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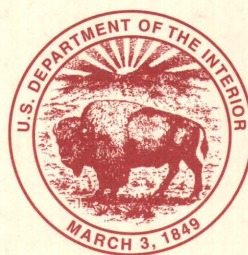
U.S. DEPARTMENT OF THE INTERIOR

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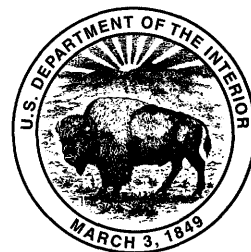
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Garnet Dissolution in Oxalic Acid—
A Possible Analog for Natural Etching of Garnet
by Dissolved Organic Matter

By Paula L. Hansley *and* Paul H. Briggs

U.S. DEPARTMENT OF THE INTERIOR

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Garnet Dissolution in Oxalic Acid—A Possible Analog for the Natural Etching of Garnet by Dissolved Organic Matter

By Paula L. Hansley *and* Paul H. Briggs

ABSTRACT

Naturally etched garnets have been interpreted to be the result of dissolution by warm (80°C–130°C), organic-acid-bearing ground water, but the mechanism of dissolution has not been investigated. Specifically, the question is whether dissolution is surface- or transport-controlled and whether it is stoichiometric (congruent) or nonstoichiometric (incongruent). In order to determine the mechanism of dissolution, laboratory conditions were set up to be as similar as possible to the assumed diagenetic environment of the naturally etched garnets. Almandine garnets were placed in Tamm's reagent (a buffered oxalic acid solution) at 80°C, and analyses of cation concentrations in the etchant in each of eight sample containers were made several times during a 150-day period by inductively coupled plasma-atomic emission spectrometry.

Although some results were ambiguous, data indicate that dissolution of the garnets is nonstoichiometric; that is, it proceeds by a two-step reaction similar to that of other aluminosilicate minerals. Apparently, hydrogen ions are first exchanged for cations in the outer layer of the garnet structure; then the residual aluminum-silicon layer is released into solution. Reductive dissolution of Fe^{3+} substituting for aluminum and the formation of strong aluminum oxalate complexes may contribute to the breakdown of the garnet structure.

At the end of the experiment, observation of the garnets by the scanning electron microscope confirmed that most originally smooth surfaces of the grains had been replaced by rounded and pointed mammillary features. The polygonal bases of the mammillary features may be the beginning of sharp etch planes and suggest that dissolution is a surface-controlled process.

INTRODUCTION

Faceted garnets (as shown in fig. 1) are present in clastic sedimentary rocks of many ages. Before the realization that diagenesis was a widespread phenomenon, these angular surfaces were thought to have formed by abrasion during transport. Only a few geologists attributed the facets to chemical etching (Bramlette, 1929; Smithson, 1941; McMullen, 1959), whereas others contended that the features were overgrowths (Sauer, 1900; Simpson, 1976; Mader, 1980; Howie and others, 1980). Most geologists now agree that these angular features are caused by dissolution during burial diagenesis (Rahmani, 1973; Hemingway and Tamar-Agha, 1975; Morton, 1979, 1984; Gravenor and Leavitt, 1981; Borg, 1986; Hansley, 1987; Morton and others, 1989). This conclusion is based on the delicate nature of the facets, crystallographic orientation of the planes, and textural relationships between the facets and authigenic minerals and on the fact that etched garnets have been created in the laboratory under diagenetic conditions.

In a study of uranium-bearing sandstone in the Upper Jurassic Morrison Formation in northwestern New Mexico, Hansley (1987) observed faceted almandine-spessartine garnets in altered sandstone (fig. 1). Oxygen and deuterium isotope data for associated authigenic clay minerals suggest that a warm (100°C–130°C), sulfate-rich fluid that migrated updip through permeable sandstone of the Morrison Formation during the middle Tertiary was responsible for the etching (Whitney and others, 1986). This conclusion is supported by paleohydrologic modeling, which indicates that waters derived from deep in the San Juan Basin moved updip into the Morrison Formation during burial (Sanford, 1993). Because of the presence of noncellular organic material most similar to humate (Hatcher and others, 1986) in the Morrison where the etched garnets are present, Hansley (1987) suggested that organic acids derived from the diagenesis of the organic material facilitated dissolution. Organic acids may also have been contained in the basinal fluids that apparently migrated updip through the Morrison because moderate to high concentrations (5,000–10,000 ppm) of organic acid anions have been reported in many deep-basin waters, especially oil-field brines (Carothers and Kharaka, 1978).

Most organic acid anions reported in oil-field brines, however, are monocarboxylic (primarily acetate) and are not good complexing agents. In a study of brines from two oil
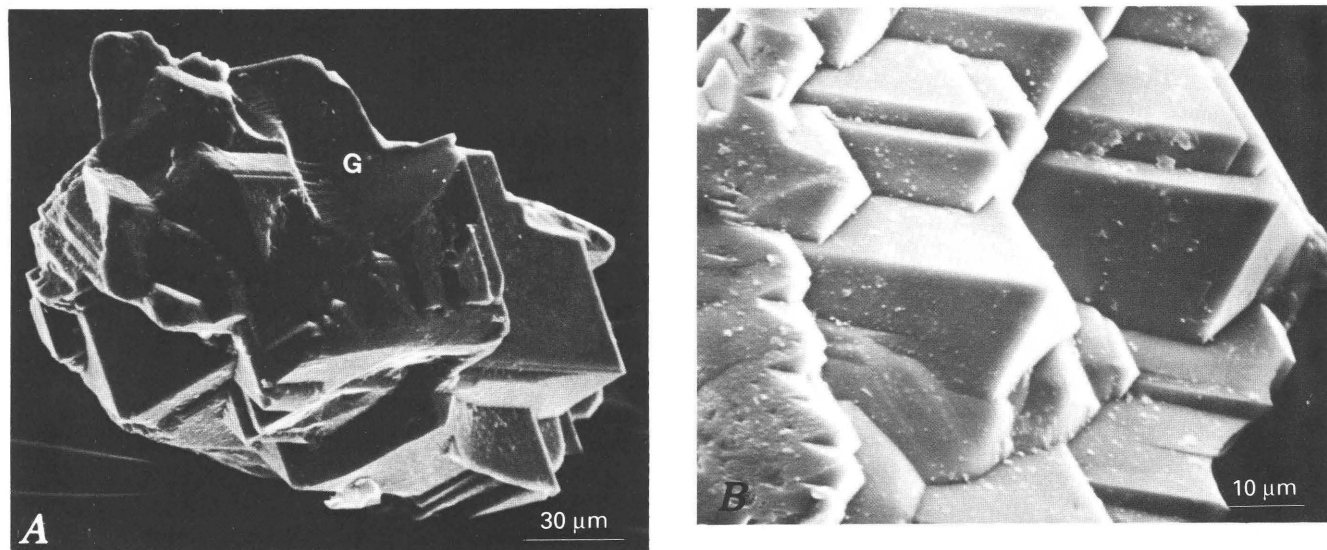
Figure 1.   Scanning electron microscope photomicrographs of naturally faceted almandine-spessartine garnets from the Upper Jurassic Morrison Formation, northwestern New Mexico. *A*, Faceted garnet showing a piece of residual detrital garnet (**G**). *B*, Closeup of faceted garnet.

fields in California, MacGowan and Surdam (1988) showed that a significant proportion of acid anions is dicarboxylic (as much as 2,640 mg/L). Kharaka and others (1993) resampled brines from the same oil fields from which MacGowan and Surdam had taken their water samples and found very low concentrations of dicarboxylic acid anions, including oxalate (0.05–0.16 mg/L), succinate (a trace to 0.22 mg/L), malonate (a trace to 0.08 mg/L), and methyl succinate (3.6–22 mg/L). The discrepancy in acid anion values may be due to different sampling techniques, the rapid rate of thermal decomposition of dicarboxylic acid anions, and the low solubility of calcium oxalate and calcium malonate (Kharaka and others, 1986). Although there is no consensus as to their natural concentrations and how much they affect chemical reactions, organic acids clearly influence diagenesis near sandstone-shale contacts, in petroleum reservoirs, and near decomposing organic matter.

