for their study and understanding. Lord Rayleigh, the great English physicist who won the 1904 Nobel Prize for his discovery of argon, among other great accomplishments, wrote in an 1892 issue of *Philosophical Magazine*: “The surfaces of bodies are the field of very powerful forces of whose action we know but little.” Wolfgang Pauli, the Austrian theoretical physicist and 1945 Nobel Prize winner best known for the exclusion principle, said, “God made the bulk; the surface was invented by the devil.”

Yet, at the same time, surfaces are radically glorious, and without them, where would we be? Consider a few prehistorical and subsequent historical events and recognitions. One can argue that making fire on demand was one of the greatest and earliest traceable inventions of all time. Archeologists generally agree that *Homo erectus*, a half million years ago, could make fire, and they did it using friction, a surface phenomenon that generates enough temporary heat to light tinder. This can be accomplished with wood on wood or mineral on mineral (quartz or flint on pyrite, for example). What are likely some of the first detailed observations of surfaces were recorded in Babylonian cuneiform dating to the second millennium BC; the inscriptions tell of the use of patterns of oil spreading on water to predict the future (I think not very successfully). Thereafter, in a number of ancient writings, it was noted that oil could smooth the surface of rough, windblown water. The accounts of Pliny the Elder, the first-century Roman naturalist, are perhaps best known. One of the



Mike and his favorite TEM instrument at Virginia Tech

most celebrated demonstrations of Pliny’s writings on this subject was performed and recorded many centuries later by Benjamin Franklin, the American patriot, politician, and scientist. Franklin’s experiment, performed in 1768, consisted of pouring a very small amount (approximately 2 cm³) of oil and observing it spread over a large area (approximately 2000 m²) of a pond in Clapham, London, England. Curiously, he did not calculate the thickness of the oil layer. Lord Rayleigh actually did that in 1890 and found the layer to be only about one nanometer thick, essentially one of the first estimates of the size of an organic molecule! Just a few decades later, in the 1820s, the German chemist Johann Döbereiner noted that hydrogen and oxygen gas, if in the presence of a platinum surface, combusted at a temperature well below that observed ordinarily. One of the greatest experimentalists who ever



FIGURE 1 Across every interface in this scene, including mineral–water interfaces, there is a complex transfer of mass, energy, protons, and electrons. This interplay results in the makeup and character of the hydrosphere, atmosphere, lithosphere, and biosphere of this planet.

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TABLE 1 PROCESSES OCCURRING AT MINERAL–WATER INTERFACES, AND THEIR CONSEQUENCES

Fundamental process	Sorption to mineral	Desorption from mineral
Possible effects	attachment of solvated ions or ionic complexes/clusters, surface diffusion, absorption, electron transfer, defect formation, island or thin film growth, mineral growth	detachment of ions or ionic complexes/clusters, electron transfer, congruent or incongruent dissolution, surface roughening
Possible consequences	sediment cementation, secondary mineral formation, reduction of permeability, solute immobility, oxidation–reduction couples, heterogeneous catalysis	weathering, increase in permeability, solute mobility, oxidation–reduction couples
Possible multiple consequences, compounded	geochemical cycling of elements, formation of clays and iron oxides, soil formation, water-chemistry variations, microbial-community impact, hydrothermal alteration, diagenesis and metamorphism, ore deposit formation	

lived, Michael Faraday, noticed the same thing in 1833, and thus the science of catalysis had begun, in this case, surface (or heterogeneous) catalysis. In the 1870s, J. Willard Gibbs, the brilliant mathematical physicist and thermodynamicist, described the thermodynamics of surfaces that we still use today.

