Weathering:

minerals, mud and microbes

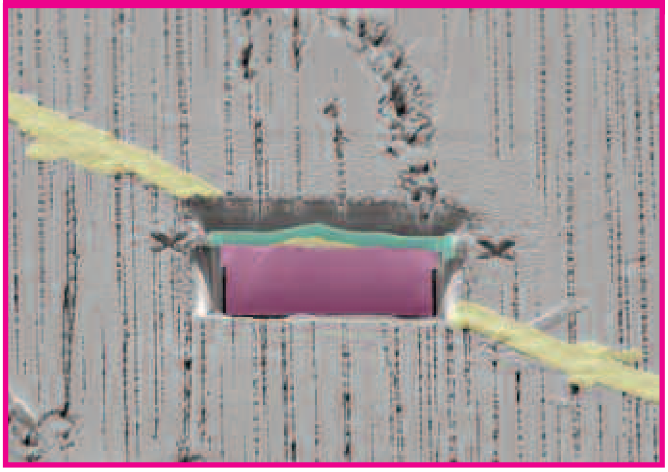
Weathering, as the name implies, is an important part of Earth's climate system. **David Brown** and **Martin Lee** describe a new technique that reveals how weathering works on a nano-scale.

One glance at an old gravestone or building shows how exposed rocks are slowly but inexorably broken down by weathering. Two related processes, which often occur in tandem, cause this decay: chemical weathering, by weakly acidic rainwater; and physical weathering, by the penetration into rocks of microbes, plant roots or even ice crystals. Although weathering is detrimental to the fabric of towns and cities it has helped to make life on Earth possible. This is because the accumulation of weathering products, known colloquially as 'mud', over thousands of years, helps to form soils.

The decay of rocks is also important to global geochemical cycles and so climate. The acidity of rain comes from its reaction with carbon dioxide in the atmosphere and the chemical weathering of rocks effectively uses up this gas. Thus, without weathering and many other natural processes, levels of carbon dioxide would steadily rise and temperatures increase. Weathering is also crucial for the release of nutrients from rocks which help make soils fertile.

Weathering takes place on a small scale. Laboratory experiments show that atoms close to the surfaces of the minerals that make up rocks react with acidic water and other compounds. This modifies the mineral's structure and chemical composition. Until recently, it has been very difficult to study how these changes take place naturally, because of the complexity of the mineral, mud and microbe mixture found in a typical soil. In collaboration with colleagues at the University of Glasgow (Maureen MacKenzie), the University of Reading (Mark Hodson) and the Natural History Museum (Caroline Smith), we have found a way of studying the chemical composition and structure of the naturally weathered surfaces of minerals on a nano-scale. We have used a newly developed technique called Focused Ion Beam (FIB) milling. Areas of interest on the surfaces of weathered minerals are initially selected using a scanning electron microscope (SEM), which forms high magnification images of the surface. The area is then coated with thin layers of gold and platinum to protect it from damage as two back-to-back trenches are cut into the surface using the high energy ion beam of the FIB. The trenches do not quite touch leaving an extremely thin slice centred on the area of interest. We remove the slice with a fine glass needle and a very steady hand. Because the slice is so thin we can look at it with a transmission electron microscope (TEM) or a scanning transmission electron

Scanning electron microscope image of a trench in a Shap feldspar. The feldspar is shown in purple, a fungal hypha (microbe) and reaction products in yellow, and the protective gold and platinum in turquoise.



Scanning transmission electron microscope (STEM) image of a FIB-produced cross-section of a Glen Feshie feldspar. The feldspar is shown in purple, fungal hyphae in yellow, reaction products including clays in red, and the protective gold and platinum in turquoise.

microscope (STEM), both of which form images at magnifications of up to half a million times by passing a high energy beam of electrons through the thinned sample.

Our work has concentrated on a mineral called feldspar, which is abundant in rocks that form the Earth's crust. Feldspar weathers relatively rapidly and so is an important source of soil nutrients. We took samples from pits dug into soils at Shap in the Lake District, and Glen Feshie in the Cairngorm Mountains of Scotland. The team dug down to bedrock and selected feldspars from a variety of soils to ensure they were weathered sufficiently.

We found that Shap grains are composed of fine-scale layers of sodium- and potassium-rich feldspar. The sodium-rich parts dissolve more rapidly to form shallow troughs. With progressive weathering these troughs grow to form tiny holes on and through the feldspar surface, called etch pits, which allow soil waters to attack the interior of the mineral grain. Therefore, for the Shap grains we can demonstrate the important influence of the internal structure and chemical composition of the mineral on the weathering process. We also used X-ray Photoelectron Spectroscopy (XPS) to analyse the chemical composition of outer surfaces of Shap feldspars. The work showed that their surface has a different chemical composition to the interior of the grain. This finding indicates that certain chemical elements are selectively removed from the feldspar crystal by weathering processes.

In contrast, slices through Glen Feshie feldspar surfaces show a complex association of clay minerals, amorphous (ie non-crystalline) reaction products and microbes, including bacteria, fungae and diatoms (a type of algae). The feldspar surfaces are often obscured by these materials and so the FIB milling technique is an ideal way of examining the feldspar surface and its relationship with released nutrients and other weathering products. The clays and amorphous reaction products are typically found directly beneath the microbes suggesting that these organisms play a key role in initiating or speeding-up weathering reactions. This was supported by an observation of minor changes to the feldspar crystal structure where it was in direct contact with the clay minerals.

In conclusion, our results illustrate the complex processes involved in mineral weathering in different soil environments. The Shap samples show the subtlety and very fine scale of

Co-workers Caroline Smith and Mark Hodson digging a soil pit in Glen Feshie, NW Scotland.

changes in the chemistry and structure of a decaying mineral, whereas Glen Feshie grains reveal the importance of microbial and chemical processes acting in tandem. Our use of the FIB milling technique in combination with high magnification electron microscopy has allowed, for the first-time, detailed observation and quantification of the nano-scale weathering processes in soils. This pioneering work will help to guide future research on weathering mechanisms and its rates, so that we can understand better how the Earth system responded to changes in atmospheric chemistry and temperature in the past. These results may then be used to help predict the impact of global warming now and in the future. ❖

Drs David J. Brown and Martin R. Lee are geologists and this work was undertaken at the department of Geographical and Earth Sciences, University of Glasgow. David Brown's current address: Department of Civil and Structural Engineering, University of Sheffield, Kroto Research Institute, email: d.j.brown@sheffield.ac.uk, martin.lee@ges.gla.ac.uk