To investigate the relative efficacy of acid for leaching garnets, Hansley (1987) conducted a series of laboratory experiments using natural garnets and a variety of inorganic and organic acids. Only oxalic acid created etch patterns identical to those on naturally etched garnets. This is an important observation because, as Honess (1927) demonstrated, the type of etch pattern created on a crystal surface is usually specific to the etching solution. An exception is a recently discovered, microbially produced etching texture on basalt that pseudomorphs bacteria in highly alkaline environments (Thorseth and others, 1992). Other experiments have demonstrated that organic acids, especially polyfunctional acids (Welch and Ullman, 1993), are excellent solvents of aluminosilicate minerals (see Stoessel and Pittman, 1990, for a review). Oxalic acid is common in natural ground waters in environments such as peat bogs

where type III kerogen is decaying. Gestsdottir and Manning (1992) found that oxalate increases the solubility of albite much more than acetate. Hajash and others (1992) concluded that oxalic acid is more effective than acetic acid at increasing the solubility of feldspar at 100°C and at pH values typical of diagenetic environments; both oxalate and acetate increase the solubility of feldspar more than inorganic acids. Grandstaff (1986) found that the dissolution rate of olivine (also an orthosilicate) increases 30 times with the addition of an organic ligand to a KCl solution at pH 4.5.

Most studies of dissolution have been conducted on feldspars. Dissolution of aluminosilicates was originally thought to be "transport controlled"; that is, controlled by the rate at which ions diffuse through a precipitated surface layer, such as a precipitated clay mineral, or by transport of ions away from the surface (Berner, 1978; Paces, 1978). Diffusion of ions through this surface layer was thought to proceed via a parabolic rate law (Wollast, 1967; Helgeson, 1971; Busenberg and Clemency, 1976). It is now accepted that parabolic-rate dissolution is probably an artifact of sample preparation caused by fine particles that are produced during grinding and adhere to the surfaces of grains.

Most scientists now agree that feldspar dissolution proceeds by a surface-controlled reaction, but it is not clear if the reaction proceeds by a one-step (stoichiometric) or a two-step (ion-exchange followed by dissolution) process. In a one-step process, ions go into solution in stoichiometric proportions. In the two-step reaction, H^+ exchanges for cations forming a protonated aluminosilicate that then breaks down more slowly. Many favor the two-step process (Berner, 1978, 1981; Dibble and Tiller, 1981; Aagard and Helgeson, 1982). Berner and Holdren

(1979) used X-ray photoelectron spectroscopy (XPS) to show that the H^+-exchanged surface layer was not "thicker than about 30Å," but their analytical technique could not have resolved thinner layers. In a subsequent study, Berner and Schott (1982) found cation-depleted layers 5Å–20Å thick that they did not consider to be diffusion limiting. They concluded that dissolution is interface controlled and takes place at sites of excess surface energy, such as dislocations, edges, microfractures, twin boundaries, or crystal defects. In an experiment in which HCl was used to study the dissolution kinetics of alkali feldspar, Holdren and Speyer (1986) concluded that feldspar dissolution was surface controlled and nonstoichiometric. Knauss and Wolery (1986) leached feldspars at 70°C and pH values ranging from 4 to 10 and interpreted the prismatic etch pits that resulted as products of a surface-controlled process. Wollast (1967) suggested that, if the etchant is not aggressive, dissolution is controlled by the thickness of the H^+-exchanged layer and the rate of diffusion of ions through this layer. Chou and Wollast (1984) proposed that a layer enriched in aluminum and silicon a few tens of angstroms thick was present on the surface of a dissolving feldspar. They concluded that the composition of the residual layer was strongly influenced by pH. Goossens and others (1989) identified a residual leached layer on the surfaces of acid-reacted feldspar, supporting their hypothesis that absorption of water is a key step in the dissolution process. Schott and others (1981) and Berner and Schott (1982) showed by XPS that such a layer is present in pyroxenes and amphiboles and that this layer is commonly less than one unit cell thick.

Results of orthosilicate dissolution experiments are ambiguous. In 1978, Grandstaff proposed that the dissolution of forsterite is controlled by the rates of surface reactions because he did not see a residual or precipitated layer thicker than the 100Å resolution of the scanning electron microscope (SEM). In transmission electron microscope (TEM) studies of orthosilicates, Westrich and others (1992) showed that dissolution of phenacite (Be_2SiO_4) proceeds as a surface-controlled reaction through a 10–20-μm-thick amorphous, hydrogen-exchanged, cation-leached layer. Their results for olivine, however, did not reveal the presence of such a layer.

Velbel (1993a) concluded that dissolution is transport controlled in saprolites because secondary minerals (iron oxides) are found on the etched surfaces of almandine garnets. Saprolites are formed, however, in environments characterized by oxidizing conditions, a lack of complexing agents, low temperatures, and saturation. The presence of precipitates on the etched garnet surfaces may be due mainly to slow ground-water flux in saprolites that does not enable dissolved ions to be transported from sites of dissolution.

The experiment described herein was an extension of the previous laboratory studies that showed the effectiveness of organic acids in dissolving garnet (Hansley, 1987). This time, however, the experiment was designed to determine the mechanism of dissolution of garnet during the etching process in a fluid thought to resemble a naturally occurring ground water containing organic acids.

CRYSTAL STRUCTURE

Garnet is an orthosilicate mineral that crystallizes in the isometric system. The general formula for the garnet group is $X_3Y_2Z_3O_{12}$, with eight formula units per unit cell (Meagher, 1982). The X-cation is coordinated by eight oxygens in a configuration that has been described as a triangular dodecahedron or distorted cube. The Y-cation is coordinated by six oxygens in the configuration of a slightly distorted octahedron. Finally, the Z-cation is coordinated by four oxygens in a distorted tetrahedron or tetragonal disphenoid. Major X-cations are calcium, manganese, Fe^{2+}, and magnesium; major Y-cations are aluminum, chromium, and Fe^{3+}; and the major Z-cation is silicon. Titanium can occur in the X- or Y-sites. The ZO_4 tetrahedra and YO_6 octahedra share corners, forming chains that parallel the "a" axes (see Meagher, 1982, fig. 3).

EXPERIMENTAL DESIGN

To determine the process involved in dissolution, we designed experiments in which the etchant was periodically analyzed for 150 days. Untreated pyrope-almandine ($[Mg,Fe]_3Al_2Si_3O_{12}$) garnets from the Barton Mines Corporation deposit in the Adirondack Mountains of New York were chosen for the experiments because of their relatively uniform composition (table 1), consistent size, and smooth, unetched surfaces (fig. 2). Magnesium and Fe^{2+} are the major X-cations in these garnets, and calcium and manganese are the minor X-cations; Al^{3+} is the major Y-cation, but, as table 1 demonstrates, substantial Fe^{3+} substitutes for aluminum in these garnets; silicon is the Z-cation. Chemical, SEM-energy dispersive system (EDS), and X-ray fluorescence (XRF) techniques were used to detect elemental abundances. X-ray fluorescence analysis of a bulk sample also detected titanium (table 2). Barton Mines' average chemical analysis differs from our XRF results mainly in percentages of calcium and magnesium (see tables 1 and 2). Based on Barton Mines' average chemical analyses (standard deviation is proprietary),
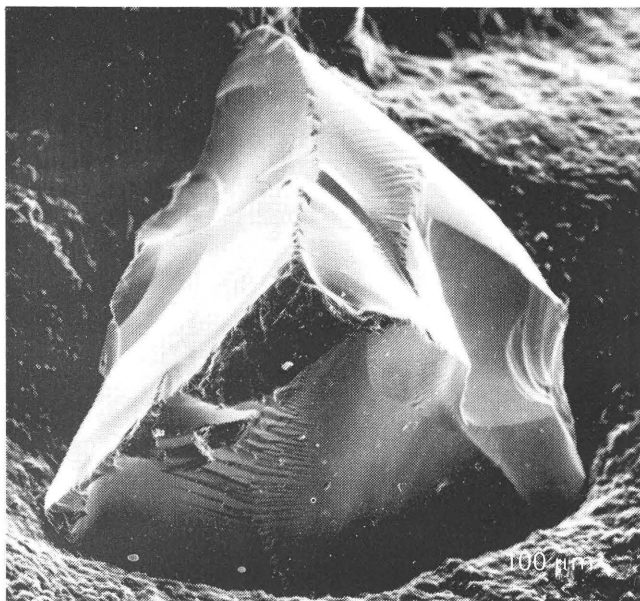
Figure 2. Scanning electron microscope photomicrograph of smooth, unetched pyrope-almandine garnet from the Barton Mines Corporation deposit in the Adirondack Mountains, New York.