The first Nobel Prize for what is essentially a surface phenomenon (for solids and liquids) went to Albert Einstein in 1921 “for his services to theoretical physics, and especially for his discovery of the law of the photoelectric effect.” The photoelectric effect is typically observed when ultraviolet light or X-rays impinge on a surface and electrons (photoelectrons) are emitted from that surface. In 1932, Irving Langmuir’s work on monomolecular films at the corporate laboratories of General Electric resulted in the first Nobel Prize in Chemistry specifically for research in the field of surface chemistry. In 1937, Clinton Davisson won the Nobel Prize in Physics for his electron diffraction work, with Lester Germer, that probed the atomic structure of surfaces, demonstrating the wave nature of electrons. In 1956, John Bardeen, Walter Brattain, and William Shockley shared the Nobel Prize in Physics for their research on semiconductors and the invention in 1949 of solid-state amplifiers (i.e. transistors), thought by many to be one of the most important inventions of all time. Transistors work because of the behavior of electrons near surfaces. Bardeen’s, Brattain’s, and Shockley’s theories, models, calculations, and observations inspired massive efforts in surface-science research, which continue to this day. Interestingly, it was also about this time, in the late 1950s, that molecular dynamics simulations first appeared, and these would in time become exceptionally important in modeling surfaces and interfaces. Returning to vital instrumentation development, Kai Siegbahn won a Nobel Prize in Physics in 1981 for X-ray photoelectron spectroscopy, and Gerd Binnig and Heinrich Rohrer won the same prize in 1986 for the scanning tunneling microscope. Both awards were for singular and revolutionary tools that probed surfaces compositionally, electronically, and structurally. In 1995, Paul Crutzen, Mario Molina, and Sherwood Rowland shared the Nobel Prize in Chemistry for their work on the atmospheric chemistry of ozone and on its alarming depletion, first observed in the late 1970s. This field includes the key reactions critical to ozone’s destruction, reactions that involve the surfaces of polar, stratospheric cloud (ice) particles. Most recently, Gerhard Ertl won the Nobel Prize in Chemistry in 2007 for his longtime and overarching studies of chemical reactions on solid surfaces.

And how exactly was the exceptional relevance of mineral surfaces and mineral–water interfaces introduced to the science of the Earth as it developed over the last few centuries? At least in part, answering this question goes back to Georgius Agricola, the remarkable 16th-century German physician and scientist, as well as the father of modern mineralogy. In his 1556 masterpiece, *De re metallica* (Latin for “On the nature of metals”), he discussed in great detail the state of the

art in mining, refining, and smelting ores. He also wrote: “When the ores are washed, the water which has been used poisons the brooks and streams and either destroys the fish or drives them away.” These observations helped provide a beginning for mineral–water interface environmental science over four centuries ago. After the beginning of the science of geology under James Hutton and other naturalists of the late 18th century, chemists, mining engineers, and early geologists, like Pierre Berthier, Gabriel Auguste Daubr e, and Jacques-Joseph Ebelmen, performed research on the dissolution of minerals (including silicates) in the early to mid 1800s. C. Newbury, W. Skey, and C. Wilkinson studied oxidation–reduction reactions at mineral–solution interfaces in the 1860s and 1870s. By this point, mineral–water interface science was well on its way to influencing the Earth sciences as these fields rapidly developed into the 20th century.

Every portion of the research described above is important to the Earth sciences today, even though much of it was not primarily intended to help us understand Earth. Yet, it is all very much relevant to this understanding. This research has taught us, and teaches us still, about the vital guiding principles that are germane to all surfaces, that is: (1) surfaces are defects; (2) interfaces are where such defects meet; (3) surface composition and atomic structure are not the same as in the bulk material; the differences may be subtle, dramatic, or in shades of gray; (4) the shape of most surfaces is complicated at the macroscopic level and all the way down to the nanoscale; (5) surface reaction pathways and kinetics depend on the surface’s atomic structure, shape, and composition, all of which may vary across a single surface; (6) the chemical reactivity of a surface generally increases as its nanotopography increases; and (7) surfaces are not static but are dynamically variable, depending on local conditions and reactions. Keep in mind that several of these principles apply also to the surface of the aqueous solution that is in contact with the mineral on the other side of the interface. To further complicate things, other entities besides the mineral and the aqueous solution may be present at the interface in natural systems, and even in laboratory experiments unbeknownst to the investigator (or maybe quite on purpose by the investigator). Such entities most commonly include, but are not limited to, adventitious compounds or materials and living organisms and their extracellular compounds.

Today, as is apparent from the themed articles in this issue of *Elements*, the processes that occur at the mineral–water interface have consequences at local, regional, and certainly global scales. These are summarized in TABLE 1. Many of the items listed in the table are described in detail, or alluded to, in this issue. But it should now be clear that the historic and scientific “forest” (see title of this paper) underpinning modern mineral–water interface chemistry is spectacularly rich with several of the greatest accomplishments and discoveries that mankind has ever produced. For a science that is so foundational to how everything works, perhaps this is not surprising. ■