## **Dissolution of Pyroxenes and Amphiboles During Weathering**

Abstract. Augite, hypersthene, diopside, and hornblende all undergo dissolution during weathering by means of the formation, growth, and coalescence of distinctive, parallel, lens-shaped etch pits. Similar etch features can be produced if these minerals are treated in the laboratory with concentrated hydrofluoric acid plus hydrochloric acid. These pits most likely form at dislocation outcrops, and their shape and orientation are controlled primarily by the crystallography of the underlying mineral. The results are similar to those found for soil feldspars and suggest that silicate weathering, in general, takes place by selective etching and not by general attack of the surface with consequent rounding as necessitated by bulk diffusiontype weathering theories.

Earlier studies (1, 2) have shown that sodium and potassium feldspars undergo dissolution during weathering by means of the development of distinctive, crystallographically controlled etch pits and not by general attack of the surface with consequent rounding. The presence of etch pits was used to support the contention that the rate-controlling step in mineral dissolution during weathering is chemical reaction at the interface between primary minerals and soil water (2, 3), and not diffusion, either in solution, in a surface precipitate layer, or within the primary minerals themselves (4). Our work on feldspars has led us more recently to the investigation of other minerals. We report here our results on the surface morphology of pyroxenes and amphiboles which have undergone dissolution as a result of weathering in soils and attack by HF in the laboratory. We have found a distinctive type of etch pitting, analogous to that in feldspars, which appears to be characteristic of chain-type silicates that have undergone dissolution under earth surface conditions (5).

Pyroxene and amphibole mineral grains were separated from in situ soils

taken by us from the following rock bodies: Coffman Hill diabase, Bucks County, Pennsylvania (augite and hypersthene); Websterite ultrabasic body, Webster, North Carolina (diopside and enstatite); Baltimore (meta) gabbro, Baltimore County, Maryland (hornblende); and Rich Mountain ultrabasic body, Ashe County, North Carolina (hornblende). In order to identify the minerals and to study their surface morphology, obscuring soil clay was removed with an ultrasonic cleaner. Grains greater than about 100  $\mu$ m were then handpicked under a binocular microscope to separate out the pyroxenes or amphiboles, or both. Each mineral separate was positively identified by x-ray diffraction and a petrographic microscope. Identified material selected for further study was mounted on stubs and examined with a scanning electron microscope (SEM) (ETEC model U-1).

In an attempt to reproduce etch features found in soil grains, we also subjected fresh, unweathered pyroxenes and amphiboles, taken from the host rocks of the above soils, to leaching in 5



Fig. 1. Photomicrographs made with the SEM of pyroxene grains from soils. (a) Lens-shaped etch pits on hypersthene. (b) Lens-shaped etch pits on augite. Note the side-by-side alignment along lamellae boundaries. (c) Deeply striated surface on diopside [detail of (d)]. (d) Single crystal of diopside showing the parallelism of striations and the c-axis of the crystal. (e) Side-by-side alignment along lamellae boundaries of lens-shaped etch pits on augite with the formation of a sawtooth-lined crack. (f) Single crystal of hypersthene showing cracks resulting from etch pit coalescence.

percent HF plus 12 percent HCl solution for periods ranging from a few minutes to 24 hours. The use of concentrated HCl was found necessary to prevent the precipitation on the mineral grains of insoluble fluorides which would otherwise obscure their surfaces. By itself, HCl produced no discernible etch features.

Examination of over a hundred photomicrographs has led us to the conclusion that pyroxenes and hornblende undergo selective etching on their surfaces, presumably at the outcrops of dislocations, with the consequent formation of similar etch features. The basic building block, found in all minerals, is the lens-shaped etch pit (Fig. 1, a and b). These pits, in every soil grain examined, were found to be oriented with their long axes parallel to one another. Where external morphology made it possible for us to determine crystallographic orientation, the lensshaped pits also paralleled the c axis of the crystal. Thus, the pits may serve as a method for determining the orientation of otherwise anhedral grains.