Table 1. Composition of pyrope-almandine garnet from the Barton Mines Corporation deposit in the Adirondack Mountains, New York, as determined by chemical analysis. [Analyses by Barton Mines Corporation]

Oxide	Weight percent
SiO_2	41.34
Al_2O_3	20.36
FeO	9.72
Fe_2O_3	12.55
MgO	12.35
CaO	2.97
MnO	0.85
Total	100.14

Table 2. Composition of pyrope-almandine garnet from the Barton Mines Corporation deposit in the Adirondack Mountains, New York, as determined by X-ray fluorescence. [Analyst, Joe Taggart]

Oxide	Weight percent
SiO_2	39.1
Al_2O_3	21.4
Fe_2O_3*	26.5
MgO	7.2
CaO	7.3
Na_2O	0.15
K_2O	<0.02
TiO_2	0.11
P_2O_5	0.05
MnO	0.78
Total	102.61

*All Fe reported as Fe^{3+} (total Fe^{3+}), although some Fe^{2+} is present.

XRF data, and SEM-EDS data, the composition of garnet probably varies by as much as 40 percent. The average diameter of each garnet was 0.5 mm and the average weight 0.1 mg. Grains were weighed on a Mettler AK 160 balance precise to ±0.0001 g.

Eight Teflon containers were filled with Tamm's reagent (0.175M $[NH_4]_2C_2O_4 \cdot H_2O$ + 0.100M $H_2C_2O_4 \cdot 2H_2O$). Tamm's reagent was chosen to be the etchant because it is an internally buffered mixture that includes both the free acid and acid anion, probably mimicking the behavior of oxalate species. The surfaces of garnet grains were cleaned ultrasonically in distilled water, and then the garnets were mounted with carbon glue on SEM carbon stubs. The glue contained only carbon, oxygen, and hydrogen. The carbon stubs are "spec pure" and contain the following elements: Al <0.1, Fe <0.2, Mg <0.2, and Si <0.1 (µmoles). Most garnets were photographed under the SEM before the experiments to ascertain the presence of smooth surfaces. Stubs and solution were placed in screw-cap, Teflon PFT containers that varied in capacity from 57 mL to 200 mL. As controls, one container (B87) contained 50.8 g (50 mL) of solution, and another container (B91) contained 50.8 g (50 mL) of solution and a carbon stub coated with carbon glue. A third container (B) had 152.3 g (150 mL) of solution and >30 garnets (>3.0 mg) mounted on a carbon stub. A fourth container (A) had 101.5 g (100 mL) of solution and 22 garnets (>2.2 mg) mounted on the stub. The other four containers each had 50.8 g (50 mL) of solution and carbon stubs carrying variable numbers of garnet grains: 86 (12 grains, 1.2 mg), 89 (30 grains, 3.0 mg), 93 (7 grains, 0.7 mg), and 94 (18 grains, 1.8 mg). All weights are approximate. The pH of the Tamm's reagent was internally buffered at 3.25 throughout the experiments. All containers were kept at 80°C in a convecting oven throughout the experiment.

Aliquots of solution were removed from each Teflon container at the beginning of the experiment and then after 4, 10, 17, 25, 34, 67 (only two containers were sampled), and 150 days. Each time a 5-mL aliquot of solution was removed, the remaining solution was stirred. To prevent adsorption on container walls and precipitation of any phases, the 5-mL aliquots were acidified with 3N HCl to approximately pH 2. The solutions were then analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) for aluminum, calcium, iron, magnesium, and silicon. Manganese was analyzed for but not detected.

At the end of the experiment, the garnets were dried. They, and their carbon stubs, were then coated with gold and observed under the SEM to compare changes in texture from the beginning to the end of the experiment. Precipitates on and around the garnets were analyzed by SEM-EDS.

Figure 3. Inductively coupled plasma-atomic emission spectrometry analysis of Tamm's reagent from container B87, which had no carbon mount or garnets.

Figure 4. Inductively coupled plasma-atomic emission spectrometry analysis of Tamm's reagent from container B91, which had a carbon mount with no garnets.

RESULTS

INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY

ICP-AES results are shown in figures 3–10 and table 3. Detection limits are as follows: Al, 0.4; Ca, 0.2; Fe, 0.4; Mg,

Figure 5. Inductively coupled plasma-atomic emission spectrometry analysis of Tamm's reagent from container A, which had garnets mounted on a carbon stub.
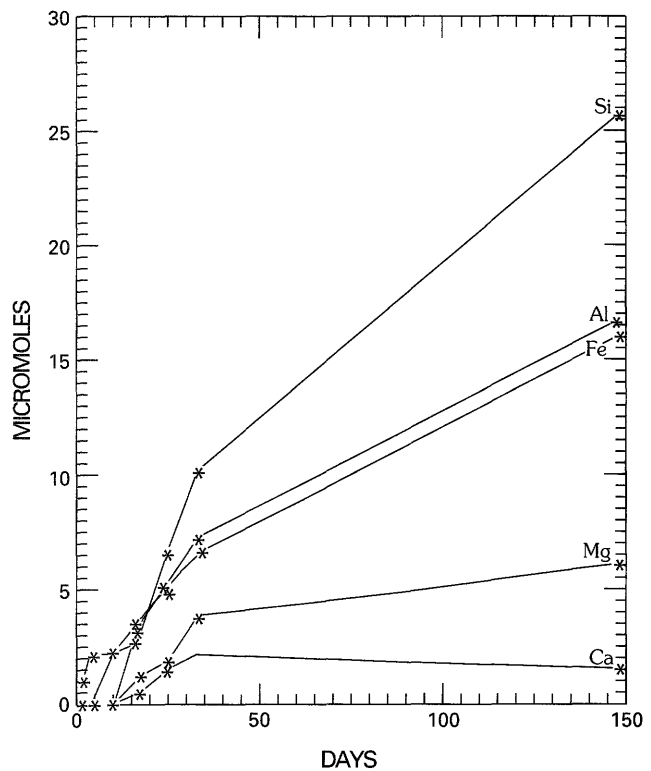
Figure 6. Inductively coupled plasma-atomic emission spectrometry analysis of Tamm's reagent from container B, which had garnets mounted on a carbon stub.

0.1; and Si, 0.2 μmoles. Analytical precision is ±10 percent relative standard deviation (RSD) and becomes less precise as the detection limit for each element is approached. As a control, the concentration of each element in container B91 (which contained solution, mount, and glue only) was subtracted from that in the other aliquots each time a measurement was made. Both control containers (B87 and B91)
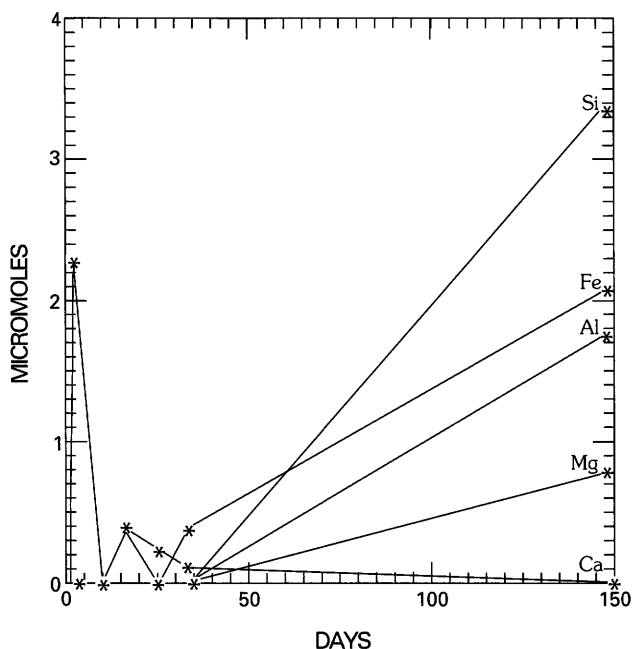
Figure 7. Inductively coupled plasma-atomic emission spectrometry analysis of Tamm's reagent from container 86, which had garnets mounted on a carbon stub.
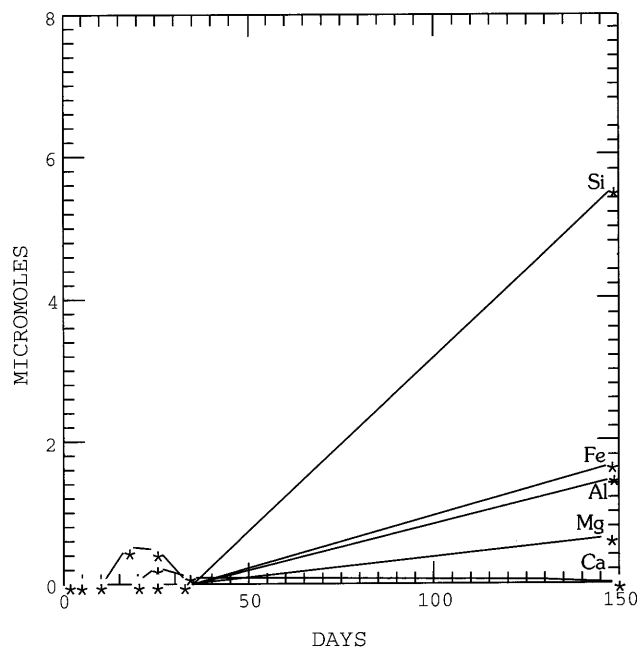
Figure 9. Inductively coupled plasma-atomic emission spectrometry analysis of Tamm's reagent from container 93, which had garnets mounted on a carbon stub.
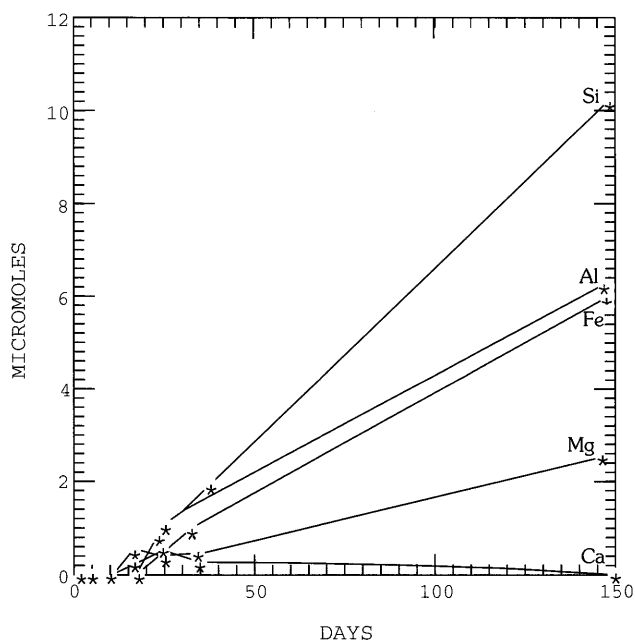
Figure 8. Inductively coupled plasma-atomic emission spectrometry analysis of Tamm's reagent from container 89, which had garnets mounted on a carbon stub.

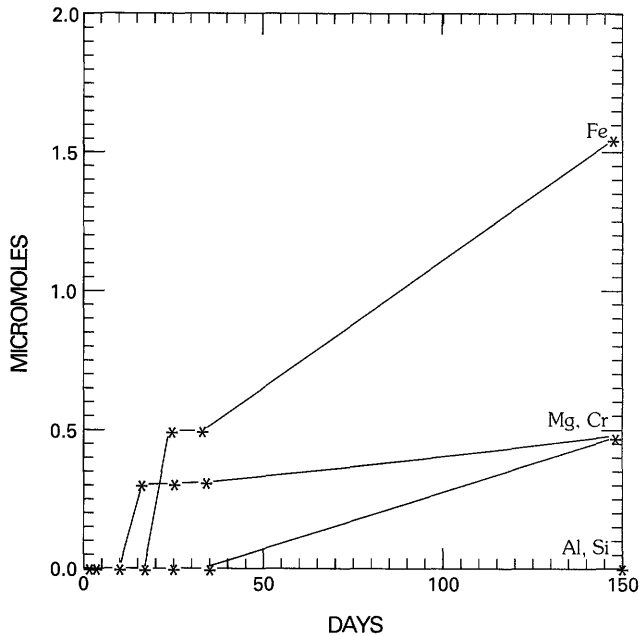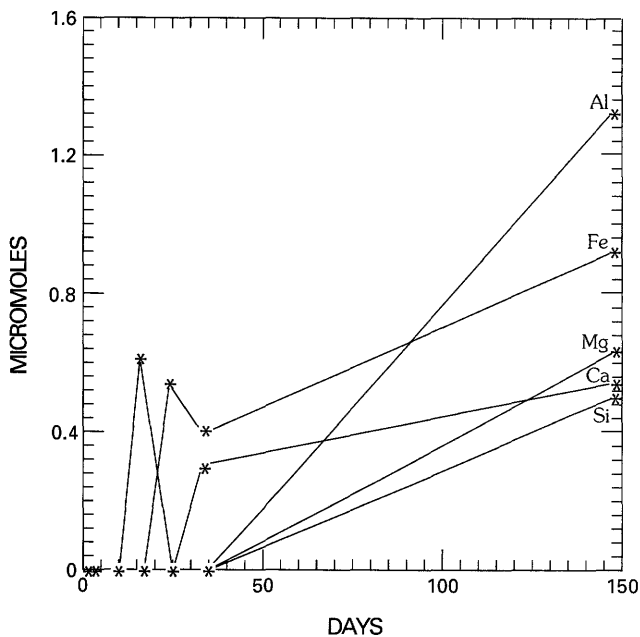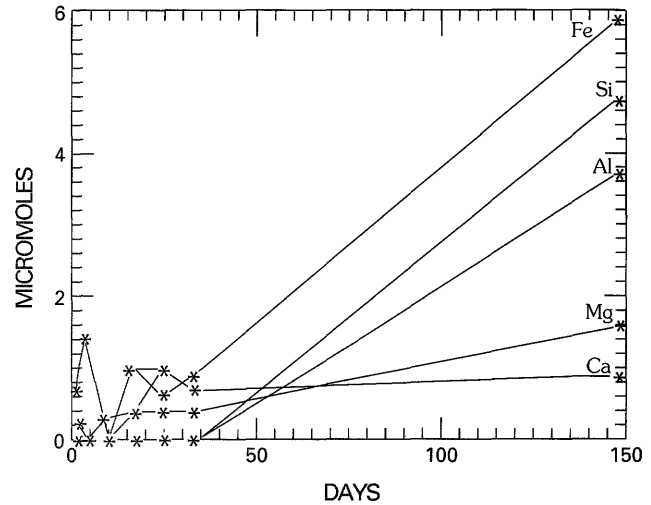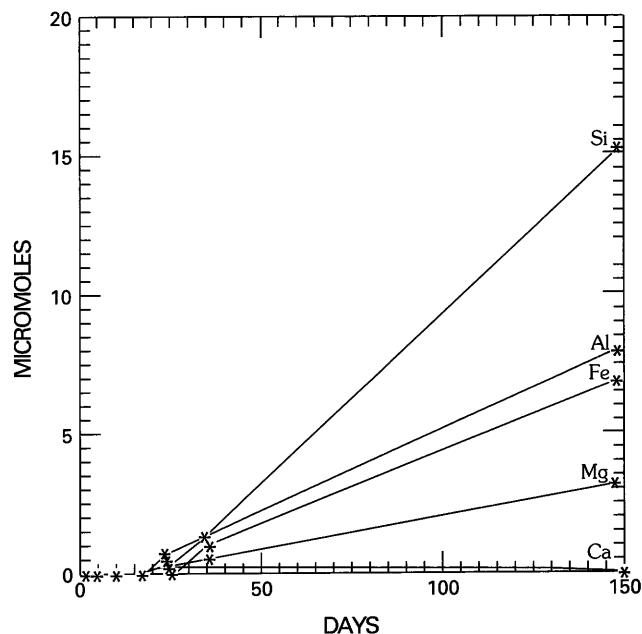**Figure 10.** Inductively coupled plasma-atomic emission spectrometry analysis of Tamm's reagent from container 94, which had garnets mounted on a carbon stub.