The lens-shaped pits were commonly found to be aligned, either along their long axes or along their short axes. Endto-end alignment along long axes (Fig. 1c) results in the formation of deeply striated surfaces (Fig. 1d). By contrast, side-by-side alignment along short axes (Fig. 1, b and e) and subsequent coalescence results in the formation of roughwalled cracks (Fig. 1, e and f). These cracks, which are usually filled with clay weathering product, were especially common in augite and hypersthene. As the pits forming the cracks enlarge and coalesce, the regions of primary undissolved mineral remaining between pits become tooth- or needle-shaped and sometimes bear a striking, albeit superficial, resemblance to cave deposits such as stalactites (Fig. 2, a and b). In augite, side-by-side alignment often occurs along the boundaries of basal lamellae (partings) (Fig. 1, b and e). This is not unexpected since these boundaries should be sites of high numbers of dislocations due to structural mismatch. In fact, parting dislocations may constitute major sites for the attack of augite by soil solutions.

Continued weathering results in the



Fig. 2. Photomicrographs made with the SEM of augite and hornblende from soils and from HF-HCl dissolution in the laboratory. (a) Augite from soil showing "cave" features. (b) Augite treated with HF-HCl in the laboratory. (c) Hornblende from soil showing "teeth." (d) Hornblende treated with HF-HCl in the laboratory.

production of more pits and cracks but at different rates for different minerals. Observations of coexisting grains from the same soil show that augite becomes extensively pitted (and thus, weathered) more rapidly than hypersthene (6). Pitting continues until a fragile "shell" of the original grain exists. During erosive transport, such shells should disintegrate and provide a source of fine-grained ferromagnesian material for further weathering.

Most all of the etch features of soil grains could be duplicated if the unweathered minerals were treated with strong HF-HCl solution (Fig. 2, a through d). This shows that the nature of the etch features is controlled primarily by crystallography and not by the type of etchant. (Natural soil acids are weaker than our HF-HCl solution and act over much longer times.) However, the degree of duplication was not as exact as we had previously found with feldspars (2), and occasional etch features were found as a result of HF-HCl treatment which did not occur on natural soil grains. This suggests some control by etchant type.

> **ROBERT A. BERNER** E. L. SJÖBERG\* MICHAEL A. VELBEL MICHAEL D. KROM

Department of Geology and Geophysics, Yale University, New Haven, Connecticut 06520

## **References and Notes**

- K. Tazaki, Pap. Inst. Thermal Spring Res., Okayama Univ. 45, 11 (1976); H. Eswaran and W. C. Bin, Soil Sci. Soc. Am. J. 42, 154 (1978); W. D. Keller, Clays Clay Miner. 24, 107 (1976); R. A. Nixon, Geology 7, 221 (1979).
   M. J. Wilson, Soil Sci. 129, 349 (1975); R. A. Berner and G. R. Holdren, Jr., Geology 5, 369 (1977); Geochim. Cosmochim. Acta 43, 1173 (1979)
- (1979)
- R. Petrović, R. A. Berner, M. B. Goldhaber 3.
- 4.
- R. Petrović, R. A. Berner, M. B. Goldhaber, Geochim. Cosmochim. Acta 40, 537 (1976).
  R. Wollast, ibid. 31, 635 (1967); R. W. Luce, R.
  W. Bartlett, G. A. Parks, ibid. 36, 35 (1972); H.
  C. Helgeson, ibid. 35, 421 (1971); T. Paces, ibid. 37, 2641 (1973); E. Busenberg and C. V. Cle-mency, ibid. 40, 41 (1976).
  Some etch features resulting from weathering are similar to those described for intrastratal so-lution [see: R. A. Rhamani, J. Sediment. Petrol. 43, 882 (1973); T. R. Walker, B. Waugh, A. J. Crone, Geol. Soc. Am. Bull. 89, 19 (1978); K. O. Stanley and L. V. Benson, in Aspects of Diagen-esis, P. A. Scholle and P. R. Schluger, Eds. (Special Publication 26, Society of Economic esis, P. A. Scholle and P. R. Schluger, Eds. (Special Publication 26, Society of Economic Paleontologists and Mineralogists, Tulsa, Okla., 1979), pp. 401-423; B. Waugh, in Scanning Electron Microscopy in the Study of Sediments, W. B. Whalley, Ed. (Geological Abstracts, Ltd., Norwich, England, 1979), pp. 329-346].
  6. This was mirrored in the laboratory by the more rapid dissolution in HF-HCl of augite (and diopside) as compared to hypersthene (and enstatite).
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- Present address: Geologiska Institutionen, Stockholms Universitet, 113 86 Stockholm,

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