showed small amounts of calcium after 17 days that remained at approximately the same level throughout the experiment. In container B87, which contained only solution, iron was detected at 25 days, magnesium was detected at 150 days, and silicon was never detected (fig. 3). Container B91, which contained only a carbon mount and glue in

solution, showed detectable iron after 25 days and aluminum, magnesium, and silicon after 150 days (fig. 4).

Iron concentrations in container A were extremely variable. ICP-AES measurements showed that iron was present initially, was undetectable after 10 days and then was present after 17 days (fig. 5). Calcium was detected

Table 3. Inductively coupled plasma-atomic emission spectrometry analyses of Tamm's reagent taken from containers holding garnet experiments.

[The blank containers, B87 and B91, had 50.8 g of solution. Container A had 101.5 g of solution, container B 152.3 g, and the rest 50.8 g. Container A began with 2.2 mg of garnets, B 3.0 mg, 86 1.2 mg, 89 3.0 mg, 93 0.7 mg, and 94 1.8 mg. Precision is ±10 percent relative standard deviation. n.d. indicates not detected. Paul H. Briggs, analyst.

Day	Container	Element (µmoles)[1]					Day	Container	Element (µmoles)[1]				
		Al	Ca	Fe	Mg	Si			Al	Ca	Fe	Mg	Si
1	B87	n.d.	n.d.	n.d.	n.d.	n.d.	25	B87	n.d.	0.3	0.5	n.d.	n.d.
	B91	n.d.	n.d.	n.d.	n.d.	n.d.		B91	n.d.	n.d.	0.5	n.d.	n.d.
	A	n.d.	0.3	0.7	n.d.	n.d.		A	n.d.	1.0	0.6	0.4	n.d.
	B	n.d.	n.d.	1.1	n.d.	n.d.		B	5.1	1.5	4.7	1.9	6.5
	86	n.d.	n.d.	n.d.	n.d.	n.d.		86	n.d.	0.3	n.d.	n.d.	n.d.
	89	n.d.	n.d.	n.d.	n.d.	n.d.		89	1.1	0.5	0.5	0.4	1.1
	93	n.d.	n.d.	n.d.	n.d.	n.d.		93	n.d.	0.3	n.d.	n.d.	n.d.
	94	n.d.	n.d.	n.d.	n.d.	n.d.		94	0.8	0.4	n.d.	0.2	0.4
4	B87	n.d.	n.d.	n.d.	n.d.	n.d.	34	B87	n.d.	0.3	0.5	n.d.	n.d.
	B91	n.d.	n.d.	n.d.	n.d.	n.d.		B91	n.d.	0.3	0.4	n.d.	n.d.
	A	n.d.	n.d.	1.5	n.d.	n.d.		A	n.d.	0.7	0.9	0.4	n.d.
	B	n.d.	n.d.	2.2	n.d.	n.d.		B	7.3	2.4	6.2	3.1	10.3
	86	n.d.	n.d.	2.3	n.d.	n.d.		86	n.d.	0.1	0.4	n.d.	n.d.
	89	n.d.	n.d.	n.d.	n.d.	n.d.		89	1.5	0.3	1.0	0.4	1.6
	93	n.d.	n.d.	n.d.	n.d.	n.d.		93	n.d.	0.1	n.d.	n.d.	n.d.
	94	n.d.	n.d.	n.d.	n.d.	n.d.		94	1.1	0.2	0.8	0.4	1.1
10	B87	n.d.	n.d.	n.d.	n.d.	n.d.	150	B87	n.d.	0.4	1.5	0.4	n.d.
	B91	n.d.	n.d.	n.d.	n.d.	n.d.		B91	1.3	0.5	0.9	0.6	0.4
	A	n.d.	0.3	n.d.	n.d.	n.d.		A	3.6	0.8	5.8	1.5	4.7
	B	n.d.	n.d.	2.2	n.d.	2.2		B	15.6	1.4	16.0	6.3	23.4
	86	n.d.	n.d.	n.d.	n.d.	n.d.		86	1.7	n.d.	2.0	0.7	2.9
	89	n.d.	n.d.	n.d.	n.d.	n.d.		89	6.4	n.d.	6.0	2.5	10.1
	93	n.d.	n.d.	n.d.	n.d.	n.d.		93	1.5	n.d.	1.6	0.7	5.9
	94	n.d.	n.d.	n.d.	n.d.	n.d.		94	7.4	n.d.	6.6	3.2	15.3
17	B87	n.d.	0.3	n.d.	n.d.	n.d.							
	B91	n.d.	0.6	n.d.	n.d.	n.d.							
	A	n.d.	0.4	1.1	0.4	n.d.							
	B	3.4	0.5	3.5	1.3	2.7							
	86	n.d.	n.d.	0.4	n.d.	n.d.							
	89	n.d.	n.d.	0.6	n.d.	n.d.							
	93	n.d.	n.d.	0.6	n.d.	n.d.							
	94	n.d.	n.d.	n.d.	n.d.	n.d.							

[1]At the end of each time period, the concentration in container B91 was subtracted from the analysis of each aliquot drawn from a container holding garnets.

initially in solution, magnesium after 17 days, and silicon and aluminum at 150 days.

Analysis of the solution in container B revealed detectable iron at the beginning of the experiment (fig. 6). The iron concentration increased after 4 days, and silicon was detected after 10 days. All elements were present in detectable concentrations by the 17th day, and both iron and silicon had increased in concentration. All elements except calcium showed the most rapid increases in concentration at 150 days (fig. 6).

In container 86, a large spike of iron was detected at 4 days, and then the concentration of iron was extremely variable over the course of the experiment (fig. 7). Measurable amounts of calcium were present after 17 days, but silicon, aluminum, and magnesium were not detected until 150 days.

Iron was first detected in solution in container 89 on day 17; the rest of the elements were detected on day 25 (fig. 8). As the experiment continued, concentrations of all elements steadily increased except calcium, which declined.

In container 93, iron was detected in solution at 17 days and then not detected until the end of the experiment (fig. 9). Calcium steadily increased in concentration but declined in concentration at the end. Aluminum, silicon, and magnesium were not present in detectable amounts until the last analysis.

In container 94, measurable amounts of aluminum, calcium, magnesium, and silicon were present after 25 days, and iron was not detected until 34 days (fig. 10). The concentration of calcium declined, whereas that of the other elements increased markedly throughout the experiment.
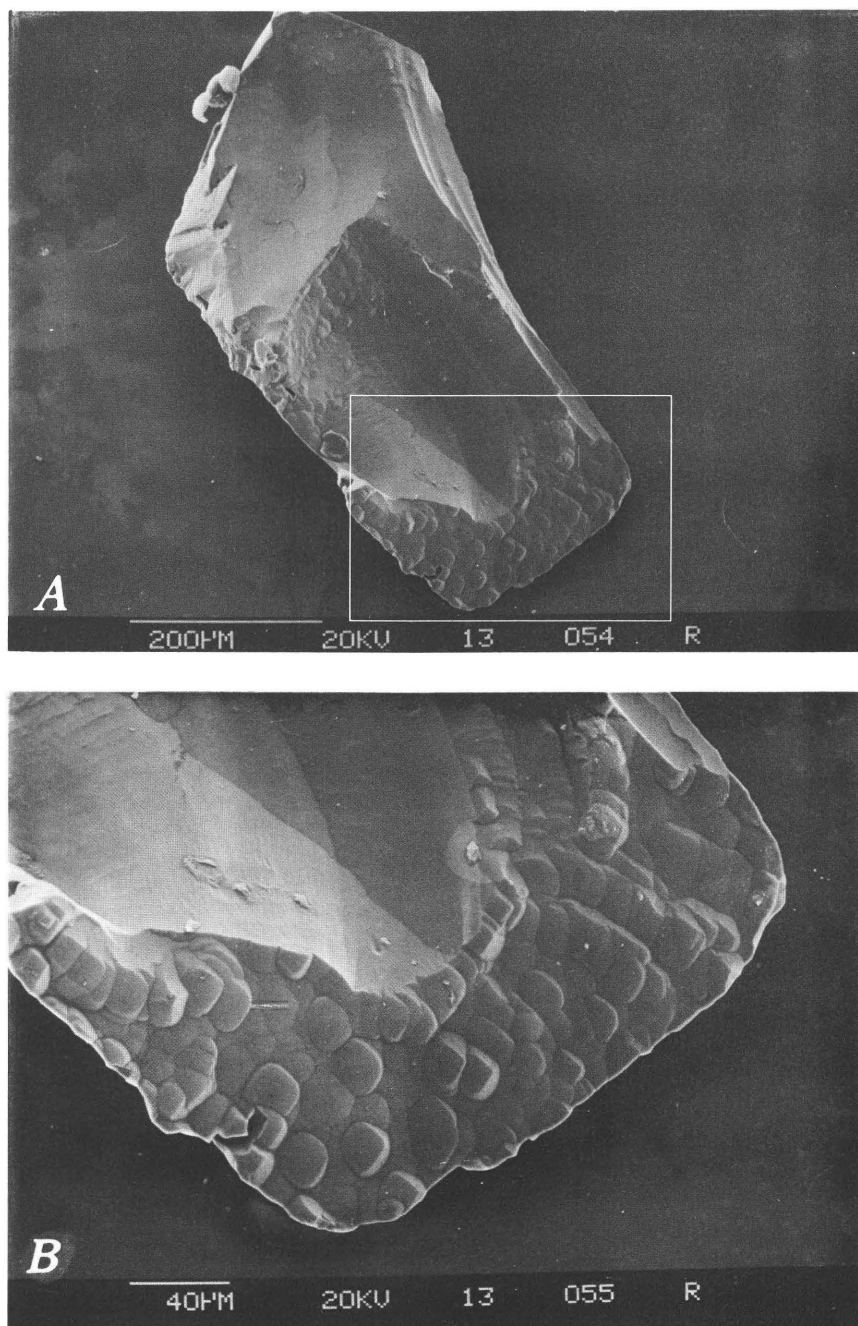
Figure 11.   Scanning electron microscope photomicrograph of garnet from container 86 at end of experiment showing that some surfaces remained smooth, whereas others have been etched. *A*, Garnet with smooth and etched surfaces. Box shows area of photomicrograph shown in *B*. *B*, Closeup of garnet in *A*.

SCANNING ELECTRON MICROSCOPY

Scanning electron microscopy observations showed that, although garnets were etched to almost the same degree, not all surfaces of the grains were etched. Some faces remained smooth, as can be seen in SEM microphotographs of a garnet from container 86 (fig. 11). Views of garnet surfaces under high magnification reveal the polygonal shapes of the etching patterns. Many of the features are rounded, and some display sharp corners (fig. 12). The presence or absence of secondary precipitates during the experiment is not known because the grains were not examined under the SEM until after the experiment had ended. At that time, white precipitates containing oxygen, carbon(?), and, presumably, hydrogen, which is not detectable with SEM-EDS, were present.

DISCUSSION

REASONS FOR FLUCTUATIONS IN CONCENTRATION

Analytical error (±10 percent RSD) may contribute to fluctuations in measured element concentrations in the solutions. The presence of iron in container B87 (solution only) after 25 days indicates that iron was being leached from the Teflon container. Although some iron also may have been derived from the other Teflon containers, it would be masked by the contribution of iron from the garnets. Calcium and magnesium also were apparently leached from the Teflon in container B87. The presence of all elements in container B91 indicates some leaching from the mounts, glue, and (or) containers. Because aluminum and silicon never were measured in B87, negligible amounts of these elements can be attributed to leaching from the mounts and (or) glue in all other containers.

Adsorption of elements on the walls of the Teflon containers could be a source of downward spikes (container 86, day 4) in the concentration curves. The large fluctuations of iron and calcium concentrations may be due to inhomogeneities in iron or calcium content on the surface of these iron- and calcium-rich garnets. SEM-EDS spectra of garnets before the experiment show variability in the analyses of iron and calcium in the garnet's structure of as much as 25 percent, more than that for the other elements.

Because iron was detected in the initial ICP-AES analyses of the solutions from containers A and B, it was derived from the carbon mount, carbon glue, or Tamm's reagent. The presence of iron and calcium in container A and iron in container B at the beginning of the experiment may be explained in part by desorption-adsorption (Mast and Drever, 1987). In what might be an analogous situation, Mast and Drever observed transient spikes of aluminum or silicon when oxalate was first added to or removed from undersaturated solutions containing oligoclase. They attributed this phenomenon to desorption-adsorption of these elements on feldspar surfaces away from sites of active dissolution.

Because iron is present in part as Fe^{3+} in the garnet structure, reductive dissolution could play a role in its rate and amount of dissolution. This process involves complex formation of Fe^{3+} with oxalate (or some other organic species), electron transfer, release of the oxidized organic product, and finally release of the reduced metal ion into solution (Stone and Morgan, 1987). The composition of the mineral, structure of the surface, nature of the electron donor, and morphology of the surface affect the rate of reductive dissolution.

Oversaturation with respect to a particular phase may explain the changes in concentration of some of the elements through time. For instance, the computer program Solmineq.88 (Kharaka and others, 1988) indicates that the solution in at least one container should be oversaturated near the end of the experiment with respect to weddelite (calcium oxalate), nontronite, hematite, and goethite (G. Breit, written commun., 1993). Precipitation of any of the iron-bearing phases might also contribute to transient downward spikes in the iron curves; however, precipitation of Fe^{3+} phases might have been prevented by reductive dissolution of Fe^{3+}. The calcium concentration curves for many of the containers tend to rise then and fall, as would be expected if a calcium-oxalate mineral were precipitating. As mentioned earlier, examination of the grains from each container under the SEM after the end of the experiment revealed precipitates containing only carbon and oxygen; however, according to Solmineq.88 modeling, only very small amounts (micrograms) of nontronite, hematite, goethite, or calcium oxalate, which may have easily been overlooked in the SEM study, would have precipitated.

STOICHIOMETRY

In the garnet structure, the number of moles of X-cations (Fe^{2+}, calcium, and magnesium) should equal the number of moles of Z cation (silicon). Stoichiometric dissolution is difficult to determine in this study because iron can also substitute in the Y-cation site. The possibility that some Fe^{2+} in solution is the result of reductive dissolution of Fe^{3+} in the Y-cation site is very likely because these ions would be included with X cations in table 3. The distribution of iron between the two oxidation states or between the two sites in each grain at the beginning of the experiment is not known. The average chemical analysis of Barton Mines' pyrope-almandine garnets (table 1) shows approximately 12.6 weight percent Fe_2O_3 and 9.7 weight percent FeO. Unfortunately, the standard deviation of these values is proprietary (Barton Mines Corporation, oral commun., 1993). Therefore, in calculations of molar ratios in this study an intermediate value of about 50 percent Fe in each cation site was assumed.

Beginning at 17 days, enough dissolution had taken place in some containers to compare X and Z molar ratios. In containers A and B, the sum of the concentrations of all X cations was higher than the concentration of silicon. Dissolution was also apparently nonstoichiometric at 25 days in all containers except for container 89 (X cations≈Z cations) because X-cations were present in higher concentrations than silicon if 50 percent of the iron is considered to be in the X-cation site. If more iron is placed in the X-cation site, dissolution also appeared to be nonstoichiometric in container 89. At 34 days, if 50 percent of the iron is arbitrarily placed in the X-cation site, dissolution is stoichiometric in containers B and 94 and nonstoichiometric in the rest. If all iron is placed in the X-cation site, dissolution is nonstoichiometric in all containers.
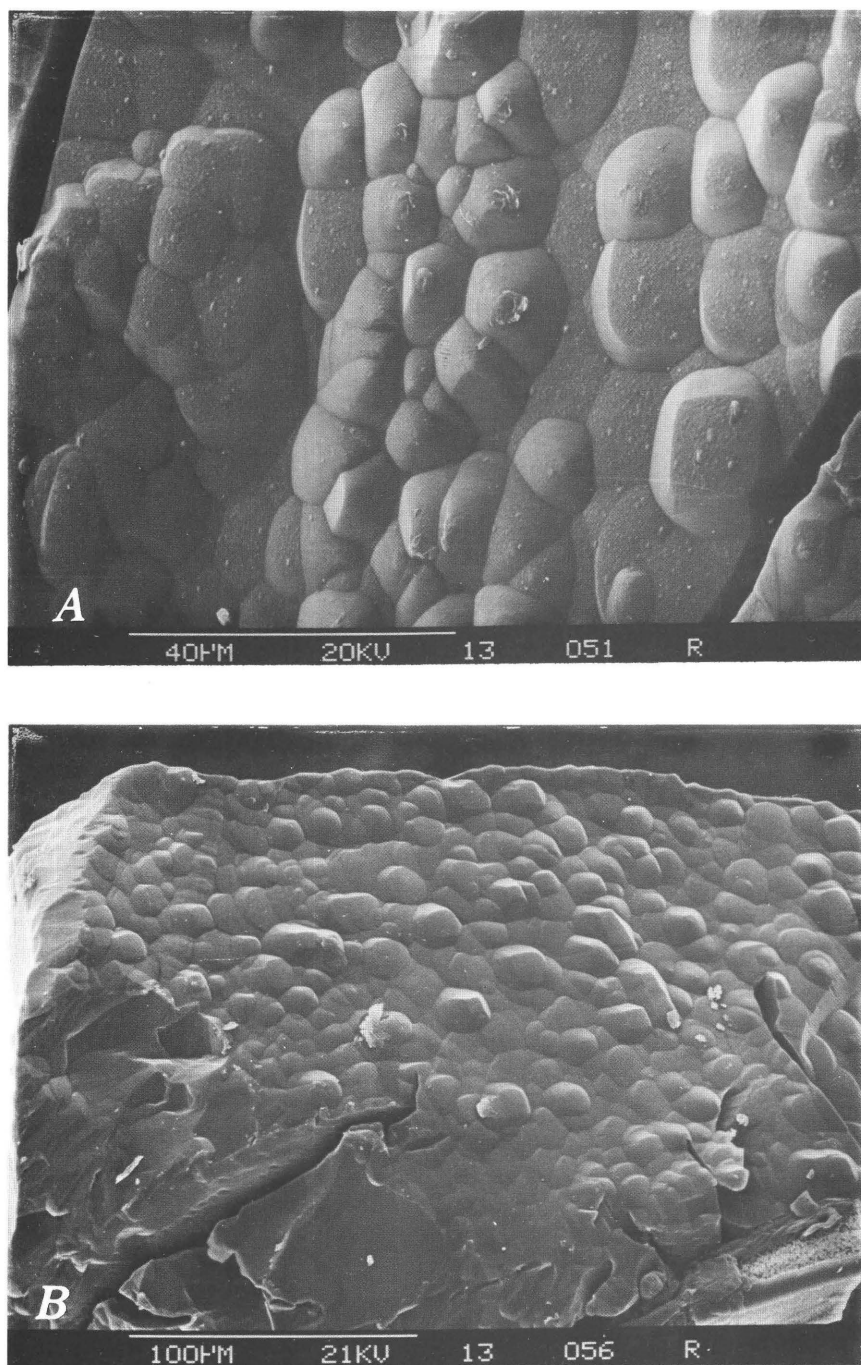
Figure 12 (above and facing page).   Scanning electron microscope photomicrographs of garnets from different containers showing examples of etched surfaces. Note pointed top of a mammillary feature in *C* and the polygonal bases and flat tops of many mammillary features in *A–D*. A, Container *86*. B, Container *89*. C, Container *93*. D, Container *94*.

The Z cation (silicon) was present in higher concentrations than the X-cation concentration in three containers, the Z-cation concentration was equal to or greater than the X-cation concentration in two containers, and the Z-cation concentration was less than the X-cation concentration in one container. These results are puzzling because they suggest that the silicon tetrahedra are breaking up faster than the other parts of the structure. The high silicon concentrations might be explained in part by reductive dissolution of Fe^{3+} substituting for aluminum in the Y-cation site. Because the Y-cation octahedra are linked to the silicon tetrahedra, breaking of octahedra would cause more silicon to dissolve. If this
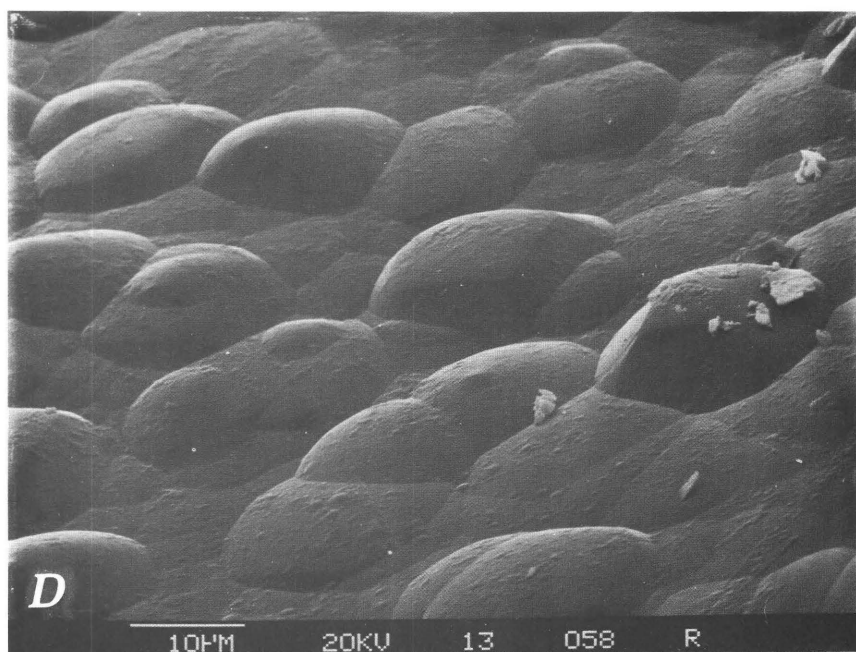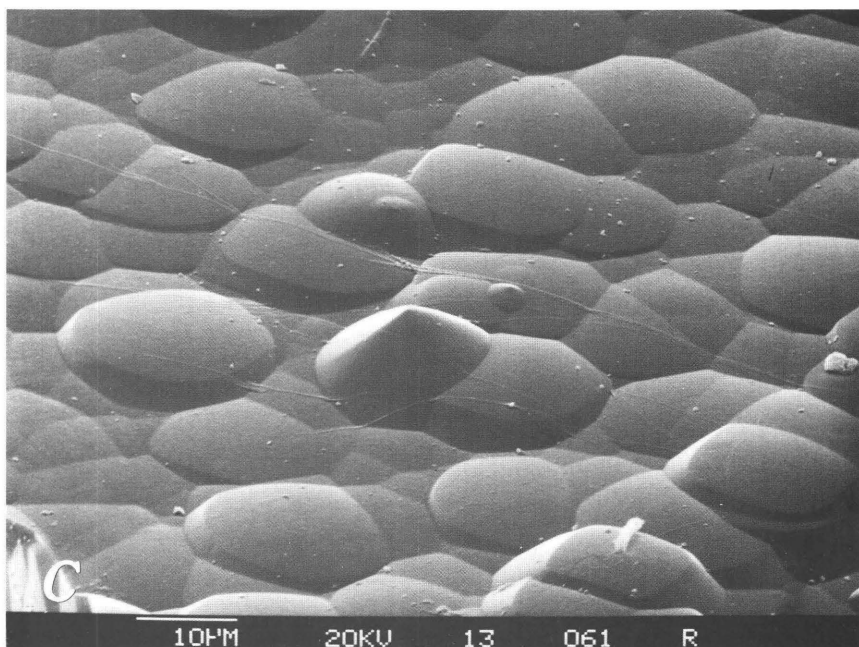
were the case, however, concentrations of other ions in solution should also be relatively higher, and they are not. The high concentration of silicon relative to iron, calcium, and aluminum in the solutions might be explained in part by precipitation of iron-, calcium-, and aluminum-bearing minerals as suggested by Solmineq.88. Finally, the higher than expected amounts of silicon also may be due to the strong complexes that aluminum forms with polyfunctional organic acid species, which are most abundant at acidic pH values (Bennett and Casey, 1994). The dissolution of aluminum would facilitate the breaking of the silicon tetrahedra;

however, the amount of aluminum in solution should then be greater, and it is not. Possibly aluminum did dissolve and then precipitate, leaving silicon in solution.

CONCLUSIONS

MECHANISM OF DISSOLUTION

Analysis by ICP-AES of concentrations in the containers with garnets at 17, 25, and 34 days suggest that garnet

dissolution either is incongruent (nonstoichometric) and proceeds by a two-step surface-controlled process because until the end of the experiment, when saturation was apparently reached, the X cations (Fe^{2+}, calcium, and magnesium) were realeased first followed by the Z cation, silicon. In this case, H^+ ions are first exchanged for Fe^{2+}, calcium, and magnesium in the garnet structure leaving an H^+-exchanged layer of unknown thickness depleted in cations on the surface of the garnets. In the next step, the aluminum octahedra-silicon tetrahedra break apart, and Al^{3+}, Fe^{3+}, and Si^{4+} go into solution. The apparent faster release of iron in some cases may be due in part to reductive dissolution. Another factor influencing the solubility of iron is that the association constants of both Fe^{3+}- and aluminum-oxalate complexes increase rapidly to temperatures as high as 90°C and those of iron oxalate complexes increase the most rapidly (Tait and others, 1992).

In saprolites, the dissolution mechanism in garnets may in fact be surface controlled, as concluded in this experiment, rather than transport controlled, as concluded by Velbel (1993a). The surface control may be masked because ground water is less effective in transporting ions away from sites of dissolution in soils. It is not possible, based on the results of the experiment, to determine whether a thin residual layer was present during dissolution (as discussed by Berner and Schott, 1982). If such a layer was present, it was probably only a few angstroms thick and did not impede the surface-controlled process of dissolution.

According to Berner (1981), the morphology of the dissolved layers should indicate whether dissolution is transport- or surface-controlled. Transport-controlled dissolution is characterized by nonspecific dissolution resulting in rounded surfaces, whereas surface-controlled dissolution is distinguished by crystallographically controlled etch pits. Using Berner's (1981) criteria, the rounded features produced in this experiment would not be the result of surface-controlled processes; however, the presence of polygonal bases and pointed tops on some rounded etch features suggests that these mammillary features may the first step in the formation of angular etch features. Saturation of the solutions with respect to certain phases may have prevented the formation of more angular forms. In addition, the fact that Tamm's reagent is an internally buffered acid may mean that it takes longer for sharp etch planes to form than in unbuffered oxalic acid. In earlier experiments, Hansley (1987) created sharp etch features that are almost certainly indicative of a surface-controlled process with 0.01M oxalic acid at 80°C in a few days.

The fact that not all surfaces of the garnets were etched (see fig. 11) indicates crystallographic (and thus surface) control of the etching process; however, the relation of etched faces to crystallographic axes is unknown because the grains were unoriented. Grandstaff (1978, fig. 2) suggested that anisotropy in the crystal structure, such as intersecting cleavage planes and lattice defects, is responsible for nonuniformity of dissolution over a crystal surface.

APPLICATION TO THE NATURAL ENVIRONMENT

In these experiments reactions almost certainly proceeded at a much faster rate than in the natural environment; however, geologic time is a factor that cannot be built into most experiments. Natural reactions are usually simulated by raising temperatures and (or) concentrations of reactants such that the reactions proceed in a reasonable amount of time, but it is assumed that the reactions proceed as in nature. Velbel (1993b) pointed out, however, that laboratory experiments typically result in dissolution rates one to two orders of magnitude higher than rates calculated in the field because natural ground waters flow in tortuous pathways and do not come in contact with all surfaces of mineral grains. In addition, the fluid-to-rock ratio is higher in the experiments. The pH value of 3.25 used in this experiment is lower than pH values in most natural waters, but pH values of 3–4 are observed in some organic-acid-bearing ground waters, such as peat bogs (Crum, 1988). The precipitation of secondary minerals, as in soils, is also more common in the natural geologic environment because pore waters tend to approach saturation. An aspect of the natural environment not tested in this experiment was the presence of microbes, which are almost certainly associated with organic matter at temperatures of less than 100°C, and their catalytic(?) effect on the etching process.

Naturally etched garnets that have mammillary surfaces virtually identical to those produced in this experiment have been observed on the periphery of zones of deeply etched garnets in sandstone of the Morrison Formation (Hansley, 1987). This pattern of etching may have resulted because the etching solution was cooler and (or) less concentrated with respect to acidity on the edges of the Morrison aquifer. Etched garnets also have been observed in the Salt Wash Member of the Morrison Formation throughout the Colorado Plateau region (Hansley, unpublished data). Breit and Meunier (1990) showed that warm, reducing, sulfate-bearing waters moved up faults in the Slick Rock area of the Colorado Plateau during the Tertiary, and petrographic evidence (Hansley, unpublished data) suggests that these waters were responsible for the etching.

Many organic acids are stronger acids and complexing agents than carbonic acid, the most common inorganic acid in sedimentary environments. Because organic acids are important dissolution agents, complexing agents, catalysts, and buffers in natural waters, it is important to consider their role whenever the diagenesis of sedimentary rocks is being studied.

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Miscellaneous Investigations Series Maps are on planimetric or topographic bases of regular and irregular areas at various scales; they present a wide variety of format and subject matter. The series also includes 7 1/2-minute quadrangle photogeologic maps on planimetric bases which show geology as interpreted from aerial photographs. The series also includes maps of Mars and the Moon.

Coal Investigations Maps are geologic maps on topographic or planimetric bases at various scales showing bedrock or surficial geology, stratigraphy, and structural relations in certain coal-resource areas.

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Miscellaneous Field Studies Maps are multicolor or black-and-white maps on topographic or planimetric bases on quadrangle or irregular areas at various scales. Pre-1971 maps show bedrock geology in relation to specific mining or mineral-deposit problems; post-1971 maps are primarily black-and-white maps on various subjects such as environmental studies or wilderness mineral investigations.

Hydrologic Investigations Atlases are multicolored or black-and-white maps on topographic or planimetric bases presenting a wide range of geohydrologic data of both regular and irregular areas; the principal scale is 1:24,000, and regional studies are at 1:250,000 scale or smaller.

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